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PERCI ODILON BONETTI HOMRICH

USO DE SOLVENTES NA DESODORIZAÇÃO DE ÓLEOS VEGETAIS COM FOCO NA OBTENÇÃO DE DADOS DE EQUILÍBRIO LÍQUIDO-LÍQUIDO

USAGE OF SOLVENTS ON VEGETABLE OILS DEODORIZATION FOCUSING ON OBTAINING LIQUID-LIQUID EQUILIBRIUM DATA

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Tese apresentada à Faculdade de Engenharia Química da Universidade Estadual de Campinas como parte dos requisitos exigidos para obtenção de título de doutor em Engenharia Química.

Orientadora: Profa. Dra. Roberta Ceriani

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Profa. Dra. Roberta Ceriani (Orientadora)

Profa. Dra. Christianne Elisabete da Costa Rodrigues

Profa. Dra. Cintia Bernardo Gonçalves

Prof. Dr. Guilherme José Máximo

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RESUMO

Visando mitigar os problemas causados por condições críticas de operação de processos industriais, a busca por diferentes tecnologias se faz necessária. A literatura apresenta a extração líquido-líquido como uma alternativa branda à desodorização de óleo vegetais, a qual atualmente é realizada a altas temperaturas (até 260 °C) e baixas pressões (aproximadamente 3 mmHg). Dentre os efeitos colaterais do atual processo, tem-se: a formação do contaminante 3-MCPD (3-monocloropropano-1,2-diol) e de ácidos graxos com isomeria *trans*, a volatilização parcial de tocoferóis e a degradação térmica de triacilgliceróis. Devido às condições operacionais amenas da extração líquido-líquido, tais efeitos são mitigados. Trabalhos prévios investigaram a remoção de ácidos graxos livres e compostos odoríferos (aldeídos e ácidos carboxílicos de cadeia curta) utilizando principalmente etanol anidro e hidratado como solventes. Devido à escolha do solvente ser crucial para otimizar o processo de extração e garantir sua segurança, a investigação de diferentes solventes para promover a extração de compostos indesejáveis de óleos vegetais ainda é um campo a ser melhorado. Nesse contexto, este trabalho de tese de doutorado teve como objetivo investigar a solubilidade mútua de diferentes compostos envolvidos na extração de odores do óleo de soja. Para isso, diagramas de equilíbrio de fases de sistemas contendo óleo de soja refinado e solventes puros (etanol anidro, ácido acético, lactato de etila e dimetilsulfóxido) ou misturas de solventes {(etanol anidro, ácido acético, lactato de etila e dimetilsulfóxido) mais água} e {(lactato de etila e dimetilsulfóxido) mais ácido fórmico} foram experimentalmente determinados. Além disso, pela coleta de dados de equilíbrio líquido-líquido, a remoção de seis compostos odoríferos foi avaliada utilizando dimetilsulfóxido como solvente. A modelagem dos dados experimentais foi realizada aplicando-se os modelos NRTL e UNIQUAC, a qual resultou em desvios globais menores que 0,59 e 0,71%, respectivamente. Os dados de equilíbrio dos sistemas investigados foram também preditos utilizando-se diferentes métodos baseados no UNIFAC, onde foi possível verificar, de uma forma geral, a não satisfatoriedade da aplicação de métodos de contribuição de grupos no cálculo do equilíbrio de fases dos sistemas investigados.

Palavras-chave: óleos vegetais, desodorização, extração líquido-líquido, solventes, cosolventes

ABSTRACT

Aiming at mitigating problems caused by critical conditions applied in industrial processes, a search for different technologies is necessary. The literature presents the liquid-liquid extraction as a mild alternative for the deodorization of vegetable oils, which is currently carried out at high temperatures (up to 260 °C) and low pressures (approximately 3 mmHg). Among side-effects of the current process, one has: 3-MPCD (3-monochloropropane-1,2-diol) contaminant and *trans* fat formation, partial volatilization of tocopherols and thermal degradation of triacylglycerols. Due to mild operational conditions of liquid-liquid extraction, such effects are mitigated. Previous works investigated the removal of free fatty acids and odoriferous compounds (aldehydes and short-chain carboxylic acids) mainly using hydrous and anhydrous ethanol as solvents. As the choice of solvent is crucial for optimizing liquid-liquid extraction process and assuring its security, investigation of different compounds to accomplish extraction of undesirable components of vegetable oils is still a field of research. In this context, this thesis aimed at investigating mutual solubilities of different compounds involved in extraction of odors from soybean oil. To achieve this purpose, equilibrium diagrams of systems containing refined soybean oil and pure solvents (anhydrous ethanol, acetic acid, ethyl lactate and dimethyl sulfoxide) or mixtures of solvents {(anhydrous ethanol, acetic acid, ethyl lactate and dimethyl sulfoxide) plus water} and {(ethyl lactate and dimethyl sulfoxide) plus formic acid} were experimentally determined. Furthermore, by collecting liquid-liquid equilibrium data, removal of six odoriferous compounds was evaluated using dimethyl sulfoxide as solvent. Experimental data modeling was assessed by applying the NRTL and the UNIQUAC models, which resulted in global deviations lower than 0.59 and 0.71%, respectively. Moreover, equilibrium data of investigated systems were predicted considering different methods based on the UNIFAC, wherein, in general, it was observed inadequacy of applying group contribution methods to calculate phase equilibria of investigated systems.

Keywords: vegetable oils, deodorization, liquid-liquid extraction, solvents, cosolvents

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INTRODUÇÃO E OBJETIVOS

O óleo de soja apresenta-se como o principal óleo produzido a partir de grãos, e figura como o segundo óleo mais utilizado para fritura em escala mundial (USDA, 2017). Durante o refino, os óleos vegetais são processados em uma sequência de etapas químicas ou físicas que visam remover compostos minoritários que alteram suas propriedades organolépticas (cor, odor, sabor e textura), bem como aqueles que diminuem sua estabilidade oxidativa e, consequentemente, sua vida de prateleira (DUNFORD, 2012). Devido às condições operacionais drásticas – em especial as aplicadas na desodorização – várias alterações indesejáveis ocorrem nos óleos vegetais (SHAHIDI, 2013; KREPS et al., 2017), necessitando-se, desta forma, a investigação de métodos alternativos brandos.

A desodorização é industrialmente realizada pelo processo de esgotamento utilizando vapor d'água como agente de arraste. A etapa é aplicada para remover principalmente compostos odoríferos, ácidos graxos livres (na desacidificação física ou aqueles remanescentes do refino químico) e pesticidas (KELLENS e GREYT, 2000; VAISALI et al., 2015). Por operar em condições operacionais drásticas (temperatura de até 260 °C e pressão de cerca de 3 mmHg), além dos compostos tipicamente removidos, a desodorização acarreta a degradação de triacilgliceróis, volatilização de compostos nutracêuticos (principalmente antioxidantes), reação de isomerização *cis-trans* e, como constatado nos últimos anos, a formação dos contaminantes clorados 3-monocloropropanodioís (3-MCPD) (ERMACORA e HRNCIRIK, 2014; SULIMAN et al., 2013; FINE et al., 2015; CHENG et al., 2017). A fim de contornar tais efeitos colaterais, a literatura apresenta processos brandos alternativos à desodorização como a separação por membranas e a extração líquido-líquido, expondo os óleos vegetais a condições operacionais brandas e reduzindo a quantidade energética requerida para a separação (RODRIGUES et al., 2007; GONÇALVES et al., 2016).

Os compostos odoríferos são principalmente provenientes da reação de oxidação (JEONG et al., 2010; ESKIN e HOEHN, 2013). Essa reação de degradação gera diferentes compostos, como aldeídos, cetonas, hidrocarbonetos, álcoois, ácidos carboxílicos de cadeia curta e polímeros, os quais variam de acordo com a composição do óleo. Sua ocorrência é verificada em diferentes situações, como na estocagem dos óleos brutos, no próprio refino – em especial nas etapas de branqueamento e desodorização – durante a fritura e na prateleira pela exposição à temperatura e luz (MAKHOUL et al., 2006; CHOE e MIN, 2006; VIEIRA et al., 2017).

Realizada em condições operacionais brandas (temperatura e pressão próximas às ambientais), a extração líquido-líquido apresenta como vantagem em relação ao processo de esgotamento a menor quantidade de energia requerida, menor perda de óleo vegetal e compostos nutracêuticos e, em comparação com a desacidificação física, menor formação de efluentes (OLIVEIRA et al., 2012). Dentre os estudos apresentados pela literatura, a extração líquido-líquido satisfatoriamente remove compostos como os ácidos graxos livres, aldeídos, ácidos carboxílicos de cadeia curta e acilgliceróis parciais utilizando principalmente etanol anidro como solvente (GONÇALVES e MEIRELLES, 2004; HOMRICH e CERIANI 2016; MAY et al., 2016; FERREIRA et al., 2015). Além disso, a hidratação do etanol anidro foi investigada para a remoção de ácidos graxos livres, resultando, assim, em uma menor solubilização mútua do par óleo vegetal-solvente, o que, consequentemente, facilita o tratamento das correntes rafinado e extrato. No tocante à remoção dos produtos da oxidação, além do etanol, também foi investigado o solvente lactato de etila para remoção de aldeídos, o qual apresentou uma região de separação bem menor que o etanol anidro (JORQUEIRA et al., 2014). Não obstante, os esforços aplicados nos estudos prévios indicam a necessidade de investigar diferentes solventes (puros ou em misturas) para a extração adequada dos compostos que alteram a palatabilidade dos óleos vegetais, visando otimizar o processo de extração líquido-líquido.

A seleção do solvente apropriado para a extração líquido-líquido é a etapa mais importante para a otimização e segurança do processo (EDEN et al., 2004; DIORAZIO et al., 2016). A partição dos compostos entre as fases e a seletividade do solvente, fornecidos a partir de dados de equilíbrio líquido-líquido, são os principais fatores utilizados na seleção de um solvente. Além disso, propriedades termofísicas como temperatura normal de ebulição, massa específica, viscosidade, tensão interfacial são levadas em conta (DATTA, 2016; BYERNE et al., 2016). Atualmente, devido às preocupações concernentes à saúde dos consumidores, a toxicidade do solvente é um parâmetro a ser considerado, especialmente nas indústrias alimentícia e farmacêutica (GIOVANOGLOU et al., 2003; TURNER e WANG, 2017).

Diante do exposto, este trabalho teve como objetivo principal a determinação de dados de equilíbrio líquido-líquido de sistemas contendo óleo de soja refinado e diferentes solventes para a remoção de compostos odoríferos. A investigação de um solvente adequado levou em consideração apenas compostos considerados de baixa toxicidade de acordo com a classificação ICH (*International Conference on Harmonisation of Technical Requirements for Registration* *of Pharmaceuticals for Human Use*) (2012). Os dados de equilíbrio foram obtidos para solventes puros e para cosolventes, bem como para sistemas pseudoternários contendo compostos odoríferos. A modelagem termodinâmica foi realizada utilizando os modelos NRTL (*Non-Random Two-Liquids*) (RENON e PRAUSNITZ, 1968) e UNIQUAC (*UNIversal QUAsiChemical*) (ABRAMS e PRAUSNITZ, 1975) e a predição de cinco métodos baseados no UNIFAC (*UNIQUAC Functional-group Activity Coefficients*) (FREDENSLUND et al., 1975) foi avaliada. Assim, o presente trabalho está estruturado da seguinte forma:

A Revisão Bibliográfica (***Capítulo 2***) apresenta o estado da arte do tema abordado nesse trabalho e os desafios a serem enfrentados a fim de contornar os atuais problemas da desodorização dos óleos vegetais.

A investigação de classes de solventes com potencial para remoção de compostos odoríferos do óleo de soja – em especial aldeídos e ácidos carboxílicos de cadeia curta – está abordada no ***Capítulo 3***, intitulado “Solvent screening using UNIFAC method to investigate the deodorization of soybean oil using a liquid solvent”. A pré-seleção de solventes para realizar a desodorização foi norteada pelo método qualitativo proposto por Cusack et al. (1991). A partir das classes orgânicas com potencialidade para a remoção dos compostos indesejáveis, 16 solventes de baixa toxicidade segundo as classificações ICH foram escolhidos. O equilíbrio líquido-líquido dos sistemas pseudoternários (óleo de soja + composto de odor + solvente) foi predito por duas abordagens do método UNIFAC: UNIFAC-LL (MAGNUSSEN, 1981) e UNIFAC-HIR (HIRATA et al., 2013).

O ***Capítulo 4*** traz o artigo intitulado “Solubility behavior of mixtures containing refined soybean oil and low-toxic solvents at different temperatures”, o qual apresenta dados experimentais de solubilidade de diferentes solventes no óleo de soja refinado. O estudo verificou a ocorrência de solubilidade total de 11 solventes no óleo de soja, a formação de emulsão persistente de dois solventes (água e ácido fórmico) e a solubilidade parcial de quatro solventes (etanol anidro, ácido acético, lactato de etila e dimetilsulfóxido). Para os sistemas parcialmente miscíveis, diagramas de equilíbrio líquido-líquido em função da temperatura foram experimentalmente obtidos e os dados foram correlacionados aos modelos NRTL (RENON e PRAUSNITZ, 1968) e UNIQUAC (ABRAMS e PRAUSNITZ, 1975). Além disso, os dados experimentais foram comparados com predições de cinco diferentes versões do método UNIFAC: UNIFAC-LL (MAGNUSSEN 1981), UNIFAC-DMD (WEIDLICH e GMEHLING, 1987; GMEHLING et al., 1993), UNIFAC-LBY (LARSEN et al.; 1987), UNIFAC-HIR (HIRATA et al.; 2013) e UNIFAC-NIST (KANG et al.; 2015).

No ***Capítulo 5*** é apresentado o artigo "Investigation of the mutual solubilities of soybean oil and low-toxic liquid-cosolvent mixtures". Nesse, dados experimentais de equilíbrio são apresentados para o sistema óleo de soja e o cosolvente ácido acético + água. Além disso, a predição utilizando os métodos UNIFAC supracitados foi realizada para diferentes cosolventes de baixa toxicidade: (etanol anidro, ou ácido acético, ou lactato de etila, ou dimetilsulfóxido) + (água ou ácido fórmico), totalizando oito sistemas. Os dados experimentais foram ajustados aos modelos NRTL e UNIQUAC.

Dados experimentais de equilíbrio do óleo de soja e diferentes cosolventes são apresentados no ***Capítulo 6***, intitulado "Phase equilibria for systems containing refined soybean oil plus cosolvents at different temperatures". Os cosolventes investigados foram: {(etanol anidro, ou lactato de etila, ou dimetilsulfóxido) + água} e {(lactato de etila, ou dimetilsulfóxido) + ácido fórmico}, totalizando cinco sistemas pseudoternários. A predição pelos métodos UNIFAC apresentaram uma melhora em relação aos solventes puros, ou seja, sem água ou ácido fórmico, gerando desvios globais para as fases extratos de aproximadamente 1%.

O ***Capítulo 7*** intitulado "Liquid-liquid equilibria and density data for pseudoternary systems of refined soybean oil + (hexanal, or heptanal, or butyric acid, or valeric acid, or caproic acid, or caprylic acid) + dimethyl sulfoxide at 298.15 K" apresenta a remoção de compostos odoríferos do óleo de soja refinado utilizando dimetilsulfóxido como solvente. Os sistemas foram ajustados aos modelos NRTL e UNIQUAC e a avaliação da predição de quatro métodos baseados no UNIFAC foi realizada.

Por fim, as Conclusões Gerais obtidas no presente trabalho estão apresentadas no ***Capítulo 8***.

CAPÍTULO 2

REVISÃO BIBLIOGRÁFICA

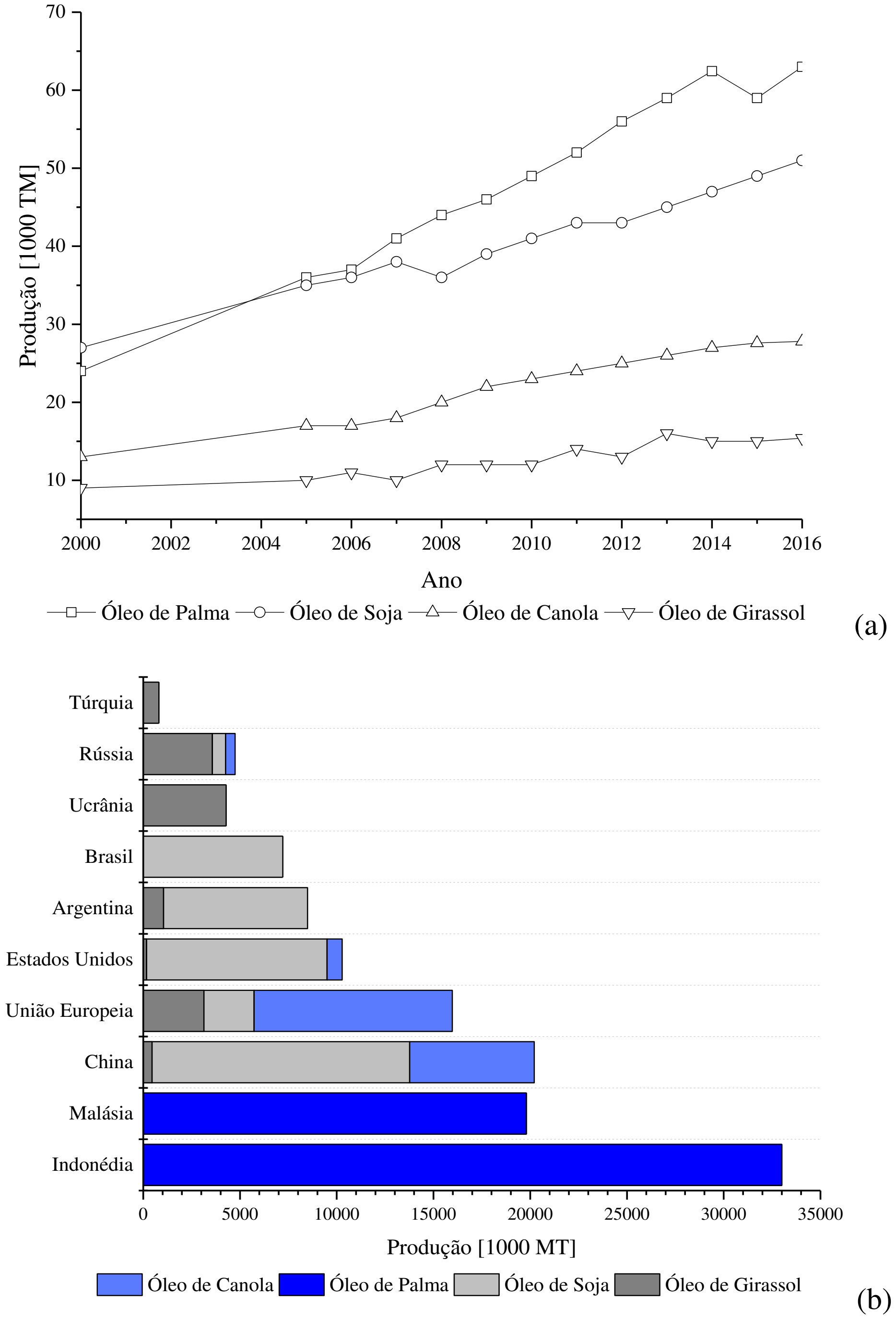
2.1 ÓLEOS VEGETAIS

Os óleos e gorduras, os quais são as maiores fontes de triacilgliceróis, apresentam elevada produção mundial, amplas aplicações industriais e, recentemente, tornaram-se uma promissora fonte de bioenergia renovável (DUNFORD, 2012; BELITS, 2009). Obtidos a partir de oleaginosas, as quais são plantas que possuem em seus grãos ou frutos uma determinada quantidade de óleo (GUNSTONE, 2013; KOZŁOWSKA et al., 2016), os óleos vegetais possuem importantes funções biológicas, como: alta fonte de energia; absorção de vitaminas lipossolúveis; isolantes térmicos e físicos; componentes estruturais de membranas biológicas; precursores de hormônios; e reguladores do colesterol (SIMOPOULOS, 2008; DHAVAMANI et al., 2014; ORSAVOVA et al., 2015). Devido ao alto consumo mundial de óleos vegetais, sua qualidade tem um impacto significativo na qualidade de vida dos consumidores, o que instiga a procura por processos de extração e refino mais brandos.

A aplicação dos óleos vegetais normalmente depende da sua composição em ácidos graxos e da presença de compostos minoritários, como os antioxidantes tocoferóis e tocotrienóis (O'BRIEN, 2008). A indústria de alimentos utiliza cerca de 80% dos óleos vegetais produzidos através de óleos de salada, óleos de fritura, margarinas, maionese, biscoitos e uma série de outros alimentos (HAMMOND, 2000; GUNSTONE, 2011). Além do uso alimentício, os óleos vegetais são utilizados na indústria farmacêutica, medicinal, como lubrificantes, como fonte de bioenergia renovável na produção de biodiesel e na obtenção de materiais poliméricos (ISSARIYAKUL e DALAI, 2014; SAGIRI et al., 2016; LLIGADAS et al., 2013).

Referente à produção, os óleos vegetais apresentam significativa importância frente aos demais comódites produzidos em escala mundial (GUNSTONE, 2011). No período 2016/2017, estima-se que a produção dos óleos vegetais no mundo seja de cerca de 187 milhões de toneladas métricas (TM), tendo destaque o óleo de palma e o de soja (USDA, 2017). A Figura 2.1-1 apresenta a produção mundial dos principais óleos no período de 2000 a 2016 e no ano de 2016 em relação aos principais países produtores.

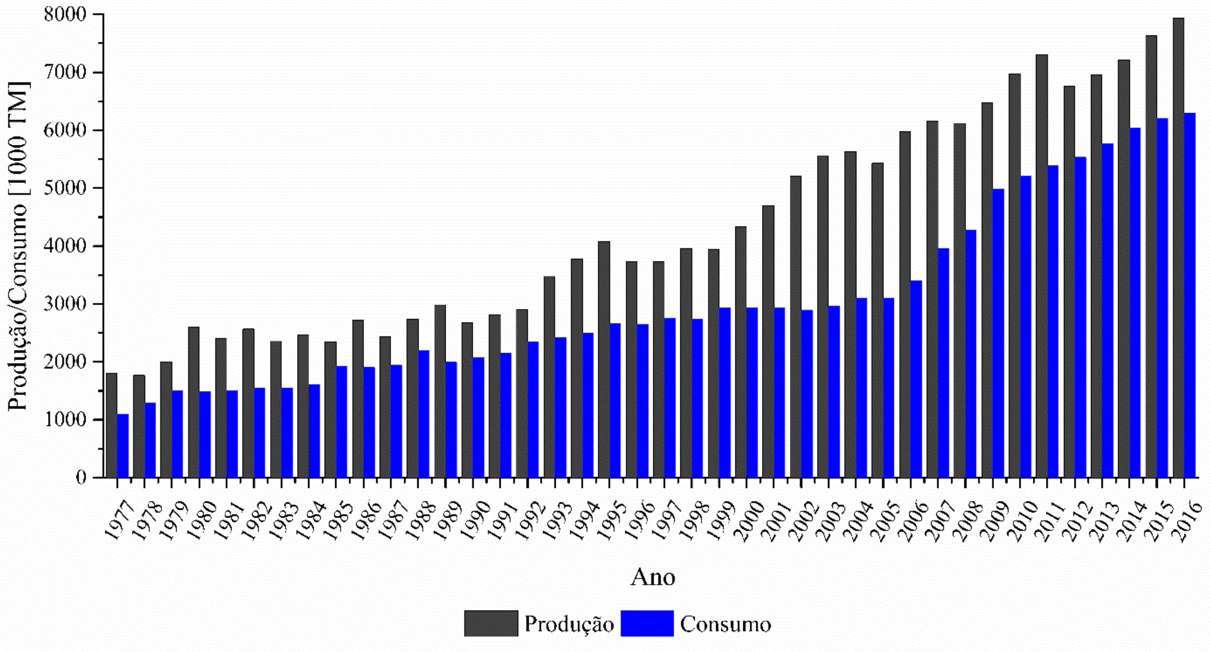
Figura 2.1-1: Produção em 1000 toneladas métricas (TM) dos principais óleos vegetais: (a) no período de 2000 a 2016; (b) no ano de 2016 para os principais países produtores.



Fonte: extraído de USDA, 2017.

Observa-se na Figura 2.1-1.a o contínuo crescimento na produção dos óleos vegetais, sendo verificado que, no intervalo de 2000 a 2016, a produção deste comódite praticamente dobrou. Até o ano de 2004, o óleo com maior produção mundial era o proveniente do grão de soja; a partir desse ano, o óleo de palma vem ganhando intensa produção, representando hoje mais da metade dos óleos produzidos em escala mundial. No que toca à produção dos óleos vegetais em diferentes países (Figura 2.1-1.b), observa-se que o Brasil é o sétimo maior produtor mundial de óleos, sendo o montante produzido praticamente o próprio óleo de soja. A Figura 2.1-2 apresenta a produção e o consumo do óleo de soja no Brasil no período de 1977 a 2016, sendo a diferença a quantidade exportada para outros países.

Figura 2.1-2: Produção e consumo (em 1000 toneladas métricas) do óleo de soja no Brasil entre os anos de 1977 e 2016.



Fonte: extraído de USDA, 2017.

Como é observado na Figura 2.1-2, o Brasil possui uma expressiva produção e consumo de óleo de soja, tornando-o o 2º maior produtor mundial do grão de soja e o 4º maior produtor mundial do óleo de soja, o que faz com que o país seja o segundo maior exportador destes produtos. Além disso, observa-se o comportamento crescente na produção durante os últimos 16 anos – corroborando com a Figura 2.1-1.a – indicando que o país vem acompanhando o crescente consumo mundial de óleo de soja.

2.1.1 Óleo de Soja

O óleo de soja é um subproduto do grão de soja (*Glycine max* (L) Merrill), sendo ambos uma expressiva fonte de alimentos no mundo (LIST, 2016; NAFZIGER, 2009). A soja pertence à classe das dicotiledôneas, à família leguminosa e à subfamília Papilionoides, destacando-se por ser a mais importante oleaginosa cultivada no mundo (HAMMOND et al., 2005; WANG, 2011). Os produtos provenientes da soja possuem amplas aplicações na indústria alimentícia, como o próprio óleo de soja, além de tofu, molho de soja, leite de soja, proteína de soja, soja em grãos e outros (HAMMOND, 2005). Além disso, o farelo de soja e o de milho são os principais ingredientes utilizados no preparo de rações animais (ESKIN e HOEHN, 2013).

Dentre todas as oleaginosas mundialmente cultivadas, a soja apresenta a maior fonte de proteínas. Por possuir uma significativa quantidade de isoflavonoides (0,5 – 3,5 mg/g), o consumo humano da proteína de soja é mundialmente encorajado (GUNSTONE, 2013). Seu alto teor de proteínas proporciona múltiplas utilizações e a formação de um complexo industrial destinado ao seu processamento, visando à produção de farelo e óleo. A Tabela 2.1-1 apresenta a composição do grão de soja e de seus subprodutos.

Tabela 2.1-1: Composição dos produtos e subprodutos do grão de soja em relação à umidade, óleo, proteínas, fibras, fosfato e carboidratos.

Composição [g.100g^{-1}]	**Grão**	**Óleo**	**Farelo**	**Casca**	**Lecitina**
Umidade	12,5	0,15	12,5	7,25	0
Óleo	19,5	99,7	2	0,77	24,2
Proteínas	36,6	0	47	8,88	0
Fibras	5,5	0	3,92	34,88	0
Impurezas	0,2	0	0	0	0
Fosfato	1,0	0,15	0,8	0,72	75,8
Carboidratos	24,7	0	33,78	51,78	0

Fonte: extraído de Dembogurski, 2003.

Como pode ser observado na Tabela 2.1-1, o grão de soja apresenta cerca de 20% em massa de óleo vegetal, o qual comumente é extraído através da sua solubilização em um solvente orgânico (comumente o hexano) (DUNFORD, 2012).

A Tabela 2.1-2 apresenta a composição da fase lipídica (óleo de soja) do grão de soja.

Tabela 2.1-2: Composição do óleo de soja em relação aos triacilgliceróis, fosfolipídios, material insaponificável, esteróis, tocoferóis, ácidos graxos livres e metais.

Componente	**Porcentagem mássica**
Triacilgliceróis	94,4
Fosfolipídios	3,7
Hidrocarbonetos	0,38
Esteróis	0,236
Tocoferóis	0,123
Ácidos graxos livres	0,3 – 0,7
Traço de metais (mg·kg^{-1} de ferro)	1 – 3

Fonte: extraído de Hammond et al., 2005.

Como é constatado na Tabela 2.1-2, o óleo de soja é composto basicamente por triacilgliceróis, sendo um óleo atrativo por, além de ser de baixo custo, ser rico em ácidos graxos insaturados. Além disso, o óleo de soja apresenta uma alta composição em fosfolipídios, o que o torna uma grande fonte de lecitina, a qual possui alto valor agregado (GUPTA, 2005; LIST, 2016). Já em relação aos antioxidantes, especialmente os tocoferóis, o óleo de soja é um dos mais ricos nesses compostos, apresentando cerca de 830 mg/kg de homólogos de tocoferóis, obtendo destaque também o óleo de milho (GLISZCZYŃSKA-ŚWIGŁO et al., 2007; FAN e ESKIN, 2015). Por fim, possuindo de 0,3 – 0,7% em massa de ácidos graxos livres, o refino do óleo de soja pode ser realizado tanto química quanto fisicamente (FARR, 2013).

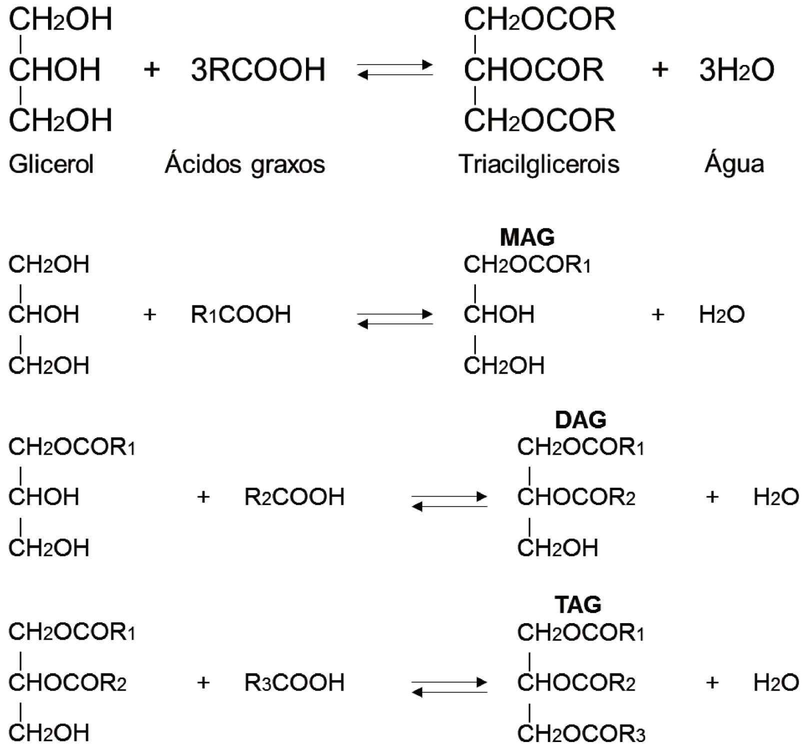
2.1.2 Composição dos óleos vegetais

Os óleos vegetais são compostos basicamente por triacilgliceróis (TAGs), os quais são formados pela esterificação de ácidos graxos às três terminações hidroxilas de uma molécula de glicerol, representando cerca de 95% da composição dos óleos (KOCHHAR, 2001; GUNSTONE, 2013). Também, há uma quantidade de ácidos graxos livres (não esterificados ao glicerol), variando sua representatividade significativamente entre os óleos (1% óleo de soja – 25% óleo do farelo de arroz) (KOSTIK et al., 2013; AZEMAN et al., 2015). Tanto os triacilgliceróis quanto os ácidos graxos livres são materiais saponificáveis, ou seja, formam sabão na reação de neutralização quando em contato com uma base (GURR et al., 2002; DEEPAM e ARUMUGHAN, 2012). Além dos compostos saponificáveis, os óleos vegetais são constituídos de uma pequena fração de material insaponificável, os quais tem grande importância frente às questões nutricionais dos óleos (GUNSTONE, 2013). Os principais materiais insaponificáveis que compõem os óleos vegetais são os esteróis, pigmentos, fosfolipídios, compostos fenólicos, tocoferóis, traços de metais, contaminantes e os produtos da oxidação (aldeídos, hidrocarbonetos, álcoois e cetonas) (HO e SHAHIDI, 2005; MEDINA et al., 2013).

2.1.2.1 Materiais saponificáveis

Como mencionado anteriormente, os TAGs são formados pela esterificação de três ácidos graxos à uma molécula de glicerol. Desta forma, a reação ocorre em três etapas formando produtos intermediários (acilgliceróis parciais) e água. A reação inversa da esterificação, hidrólise dos acilgliceróis, forma acilgliceróis parciais, glicerol e ácidos graxos livres (AGLs) (SCRIMGEOUR, 2005). Essas reações estão apresentadas na Figura 2.1-3.

Figura 2.1-3: Reações de esterificação e hidrólise envolvidas na formação de triacilgliceróis (TAGs), diacilgliceróis (DAGs) e monoacilgliceróis (MAGs).



Fonte: própria autoria.

Como apresenta a Figura 2.1-3, a quantidade de AGLs está diretamente relacionada com a quantidade de acilgliceróis parciais (mono e diacilglicerol). Assim, como há uma significativa variação de acidez entre os óleos vegetais, há uma alta faixa de composição em MAG e DAG (KOCHHAR, 2001).

A composição dos óleos vegetais em TAGs pode ser calculada estatisticamente por métodos computacionais que determinam a provável disposição dos AGs quando esterificados ao glicerol (ANTONIOSI FILHO et al., 1995; VAN VLIET e VAN KEMPEN, 2004). Por exemplo, o método baseado na hipótese 1,2,3-casual considera que os ácidos graxos possuem a mesma probabilidade de se distribuírem em cada uma das posições das hidroxilas do glicerol. Porém, os AGs não se distribuem de maneira aleatória na molécula do glicerol, sendo praticamente inexistente AGs saturados na posição 2. Outra constatação que indica a não aleatoriedade da distribuição dos AGs nos TAGS é que o ácido linoleico é praticamente encontrado apenas na posição central do glicerol (GROMPONE, 2005). A fim de melhor representar a disposição dos AGs, o método estatístico desenvolvido por Antoniossi Filho et al. (1995) consiste na teoria da distribuição “casual” e “1,3-casual 2-casual”, ou seja, nesse caso considera-se que os ácidos graxos se distribuem de forma aleatória primeiramente nas hidroxilas das posições 1 e 3 da molécula do glicerol, e posteriormente na posição 2. Prováveis composições de TAGs dos óleos de soja, milho, girassol, canola, amendoim e algodão estão expostas na Tabela 2.1-3.

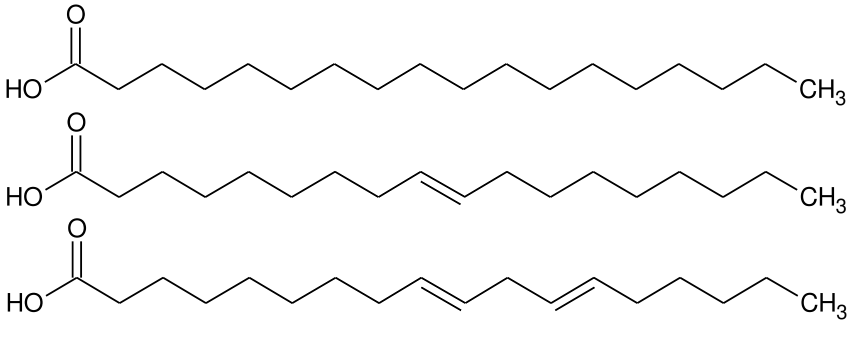
Tabela 2.1-3: Composição em triacilgliceróis (TAGs) de alguns óleos vegetais.

Composição		**Óleos Vegetais**					
AG	*Grupo*	*Soja*	*Milho*	*Girassol*	*Canola*	*Amendoim*	*Algodão*
POL	52:3	9,2	3,9	6,0	6,7	12,9	14,3
PLL	52:4	9,3	16,8	3,7	2,0	5,1	26,6
OOO	54:3	2,5	2,6	1,9	26,1	11,8	4,2
OOL	54:4	15,4	9,9	17,6	22,9	19,4	5,7
OLL	54:5	21,6	22,9	31,8	9,1	18,3	10,4
LLL	54:6	16,3	26,5	25,0	2,2	2,0	12,9

Fonte: extraído de Firestone, 2006.

Na Tabela 2.1-3, observa-se a preponderância dos ácidos graxos oleico (O), linoleico (L), os quais possuem 18 carbonos, e palmítico (P), o qual possui 16 carbonos, na composição dos óleos vegetais. Outro importante fator é que, quando as moléculas apresentam insaturações, estão naturalmente em sua isomeria *cis* (KOCHHAR, 2001). Por possuírem um maior ponto de fusão, os óleos saturados são sólidos a temperatura ambiente, já os insaturados são encontrados como líquidos (GURR et al., 2002; GUNSTONE, 2013). A Figura 2.1-4 ilustra a estrutura dos ácidos graxos saturados e insaturados com 18 carbonos na configuração linear (*trans*).

Figura 2.1-4: Estruturas moleculares dos ácidos graxos esteárico, oleico e linoleico.



Fonte: própria autoria.

Como mostra a Figura 2.1-4, os ácidos graxos de 18 carbonos (esteárico, oleico e linoleico) apresentam moléculas muito semelhantes, diferindo apenas em relação à quantidade de insaturações. Além disso, se tratando do ácido oleico e do linoleico, ambos apresentam algumas propriedades físicas semelhantes, como apresenta a Tabela 2.1-4, a qual sumariza o ponto de fusão e ebulição, a massa específica e massa molar de alguns ácidos graxos.

Tabela 2.1-4: Propriedades físicas massa molar (MM), massa específica (ρ), temperatura de fusão (T_F) e temperatura normal de ebulição (T_B) de alguns ácidos graxos.

Ácido Graxo	**Cx:y**	**MM [g.mol^{-1}]**	**ρ [g.cm^{-3}]**	**T_F [ºC]**	**T_B [ºC]**
Láurico	C12:0	200,32	1,007	44	331
Palmítico	C16:0	256,43	0,852	63	390
Oleico	C18:1	282,5	0,895	14	390
Linoleico	C18:2	280,5	0,900	-12	408
Linolênico	C18:3	278,4	0,916	-12	408

Fonte: extraído de Firestone, 2006.

De acordo com a Tabela 2.1-4, os ácidos graxos comumente presentes nos óleos vegetais – oleico e linoleico – possuem uma massa molar e uma massa específica muito próximas, sendo essas, além da configuração molecular (tamanho da cadeira carbônica e instaurações) as principais propriedades envolvidas na solubilização de diferentes compostos (como no caso da extração líquido-líquido); já a propriedade de temperatura de ebulição é de grande importância para processos de separação que envolvem a volatilidade dos compostos, como a destilação. A Tabela 2.1-5 sumariza a composição em ácidos graxos de diversos óleos vegetais provenientes de grãos, frutos e cereais.

Tabela 2.1-5: Composição em ácidos graxos e massa específica de diferentes óleos vegetais.

Óleos vegetais	**Ácidos graxos saturados (g.100g^{-1})**			**Ácidos graxos insaturados (g.100g^{-1})**				**Massa específica [g.cm^{-3}] (25 °C)**
	Láurico C12:0	*Palmítico C16:0*	*Total*	*Oleico C18:1*	*Linoleico C18:2*	*Linolenico C18:3*	*Total*	
Babaçu	40 - 55	5 - 11	54	9 - 20	1 - 7	–	19	0,914 - 0,917
Coco	45 - 51	8 - 10	56	5 - 10	1 - 2	–	9	0,908 - 0,921
Girassol	–	5 - 8	7	13 - 40	48 - 74	–	88	0,918 - 0,923
Canola	–	2 - 6	4	8 - 60	11 - 23	5 - 13	60	0,910 - 0,920
Soja	–	10 - 13	12	18 - 29	50 - 57	6 - 10	85	0,919 - 0,925
Algodão	–	18 - 26	22	14 - 22	56 - 62	–	77	0,918 - 0,926
Amendoim	–	8 - 14	11	36 - 67	14 - 43	–	80	0,914 - 0,917
Óleo de Uva	–	6 - 11	9	12 - 28	58 - 78	–	88	0,923 - 0,926
Gergelim	–	8 - 10	9	34 - 44	40 - 51	0,3 - 0,7	85	0,915 - 0,923
Castanha do Brasil	–	14 - 16	15	29 - 48	30 - 47	–	77	0,910 - 0,912
Nozes de Macadamia	–	8 - 9	9	56 - 59	2 - 3	–	60	0,909 - 0,915
Gérmen de trigo	–	12 - 20	16	13 - 23	50 - 59	2 - 9	78	0,925 - 0,933
Farelo de arroz	–	16 - 28	22	38 - 48	16 - 36	0,5 - 2	69	0,916 - 0,921
Óleo de milho	–	9 - 17	13	20 - 42	40 - 66	0,5 - 1,5	84	0,917 - 0,925
Óleo de palma	–	40 - 48	44	36 - 44	7 - 12	–	50	0,891 - 0,899
Azeite de oliva	–	8 - 20	14	55 - 83	4 - 21	0 - 1,5	82	0,910 - 0,916
Jatropha Curcas	–	3 - 17	10	34 - 64	18 - 45	–	81	0,914 - 0,917

Fonte: extraído de Firestone, 2006.

Como apresenta a Tabela 2.1-5, os óleos de girassol, soja, algodão, amendoim, uva, gergelim, castanha do Brasil, gérmen de trigo, milho e o azeite de oliva possuem praticamente 80g/100g dos ácidos graxos oleico (C18:1) e linoleico (C18:2). Além disso, constata-se a grande similaridade da massa específica entre os diversos óleos vegetais, propriedade de extrema importância em processos de separação como a extração líquido-líquido.

Outro fator importante concernente à composição dos óleos vegetais é a variação do perfil de ácidos graxos em função de condições climáticas e do período de cultivo das plantas oleaginosas (ONEMLI, 2010; SINGH e GULERIA, 2013). Além dos triacilgliceróis, a composição em tocoferóis também é altamente afetada, sendo a taxa do amadurecimento da semente – a qual é sobretudo função do clima – o principal fator interferente na concentração destes compostos (KODAD et al., 2011, 2014). Em climas frios, há um decréscimo na taxa de amadurecimento da semente propiciando a formação de ácido linoleico; em climas quentes, há o favorecimento da formação de ácido oleico. Não obstante a alteração da composição dos óleos vegetais, a razão tocoferol/ácido graxo se mantém praticamente inalterada (IZQUIERDO et al., 2007). Além de efeitos climáticos, ionização, radiação e agente mutagênico químico também podem alterar a composição dos ácidos graxos nos óleos vegetais (LALAS et al., 2007), obtendo-se assim, óleos provenientes da mesma oleaginosa com diferentes composições e, consequentemente, diversas aplicações (GUNSTONE, 2013).

2.1.2.2 Materiais insaponificáveis

Uma pequena fração da composição dos óleos vegetais é representada por materiais insaponificáveis. Esses compostos, os quais podem conferir ao óleo efeitos desejáveis ou indesejáveis, possuem extrema importância em relação ao uso e à qualidade dos óleos vegetais. Entre os principais compostos minoritários dos óleos vegetais, tem-se: esteróis, os quais podem constituir a maior fração de material insaponificável dos óleos vegetais (até 1% em massa) (FIRESTONE, 2006); pigmentos, como carotenoides e clorofilas (HEREDIA et al., 2010); fosfolipídios, os quais, além de possuírem propriedades emulsificantes, podem conferir cor e sabor ao óleo se não forem removidos de forma eficiente (DUNFORD, 2012); compostos fenólicos, como os ácidos vanílico e cafeico, os quais contribuem para a estabilidade oxidativa dos óleos (PURCARO et al., 2016); tocoferóis (vitamina E), compostos que existem como quatro homólogos (α, β, γ, δ) e possuem propriedades antioxidantes e anticancerígenas (DAS GUPTA e SUH, 2016; PURCARO et al., 2016); traços de metais, como cobre, ferro, manganês e níquel, os quais são iniciadores da oxidação dos óleos vegetais (FARZIN e MOASSESI, 2014); contaminantes, como pesticidas e 3-MCPD (ZAYATS et al, 2016; STADLER, 2015); e os produtos da oxidação, como aldeídos, hidrocarbonetos, ácidos carboxílicos e cetonas, indesejáveis nos óleos vegetais por gerarem odor e sabor desagradáveis (SGHAIER et al., 2016).

2.2 OXIDAÇÃO DOS ÓLEOS VEGETAIS

A reação de oxidação é uma das causas da degradação dos óleos vegetais e resulta na formação de uma série de compostos que alteram principalmente o odor, o sabor e a textura dos óleos vegetais, conferindo a esses o aspecto de rancidez (ESKIN e HOEHN, 2013). Essa reação pode ocorrer de diferentes formas, como: rancificação por oxidação enzimática (lipoxigenases); rancificação por hidrólise enzimática (lipases, hidrolases); rancificação por foto-oxidação (reação com oxigênio singlete); e rancificação por radicais livres (reação com oxigênio triplete).

A oxidação ocorre em diferentes situações, como na estocagem do óleo bruto, no refino (como na etapa de clarificação e desodorização), na prateleira e durante a fritura (MATTHÄUS, 2010; WANG et al., 2016), sendo influenciada por fatores como: concentração de oxigênio, temperatura, luz e composição do óleo vegetal em triacilgliceróis e antioxidantes (RAMÍREZ et al., 2001; GILLAT, 2001; OAKLEY et al., 2018). A reação acontece essencialmente nos ácidos graxos insaturados que compõem os óleos vegetais, como naqueles esterificados às moléculas de glicerol (mono-, di-, e triacilgliceróis) (MAHUNGU et al., 1999), nos AGs dos fosfolipídios, das ceras e nos próprios ácidos graxos livres (CHOE e MIN, 2006). Outro fator importante é a susceptibilidade dos ácidos graxos sofrerem a oxidação em função de suas insaturações. Assim, há uma grande variação da taxa da reação de oxidação para os diferentes óleos vegetais, ocorrendo na proporção de 1:12:25 para os AGs C18:1, C18:2 e C18:3, respectivamente (WHITE, 2000). Quando se trata dos ácidos graxos saturados, a presença desses praticamente não altera a taxa de oxidação. Além da composição dos óleos vegetais em ácidos graxos, outro fator que altamente influencia a oxidação e, consequentemente, seus produtos, é a presença de compostos anti e pró oxidantes, os quais diminuem ou aumentam a taxa da reação, respectivamente (REISCHE et al., 2002, CHEN et al., 2011).

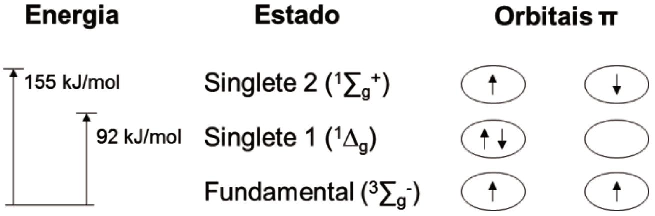
Portanto, devido à variação de todos esses fatores, em destaque a grande faixa de composição em ácidos graxos dos óleos vegetais, uma grande variabilidade de compostos é formada pela reação de oxidação (GILLAT, 2001). Para representar a reação de oxidação, mecanismos teóricos foram elaborados para descrever as etapas que ocorrem na degradação dos óleos vegetais e a consequente formação dos compostos organolépticos (SCHAICH, 2005).

2.2.1 Mecanismos e produtos da reação de oxidação lipídica

A reação de oxidação acontece quando há a presença de um iniciador (etapa de iniciação), o qual forma o O_2 singlete, o qual é um estado extremamente reativo da molécula de oxigênio (CHOE e MIN, 2006; HALVORSEN e BLOMHOFF, 2011). Assim, há a abstração de um hidrogênio adjacente à dupla ligação do ácido graxo acarretando na formação de radicais livres e, consequentemente, em uma reação autocatalítica, a qual se auto-acelera e autopropaga (SCHAICH, 2005).

Como a oxidação não é uma reação termodinamicamente espontânea, a presença do iniciador é fundamental para ocorrer a degradação dos lipídios. Desta forma, o oxigênio fundamental (triplete) não possui energia suficiente para quebrar a molécula do ácido graxo, sendo o iniciador responsável pelo início da reação (SCHAICH, 2005). O iniciador comumente é luz, calor ou metais, os quais interagem com o oxigênio desemparelhando seus *spins* da camada de valência, deixando-o em seu estado excitado (CHOE e MIN, 2006; OAKLEY et al., 2018). A esquematização da formação do O_2 singlete a partir do triplete está apresentada na Figura 2.2-1.

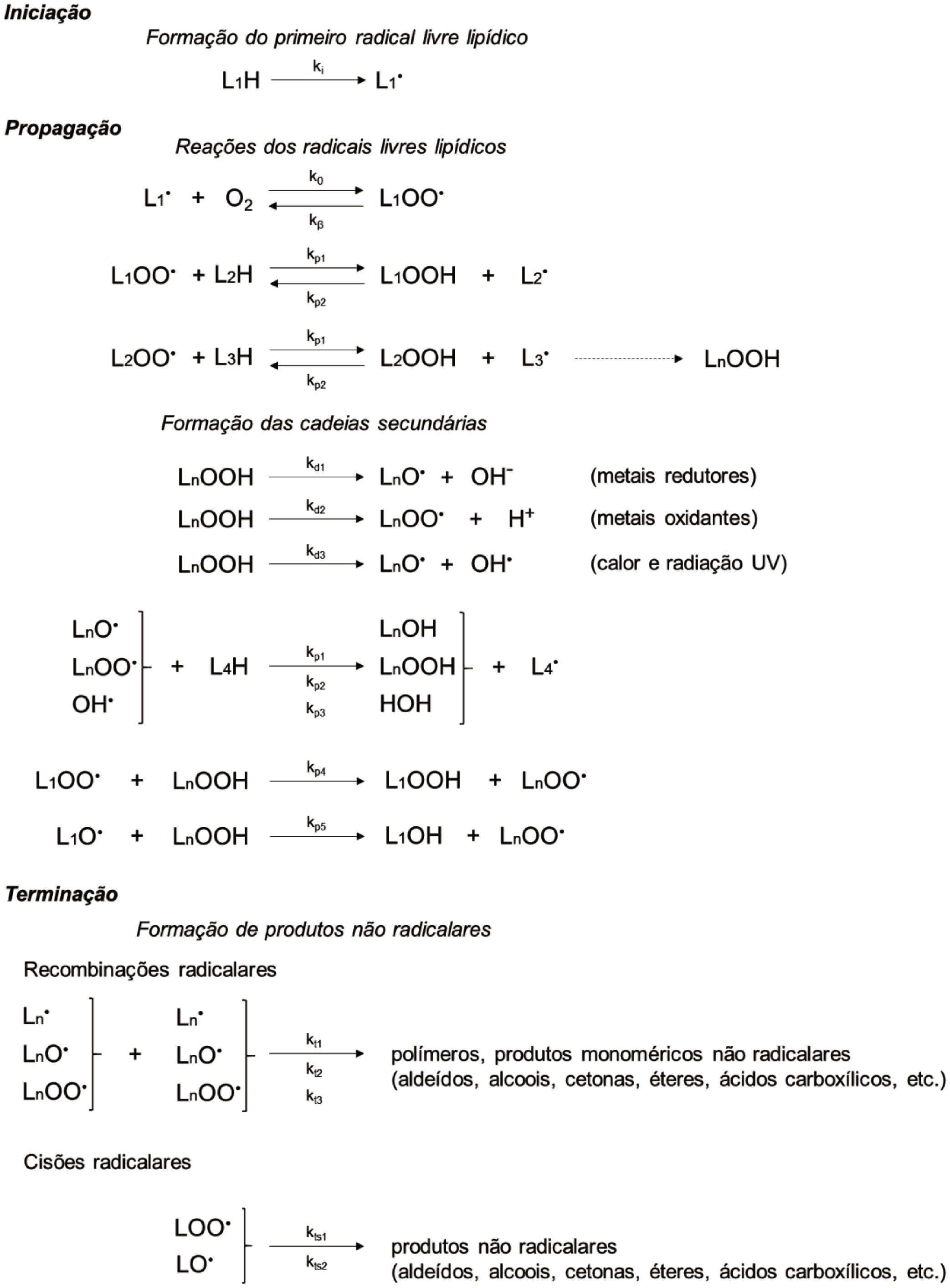
Figura 2.2-1: Formação do oxigênio singlete.



Fonte: própria autoria.

Após a formação do oxigênio singlete, um hidrogênio do AG é abstraído e forma-se o primeiro radical livre (etapa de iniciação), o qual reage com outros ácidos graxos formando os primeiros hidroperóxidos (produtos primários da oxidação) (PESSOA, 2010; OAKLEY et al., 2018). A etapa de iniciação é caracterizada por um baixo consumo de O_2, baixa formação de hidroperóxidos e um aumento significativo na concentração dos radicais livres. Subsequentemente, inicia-se a etapa de propagação (reação dos radicais livres), formando uma série de compostos intermediários, além dos próprios hidroperóxidos, que variam conforme o tempo e as condições reacionais (GUILLEN e GOICOECHEA, 2008). Os hidroperóxidos são extremamente instáveis e reativos, degradando outros ácidos graxos e formando mais radicais livres. Nessa etapa, há um alto consumo de O_2, uma alta formação de hidroperóxidos e iniciamse as alterações organolépticas como o odor e o sabor (SHAHIDI e ZHONG, 2005; VIEIRA et al., 2017). Por fim, quando a reação entre os radicais livres ou hidroperóxidos formam os produtos secundários da oxidação, inicia-se a etapa de terminação. Assim, diminui-se o consumo de O_2 e a concentração de hidroperóxidos e há a formação de uma série de compostos voláteis ou não voláteis, interferindo drasticamente na palatabilidade dos óleos vegetais (DUARTE e QUINTANAR, 2009; KIRALAN e RAMADAN, 2016). A Figura 2.2-2 apresenta as etapas da reação de oxidação dos óleos vegetais.

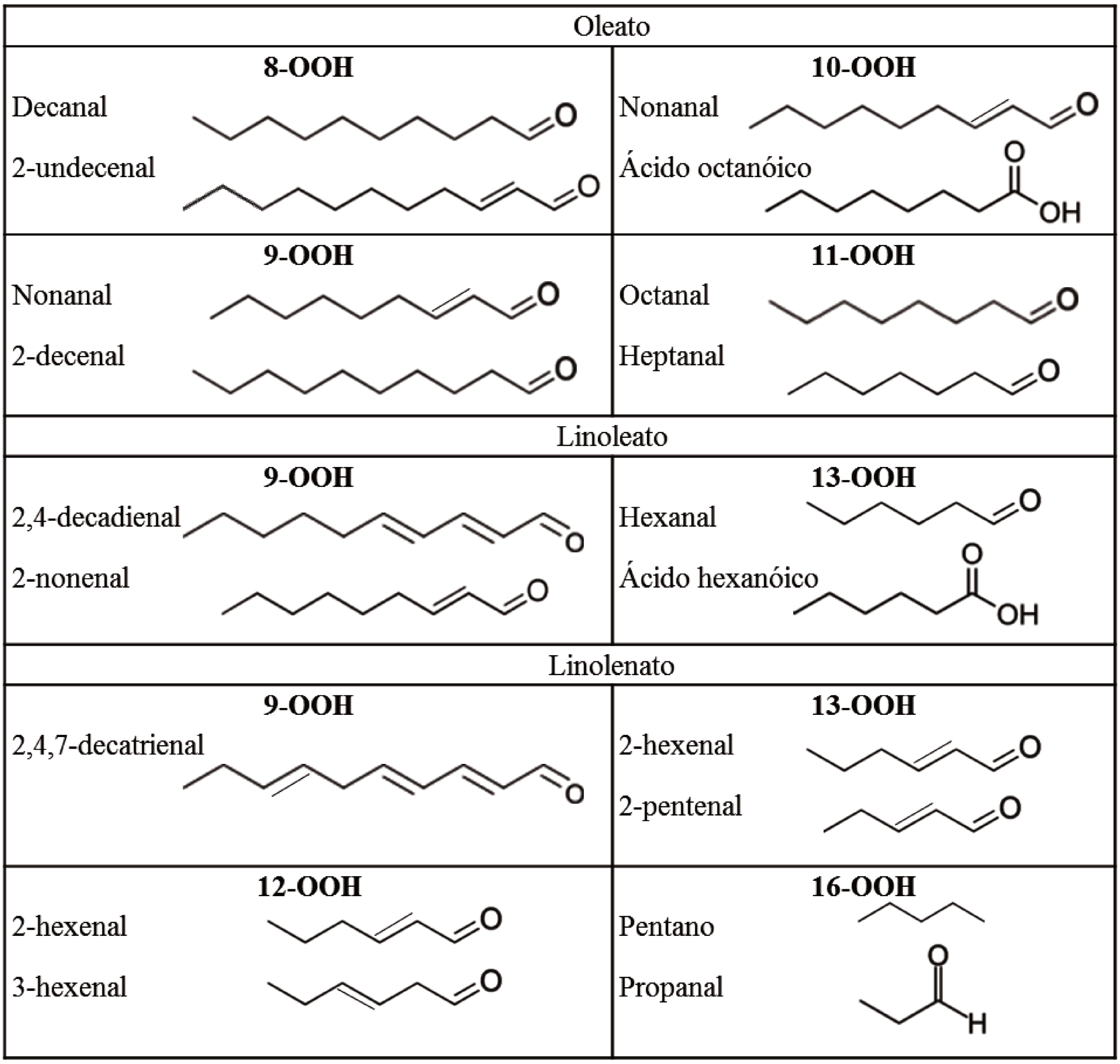
Figura 2.2-2: Mecanismo teórico da reação de oxidação lipídica por radicais livres.



Fonte: adaptado de Schaich, 2005.

Na Figura 2.2-2, L_nH e L_nOOH representam, respectivamente, o ácido graxo ou seu éster e o hidroperóxido, e $Ln^•$, $LOO^•$ e $LO^•$ os radicais alquila, peroxila e alcoxila, respectivamente. Como pode ser observado na Figura 2.2-2, a abstração de apenas um hidrogênio da molécula de ácido graxo insaturado forma um grande número de outros radicais livres, os quais rapidamente propagam a reação e, consequentemente, a degradação dos óleos vegetais. A Figura 2.2-3 apresenta alguns compostos resultantes da degradação de diferentes hidroperóxidos provenientes dos ácidos graxos oleico (C18:1), linoleico (C18:2) e linolênico (C18:3).

Figura 2.2-3: Produtos secundários da oxidação lipídica de diferentes hidroperóxidos gerados a partir dos ácidos graxos oleico, linoleico e linolênico.



Fonte: própria autoria.

Como observa-se na Figura 2.2-3, os aldeídos possuem significativa representatividade frente aos compostos formados na oxidação lipídica. Sendo os ácidos graxos oleico e linoleico os principais constituintes de grande parte dos óleos vegetais, os compostos hexanal, 2,4-decadienal, heptanal, 2-nonenal, nonanal e 2-decenal são encontrados em vários óleos, como o de girassol, de soja, de milho e de canola (WANG et al., 2016; KIRALAN e RAMADAN, 2016; OAKLEY et al., 2018). Além de indicarem a ocorrência da reação de oxidação, o perfil de aldeídos, cetonas, álcoois e outros é amplamente utilizado para a detecção de adulteração em óleos vegetais, como no caso do azeite de oliva (MILDNER-SZKUDLARZ e JELEŃ, 2010).

Outra questão importante é que os próprios compostos formados pela oxidação (aldeídos, cetonas, álcoois, etc.) podem sofrer alterações pela presença dos radicais livres (MARMESAT, 2009). Desta forma, compostos como ácidos carboxílicos podem vir a contribuir às propriedades organolépticas dos óleos vegetais, como os ácidos hexanóico, octanóico e octenóico (HU e JACOBSEN, 2016). Quando há essas alterações nos grupos funcionais das moléculas, 99,3% do hexanal oxidado forma ácido hexanóico, 97,5% do octanal forma ácido octanóico e 78,2% do 2-octenal forma ácido octenóico. Também essas alterações podem ocorrer apenas em relação ao tamanho da molécula, como no caso do 2,4-decadienal; quando esse reage com algum radical livre, 49,5% dos produtos é o n-hexanal (PRZYBYLSKI e ESKIN, 1995), importante composto utilizado na detecção da reação de oxidação lipídica.

Em relação à palatabilidade dos óleos vegetais, a contribuição dos produtos da oxidação está diretamente relacionada com a volatilidade e com o valor de limiar de odor e sabor – concentração necessária do composto para detecção de odor ou sabor (WHITE, 2000; HO e SHAHIDI, 2005). Assim, por possuírem um baixo valor de limiar de odor e sabor, os aldeídos e cetonas contribuem altamente a esses dois aspectos, influenciando drasticamente a aparência e sabor dos óleos. Também, os hidrocarbonetos, como o pentano, por ser muito volátil e apresentar um baixo valor de limiar de odor, é muitas vezes utilizado para a detecção de oxidação em óleos vegetais; porém suas contribuições ao sabor e à rancidez dos óleos vegetais são praticamente insignificantes (KALUA et al., 2007).

Desta forma, por diminuírem a qualidade sensorial dos óleos vegetais, os compostos da oxidação devem ser removidos dos óleos vegetais, sendo essa remoção atualmente realizada por processo de esgotamento utilizando vapor d'água como agente de arraste.

2.3 REFINO DOS ÓLEOS

O refino dos óleos vegetais é necessário a fim de remover compostos indesejáveis presentes no material bruto, tornando-o comestível (DUNFORD, 2012). Assim, o óleo extraído da oleaginosa utilizando um solvente passa por uma série de etapas de separação física ou química, as quais resultam em um produto com maior aceitação dos consumidores (FARR, 2013). Todavia, as condições operacionais aplicadas às etapas do refino, bem como os agentes de separação utilizados na remoção dos compostos indesejáveis acarretam na perda de compostos nutracêuticos, diminuindo, consequentemente, o valor nutricional dos óleos vegetais refinados (CMOLIK e POKORNY, 2000; EL-MALLAH et al., 2011).

O refino dos óleos vegetais brutos pode ser feito de duas maneiras, as quais dependem da quantidade de ácidos graxos livres e fosfolipídios presentes no material (JOHNSON, 2000). Desta forma, óleos vegetais que apresentam uma baixa quantidade desses compostos são desacidificados quimicamente, e aqueles que contém uma alta quantidade são desacidificados fisicamente (SULIMAN et al., 2013). Assim, o refino ocorre basicamente nas seguintes etapas:

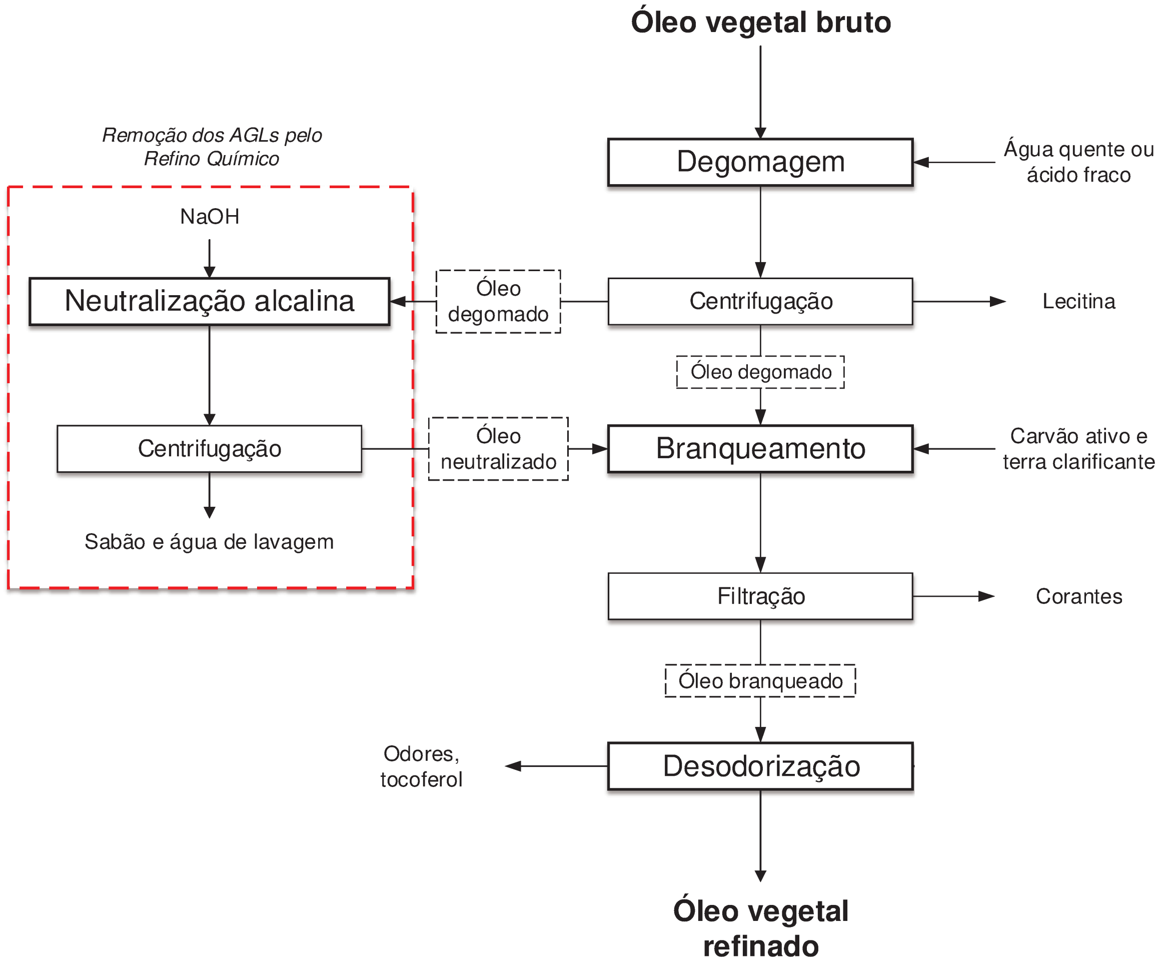
a) degomagem: através de lavagem com água (agente de degomagem) com um composto quelante – comumente ácido fosfórico, ácido cítrico, ácido málico ou outros agentes – remove principalmente fosfolipídios, proteínas e outros compostos coloidais presentes no óleo vegetal bruto (FARR, 2013). Pela centrifugação da mistura, obtém-se como principal subproduto a lecitina do óleo, a qual possui alto valor comercial agregado (SHAHIDI, 2013). Quando é aplicado o refino químico, o óleo degomado é submetido à etapa de neutralização; já para o refino físico, o óleo degomado é subsequentemente clarificado;
b) neutralização: para óleos com baixo teor de acidez, a remoção dos ácidos graxos livres é realizada pela adição de uma solução alcalina, comumente a soda cáustica. Assim, os AGLs são convertidos em sabões, os quais são posteriormente separados por centrifugação (HAMM e HAMILTON, 2000). Devido à grande quantidade de sabão que é formada pela neutralização de um óleo vegetal bruto com alto teor de acidez e, consequentemente, a decorrente perda de óleo vegetal neutro pelo arraste deste pelo sabão, os AGLs desses óleos são removidos por esgotamento (etapa concomitante à desodorização) no refino físico;
c) clarificação: os compostos que conferem cor aos óleos vegetais – além de traços de metais, sabão proveniente do refino químico e contaminantes (pesticidas e hidrocarbonetos aromáticos policíclicos) – são removidos através da adsorção em uma mistura de carvão ativado e argilas naturais, denominada como terra branqueadora (ZSCHAU, 2000). Ocasionalmente, são adicionadas às terras branqueadoras alumina, ácido silícico, silicato de alumínio/magnésio, sílica gel ou silicatos sintéticos (DUNFORD, 2012). Após a clarificação, o óleo é então filtrado e submetido à etapa de desodorização;

d) desodorização: no refino químico, essa etapa é aplicada para a remoção de compostos da oxidação (os quais conferem odor e sabor) e traços de pesticidas através de uma corrente de vapor de arraste em um processo de esgotamento (GREYT e KELLENS, 2005). Quando é aplicado o refino físico, além dos compostos supracitados, a desodorização/desacidificação física remove também os AGLs. Frente às demais etapas do refino dos óleos vegetais, a desodorização é aquela que opera com as condições de temperatura e pressão mais drásticas, acarretando em perdas de compostos nutracêuticos, degradação dos triacilgliceróis e formação de ácidos graxos com isomeria *trans* e dos contaminantes clorados 3-MCPD (TASAN e MEHMET, 2003; ERMACORA e HRNCIRIK, 2014).

A Figura 2.3-1 apresenta a esquematização do refino químico dos óleos vegetais brutos. Já a

Tabela **2.3-1** apresenta as condições operacionais e os agentes de separação utilizados nas etapas de degomagem, neutralização, clarificação e desodorização.

Figura 2.3-1: Esquematização do refino químico de óleos vegetais.



Fonte: própria autoria.

Tabela 2.3-1: Condições operacionais das etapas envolvidas no refino dos óleos vegetais.

Etapa do refino	**Condições operacionais**		**Agente de separação**
	Temperatura [°C]	*Pressão [mmHg]*	
Degomagem	90	760	Água e ácido fraco
Neutralização	50	760	Soda cáustica
Branqueamento	90 – 125	50 – 125	Terra branqueadora
Desodorização	260	3	Vapor d'água

Fonte: extraído de Hamm e Hamilton, 2000.

Como pode ser constatado, a desodorização é a etapa que envolve as condições operacionais de temperatura e pressão mais drásticas, alterando consideravelmente a composição dos óleos vegetais durante o processamento.

2.3.1 Alteração dos óleos vegetais durante a desodorização

Devido às condições drásticas da desodorização, além dos compostos tipicamente volatilizados durante esse processo, uma série de outros compostos são removidos ou sofrem reações químicas (KELLENS e GREYT, 2000; FINE et al., 2015). Desta forma, a desodorização pelo processo de esgotamento é considerada uma etapa crítica do refino dos óleos vegetais, requerendo alto consumo de energia e diminuindo a qualidade do produto final. O Quadro 2.3-1 sumariza alguns compostos removidos/degradados durante a etapa da desodorização.

Quadro 2.3-1: Compostos removidos física ou quimicamente durante a desodorização dos óleos vegetais.

Remoção física	
Parcialmente removidos	Tocoferóis, esteróis, pesticidas, hidrocarbonetos aromáticos policíclicos, monoacilgliceróis
Removidos a níveis aceitáveis	Compostos de odor e sabor
Quase completamente removidos	Ésteres metílicos/etílicos
Reações Químicas	
Parcialmente decompostos	Ácidos graxos oxidados, carotenoides, hidroperóxidos
Completamente decompostos	Sabões
Formação do 3-MCPD	Compostos clorados e DAG e MAG
Isomerização *cis-trans*	Ácidos graxos insaturados

Fonte: adaptado de Brench (2002)

Em relação aos compostos organolépticos, os aldeídos, sob condições típicas de operação, normalmente apresentam fatores de remoção de 10^4 a 10^5, alcançando níveis desejáveis de detecção sensorial (BRENCH, 2002). Também, o tempo necessário para a remoção dos compostos que alteram a palatabilidade dos óleos vegetais durante a desodorização é de cerca de 1 hora, sendo constatado que durante essa etapa do refino, os óleos vegetais sofrem a oxidação por radicais livres, formando ainda mais produtos secundários da oxidação (HO e SHAHIDI, 2005).

Concernente aos pesticidas, os compostos organoclorados são comumente encontrados nos óleos vegetais brutos e frequentemente apresentam uma remoção de aproximadamente 70% quando aplicada a desodorização em batelada (BRENCH, 2002). Já para a desodorização em processo semicontínuo, esses contaminantes são removidos à níveis de concentração que não são detectados (MIYAHARA e SAITO, 1993). Porém, vale salientar que os óleos vegetais refinados apresentam traços de pesticidas, pois o refino do material bruto não é capaz de removê-los completamente. Além dos pesticidas, outros contaminantes removidos durante a desodorização são os hidrocarbonetos aromáticos policíclicos (HAPs), os quais são carcinogênicos e, consequentemente, precisam ser removidos dos óleos vegetais durante o processamento (BRENCH, 2002). Esses compostos são encontrados principalmente no óleo de coco e, eventualmente, nos óleos de canola e de semente de girassol (HOSSAIN e SALEHUDDIN, 2012). Durante a desodorização, aproximadamente 80% dos HAPs de cadeia carbônica curta (compostos mais leves) são removidos, enquanto os HAPs de maior massa molar necessitam ser removidos por adsorção em carvão ativado (BRENCH, 2002).

Outro composto que é parcialmente removido durante a desodorização é o tocoferol, sendo encontrado no destilado da coluna de desodorização frações dos quatro isômeros desse antioxidante (α-, β-, γ- e δ-tocoferol) (SULIMAN et al., 2013). Quanto ao refino do óleo de soja – o qual apresenta significativa quantidade de tocoferol – o destilado deste óleo serve como uma fonte natural de vitamina E, o qual pode ser adicionado em outros produtos (alimentos, cosméticos, entre outros) ou comercializado de forma isolada, apresentando alto valor agregado (OLIVEIRA et al., 2005). Pode-se considerar que um óleo de soja desodorizado de forma adequada resulta em um destilado contendo cerca de 900 – 1000 $mg \cdot kg^{-1}$ de tocoferol (BRENCH, 2002).

Por fim, recentemente foi verificado que a etapa de desodorização é a principal contribuinte para a formação de contaminantes clorados, principalmente os 3-MCPD (ZULKURNAIN et al., 2012). Esses compostos são provenientes de reações entre os acilgliceróis parciais (mono e diacilglicerol) com compostos clorados presentes nos agentes de separação utilizados durante o refino, como no hidróxido de sódio, ácido fosfórico, ácido cítrico e na sílica ácida (ERMACORA e HRNCIRIK, 2014). Também, constatou-se que a temperatura é o principal parâmetro de operação que afeta a formação dos 3-MCPD, o que instiga a investigação de um processo de desodorização operado à temperaturas próximas às ambientes (FREUDENSTEIN et al., 2013).

2.4 EXTRAÇÃO LÍQUIDO-LÍQUIDO

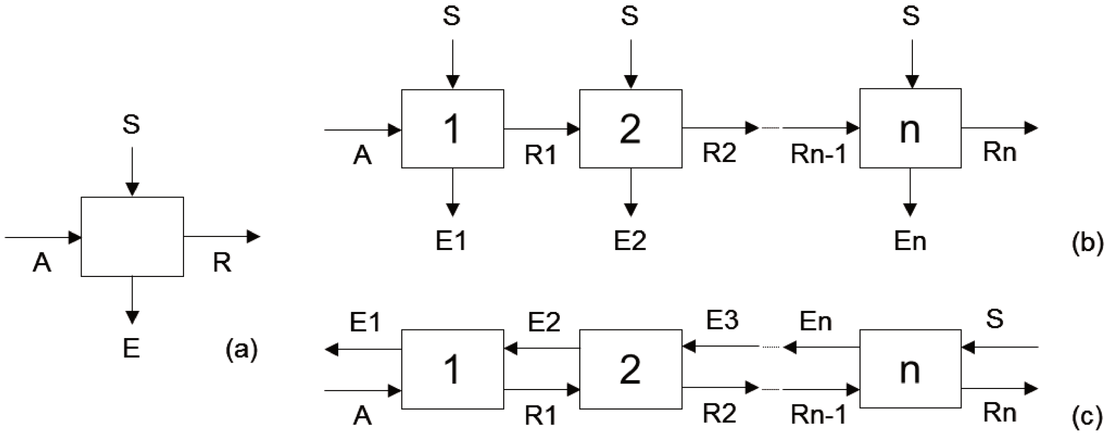
Dentre as operações unitárias de separação, um dos métodos amplamente aplicado nas indústrias química, alimentícia e farmacêutica é a extração líquido-líquido (SEADER e HENLEY, 1998; MOLDOVEANU e DAVID, 2015). Normalmente operando em condições próximas às ambientes (temperatura e pressão), esse processo é uma alternativa aos métodos de separação (como a destilação e o esgotamento) que apresentam limitações operacionais frente à mistura a ser separada, como: a baixa volatilidade relativa entre os compostos do sistema; a formação de pontos azeotrópicos; substâncias inorgânicas dissolvidas em soluções orgânicas ou aquosas; e a susceptibilidade de degradação dos componentes pela alta temperatura de operação (BRUNT, 2004).

O processo de extração líquido-líquido consiste na separação de um composto (soluto) diluído em sua matriz líquida (diluente) utilizando um outro líquido (solvente), sendo o solvente determinado visando extrair o soluto solubilizando minimamente o diluente (LO e BAIRD, 2001; ZHANG e HU, 2013). Para isso, os compostos são colocados em contato em um determinado número de estágios dependendo de parâmetros como a recuperação de soluto desejada e a seletividade do solvente (FOUST, 1980). Desta forma, a extração líquido-líquido pode operar de três maneiras:

a) em um único estágio: o contato íntimo da mistura é promovido em um tanque agitador-misturador. Essa configuração é aplicada para sistemas que possuem uma quantidade de soluto muito diluída, tendo como vantagens o bom contato entre as fases, alta eficiência e como desvantagens o alto investimento e alto consumo energético (SEADER e HENLEY, 1998);
b) em multiestágios cruzados: nessa configuração, através de colunas de pratos ou de recheio, a fase rafinado é novamente misturada com solvente puro em cada estágio tantas vezes quantas forem necessárias para extrair o soluto até atingir a pureza do diluente desejada (GEANKOPLIS, 2003). Embora apresente uma eficiência menor que a extração por multiestágios contracorrente, a alimentação de um solvente puro a cada estágio da separação permite ter uma distribuição de diferentes solutos nas diferentes fases extrato, o que é atrativo quando há vários solutos de interesse na mistura (SEADER e HENLEY, 1998);
c) em multiestágios contracorrentes: essa configuração consiste em extrair o soluto desejado através de colunas de pratos ou de recheio, nas quais a alimentação e o solvente são adicionados às extremidades do equipamento. Desta forma, uma corrente ascende a coluna e a outra descende, e o contato entre as fases ocorre em todos os estágios (SEADER e HENLEY, 1998). Essa configuração apresenta como vantagem em relação à de multiestágios cruzadas a obtenção de um gradiente de potencial químico entre as fases mais propício à transferência de massa (FOUST, 1980).

A Figura 2.4-1 apresenta a esquematização das três possíveis configurações utilizadas no processo de extração líquido-líquido.

Figura 2.4-1: Configurações de operação da extração líquido-líquido: (a) em um único estágio; (b) em multiestágios cruzados; (c) em multiestágios concorrentes.



Fonte: própria autoria.

Como pode ser observado na Figura 2.4-1, pelo contato da alimentação (A), composta pelo diluente e pelo soluto, com o solvente (S), há a formação de duas fases, a rafinado (R) e a extrato (E), contendo majoritariamente diluente e solvente, respectivamente. Assim, as correntes de saída do equipamento de extração devem ser tratadas para separar os compostos de interesse, como a purificação do diluente e/ou soluto e a separação do solvente para ser reutilizado na extração (SEADER e HENLEY, 1998). Comumente, o tratamento das correntes é realizado por destilação, a qual tem grande importância frente à seleção do solvente adequado ao processo, como em relação à temperatura normal de ebulição e à volatilidade relativa frente aos demais compostos da mistura (GEANKOPLIS, 2003).

2.4.1 Seleção de Solvente

O solvente utilizado na extração líquido-líquido é o fator que mais interfere na eficiência, otimização e segurança do processo (BYRNE et al., 2016; GIOVANOGLOU et al., 2003). Assim, por um estudo comparativo de diferentes solventes no processo extrativo, obtém-se um solvente (puro ou mistura) que atende a parâmetros e fatores determinantes, como: seletividade e distribuição dos compostos entre as fases, indicados por dados de equilíbrio líquido-líquido, propriedades termofísicas dos compostos (massa específica, tensão superficial, viscosidade, entre outros); e, em especial nas indústrias alimentícia e farmacêutica, especificações relacionadas à periculosidade dos solventes, como toxicidade, flamabilidade e estabilidade (EDEN et al., 2004; BYERNE et al., 2016; DIORAZIO et al., 2016).

O método escolhido para a seleção de um solvente depende significativamente do quanto a mistura está distante da idealidade. Assim, para sistemas que são bem representados por métodos termodinâmicos preditivos, como o UNIFAC (*UNIQUAC Functional-group Activity Coefficients*) (FREDENSLUND et al., 1975) e o ASOG (*Analytical Solution of Groups*) (KOJIMA e TOCHIGI, 1990), a seleção de um solvente adequado ao processo de extração pode ser realizada pela predição de dados de equilíbrio líquido-líquido e das propriedades físicas das diferentes misturas (GANI et al., 1991; PRETEL et al., 1994). Métodos computacionais avançados têm a capacidade de avaliar o equilíbrio de fases de diversos sistemas e indicar um solvente adequado para a purificação desejada (DATTA, 2016; DIORAZIO et al., 2016). No caso de sistemas muito distantes da idealidade – como a mistura óleo vegetal (composto apolar) com solventes orgânicos polares – há a necessidade da coleta de dados experimentais, pois a predição dos dados termodinâmicos por métodos como o UNIFAC pode apresentar desvios significativos (HOSTRUP et al., 1999; KARUNANITHI et al., 2005). Nesses casos, um norteamento inicial pode ser alcançado por métodos qualitativos que avaliam o comportamento de determinada substância quando em contato com outra de diferente espécie química (CUSACK et al., 1991). A fim de exemplificar, a Tabela 2.4-1 apresenta o método qualitativo baseado no comportamento do coeficiente de atividade desenvolvido por Cusack et al. (1991).

Tabela 2.4-1: Método qualitativo baseado no comportamento do coeficiente de atividade para a seleção de solvente.

Soluto (*i*)		**Solvente (*j*)**								
		1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1	Ácido, aromático contendo OH	0	–	–	–	–	0	+	+	+
2	Álcool parafínicos, água, amida ou amina com H ativo	–	0	+	+	+	+	+	+	+
3	Cetona, nitrato aromático, amina terciária, piridina, sulfona, trialquil fosfato	–	+	0	+	+	–	0	+	+
4	Éster, aldeído, carbonato, nitrito ou nitrato, fosfatos, amida sem H ativo	–	+	+	0	+	–	+	+	+
5	Éter, óxido	–	+	+	+	0	–	0	+	+
6	Parafina multi-halogenada com H ativo	0	+	–	–	–	0	0	+	0
7	Aromático, aromático halogenado, olefina	+	+	0	+	0	0	0	0	0
8	Parafina	+	+	+	+	+	+	0	0	0
9	Parafina ou olefina mono-halogenada	+	+	+	+	+	0	0	+	0

O método de Cusack et al. (1991) (Tabela 2.4-1) consiste em comparar o efeito do contato de diferentes substâncias em seus coeficientes de atividade, representados pelo método como efeito positivo (repulsão das moléculas), efeito desprezível e efeito negativo (atração das moléculas). Esta análise pode ser feita considerando-se tanto o par soluto-solvente, quanto o par diluente-solvente, o que possibilita verificar a solubilidade mútua das fases rafinado e extrato, desejando-se que, no caso diluente-solvente, haja um aumento no coeficiente de atividade. Desta forma, almeja-se obter um solvente que diminua o coeficiente de atividade do soluto e que aumente esse parâmetro em relação ao diluente, maximizando a extração do composto desejado e minimizando a solubilização dos componentes chaves das fases em equilíbrio (CUSACK et al., 1991).

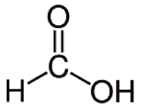
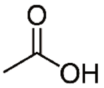
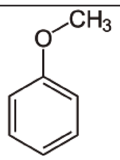
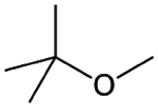
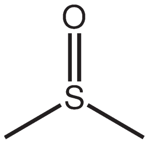
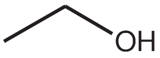
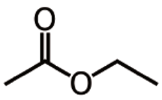
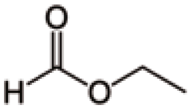
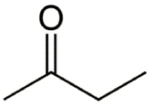
2.4.1.1 Classe de solventes

Levando-se em consideração a necessidade de haver uma conscientização referente aos efeitos causados pelo uso de compostos de alta periculosidade envolvidos nos processos industriais – sobretudo nas indústrias alimentícia e farmacêutica – uma propriedade que tem grande importância e impacto é a toxicidade dos solventes (KERTON, 2009; DIORAZIO et al., 2016). Desta forma, os solventes podem ser classificados em três diferentes classes:

a) Classe 1: compostos que apresentam alta toxicidade e efeitos nocivos ao meio ambiente. Assim, esses compostos apresentam aplicações extremamente restritas, sendo evitados ao máximo principalmente nas indústrias farmacêutica e alimentícia. Dentre esses solventes, tem-se o benzeno, o tetracloreto de carbono e o 1,2-dicloroetano (ICH, 2016);
b) Classe 2: compostos que apresentam toxicidade e efeitos nocivos ao meio ambiente moderados. Esses compostos são aceitáveis em processos industriais quando a quantidade de exposição diária não ultrapassa os limites característicos de cada composto (KERTON, 2009; BYRNE et al., 2016). Dentre esses solventes, tem-se o hexano, o metanol, o etilenoglicol e o tolueno (ICH, 2016);
c) Classe 3: compostos que apresentam baixa toxicidade, baixo impacto ambiental e os menores riscos à saúde humana. São tidos como solventes preferenciais nas indústrias farmacêutica e alimentícia, podendo ser utilizados em diversos processos de separação (RANU, 2010). Dentre esses solventes, tem-se o etanol, o 1-propanol, o acetato de etila, o ácido acético e o éter etílico (ICH, 2016).

Alguns solventes de Classe 2 estão apresentados na Tabela 2.4-2, juntamente com propriedades físicas e seus respectivos diagramas de Hommel (diagrama de risco).

Tabela 2.4-2: Propriedades físicas temperatura normal de ebulição (Tb), massa molar (MM), ponto de fusão (Pf) massa específica (ρ) à 25 °C e o diagrama de Hommel de solventes de baixa toxicidade de acordo com classificações ICH.

Solvente	**Estrutura molecular**	**Propriedades Físicas**				**Diagrama de Hommel**[a]
		T_b [°C]	**MM [g·mol^{-1}]**	**P_f [°C]**	**ρ [g·cm^{-3}]**	
Ácido fórmico		100	46	8,3	1,22	
Ácido acético		118	60	17	1,05	
Anisol		154	108	-37	0,99	
Éter metil-terc-butílico		55	88	-109	0,74	
Dimetilsulfóxido		189	78	19	1,10	
Etanol		78	46	-114	0,79	
Acetato de etila		77,1	88	-84	0,90	
Formato de etila		54	74	-80	0,92	
Metil-etil cetona		80	72	-86	0,81	

[a] Diagrama de Hommel: azul: risco à saúde; vermelho: inflamabilidade; amarelo: reatividade; branco: riscos específicos.

Desta forma, levando em consideração os riscos à saúde humana e os efeitos deletérios ao meio ambiente, tanto resultantes do manuseio dos solventes quanto pela presença de traços desses compostos nos produtos finais, a seleção de um solvente seguro é de grande importância para o processo de extração líquido-líquido, mormente aos processos de separação aplicados à indústria alimentícia, como é o caso do processamento dos óleos vegetais.

2.4.2 Aplicação da extração líquido-líquido no refino de óleos vegetais

Uma série de estudos investigou métodos alternativos às etapas que mais acarretam consumo de energia, degradação e perdas dos óleos vegetais e de compostos nutracêuticos, como a desacidificação e a desodorização. Dentre os processos estudados, a extração líquido-líquido apresenta-se como uma alternativa branda à remoção de ácidos graxos livres (BATISTA et al., 1999b; RODRIGUES et al., 2007), acilgliceróis parciais (FERREIRA et al., 2015) e compostos da oxidação lipídica, como aldeídos (HOMRICH e CERIANI, 2016; JORQUEIRA et al., 2014) e ácidos carboxílicos de cadeia curta (MAY et al., 2016). Operando em condições próximas as ambientes, a extração com um solvente tem como vantagens frente à desacidificação com álcali e à desodorização a menor quantidade de efluentes geradas, menor degradação e perda de compostos nutracêuticos e triacilgliceróis e menor quantidade térmica requerida (RODRIGUES et al., 2006).

Concernente à neutralização, a remoção dos ácidos graxos livres foi estudada pela investigação da solubilidade mútua de diferentes solventes orgânicos na presença de uma mistura contendo óleos vegetais e ácidos graxos livres (CUEVAS et al., 2009; GONÇALVES; MEIRELLES, 2004). Os solventes estudados foram principalmente os álcoois, como o metanol, etanol e isopropanol, os quais apresentaram satisfatórios valores de coeficiente de partição do soluto e de seletividade do solvente, em especial o metanol e o etanol (BATISTA et al., 1999). Pelas vantagens do etanol frente o metanol, como a menor toxicidade e maior acessibilidade, vários estudos determinaram os dados de equilíbrio líquido-líquido de misturas contendo diferentes óleos vegetais, diferentes ácidos graxos livres, diferentes graus de hidratação do etanol e diferentes temperaturas (GONÇALVES et al., 2016; OLIVEIRA et al., 2012; MOHSEN-NIA et al., 2008; CHIYODA et al., 2010). Além disso, a desacidificação com etanol hidratado foi realizada em escala laboratorial em uma coluna de pratos rotativos (PINA e MEIRELLES, 2000; RODRIGUES et al., 2014). Recentemente, a remoção de ácidos graxos livres também foi investigada utilizando solventes eutéticos. A extração de ácido palmítico do óleo de palma foi realizada utilizando misturas de betaína monoidratada com diferentes compostos doadores de pontes de hidrogênio, como glicerol e propilenoglicol, e apresentou uma eficiência de aproximadamente 50%. Além da avaliação do coeficiente de distribuição do soluto, o processo de separação foi otimizado utilizando metodologia de superfície de resposta (ZAHRINA et al. 2017; ZAHRINA e MULIA, 2018).

Atinente à remoção dos produtos secundários da oxidação lipídica, dados de equilíbrio líquido-líquido envolvendo compostos odoríferos (aldeídos e ácidos carboxílicos de cadeia curta), óleo de semente de girassol e solventes foram coletados (HOMRICH e CERIANI, 2016; JORQUEIRA et al., 2014; MAY et al., 2016). Aldeídos, como hexanal e 2-nonenal, e ácidos carboxílicos, como os ácidos valérico e caprílico, foram removidos utilizando-se etanol anidro como solvente. Além disso, a remoção de heptanal com lactato de etila foi estudada. O etanol anidro apresentou bom coeficiente de partição para os solutos e boa seletividade, extraindo os compostos de forma satisfatória a temperatura de 25 °C (HOMRICH e CERIANI 2016). Já para o sistema contendo lactato de etila, por esse solvente apresentar uma solubilidade maior com o óleo, uma região de separação menor foi obtida, necessitando-se, assim, operar em uma temperatura menor (20 °C) (JORQUEIRA et al., 2014). Tais estudos confirmam a possibilidade de remover compostos da oxidação lipídica pelo contato com um solvente líquido, instigando a investigação de dados de equilíbrio líquido-líquido envolvendo óleos vegetais e diferentes solventes (puro ou mistura) e que apresentem-se adequados para a remoção dos compostos atualmente removidos na desodorização.

2.5 EQUILÍBRIO DE FASES

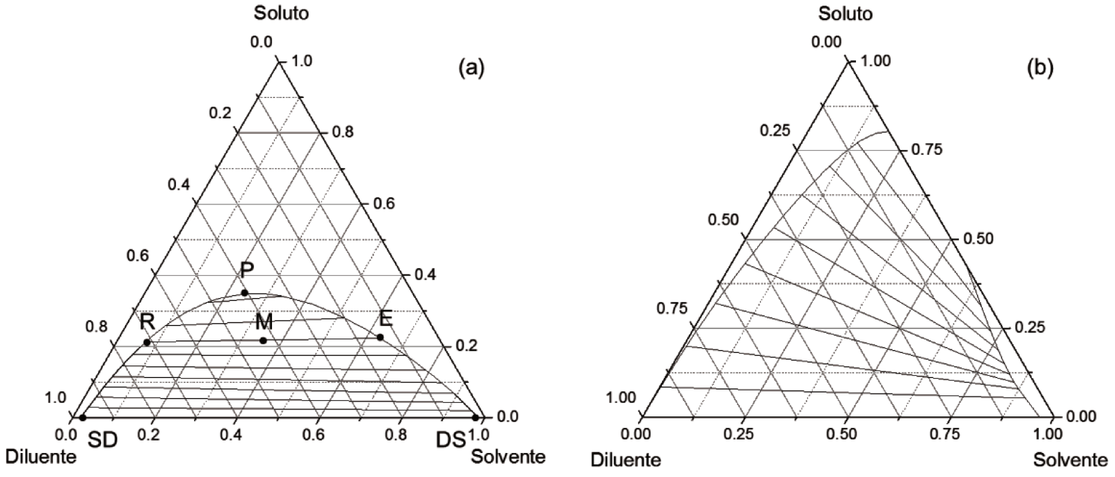
O equilíbrio de fases faz-se presente em vários processos industriais de separação, como na destilação, na absorção, na lixiviação, e na extração líquido-líquido (GEANKOPLIS, 2003). Assim, sendo conhecido o equilíbrio termodinâmico entre as fases em contato envolvidas nesses processos, há a possibilidade de projetar equipamentos de separação, modelar e otimizar o processo (HENLEY e SEADER, 1981).

Quando se trata da extração líquido-líquido, sabendo-se que esse processo comumente envolve o tratamento das fases rafinado e extrato por destilação, o conhecimento do equilíbrio líquido-líquido e líquido-vapor é essencial para determinar parâmetros e fatores como: melhor solvente para realizar a extração; número de estágios necessários para a extração e para as conseguintes purificações das fases resultantes; e dimensionamento dos equipamentos de separação (SEADER e HENLEY, 1998; ZHANG e HU, 2013). O equilíbrio de fases pode ser representado por diagramas, os quais facilitam a visualização da solubilidade mútua dos compostos envolvidos na mistura em uma determinada temperatura e pressão.

2.5.1 Diagramas do equilíbrio de fases líquido-líquido

Os diagramas de equilíbrio líquido-líquido são comumente representados em coordenadas triangulares, trazendo as composições de uma mistura ternária distribuída entre duas fases em equilíbrio (MATOUS, 2005). Assim, estes diagramas informam o tamanho da região heterogênea da mistura, como o solvente e o diluente se distribuem nas correntes rafinado e extrato, respectivamente, bem como informam a distribuição do soluto em ambas as fases (DEMIREL, 2007). A Figura 2.5-1 apresenta os diferentes tipos de diagramas do equilíbrio líquido-líquido que são obtidos dependendo da solubilidade mútua dos compostos envolvidos.

Figura 2.5-1: Diagramas ternários de equilíbrio líquido-líquido: (a) Tipo I; (b) Tipo II.



Fonte: própria autoria.

De acordo com a Figura 2.5-1, o diagrama do tipo I possui apenas um par parcialmente solúvel, já o do tipo II possui dois pares parcialmente solúveis. Na prática, o diagrama do tipo I é o mais comum, sendo este descrito da seguinte maneira:

a) a curva $\overline{SDRPEDS}$ delimita as regiões homogênea (acima da curva) e heterogênea (abaixo da curva);
b) os pontos DS e SD identificam, respectivamente, a solubilidade de diluente no solvente e do solvente no diluente;
c) o ponto M traz a composição de uma mistura heterogênea, a qual se divide em duas fases: ponto R (fase rafinado) e ponto E (fase extrato), conectadas pela linha de amarração $\overline{RME}$;

d) à medida que a quantidade de soluto aumenta, o tamanho das linhas de amarração diminui, ou seja, as fases cada vez possuem composições mais parecidas até atingirem o *plait point* (ponto P), no qual as duas fases são compostas pelas mesmas composições; portanto, acima deste ponto há a presença de apenas uma fase.

Outra constatação importante que pode ser observada nos diagramas do equilíbrio líquido-líquido são o coeficiente de partição (k_i) dos compostos e a seletividade do solvente ($S_{i/j}$), representados pelas Equações 2.5-1 e 2.5-2, respectivamente.

$$k_i = \frac{w_i^{II}}{w_i^{I}} \tag{2.5-1}$$

$$S_{i/j} = \frac{k_i}{k_j} \tag{2.5-2}$$

nas quais w_i é a fração mássica do componente i e os sobrescritos I e II são as fases em equilíbrio.

De acordo com a Equação 2.5-1, o coeficiente de partição do componente i indica como este se distribui nas fases rafinado (fase I) e na fase extrato (fase II). Desta forma, tendo como exemplo o coeficiente de partição do soluto, para valores maiores que a unidade, o composto tende a interagir mais com o solvente do que com o diluente; já quando esse parâmetro é a unidade, o composto se distribui de forma igualitária entre as duas fases e, quando o k é menor que a unidade, o soluto está preferencialmente na fase rafinado. Qualitativamente, esse parâmetro está representado pelas inclinações das linhas de amarração, sendo desejável que estas estejam inclinadas para a fase extrato.

Já em relação à seletividade do solvente (Equação 2.5-2), sendo i o soluto e j o diluente, este parâmetro indica como o solvente solubiliza o soluto e o diluente. Assim, para altos valores de S, há uma alta solubilização do soluto e uma baixa solubilização do diluente no solvente, o que é desejado. Já para baixos valores de S, há uma significativa solubilização do diluente no solvente, o que acarreta em maiores perdas dos materiais envolvidos na extração líquido-líquido e em um maior tratamento das fases rafinado e extrato. Qualitativamente, esse parâmetro está indicado nos diagramas líquido-líquido pelo tamanho das linhas de amarração, ou seja, quanto maior a linha de amarração, menor a solubilização do par diluente/solvente e, consequentemente, maior a seletividade do solvente.

Portanto, como pode ser observado, os diagramas de equilíbrio líquido-líquido informam como o solvente irá extrair o soluto de sua matriz líquida (diluente), bem como a composição que as fases rafinado e extrato sairão do extrator, dado esse de extrema importância para o projeto, simulação e otimização tanto do processo de extração líquido-líquido quanto do tratamento das correntes por destilação (DEMIREL, 2007). Os dados do equilíbrio líquido-líquido podem ser descritos matematicamente pela relação entre a temperatura, pressão e composição através da modelagem termodinâmica do equilíbrio de fases, possibilitando, desta forma, a simulação e otimização dos processos de separação.

2.6 MODELAGEM TERMODINÂMICA DO EQUILÍBRIO DE FASES

O equilíbrio termodinâmico de fases para um determinado sistema é atingido quando não há mais nenhuma tendência espontânea de transferência de calor, momento e massa entre as fases envolvidas (TOSUN, 2013). Assim, para uma dada temperatura (T) e pressão (P), o sistema atinge o seu equilíbrio quando o potencial químico dos compostos (μ_i) é igual em todas as fases (π). Essas condições estão expressas nas Equações 2.6-1, 2.6-2 e 2.6-3, respectivamente.

$$T^{I} = T^{II} = \ldots = T^{\pi} \tag{2.6-1}$$

$$P^{I} = P^{II} = \ldots = P^{\pi} \tag{2.6-2}$$

$$\mu_i^{I} = \mu_i^{II} = \ldots = \mu_i^{\pi} \tag{2.6-3}$$

Assim, para uma determinada temperatura e pressão, o potencial químico é definido como o diferencial da energia de Gibbs para uma certa espécie contida em um sistema envolvendo fases em contato. Desta forma, o equilíbrio de fases ocorre quando não há mais variação da energia de Gibbs para determinado composto entre as diferentes fases, cessando a transferência de massa na interface do sistema (DEMIREL, 2007). O potencial químico em função da variação da energia de Gibbs está exposto na Equação 2.6-4.

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \qquad (2.6\text{-}4)$$

na qual G é a energia de Gibbs, n_i é a quantidade de matéria do componente i, n_j é a quantidade de matéria do componente j, T é a temperatura e P é a pressão.

De forma equivalente à Equação 2.6-4, o equilíbrio de fases pode ser representado em função da fugacidade das fases (f), como apresenta a Equação 2.6-5.

$$f^{I} = f^{II} = \ldots = f^{\pi} \qquad (2.6\text{-}5)$$

Considerando um sistema composto por duas fases (I, II), a fugacidade em solução ($\hat{f}$) do componente i é igual em todas as fases, como apresenta a Equação 2.6-6.

$$\hat{f}_i^{I} = \hat{f}_i^{II} \qquad (2.6\text{-}6)$$

Relacionando a fugacidade em solução do componente i com o coeficiente de atividade (γi) e a fração molar (x_i) do componente i, tem-se (Equação 2.6-7):

$$\left(\gamma_i x_i f_i^0\right)^{I} = \left(\gamma_i x_i f_i^0\right)^{II} \qquad (2.6\text{-}7)$$

Muitas expressões semi-empíricas têm sido propostas na literatura para relacionar os coeficientes de atividade à composição e temperatura da mistura. Essas expressões (NRTL, UNIQUAC e UNIFAC, por exemplo) contém parâmetros ajustáveis a dados experimentais, e serão brevemente descritas a seguir.

2.6.1 Modelos moleculares

2.6.1.1 Modelo NRTL (Non-Random, Two-Liquid)

A equação do modelo NRTL (*Non-Random, Two-Liquid*) (Equação 2.6-8) desenvolvida por Renon e Prausnitz (1968) parte do conceito elaborado por Wilson estendendo-o para sistemas de líquidos imiscíveis através da inserção de uma terceira constante desenvolvida experimentalmente para cada binário. A equação NRTL pode ser aplicada para sistemas multicomponentes vapor-líquido, líquido-líquido e vapor-líquido-líquido (HENLEY e SEADER, 1981; TOSUN, 2013b).

$$\ln \gamma_i^{\alpha} = \frac{\sum_{j}^{C} \frac{\tau_{ji} G_{ji} w_j}{M_j}}{\sum_{k}^{C} \frac{\tau_{ki} G_{ki} w_k}{M_k}} + \sum_{j=1}^{C} \left[\frac{w_j G_{ij}}{M_j \sum_{k}^{n} \frac{G_{kj} w_k}{M_k}} \left(\tau_{ij} - \frac{\sum_{r}^{C} \frac{\tau_{ri} G_{rj} w_k}{M_k}}{\sum_{k}^{C} \frac{G_{kj} w_k}{M_k}} \right) \right] \qquad (2.6\text{-}8)$$

Sendo:

$$G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right) \qquad (2.6\text{-}9)$$

$$\tau_{ij} = \frac{A_{ij}}{T} \qquad (2.6\text{-}10)$$

$$\alpha_{ij} = \alpha_{ji} \qquad (2.6\text{-}11)$$

Nas quais: γ_i: coeficiente de atividade; M: massa molar; w: fração mássica; A_{ij} e A_{ji}: parâmetros ajustáveis aos dados experimentais do equilíbrio; α_{ij} e α_{ji}: parâmetro que representa a não aleatoriedade da mistura.

2.6.1.2 *Modelo UNIQUAC* (Universal Quasi-Chemical)

A equação do modelo UNIQUAC (*Universal Quasi-Chemical*), desenvolvida por Abrams e Prausnitz (1975), foi elaborada a partir de mecanismos estatísticos para obter uma nova expressão para a energia livre em excesso. O modelo parte de uma generalização de uma análise prévia desenvolvida por Guggenheim e é estendida para misturas de moléculas que diferem significativamente em relação ao tamanho e forma (HENLEY e SEADER, 1981). O cálculo do coeficiente de atividade pela equação de UNIQUAC, como pode ser observado na Equação 2.6-12, considera dois efeitos: o termo combinatorial, o qual está relacionado com o tamanho e forma das moléculas dos componentes da mistura, e o termo residual, o qual leva em consideração a energia de interação dos componentes das fases.

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res} \tag{2.6-12}$$

Assim, o termo combinatorial pode ser determinado pela Equação 2.6-13.

$$\ln \gamma_i^{comb} = \frac{\ln \psi_i^{'}}{\ln\left(\dfrac{w_i}{\xi \overline{M}_i}\right)} + 1 - \frac{\xi \overline{M}_i \psi_i^{'}}{w_i} + \frac{z}{2}\overline{M}_i q_i^{'} \ln\left(\frac{\theta_i^{'}}{\psi_i^{'}}\right) - \frac{z}{2}\overline{M}_i q_i^{'}\left(1 - \frac{\psi_i^{'}}{\theta_i^{'}}\right) \tag{2.6-13}$$

Sendo:

$$\xi = \sum_{j=1}^{k} \frac{w_i}{\overline{M}_i} \tag{2.6-14}$$

$$\theta_i^{'} = \frac{q_i^{'} w_i}{\sum_{j=1}^{k} q_j^{'} w_j} \tag{2.6-15}$$

$$\psi_i^{'} = \frac{r_i^{'} w_i}{\sum_{j=1}^{k} r_j^{'} w_j} \tag{2.6-16}$$

$$q_i^{'} = \frac{1}{M_j} \sum_k v_k^{(i)} Q_k \tag{2.6-17}$$

$$r_i^{'} = \frac{1}{M_j} \sum_k v_k^{(i)} R_k \tag{2.6-18}$$

E o termo residual é determinado pela Equação 2.6-19:

$$\ln \gamma_i^{res} = \overline{M}_i q_i^{'} \left[1 - \ln\left(\sum_{j=1}^{k} \theta_j^{'} \tau_{ji} \right) - \frac{\sum_{j=1}^{k} \theta_i^{'} \tau_{ij}}{\sum_{k=1}^{k} \theta_k^{'} \tau_{kj}} \right] \tag{2.6-19}$$

Na qual:

$$\tau_{ij} = -\frac{u_{ij} - u_{ji}}{RT} \exp\left(-\frac{A_{ij}}{T}\right) \tag{2.6-20}$$

na qual: $\theta_i^{'}$: fração de volume do componente *i*; $\psi_i^{'}$: fração de área do componente *i*; w_i: fração mássica do componente *i*; $q_i^{'}$: parâmetro de área do componente *i*; $r_i^{'}$: parâmetro de volume do componente *i*; $\overline{M}_i$: massa molar média do componente *i*; Q_k: volume de van der Waals do grupo *k*; R_k: área de van der Waals do grupo *k*; $\nu_k^{(i)}$: número de vezes que o grupo *k* está contido na molécula *i*; τ_{ij} e τ_{ji} parâmetros de interação entre os componentes *i* e *j*; $u_{ij} - u_{ji}$: diferença entre as energias de interação entre as moléculas *i* e *j*; *R*: constante universal dos gases ideais; *T*: temperatura absoluta.

2.6.2 Métodos preditivos de contribuição de grupos

A predição de propriedades termofísicas e do equilíbrio de fases através de métodos de contribuição de grupo baseia-se nas interações que ocorrem entre os grupos funcionais das moléculas do sistema. Tais interações, previamente ajustadas utilizando bancos de dados obtidos experimentalmente para diferentes sistemas, possibilitam calcular o coeficiente de atividade dos compostos e das fases envolvidas no sistema através de equações matemáticas, como os métodos ASOG (*Analytical Solution of Groups*) (KOJIMA e TOCHIGI, 1990) e UNIFAC (*UNIQUAC Functional-group Activity Coefficients*) (FREDENSLUND et al. 1975).

O método UNIFAC (Eq. A.2.3), inicialmente parametrizado para equilíbrio líquido-vapor, determina as propriedades termodinâmicas através das contribuições combinatorial e residual, da mesma maneira que o modelo UNIQUAC (Equação 2.6-12). Várias modificações e parametrizações foram estabelecidas e são continuamente aprimoradas. Dentre elas, citam-se as diferentes abordagens do método UNIFAC utilizadas nesse trabalho:

a) UNIFAC-LL (MAGNUSSEN, 1981): parametrização do método UNIFAC original (Eq. A.2.3) que considera dados de sistemas binários e ternários de equilíbrio líquido-líquido contendo hidrocarbonetos, água, álcoois, ácidos orgânicos, entre outros;

b) UNIFAC-Dortmund (WEIDLICH e GMEHLING, 1987; GMEHLING et al., 1993): modificação do termo residual do método UNIFAC original, apresentada na Equação A.2.4. O método foi ajustado para dados dos equilíbrios líquido-vapor e líquido-líquido, além de entalpia molar em excesso, coeficiente de atividade em diluição infinita, poder calorífico em excesso e solubilidade de gases;
c) UNIFAC-Lyngby (LARSEN, 1987): modificação do termo residual do método UNIFAC original, apresentada na Equação A.2.5. A parametrização foi realizada utilizando dados experimentais dos equilíbrios líquido-vapor e líquido-líquido e entalpia molar em excesso;
d) NIST-UNIFAC (KANG et al., 2015): parametrização do método UNIFAC-Dortmund (Eq A.2.4) ajustada a um banco de dados recentemente obtido através do Instituto Nacional de Padrões e Tecnologia – do inglês *National Institute of Standards and Technology* (NIST). O ajuste levou em consideração os equilíbrios líquido-vapor e líquido-líquido e as mesmas propriedades consideradas pelo método UNIFAC-Dortmund. Além disso, vários grupos funcionais foram adicionados;
e) UNIFAC (Hirata et al., 2013): parametrização do método UNIFAC original (Eq. A.2.3) baseada em dados de equilíbrio líquido-líquido de sistemas envolvidos na desacidificação de óleos vegetais utilizando principalmente etanol como solvente.

2.7 CONSIDERAÇÕES FINAIS

O atual processo de desodorização ao qual os óleos vegetais são submetidos possui efeitos deletérios devido às condições operacionais críticas, como temperatura e pressão. A fim de evitar tais efeitos, estudos buscam processos alternativos para efetuarem a remoção dos compostos atualmente removidos na desodorização, como os ácidos graxos livres e compostos odoríferos. Dentre esses estudos, devido às condições de operação próximas às ambientes aplicadas à extração líquido-líquido, esse processo apresenta como principais vantagens frente ao atual processo de desodorização o menor consumo de energia e a prevenção de efeitos indesejáveis, como a formação do contaminante 3-MCPD e a degradação de triacilgliceróis.

Como discutido nesse capítulo, o solvente aplicado à extração líquido-líquido é o principal fator que influencia a eficiência e a segurança do processo. Embora esforços têm sido aplicados à investigação da extração de compostos odoríferos e ácidos graxos livres dos óleos vegetais com solvente, os estudos focaram principalmente nos solventes etanol anidro e aquoso. Assim, a investigação da solubilização de diferentes solventes e cosolventes em óleos vegetais é uma lacuna a ser preenchida. Nesse sentido, este trabalho objetivou investigar a solubilidade mútua de diferentes compostos envolvidos na extração de odores do óleo de soja. Para isso, diagramas de equilíbrio de fases de sistemas contendo óleo de soja refinado e solventes (quatro solventes puros e seis misturas de solventes) foram experimentalmente determinados e modelados termodinamicamente. Além disso, pela coleta de dados de equilíbrio líquido-líquido, a remoção de seis compostos odoríferos utilizando dimetilsulfóxido foi avaliada. Também, faz-se válida a análise da predição dos dados de solubilidade pelos métodos baseados no UNIFAC, a fim de verificar as aplicabilidades e limitações de tais métodos.

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CAPÍTULO 3

SOLVENT SCREENING USING UNIFAC METHOD TO INVESTIGATE THE DEODORIZATION OF SOYBEAN OIL USING A LIQUID SOLVENT

Perci. O. B. Homrich, Roberta Ceriani

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ABSTRACT: Removal of secondary oxidation products from edible oils, currently achieved by steam stripping in the deodorization process, may be conducted under mild conditions with a liquid solvent. Solvent screening can be used to determine more suitable solvents for removing undesirable compounds. In order to investigate the removal of n-hexanal, 2,4-decadienal and hexanoic acid, odor compounds of soybean oil, 16 solvents with low toxicity were preselected by using the qualitative method of Cusack et al. (1991). Solubility data of pseudoternary (diluent + solute + solvent) and binary (solvent + solvent) systems were predicted using UNIFAC at 298.15 K and under 1 atm in Aspen Plus. Two versions of UNIFAC were considered, namely, Magnussen et al. (1981) and Hirata et al. (2013). This last version is specifically adjusted for lipid technology systems. In general, the results indicated that 7 solvents presented a separation region (type I or II), with different mutual solubility for the solvent/diluent pair. In addition, a partial miscibility were verified for three binary systems of solvents and water. This simulated screening was a guidance for sets of experiments involving liquid-liquid equilibria under investigation currently in our lab.

3.1 INTRODUCTION

The deodorization of vegetable oils causes various deleterious consequences, such as the removal of nutraceutical compounds, the degradation of triacylglycerol, the undesirable reactions of oxidation and cis-trans isomerization, and the 3-MCPD (3-monochloropropane-1,2-diol) contaminant formation (Suliman and Jiang, 2013; Szydłowska-Czerniak *et al.*, 2011; Ermacora and Hrncirik, 2014). As shown in the literature, liquid-liquid extraction can remove some compounds that are currently vaporized from the oil in the deodorization step in milder conditions in terms of temperature, such as secondary oxidation products (Homrich and Ceriani, 2015; Jorqueira, 2015) and free fatty acids (Oliveira *et al.*, 2013; Rodrigues *et al.*, 2014). The use of a liquid solvent avoids mainly the degradation of nutraceutical and triacylglycerol compounds, and the undesirable reactions that occur in steam stripping.

In order to design liquid-liquid extraction, solvent screening can be applied to determine an adequate solvent for removing some particular compounds (Papadopoulos and Linke, 2006). Commonly, solvent screening is conducted by predicting equilibrium data using group contribution methods, such as UNIFAC and ASOG, and indicates potential solvents capable of promoting desirable extraction (Frank *et al.*, 2007; Birajdar *et al.*, 2014). For systems well described by group contribution methods, it is usual to generate by molecular design a large number of molecules that obeys some predetermined characteristics, such as the number of carbons, unsaturations and ramifications, toxicology and physical properties (Gani and Brignole, 1983; Cismondi *et al.*, 2003). However, when the non-ideality of the system is unsatisfactorily predicted by group contribution methods, as is the case of fatty systems, solvent screening requires a combination of different steps, including frequently experimental collection of equilibrium data. In this way, when experimental data is required, a qualitative preselection of solvents is applied as a guidance for a limited number of potential solvents, decreasing experimental work in the laboratory. Among available tools used for solvent screening, one developed by Cusack *et al.* (1991) is of particular interest. It is based on the behavior of the activity coefficients of components in a mixture, and it indicates qualitatively which classes of compounds (acids, ethers, etc.) may promote the chosen separation. Other factor that can be taken into account, especially in processes of pharmaceutical and food industries, is solvent toxicity. According to the International Conference on Harmonization of Technical Requirements for Registration of Pharmaceuticals for Human Use (ICH, 2012), preferred solvents for these industries are ethanol, water, acetic acid and ethyl acetate, among others. Although UNIFAC method does not satisfactorily predict the equilibrium data of fatty systems (global deviations of ± 10 % are cited by Hirata *et al.*, 2013), it can be used as a first estimation of relevant factors in liquid-liquid extraction, such as the existence of an heterogeneous region, type of liquid-liquid equilibria (i.e., type I, type II…), and the possibility of blends of solvents.

In this context, the aim of this work was to indicate suitable solvents for removing n-hexanal, 2,4-decadienal and hexanoic acid (odor compounds) from soybean oil at 298.15 K and under 1 atm. To achieve this objective, the method of Cusack *et al.* (1991) was applied for indicating which classes of compounds would be more suitable for removing theses solutes. Among them, 16 organic solvents presenting low toxicity were chosen. Liquid-liquid equilibria of the preselected pseudoternary (diluent + solute + solvent) and binary (solvent + solvent) systems were predicted by the UNIFAC (UNIQUAC Functional-group Activity Coefficients) method (Fredenslund *et al.*, 1975), using the set of parameters reported by Magnussen *et al.* (1981) for liquid-liquid systems (UNIFAC-LL) and by Hirata *et al.* (2013) for lipid technology systems (UNIFAC-FS).

3.2 METHODS

3.2.1 Solvent screening based on activity coefficients

The first step of solvent screening for removing some odoriferous compounds of soybean oil (aldehydes and carboxylic acid) was accomplished by using the method of Cusack *et al.* (1991). Following its guidelines, a suitable solvent should lower the activity coefficient of solute relative to its value in the feed, and, consequently, increase its distribution coefficient (preferred phase is the extract phase). On the other hand, the opposite behavior is desired for the diluent (soybean oil, in this case), i.e., an increase in its activity coefficient, indicating that the preferred phase for this compound is the raffinate phase.

After chosen more suitable classes of compounds for removing the secondary oxidation products from soybean oil, 16 solvents were selected based on their toxicity (ICH, 2012), pursuing security during oil refining process and health aspects related to human consumption.

3.2.2 Prediction of liquid-liquid equilibrium

Liquid-liquid equilibria for the pseudoternary systems (soybean oil + solute + solvent) were predicted with UNIFAC-LL and UNIFAC-FS methods for activity coefficients at 298.15 K and 1 atm. These data were obtained in *Aspen Plus V8.4* with the structural parameters (r and

q) for UNIFAC calculated considering the following functional groups: CH_3, CH_2, CH, COOC, COOH, HC=CH, CHO, $(CH_3)_2SO$, OH and H_2O.

Soybean oil were represented by triacylglycerol triolein (2,3-Bis[[(Z)-octadec-9-enoyl]oxy]propyl (Z)-octadec-9-enoate), which presents a molecular weight of 885.432 g/mol. A total of 48 pseudoternary systems containing triolein, as diluent (soybean oil), plus n-hexanal, or 2,4-decadienal, or hexanoic acid, as the solutes, plus one at a time of the 16 preselected solvents were predicted. Complimentary, miscibility between solvents (binary mixtures) were also evaluated.

3.3 RESULTS AND DISCUSSIONS

3.3.1 Preselection of organic solvents

The method of Cusack *et al.* (1991) indicated that for aldehyde solutes (n-hexanal and 2,4-decadienal), suitable classes of solvents were acids and esters, while for acid solute (hexanoic acid), appropriate classes were paraffinic alcohols, water, ketones and sulfoxides. Among these classes of solvents, 16 compounds that present low toxicity according to ICH (2012) were selected: acetic acid, formic acid, ethyl acetate, ethyl formate, butyl acetate, isobutyl acetate, methyl acetate, propyl acetate, ethanol, water, methyl ethyl ketone, methyl isobutyl ketone, anisole, tert-butyl methyl ether, dimethyl sulfoxide and ethyl ether.

3.3.2 Prediction of liquid-liquid equilibria

Liquid-liquid equilibria for the preselected pseudoternary and binary systems were predicted at 298.15 K and 1 atm using *Aspen Plus V8.4* with parameters of UNIFAC-LL and UNIFAC-LS for comparison purposes. It was possible to verify the mutual solubility between the diluent (soybean oil represented by triolein) and the 16 solvents, the existence of a heterogeneous region for the pair solvent-diluent and the type of the diagram (type I or type II) for each solute.

Among the 16 preselected solvents, 7 solvents presented a heterogeneous region, ensuring the possibility of liquid-liquid extraction: formic acid, water, ethanol, dimethyl sulfoxide, anisole, methyl isobutyl ketone, and methyl ethyl ketone. In the case of methyl isobutyl ketone and methyl ethyl ketone, the UNIFAC-LL and UNIFAC-FS gave controversial results, i.e., the UNIFAC-LL predicted a heterogeneous region. Table 3.3-1 presents mutual solubility values predicted using the UNIFAC-LL and UNIFAC-FS for diluent (triolein) and solvents. The other 9 solvents investigated, acetic acid, ethyl acetate, ethyl formate, butyl acetate, isobutyl acetate, methyl acetate, propyl acetate, tert-butyl methyl ether and ethyl ether, were predicted to dissolve completely in triolein for both methods.

Table 3.3-1: Predicted mutual solubility values expressed in mass fraction (w) for the binary systems soybean oil (1) and solvents (2) using UNIFAC-LL and UNIFAC-FS at 298.15 K and 1 atm.

Solvent	**UNIFAC-LL**				**UNIFAC-FS**			
	Phase I		**Phase II**		**Phase I**		**Phase II**	
	w_1	w_2	w_1	w_2	w_1	w_2	w_1	w_2
Formic acid	0.9189	0.0811	0.0000	1.0000	0.8566	0.1434	0.0000	1.0000
Water	0.9991	0.0009	0.0000	1.0000	0.9999	0.0001	0.0000	1.0000
Ethanol	0.9035	0.0965	0.0009	0.9991	0.8496	0.1504	0.0747	0.9253
Dimethyl sulfoxide	0.9932	0.0068	0.0000	1.0000	0.9875	0.0125	0.0000	1.0000
Anisole	0.8826	0.1174	0.0000	1.0000	0.7935	0.2065	0.0000	1.0000
Methyl isobutyl ketone	0.7543	0.2457	0.0026	0.9974	–	–	–	–
Methyl ethyl ketone	0.8308	0.1692	0.0009	0.9991	–	–	–	–

As one can see, primary results showed in Table 3.3-1 demonstrate the potential of these 7 organic low-toxic solvents to be applied in edible oil deodorization by liquid-liquid extraction, considering the low miscibility values (or immiscibility in certain cases) for the pair solvent-diluent. Besides the discrepancy between UNIFAC-LL and UNIFAC-FS predictions for methyl isobutyl ketone and methyl ethyl ketone systems, it was also noted an important difference among predicted values for systems containing ethanol as solvent, which may be a consequence of the existence of this compound in the databank of Hirata *et al.* (2013) for UNIFAC-FS parameter regressions.

In relation to pseudoternary systems, diagrams of type I (one partially miscible pair) and type II (two partially miscible pairs) were generated by the UNIFAC-LL and UNIFAC-FS methods. As examples, Figure 3.3-1 shows these two types of diagrams obtained for systems composed by soybean oil + 2,4-decadienal + methyl ethyl ketone (Figure 3.3-1–A) and soybean oil + n-hexanal + formic acid (Figure 3.3-1–B) at 298.15 K and 1 atm using the UNIFAC-LL[a].

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[a] A predição para os demais sistemas está apresentada no Apêncice A.1.

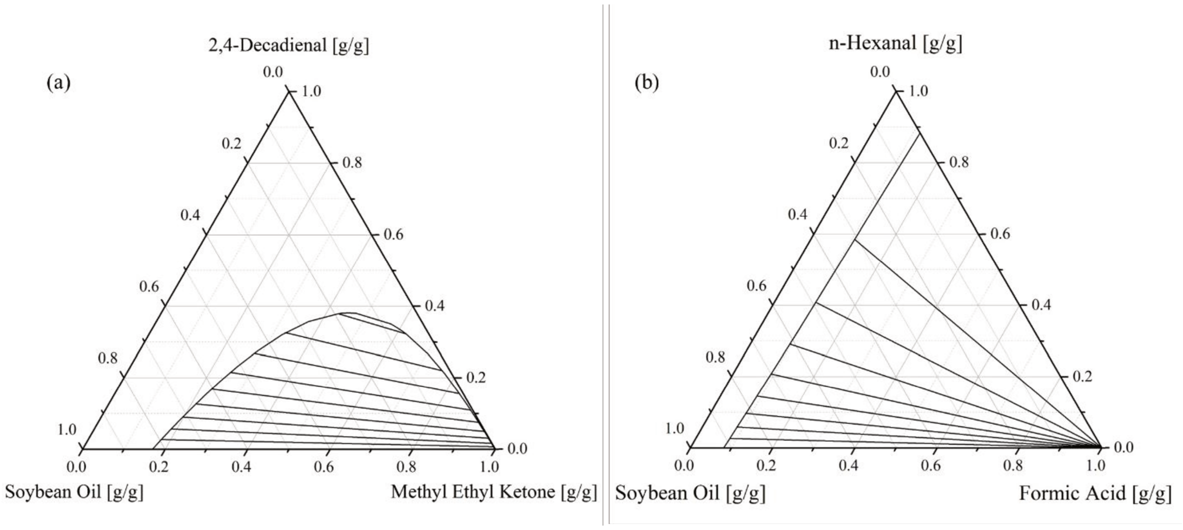

Figure 3.3-1: Diagrams of type I (a) [soybean oil + 2,4-decadienal + methyl ethyl ketone] and of type II (b) [soybean oil + n-hexanal + formic acid] at 298.15 K and 1 atm predicted with the UNIFAC-LL.

The diagram of type I (Figure 3.3-1–A) exhibits the partial miscibility for the pair diluent-solvent (soybean oil-methyl ethyl ketone), and Figure 3.3-1–B presents the partial miscibility between pair diluent-solvent (soybean oil-formic acid) and solute-solvent (n-hexanal-formic acid). This last behavior limits liquid-liquid extraction because at low concentrations of solute, as it is the case of odor compounds, solute would be immiscible in solvent.

Figure 3.3-2 compares the prediction of the UNIFAC-LL and UNIFAC-FS for the system containing soybean oil + hexanoic acid + ethanol at 298.15 K and 1 atm. Predicted data depicted in Figure 3.3-2 illustrates the difference encountered for this particular system. The UNIFAC-FS (Figure 3.3-2–B) predicted more feasible values than the UNIFAC-LL (Figure 3.3-2–A) in comparison to results of Oliveira et al. (2012) and Rodrigues et al. (2014) as a consequence of the presence of carboxylic acids (fatty acids) and ethanol in the databank regressed by Hirata *et al.* (2013). As one can see, the heterogeneous region in Figure 3.3-2–B is smaller than the one predicted by UNIFAC-LL, but it still indicates the possibility of liquid-liquid extraction of hexanoic acid.

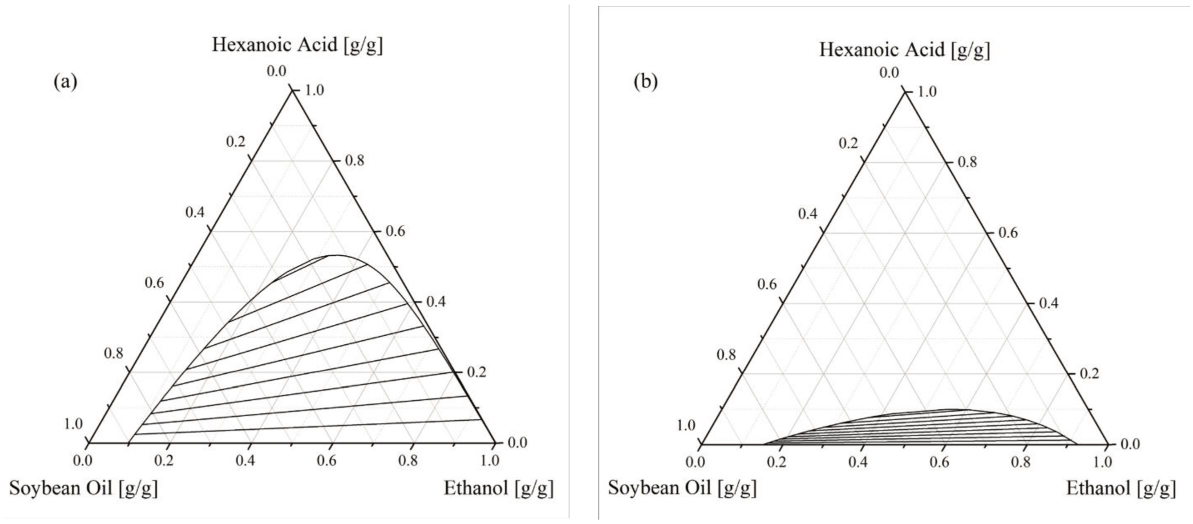

Figure 3.3-2: Predicted liquid-liquid equilibrium for the system soybean oil + hexanoic acid + ethanol at 298.15 K and 1 atm using the UNIFAC-LL (a) and UNIFAC-FS (b).

Regarding distribution coefficients of solutes, Figure 3.3-1 and Figure 3.3-2 shows that inclinations of tie-lines vary considerably among different solvents, which would affect the design of the liquid-liquid extraction process in terms of solvent flow rate, number of equilibrium stages and type of extractor. Nevertheless, as observed by Hirata *et al.* (2013), the UNIFAC-LL inverts tie-line inclinations for some fatty systems. This fact confirms the need for determining new experimental data for lipid technology systems.

Finally, considering the possibility of using mixed solvents as the separating agent in liquid-liquid extraction, binary solubility values between solvents were predicted using the UNIFAC-LL method. It was noted that the majority of the binary systems were completely miscible. Only solvents methyl ethyl ketone, methyl isobutyl ketone and anisole were predicted to be partially miscible in water (Table 3.3-2).

Table 3.3-2: Predicted binary solubility values expressed in mass fraction (w) for water (solvent 1) plus anisole or methyl isobutyl ketone or methyl ethyl ketone (solvent 2) at 298.15 K and 1 atm using the UNIFAC-LL.

Solvent 2	**Aqueous phase**		**Organic phase**	
	w_{water}	$w_{\text{solvent 2}}$	w_{water}	$w_{\text{solvent 2}}$
Anisole	0.9979	0.0021	0.0061	0.9939
Methyl isobutyl ketone	0.9809	0.0191	0.0166	0.9834
Methyl ethyl ketone	0.8515	0.1485	0.1202	0.8798

Data presented in Table 3.3-2 indicate that binary mixtures composed by water plus anisole, or methyl ethyl ketone are slightly miscible, fact that would limit blending these solvents.

3.4 CONCLUSION

Solvent screening for removing some odor compounds from soybean oil was qualitatively accomplished using the method of Cusack *et al.* (1991) in combination with the UNIFAC-LL and UNIFAC-FS methods. The method of Cusack *et al.* (1991) indicated that n-hexanal, 2,4-decadienal and hexanoic acid would be removed using solvents of acid, ester, paraffinic alcohol, ketone, sulfoxide classes, and water. Liquid-liquid equilibria (types I and II) were predicted for 16 selected low-toxicity solvents, and formic acid, water, ethanol, anisole, dimethyl sulfoxide, methyl ethyl ketone and methyl isobutyl ketone were partial miscible with soybean oil, enabling liquid-liquid extraction. Complementarily, binary solubility values between solvents were predicted using UNIFAC-LL, which indicated that only anisole, methyl ethyl ketone and methyl isobutil ketone are partially miscible in water. The results achieved in this work allowed preselecting a limited number pure and mixed solvents to be further used in the experimental investigation of liquid-liquid extraction as an alternative process for deodorization of edible oils.

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CAPÍTULO 4

SOLUBILITY BEHAVIOR OF MIXTURES CONTAINING REFINED SOYBEAN OIL AND LOW-TOXIC SOLVENTS AT DIFFERENT TEMPERATURES

Homrich, P. O. B.; Mariutti, L. R.; Bragagnolo, N.; Ceriani, R. Solubility behavior of mixtures containing refined soybean oil and low-toxic solvents at different temperatures. *Fluid Phase Equilibria.* **2017**, *442*, 87–95. DOI: 10.1016/j.fluid.2017.03.013

ABSTRACT: Solubility behavior of refined soybean oil (RSO) plus seventeen low toxic solvents was determined experimentally, and was predicted using five versions of the UNIFAC method. Qualitative results obtained by cloud point detection at a temperature *T* of 278.15 K showed that eleven systems were completely miscible, two formed stable emulsions, and four resulted in biphasic mixtures. Mutual solubility at different temperatures of pseudobinary partially miscible systems (RSO plus solvent) was measured either by the cloud point method or by direct tie line quantification: RSO plus anhydrous ethanol, or acetic acid, or ethyl lactate, or dimethyl sulfoxide (DMSO). Liquid-liquid equilibrium data were satisfactorily correlated by the NRTL and UNIQUAC models, which were also used for determining the upper critical solution temperatures (UCST) by liquid-liquid flash calculations. Further, the predictive capacity of five versions of the UNIFAC method was verified and comparisons among them were achieved.

Keywords: liquid-liquid extraction, low-toxic solvent, deodorization, refined soybean oil

4.1 INTRODUCTION

Concerns related to food quality instigate searching for milder variables of processing, focusing on their effects in the final acceptance of ordinary consumers [1,2]. Liquid-liquid extraction is a potential separation process in edible oil refining for removing undesirable compounds from crude vegetable oils, including free fatty acids and odoriferous molecules [3–7], in the deacidification and the deodorization steps, respectively. In this way, objectionable effects, such as volatilization of nutraceutical compounds, thermal degradation of triacylglycerols, *trans*–fat formation, oxidation reactions, and formation of 3-MCPD (3-monochloropropane-1,2-diol) contaminant [8–11], caused by high temperatures (220 – 265 °C) and low pressures (0.2 – 0.4 kPa) applied in the traditional process (steam stripping) [12], are avoided.

Removal of long-chain fatty acids (free fatty acids) and odoriferous compounds, such as aldehydes and short-chain carboxylic acids, using organic solvents (mainly anhydrous and hydrous ethanol) has been investigated previously in the literature [3–7,13,14]. These studies verified that ethanol as a solvent allows suitable coefficients of partition of solutes, and reasonable solvent selectivities, for different edible and nonedible oils playing as the diluent. To the best of our knowledge, only few studies considered other solvents: methanol [15,16], 2-propanol [15], n-propanol [15], and ethyl lactate [17,18]. In addition, little attention was given to mutual solubility behavior of edible oils within different solvents at different temperatures [15–20].

Solvent screening is essential for the design of liquid-liquid extraction process. Liquid-liquid equilibrium (LLE) data are taken into account for evaluating candidates that have a high capacity for dissolving the solute, and a high selectivity for the solute relative to the diluent, generating more efficient solvent extraction processes [21–23]. Additionally to these two factors, other thermophysical properties are also considered, as density, boiling point, viscosity, and interfacial tension, as well as, availability, flammability, stability, toxicity, and solvent compatibility within the solute and the diluent [21]. In the case of food, pharmaceutical, and biomedical industries [24], solvent toxicity features as a main concern.

Qualitative tools, such as the method of Cusack et al. [25], comprise initial solvent-selection methods, and are used as a guide for preselecting a limited group of candidates (substances) to act as solvents for a certain solute-diluent system. Cusack et al. [25] method chooses a solvent that lowers the value of the solute activity coefficient relative to its value in the solute-diluent mixture (initial mixture) [21]. Group contribution methods, such as the

UNIQUAC Functional-group Activity Coefficients (UNIFAC) method [26], can be used for estimating activity coefficients of compounds within the mixture, based on their functional groups. Particularly, in the case of fatty systems, poorly predictive capacity of the UNIFAC method, in its different versions, has been pointed out in the literature [6,27,28]. Efforts have been made toward suiting the UNIFAC parameter matrix for selected branches of mixtures [27,28] based on available experimental data.

In this context, this work goals at determining solubility behavior of refined soybean oil and seventeen organic solvents for removal of odoriferous compounds. Solubility for each of these pseudobinary systems was measured at 278.15 K, and experimental results indicated that eleven systems were completely miscible, two formed stable emulsions and four were partially miscible. Then, phase diagrams for the four partially miscible systems (RSO + anhydrous ethanol, or acetic acid, or ethyl lactate, or dimethyl sulfoxide) were obtained by cloud point detection using either the constant-temperature method [17,29] or the constant-composition method [29,30], and by direct quantification of tie lines using either a gravimetric procedure (vacuum oven) [7] or the gas chromatography-mass spectrometry (GC-MS). Data were collected at different temperatures, ranging from 278.15 to 336.45 K with $u(T) = 0.05$ K. The NonRandom Two-Liquids (NRTL) [31] and the UNIversal QUAsiChemical (UNIQUAC) [32] models were used for correlating measured data. When suitable, upper critical solution temperature (UCST) was determined by liquid-liquid flash calculations [16,33] with regressed parameters of the NRTL and UNIQUAC models. Further, the predictive capacity of five versions of the UNIFAC method [26] were verified for pseudobinary systems composed of RSO and preselected solvents indicated by Cusack et al. [25], namely: UNIFAC-LL [34], UNIFAC-HIR [27], UNIFAC-Dortmund [35,36], NIST-modified UNIFAC [37] and UNIFAC-Lyngby [38].

4.2 SOLVENT SCREENING FOR LIQUID-LIQUID EXTRACTION

In this work, the method of Cusack et al. [25] was used for choosing potential candidates (solvents) for removing two classes of odoriferous compounds (aldehydes and short-chain carboxylic acids) from RSO in a liquid-liquid extraction process. The method indicated that acids and esters are preferred to extract aldehydes, while paraffinic alcohols, water, ketones, ethers, and sulfoxides favor extraction of carboxylic acids. Among these classes, seventeen compounds were preselected taking into account recommendations of ICH [39], regarding solvents in Class 3 (less toxic and of lower risk to human health). Preselected solvents were then: anhydrous ethanol, acetic acid, ethyl lactate, dimethyl sulfoxide (DMSO), formic acid, methyl acetate, ethyl acetate, ethyl formate, butyl acetate, isobutyl acetate, propyl acetate, water, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), anisole, tert-butyl methyl ether, and ethyl ether.

4.3 EXPERIMENTAL SECTION

4.3.1 Material

Refined soybean oil (Liza™, Cargill, Brazil) was purchased in a local market. Official AOCS methods Ce 1f-96 and Ce 1-62 [40] were applied for determining its fatty acids profile, which is presented in Table A.2.1 (*Supplementary Material*). Results in Table A.2.1 show that RSO is rich in polyunsaturated fatty acids (54% m/m, mainly linoleic acid), followed by monounsaturated fatty acids (22.9% m/m, mainly oleic acid). Fatty acids with 18 carbons sum up 85 % m/m, approx., distributed among stearic, oleic, linoleic and linolenic acids, with presence of a small content of *trans* isomers.

From Table A.2.1, a probable triacylglycerol (TAG) profile (Table A.2.2) of RSO was estimated using the statistical procedure of Antoniosi Filho et al. [41]. An equivalent TAG for this probable profile is formed by two linoleic acids and one oleic acid (LiLiO), named {3-[(9Z)-9-Octadecenoyloxy]-1,2-propanediyl-(9Z,12Z,9'Z,12'Z)bis(-9,12-octadecadienoate)}, with a molecular weight of 874.5 g.gmol^{-1}. Since RSO is a multicomponent mixture containing mainly TAGs with 18 carbons, it was possible to represent RSO as a pseudocomponent (LiLiO) both in modeling and prediction of LLE data [6,7,15,42–45].

Free fatty acids (FFA) content of RSO was obtained by titration (official method 2201 of the IUPAC [46]), given a very low value of 0.12 with u(FFA) = 0.01, expressed as percentage of linoleic acid. The oil stability index (OSI) was accomplished with the AOCS Method Cd 12b-92 [40] with a Rancimat instrument (Metrohm, model 743) at 100 ºC and 20 L/h of air flow rate. The OSI of RSO was 10.6 h with u(OSI) = 0.1 h, indicating that RSO had almost 11 h of natural resistance to oxidation reactions.

Table 4.3-1 lists the reagents used as solvents in this work (CAS Registry numbers, purities in mass fraction, IUPAC names and suppliers). Besides these compounds, deionized water (Milli-Q, Millipore) was also investigated as a potential solvent. All chemicals were utilized without any further purification step.

Table 4.3-1: Source and purity of chemicals used in this work.

Compounds	**IUPAC name**	**CAS Registry No.**	**Supplier**	**Purity (mass fraction)**
Anhydrous ethanol	Ethanol	64-17-5	Sigma-Aldrich	> 0.995
Acetic acid	Ethanoic acid	64-19-7	Êxodo	0.997
Ethyl lactate	Ethyl 2-hydroxypropanoate	97-64-3	Fluka	> 0.99
Dimethyl sulfoxide	Methanesulfinylmethane	67-68-5	Sigma-Aldrich	> 0.997
Formic acid	Methanoic acid	64-18-6	Êxodo	0.99
Methyl ethyl ketone	Butan-2-one	78-93-3	Êxodo	0.99
Methyl isobutyl ketone	4-Methyl-2-pentanone	108-10-1	Êxodo	0.985
Ethyl acetate	Ethyl ethanoate	141-78-6	Sigma-Aldrich	> 0.995
Ethyl formate	Ethyl methanoate	109-94-4	Sigma-Aldrich	> 0.995
Butyl acetate	Butyl acetate	123-86-4	Sigma-Aldrich	> 0.995
Isobutyl acetate	2-methylpropyl acetate	110-19-0	Sigma-Aldrich	0.99
Methyl acetate	Methyl acetate	79-20-9	Sigma-Aldrich	0.99
Propyl acetate	Propyl ethanoate	109-60-4	Sigma-Aldrich	> 0.995
Anisole	Methoxybenzene	100-66-3	Sigma-Aldrich	0.99
Tert-butyl methyl ether	2-Methoxy-2-methylpropane	1634-04-4	Sigma-Aldrich	0.99
Ethyl ether	Ethoxyethane	60-29-7	Êxodo	> 0.995
2-propanol	Propan-2-ol	60-63-0	Sigma-Aldrich	0.999

[a]: Purity expressed as mass fraction.

4.3.2 Solubility Behavior of RSO and Preselected Solvents

To determine whether the 17 pseudobinary systems (preselected solvents and RSO) were miscible, partially miscible or immiscible, the constant-temperature method [29] for cloud point detection was used at 278.15 K with $u(T) = 0.05$ K. A known amount of RSO (or organic solvent), measured using an analytical balance (Radwag, Model AS 220.R2) accurate to ± 0.0001 g, was placed in an equilibrium sealed-glass cell (23 mL) connected to an ultra-thermostatic bath (Marconi, Model MA-184). Then, liquid was vigorously agitated with a magnetic stirrer (Fisatom, Model 752), while the other compound (organic solvent or RSO) was added dropwise to the homogeneous solution. The coexistence of two phases was verified by visual detection of mixture turbidity. On the other hand, a persistent translucency regardless of the added amount of the second compound indicated that the pseudobinary system was completely miscible, disabling the usage of such solvents for T-w diagrams determination.

4.3.3 Determination of Phase Diagrams

Experimental procedures described below were only used for the pseudobinary systems detected as partially miscible: RSO plus anhydrous ethanol, or acetic acid, or ethyl lactate, or DMSO. Although water and formic acid were very poorly miscible with RSO, stable emulsions were formed in both cases. Temperatures up to 338.15 K with $u(T) = 0.05$ K were also tested, but emulsions persisted, which certainly disables the application of these two solvents.

Binodal curves, presented as T–w diagrams, in which w is the mutual solubilities in mass fraction, were measured by cloud point detection following two different procedures, according to Treybal [29]. In the case of temperatures located far from the region of the upper critical solution temperature (UCST), the constant-temperature method was used. On the contrary, the constant-composition method was successfully applied. These methods were used for pseudobinary systems of RSO (1) plus anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4) in triplicate. In the case of RSO plus DMSO (5) system, experimental difficulties for detecting the cloud point arose, and direct quantification of tie lines was applied using either a gravimetric procedure (vacuum oven) or gas chromatography-mass spectrometry (GC-MS). On the basis of LLE data, partition coefficients of the diluent (k_1) in Eq. 4.3-1 were calculated to assess distribution of RSO between extract (E) and raffinate (R) phases at different temperatures. For the diluent, lower partition coefficients are desirable.

$$k_1 = \frac{w_1^E}{w_1^R} \tag{4.3-1}$$

4.3.4 Cloud point detection by using the constant-temperature method

The procedure of constant-temperature method previously described was used for temperatures below the UCST region. For each solvent, an initial temperature (T_i) with $u(T_i) = 0.05$ K was set according to the size of its biphasic region with RSO at 278.15 K (previously determined), and avoiding air moisture condensation on the external surface of sealed-glass cell. Thus, for anhydrous ethanol and acetic acid: $T_i = 288.15$ K, and for ethyl lactate: $T_i = 283.15$ K. After cloud point detection by adding the second compound (RSO or solvent), temperature T was increased by 2.5 K for ethyl lactate system and by 5.0 K for anhydrous ethanol and acetic acid systems, causing disappearance of turbidity. Again, addition of drops of the second component caused formation of a second phase (cloud point). This procedure was repeated until cloud point temperature approached the UCST.

4.3.5 Cloud point detection by using the constant-composition method

The constant-composition method was applied to determine cloud points at temperatures near to the UCST, where d*T*/d*w* is close to zero. In brief, for each solvent, a turbid liquid mixture with known composition was prepared in a sealed-glass cell connected to an ultra-thermostatic bath set at a temperature close to the UCST, and was agitated vigorously. At constant stirring, liquid temperature was increased by 0.5 K intervals until disappearance of turbidity. Then liquid temperature was varied in ± 0.1 K, and the corresponding binodal point was detected, with alternation between turbidity and clearness, confirming cloud point temperature.

4.3.6 Direct tie line quantification using a gravimetric procedure (vacuum oven)

Samples of 20 g of pseudobinary mixtures containing RSO (1) plus DMSO (5) were prepared in sealed-glass cells, stirred vigorously for 2 h, and allowed to settle, for at least 12 h, at selected temperatures: 293.15 to 333.15 K with $u(T) = 0.05$ K in a 5.0 K interval. After phase split, top and bottom phases were sampled using syringes with stainless steel needles. Three aliquots of about 1 g of each sample of each phase were placed in Petri dishes and kept in a vacuum oven (Marconi, Model MA030) for vaporization of DMSO, until constant mass [7]. Then, tie line compositions in terms of mass fractions of DMSO and RSO were determined. Vaporization of RSO can be considered nonexistent at experimental conditions in vacuum oven (393.15 K and 1.3 kPa of absolute pressure), and it was confirmed by preliminary tests.

4.3.7 Direct tie line quantification using gas chromatography-mass spectrometry (GC-MS)

To quantify concentrations of DMSO in raffinate phase (RP) and extract phase (EP) of three selected temperatures (293.15, 308.15 and 323.15 K), samples of each phase were collected with syringes and then diluted in 2-propanol in the following ratios: 1:100 for the raffinate phase; and 1:2000 for the extract phase. These samples were injected into the GC-MS, and mass fractions of DMSO of each phase were calculated using the analytical curve. GC-MS was only applied for selected temperatures, considering that from the *t test* [46] it was inferred that the differences between mass fractions obtained by both methods for each of these samples were not statistically significant at 95 % of confidence.

A gas chromatograph (GC) coupled to a mass spectrometer (MS, GCMS-QP2010 Ultra Shimadzu, Kyoto, Japan) was used in the experiments. Samples were injected in splitless mode at 250 °C. Separation was achieved in a RTX-Wax capillary column (30 m × 0.25 mm inner diameter, 0.20 μm thick stationary phase, polyethylene glycol, Restek, Bellefonte, PA), helium was used as the carrier gas in the linear flow control mode with a constant column flow of 1.22 mL/min. The oven temperature program started at 50 °C for 5 min, followed by heating at 5 °C/min to 150 °C, then heating at 10 °C/min to 250 °C, and maintaining at this temperature for 5 min, giving a total time of 40 min [47]. Detection was carried out by mass spectrometry using an ion source in the electron ionization (EI) mode at 70 eV and 250 °C. The mass/charge (*m/z*) analyzer was a quadrupole, operating in the scanning mode (SCAN = *m/z* 35−350) to identify the compounds and in the selected ion monitoring (SIM) mode for quantification (63 *m/z*). Equipment control and data processing was performed in a GCMS Solution workstation (Shimadzu, Kyoto, Japan).

The analytical curve (Figure A.2.1) was constructed by diluting dimethyl sulfoxide (DMSO) in 2-propanol at twelve ratios (1:1250; 1:1500; 1:2000; 1:2500; 1:2500; 1:2750; 1:3000; 1:3500; 1:4000; 1:4500; 1:5000; 1:6000) in quadruplicate. Regressed parameters of the analytical curve and their deviation are presented in Table A.2.3, as well as the detection and quantification limits, calculated following Equations A.2.1 and A.2.2 [48]. Densities of reagents DMSO, 2-propanol and of equilibrium phases (raffinate and extract phases) were measured using a densitometer (Mettler-Toledo, Model DM45) and are presented in Table A.2.4.

4.4 DATA CORRELATION WITH THE NRTL AND UNIQUAC MODELS AND PREDICTION OF THE UNIFAC METHOD

Experimental LLE data of pseudobinary systems composed of RSO (1) plus anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4), or DMSO (5) were correlated with the NRTL and the UNIQUAC models on the molar basis. Binary parameters (a_{ij}/J·K^{-1}mol^{-1}, b_{ij}/J·mol^{-1} and c_{ij}/J·K^{-1}mol^{-1}) for the NRTL (Eq. 4.4-1) and the UNIQUAC (Eq. 4.4-2) models, and the nonrandomness parameter (α_{ij}) for the NRTL model, were obtained by using software *Aspen Plus v.8.4.*

$$\tau_{ij} = a_{ij} + {b_{ij}}/{T} + c_{ij} \ln T \qquad (4.4\text{-}1)$$

$$\tau_{ij} = \exp\left(a_{ij} + {b_{ij}}/{T} + c_{ij} \ln T \right) \qquad (4.4\text{-}2)$$

Adjustment of parameters was achieved by using the Britt-Luecke algorithm with the Deming initialization method. Regression of parameters was accomplished using the maximum-likelihood objective function, which considered all measured variables (temperatures, mole fractions and pressure). The adjusted binary parameters were used in the determination of the UCST by liquid-liquid flash calculations [33,16].

Further, phase diagrams for the 17 systems (RSO plus preselected solvents) were predicted using the UNIFAC method considering five versions: UNIFAC-LL of Magnussen et al. [34], UNIFAC-HIR of Hirata et al. [27], UNIFAC-Dortmund of Weidlich and Gmehling [35], and Gmehling et al. [36], NIST-modified UNIFAC [37] of Kang et al. and UNIFAC-Lyngby of Larsen et al. [38].

Agreement between experimental and calculated (or predicted) mass fractions for the NRTL and UNIQUAC models and for the UNIFAC method versions were evaluated by global deviations (δw) according to Eq. 4.4-3.

$$\delta w = 100\sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{P}\left\{\left(w_{i,n}^{\mathrm{R,exp}} - w_{i,n}^{\mathrm{R,calc}}\right)^2 + \left(w_{i,n}^{\mathrm{E,exp}} - w_{i,n}^{\mathrm{E,calc}}\right)^2\right\}}{2NP}} \qquad (4.4\text{-}3)$$

where N is the total number of tie lines in each system, P is the total number of components in each system, the superscripts E and R refer to extract phase and raffinate phases, and the superscripts exp and calc refer to experimental and calculated (or predicted) values, respectively.

4.4.1 The UNIFAC Method

Several modifications of the UNIFAC method [26] (Eq. A.2.3) have been designed, in which readjusted group-group binary parameters of Eq. A.2.3 were provided for specific data banks (UNIFAC-LL [34], UNIFAC-HIR [27], NIST-modified UNIFAC [35]), and those in which modifications in relation to combinatorial term were considered (UNIFAC-Dortmund (Eq. A.2.4) [36,37] and UNIFAC-Lyngby Eq. (Eq. A.2.5) [38]).

Magnussen et al. [34] readjusted Eq. A.2.3 considering LLE data of binary and ternary systems containing hydrocarbons, water, alcohols, organic acids, halogenated hydrocarbons, to name a few. On the other hand, Hirata et al. [27] considered only LLE data of pseudoternary and pseudoquaternary systems composed of edible and non-edible vegetable oils, long-chain carboxylic acids, and alcoholic solvents, specially anhydrous and hydrous ethanol. Very recently, Kang et al. [37] readjusted Eq. A.2.4 considering experimental data of vapor-liquid equilibrium (VLE), LLE, molar excess enthalpy (h^E), activity coefficient at infinite dilution (γ^∞), gas solubilities, and excess heat capacity (CPE). In addition, several new groups were introduced to improve data prediction.

In the case of the UNIFAC-Dortmund method [35,36] (Eq. A.2.4) and the UNIFAC-Lyngby method [38] (Eq. A.2.5), terms related to the combinatorial and residual parts of the original UNIFAC were modified, and group-group interaction parameters were readjusted. Data such as VLE, LLE, and h^E were considered by both methods, while γ^∞, gas solubilities and excess heat capacity (CPE) were only considered by the UNIFAC-Dortmund method.

4.4.2 Division of molecules in functional groups, volume and area values and group-group interaction parameters

Table A.2.5 presents the subdivision form of all solvents and of RSO (TAG LiLiO) using the following functional subgroups: CH_3, CH_2, CH, C, CH_2COO, CH_3COO, HCO, OH, COOH, HCOOH, HCOO, COO, $(CH_3)_2SO$ (DMSO), CH_2O, CH_3O, CH_3CO, AC, ACH, H_2O and HC=CH. Values for relative van der Waals surface area (Q_k) and volume (R_k) of above-mentioned subgroups used by the UNIFAC versions considered in this work (five in total) are presented in Table A.2.6. Structural parameters q and r of the UNIFAC versions for each compound are listed in Table S.7.

As shown in Table A.2.6, formic acid molecule (HCOOH) plays as a main group in the UNIFAC-Dortmund method, while in the UNIFAC-LL method, it is considered as sub-group of the main group COOH. Furthermore, the following groups are not considered for specific UNIFAC versions: HCOO (ethyl formate) for the UNIFAC-LL, and HCOO, HCOOH (formic acid), and DMSO (dimethyl sulfoxide) for the UNIFAC-Lyngby. All available group-group interaction parameters for studied UNIFAC versions are presented in Tables A.2.8 to A.2.12.

4.5 RESULTS AND DISCUSSION

Table 4.5-1 presents results of solubility behavior (P: partially miscible, M: miscible) of RSO plus low-toxic solvents at 278.15 K obtained experimentally and using the predictive methods (UNIFAC-LL, UNIFAC-HIR, UNIFAC-Dortmund, NIST-modified UNIFAC and UNIFAC-Lyngby).

Table 4.5-1: Qualitative solubility behaviors at 278.15 K between refined soybean oil (RSO) and the 17 preselected solvents: experimental and predicted results for the UNIFAC-LL, UNIFAC-HIR, UNIFAC-Dortmund, NIST-modified UNIFAC and UNIFAC-Lyngby methods.

Solvent	Exp.[a,b]	UNIFAC-LL	UNIFAC-HIR	UNIFAC-Dortmund	NIST-modified UNIFAC	UNIFAC-Lyngby
Anhydrous Ethanol	P	P	P	P	P	P
Acetic Acid	P	M	M	P	P	P
Ethyl Lactate	P	P	M	P	P	P
Dimethyl sulfoxide	P	P	P	P	P	NA[c]
Water[d]	P	P	P	P	P	P
Formic Acid[d]	P	P	P	P	P	NA[c]
Methyl Acetate	M	M	M	P	P	P
Ethyl Formate	M	NA[c]	NA[c]	P	M	NA[c]
Ethyl Acetate	M	M	M	P	P	M
Butyl acetate	M	M	M	M	M	M
Isobutyl Acetate	M	M	M	M	M	M
Propyl Acetate	M	M	M	M	M	M
Ethyl Ether	M	M	M	M	M	M
Tert-butyl Methyl Ether	M	M	M	M	M	M
Methyl Ethyl Ketone	M	P	P	M	M	P
Methyl Isobutyl Ketone	M	P	M	M	M	M
Anisole	M	P	P	M	P	P
Partially miscible systems (Total)	6	8	6	9	9	7
Agreements (Total)		12	12	14	14	11

[a] P: partially miscible; [b] M: miscible; [c] NA: not applicable due to lack of group-group interaction parameters; [d] stable emulsion formation.

As shown in Table 4.5-1, qualitative agreements (partially miscible, P, or miscible, M) were concomitantly achieved by all UNIFAC versions for 7 out of 17 pseudobinary systems: P – anhydrous ethanol, DMSO, water, and formic acid; M –butyl acetate, isobutyl acetate, propyl acetate, ethyl ether and tert-butyl methyl ether. For ethyl lactate, agreements for solubility behaviors at 278.15 K were not achieved only for the UNIFAC-HIR method, while for acetic acid, both the UNIFAC-LL and UNIFAC-HIR methods failed. As exposed, the UNIFAC method is not capable to determine qualitatively when RSO and solvents are miscible. Phase diagrams for partially miscible systems were generated using predicted LLE data for all the UNIFAC versions presented in Table 4.5-1, and are depicted in Fig. A.2.2.

Table 4.5-2 summarize experimental LLE data under atmospheric pressure measured for pseudobinary model systems that were partially miscible according to Table 4.5-1, that is:

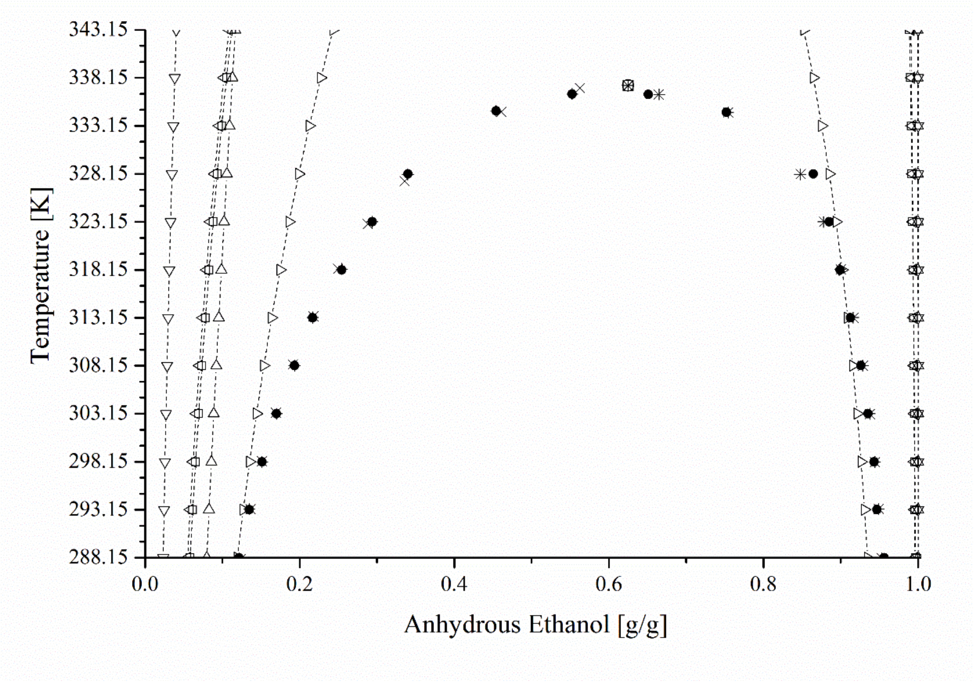
RSO (1) plus anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4), or DMSO (5). It is of note that selected results of solvent mass fractions (*w*) reported in Table 4.5-2 for anhydrous ethanol (2), acetic acid (3), and ethyl lactate (4), namely three cloud point values for each solvent, were confirmed by solvent vaporization in vacuum oven as described in item 4.3.6, but with its temperature set at 353.15 K.

Figure 4.5-2 shows experimental data, the NRTL and UNIQUAC models correlation and the prediction by the UNIFAC method versions. It also depicts the UCST obtained using liquid-liquid flash calculations considering the regressed parameters for the NRTL and UNIQUAC models.

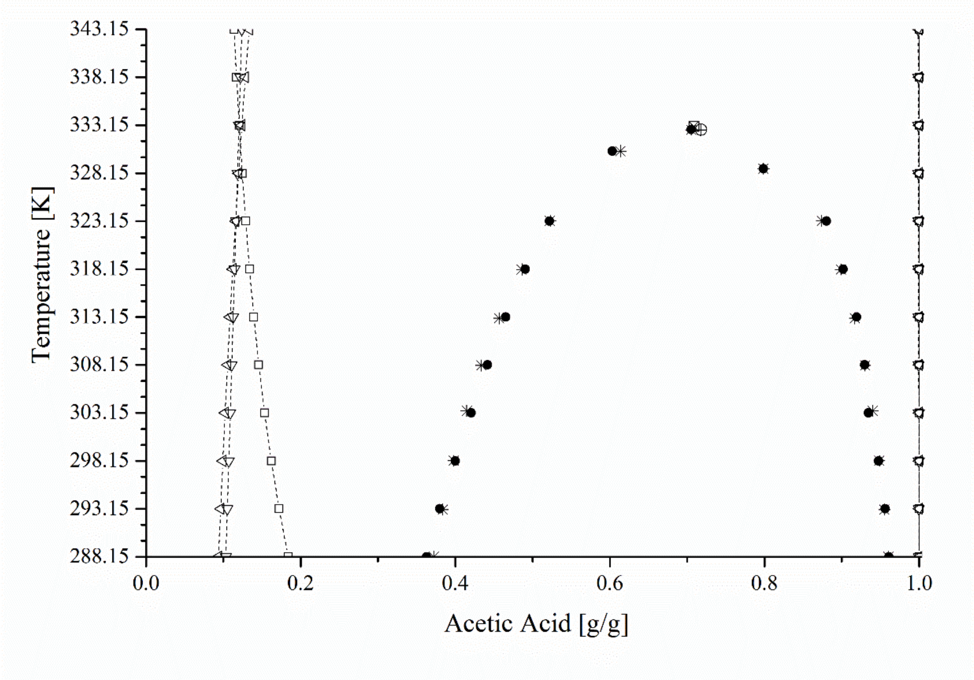
Table 4.5-2: Experimental liquid-liquid equilibrium data (mass fractions w) for pseudobinary systems composed of refined soybean oil (1) plus anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4), or dimethyl sulfoxide (5) at p = 94.2 kPa[a].

Anhydrous Ethanol (2)			**Acetic Acid (3)**			**Ethyl Lactate (4)**			**Dimethyl Sulfoxide (5)**		
T [K]	$u(T)$	w_2	T [K]	$u(T)$	w_3	T [K]	$u(T)$	w_4	T [K]	$u(T)$	w_5
Constant-temperature method									*Gravimetric procedure*		
288.15	0.05	0.122	288.15	0.05	0.363	283.15	0.05	0.307	293.15	0.05	0.052
293.15		0.135	293.15		0.380	285.65		0.324	298.15		0.052
298.15		0.151	298.15		0.401	288.15		0.346	303.15		0.052
303.15		0.170	303.15		0.421	290.65		0.371	308.15		0.053
308.15		0.193	308.15		0.442	293.15		0.410	313.15		0.057
313.15		0.217	313.15		0.465	295.65		0.450	318.15		0.056
318.15		0.255	318.15		0.491	298.15		0.487	323.15		0.055
323.15		0.294	323.15		0.522	300.65		0.539	328.15		0.055
328.15		0.340	323.15		0.880	300.65		0.846	333.15		0.057
328.15		0.865	318.15		0.902	298.15		0.883	333.15		0.995
323.15		0.885	313.15		0.919	295.65		0.901	328.15		0.995
318.15		0.899	308.15		0.930	293.15		0.908	323.15		0.995
313.15		0.913	303.15		0.935	290.65		0.928	318.15		0.994
308.15		0.926	298.15		0.947	288.15		0.937	313.15		0.996
303.15		0.935	293.15		0.956	285.65		0.948	308.15		0.995
298.15		0.943	288.15		0.961	283.15		0.953	303.15		0.997
293.15		0.947							298.15		0.996
288.15		0.956							293.15		0.996
Constant-composition method									*GC-MS method*		
334.55	0.05	0.752	328.6	0.3	0.799	301.5	0.2	0.800	293.15	0.05	0.055
334.7	0.2	0.454	330.4	0.2	0.603	301.7	0.2	0.606	308.15		0.054
336.4	0.1	0.651	332.7	0.2	0.705	302.5	0.2	0.700	323.15		0.056
336.5	0.1	0.552							323.15		1.02
									308.15		1.01
									293.15		0.99

[a] Standard uncertainties u are $u(p)$ = 0.5 kPa, $u(w_2) \leq 0.008$, $u(w_3) \leq 0.005$, $u(w_4) \leq 0.008$, $u(w_5) \leq 0.002$ using gravimetric in vacuum oven, $u(w_5) \leq 0.008$ with coefficient of variation (CV)[b] ≤ 14.89% (raffinate phase), and $u(w_5) \leq 0.05$ with CV ≤ 4.99% (extract phase) using GC-MS. [b] Coefficient of variation is calculated as: $CV(\%) = (u(w)/w).100$

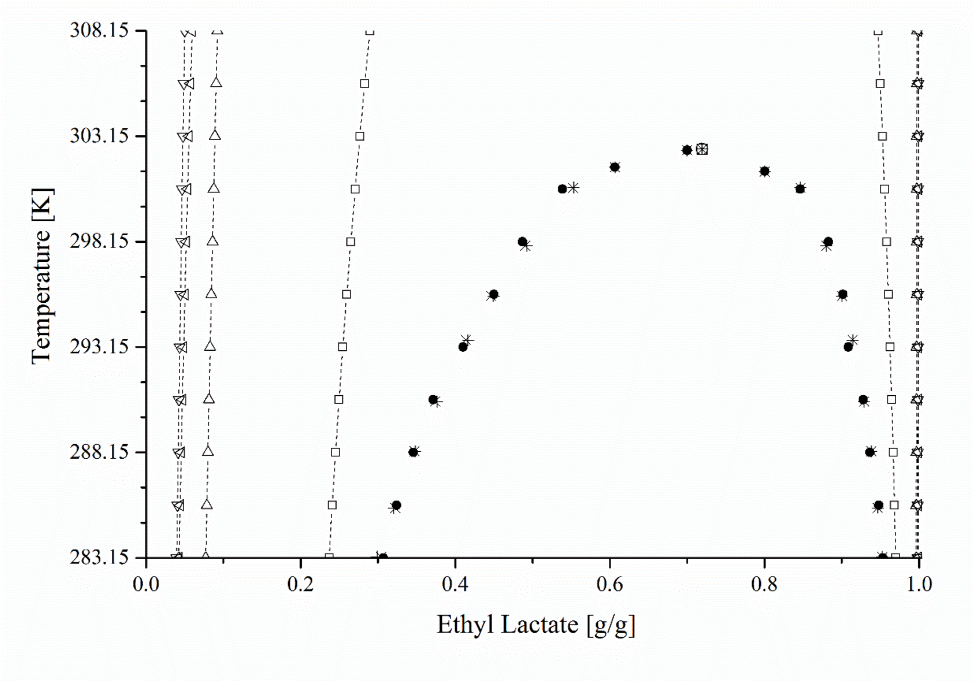


(A)

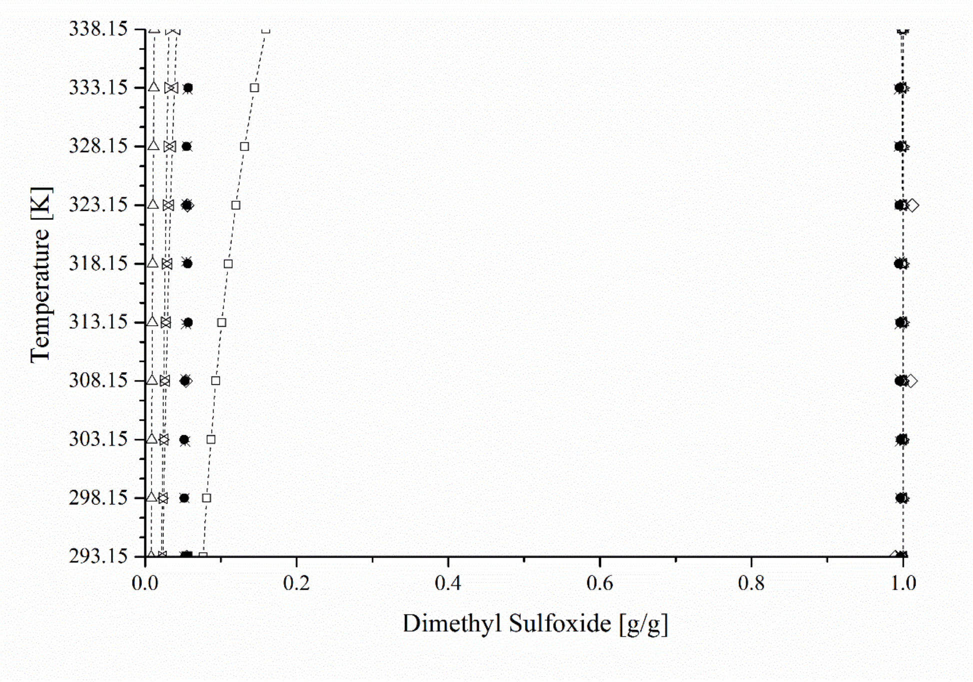


(B)

Figure 4.5-1 (A-B): Liquid-liquid equilibrium data and calculated upper critical solution temperatures (UCST) for pseudobinary systems composed of refined soybean oil (1) + organic solvents under atmospheric pressure: (A) anhydrous ethanol (2), (B) acetic acid (3), (C) ethyl lactate (4) and (D) dimethyl sulfoxide (5). Legend: (●) experimental data obtained by either cloud point or gravimetric procedure; (◇) experimental data obtained by GC-MS for DMSO; (×) NRTL; (+) UNIQUAC; (⊠) UCST by the NRTL model; (⊕) UCST by the UNIQUAC model; (△) UNIFAC-LL; (▷) UNIFAC-HIR; (□) UNIFAC-Dortmund; (◁) NIST-modified UNIFAC; (▽) UNIFAC-Lyngby.



(C)



(D)

Figure 4.5-2 (C-D): Liquid-liquid equilibrium data and calculated upper critical solution temperatures (UCST) for pseudobinary systems composed of refined soybean oil (1) + organic solvents under atmospheric pressure: (A) anhydrous ethanol (2), (B) acetic acid (3), (C) ethyl lactate (4) and (D) dimethyl sulfoxide (5). Legend: (●) experimental data obtained by either cloud point or gravimetric procedure; (◇) experimental data obtained by GC-MS for DMSO; (×) NRTL; (+) UNIQUAC; (⊠) UCST by the NRTL model; (⊕) UCST by the UNIQUAC model; (△) UNIFAC-LL; (▷) UNIFAC-HIR; (□) UNIFAC-Dortmund; (◁) NIST-modified UNIFAC; (▽) UNIFAC-Lyngby.

Among the four solvents considered, anhydrous ethanol and DMSO generated largest biphasic regions within the diluent (RSO) (Figure 4.5-2). In the solvent-rich phase (extract phase E), low solubilities of RSO were found. On the contrary, different ranges of solubilities of each solvent in RSO-rich phase (raffinate phase R) were revealed by experiments. Solubilities for solvents in raffinate phase decreased in the following order: ethyl lactate > acetic acid > anhydrous ethanol > DMSO. Phase diagrams of RSO (1) plus anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4) are of type I [49], while for RSO (1) plus DMSO (5), a small temperature effect in mutual solubilities was found.

Table 4.5-3 and Table 4.5-4 list binary parameters of the NRTL and UNIQUAC models, respectively, as well as global deviations (δ_w) and average absolute deviation (AAD) between experimental and calculated data.

Table 4.5-3: Binary parameters for the NRTL model, global deviations (δ_w) (Eq. 4.4-3) and average absolute deviation (AAD) for each phase (raffinate and extract) for refined soybean oil (1) plus organic solvents {anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4), or dimethyl sulfoxide (5)}.

Pair ij	a_{ij}**/J.(mol.K)$^{-1}$**	b_{ij}**/J.(mol)$^{-1}$**	c_{ij}**/J.(mol.K)$^{-1}$**	α_{ij}	δ_w	**AAD (%)^a**
12	548.19	-921.93	-96.26	0.45	0.59	0.0042
21	121.96	-3659.06	-11.75			
13	598.09	-18720.79	-95.26	0.59	0.51	0.0039
31	641.66	-20697.87	-93.39			
14	1109.28	-16780.43	-186.06	0.49	0.40	0.0030
41	-1623.44	79557.39	244.22			
15	-656.64	-3301.88	132.05	0.27	0.10	0.0008
51	-665.12	39976.12	104.11			

^{a} Average Absolute Deviation (AAD) is calculated as: $\mathrm{AAD} = \frac{1}{M} . \sum_{i=1}^{M} \left| w_{\exp} - w_{calc} \right|$.

Table 4.5-4: Binary parameters for the UNIQUAC model, global deviations (δ_w) (Eq. 4.4-3) and average absolute deviation (AAD) of mass fraction (w) for refined soybean oil (1) plus organic solvents {anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4), or dimethyl sulfoxide (5)}.

Pair ij	a_{ij}**/J.(mol.K)$^{-1}$**	b_{ij}**/J.(mol)$^{-1}$**	c_{ij}**/J.(mol.K)$^{-1}$**	δ_w	**AAD (%)^a**
12	9198.18	-334.09	51.61	0.61	0.0042
21	697.50	6.90	-1.45		
13	-82.77	3536.68	11.58	0.53	0.0040
31	-74.06	2656.98	11.39		
14	3126.58	-175.22	28.48	0.49	0.0038
41	881.41	19.19	-3.88		
15	-156.93	6704.19	21.71	0.10	0.0007
51	114.45	-5468.54	-16.61		

^{a} Average Absolute Deviation (AAD) is calculated as: $\mathrm{AAD} = \frac{1}{M} . \sum_{i=1}^{M} \left| w_{\exp} - w_{calc} \right|$.

In general, the NRTL and UNIQUAC models satisfactorily correlated experimental LLE data, generating δ_w lower than 0.59% and 0.61%, respectively. UCST values and critical mass fraction of RSO (w_{1C}) obtained by liquid-liquid flash calculations using either the NRTL or UNIQUAC models with regressed parameters from Table 4.5-3 and Table 4.5-4, respectively, are presented in Table 4.5-5.

Table 4.5-5: Upper critical solution temperature (UCST) and critical mass fraction of refined soybean oil (w_{1C}) for pseudobinary systems of refined soybean oil (1) plus anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4) obtained by flash calculations using the NRTL and UNIQUAC models.

Solvent	**NRTL**		**UNIQUAC**		**Average value**			
	UCST/K	w_{1C}	UCST/K	w_{1C}	UCST/K	u(UCST)/K [a]	w_{1C}	$u(w_{1C})$[a]
2	337.33	0.375	337.36	0.377	337.35	0.02	0.376	0.001
3	333.04	0.291	332.67	0.282	332.86	0.26	0.287	0.006
4	302.53	0.281	302.54	0.282	302.54	0.01	0.282	0.001

[a] UCST and w_{1C} deviations are calculated as: $u(x)=\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i-\bar{x})^2}$

As shown in Table 4.5-5, all the UCST were higher than 298.15 K (ambient condition). For each solvent, it was found concordance between the calculated UCST and w_{1C} values using either the NRTL or UNIQUAC models, confirming their similar predictive capacity.

Regarding predicted phase diagrams, Figure 4.5-2 depicts inadequacy of all the UNIFAC versions in representing LLE data of studied fatty systems. In most cases, predicted values indicated that RSO is virtually immiscible in solvents, and larger heterogeneous regions than experimental ones were generated. This fact may be a consequence of the size and shape of TAG molecule, in which common functional groups appear in uncommon ways and/or are repeated many times to describe the molecule entirely. In general, absence of the UCST within investigated temperature ranges were predicted. Other failures related to predictions are missing group-group interaction parameters for DMSO using the UNIFAC-Lyngby method, and prediction of complete miscibility with RSO given by the UNIFAC-HIR method for acetic acid and for ethyl lactate as solvents, and by the UNIFAC-LL method for acetic acid as solvent. Also, in the case of the UNIFAC-Dortmund method for acetic acid as solvent, predicted solubilities decreased with temperature, which is in total disagreement with experimental results.

On the other hand, reasonable predictions were found in the following cases:

(i) the UNIFAC-HIR method, which was adjusted specially for deacidification of vegetable oils with alcoholic solvents, as expected, generated reasonable values of mutual solubilities for the anhydrous ethanol/RSO pair (Figure 4.5-2–A) for temperatures between 288.15 K and 328.15 K. It is a consequence of database considered by Hirata et al. [27], which was within this temperature interval;

(ii) the UNIFAC-Dortmund method reasonably predicted LLE of ethyl lactate with RSO (Figure 4.5-2–**C**) at lower temperatures (283.15 to 288.15 K), presenting higher discrepancies at higher temperatures;

(iii) for DMSO system, due to a large heterogeneous region between this solvent and RSO found experimentally, satisfactory predictions of DMSO-rich phase were verified, and for RSO-rich phase reasonable results were also achieved;

(iv) in general, low values of mass fractions of RSO in the extract phases were found experimentally, and predicted values given by the five UNIFAC versions used followed. On the other hand, considerable differences in solvent mass fractions RSO-rich phase were observed.

Global deviations (Eq. 4.4-3) between experimental and predicted values for the UNIFAC method versions used in this work are shown in Table 4.5-6.

Table 4.5-6: Global deviations (Eq. 4.4-3) between experimental and predicted results for the UNIFAC-LL, UNIFAC-HIR, NIST-modified UNIFAC, UNIFAC-Dortmund and UNIFAC-Lyngby methods for refined soybean oil (RSO) (1) plus anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4), or dimethyl sulfoxide (5).

Solvent	δ_w				
	UNIFAC-LL	UNIFAC-HIR	UNIFAC-Dortmund	NIST-modified UNIFAC	UNIFAC-Lyngby
Anhydrous Ethanol (2)	16.7	10.0	16.9	16.2	19.2
Acetic Acid (3)	NA[a]	NA[a]	30.4	32.2	31.9
Ethyl Lactate (4)	26.6	NA[a]	18.2	22.6	26.6
DMSO (5)	3.2	2.1	3.9	1.8	NA[b]

[a] Predicted as completely soluble, see Table 2 (NA: not applicable); [b] Not applicable due to lack of group-group interaction parameters.

High values of global deviations were obtained for all five UNIFAC method versions tested. As expected, the UNIFAC-HIR method provided better results for systems of RSO plus anhydrous ethanol, which is the kind of system used for readjustments of their group-group interaction parameters. For system composed of RSO plus DMSO, global deviations given by the UNIFAC-LL, UNIFAC-HIR and UNIFAC-Dortmund methods were lower than 3.9%. For this system experimental heterogeneous region was larger than the region predicted by the UNIFAC-Dortmund method.

Finally, experimental behaviors of partition coefficients of RSO (k_1) within different solvents at selected temperatures (Table A.2.13) are illustrated in Figure 4.5-3. Comparisons between experimental, correlated and predicted behaviors of partition coefficients of RSO (k_1) within different solvents are depicted in Figure A.2.3.

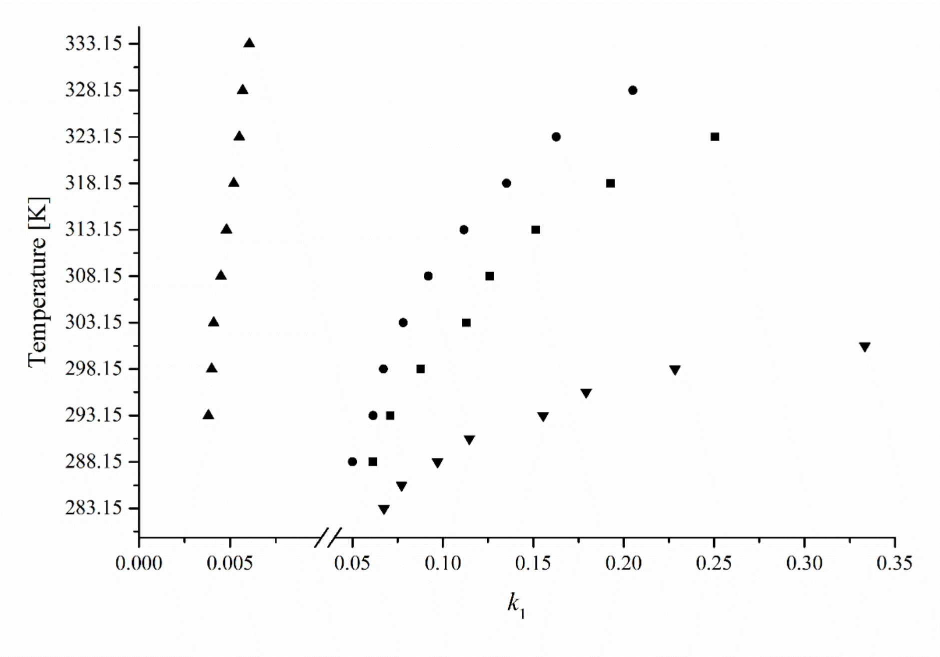


Figure 4.5-3: Partition coefficients of refined soybean oil (RSO) (k_1, Eq. 4.4-3) for pseudobinary systems composed of refined soybean oil (1) plus organic solvents: (●) anhydrous ethanol (2); (■) acetic acid (3); (▼) ethyl lactate (4); and (▲) dimethyl sulfoxide (5).

Figure 4.5-3 illustrates the potential of anhydrous ethanol and DMSO as solvents for extracting undesirable compounds from refined soybean oil. At a given temperature, ethyl lactate provided highest values of k_1, followed by acetic acid, anhydrous ethanol, and DMSO. Figure 4.5-3 also reveals relevant influence of temperature in k_1 for all solvents, except DMSO. At temperatures close to 288.15 K, similar values of k_1 were found for ethyl lactate, acetic acid and anhydrous ethanol, but they differ considerably as temperature increases. In general, values of k_1 for DMSO as solvent were very low (< 0.006) despite of temperature. Concerning the predicted values of k_1 for the investigated solvents, Figure A.2.3 emphasizes failures of the UNIFAC versions used in this work to predict LLE data. Lower values of k_1 were always predicted for all solvents at a given temperature, but anhydrous ethanol with the UNIFAC-HIR method for temperatures below 308.15 K. These results reinforce the need of collecting experimental data for systems in edible and nonedible oils regarding its main functional groups.

4.6 CONCLUSION

A search for potential solvents for removing odoriferous compounds was conducted by investigating solubility behavior of seventeen low toxic solvents and refined soybean oil (RSO). Eleven solvents were completely miscible within oil, two formed stable emulsions (water and formic acid) and four formed biphasic mixtures. For partially miscible systems (RSO plus anhydrous ethanol, or acetic acid, or ethyl lactate, or DMSO), LLE data were collected by means of either cloud point detection or by tie line quantification. Based on LLE data, it was found that DMSO and anhydrous ethanol are potential solvents for removing aldehydes and short chain carboxylic acids (odoriferous compounds) from soybean oil, providing largest biphasic regions. On the other hand, mutual solubilities between RSO plus acetic acid or ethyl lactate are indicatives that these solvents would not be first choices. The NRTL and UNIQUAC models satisfactorily correlated experimental data, providing very low global deviations. The UCST values were determined by liquid-liquid flash calculations using the NRTL and UNIQUAC regressed parameters, and good agreement were verified between the two models.

Concerning the UNIFAC method predictions, the five investigated versions failed to predict solubilities in both qualitative and quantitative ways. Exceptions were found for specific cases, as the UNIFAC-HIR method for anhydrous ethanol and the UNIFAC-Dortmund method for ethyl lactate. Prediction results emphasize failures on the capability of the UNIFAC method to predict LLE data in systems involving vegetable oils, and reinforce the need of collecting experimental data for systems in this area of research in order to readjust the UNIFAC method group-group binary parameters and improve its predictive capacity.

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CAPÍTULO 5

INVESTIGATION OF THE MUTUAL SOLUBILITIES OF SOYBEAN OIL AND LOW-TOXIC LIQUID-COSOLVENT MIXTURES

Perci O. B. Homrich, Roberta Ceriani

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ABSTRACT: Liquid-liquid extraction is a potential alternative for removing mildly odoriferous compounds from vegetable oils. An improvement in process performance can be achieved by using an adequate cosolvent which provides a maximum solute removal with minimum diluent loss, as well as presents important thermophysical properties suited to facilitate mass transfer among target components and solvent recovery. Furthermore, in food and pharmaceutical industries, toxicity is a relevant concern. Thus, in order to evaluate mutual solubilities of soybean oil within different low-toxic cosolvents, liquid-liquid equilibrium data was experimentally measured for system composed of refined soybean oil + acetic acid + water, and was predicted for cosolvents ({acetic acid, or ethanol, or ethyl lactate, or dimethyl sulfoxide} + {water or formic acid}) at different temperatures. For accessing feasible values of water and formic acid to be added to ethanol, or acetic acid, or ethyl lactate, or dimethyl sulfoxide, the amount of added water was experimentally determined aiming to avoid persistent emulsion formation at 298.15 K, and for the addition of formic acid we follow instructions of the CLP regulation in order to avoid corrosion. Experimental data were correlated by the NRTL and UNIQUAC models, and predictions were accomplished by using five different versions of the UNIFAC method, namely: UNIFAC-LL, UNIFAC-DMD, UNIFAC-LBY, UNIFAC-HIR, and UNIFAC-NIST.

Keywords: cosolvents, deodorization, liquid-liquid extraction, refined soybean oil.

5.1 INTRODUCTION

Liquid-liquid extraction has been researched as a mild alternative process for removing some undesirable compounds from vegetable oils, such as odor components (May et al., 2016; Homrich and Ceriani, 2016) and free fatty acids (Ferreira et al., 2015; Gonçalves et al., 2016). Due to ambient condition, this separation method avoids some deleterious consequences found in steam stripping process, which is currently applied in the deodorization step, as well as requires lower energy consumption (Rodrigues et al., 2007; Cuevas et al., 2009). Several studies have shown that severe conditions of temperature (220 – 265 °C) and pressure (0.2 – 0.4 kPa) applied in stripping are responsible for triacylglycerols and nutraceutical compounds degradation (Suliman and Jiang, 2013; Fine et al. 2015), cis-trans isomerization (Ceriani and Meirelles, 2007; Martin et al., 2006), and formation of the 3-MCPD contaminant (Ermacora and Hrncirik, 2014).

Knowledge of liquid-liquid equilibrium (LLE) data allows selection of appropriate solvents or cosolvents to improve removal of a solute from a diluent of industrial interest. Cosolvents have been highly analyzed for possessing the advantages of reducing miscibility between solvent and diluent, as well as facilitating mixing and separation of phases by thermophysical property improvement (Rocha et al., 2017; Yang et al., 2012. Bandlamudi et al., 2017). Furthermore, cosolvent selection may also mitigates human health impacts and process safety risks by taking into account solvent safety features as corrosivity, flammability, and toxicity, wherein this last one is especially considered in food and pharmaceutical industries (ICH, 2012; Byrne et al., 2016; Diorazio et al., 2016).

Literature presents few works which investigated solubility behavior of edible oils within different cosolvents, mainly mixtures of ethanol and water (Huang et al., 2015; Silva et al., 2010). Recently, we reported LLE data of refined soybean oil with low-toxic solvents, in which it was found that dimethyl sulfoxide and anhydrous ethanol exhibited lowest miscibilities within oil, followed by acetic acid and ethyl lactate (Homrich et al., 2017). Although efforts have been made in this area, scarce LLE data of vegetable oils and different cosolvents are found. Accordingly, in order to progress towards determination of suitable compounds for removing undesirable components (aldehydes and short-chain carboxylic acids) from vegetable oils, an in-depth search for cosolvents that are selective for odor compounds over vegetable oils is necessary.

In this context, this work aimed at investigating liquid-liquid phase diagrams for refined soybean oil (RSO) plus different cosolvents, classified as low-toxic by the ICH guidance

(ICH, 2012). Used solvents were previously selected for having solvating characteristics with aldehydes and short-chain carboxylic acids. LLE data were experimentally collected for system containing RSO plus acetic acid plus water at temperatures varying from 293.15 to 333.15 K with $u(T)$ = 0.05 K, and correlated by the NonRandom Two Liquids (NRTL) (Renon and Prausnitz, 1968) and UNIversal QUAsiChemical (UNIQUAC) (Abrams and Prausnitz, 1975) models. Additionally, phase diagrams of RSO with eight cosolvents {(acetic acid, or ethanol, or ethyl lactate, or dimethyl sulfoxide) + (water or formic acid)} were predicted using five different versions of the UNIFAC method (Fredenslund et al., 1975), specifically: UNIFAC-LL (Magnussen, 1981), UNIFAC-DMD (Weidlich and Gmehling, 1987; Gmehling et al., 1993), UNIFAC-LBY (Larsen, 1987), UNIFAC-HIR (Hirata et al., 2013) and UNIFAC-NIST (Kang et al., 2015). The amount of water added to each solvent was determined aiming to avoid persistent emulsion formation; for formic acid addition, we followed guidelines from the Classification, Labelling and Packaging (CLP) regulation to avoid corrosion (CLP, 2008).

5.2 METHODOLOGY

5.2.1 Materials

Refined soybean oil (Liza brand) was purchased in a local market. Its fatty acid and triacylglycerol (TAG) profiles, as well as its acidity and oil stability index (OSI) can be found elsewhere (Homrich et al., 2017). Chemicals used in this work are presented in Table 5.2-1. Also, deionized water (Milli-Q, Millipore) was utilized in preparation of cosolvents.

Table 5.2-1: Source and purity of chemicals used in this work.

Compounds	IUPAC name	CAS Registry No.	Supplier	Purity (mass fraction)
Anhydrous ethanol	Ethanol	64-17-5	Sigma-Aldrich	> 0.995
Acetic acid	Ethanoic acid	64-19-7	Êxodo	0.997
Ethyl lactate	Ethyl 2-hydroxypropanoate	97-64-3	Fluka	> 0.99
Dimethyl sulfoxide	Methanesulfinylmethane	67-68-5	Sigma-Aldrich	> 0.997
Formic acid	Methanoic acid	64-18-6	Êxodo	0.99

5.2.2 Preparation of cosolvents

Cosolvents were prepared by mixing {water or formic acid} with {ethanol, or acetic acid, or ethyl lactate, or dimethyl sulfoxide}. Maximum amount of water added in each solvent was determined to avoid stable emulsion formation at 298.15 K after a period of 12 h of phase separation. Thus, different mixtures containing water and solvent were prepared directly in a sealed equilibrium glass cell (23 mL) in an analytical balance (Radwag, Model AS 220.R2) accurate to ± 0.0001 g. Mixtures composed of oil/cosolvent in mass ratio of 1:1 were vigorously agitated using magnetic stirrers (Fisatom, Model 752) for 1 h and rested for 12 h for phase split. Temperature was controlled using an ultra-thermostatic bath (Marconi, Model MA-184) with a precision of 0.05 K. Translucent phases with maximum water quantity were verified for the following cases: {ethanol, or acetic acid, or ethyl lactate} plus water (10% m/m) and dimethyl sulfoxide plus water (25% m/m). For the amount of formic acid added to the solvents, we followed guidelines of CPL regulation (CPL, 2008), which states that a formic acid concentration higher than 10% m/m provides corrosion.

5.2.3 Experimental determination of liquid-liquid equilibrium data

Mixtures containing RSO plus cosolvent {acetic acid plus water}, in oil/cosolvent mass ratio of 1:1, were vigorously agitated for 1 h and allowed to settle for 12 h. Temperature varied from 293.15 to 333.15 K with $u(T) = 0.05$ K. After phase split, aliquots of each equilibrium phase were collected using syringes with stainless steel needles. For RSO quantification, samples of about 1 g of each phase were placed in Petri dishes and kept in a vacuum oven (Marconi, Model MA030) at 383.15 K for vaporization of water and solvent, until constant mass. Water content was determined by Karl Fischer titration, according to AOCS method Ca 23–55, with a KF Coulometer (Metrohm, Model 831). Acetic acid mass fraction was obtained by difference.

5.2.4 Thermodynamic modeling

Both in modeling and prediction, RSO was represented as a pseudocomponent of a unique triacylglycerol molecule containing two linoleic acids and one oleic acid (LLO), named {3-[(9Z)-9-Octadecenoyloxy]-1,2-propanediyl-(9Z,12Z,9'Z,12'Z)bis(-9,12-octadecadienoate)}, with a molecular weight of 874.5 g.gmol^{-1} (Homrich et al., 2017). Experimental LLE data were correlated by using the NRTL and the UNIQUAC models. Binary parameters (a_{ij}/J·K^{-1}mol^{-1}, b_{ij}/J·mol^{-1}) for the NRTL (Eq. 5.2-1) and the UNIQUAC (Eq. 5.2-2) models, and the nonrandomness parameter (α_{ij}) for the NRTL model, were obtained by using the Britt-Luecke algorithm with the Deming initialization method (Homrich et al., 2017). Regression of parameters was accomplished using the maximum-likelihood objective function, which considered all measured variables (temperatures, mole fractions and pressure). All modelling was achieved by using the software *Aspen Plus v.8.4.*

$$\tau_{ij} = a_{ij} + {}^{b_{ij}}\!/_{T} \tag{5.2-1}$$

$$\tau_{ij} = \exp\left(a_{ij} + {}^{b_{ij}}\!/_{T} \right) \tag{5.2-2}$$

Prediction of phase diagrams was achieved by applying five UNIFAC versions, namely: UNIFAC-LL (Magnussen, 1981), UNIFAC-DMD (Weidlich and Gmehling, 1987; Gmehling et al., 1993), UNIFAC-LBY (Larsen, 1987), UNIFAC-HIR (Hirata et al., 2013) and UNIFAC-NIST (Kang et al., 2015). It is worthwhile mentioning that for the UNIFAC-HIR, it was adjusted group-group parameters using a databank containing LLE data involved on the solvent deacidification of edible oils, comprising specially hydrous and anhydrous short-chain alcohols as solvents, and long-chain carboxylic acids as solutes. Since functional groups of ethyl lactate, formic acid and DMSO were not considered in the UNIFAC-HIR, we used binary parameters adjusted by Magnussen (1981) (UNIFAC-LL). Subdivision form of all solvents and of RSO (TAG LiLiO) considered the following functional subgroups: CH_3, CH_2, CH, CH_2COO, OH, COOH, HCOOH, $(CH_3)_2SO$ (DMSO), H_2O and HC=CH. Global deviation between experimental and calculated (or predicted) data for the system RSO plus acetic acid plus water was calculated according to Equation 5.2-3.

$$\delta w = 100\sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{P}\left\{\left(w_{i,n}^{\mathrm{R,exp}} - w_{i,n}^{\mathrm{R,calc}}\right)^2 + \left(w_{i,n}^{\mathrm{E,exp}} - w_{i,n}^{\mathrm{E,calc}}\right)^2\right\}}{2NP}} \tag{5.2-3}$$

where *N* is the total number of tie lines in each system, *P* is the total number of components in each system, the superscripts E and R refer to extract phase and raffinate phases, and the superscripts exp and calc refer to experimental and calculated (or predicted) values, respectively. Based of experimental and predicted LLE data, partition coefficients of RSO (k_{RSO}) in Eq. 5.2-4 were calculated for evaluating distribution of oil (diluent) between extract (E) and raffinate (R) phases at different temperatures. For diluent, lower values of partition coefficients are desirable.

$$k_{RSO} = \frac{w_{RSO}^{E}}{w_{RSO}^{R}} \qquad (5.2\text{-}4)$$

5.3 RESULTS

Table 5.3-1 shows experimental liquid-liquid equilibrium data and partition coefficients of RSO (k_{RSO}) for system containing RSO plus acetic acid plus water at different temperatures and atmospheric pressure. Figure 5.3-1 depicts liquid-liquid phase diagrams for the RSO plus low-toxic cosolvents at different temperatures, including experimental and predicted data.

Table 5.3-1: Experimental liquid-liquid equilibrium data (mass fractions *w*) and partition coefficient of RSO (k_{RSO}) for refined soybean oil (RSO) (1) + acetic acid (2) + water (3) at 94.2 kPa[a].

T/*K*	**Overall mixture (OM)**			**Raffinate phase (RP)**			**Extracted phase (EP)**			**k_{RSO}**
	w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3	
293.15	0.5018	0.4484	0.0499	0.878	0.117	0.0044	0.0043	0.875	0.121	0.005
298.15	0.4995	0.4505	0.0501	0.873	0.122	0.0047	0.0047	0.872	0.123	0.005
303.15	0.5002	0.4498	0.0500	0.866	0.129	0.0049	0.0056	0.869	0.125	0.006
308.15	0.4979	0.4519	0.0502	0.862	0.132	0.0054	0.0065	0.870	0.123	0.008
313.15	0.4986	0.4512	0.0502	0.855	0.139	0.0065	0.0070	0.873	0.120	0.008
318.15	0.5014	0.4487	0.0499	0.850	0.142	0.0071	0.0073	0.876	0.117	0.009
323.15	0.4994	0.4505	0.0501	0.845	0.147	0.0080	0.0083	0.870	0.121	0.010
328.15	0.5006	0.4494	0.0500	0.843	0.149	0.0087	0.0091	0.867	0.123	0.011
333.15	0.4997	0.4502	0.0501	0.836	0.155	0.0094	0.0096	0.864	0.127	0.012

[a] Standard uncertainties u are u(T) = 0.05 K, u(p) = 0.5 kPa, $u(w^{OM}) = 0.00001$, $u(w_1^{RP}) \leq 0.006$, $u(w_3^{RP}) \leq 0.0001$, $u(w_1^{EP}) \leq 0.0006$, $u(w_3^{EP}) \leq 0.002$, $u(k_{\mathrm{RSO}}) \leq 0.001$.

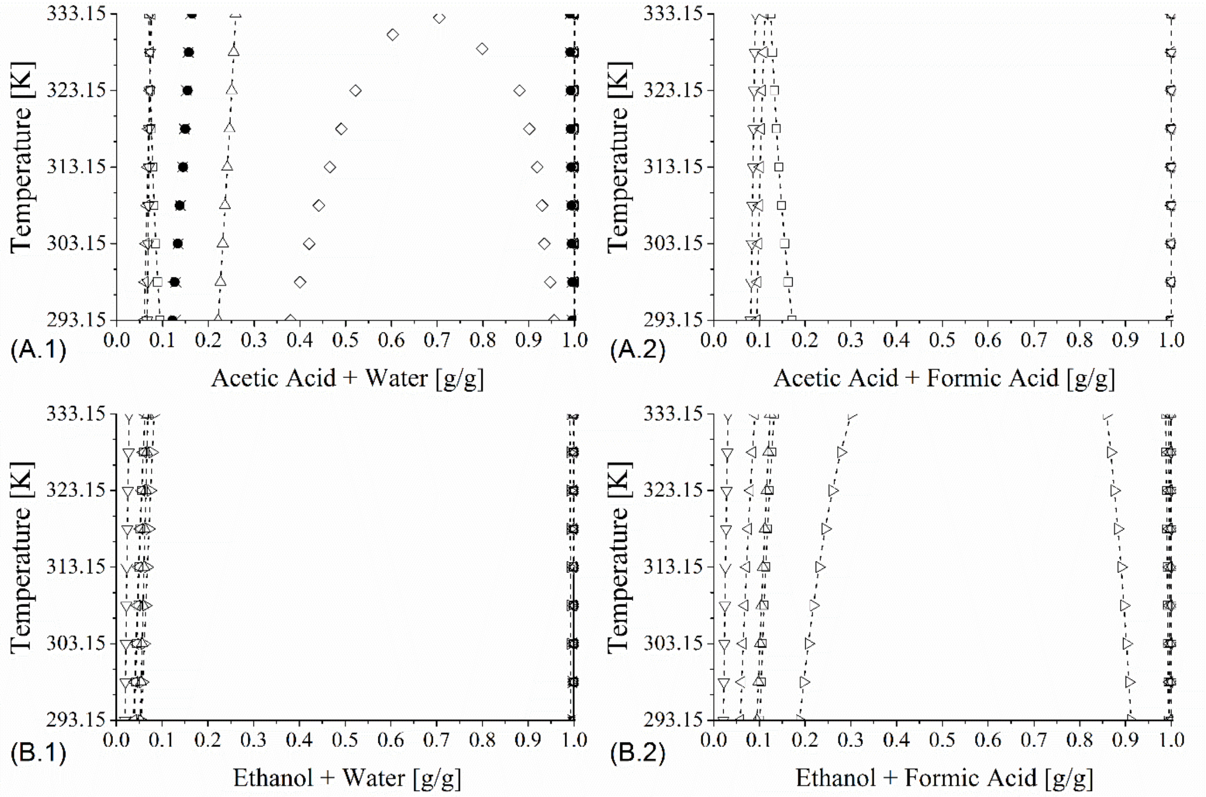

Figure 5.3-1 (A-B): Liquid-liquid equilibrium data for systems composed of refined soybean oil (RSO) + cosolvents ({acetic acid, or ethanol, or ethyl lactate, or dimethyl sulfoxide} + {water or formic acid}). Legend: (●) experimental data; (×) NRTL; (+) UNIQUAC; (△) UNIFAC-LL; (▷) UNIFAC-HIR; (□) UNIFAC-DMD; (◁) NIST-UNIFAC; (▽) UNIFAC-LBY; (◇) Experimental data for RSO + water-free acetic acid from Homrich et al. (2017).

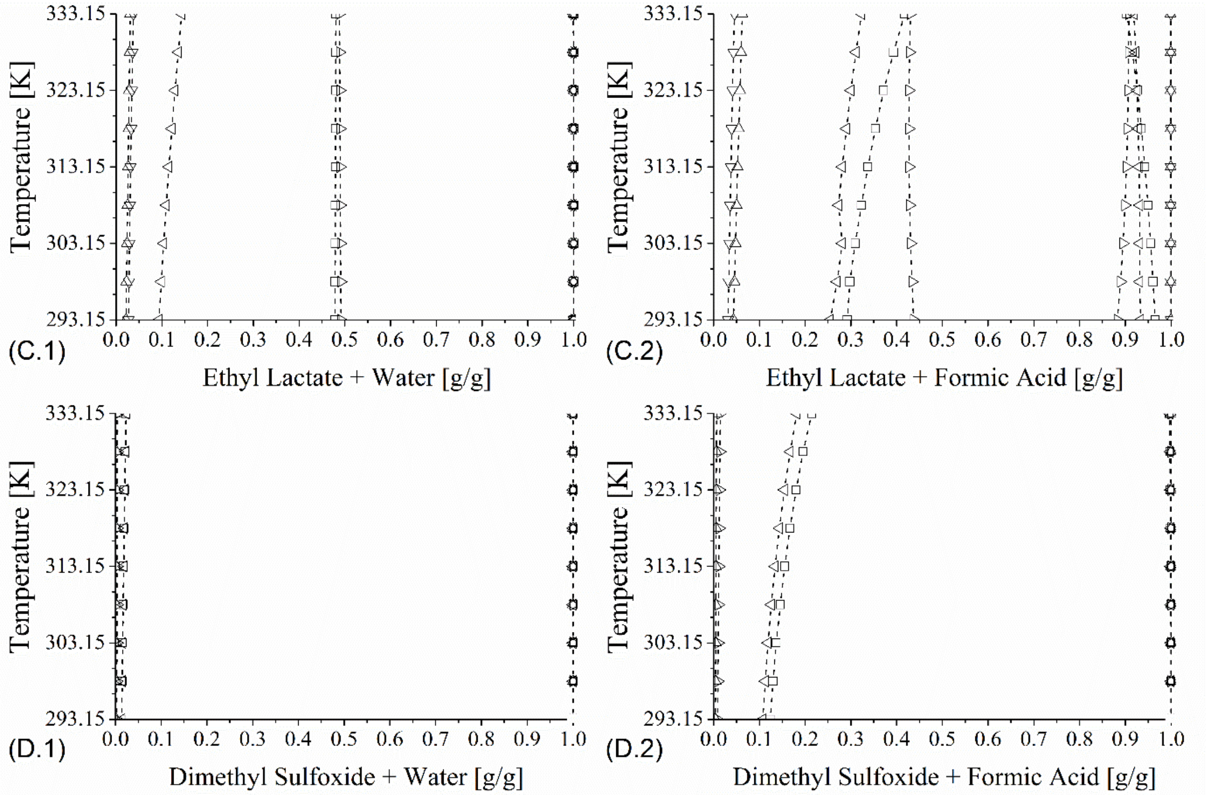

Figure 5.3-2 (C-D): Liquid-liquid equilibrium data for systems composed of refined soybean oil (RSO) + cosolvents ({acetic acid, or ethanol, or ethyl lactate, or dimethyl sulfoxide} + {water or formic acid}). Legend: (●) experimental data; (×) NRTL; (+) UNIQUAC; (△) UNIFAC-LL; (▷) UNIFAC-HIR; (□) UNIFAC-DMD; (◁) NIST-UNIFAC; (▽) UNIFAC-LBY; (◇) Experimental data for RSO + water-free acetic acid from Homrich et al. (2017).

Table 5.3-2 and Table 5.3-3 present adjusted binary parameters of the NRTL and UNIQUAC models, respectively. Table 5.3-4 exhibits global deviations between experimental and predicted data using the five evaluated versions of the UNIFAC method.

Table 5.3-2: Binary parameters for the NRTL model, global deviations (δw) (Eq. 5.2-3) and average absolute deviation (AAD) for refined soybean oil (1) plus acetic acid (2) plus water (3).

Pair ij	a_{ij}/J.(mol.K)$^{-1}$	b_{ij}/J.(mol)$^{-1}$	α_{ij}	δ_w	AAD (%)[a]
12	109.38	18593.55	0.6	0.27	0.19
21	32.03	1544.83			
13	305.27	-77803.38	0.2		
31	298.60	-44278.51			
23	-11.79	5327.68	0.6		
32	-29.14	19625.52			

[a] Average Absolute Deviation (AAD) is calculated as: $\text{AAD}(\%)=\frac{100}{M}.\sum_{i=1}^{M}\left|w_{\exp}-w_{calc}\right|$.

Table 5.3-3: Binary parameters for the UNIQUAC model, global deviations (δw) (Eq. 5.2-3) and average absolute deviation (AAD) for refined soybean oil (1) plus acetic acid (3) plus water.

Pair ij	a_{ij}**/J.(mol.K)$^{-1}$**	b_{ij}**/J.(mol)$^{-1}$**	δ_w	**AAD (%)[a]**
12	2.97	3293.12	0.25	0.18
21	-22.05	-4241.94		
13	40.33	11455.30		
31	-65.92	-15645.82		
23	147.61	44843.81		
32	-29.38	12655.01		

[a] Average Absolute Deviation (AAD) is calculated as: $\mathrm{AAD}=\frac{100}{M}.\sum_{i=1}^{M}\left|w_{\exp}-w_{calc}\right|$.

Table 5.3-4: Global deviations (δw) (Eq. 5.2-3) and Average Absolute Deviation (AAD) between experimental and predicted results for the UNIFAC-LL, UNIFAC-HIR, NIST-UNIFAC, UNIFAC-DMD and UNIFAC-LBY methods for refined soybean oil (RSO) plus acetic acid plus water.

UNIFAC version	**Oil-rich Phase**	**Cosolvent-rich Phase**	**Global**
	AAD (%)[a]		δ_w
UNIFAC-LL	6.76	1.27	5.83
UNIFAC-DMD	4.23	1.14	3.88
UNIFAC-LBY	4.89	1.49	4.29
UNIFAC-HIR	NA[b]	NA[b]	NA[b]
UNIFAC-NIST	5.05	1.54	4.42

[a] Average Absolute Deviation (AAD) is calculated as: $\mathrm{AAD}=\frac{100}{M}.\sum_{i=1}^{M}\left|w_{\exp}-w_{calc}\right|$. [b] Predicted as completely soluble.

Experimental LLE data (Figure 5.3-1–A.1) showed that addition of water considerably decreased mutual solubility between RSO and acetic acid. As one can see, low amounts of RSO were found in the cosolvent region at investigated temperature range, which indicates low oil loss and consequently an easier solvent recovery. Also, temperature slightly influences the solubility of both equilibrium phases. Furthermore, it were found good agreements between experimental and calculated LLE data for both the NRTL and UNIQUAC models, which presented global deviations of 0.27 and 0.25%, and average absolute deviations of 0.19 and 0.18%, respectively.

Comparing experimental data with predicted ones, good agreement was found for the cosolvent-rich region for the UNIFAC-LL, UNIFAC-DMD, UNIFAC-NIST and UNIFAC-LBY methods, as shown by the low global deviation for that phase (Table 5.3-4). For the RSO-rich region, higher differences between experimental and calculated data were achieved. In general, a considerable improvement on the UNIFAC prediction was surprisingly verified when water was added to acetic acid. Reported global deviations of the UNIFAC methods (Homrich et al., 2017) for the RSO plus water-free acetic acid were approximately 30%.

Concerning the predictions of the liquid-liquid phase diagrams for systems of RSO plus cosolvents ({water or formic acid} + {acetic acid, or ethanol, or ethyl lactate, of dimethyl sulfoxide}), large biphasic regions were found in comparison with systems with one solvent. Furthermore, an unexpected decrease in the solubility of the cosolvent ({water or formic acid} + acetic acid) in the RSO-rich region was predicted by the UNIFAC-DMD. A similar result was also encountered for mutual solubility of cosolvent formic acid + ethyl lactate for the UNIFAC-HIR. Lastly, at the investigated temperature interval, no upper critical temperature (UCST) was found for any system.

Figure 5.3-3 presents the influence of adding water or formic acid to solvents on partition coefficients of RSO.

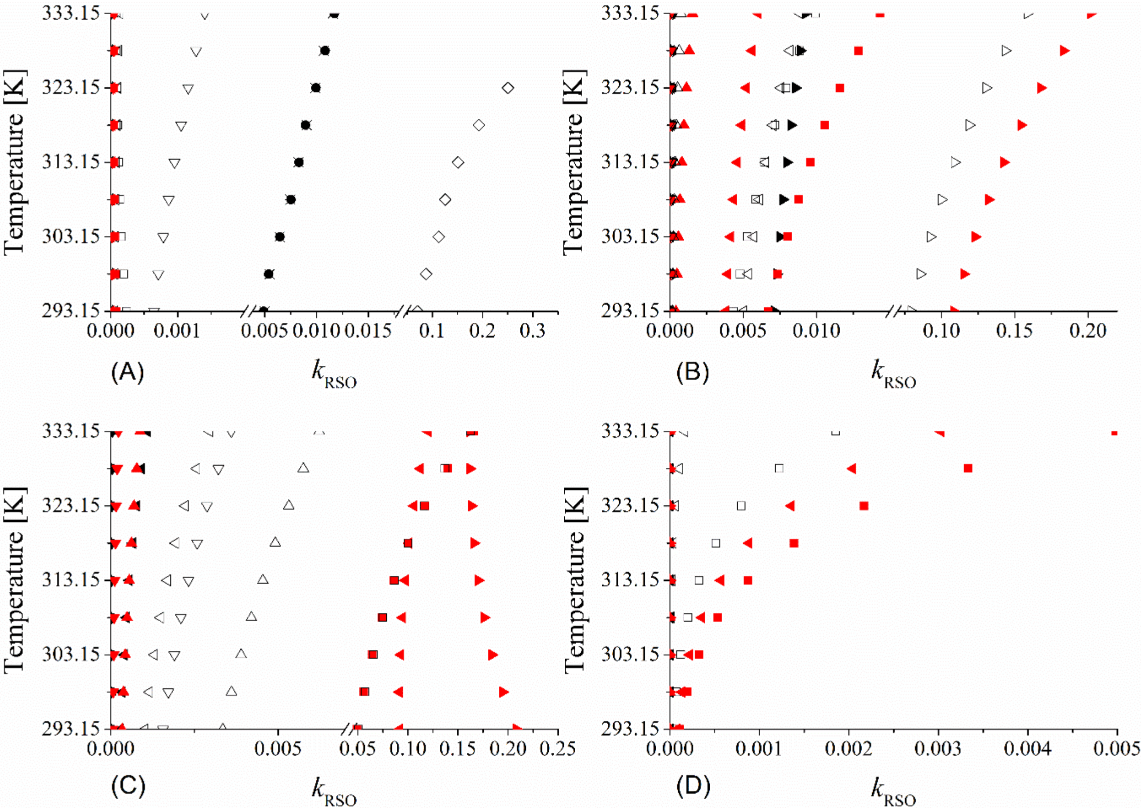

Figure 5.3-3: Partition coefficients of refined soybean oil (RSO) (k_{RSO}) (Eq. 5.2-4) for systems composed of RSO plus {water (black) or formic acid (red)} plus organic solvents: (A) acetic acid; (B) anhydrous ethanol; (C) ethyl lactate; and (D) dimethyl sulfoxide; (●) experimental data; (×) NRTL; (+) UNIQUAC; (△) UNIFAC-LL; (▷) UNIFAC-HIR; (□) UNIFAC-DMD; (◁) NIST-UNIFAC; (▽) UNIFAC-LBY. (◇)

Experimental data in Figure 5.3-3 exhibit a considerable decrease in partition coefficients of RSO when water was added in acetic acid. It is also depicted improvements on the UNIFAC prediction for the liquid-cosolvent mixture of acetic acid plus water when compared with the water-free acetic acid system, considering that experimental data of the cosolvent system were closer to predicted ones. Concerning the predicted k_{RSO} for the eight investigated cosolvents, in general low values were found. An increase in the partition coefficient of RSO when formic acid was added to the solvents occurred for the following cases: UNIFAC-Dortmund (ethanol and DMSO); UNIFAC-HIR (ethanol); and UNIFAC-NIST (ethyl lactate and DMSO). It was previously predicted (Homrich et al., 2017) by using the five UNIFAC versions that RSO and formic acid were immiscible. So these results were unexpected. Concerning discrepancies of the UNIFAC-HIR predictions, they were probably due to the fact that formic acid and ethyl lactate were not considered in the adjustment of group-group binary parameters. As already mentioned, in this case we used binary parameters of the UNIFAC-LL method.

5.4 CONCLUSION

A study of low-toxic cosolvents for removing odor compounds from soybean oil has been conducted. Experimental liquid-liquid equilibrium data for the pseudoternary system composed of refined soybean oil plus acetic acid plus water presented a significant increase in the biphasic region when compared with water-free acetic acid solvent, with very low amounts of RSO in the cosolvent-rich region. Moreover, the NRTL and UNIQUAC models satisfactorily adjusted experimental data, presenting global deviations of 0.27 and 0.25%, respectively. The UNIFAC methods presented global deviations that varied from 3.88 to 5.83%; however, the cosolvent-rich region presented average absolute deviations of approximately 1.2%, indicating good agreement. Regarding the prediction of phase diagrams for the systems RSO plus low-toxic cosolvents ({acetic acid, or ethanol, or ethyl lactate, or dimethyl sulfoxide} plus {water or formic acid}), in general large biphasic regions and low values of partition coefficient of RSO were encountered. Preliminary results showed an important benefit of using a cosolvent for removing undesirable compounds of vegetable oils, entailing a simpler and more economical solvent recovery and purification of the raffinate phase.

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CAPÍTULO 6

PHASE EQUILIBRIA FOR SYSTEMS CONTAINING REFINED SOYBEAN OIL PLUS COSOLVENTS AT DIFFERENT TEMPERATURES

Homrich, P. O. B.; Ceriani, R. Phase Equilibria for Systems Containing Refined Soybean Oil plus Cosolvents at Different Temperatures. *Journal of Chemical and Engineering Data.* **2018**, *63*, 1937–1945. DOI: 10.1021/acs.jced.7b01051

ABSTRACT: Investigation of mutual solubility between vegetable oil and five low-toxic cosolvents is assessed. Liquid-liquid equilibrium data were experimentally collected for systems containing refined soybean oil plus cosolvents composed of {(anhydrous ethanol, or ethyl lactate, or dimethyl sulfoxide) plus water} and {(ethyl lactate, or dimethyl sulfoxide) plus formic acid} at different temperatures. Comparing with pure solvents-oil systems (previous results), it was observed that addition of water or formic acid decreases the mutual solubilities of cosolvents-oil systems. Low quantities of the oil were found in cosolvent-rich phases and very poorly solubility occurs for the system containing oil plus dimethyl sulfoxide plus water. Experimental data were satisfactorily correlated by the NRTL and UNIQUAC models, presenting global deviations lower than 0.29%. Furthermore, prediction using five different versions of the UNIFAC method (UNIFAC-LL, UNIFAC-DMD, UNIFAC-LBY, original UNIFAC with parameters of Hirata et al., and UNIFAC-NIST) agreed for some cases. However, results showed a necessity to improve the predictive capacity of the UNIFAC methods for fatty systems.

Keywords: cosolvents, liquid-liquid extraction, refined soybean oil, UNIFAC, deodorization

6.1 INTRODUCTION

Mild and safe alternative processes have been researched attempting to attenuate safety, health, and environmental impacts and to improve product quality. In chemical industry, solvents (pure or mixtures) are used in large quantities, and their types mainly affect process efficiency and security, especially in liquid-liquid extraction (LLEx) [1,2]. Distribution of components between equilibrium phases and solvent selectivity, indicated by equilibrium data, figure as key factors. Aiming at designing a mild process, safety regulations and solvent standards help to get information as toxicity, flammability, corrosivity and stability [3-5].

For presenting a direct impact on consumer health, food, cosmetic and pharmaceutical industries are the focus of several researches towards soften alternative processes [6,7]. Regarding food industries, edible oil is relevant due to its high consumption by humans. Soybean oil, which is the second most consumed vegetable oil, has an estimated worldwide production in the period 2016/2017 of 53.8 thousand metric tons (MT) [8], of which 80% are processed to become edible and to extend its shelf life [9]. During refining, particularly in the deodorization step, which is applied to remove odoriferous compounds, free fatty acids (physical refining), and trace of pesticides and soap, a series of negative consequences occur. Nutraceutical compounds as sterol and tocopherols may be extensively removed (up to 40%), specially due to the high temperatures (220–265 °C) and very low pressures (0.2–0.4 kPa) applied, and tocopherol esters and fatty acids polymers are formed [10-13] Also, drastic operational conditions are responsible for thermal degradation of triacylglycerols (TAGs) and formation of 3-MCPD (3–monochloropropane-1,2-diol) contaminant and trans-fat [14,15]. Moreover, high energy consumption, and the inability of deodorization step to completely remove pesticides [16], reinforce necessity of an alternative process investigation to deodorize vegetable oils.

Liquid-liquid equilibrium data provided by previous works [17-19] showed that a liquid solvent can softly remove flavor components and free fatty acids from vegetable oils. As liquid-liquid extraction efficiency and safety mainly depend on solvent choice, mutual solubility of vegetable oils and different solvents have been investigated. Solvents as anhydrous and hydrous ethanol, dimethyl sulfoxide and methanol present low solubility within vegetable oils [20,21]; however, the applicability of methanol is avoided due to its high toxicity. Solvents as ethyl lactate, acetic acid and propanol were also investigated, but their solubility in soybean oil were considerably high, which disables their applicability as pure solvents.

Since vegetable oils are mainly composed by non-polar molecules (TAGs), addition of high polar substances, such as water, in organic solvents tends to decrease the mutual solubility of the system, as occur when anhydrous ethanol plus water is mixed with vegetable oils [22,23]. By combining two or more components, characterizing a cosolvent, an ability to generate a more efficient and economical chemical processes is enabled. As water, formic acid is a high polar compound and it is considered as low-toxic solvent by the ICH classifications [4], becoming attractive for its investigation as a cosolvent. As far as we know, besides for the cosolvent hydrous ethanol, no information of liquid-liquid equilibrium of vegetable oils and different low-toxic cosolvents was provided in the open literature, which instigates an in-depth research in this field.

In the present study, liquid-liquid equilibrium (LLE) data were collected for refined soybean oil (RSO) plus five cosolvents {(anhydrous ethanol, or ethyl lactate, or dimethyl sulfoxide) plus water} and {(ethyl lactate, or dimethyl sulfoxide) plus formic acid}. We followed guidelines from the method of Cusack et al. (1991) [24] and from ICH classifications [4], for choosing solvents with solvating characteristics with odoriferous compounds and of low toxicity, respectively. The amount of water added to each solvent was determined for avoiding persistent emulsion formation; for formic acid addition, guidelines from the Classification, Labelling and Packaging (CLP) regulation [5] were followed to avoid corrosion. Experiments were carried out at temperatures varying from 293.15 to 333.15 K with u(T) = 0.05 K. Thermodynamic modeling was achieved by using the NonRandom Two Liquids (NRTL) [25] and the UNIversalQUAsiChemical (UNIQUAC) [26] models. Furthermore, prediction capability was analyzed for five versions of the UNIQUAC Functional-group Activity Coefficients (UNIFAC) method [27], specifically: UNIFAC-LL [28], UNIFAC-DMD [29,30], UNIFAC-LBY [31], UNIFAC-HIR [32] and UNIFAC-NIST [33].

6.2 EXPERIMENTAL SECTION

6.2.1 Material

Refined soybean oil (Liza brand) was utilized in this work, for which information about its acidity, oil stability index (OSI), and its fatty acid and triacylglycerol (TAG) profiles are presented elsewhere [20]. Chemicals used in this work are presented in Table 6.2-1. Also, deionized water (Milli-Q, Millipore) was utilized in preparation of cosolvents.

Table 6.2-1. Source and purity of chemicals used in this work.

Compounds	IUPAC name	CAS Number	Supplier	Purity (g/g)[a]
Anhydrous ethanol	Ethanol	64-17-5	Sigma-Aldrich	0.9995
Ethyl lactate	Ethyl 2-hydroxypropanoate	97-64-3	Fluka	0.998
Dimethyl sulfoxide	Methanesulfinylmethane	67-68-5	Sigma-Aldrich	0.9997
Formic acid	Methanoic acid	64-18-6	Êxodo	0.996

[a] Purity provided by the manufacturer.

Cosolvents consisted of mixtures of {(anhydrous ethanol, or ethyl lactate, or dimethyl sulfoxide (DMSO)) plus water} in a mass fraction ratio (solvent:water) of (0.9:0.1), (0.9:0.1) and (0.75:0.25), respectively, and {(ethyl lactate, or DMSO) plus formic acid}, both with a mass fraction ratio (solvent:formic acid) of (0.9:0.1). Quantities of water in cosolvents were determined for avoiding emulsion formation for system (RSO plus cosolvent) under vigorous agitation for a period of 1 h followed by phase separation of 12 h at 298.15 K. The amount of formic acid in cosolvents was based on a CPL regulation [5], which defines that a quantity higher than 10% m/m can cause corrosion. Cosolvent formic acid plus anhydrous ethanol was not investigated due to occurrence of esterification reaction.

6.2.2 Experimental determination of liquid-liquid equilibrium data and quality test

Cosolvents containing anhydrous ethanol or DMSO were mixed with RSO in mass ratio (cosolvent:RSO) of 1:1, while cosolvents containing ethyl lactate were mixed in mass ratio (cosolvent:RSO) of 1.5:1. Cosolvents and RSO were weighted directly in a sealed equilibrium glass cell (23 mL) using an analytical balance (Radwag, Model AS 220.R2) accurate to ± 0.0001 g. Mixtures were vigorously agitated by magnetic stirrers (Fisatom, Model 752) for 1 h, and left to settle for 12 h, enabling complete phase-split, as follow by Homrich et al. [20]. Temperature was controlled by an ultra-thermostatic bath (Marconi, Model MA-184) with a precision of 0.05 K. Temperature varied from 293.15 to 333.15 K with $u(T) = 0.05$ K. After phase split, aliquots of each equilibrium phase were collected using syringes with stainless steel needles for posterior quantification.

RSO was gravimetrically quantified in a vacuum oven (Marconi, Model MA030) at 383.15 K, in which Petri dishes containing samples of about 1 g of each phase were kept for cosolvent evaporation, until constant mass. For cosolvents containing water plus (anhydrous ethanol or ethyl lactate), water content was determined by Karl Fischer titration, according to AOCS method Ca 23–55 [34], with a KF Coulometer (Metrohm, Model 831), while for cosolvent (water plus DMSO), water content was determined in a volumetric Karl Fischer

(Mettler-Toledo, Model DL 31). Formic acid was quantified by titration, following the AOCS methods Ce 1f-96 and Ce 1-62 [34]. Anhydrous ethanol, ethyl lactate and DMSO mass fractions were obtained by difference. All quantification techniques were performed at least in triplicate.

Quality test of collected ELL data was assessed by a method developed by Marcilla et al. [35]. The procedure is based on mass balance and calculates the mass of each phase considering experimental equilibrium mass fractions *w* and masses of component *i* in overall mixtures. For each component *i* of the system, a mass balance can be written (Eq. 6.2-1).

$$m^{OM} w_i^{OM} = m^{EP} w_i^{EP} + m^{RP} w_i^{RP} \tag{6.2-1}$$

wherein *m* stands for mass, w_i is the mass fraction of component *i*, the superscript *OM* refers to overall mixture, and the superscripts *EP* and *RP* refer to the extract and raffinate phases, respectively. Using least-squares fitting, m^{EP} and m^{RP} can be calculated from experimental values of w_i^{EP} and w_i^{RP}. Thus, a matrix **P** formed by the mass of each phase in equilibrium (m^{EP} and m^{RP}) can be calculated according to Eq. 6.2-2:

$$\mathbf{P} = \left(\mathbf{B^T B}\right)^{\mathbf{-1}} \mathbf{B^T M} \tag{6.2-2}$$

in which **M** is a matrix formed by the values of w_i^{OC}, **B** is the transformation matrix containing w_i^{EP} and w_i^{RP}, $\mathbf{B^T}$ is the transpose matrix of **B**, and $\mathbf{(B^T B)^{-1}}$ is the inverse matrix of $\mathbf{(B^T B)}$. To assess quality, relative deviations (*RD*) between calculated and actual total mass are calculated according to Eq. 6.2-3.

$$RD(\%) = 100 \frac{\left(m^{EP} + m^{RP} - m^{OM}\right)}{m^{OM}} \tag{6.2-3}$$

6.2.3 Thermodynamic modeling

Thermodynamic correlation using the NRTL and UNIQUAC models and prediction by the five versions of the UNIFAC method were accomplished using the software *Aspen Plus v.8.4.* RSO was represented as a pseudocompound, the triacylglycerol LLO [20], which contains two linoleic acids (L) and one oleic acid (O). A molecular weight of 874.5 g·mol^{-1}, previously determined as the average molecular weight of the utilized RSO, was considered in modelling and prediction [20]. Both representative TAG (LLO) and RSO's average molecular weight were previously determined by using a statistical method developed by Antoniosi Filho et al [36].

Binary parameters (a_{ij}/J·mol^{-1}·K^{-1} and b_{ij}/J·mol^{-1}) for the NRTL (Eq. (6.2-4)) and the UNIQUAC (Eq. (6.2-5)) models, and the nonrandomness parameter (α_{ij}) for the NRTL model, were obtained by using the Britt-Luecke algorithm with the Deming initialization method. Regression of parameters was accomplished using the maximum-likelihood objective function, which considered all measured variables (temperatures, mole fractions and pressure).

$$\tau_{ij} = a_{ij} + {}^{b_{ij}}\!/_{T} \qquad (6.2\text{-}4)$$

$$\tau_{ij} = \exp\left(a_{ij} + {}^{b_{ij}}\!/_{T} \right) \qquad (6.2\text{-}5)$$

wherein τ_{ij} is the molecular energy interaction between components i and j and T is temperature.

RSO (TAG LLO) and cosolvents were subdivided using the following functional subgroups: CH_3, CH_2, CH, CH_2COO, COO, OH, COOH, HCOOH, $(CH_3)_2SO$ (DMSO), H_2O and HC=CH. Binary parameters adjusted by Magnussen [28] (UNIFAC-LL) for functional groups of ethyl lactate, formic acid and DMSO were used in the UNIFAC-HIR prediction, since this last method did not include such groups in its parametrization. UNIFAC-HIR [32] adjusted binary parameters for deacidification of vegetable oils by liquid-liquid extractions using alcoholic solvents. Global deviation between experimental and calculated (or predicted) data for the system RSO plus cosolvents was calculated according to Equation 6.2-6.

$$\delta w = 100 \sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{P}\left\{\left(w_{i,n}^{\mathrm{R,exp}} - w_{i,n}^{\mathrm{R,calc}}\right)^2 + \left(w_{i,n}^{\mathrm{E,exp}} - w_{i,n}^{\mathrm{E,calc}}\right)^2\right\}}{2NP}} \qquad (6.2\text{-}6)$$

in which N is the total number of tie lines in each system, P is the total number of components in each system, w is the mass fraction of component i, the superscripts E and R refer to extract phase and raffinate phases, and the superscripts exp and calc refer to experimental and calculated (or predicted) values, respectively.

Based of experimental and predicted LLE data (w), partition coefficients of RSO (k_{RSO}) (Eq. 6.2-7) were calculated for assessing distribution of oil (diluent) between extract (E) and raffinate (R) phases at different temperatures.

$$k_{RSO} = \frac{w_{RSO}^{E}}{w_{RSO}^{R}} \qquad (6.2\text{-}7)$$

6.3 RESULTS AND DISCUSSION

Experimental LLE data and partition coefficients of RSO (k_{RSO}) for cosolvents containing water and formic acid are listed in Table 6.3-1 and Table 6.3-2, respectively.

Table 6.3-1. Experimental liquid-liquid equilibrium data (mass fractions w) and partition coefficient of RSO (k_{RSO}) for refined soybean oil (RSO) (1) plus {(anhydrous ethanol (2), or ethyl lactate (3), or dimethyl sulfoxide (4)) plus water (5)} at 94.2 kPa[a].

T/*K*	Overall mixture (OM)			Raffinate phase (RP)			Extract phase (EP)			k_{RSO}
	w_1	w_2	w_5	w_1	w_2	w_5	w_1	w_2	w_5	
293.15	0.505	0.445	0.050	0.966	0.031	0.003	0.007	0.873	0.120	0.007
298.15	0.497	0.452	0.051	0.958	0.038	0.004	0.007	0.872	0.121	0.007
303.15	0.502	0.448	0.050	0.951	0.045	0.004	0.007	0.872	0.120	0.008
308.15	0.502	0.448	0.050	0.943	0.052	0.005	0.008	0.871	0.122	0.008
313.15	0.504	0.445	0.050	0.933	0.062	0.005	0.008	0.871	0.121	0.009
318.15	0.495	0.454	0.051	0.925	0.069	0.007	0.009	0.870	0.121	0.009
323.15	0.508	0.442	0.050	0.913	0.077	0.009	0.009	0.872	0.119	0.010
328.15	0.501	0.448	0.051	0.902	0.087	0.011	0.009	0.872	0.119	0.010
333.15	0.498	0.451	0.051	0.894	0.093	0.013	0.010	0.869	0.120	0.012
	w_1	w_3	w_5	w_1	w_3	w_5	w_1	w_3	w_5	
293.15	0.398	0.544	0.057	0.850	0.146	0.003	0.009	0.869	0.122	0.011
298.15	0.401	0.541	0.057	0.834	0.162	0.004	0.011	0.867	0.122	0.013
303.15	0.398	0.545	0.057	0.826	0.170	0.004	0.011	0.867	0.122	0.014
308.15	0.401	0.542	0.057	0.816	0.180	0.004	0.012	0.864	0.124	0.015
313.15	0.405	0.538	0.057	0.807	0.189	0.004	0.015	0.861	0.123	0.019
318.15	0.398	0.545	0.057	0.801	0.194	0.005	0.015	0.865	0.121	0.018
323.15	0.398	0.545	0.057	0.792	0.202	0.006	0.016	0.860	0.124	0.020
328.15	0.407	0.536	0.057	0.789	0.204	0.006	0.019	0.857	0.124	0.024
333.15	0.397	0.546	0.058	0.779	0.214	0.007	0.022	0.854	0.124	0.028
	w_1	w_4	w_5	w_1	w_4	w_5	w_1	w_4	w_5	
293.15	0.502	0.374	0.124	0.996	0.003	0.001	0.001	0.755	0.244	0.001
298.15	0.503	0.373	0.124	0.998	0.001	0.001	0.002	0.751	0.247	0.002
303.15	0.499	0.376	0.125	0.997	0.003	0.001	0.002	0.748	0.250	0.002
308.15	0.502	0.373	0.124	0.998	0.001	0.001	0.002	0.749	0.249	0.002
313.15	0.499	0.376	0.125	0.998	0.001	0.001	0.003	0.750	0.248	0.003
318.15	0.503	0.373	0.124	0.998	0.001	0.001	0.003	0.748	0.249	0.003
323.15	0.498	0.376	0.125	0.997	0.001	0.001	0.003	0.748	0.249	0.003
328.15	0.499	0.375	0.126	0.994	0.005	0.002	0.004	0.747	0.249	0.004
333.15	0.500	0.374	0.125	0.994	0.005	0.002	0.005	0.747	0.248	0.005

[a] Standard uncertainties u are $u(p)$ = 0.5 kPa and $u(T)$ = 0.05 K. Relative standard uncertainties are $u_r(w_1^{RP}) \leq 0.005$, $u_r\,(w_5^{\;RP}) \leq 0.085$, $u_r(w_1^{EP}) \leq 0.143$, $u_r(w_5^{\;EP}) \leq 0.024$ and $u_r(k_{RSO}) \leq 0.172$. u_r is calculated as $u_r(w) = 100.(u(w)/w)$.

Table 6.3-2. Experimental liquid-liquid equilibrium data (mass fractions *w*) and partition coefficient of RSO (k_{RSO}) for refined soybean oil (RSO) (1) plus {(ethyl lactate (3), or dimethyl sulphoxide (4)) plus formic acid (6)} at 94.2 kPa[a].

T/*K*	**Overall mixture (OM)**			**Raffinate phase (RP)**			**Extracted phase (EP)**			**k_{RSO}**
	w_1	w_3	w_6	w_1	w_3	w_6	w_1	w_3	w_6	
293.15	0.401	0.539	0.060	0.743	0.234	0.022	0.034	0.845	0.121	0.046
298.15	0.399	0.541	0.060	0.726	0.251	0.023	0.044	0.832	0.124	0.061
303.15	0.400	0.540	0.060	0.695	0.281	0.024	0.052	0.823	0.125	0.074
308.15	0.401	0.539	0.060	0.674	0.302	0.024	0.061	0.816	0.122	0.091
313.15	0.400	0.540	0.060	0.657	0.318	0.026	0.072	0.806	0.122	0.110
318.15	0.400	0.540	0.060	0.621	0.351	0.028	0.085	0.792	0.123	0.137
323.15	0.400	0.540	0.060	0.598	0.372	0.030	0.093	0.785	0.122	0.155
328.15	0.399	0.540	0.060	0.563	0.404	0.033	0.110	0.767	0.123	0.196
333.15	0.399	0.541	0.060	0.538	0.423	0.039	0.133	0.743	0.124	0.247
	w_1	w_4	w_6	w_1	w_4	w_6	w_1	w_4	w_6	
293.15	0.504	0.447	0.050	0.964	0.033	0.004	0.004	0.874	0.122	0.004
298.15	0.501	0.450	0.050	0.967	0.032	0.001	0.005	0.871	0.125	0.005
303.15	0.496	0.453	0.050	0.962	0.035	0.003	0.005	0.867	0.128	0.005
308.15	0.497	0.453	0.050	0.957	0.040	0.003	0.006	0.867	0.128	0.006
313.15	0.502	0.448	0.050	0.954	0.043	0.003	0.007	0.866	0.127	0.007
318.15	0.497	0.453	0.050	0.953	0.044	0.004	0.009	0.865	0.126	0.009
323.15	0.506	0.445	0.049	0.944	0.052	0.004	0.010	0.866	0.124	0.010
328.15	0.495	0.454	0.050	0.943	0.053	0.004	0.011	0.863	0.127	0.011
333.15	0.503	0.447	0.050	0.941	0.054	0.004	0.012	0.864	0.124	0.013

[a] Standard uncertainties *u* are $u(p) = 0.5$ kPa and $u(T) = 0.05$ K. Relative standard uncertainties are $u_r(w_1^{RP}) \leq 0.007$, $u_r\,(w_6^{\,RP}) \leq 0.057$, $u_r(w_1^{EP}) \leq 0.109$, $u_r(w_6^{\,EP}) \leq 0.033$ and $u_r(k_{RSO}) \leq 0.109$. u_r is calculated as $u_r(w) = 100.(u(w)/w)$.

Relative deviations obtained by the mass balance procedure [35] for the systems containing RSO plus {(anhydrous ethanol, or ethyl lactate, or DMSO) plus water} or {(ethyl lactate, or DMSO) plus formic acid} were lower than 0.96%, 0.94%, 0.25%, 1.09% and 1.32%, respectively. Interaction parameters of the NRTL (Table 6.3-3) and UNIQUAC (Table 6.3-4) models were satisfactorily adjusted, presenting global deviations (δ_w) (Table 6.3-5) a between calculated and experimental LLE data lower than 0.22% and 0.29%, respectively.

Table 6.3-3. Binary parameters of the NRTL model.

Pair ij^a	a_{ij}/J·mol^{-1}·K^{-1}	a_{ji}/J·mol^{-1}·K^{-1}	b_{ij}/J·mol^{-1}	b_{ji}/J·mol^{-1}	α_{ij}
12	5.66	544.25	1858.83	-83134.01	0.14
13	-84.58	76.25	8885.67	20573.94	0.10
14	-63.45	118.68	12366.31	-3963.67	0.10
15	62.45	46.95	-13794.14	-7764.93	0.61
16	-56.86	-24.33	23030.36	17652.61	0.30
25	-156.66	-215.01	79384.46	82997.05	0.31
35	39.31	35.10	-13083.45	-11656.17	0.90
36	261.25	-12.50	-82890.27	9233.47	0.10
45	31.34	-22.63	-15183.47	-1410.73	0.39
46	333.04	-129.20	-82813.11	50042.17	0.30

[a] Refined soybean oil (1); anhydrous ethanol (2); ethyl lactate (3); dimethyl sulfoxide (4); water (5); formic acid (6).

Table 6.3-4. Binary parameters of the UNIQUAC model.

Pair ij^a	a_{ij}/J·mol^{-1}·K^{-1}	a_{ji}/J·mol^{-1}·K^{-1}	b_{ij}/J·mol^{-1}	b_{ji}/J·mol^{-1}
12	29.39	-13.10	-11945.72	3630.70
13	-29.25	-61.67	12230.10	14035.55
14	-104.57	54.88	32304.91	-18611.22
15	8.14	6.92	-11713.53	-182.54
16	-180.88	-36.80	-48094.21	15662.36
25	-554.42	9.71	-81379.64	-1154.11
35	-65.64	-9.23	-2971.59	1810.78
36	-794.62	-114.23	-83130.52	42972.64
45	-66.78	-22.46	23032.42	13663.43
46	-224.68	-163.64	68316.53	57739.99

[a] Refined soybean oil (1); anhydrous ethanol (2); ethyl lactate (3); dimethyl sulfoxide (4); water (5); formic acid (6).

Table 6.3-5. Global deviations (δ_w) (Eq. (6.3-6)) for the NRTL and UNIQUAC models.

System	δ_w	
	NRTL	UNIQUAC
Refined soybean oil + anhydrous ethanol + water	0.11	0.15
Refined soybean oil + ethyl lactate + water	0.19	0.29
Refined soybean oil + dimethyl sulfoxide + water	0.14	0.18
Refined soybean oil + ethyl lactate + formic acid	0.22	0.21
Refined soybean oil + dimethyl sulfoxide + formic acid	0.12	0.16

Figure 6.3-1 and Figure 6.3-3 depict liquid-liquid phase diagrams for the RSO plus low-toxic solvents (anhydrous ethanol, ethyl lactate and DMSO) plus water or formic acid, respectively, including experimental and predicted data, as well as LLE data previously obtain for pure solvents (anhydrous ethanol, ethyl lactate and DMSO) [20]. Only the NRTL data are depicted in Figs. 6.3-1 and 6.3-2 as both models presented similar values of w and large part of their binodal curves overlapped. Also, only the best predicted data using the versions based on the UNIFAC method are displayed. These data are presented in Tables A.3.1 to A.3.3 (Supporting Information).

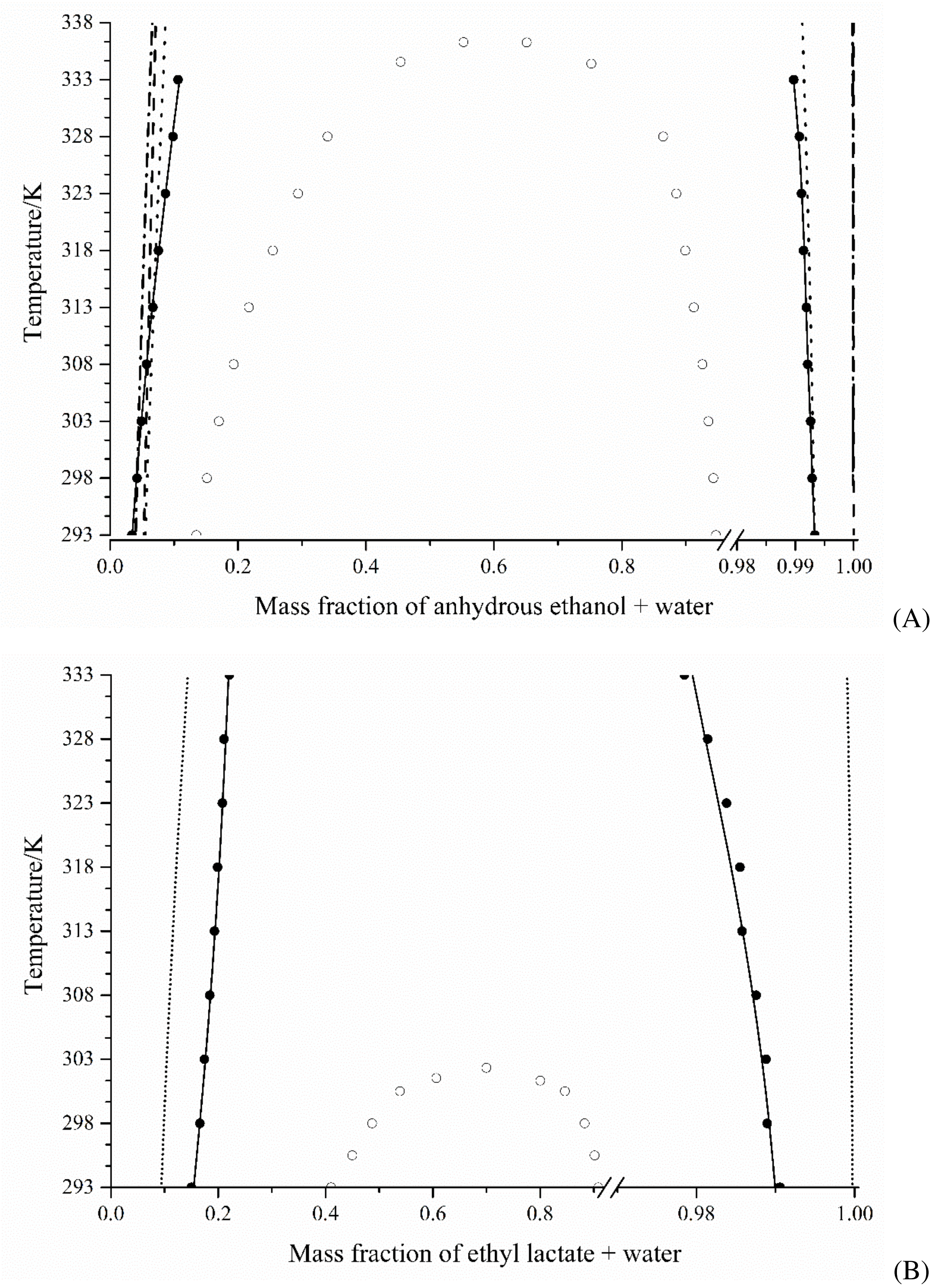
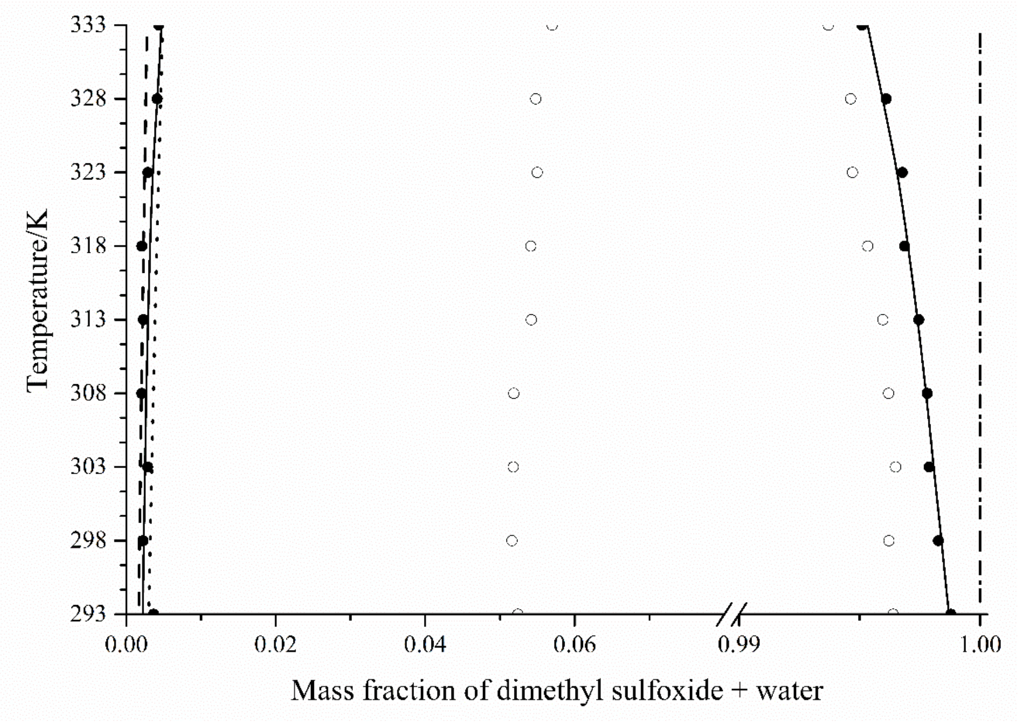


Figure 6.3-1 (A-B). Liquid-liquid equilibrium data for systems composed of refined soybean oil (1) plus cosolvents under atmospheric pressure: (A) anhydrous ethanol (2) plus water (5) (10% m/m), (B) ethyl lactate (4) plus water (5) (10% m/m), (C) dimethyl sulfoxide (4) plus water (5) (25% m/m). Legend: (●) experimental data; (solid line) NRTL; (dash) UNIFAC-LL; (dot) UNIFAC-HIR; (dash dot) UNIFAC-DMD; (short dosh) NIST-UNIFAC; (dash dot dot) UNIFAC-LBY; (○) water-free solvents [20].



(C)

Figure 6.3-2 (C). Liquid-liquid equilibrium data for systems composed of refined soybean oil (1) plus cosolvents under atmospheric pressure: (A) anhydrous ethanol (2) plus water (5) (10% m/m), (B) ethyl lactate (4) plus water (5) (10% m/m), (C) dimethyl sulfoxide (4) plus water (5) (25% m/m). Legend: (●) experimental data; (solid line) NRTL; (dash) UNIFAC-LL; (dot) UNIFAC-HIR; (dash dot) UNIFAC-DMD; (short dosh) NIST-UNIFAC; (dash dot dot) UNIFAC-LBY; (○) water-free solvents [20].

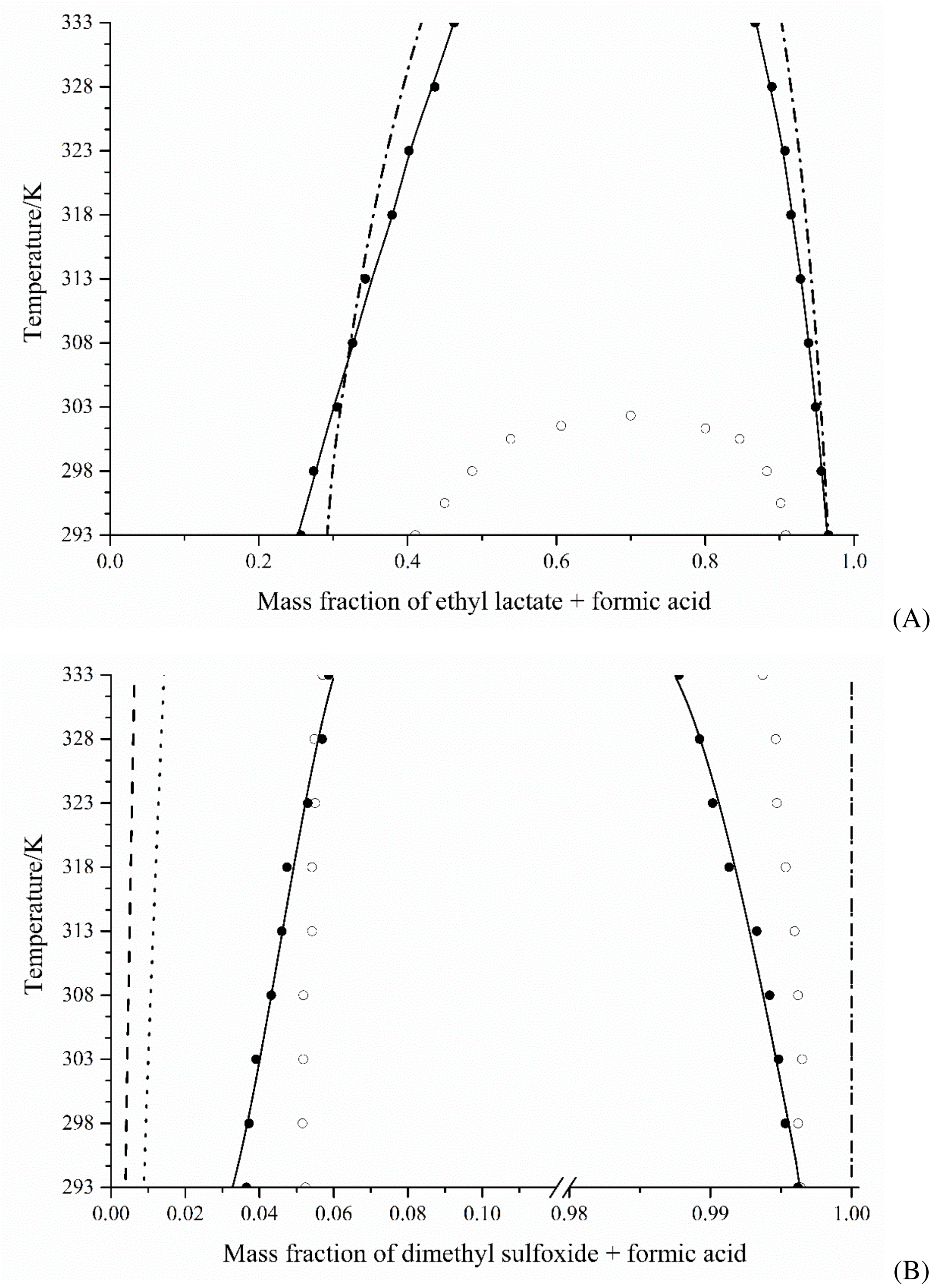


Figure 6.3-3. Liquid-liquid equilibrium data for systems composed of refined soybean oil (1) plus cosolvents under atmospheric pressure: (A) ethyl lactate (3) plus formic acid (6) (10% m/m), (B) dimethyl sulfoxide (4) plus formic acid (6) (10% m/m). Legend: (●) experimental data; (solid line) NRTL; (dash) UNIFAC-LL; (dot) UNIFAC-HIR; (dash dot) UNIFAC-DMD; (short dosh) NIST-UNIFAC; (dash dot dot) UNIFAC-LBY; (○) water-free solvents [20].

As one can see in Figure 6.3-1 and Figure 6.3-3, addition of water or formic acid in the investigated solvents generated an increase in biphasic regions, except in the case of DMSO plus formic acid, which presented similar results within the ELL data of pure DMSO. Higher improvements were found for systems containing ethyl lactate, which as a pure solvent presents an upper critical solution temperature (UCST) lower than 303 K [19]. For systems containing anhydrous ethanol and DMSO, very low concentration of RSO can be verified in extract phases, resulting in very low values of loss of RSO during solvent extraction process. In the case of DMSO plus water, raffinate phases containing low quantities of cosolvent were obtained, which indicates a very good potential for this cosolvent.

In general, for solvent plus water systems, temperature had slightly affected mutual solubility of compounds, indicating very low solubility of water in RSO at the studied temperature range. Similar result was verified for cosolvent DMSO plus formic acid. However a slight effect of temperature in this case was due to low mutual solubility of DMSO and RSO. Comparing pure solvents anhydrous ethanol and ethyl lactate with their cosolvents investigated in this work, a significant decrease in the mutual solubility was achieved at higher temperatures.

Concerning the UNIFAC method predictions, satisfactory results were found in some cases. Table 6.3-6 presents global deviations and average absolute deviation of each equilibrium phase (raffinate and extract) between experimental and predicted data.

Table 6.3-6. Global deviations (δw) (Eq.6.2-6) and Average Absolute Deviation (AAD) for raffinate phase (RP) and extract phase (EP) between experimental and predicted results by the UNIFAC-LL, UNIFAC-DMD, UNIFAC-LBY UNIFAC-HIR and NIST-UNIFAC methods for systems containing refined soybean oil (RSO) plus cosolvents.

System	**UNIFAC-LL**			**UNIFAC-DMD**			**UNIFAC-LBY**			**UNIFAC-HIR**			**UNIFAC-NIST**		
	RP	**EP**	**Global**	**RP**	**EP**	**Global**	**RP**	**EP**	**Global**	**RP**	**EP**	**Global**	**RP**	**EP**	**Global**
	AAD(%)[a]		δ_w	AAD(%)[a]		δ_w	AAD(%)[a]		δ_w	AAD(%)[a]		δ_w	AAD(%)[a]		δ_w
RSO + anhydrous ethanol + water	1.20	1.52	1.58	1.32	1.62	1.77	2.99	1.78	3.01	1.01	1.00	1.21	1.34	1.65	1.81
RSO + ethyl lactate + water	10.88	2.35	9.54	19.34	56.46	51.24	10.50	2.34	9.23	20.03	58.48	52.93	4.85	1.79	4.41
RSO + DMSO + water	0.13	0.23	0.24	0.98	0.38	0.90	NA[b]	NA[b]	NA[b]	0.15	0.25	0.24	0.99	0.37	0.92
RSO + ethyl lactate + formic acid	20.07	6.94	18.15	2.31	4.53	4.10	21.04	6.36	18.63	5.79	3.59	6.28	4.60	2.90	5.27
RSO + DMSO + formic acid	2.74	2.19	2.91	7.65	4.37	7.00	NA[b]	NA[b]	NA[b]	2.32	2.18	2.62	6.15	3.41	5.61

[a] Average Absolute Deviation (AAD) is calculated as: $\mathrm{AAD} = \frac{100}{M} . \sum_{i=1}^{M} \left| w_{\exp} - w_{calc} \right|$; [b] NA: not applicable due to lack of group-group interaction parameters.

Following Table 6.3-6, some considerations can be highlighted:

(i) For systems containing water, DMSO was well represented by the five UNIFAC versions. With global deviations lower than 0.92%,. the UNIFAC-HIR performed well for the prediction of cosolvent containing anhydrous ethanol, presenting a global deviation of 1.21%. Ethyl lactate system was only reasonably predicted by the UNIFAC-NIST method, with a global deviation of 4.41%;

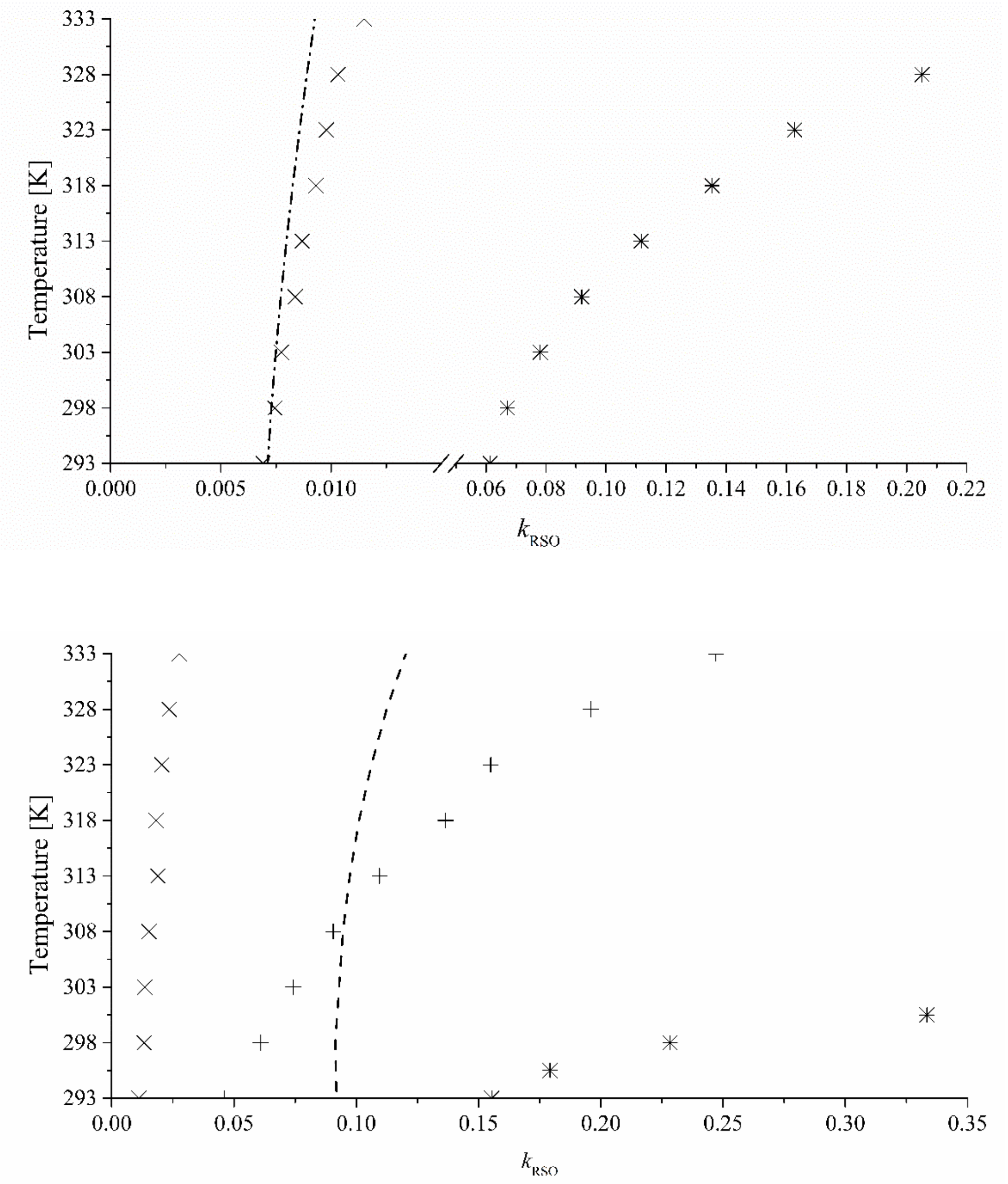
(ii) For cosolvents containing formic acid, neither ethyl lactate nor DMSO systems were satisfactorily predicted. The UNIFAC-DMD and UNIFAC-NIST presented reasonable results for ethyl lactate, while the UNIFAC-LL and UNIFAC-HIR showed some agreement with experimental data for DMSO system;

(iii) With some exceptions, the extract phase was satisfactorily predicted. Main deviations were found for systems containing ethyl lactate plus formic acid (UNIFAC-LL and UNIFAC-LBY) and plus water (UNIFAC-DMD and UNIFAC-HIR). Regarding raffinate phases, only systems containing anhydrous ethanol or DMSO plus water presented low AAD by using the UNIFAC-LL, UNIFAC-DMD, UNIFAC-HIR and UNIFAC-NIST;

(iv) A somewhat consistency among results for the investigated systems only occurred for the UNIFAC-NIST method, since no high global deviations were found for the other methods. Moreover, the UNIFAC-LBY was the only method which did not present global deviations lower than 1%. High deviations found for the UNIFAC-HIR model were probably due to the fact that we combined this method with the UNIFAC-LL for missing parameters;

(v) Finally, a significant improvement for UNIFAC predictions was found in some cases when compared cosolvents with pure solvents systems [20]. However, the current group-group parameters banks available for the UNIFAC methods still remained unreliable for the investigation of phase equilibrium of different liquid compounds (as solvents and solutes) and vegetable oils.

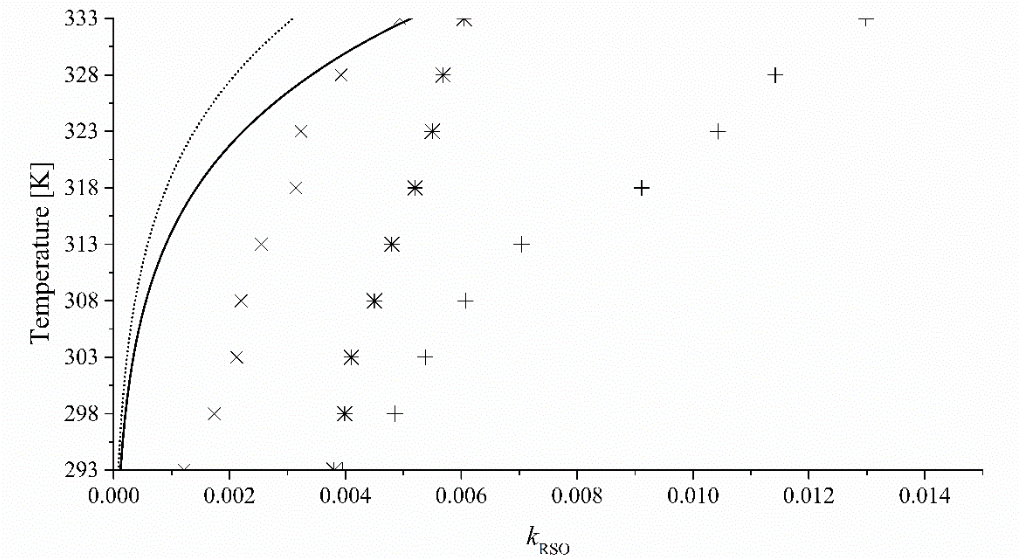
Experimental k_{RSO} of investigated systems, as well as predicted behavior and those previously obtained for pure solvents (anhydrous ethanol, ethyl lactate and DMSO) are given in Figure 6.3-4.



(A)

(B)

Figure 6.3-4 (A-B). Partition coefficients of refined soybean oil (RSO) (kRSO) for systems containing cosolvents under atmospheric pressure. (A) anhydrous ethanol; (B) ethyl lactate; (C) dimethyl sulfoxide. Legend: (×) experimental data (solvent plus water); (+) experimental data (solvent plus formic acid); (dash dot) UNIFAC-HIR (anhydrous ethanol plus water); (dash) UNIFAC-DMD (ethyl lactate plus formic acid); (solid) UNIFAC-DMD (dimethyl sulfoxide plus formic acid); (short dot) NIST-UNIFAC (dimethyl sulfoxide plus formic acid); (✳) pure solvent data [20].



(C)

Figure 6.3-5 (C). Partition coefficients of refined soybean oil (RSO) (kRSO) for systems containing cosolvents under atmospheric pressure. (A) anhydrous ethanol; (B) ethyl lactate; (C) dimethyl sulfoxide. Legend: (×) experimental data (solvent plus water); (+) experimental data (solvent plus formic acid); (dash dot) UNIFAC-HIR (anhydrous ethanol plus water); (dash) UNIFAC-DMD (ethyl lactate plus formic acid); (solid) UNIFAC-DMD (dimethyl sulfoxide plus formic acid); (short dot) NIST-UNIFAC (dimethyl sulfoxide plus formic acid); (✳) pure solvent data [20].

Figure 6.3-3 clearly exhibits the effect of adding water or formic acid in the investigated solvents. For system containing anhydrous ethanol, addition of water considerably improved the biphasic region, as previously verified. Ethyl lactate plus water or formic acid (Figure 6.3-4-B) presented very low k_{RSO} when compared with pure ethyl lactate, significantly improving applicability of this solvent for removing undesirable compounds from vegetable oils. Figure 3-C evidences the effect of formic acid in DMSO, which had an increase in k_{RSO} due to the higher solubility of the system. On the other hand, water in DMSO was capable to generate very low values of k_{RSO}, which is desirable to improve process efficiency. Concerning the UNIFAC prediction, Figure 6.3-4 enables an understanding of which model represented better studied systems. Corroborating with global deviation values presented in Table 6.3-7, anhydrous ethanol plus water was satisfactorily represented by the UNIFAC-HIR and ethyl lactate plus formic acid by the UNIFAC-DMD. Even though DMSO plus water presented some deviations between experimental and calculated data, such observation can be due to the very low values of k_{RSO}, which generates higher discrepancies.

Experimental results demonstrated advantages of adding water or formic acid in solvents of low-toxicity, providing raffinate and extract phases with low quantities of solvent and RSO, respectively, which highly facilitates handling of streams after liquid-liquid extraction process. In addition, regardless of some agreement between experimental and calculated data, lack of reliability of the five UNIFAC versions was verified, emphasizing a necessity of a parameterization considering various classes of solvents and solutes involved in vegetable oils refining.

6.4 CONCLUSION

Liquid-liquid equilibrium data for systems containing refined soybean oil plus five low-toxic solvents were collected. Obtained results showed the benefits of mixing liquid solvents for possibly removing undesirable compounds from vegetable oils. Cosolvents containing water, especially with DMSO, presented very low mutual solubility and, therefore, may be an attractive alternative to improve process efficiency. Moreover, the applicability of ethyl lactate was highly improved comparing cosolvent systems with LLE data for pure ethyl lactate, which previously presented a considerable solubility with vegetable oils.

All investigated systems were well adjusted by the NRTL and UNIQUAC models, presenting global deviation lower than 0.35% and 0.26%, respectively. Predictions using five versions of the UNIFAC method resulted in satisfactory data in some cases, however the applicability of a group-contribution method to investigate fatty systems is still not well grounded. Such observations instigate a parametrization including different classes of compounds involved in vegetable oils refining, enabling design, optimization and simulation of purification processes of fatty industries.

Supporting Information

Liquid-liquid equilibrium data predicted by the methods based on UNIFAC.

AUTHOR INFORMATION

Corresponding Author

*E-mail: rceriani@feq.unicamp.br. Tel +55 19 35213961. Fax: +55 19 35213965.

ORCID

Roberta Ceriani: 0000-0001-8490-4960

Perci O. B. Homrich: 0000-0002-9677-9869

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CAPÍTULO 7

LIQUID-LIQUID EQUILIBRIA AND DENSITY DATA FOR PSEUDOTERNARY SYSTEMS OF REFINED SOYBEAN OIL + (HEXANAL, OR HEPTANAL, OR BUTYRIC ACID, OR VALERIC ACID, OR CAPROIC ACID, OR CAPRYLIC ACID) + DIMETHYL SULFOXIDE AT 298.15 K

Perci O. B. Homrich, Láisa G. Dias, Lilian R. B. Mariutti, Neura Bragagnolo, Roberta Ceriani

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ABSTRACT: Odoriferous compounds and free fatty acids can be mildly removed from vegetable oils using organic liquid solvents. Liquid-liquid equilibrium data are presented for extraction of odoriferous compounds (hexanal, heptanal, butyric acid, valeric acid, caproic acid, and caprylic acid) from refined soybean oil using dimethyl sulfoxide. Six tie lines were collected for each system at 298.15 K and under atmospheric pressure. Quantification of mass fractions were carried out by gas chromatography-mass spectrometry (GC-MS) for hexanal and heptanal, by gravimetry in a vacuum oven for refined soybean oil, and by titration for carboxylic acids. Collected data showed a high extraction of short-chain carboxylic acids and very low amounts of oil in solvent-rich phases. Coefficients of partition lower than 1 were found for aldehydes. Satisfactory agreements were found for thermodynamic correlation by using the NonRandom Two-Liquids (NRTL) and the UNIversal QUAsiChemical (UNIQUAC) models, which presented global deviations lower than 0.55 and 0.71%, respectively. Moreover, four versions of the UNIFAC method were tested (UNIFAC-LL, UNIFAC-HIR, UNIFAC-DMD, and NIST-UNIFAC), wherein reasonable agreements were found for few cases.

Keywords: liquid-liquid extraction, odoriferous compounds, refined soybean oil, dimethyl sulfoxide

7.1 INTRODUCTION

Consumer acceptance and longer shelf life of edible oils are attained by the refining for improving oxidation resistance and organoleptic properties. In the deodorization step, wherein odoriferous compounds and free fatty acids (physical refining) are stripped off from crude oil, a series of damages caused to drastic operational conditions occurs [1,2]. For instance, process residual chlorides used throughout refining react with glycerol and partial diacylglycerols during deodorization and form glycidyl esters compounds and 3-monochloropropane-1,2-diol (3-MCPD) [3,4], which are carcinogenic contaminants also found in animal fats [5] and infant formulas [6]. Alternative approaches have been considered for performing deodorization process, as stripping at mild temperatures [7,8], nanofiltration membrane [9], and liquid-liquid extraction [10,11]. Moreover, different technologies have also been proposed for degumming [12], bleaching [13] and chemical deacidification [14].

Liquid-liquid extraction occurs based on mutual solubilities between diluent (oil), solute (undesirable molecules) and a liquid solvent. A solvent that maximizes solute extraction with minimum oil loss is desired. Furthermore, toxicity, reactivity, flammability, and thermophysical properties as density, viscosity and normal boiling point can be taken into consideration [15,16]. Liquid-liquid equilibrium (LLE) data showed that FFAs and sensory compounds (mainly aldehydes and short-chain carboxylic acids) can be satisfactorily removed from vegetable oils using ethanol as solvent [17–19]. For mutual solubility of different solvents and cosolvents within edible oils, some compounds were investigated, as: NADES (natural deep eutectic solvents) [20,21], methanol, propanol [22], mixtures of ethanol or methanol and water [23] and pure and hydrated ethyl lactate, acetic acid, ethanol, and dimethyl sulfoxide (DMSO) [24,25]. As we showed in our previous works [24,25], both pure and hydrated DMSO presented very poorly mutual solubility within soybean oil, as well as its mixture with formic acid. It is noteworthy that DMSO is classified as low toxic by the ICH classifications [26], presenting low risks to human health. To the best of our knowledge, liquid-liquid equilibrium data of oils, plus odoriferous molecules plus DMSO have not been investigated.

Among undesirable compounds of unprocessed oils, secondary oxidation products (aldehydes, ketones, short-chain carboxylic acids, to name a few) figure as the main contributors to oil flavor [27,28]. Their formation typically occurs during storage, but also appears during processing [29] and deep frying [30,31]. Also, aldehydes, as hexanal, can undergo oxidation and its equivalent carboxylic acid is formed, namely caproic acid [32]. A natural prevention of oxidation reactions occurs by antioxidants molecules, as tocopherols, that are suggested to reduce risk of cancer [33]. However, quantities of tocopherols and other nutraceutical compounds are lost during deodorization by volatilization and thermal degradation [34–36]. Furthermore, not only secondary oxidation products influence oil odor, but some of them, as acetaldehyde, damage genes that prevent cancer from developing [37]. Thus, a mild way to remove these compounds is necessary for producing safe edible oils with higher quality in a process with mitigated environmental damages.

In this context, LLE equilibrium data of refined soybean oil (RSO) plus odoriferous compounds plus DMSO was experimental collected at 298.15 K and under atmospheric pressure. Six different solutes were studied, namely: hexanal, heptanal, butyric acid, valeric acid, caproic acid, and caprylic acid. Hexanal and heptanal were quantified by gas chromatography-mass spectrometry (GC-MS), RSO by gravimetry in a vacuum oven, and carboxylic acids by titration. Marcilla et al. [38] procedure was applied for data quality assessment. Thermodynamic correlation was performed using the NonRandom Two-Liquids (NRTL) [39] and the UNIversal QUAsiChemical (UNIQUAC) [40] models. Moreover, four versions of the UNIFAC method [41] were considered for LLE prediction, namely: UNIFAC-LL [42], UNIFAC-DMD [43,44], NIST-UNIFAC [45], and UNIFAC-HIR [46].

7.2 EXPERIMENTAL SECTION

7.2.1 Material

Table 7.2-1 lists the chemicals in this work (CAS Registry numbers, purities, density, IUPAC names and suppliers). All reagents were utilized without any further purification step.

Table 7.2-1. Source, purity and density ρ at 298.15 K of chemicals used in this work.

Compounds	**IUPAC name**	**CAS number**	**Supplier**	**Purity**^{a}	**ρ/kg·m^3 at 298.15 K**	
					This work	Literature
Hexanal	Hexanal	66-25-1	Sigma-Aldrich	0.99	830.01	833.12 [47]
Heptanal	Heptanal	111-71-7	Sigma-Aldrich	0.971	822.75	821.62 [48]
Butyric acid	Butanoic acid	107-92-6	Sigma-Aldrich	0.998	953.05	952.77 [49]
Valeric acid	Pentanoic acid	109-52-4	Sigma-Aldrich	0.998	934.75	933.90 [49]
Caproic acid	Hexanoic acid	142-62-1	Sigma-Aldrich	0.9976	923.07	922.06 [50]
Caprylic acid	Octanoic acid	124-07-2	Sigma-Aldrich	0.995	906.00	906.02 [50]
DMSO^b	Methanesulfinylmethane	67-68-5	Sigma-Aldrich	0.9997	1095.34	1095.32 [50]
2-propanol	Propan-2-ol	67-63-0	Sigma-Aldrich	0.999	780.69	780.91 [51]
RSO^b					917.20	916.59 [52]

^{a}Purity in mass fraction provided by manufacture (certificate analysis). ^{b}DMSO: Dimethyl sulfoxide; RSO: refined soybean oil.

Refined soybean oil (Liza™, Cargill, Brazil) was purchased in a local market. Its fatty acids profile (Table A.4.1) (Supplementary Material) was determined by using the Official AOCS methods Ce 1f-96 [53] and Ce 1-62 [54]. Triacylglycerols profile (Table A.4.2) was calculated using the procedure of Antoniosi Filho et al. [55], which statistically describes how the fatty acids (Table A.4.1) are distributed in the TAGs. Titration (official method 2201 of the IUPAC [56]) was applied for free fatty acids (FFA) determination. A value of 0.16 with u(FFA) = 0.01, expressed as percentage of linoleic acid, was found for RSO. Furthermore, the oil stability index (OSI) was assessed following the AOCS Method Cd 12b-92 [57] with a Rancimat instrument (Metrohm, model 743) at 100 ºC and 20 L/h of air flow rate. An OSI of 9.77 h with u(OSI) = 0.15 h was determined, indicating a natural resistance of RSO to oxidation reactions of almost 10 h.

7.2.2 Liquid-liquid equilibrium data measurement and quality test

Mixtures of feed (RSO plus solute) and DMSO were prepared in the mass fraction ratio of 1:1. Six different quantities of solute, varying from 4 to 30% in mass, were added in the RSO. Compounds were weighted directly in an equilibrium glass cell (40 mL) using an analytical balance (Tecnal, model 210A) accurate to ± 0.0001 g. Experiments were carried out at 298.15 K controlled by an ultrathermostatic bath (Marconi, model MA-184) with a precision of 0.05 K. Mixtures were vigorously agitated by magnetic stirrers (Fisatom, model 752) for 1 h, and left to settle for 12 h, wherein two translucent phases were formed. Aliquots of each equilibrium phase were collected using syringes with stainless steel needles. Densities were measured using a densitometer (Mettler-Toledo, model DM45).

RSO was gravimetrically quantified in a vacuum oven (Marconi, model MA030) at 383.15 K and 1.3 kPa of absolute pressure [17,24]. Petri dishes containing samples of about 1 g of raffinate phases and 2 g of extract phases were placed into the vacuum oven until constant mass for solvent and solute evaporation. Carboxylic acids (butyric, valeric, caproic, and caprylic acids) were quantified by titration, following the AOCS methods Ce 1f-96 [53] and Ce 1-62 [54] using a bottletop burette (BrandTech, model Titrette 25 mL) accurate to ± 0.001 mL.

Hexanal and heptanal were quantified using a gas chromatograph (GC) coupled to a mass spectrometer (MS, GCMS-QP2010 Ultra Shimadzu, Kyoto, Japan) [24,58]. Samples of each phase were diluted in 2-propanol in the following ratios: 1:49 for the raffinate phase; and 1:199 for the extract phase. Analytical curves (Figures A.4.1 and A.4.2) were constructed by diluting RSO, DMSO, and hexanal or heptanal in 2-propanol at eight ratios (1:49; 1:59; 1:69; 1:89; 1:114; 1:169; 1:339; 1:7999) in triplicate. Adjusted parameters of analytical curves and their deviations are presented in Table A.4.3, as well as limits of detection (LD) and quantification (LQ) [59]. Detection was carried out by mass spectrometry with a quadrupole mass/charge (m/z) analyzer, operating in the scanning mode (SCAN = m/z 35−350) to identify the compounds and in the selected ion monitoring (SIM) mode for quantification (43 and 42 m/z for hexanal and heptanal, respectively). Further injection and instrumental details can be found elsewhere [24].

Quality test of collected LLE data was assessed by applying a method developed by Marcilla et al. [38]. The procedure considers experimental equilibrium mass fractions *w* to calculate masses in grams of each phase (raffinate (m^{RP}) and extract (m^{EP})) and compares their sum with measured masses of the overall mixtures (m^{OM}). Relative deviations (RD) between calculated and measured mass of overall mixture are calculated according to Eq. (7.2-1).

$$RD(\%) = 100\frac{\left(m^{EP} + m^{RP} - m^{OM}\right)}{m^{OM}} \tag{7.2-1}$$

Finally, liquid-liquid extraction efficiency was assessed by the distribution coefficient k_i (Eq. (7.2-2)) and solvent selectivity $S_{solute/\mathrm{RSO}}$ (Eq. (7.2-3)).

$$k_i = \frac{w_i^{EP}}{w_i^{RP}} \tag{7.2-2}$$

$$S_{solute/RSO} = \frac{k_{solute}}{k_{RSO}} \tag{7.2-3}$$

wherein *k* stands for the distribution coefficient of compound *i*, *w* is the mass fraction of compound *i* and the superscripts EP and RP refer to extract and raffinate phases, respectively.

7.2.3 Thermodynamic modeling and prediction of phase equilibria

Binary parameters b_{ij} of the NRTL (Eq. (7.2-4)) and the UNIQUAC (Eq. (7.2-5)) models, and the nonrandomness parameter (α_{ij}) for the NRTL model, were calculated by minimizing a maximum-likelihood objective function by using the Britt-Luecke algorithm with the Deming initialization method. [24]

$$\tau_{ij} = {b_{ij}}/{T} \tag{7.2-4}$$

$$\tau_{ij} = \exp\left({b_{ij}}/{T} \right) \qquad (7.2\text{-}5)$$

wherein τ_{ij} is the molecular energy interaction between components i and j, and T is temperature.

RSO was represented by the triacylglycerol LLO, which contains two linoleic acids (L) and one oleic acid (O), as it is the major TAG presented in the RSO according to Table A.4.2. Also, from the TAGs profile, an average molar weight of 873.8 g·mol was calculated and considered in modeling and prediction. For both the UNIQUAC modeling and the UNIFAC predictions, RSO, solutes (aldehydes and carboxylic acids), and DMSO were subdivided into functional groups according to Table A.4.4. Group volume (R_k) and surface area (Q_k) parameters and structural parameters q (surface area) and r (volume) of RSO, solutes, and DMSO are showed in Tables A.4.5 and A.4.6, respectively.

Four different versions of the UNIFAC method were considered, namely: UNIFAC-LL [42], UNIDAC-DMD [43,44], NIST-UNIFAC [45], and UNIFAC-HIR [46], which is a parametrization of the UNIFAC-LL method considering data involved in the deacidification of vegetable oils using mainly alcoholic liquid solvents. Since UNIFAC-HIR did not adjust DMSO and CHO (aldehyde) groups, we combined this method with the UNIFAC-LL for assessing predicted equilibrium data. All modeling and prediction was accomplished by using the software *Aspen Plus v.8.4.* Global deviation between experimental and calculated (or predicted) data was calculated according to Eq. (7.2-6).

$$\delta w = 100\sqrt{\frac{\sum_{n=1}^{N}\sum_{i=1}^{P}\left\{\left(w_{i,n}^{\mathbf{RP,exp}} - w_{i,n}^{\mathbf{RP,calc}}\right)^2 + \left(w_{i,n}^{\mathbf{EP,exp}} - w_{i,n}^{\mathbf{EP,calc}}\right)^2\right\}}{2NP}} \qquad (7.2\text{-}6)$$

in which N is the total number of tie lines in each system, P is the total number of components in each system, w is the mass fraction of component i, the superscripts EP and RP refer to extract and raffinate phases, respectively, and the superscripts exp and calc refer to experimental and calculated (or predicted) values, respectively.

7.3 RESULTS AND DISCUSSION

Table 7.3-1 exhibits experimental liquid-liquid equilibrium data, solutes distribution coefficient k_x, and density ρ for pseudoternary systems composed of refined soybean oil, odoriferous compounds, and DMSO.

Table 7.3-1. Experimental liquid-liquid equilibrium data (mass fractions w), density ρ, and coefficient of distribution k_x (Eq. (7.2-2)) for pseudoternary systems composed of refined soybean oil (1) plus odoriferous compounds (x) plus dimethyl sulfoxide (8) at T = 298.15 K and p = 94.2 kPa.[a]

Tie	**Overall mixture**		**Raffinate phase**			**Extract phase**			k_x
line	w_1	w_x	w_1	w_x	ρ/kg·m^3	w_1	w_x	ρ/kg·m^3	
	Refined soybean oil (1) + hexanal (2) + dimethyl sulfoxide (8)								
1	0.480	0.021	0.925	0.027	923.77	0.003	0.020	1088.17	0.74
2	0.449	0.050	0.887	0.059	921.56	0.003	0.045	1078.06	0.76
3	0.425	0.075	0.853	0.088	919.79	0.004	0.071	1069.90	0.81
4	0.400	0.100	0.825	0.111	918.96	0.004	0.098	1063.67	0.88
5	0.375	0.125	0.792	0.136	917.53	0.007	0.121	1053.81	0.89
6	0.350	0.151	0.760	0.160	914.24	0.007	0.149	1045.36	0.93
	Refined soybean oil (1) + heptanal (3) + dimethyl sulfoxide (8)								
1	0.479	0.021	0.927	0.028	927.03	0.003	0.014	1089.73	0.50
2	0.448	0.052	0.871	0.077	926.38	0.003	0.026	1084.60	0.32
3	0.425	0.075	0.824	0.119	921.99	0.003	0.035	1079.19	0.30
4	0.400	0.100	0.781	0.159	924.66	0.003	0.045	1073.76	0.28
5	0.376	0.125	0.734	0.198	921.77	0.004	0.061	1069.75	0.31
6	0.350	0.151	0.690	0.239	920.72	0.004	0.073	1065.51	0.31
	Refined soybean oil (1) + butyric acid (4) + dimethyl sulfoxide (8)								
1	0.472	0.028	0.950	0.003	925.19	0.003	0.053	1088.46	15.28
2	0.452	0.052	0.945	0.007	925.76	0.003	0.093	1082.44	12.55
3	0.425	0.075	0.942	0.010	925.77	0.004	0.128	1077.90	12.20
4	0.400	0.101	0.933	0.016	927.37	0.007	0.164	1073.12	10.58
5	0.374	0.127	0.927	0.019	927.03	0.005	0.195	1068.48	10.23
6	0.350	0.150	0.924	0.024	927.35	0.008	0.226	1065.00	9.27
	Refined soybean oil (1) + valeric acid (5) + dimethyl sulfoxide (8)								
1	0.474	0.026	0.948	0.005	925.28	0.004	0.045	1081.05	9.53
2	0.449	0.050	0.942	0.011	925.26	0.005	0.090	1079.91	8.47
3	0.424	0.076	0.940	0.014	924.27	0.006	0.129	1078.12	9.08
4	0.400	0.100	0.932	0.020	927.17	0.006	0.159	1074.98	7.78
5	0.375	0.125	0.930	0.026	926.12	0.009	0.195	1069.49	7.51
6	0.350	0.149	0.922	0.033	926.76	0.012	0.223	1066.12	6.86
	Refined soybean oil (1) + caproic acid (6) + dimethyl sulfoxide (8)								
1	0.475	0.025	0.945	0.007	925.16	0.004	0.042	1086.09	6.18
2	0.442	0.050	0.931	0.012	925.69	0.005	0.080	1078.93	6.58
3	0.426	0.075	0.919	0.019	927.72	0.006	0.123	1070.90	6.53
4	0.401	0.100	0.911	0.024	926.30	0.008	0.154	1064.50	6.29
5	0.377	0.125	0.897	0.033	929.43	0.012	0.193	1058.46	5.92
6	0.351	0.150	0.883	0.042	930.38	0.015	0.218	1052.24	5.23
	Refined soybean oil (1) + caprylic acid (7) + dimethyl sulfoxide (8)								
1	0.479	0.021	0.951	0.008	925.38	0.005	0.034	1085.94	4.42
2	0.448	0.052	0.929	0.020	927.04	0.008	0.082	1076.01	4.03
3	0.425	0.075	0.904	0.032	927.46	0.010	0.114	1069.12	3.55
4	0.400	0.100	0.884	0.041	929.87	0.012	0.149	1060.29	3.60
5	0.375	0.126	0.863	0.054	930.23	0.017	0.184	1052.79	3.41
6	0.348	0.151	0.847	0.065	930.96	0.026	0.213	1045.08	3.29

[a] Standard uncertainties u are $u(p)$ = 0.5 kPa, $u(w_1^{RP}) \leq 0.007$, $u(w_1^{EP}) \leq 0.003$, $u(w_2) \leq 0.008$, $u(w_3) \leq 0.005$, $u(w_4) \leq 0.002$, $u(w_5) \leq 0.005$, $u(w_6) \leq 0.003$, $u(w_7) \leq 0.007$, $u(k_2) \leq 0.12$, $u(k_3) \leq 0.15$, $u(k_4) \leq 1.15$, $u(k_5) \leq 1.25$, $u(k_6) \leq 0.22$, $u(k_7) \leq 0.15$, $u(\rho) \leq 0.74$.

Relative deviations calculated by the mass balance procedure [38] for the systems containing RSO plus (hexanal, or heptanal, or butyric acid, or valeric acid, or caproic acid, or caprylic acid) plus DMSO were lower than 0.36%, 0.37%, 0.21%, 0.27%, 0.25% and 0.34%, respectively, indicating the good quality of collected data.

Table 7.3-2 presents interaction parameters of the NRTL and UNIQUAC models. Their global deviations (δ_w) are presented in Table 7.3-3, which also shows δ_w of UNIFACs predictions. Experimental, calculated and the best predicted LLE (lowest values of δ_w) are depicted in Fig. 7.3-1. All predicted data are presented in Table A.4.7 and depicted in Fig. A.4.3.

Table 7.3-2. Binary parameters of the NRTL and UNIQUAC models.

	NRTL			**UNIQUAC**	
Pair *ij*[a]	**b_{ij}/J·mol^{-1}**	**b_{ji}/J·mol^{-1}**	**α_{ij}**	**b_{ij}/J·mol^{-1}**	**b_{ji}/J·mol^{-1}**
12	-4228.49	9125.44	0.30	248.68	-1691.21
13	-2632.01	3726.64	0.30	-4081.09	2151.14
14	-2547.51	12799.35	0.30	-1476.78	89.30
15	-5102.16	9080.31	0.30	-1476.78	89.30
16	-107.82	6027.75	0.40	-2295.77	928.06
17	-10637.20	5741.39	0.30	-774.72	762.33
18	2392.96	18770.70	0.30	-3298.97	410.44
28	869.08	4788.84	0.30	-2017.57	-513.54
38	4348.70	5729.80	0.40	-17059.02	1062.69
48	-3576.62	2478.86	0.40	1113.43	-1069.02
58	711.22	-3495.61	0.30	1113.43	-1069.02
68	-2339.48	4146.39	0.30	-3965.33	1567.52
78	-2390.97	-5413.63	0.20	634.75	-370.59

[a] Refined soybean oil (1); hexanal (2); heptanal (3); butyric acid (4); valeric acid (5); caproic acid (6); caprylic acid (7); dimethyl sulfoxide (8).

Table 7.3-3. Global deviations (δ_w) (Eq. (7.2-6)) between experimental and calculated data for the NRTL and UNIQUAC models and for the UNIFAC methods.

System[a]	**δ_w (%)**					
	NRTL	**UNIQUAC**	**UNIFAC-LL**	**UNIFAC-HIR**	**UNIFAC-DMD**	**NIST-UNIFAC**
RSO + hexanal + DMSO	0.36	0.39	4.10	5.58	2.60	4.25
RSO + heptanal + DMSO	0.31	0.36	2.23	2.40	2.93	3.38
RSO + butyric acid + DMSO	0.29	0.56	3.34	12.75	5.47	1.24
RSO + valeric acid + DMSO	0.23	0.27	4.09	12.76	6.37	1.47
RSO + caproic acid + DMSO	0.55	0.50	5.00	12.24	6.20	1.71
RSO + caprylic acid + DMSO	0.33	0.71	6.90	11.56	7.33	2.53

[a] RSO: refined soybean oil; DMSO: dimethyl sulfoxide.

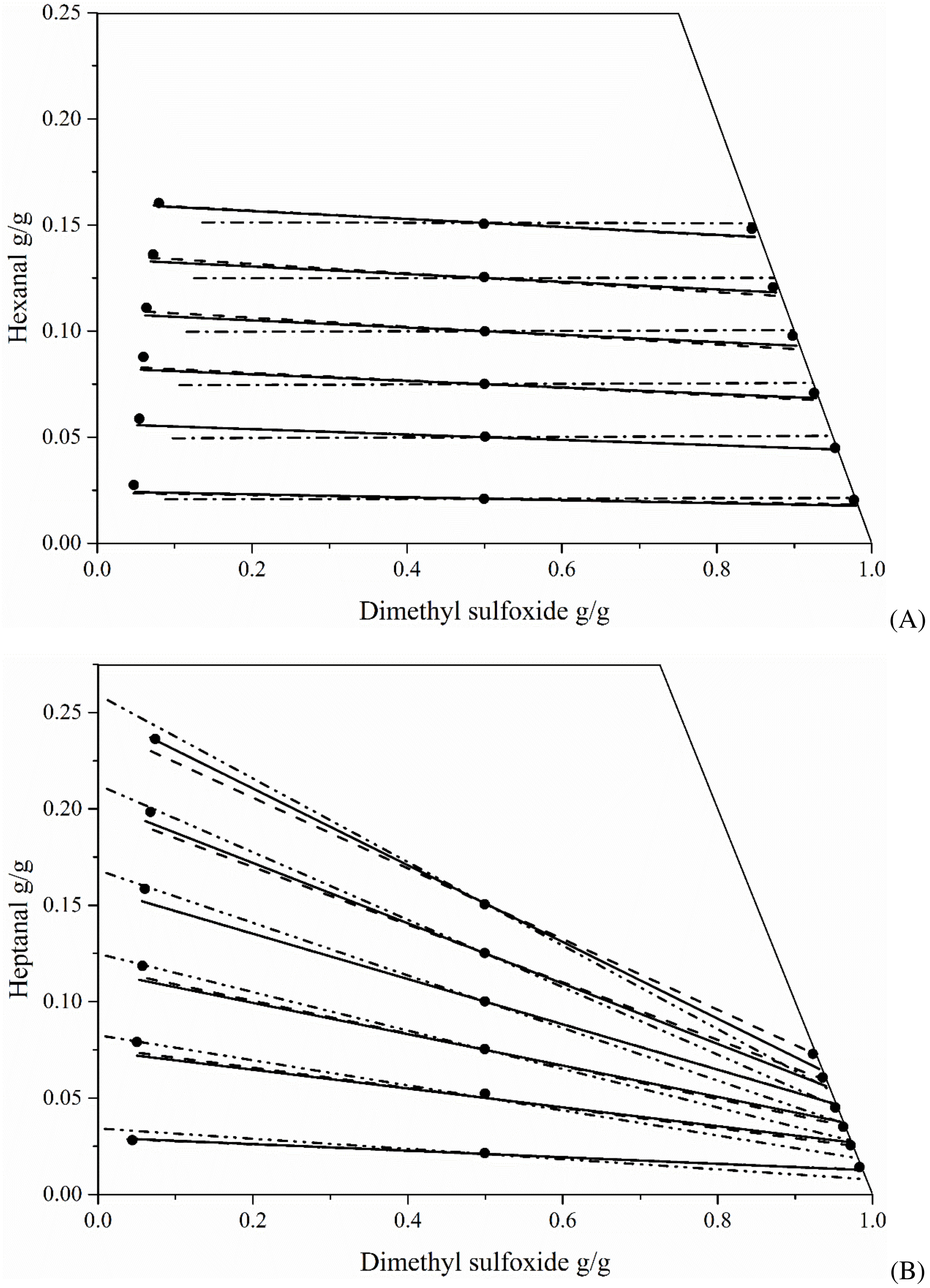

Figure 7.3-1 (A-B). Liquid-liquid equilibrium data for pseudoternary systems composed of refined soybean oil plus odoriferous compounds plus dimethyl sulfoxide (8) at 298.15 K and under atmospheric pressure: (A) hexanal, (B) heptanal, (C) butyric acid, (D) valeric acid, (E) caproic acid and (F) caprylic acid. Legend: (●) experimental data; (solid) NRTL; (dash) UNIQUAC; (dash dot dot) UNIFAC-LL; (dash dot) UNIFAC-DMD; (dot) NIST-UNIFAC.

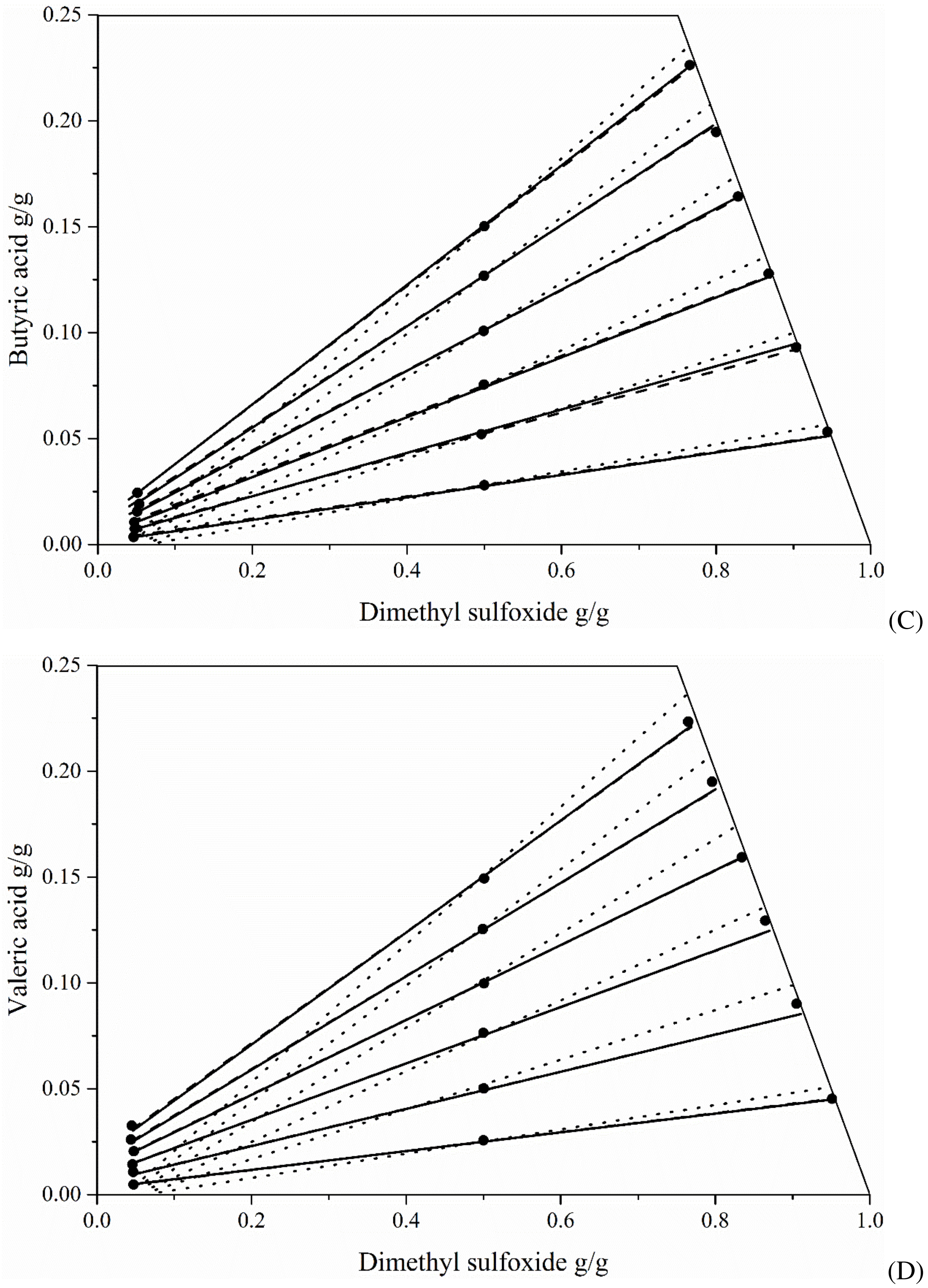

Figure 7.3-2 (C-D). Liquid-liquid equilibrium data for pseudoternary systems composed of refined soybean oil plus odoriferous compounds plus dimethyl sulfoxide (8) at 298.15 K and under atmospheric pressure: (A) hexanal, (B) heptanal, (C) butyric acid, (D) valeric acid, (E) caproic acid and (F) caprylic acid. Legend: (●) experimental data; (solid) NRTL; (dash) UNIQUAC; (dash dot dot) UNIFAC-LL; (dash dot) UNIFAC-DMD; (dot) NIST-UNIFAC.

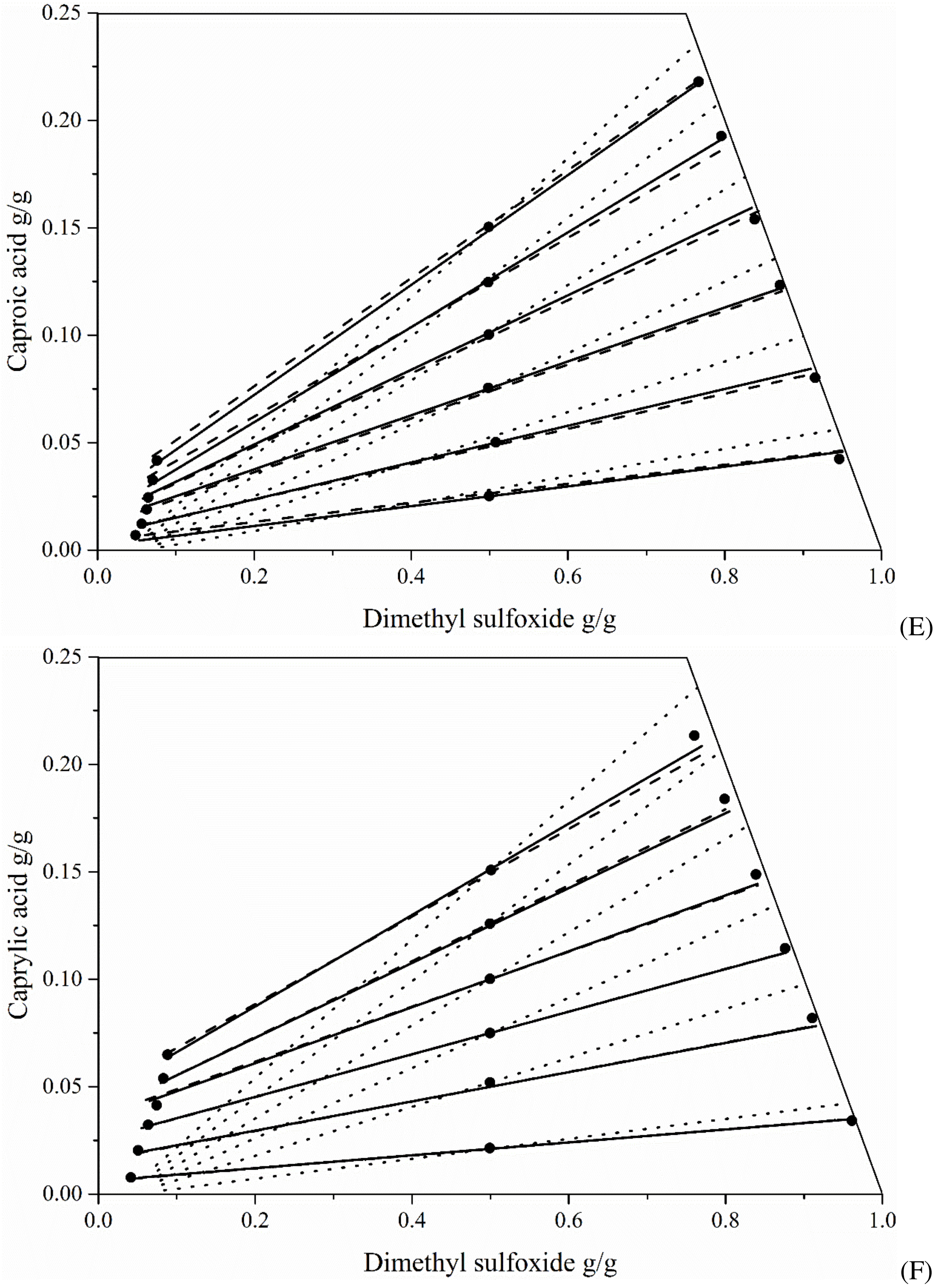

Figure 7.3-3 (E-F). Liquid-liquid equilibrium data for pseudoternary systems composed of refined soybean oil plus odoriferous compounds plus dimethyl sulfoxide (8) at 298.15 K and under atmospheric pressure: (A) hexanal, (B) heptanal, (C) butyric acid, (D) valeric acid, (E) caproic acid and (F) caprylic acid. Legend: (●) experimental data; (solid) NRTL; (dash) UNIQUAC; (dash dot dot) UNIFAC-LL; (dash dot) UNIFAC-DMD; (dot) NIST-UNIFAC.

Solubility behaviors of investigated mixtures (Fig. 7.3-1) reveal tendencies of solutes migration between equilibrium phases. For aldehydes as solutes, hexanal and heptanal showed higher mass fractions in raffinate phases, indicating a lower interaction with DMSO in comparison with carboxylic acids. As one can see, carbon-chain length of aldehydes highly alters tie lines inclination, considering that similar quantities of hexanal were found between equilibrium phases, whereas heptanal showed a high tendency to remain in oily phase. Thus, k values (Table 7.3-1) were lower than unit for both solutes. On the other hand, for carboxylic acids, even at lower concentrations, important transfer of solutes from RSO to DMSO occurred, as observed by tie lines inclination. This behavior was affected by carbon-chain length of carboxylic acids, as tie lines inclinations decrease as molecular chain increases. Corroborating with satisfactory k values presented in Table 7.3-1, carboxylic acids were easily removed from RSO using DMSO as solvent, which agrees with Cusack et al. [60] who suggests solvent selection based on activity coefficient behaviors.

In investigated heterogeneous region, increases of mass fractions of hexanal, heptanal, butyric acid, and valeric acid in overall mixtures barely influenced mutual solubility of the pair RSO:DMSO, as tie line lengths remained similar throughout diagrams (Fig. 7.3-1). Even at higher quantities of solute in extract phases, very low amounts of RSO were found, revealing a high repulsion between diluent and solvent. Analogous behavior was previously observed for the solubility between RSO and DMSO at different temperatures, wherein temperature virtually did not impact on mutual solubility of this pair [24]. For caproic and caprylic acids, a somewhat increase of DMSO in the RSO-rich phase occurred, as showed by binodal curve inclinations.

Concerning LLE predictions, the UNIFAC-DMD method showed reasonable results for the system containing hexanal. The UNIFAC-LL method reasonably predicted LLE of heptanal system, and good agreements were found for miscibility data of butyric acid and valeric acid systems calculated by the NIST-UNIFAC method. For such cases, higher differences between experimental and predicted data were found for the RSO-rich phases, which affected biphasic region sizes. Furthermore, predicted tie line inclinations presented a somewhat discrepancy between experimental ones. Even though reasonable agreements were found for cited systems, the UNIFAC-LL, UNIFAC-DMD, and NIST-UNIFAC methods failed to predict miscibility data for systems containing same functional groups. As observed in Fig. S.3, none of the UNIFAC methods was capable to predict the effect of the carbon chain length on liquid-liquid equilibrium of investigated systems. For instance, similar data were predicted between LLE of hexanal and heptanal systems, which highly disagrees with experimental results. Moreover, predicted distribution of solutes between equilibrium phases (Fig. A.4.4) also shows clearly inefficiency of the applied group contribution methods to describe miscibility data of RSO, odoriferous compounds and DMSO. Thus, in general the UNIFACs methods studied in this work are not reliable tools to predict extraction of odoriferous compounds from RSO using DMSO.

Experimental distribution of compounds between raffinate and extract phases for investigated systems is depicted in Fig. 7.3-2. Also, comparisons with removal of odoriferous compounds (hexanal, and butyric, valeric and caprylic acids) from sunflower seed oil using anhydrous ethanol as solvent are presented. Solvents selectivity is shown in Table 7.3-4.

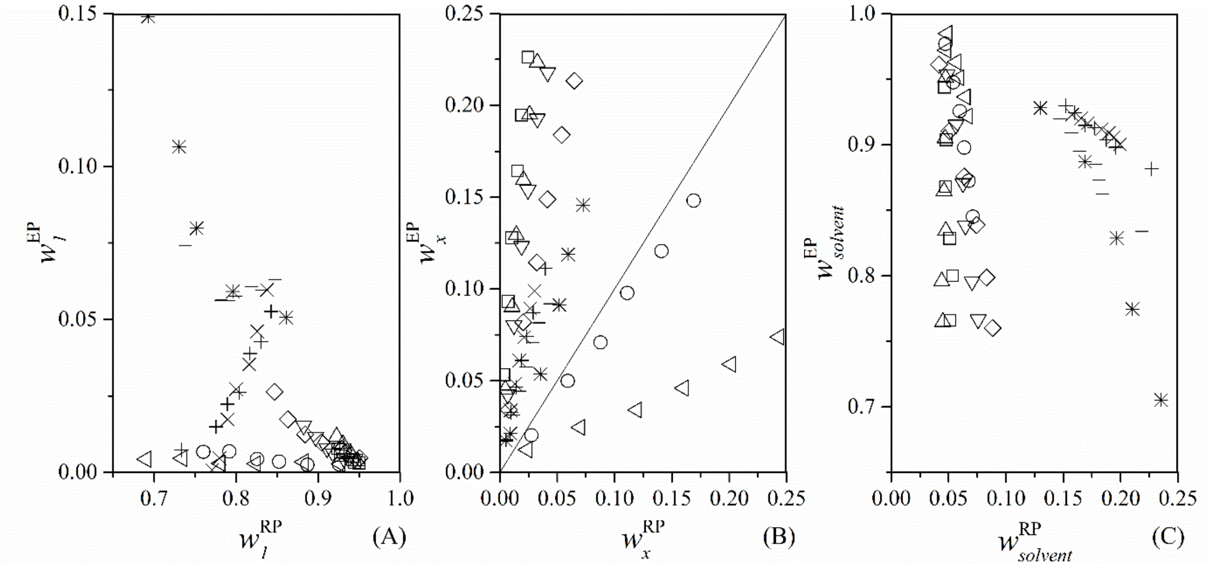

Figure 7.3-4. Distribution of refined soybean oil (1), solutes (*x*), and dimethyl sulfoxide (8) between raffinate (RP) and extract (EP) phases at 298.15 K. Solutes *x*: (○) hexanal; (◁) heptanal (□) butyric acid; (▽) valeric acid; (△) caproic acid; and (◇) caprylic acid; Comparison data of sunflower seed oil plus solutes plus anhydrous ethanol: (✳) hexanal; (╳) butyric acid; (+) valeric acid; (–) caprylic acid [17,24].

Table 7.3-4. Solvent selectivity ($S_{x/1}$) (Eq. (7.2-3)) for systems containing refined soybean oil (1), odoriferous compounds (*x*), and dimethyl sulfoxide (8) at 298.15 K.

Tie line	$S_{2/1}$	$u(S_{2/1})$	$S_{3/1}$	$u(S_{3/1})$	$S_{4/1}$	$u(S_{4/1})$	$S_{5/1}$	$u(S_{5/1})$	$S_{6/1}$	$u(S_{6/1})$	$S_{7/1}$	$u(S_{7/1})$
	Hexanal		Heptanal		Butyric acid		Valeric acid		Caproic acid		Caprylic acid	
1	253	61	174	62	4803	3121	2445	811	1354	835	892	141
2	270	53	97	36	3659	861	1638	247	1328	126	486	59
3	194	26	87	25	2741	361	1407	126	967	47	328	17
4	165	14	74	32	1350	583	1153	92	729	184	255	10
5	102	8	59	11	1752	132	750	61	457	14	170	14
6	104	7	49	25	1107	91	537	46	301	9	106	6

Distributions of solutes in equilibrium phases (Fig. 7.3-2.B) display high tendency of carboxylic acids to migrate from RSO to DMSO. An increase in w of solutes in extract phases is verified as carbon chain length of molecules decreases, corroborating with tie line inclinations depicted in Fig. 7.3-1. Also, considerable difference between the k value of hexanal and heptanal verified in Fig. 7.3-1 is shown in Fig. 7.3-2. RSO distributions (Fig. 7.3-2.A) presented low quantities of the oil in the DMSO-rich phase, despite solutes concentrations. Same behavior occurs for the DMSO distribution (Fig. 7.3-2.C), wherein its quantity in RSO:rich phases varied between approximately 5 and 7.5% in mass for the investigated diagram region.

Comparing anhydrous ethanol [17,18] and DMSO as solvents, higher affinity of carboxylic acids with solvent was found in the present work. On the other hand, hexanal presented higher distribution coefficient in anhydrous ethanol than in DMSO, as verified by higher concentrations of hexanal in alcohol-rich phases. Furthermore, considerable improvements were found for both RSO and DMSO distributions using DMSO as solvent, as higher mutual solubilities of diluent and solvent were found for anhydrous ethanol systems.

Regarding solvent selectivity (Table 7.3-4), high values were found for removal of odoriferous compounds from RSO. As one can see, chain length of solutes highly influences the extraction performance, since DMSO selectivity for investigated systems decreases in the following order: $S_{4/1} > S_{5/1} > S_{6/1} > S_{7/1} > S_{2/1} > S_{3/1}$, wherein subscripts i and j stand for RSO (1), hexanal (2), heptanal (3), butyric acid (4), valeric acid (5), caproic acid (6) and caprylic acid (7). Furthermore, higher selectivity values were found for lower concentrations of odoriferous compounds in overall mixtures, as lowest miscibilities between RSO and DMSO occurred within this region. Comparing with anhydrous ethanol, previous studies reported selectivity values lower than 3050, 282, 40, and 40 for removal of butyric acid, valeric acid, caprylic acid, and hexanal from sunflower seed oil, respectively [17,18]. Furthermore, regardless of lower k values for extraction of hexanal using DMSO, considerable higher values for solvent selectivity were found in the present work when comparing with extraction using anhydrous ethanol. Such occurrence is mainly due to low mutual miscibility of the pair DMSO:RSO, which remain very low throughout investigated LLE region.

7.4 CONCLUSION

Liquid-liquid equilibrium and density data were collected to investigate extraction of six odoriferous compounds (hexanal, or heptanal, or butyric acid, or valeric acid, or caproic acid, or caprylic acid) from refined soybean oil using DMSO as solvent. Results revealed that DMSO is very suitable for extracting carboxylic acids from RSO, presenting high values of k

and *S*. For hexanal system, tie lines were slightly inclined to raffinate phases; for heptanal, its distribution between equilibrium phases considerably increased towards RSO-rich phase, resulting in low values of *k*. Furthermore, mutual solubilities of the pair RSO:DMSO were barely affected by solute quantities in overall mixtures. Extracted phases presented very low amounts of oil even at high quantities of solutes, indicating low affinity between RSO and DMSO molecules. Correlation of the NRTL and the UNIQUAC methods were successfully achieved for all systems, presenting global deviations lower than 0.55 and 0.71%, respectively.

In general, a low predictive capacity was found for the UNIFAC method prediction. The UNIFAC-NIST satisfactorily predicted solubility data for systems containing butyric and valeric acids, especially for DMSO-rich phases. For caproic and caprylic acids systems, reasonable data were generated by the UNIFAC-NIST method. However, despite good agreements in extract phases for butyric acid and valeric acid systems, higher deviations were found for acids of longer molecular chains, indicating a lack of predictability for systems containing same functional groups. Also, DMSO-rich phase of system containing hexanal was adequately calculated by the UNIFAC-DMD; a somewhat consistency was found for the RSO-rich phase, wherein predicted solvent quantities were higher than experimental ones. For LLE of heptanal system, reasonable predictions were achieved by the UNIFAC-LL method. All other cases presented deficiency in predicting ternary solubility behavior for the extraction of odoriferous compounds from RSO using DMSO as solvent.

AUTHOR INFORMATION

Corresponding Author

*E-mail: rceriani@feq.unicamp.br. Tel +55 19 35213961. Fax: +55 19 35213965.

ORCID

Roberta Ceriani: 0000-0001-8490-4960

Perci O. B. Homrich: 0000-0002-9677-9869

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CAPÍTULO 8

CONCLUSÕES GERAIS

O presente trabalho investigou a solubilidade de diferentes solventes e cosolventes no óleo de soja a fim de realizar a desodorização. Como abordado no ***Capítulo 2***, as condições operacionais do atual processo de desodorização dos óleos vegetais acarretam em efeitos negativos nos óleos, como formação de gordura *trans* e do contaminante 3-MCPD. Como alternativa ao atual processo, estudos indicam que a extração líquido-líquido apresenta potencial para remover compostos odoríferos e ácidos graxos livres, atualmente volatilizados durante a desodorização. Não obstante a intensa coleta de dados experimentais focados na extração com solvente para refinar óleos vegetais, a investigação de diferentes solventes para desodorizar óleos vegetais se faz necessária.

Os resultados obtidos nos ***Capítulos 3*** e ***4*** indicaram que, dentre os 17 solventes de baixa toxicidade pré-selecionados considerando o método qualitativo de Cusack et al. (1991), etanol, ácido acético, lactato de etila e dimetilsulfóxido são parcialmente miscíveis no óleo de soja. Além disso, água e ácido fórmico formam emulsão persistente através de agitação com o óleo, impossibilitando a aplicação destes solventes em suas formas puras. Quatro diagramas de equilíbrio foram obtidos, havendo destaque para os solventes DMSO e etanol por apresentarem menor solubilidade no óleo de soja. Também, para o sistema contendo DMSO com solvente, as fases extratos apresentaram uma concentração muito baixa de óleo de soja e cerca de 5% em massa de solvente foi encontrado nas fases rafinados, indicando uma baixa solubilidade do par óleo e solvente. Além disso, a temperatura não apresentou um efeito significativo na miscibilidade mútua de tal sistema. De maneira geral, a predição pelos métodos baseados no UNIFAC não foi satisfatória tanto quantitativa quando qualitativamente.

A fim de investigar a aplicação de cosolventes para desodorizar óleos vegetais, os resultados apresentados nos ***Capítulos 5*** e ***6*** apresentam a solubilidade entre o óleo de soja refinado e 6 diferentes cosolventes: {(etanol, ou ácido acético, ou lactato de etila, ou dimetilsulfóxido) + água} e {(lactato de etila, ou dimetilsulfóxido) + ácido fórmico}. Os dados de equilíbrio líquido-líquido obtidos apresentam a vantagem de adicionar água ou ácido fórmico nos solventes devido à diminuição da solubilidade mútua dos compostos, facilitando a purificação das fases rafinado e extrato. Para esta etapa, as fases extratos de todos os solventes apresentaram um quantidade muito baixa de óleo, a qual permaneceu baixa em toda a faixa de temperatura estudada. Para o sistema contendo DMSO, concentrações muito baixas de solvente foram encontradas nas fases ricas em óleo, propiciando a posterior purificação das correntes extrato e rafinado. Além disso, uma melhora acentuada na predição dos diagramas de equilíbrio foi verificada para os métodos UNIFAC quando comparada com a predição dos sistemas contendo óleo de soja e solventes puros. Para as fases extratos, foram encontrados valores de desvios globais de aproximadamente 1%.

Em relação ao estudo do equilíbrio líquido-líquido dos sistemas contendo óleo de soja refinado, compostos odoríferos (hexanal, heptanal, ácidos butírico, ácido valérico, ácido capróico e ácido caprílico) e dimetilsulfóxido apresentado no ***Capítulo 7***, observou-se a alta seletividade do solvente para a remoção dos solutos, em especial para os ácidos carboxílicos. A miscibilidade mútua do par solvente e diluente permaneceu baixa independentemente da concentração de soluto na mistura inicial, indicando a baixa afinidade do DMSO e do óleo. Tal comportamento também foi verificado para diferentes temperaturas (***Capítulo 5***). Além disso, comparações da distribuição dos compostos entre as fases em equilíbrio e da seletividade do solvente foram realizadas para a remoção de odores do óleo utilizando etanol anidro. Tanto aldeídos quanto ácidos carboxílicos apresentaram valores de seletividade do solvente significativamente maiores para os sistemas estudados no presente trabalho, em que foi possível verificar uma menor solubilização do par solvente e diluente em comparação com o solvente alcoólico. Por fim, a predição utilizando quatro métodos baseados no UNIFAC (UNIFAC-LL, UNIFAC-DMD, UNIFAC-HIR e NIST-UNIFAC) apresentou-se falha para a maioria dos sistemas. Tais resultados obtidos pela predição reforçam a não adequabilidade dos métodos de contribuição de grupos utilizados no presente trabalho para a representação do equilíbrio líquido-líquido de sistemas envolvidos nas indústrias de óleos vegetais, indicando a necessidade de parametrização de métodos preditivos com foco em sistemas graxos.

De uma maneira geral, o presente trabalho indicou diferentes possibilidades de solventes para serem aplicados em processos de purificação de óleos vegetais. Os dados experimentais obtidos colaboram para um maior entendimento do comportamento de sistemas que apresentam um alto desvio da idealidade, como é o caso das misturas investigadas. Considerando-se os resultados obtidos, a extração líquido-líquido pode servir como um pré-tratamento dos óleos vegetais aplicado anteriormente à atual etapa de desodorização, permitindo assim, condições de operação mais brandas na coluna de esgotamento e também um menor tempo requerido em tal etapa. A fim de haver uma total substituição do processo de esgotamento, há a necessidade de investigar a aplicabilidade da extração líquido-líquido para extrair outros compostos atualmente removidos na desodorização, como pesticidas, traços de metais e sabões e ácidos graxos livres remanescentes do refino químico. Por fim, os dados de equilíbrio líquido-líquido obtidos contribuem para a elaboração de bancos de dados visando uma parametrização mais robusta de métodos preditivos para melhor representarem os sistemas graxos.

SUGESTÕES PARA TRABALHOS FUTUROS

- Estudar a remoção por solvente de diferentes compostos envolvidos no refino dos óleos vegetais, como pesticidas, tocoferóis, acilgliceróis parciais, entre outros;
- Estudo comparativo de propriedades físicas, como massa específica, viscosidade, tensão interfacial e temperatura normal de ebulição de diferentes solventes e seus impactos no processo de refino;
- Investigar a solubilidade mútua entre solventes e óleos vegetais que contém um maior teor de ácidos graxos saturados, como os óleos de palma e de coco;
- Realizar um estudo comparativo da análise econômica do processo de extração líquido-líquido para a desodorização de óleos vegetais envolvendo diferentes solventes;
- Estudar o equilíbrio líquido-vapor entre os compostos para investigar a recuperação do solvente e a purificação da corrente óleo;
- Comparar a recuperação do solvente e o tratamento da corrente rafinado considerando-se diferentes solventes;
- Obter dados suficientes de equilíbrio visando o projeto de um equipamento de extração, bem como modelar e simular o processo de desodorização;
- Aperfeiçoar métodos preditivos, como o UNIFAC-LL (MAGNUSSEN, 1981), UNIFAC-DMD (WEIDLICH e GMEHLING, 1987; GMEHLING et al., 1993) e UNIFAC-LYB (LARSEN, 1987) visando uma melhor relação com sistemas contendo óleos vegetais e solventes líquidos.

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APÊNDICE A.1

Predição do equilíbrio líquido-líquido dos sistemas envolvidos no **Capítulo 3.**

Figura A.1.1: Diagramas de equilíbrio líquido-líquido dos sistemas óleo de soja, n-hexanal e (ou água, ou anisol, ou dimetilsulfóxido, ou metil-isobutil-cetona, ou metil-etil-cetona) a 25 °C sob pressão atmosférica preditos pelo método UNIFAC com os parâmetros ajustados por Magnussen et al. (1981).

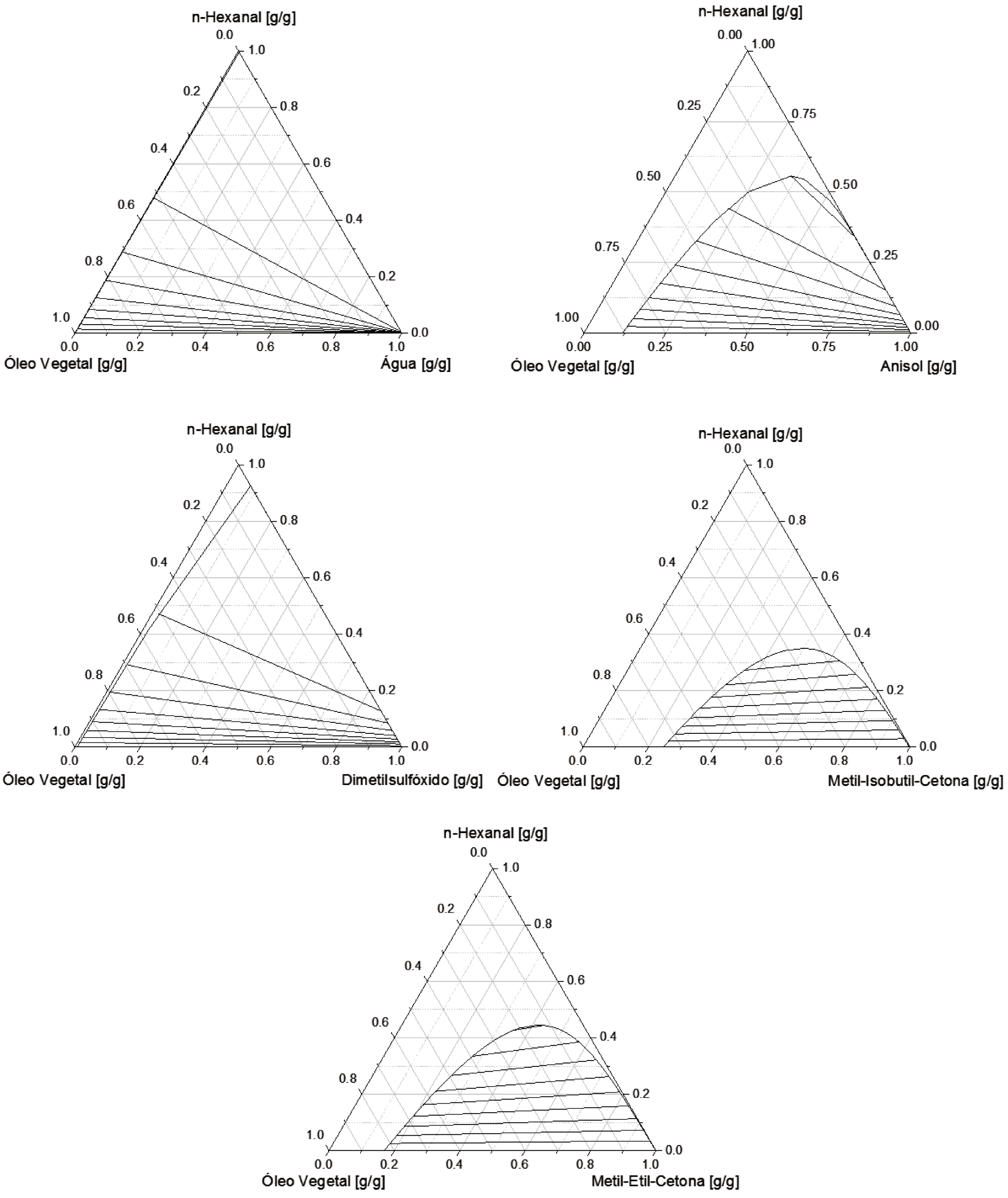


Figura A.1. 2: Diagramas de equilíbrio líquido-líquido dos sistemas óleo de soja, 2,4-decadienal e (ou água, ou anisol, ou dimetilsulfóxido, ou metil-isobutil-cetona, ou metil-etil-cetona) a 25 °C sob pressão atmosférica preditos pelo método UNIFAC com os parâmetros ajustados por Magnussen et al. (1981).

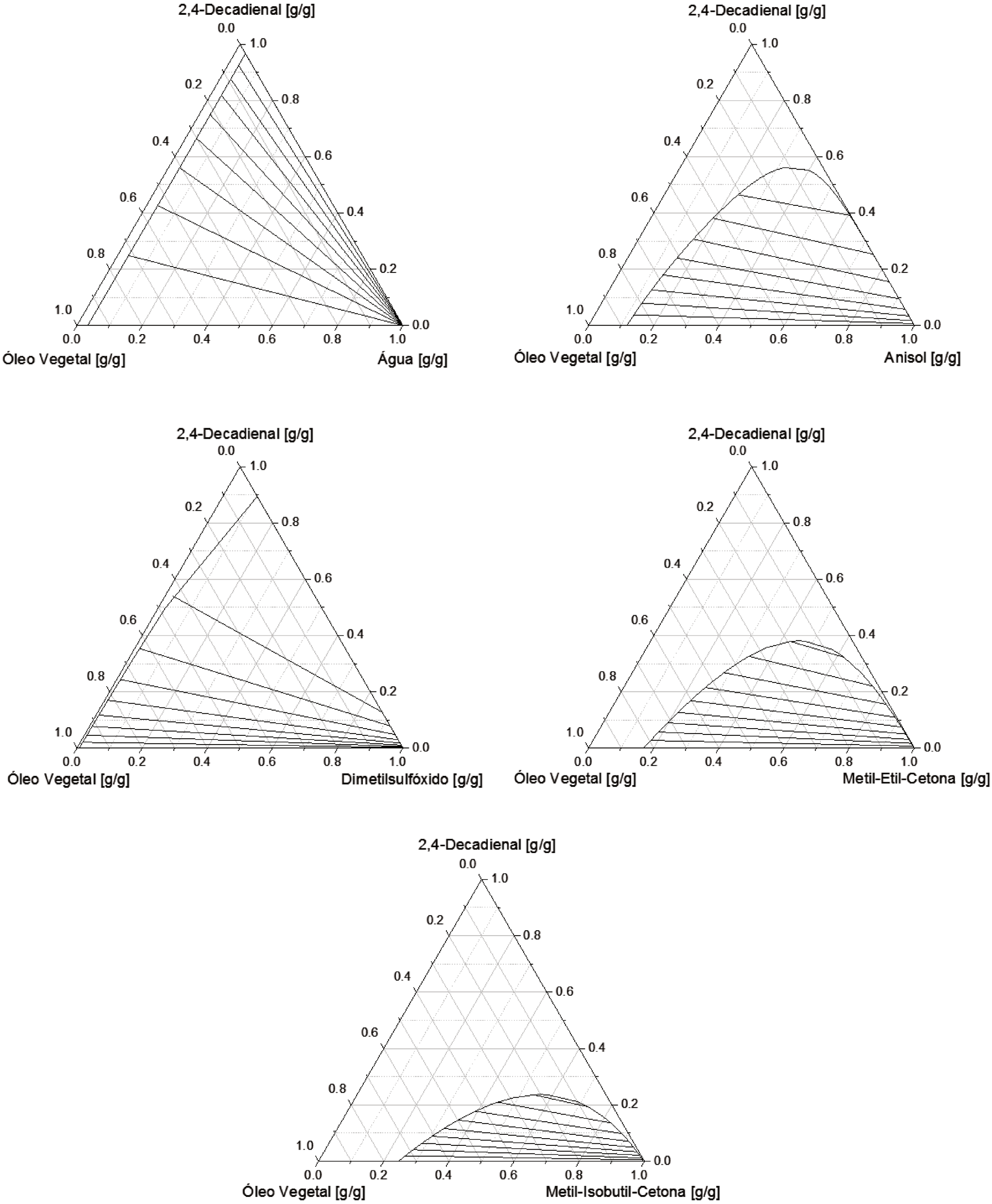


Figura A.1. 3: Diagramas de equilíbrio líquido-líquido dos sistemas óleo de soja, n-hexanal e (ou água, ou anisol, ou dimetilsulfóxido) a 25 °C sob pressão atmosférica preditos pelo método UNIFAC com os parâmetros ajustados por Hirata et al. (2013).

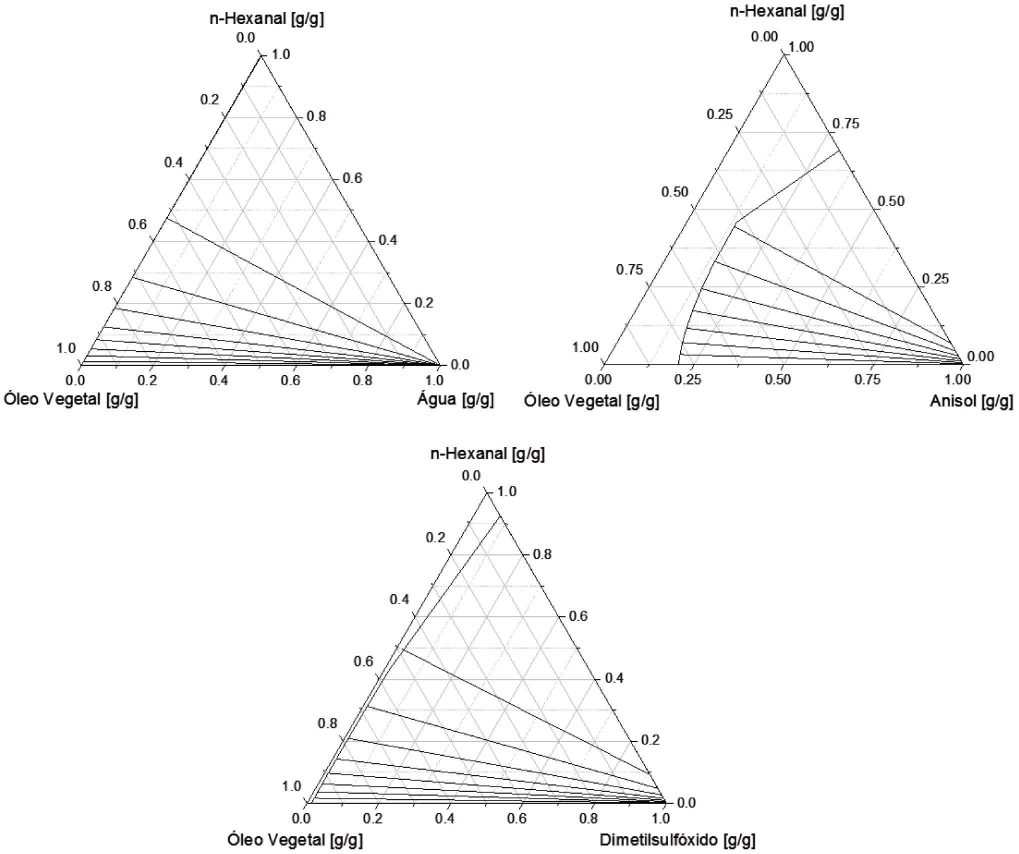


Figura A.1. 4: Diagramas de equilíbrio líquido-líquido dos sistemas óleo de soja, 2,4-decadienal e (ou água, ou anisol, ou dimetilsulfóxido) a 25 °C sob pressão atmosférica preditos pelo método UNIFAC com os parâmetros ajustados por Hirata et al. (2013).

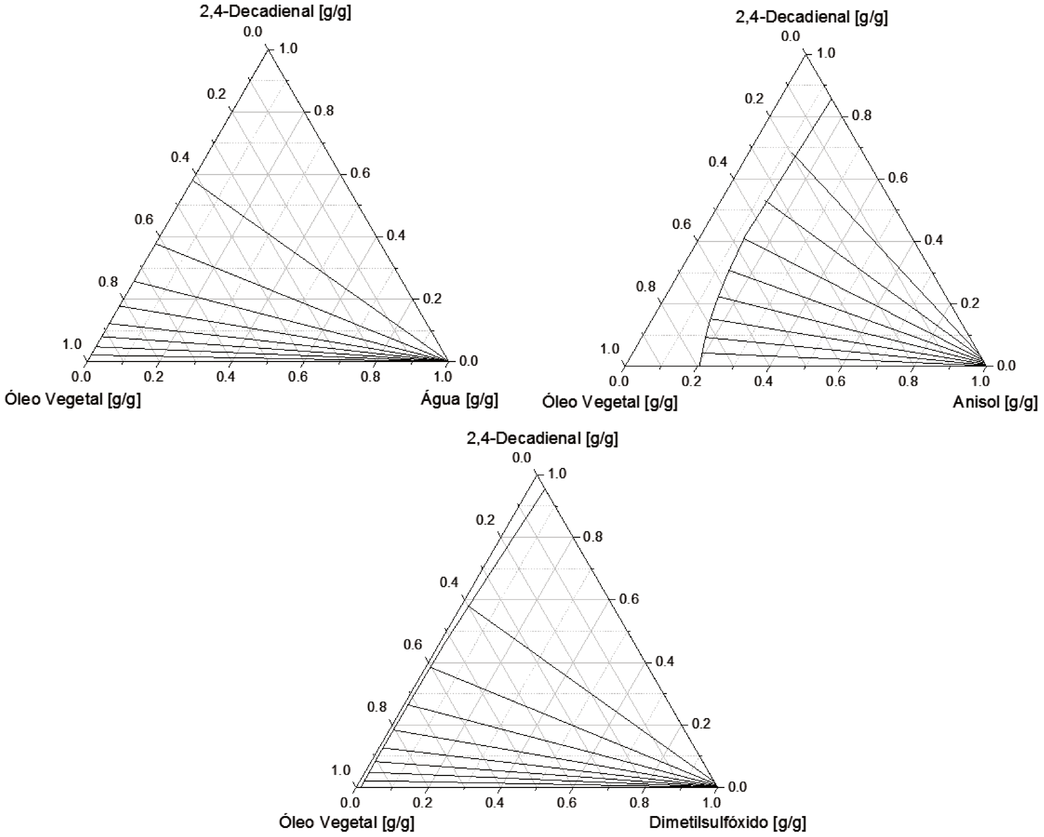
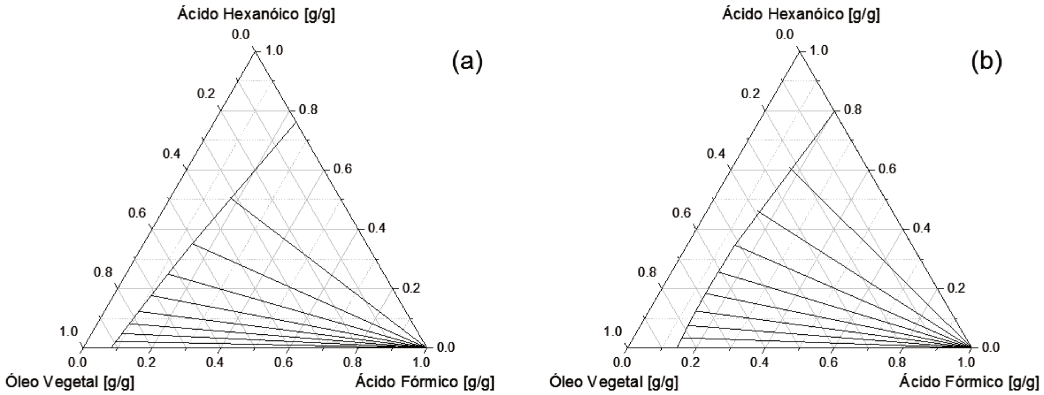


Figura A.1. 5: Diagramas de equilíbrio líquido-líquido dos sistemas óleo de soja, ácido hexanoico e ácido fórmico a 25 °C sob pressão atmosférica preditos pelo método UNIFAC com os parâmetros ajustados por Magnussen et al. (1981) (a) e Hirata et al. (2013) (b).



APÊNDICE A.2

Material suplementar do artigo “Solubility behavior of mixtures containing refined soybean oil and low-toxic solvents at different temperatures”.

Table A.2. 1: Composition of refined soybean oil in terms of its fatty acid profile.

Symbol	Fatty acid	CX:Y [a]	MW/g.mol^{-1} [b]	% mass	% molar
M	Myristic	14:0	228.38	0.08	0.10
P	Palmitic	16:0	256.43	10.98	11.95
Po	Palmitoleic (ω 7)	16:1	254.41	0.09	0.10
S	Stearic	18:0	284.48	3.66	3.59
O	Oleic (ω 9)	18:1	282.47	22.94	22.66
t–L	*Trans* Linoleic (ω 6)	18:2	328.45	0.64	0.54
L	Linoleic (ω 6)	18:2	280.45	54.34	54.07
A	Arachidic	20:0	312.54	0.35	0.31
t–Ln	*Trans* Linolenic (ω 3)	18:3	278.44	0.27	0.27
Ln	Linolenic (ω 3)	18:3	278.44	5.48	5.49
Ga	Cis–11–Eicosenoic (ω 11)	20:1	310.51	0.49	0.44
Be	Behenic	22:0	340.59	0.43	0.35
Lg	Lignoceric	24:0	368.63	0.17	0.13

[a] X = number of carbons, Y = number of double bonds. [b] Molecular weight.

Table A.2. 2: Probable triacylglycerol (TAG) profile of refined soybean oil.

TAG	CX:Y [a]	MW/g.gmol^{-1} [b]	% mass	% molar
PLP	50:2	831.35	2.18	2.29
OOP	52:2	859.41	3.46	3.51
PLO	52:3	857.39	10.32	10.50
SLO	54:3	885.44	4.57	4.50
LLP	52:4	855.38	13.32	13.59
OOL	54:4	883.43	13.00	12.84
PLnL	52:5	853.36	2.63	2.69
LLO	54:5	881.41	23.16	22.92
LLL	54:6	879.40	21.70	21.53
LLLn	54:7	877.38	5.66	5.63

[a] X = number of carbons, Y = number of double bonds. [b] Molecular weight.

Figure A.2. 1: Curve calibration of dimethyl sulfoxide in 2-propanol.

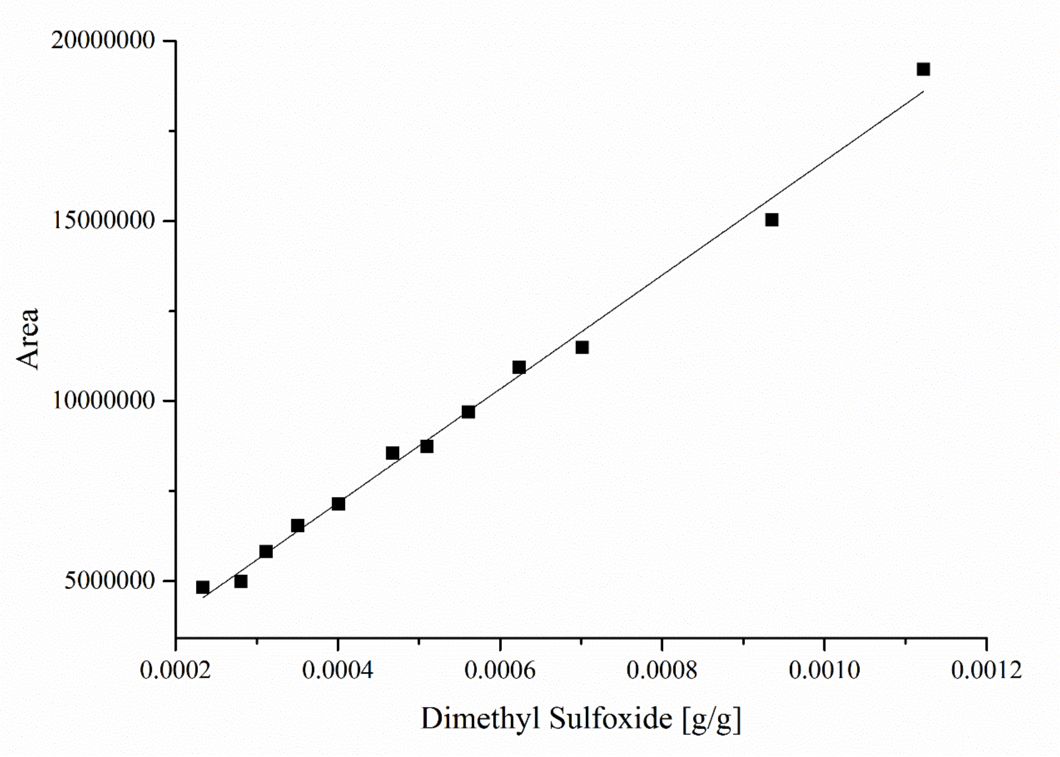


Table A.2. 3: Parameters of the curve calibration, their standard error and the limits of detection (LD) and quantification (LQ).

Parameter	Value	Standard error
Slope	15833500000	404369000
Intercept	837069.7	242649
Limit of detection (LD)	0.0000506	
Limit of quantification (LQ)	0.0001533	

Limits of detection (LD) and of quantification (LQ):

$$LD = 3.3\frac{s}{S} \qquad \text{(Eq. A.2.1)}$$

$$LQ = 10\frac{s}{S} \qquad \text{(Eq. A.2.2)}$$

in which: *s* is the standard error of the intercept value of the curve calibration, and *S* is the slope of the curve calibration.

Table A.2. 4: Experimental densities at 298.15 K of dimethyl sulfoxide and 2-propanol and of the raffinate (RP) and extract phases (EP) of the pseudobinary systems containing dimethyl sulfoxide plus refined soybean oil.

Compound	**ρ [g.cm^3]**	**u(ρ)**
Dimethyl sulphoxide	1.09565	0.00001
2-propanol	0.78069	0.00001
RP at 293.15 K	0.92465	0.00001
RP at 308.15 K	0.92422	0.00002
RP at 323.15 K	0.92477	0.00001
EP at 293.15 K	1.09497	0.00001
EP at 308.15 K	1.09421	0.00001
EP at 323.15 K	1.09388	0.00001

Equations of the original UNIFAC method used by the UNIFAC-LL and UNIFAC-HIR:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \qquad \text{(Eq. A.2.3)}$$

Residual term:

$$\ln \gamma_i^c = 1 - \phi_i + \ln \phi_i - 5q_i \left[\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right] \qquad \text{(Eq. A.2.3.1)}$$

$$\theta_i = \frac{q_i}{\sum_j x_j q_j} \qquad \text{(Eq. A.2.3.2)}$$

$$\phi_i = \frac{r_i}{\sum_j x_j r_j} \qquad \text{(Eq. A.2.3.3)}$$

Combinatorial term:

$$\ln \gamma_i^r = \sum_K^{groups} v_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \qquad \text{(Eq. A.2.3.4)}$$

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}} \right] \qquad \text{(Eq. A.2.3.5)}$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad \text{(Eq. A.2.3.6)}$$

$$X_m = \frac{\sum_i^M v_m^{(i)} x_i}{\sum_i^M \sum_j^N v_j^{(i)} x_i} \qquad \text{(Eq. A.2.3.7)}$$

$$\psi_{nm} = \exp\left(-\frac{a_{nm}}{T} \right) \qquad \text{(Eq. A.2.3.8)}$$

Equations of the modified UNIFAC-Dortmund (also used by the NIST-modified UNIFAC):

$$\ln \gamma_i^c = 1 - \phi_i^{'} + \ln \phi_i^{'} - 5q_i \left[\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right] \qquad \text{(Eq. A.2.4)}$$

$$\phi_i = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \qquad \text{(Eq. A.2.4.1)}$$

$$\psi_{nm} = \exp\left(-\frac{\left(a_{nm} + b_{nm} T + c_{nm} T^2 \right)}{T} \right) \qquad \text{(Eq. A.2.4.2)}$$

Equations of the modified UNIFAC-Lyngby:

$$\ln \gamma_i^c = \ln \frac{\psi_i}{x_i} + 1 - \frac{\psi_i}{x_i} \qquad \text{(Eq. A.2.5)}$$

$$\psi_i = \frac{r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \qquad \text{(Eq. A.2.5.1)}$$

$$\ln \Gamma_k = \frac{z}{2} Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}} \right] \qquad \text{(Eq. A.2.5.2)}$$

$$\theta_m = \frac{Q_m \frac{z}{2} Q_m}{\sum_n Q_n \frac{z}{2} Q_n} \qquad \text{(Eq. A.2.5.3)}$$

$$\psi_{nm} = \exp\left(- \frac{\left(a_{nm} + b_{nm}(T - T_0) + c_{nm}\left(T \ln \frac{T_0}{T} + T - T_0 \right) \right)}{T} \right) \qquad \text{(Eq. A.2.5.4)}$$

Table A.2. 5: Sub-division of refined soybean oil and organic solvents into functional groups.

Main group	**1**				**2**	**3**		**4**		**5**	**6**	**7**		**8**		**9**	**10**		**11**
	CH_2				**C=C**	**ACH**		**OH**		**H_2O**	**CH_3CO**	**COOH**		**COOC**		**HCOO**	**CH_2O**		**DMSO**
Sub-group	1	2	3	4	5	6	7	8	8.1	9	10	11	12	13	14	15	16	17	18
	CH_3	CH_2	CH	C	CH=CH	ACH	AC	OH (P)	OH (S)	H_2O	CH_3CO	COOH	HCOOH	CH_3COO	CH_2COO	HCOO	CH_3O	CH_2O	DMSO
Refined Soybean Oil (LLO)	3	37	1		5										3				
Anhydrous ethanol	1	1						1											
Acetic acid	1											1							
Ethyl lactate[a]	2		1						1						1				
Ethyl lactate[b]	2		1					1							1				
Dimethyl sulfoxide																			1
Formic acid													1						
Methyl ethyl ketone	1	1									1								
Methyl isobutyl ketone	2	1	1								1								
Ethyl acetate	1	1												1					
Ethyl formate	1	1														1			
Butyl acetate	1	3												1					
Isobutyl acetate	2	1	1											1					
Methyl acetate	1													1					
Propyl acetate	1	2												1					
Anisole						5	1										1		
Tert-butyl methyl ether	3			1													1		
Ethyl ether	2	1																1	
Water										1									

[a] Sub-groups considered by UNIFAC-LL, UNIFAC-HIR, UNIFAC-Dortmund and NIST-modified UNIFAC; [b] Sub-groups considered by UNIFAC-Lyngby.

Table A.2. 6: Group volume (R_k) and surface area (Q_k) parameters.

Group		**UNIFAC version**					
		UNIFAC-LL and UNIFAC-HIR		**UNIFAC-Dortmund and NIST-modified UNIFAC**		**UNIFAC-Lyngby**	
Main group	Sub-group	R_k	Q_k	R_k	Q_k	R_k	$(z/2)Q_k$
(1) CH_2	(1) CH_3	0.9011	0.8480	0.6325	1.0608	0.9011	0.8480
	(2) CH_2	0.6744	0.5400	0.6325	0.7081	0.6744	0.5400
	(3) CH	0.4469	0.2280	0.6325	0.3554	0.4469	0.2280
	(4) C	0.2195	0.0000	0.6325	0.0000	0.2195	0.0000
(2) C=C	(5) CH=CH	1.1167	0.8670	1.2832	1.2489	1.1167	0.8670
(3) ACH	(6) ACH	0.5313	0.4000	0.3763	0.4321	0.5313	0.4000
	(7) AC	0.3652	0.1200	0.3763	0.2113	0.3652	0.1200
(4) OH	(8) OH (P)	1.0000	1.2000	1.2302	0.8927	1.0000	1.2000
	(8.1) OH (S)	3.2391	3.1240	1.0630	0.8663	N.A	N.A
(5) H_2O	(9) H_2O	0.9200	1.4000	1.7334	2.4561	0.9200	1.4000
(6) CH_2CO	(10) CH_3CO	1.6724	1.4880	1.7048	1.6700	1.6724	1.4880
(7) COOH	(11) COOH	1.3013	1.2240	0.8000	0.9215	1.3013	1.2240
	(12) HCOOH[a]	1.5280	1.5320	0.8000	1.2742	N.A	N.A
(8) COOC	(13) CH_3COO	1.9031	1.7280	1.2700	1.6286	1.9031	1.7280
	(14) CH_2COO	1.6764	1.4200	1.2700	1.4228	1.6764	1.4200
(9) HCOO	(15) HCOO	N.A	N.A	1.9000	1.8000	N.A	N.A
(10) CH_2O	(16) CH_3O	1.1450	1.0880	1.1434	1.6022	1.1450	1.0880
	(17) CH_2O	0.9183	0.7800	1.1434	1.2495	0.9183	0.7800
(11) DMSO	(18) DMSO	2.8266	2.4720	3.6000	2.6920	N.A	N.A

[a] Sub-group HCOOH was considered in UNIFAC-Dortmund as a main group. It is identified as main group (7.1) in Tables A.2.8 and A.2.9.

Table A.2. 7: Structural parameters *q* (surface area of component *i*) and *r* (volume of component *i*) of refined soybean oil and the seventeen solvents.

Compound	**UNIFAC version**					
	UNIFAC-LL and UNIFAC-HIR		**UNIFAC-Dortmund and NIST-modified UNIFAC**		**UNIFAC-Lyngby**	
	r	*q*	*r*	*q*	*r*	*q*
Refined Soybean Oil (LLO)	38.7157	31.3470	36.1585	40.2504	38.7157	31.3470
Anhydrous ethanol	2.5755	2.5880	2.4952	2.6616	2.5755	2.5880
Acetic acid	1.2663	0.9680	1.0088	1.9298	1.2663	0.9680
Ethyl lactate (OH (S))[a]	7.1646	6.4680	4.2305	1.2217	–	–
Ethyl lactate (OH (P))[b]	–	–	–	–	4.9255	4.5440
Dimethyl sulfoxide	2.8266	2.4720	3.6000	2.9189	N.A[c]	N.A[c]
Formic acid	1.5280	1.5320	0.8000	2.6025	N.A[c]	N.A[c]
Methyl ethyl ketone	3.2479	2.8760	2.9698	1.9176	3.2479	2.8760
Methyl isobutyl ketone	4.5959	3.9520	4.2348	2.7326	4.5959	3.9520
Ethyl acetate	3.4786	3.1160	2.5350	3.1818	3.4786	3.1160
Ethyl formate	N.A[c]	N.A[c]	3.5933	2.8608	N.A[c]	N.A[c]
Butyl acetate	4.8274	4.1960	3.8000	4.8137	4.8274	4.1960
Isobutyl acetate	4.8266	4.1920	3.8000	4.8137	4.8266	4.1920
Methyl acetate	1.5755	1.3880	1.2650	1.7689	1.5755	1.3880
Propyl acetate	4.1530	3.6560	3.1675	4.1056	4.1530	3.6560
Anisole	4.1667	3.2080	3.4012	3.9740	4.1667	3.2080
Tert-butyl methyl ether	4.0678	3.6320	3.6734	4.7846	4.0678	3.6320
Ethyl ether	3.3949	3.0160	3.0409	4.0792	3.3949	3.0160
Water	0.9200	1.4000	1.7334	2.4561	0.9200	1.4000

[a] OH (S) was considered in ethyl lactate by UNIFAC-LL, UNIFAC-HIR, UNIFAC-Dortmund and NIST-modified UNIFAC; [b] OH (P) was considered in ethyl lactate by UNIFAC-Lyngby; [c] NA: not applicable due to lack of group-group interaction parameters.

Table A.2. 8: Matrix of UNIFAC-LL interaction parameters (Eq. A.2.3).

Group i/j	**CH_2 (1)**	**HC=HC (2)**	**ACH (3)**	**OH (4)**	**H_2O (5)**	**CH_2CO (6)**	**COOH (7)**	**COOC (8)**	**CH_2O (10)**	**DMSO (11)**
(1) CH_2	0	74.54	-114.8	644.6	1300	472.6	139.4	972.4	662.1	956.5
(2) HC=HC	292.3	0	38.81	724.4	896	343.7	1647	-577.5	214.5	265.4
(3) ACH	156.5	3.446	0	703.9	859.4	593.7	461.8	5.994	32.14	84.16
(4) OH	328.2	470.7	-9.21	0	28.73	67.07	-104	195.6	262.5	0
(5) H_2O	342.4	220.6	372.8	-122.4	0	-171.8	-465.7	-6.32	64.42	0
(6) CH_2CO	66.56	306.1	-78.31	216	634.8	0	1247	258.7	-103.6	0
(7) COOH	1744	-48.52	75.49	118.4	652.3	-101.3	0	-117.6	-96.62	0
(8) COOC	-320.1	485.6	85.84	180.6	385.9	58.84	1417	0	-235.7	0
(10) CH_2O	1571	26.51	52.13	137.1	212.8	191.1	1402	461.3	0	0
(11) DMSO	36.42	60.82	29.77	0	0	0	0	0	0	0

Table A.2. 9: Matrix of UNIFAC-HIR group-group interaction parameters (Eq. A.2.3).

Group i/j	**CH_2 (1)**	**HC=HC (2)**	**ACH (3)**	**OH (4)**	**H_2O (5)**	**CH_2CO^a (6)**	**COOH (7)**	**COOC (8)**	**CH_2O^a (10)**	**$DMSO^a$ (11)**
(1) CH_2	0	-323.03	-114.8	927.60	1888.63	472.6	17.35	14726.95	662.1	956.5
(2) HC=HC	267.19	0	38.81	798.95	1458.48	343.7	1634.71	300.39	214.5	265.4
(3) ACH	156.5	3.446	0	703.9	859.4	593.7	461.8	5.994	32.14	84.16
(4) OH	-27.03	76.26	-9.21	0	358.76	67.07	-301.27	181.89	262.5	0
(5) H_2O	26526.91	-199.06	372.8	-292.63	0	-171.8	6.88	-20.15	64.42	0
(6) CH_2CO^a	66.56	306.1	-78.31	216	634.8	0	1247	258.7	-103.6	0
(7) COOH	-418.37	-790.67	75.49	-391.64	-435.16	-101.3	0	-175.89	-96.62	0
(8) COOC	-500.77	66.66	85.84	271.05	871.55	58.84	209.16	0	-235.7	0
(10) CH_2O^a	1571	26.51	52.13	137.1	212.8	191.1	1402	461.3	0	0
(11) $DMSO^a$	36.42	60.82	29.77	0	0	0	0	0	0	0

[a] Group-group interaction parameters were the same provided by Magnussen et al. [36].

Table A.2. 10 (part 1): Matrix of UNIFAC-Dortmund group-group interaction parameters (Eq. A.2.4).

Group		**m**					
n		**CH_2 (1)**	**C=C (2)**	**ACH (3)**	**OH (4)**	**H_2O (5)**	**CH_2CO (6)**
(1) CH_2	$a_{n,m}$	0	189.66	114.2	2777	1391.3	433.6
	$b_{n,m}$	0	-0.27232	0.0933	-4.674	-3.6156	0.1473
	$c_{n,m}$	0	0	0	0.001551	0.001144	0
(2) C=C	$a_{n,m}$	-95.418	0	980.74	2649	-2026.1	-174.6
	$b_{n,m}$	0.061708	0	-2.4224	-6.508	8.1549	1.96
	$c_{n,m}$	0	0	0	0.004822	0	0
(3) ACH	$a_{n,m}$	16.07	-157.2	0	3972	792	146.2
	$b_{n,m}$	-0.2998	0.6166	0	-13.16	-1.726	-1.237
	$c_{n,m}$	0	0	0	0.01208	0	0.004237
(4) OH	$a_{n,m}$	1606	1566	3049	0	-801.9	-250
	$b_{n,m}$	-4.746	-5.809	-12.77	0	3.824	2.857
	$c_{n,m}$	0.0009181	0.005197	0.01435	0	-0.007514	-0.006022
(5) H_2O	$a_{n,m}$	-17.253	-1301	332.3	1460	0	190.5
	$b_{n,m}$	0.8389	4.072	1.158	-8.673	0	-3.669
	$c_{n,m}$	0.0009021	0	0	0.01641	0	0.008838
(6) CH_2CO	$a_{n,m}$	199	91.811	-57.53	653.3	770.6	0
	$b_{n,m}$	-0.8709	-0.71715	1.212	-1.412	-0.5873	0
	$c_{n,m}$	0	0	-0.003715	0.000954	-0.003252	0
(7) COOH	$a_{n,m}$	2017.7	-347.5	613.32	1525.8	624.97	178.22
	$b_{n,m}$	-9.0933	1.216	-1.595	-4.9155	-4.6878	-0.91676
	$c_{n,m}$	0.010238	0	0	0	0.0052371	0
(7.1) HCOOH	$a_{n,m}$	-21.23	0	-1141.6	0	594.45	0
	$b_{n,m}$	0	0	8.6562	0	-2.2535	0
	$c_{n,m}$	0	0	-0.015439	0	0	0
(8) COOC	$a_{n,m}$	632.22	-582.82	622.73	310.4	311.974	33.415
	$b_{n,m}$	-3.3912	1.6732	-1.7605	1.538	-1.3412	0.21913
	$c_{n,m}$	0.0039282	0	0	-0.004885	0.001074	0
(9) HCOO	$a_{n,m}$	238.5	-28.63	108.3	839.6	53.284	101.3
	$b_{n,m}$	-0.5358	0	-0.262	-1.215	0	0
	$c_{n,m}$	0	0	0	0	0	0
(10) CH_2O	$a_{n,m}$	-9.654	-844.3	179	650.9	433.207	695.8
	$b_{n,m}$	-0.03242	2.945	0.05615	-0.7132	-0.605276	-0.9619
	$c_{n,m}$	0	0	0	0.000815	-0.000914	-0.002462
(11) DMSO	$a_{n,m}$	477.1	154	-345.6	-452.3	-370.8	38.06
	$b_{n,m}$	-2.175	-1.303	1.545	1.956	0.1043	-0.5189
	$c_{n,m}$	0	0	0	0	0	0

Table A.2. 10 (part 2): Matrix of UNIFAC-Dortmund group-group interaction parameters (Eq. A.2.4).

Group		**m**					
n		**COOH (7)**	**HCOOH (7.1)**	**COOC (8)**	**HCOO (9)**	**CH_2O (10)**	**DMSO (11)**
(1) CH_2	$a_{n,m}$	1182.2	1935.7	98.656	508.4	233.1	-547.5
	$b_{n,m}$	-3.2647	0	1.9294	-0.6215	-0.3155	3.457
	$c_{n,m}$	0.009198	0	-0.0031331	0	0	0
(2) C=C	$a_{n,m}$	0	179.8	309.8	174.1	733.3	778.3
	$b_{n,m}$	0	0.69911	0	-0.5886	-2.509	0.1482
	$c_{n,m}$	0	0	0	0	0	0
(3) ACH	$a_{n,m}$	69.561	-1172	-274.54	170.5	-87.08	347.6
	$b_{n,m}$	1.8881	10.106	0.91491	-0.02393	-0.1859	-1.43
	$c_{n,m}$	0	-0.01428	0	0	0	0
(4) OH	$a_{n,m}$	-1295	0	973.8	235.9	816.7	190.4
	$b_{n,m}$	4.3634	0	-5.633	-0.5874	-5.092	-1.2
	$c_{n,m}$	0	0	0.00769	0	0.006065	0
(5) H_2O	$a_{n,m}$	-1795.2	-804.28	-433.288	140.71	177.665	117
	$b_{n,m}$	12.708	2.828	3.0862	0	-3.72906	-0.611
	$c_{n,m}$	-0.015455	0	-0.002012	0	0.010763	0
(6) CH_2CO	$a_{n,m}$	-109.51	0	-16.486	-83.57	3645	-76.87
	$b_{n,m}$	0.96888	0	-0.27924	0	-26.91	0.5372
	$c_{n,m}$	0	0	0	0	0.04757	0
(7) COOH	$a_{n,m}$	0	-65.631	59.594	0	-310.82	0
	$b_{n,m}$	0	0	-0.71198	0	0	0
	$c_{n,m}$	0	0	0	0	0	0
(7.1) HCOOH	$a_{n,m}$	-14.016	0	-447.04	-441.01	310.75	0
	$b_{n,m}$	0	0	0	0	0	0
	$c_{n,m}$	0	0	0	0	0	0
(8) COOC	$a_{n,m}$	62.031	745.4	0	342.4	195.3	296.8
	$b_{n,m}$	1.0567	0	0	0	-9.75	-1.264
	$c_{n,m}$	0	0	0	0	0.04051	0
(9) HCOO	$a_{n,m}$	0	489.15	-251.7	0	0	0
	$b_{n,m}$	0	0	0	0	0	0
	$c_{n,m}$	0	0	0	0	0	0
(10) CH_2O	$a_{n,m}$	521.48	-454.92	824.2	0	0	0
	$b_{n,m}$	0	0	-6.009	0	0	0
	$c_{n,m}$	0	0	0.008271	0	0	0
(11) DMSO	$a_{n,m}$	0	0	-337.1	0	0	0
	$b_{n,m}$	0	0	0.8843	0	0	0
	$c_{n,m}$	0	0	0	0	0	0

Table A.2. 11 (part 1): Matrix of NIST-modified UNIFAC group-group interaction parameters (Eq. A.2.4).

Group		**m**					
n		**CH_2 (1)**	**C=C (2)**	**ACH (3)**	**OH (4)**	**H_2O (5)**	**CH_2CO (6)**
(1) CH_2	$a_{n,m}$	0	257.05	137.14	3119.2	1391.3	175.24
	$b_{n,m}$	0	-0.1011	-0.32	-6.073	-3.6156	1.1209
	$1000c_{n,m}$	0	0	1.2503	2.3986	1.144	0
(2) C=C	$a_{n,m}$	-125.99	0	-116.5	2529.96	615.44	330.13
	$b_{n,m}$	-0.1271	0	0.2659	-5.9572	-1.1646	0.3412
	$1000c_{n,m}$	0	0	0	4.8653	0	0
(3) ACH	$a_{n,m}$	65.28	146.29	0	3851.36	792	208.29
	$b_{n,m}$	-0.4342	-0.3015	0	-12.7673	-1.726	-0.891
	$1000c_{n,m}$	-0.194	0	0	12.019	0	0.82427
(4) OH	$a_{n,m}$	1857.23	1433.2	2866.4	0	-513.48	-288.13
	$b_{n,m}$	-8.7982	-6.2819	-14.2748	0	1.25	2.2923
	$1000c_{n,m}$	10.757	7.5645	20.523	0	-2.1501	-3.7772
(5) H_2O	$a_{n,m}$	-17.25	38.11	332.3	1651.05	0	206.26
	$b_{n,m}$	0.8389	0.9518	1.158	-8.9104	0	-3.9629
	$1000c_{n,m}$	0.9021	0	0	14.679	0	9.306
(6) CH_2CO	$a_{n,m}$	282.42	221.24	-225.48	668.98	867.04	0
	$b_{n,m}$	-1.2006	-1.0604	1.4676	-0.7227	-0.7877	0
	$1000c_{n,m}$	0	0	-0.87633	-1.6635	-3.0305	0
(7) COOH	$a_{n,m}$	1874.82	1239.81	-51.56	995.65	195.87	254.62
	$b_{n,m}$	-5.2344	-3.9068	2.833	-8.4974	-1.9941	-1.5161
	$1000c_{n,m}$	0.82871	0	-7.2836	11.205	2.4708	0
(7.1) HCOOH	$a_{n,m}$	803.79	-46.47	-1113.41	-846.8	9.72	-151.13
	$b_{n,m}$	-2.2809	0	8.4775	4.7834	-0.3228	0
	$1000c_{n,m}$	0	0	-15.256	0	0	0
(8) COOC	$a_{n,m}$	737	77.02	834.28	252.79	-12.36	-19.76
	$b_{n,m}$	-3.0713	0.1425	-3.3669	2.6565	-0.408	0.96
	$1000c_{n,m}$	3.1041	0	3.0476	-7.9064	-0.16248	0
(9) HCOO	$a_{n,m}$	237.35	322.48	123.43	-233.71	1274.05	501.24
	$b_{n,m}$	-0.7084	-1.0911	-0.525	5.3056	-0.2557	0
	$1000c_{n,m}$	-0.19047	0	0	-9.9789	-3.0377	0
(10) CH_2O	$a_{n,m}$	-0.39	193.05	-125	650.9	-44.29	737.4
	$b_{n,m}$	0.3745	-0.1982	0.7224	-0.7132	0.5553	-0.6434
	$1000c_{n,m}$	0	0	0	0.82	0.96627	-2.7909
(11) DMSO	$a_{n,m}$	460.82	52.88	58.36	-350.93	-361.72	1179.84
	$b_{n,m}$	-2.1701	-1.0493	-0.6666	1.2858	0.07	-4.0045
	$1000c_{n,m}$	0	0	0	0	0	0

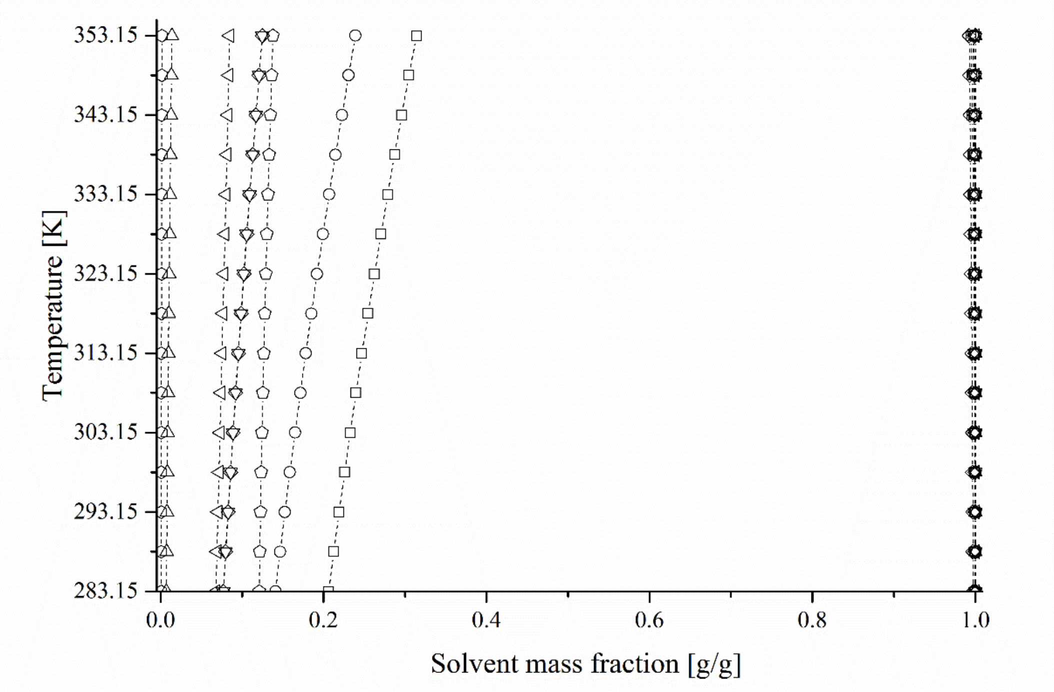
Table A.2. 11 (part 2): Matrix of NIST-modified UNIFAC group-group interaction parameters (Eq. A.2.4).

Group		**m**					
n		**COOH (7)**	**HCOOH (7.1)**	**COOC (8)**	**HCOO (9)**	**CH_2O (10)**	**DMSO (11)**
(1) CH_2	$a_{n,m}$	1443.33	-1576.18	113.19	521.38	204.31	-498.67
	$b_{n,m}$	-4.902	6.6648	1.8837	-0.5881	-0.5302	3.6653
	$1000c_{n,m}$	11.595	0	-3.8391	0.3446	0	0
(2) C=C	$a_{n,m}$	1701.95	1632.01	284.78	-29.63	-42.31	-237.28
	$b_{n,m}$	19.6463	0	-0.7037	0.8242	-0.0428	2.4268
	$1000c_{n,m}$	0	0	0	0	0	0
(3) ACH	$a_{n,m}$	332.11	-1366.87	-436.58	113.93	-6.13	-17.89
	$b_{n,m}$	0.7276	10.5751	2.5648	0.3235	-0.2221	0.7819
	$1000c_{n,m}$	3.2011	-13.93	-3.1523	0	0	0
(4) OH	$a_{n,m}$	-1547.97	-41.16	1097.75	292.25	816.7	59.12
	$b_{n,m}$	9.2465	-1.8128	-7.8816	-0.7058	-5.092	-0.5521
	$1000c_{n,m}$	3.6126	0	13.497	0.10613	6.07	0
(5) H_2O	$a_{n,m}$	82.33	-122.47	3.28	-67.62	-46.96	55.26
	$b_{n,m}$	1.0692	0.5285	2.1301	-0.0932	-0.3124	-0.4555
	$1000c_{n,m}$	-1.5475	0	-0.56037	-0.025332	1.7411	0
(6) CH_2CO	$a_{n,m}$	-561.05	-134	61.56	-286.8	3646.91	-1156.26
	$b_{n,m}$	3.3419	0	-0.8304	0	-26.9306	3.733
	$1000c_{n,m}$	0	0	0	0	46.438	0
(7) COOH	$a_{n,m}$	0	0.6	-250.76	-	115.14	-296.06
	$b_{n,m}$	0	-0.6722	0.5169	-	-1.4055	-0.6339
	$1000c_{n,m}$	0	0	0	-	0	0
(7.1) HCOOH	$a_{n,m}$	25.68	0	-88.85	-161.36	345.03	-
	$b_{n,m}$	0.9946	0	0	0	0	-
	$1000c_{n,m}$	0	0	0	0	0	-
(8) COOC	$a_{n,m}$	565.9	10.95	0	-167.65	428.62	-49.6
	$b_{n,m}$	-1.0278	0	0	0	-11.4456	-0.3743
	$1000c_{n,m}$	0	0	0	0	51.758	0
(9) HCOO	$a_{n,m}$	-	85.56	101.8	0	15.66	-
	$b_{n,m}$	-	0	0	0	0	-
	$1000c_{n,m}$	-	0	0	0	0	-
(10) CH_2O	$a_{n,m}$	-210.79	-335.44	297.18	-81	0	620.88
	$b_{n,m}$	2.1044	0	-2.7538	0	0	0
	$1000c_{n,m}$	0	0	3.4779	0	0	0
(11) DMSO	$a_{n,m}$	-376.15	-	149.52	-	-471.41	0
	$b_{n,m}$	0.6168	-	-0.1905	-	0	0
	$1000c_{n,m}$	0	-	0	-	0	0

Table A.2. 12: Matrix of UNIFAC-Lyngby group-group interaction parameters (Eq. A.2.5).

Group		**m**								
n		**CH_2 (1)**	**C=C (2)**	**ACH (3)**	**OH (4)**	**H_2O (5)**	**CH_2CO (6)**	**COOH (7)**	**COOC (8)**	**CH_2O (10)**
(1) CH_2	$a_{n,m}$	0	76.46	62.88	972.8	1857	414	664.1	329.1	230.5
	$b_{n,m}$	0	-0.1834	-0.2493	0.2687	-3.322	-0.5165	1.317	-0.1518	-1.328
	$c_{n,m}$	0	-0.3659	1.103	8.773	-9	1.803	-4.904	-1.824	-2.476
(2) C=C	$a_{n,m}$	-46.45	0	35.07	633.5	1049	577.5	186	-24.65	321.6
	$b_{n,m}$	-0.1817	0	-0.08042	0	-3.305	0	0	0	4.551
	$c_{n,m}$	-0.4888	0	-0.3761	0	0	0	0	0	0
(3) ACH	$a_{n,m}$	-1.447	-0.02772	0	712.6	1055	87.64	537.4	97.3	82.86
	$b_{n,m}$	0.05638	-0.07129	0	-1.459	-2.968	-0.4616	0	0.1902	0.6106
	$c_{n,m}$	-1.612	-0.3407	0	9	9.854	6.691	0	-0.7515	-0.7392
(4) OH	$a_{n,m}$	637.5	794.7	587.3	0	155.6	161	61.78	169.1	227
	$b_{n,m}$	-5.832	0	-0.6787	0	0.3761	0.7501	0	0.1902	1.364
	$c_{n,m}$	-0.8703	0	9	0	-9	9	0	4.625	3.324
(5) H_2O	$a_{n,m}$	410.7	564.4	736.7	-47.15	0	40.2	8.621	218	19.54
	$b_{n,m}$	2.868	0	1.965	-0.4947	0	1.668	-1.709	-0.4269	1.293
	$c_{n,m}$	9	0	0	8.65	0	-1.994	6.413	-6.092	-8.85
(6) CH_2CO	$a_{n,m}$	71.93	-144.3	92.19	179.6	272.4	0	230	-11.93	-48
	$b_{n,m}$	-0.796	0	0.6129	-1.285	-1.842	0	0	-0.04056	-0.5097
	$c_{n,m}$	-2.916	0	-8.963	4.007	0.3303	0	0	0	0
(7) COOH	$a_{n,m}$	171.5	227.3	62.32	-92.21	86.44	-151.7	0	-224.6	-248.1
	$b_{n,m}$	-1.463	0	0	0	0.9941	0	0	-0.7234	0
	$c_{n,m}$	0.6759	0	0	0	-12.74	0	0	0	0
(8) COOC	$a_{n,m}$	44.43	200.3	8.346	266.9	245	43.65	557.9	0	277
	$b_{n,m}$	-0.9718	0	-0.5254	-1.054	-0.0717	0.1905	1.377	0	0.3255
	$c_{n,m}$	0.5518	0	0	3.586	2.754	0	0	0	0
(10) CH_2O	$a_{n,m}$	369.9	-17.23	125.2	137.1	183.1	160.4	286.6	-129.4	0
	$b_{n,m}$	-1.542	-1.648	-1.093	-1.115	-2.507	0.5484	0	-0.04136	0
	$c_{n,m}$	-3.228	0	0.5898	4.438	0	0	0	0	0

Figure A.2. 2: Predicted liquid-liquid equilibria for pseudobinary systems composed of refined soybean oil (RSO) (1) plus organic solvents at selected temperatures (only partially miscible systems, P, in Table 7): (▽) anhydrous ethanol; (◫) acetic acid; (◇) ethyl lactate; (△) DMSO; (○) MEK; (□) MIBK; (◁) formic acid; (▷) ethyl formate; (▯) anisole; (▯) water; (⊖) methyl acetate; (⊕) ethyl acetate. (A) UNIFAC-LL, (B) UNIFAC-HIR, (C) UNIFAC-Dortmund, (D) NIST-modified UNIFAC and (E) UNIFAC-Lyngby.



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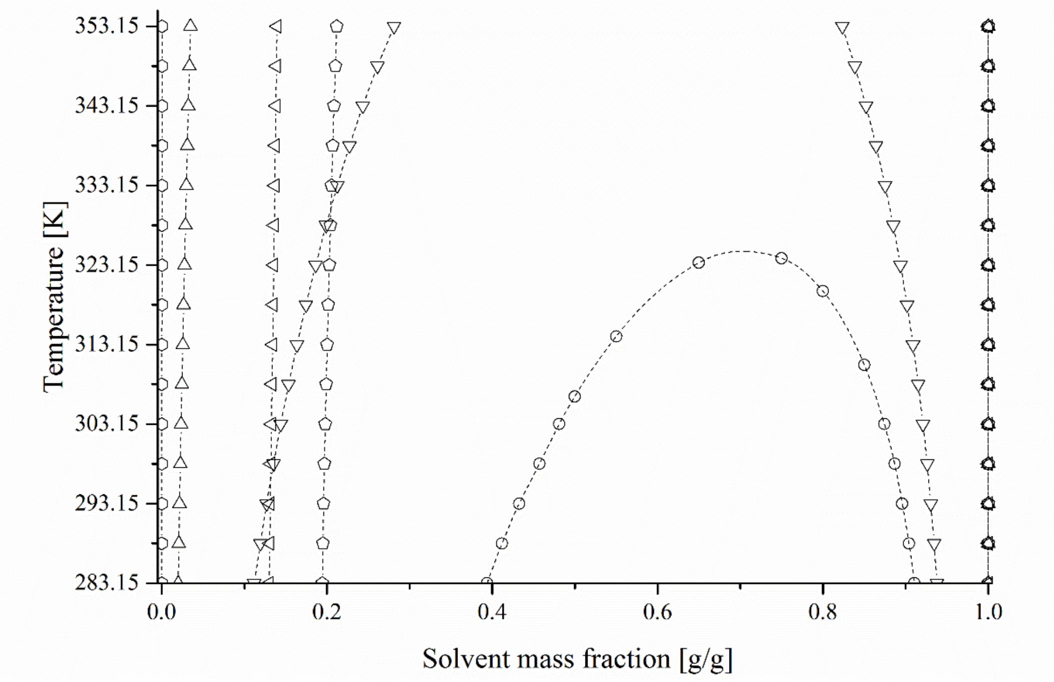

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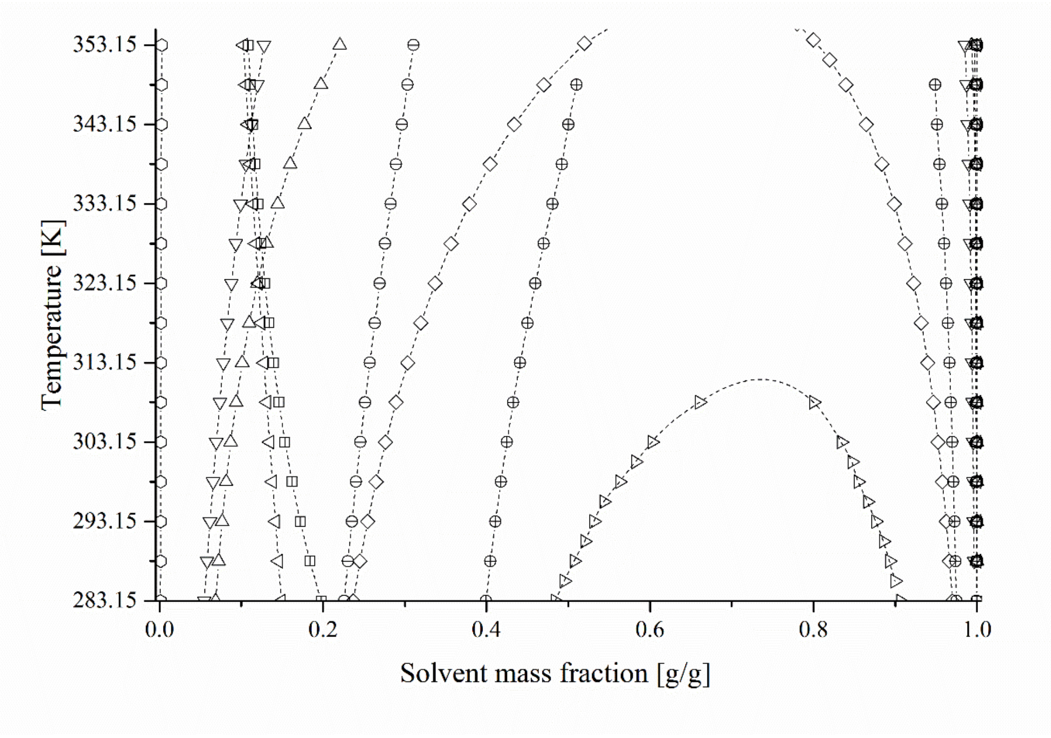
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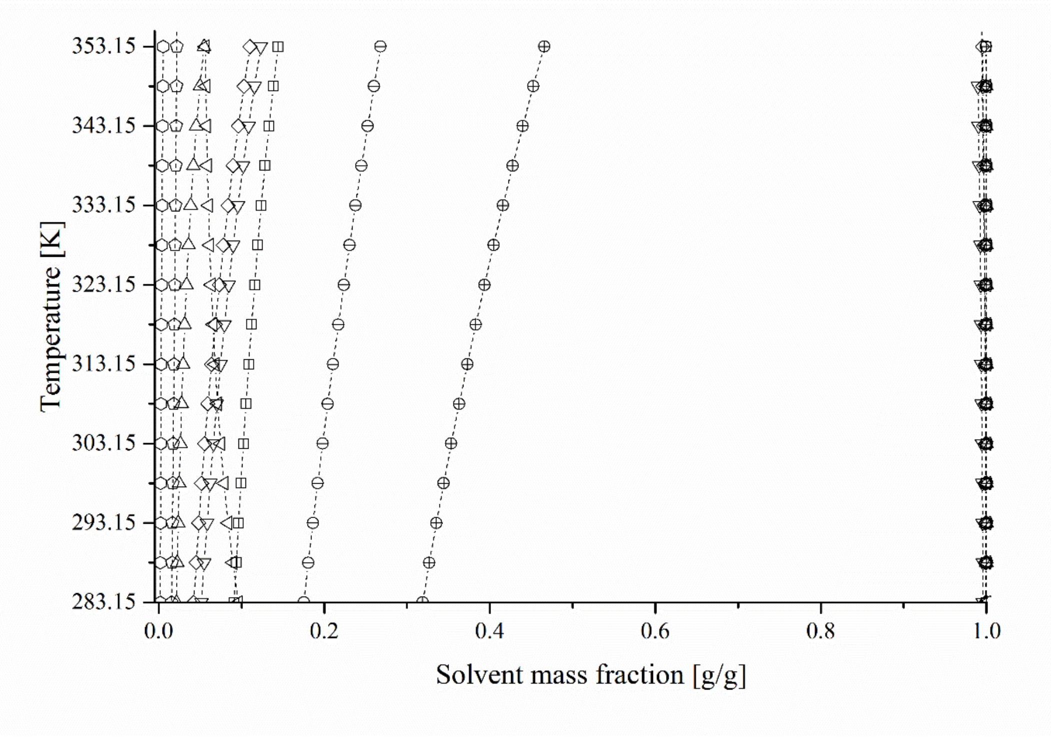
Solvent mass fraction [g/g]

(C)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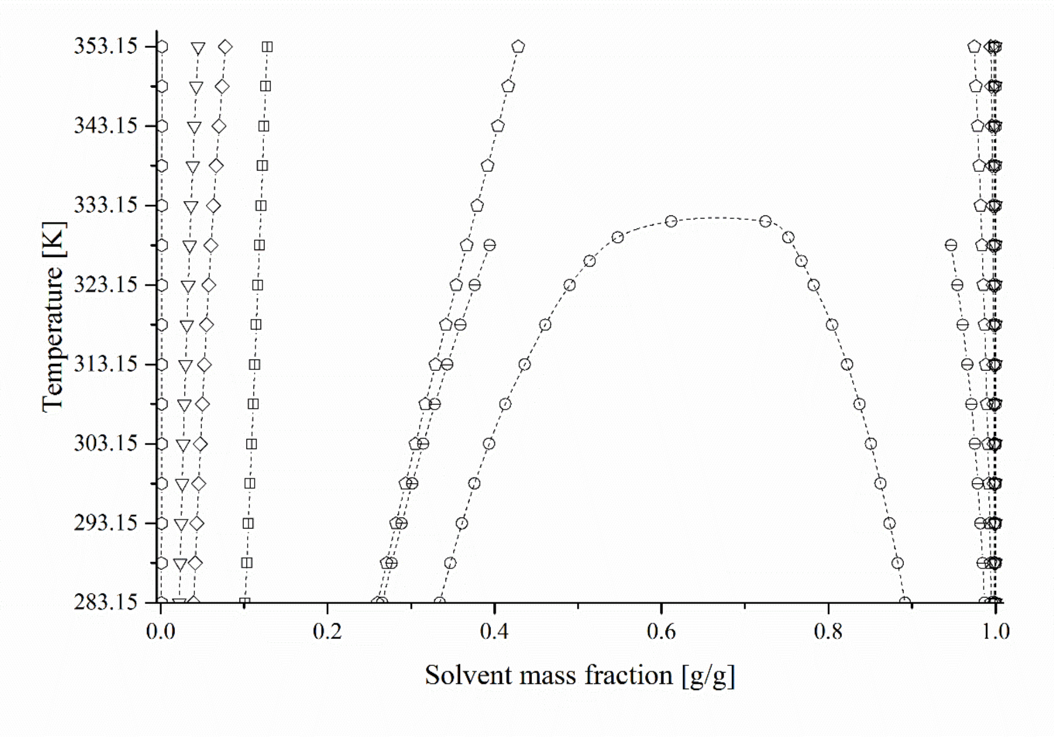
Solvent mass fraction [g/g]

(D)

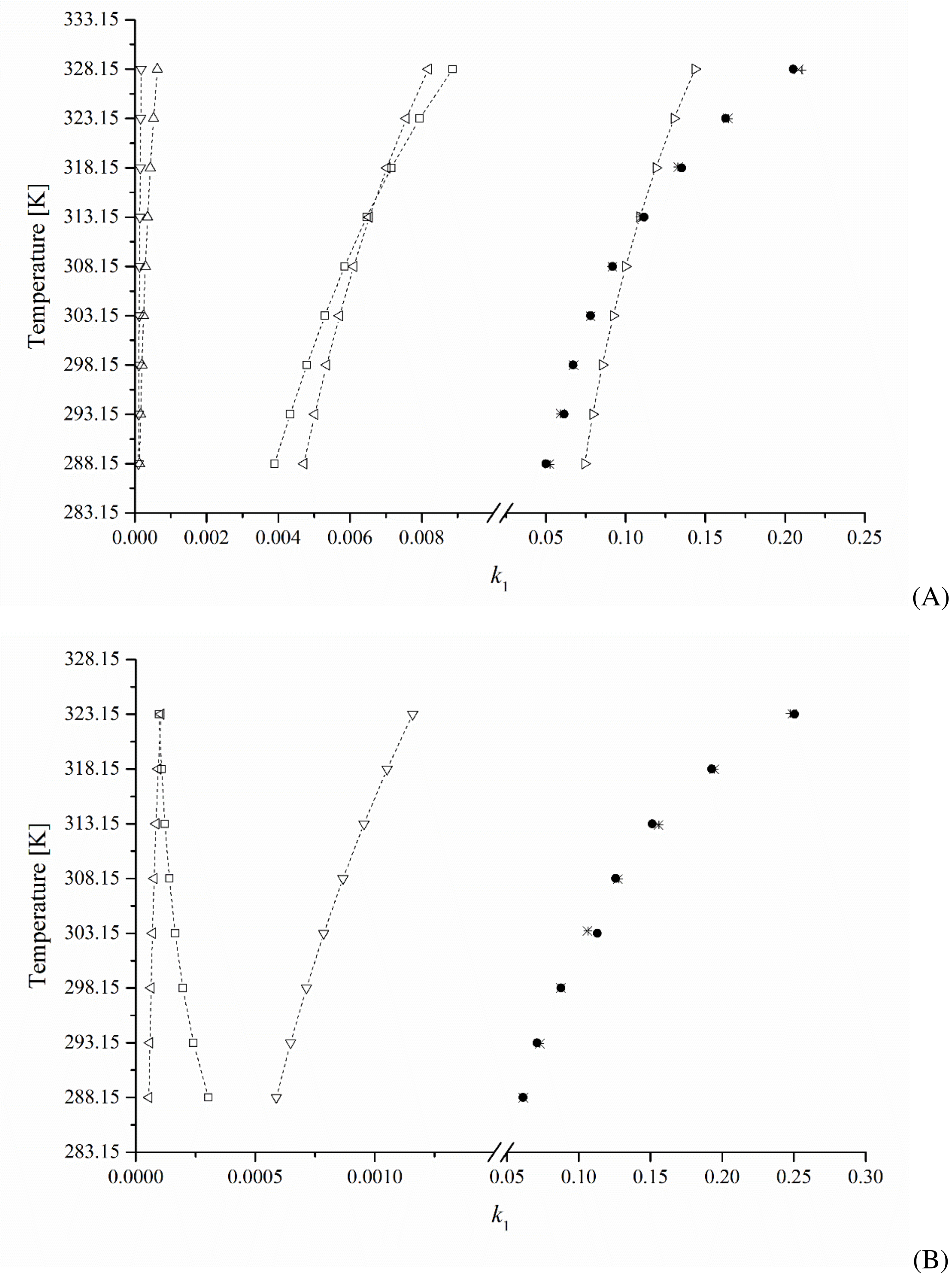


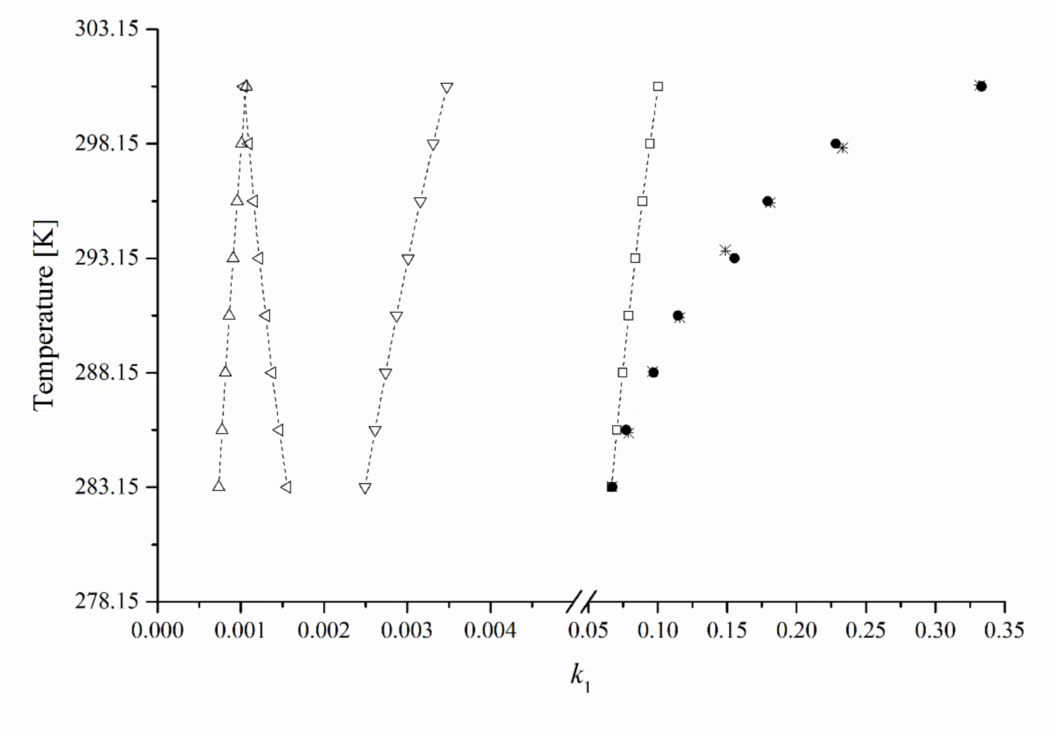
(E)

Table A.2. 13: Coefficients of partition (Eq. 4.3-1) of refined soybean oil (RSO) (k_1) for pseudobinary systems composed of refined soybean oil (1) plus anhydrous ethanol (2), or acetic acid (3), or ethyl lactate (4), or dimethyl sulfoxide (5).

Anhydrous Ethanol		**Acetic Acid**		**Ethyl Lactate**		**Dimethyl Sulfoxide**	
***T* [K]**	***k*₁**	***T* [K]**	***k*₁**	***T* [K]**	***k*₁**	***T* [K]**	***k*₁**
288.15	0.05	288.15	0.06	283.15	0.07	293.15	0.004
293.15	0.06	293.15	0.07	285.65	0.08	298.15	0.004
298.15	0.07	298.15	0.09	288.15	0.10	303.15	0.004
303.15	0.08	303.15	0.11	290.65	0.11	308.15	0.005
308.15	0.09	308.15	0.13	293.15	0.16	313.15	0.004
313.15	0.11	313.15	0.15	295.65	0.18	318.15	0.006
318.15	0.14	318.15	0.19	298.15	0.23	323.15	0.006
323.15	0.16	323.15	0.25	300.65	0.33	328.15	0.006
328.15	0.21					333.15	0.005

Figure A.2. 3: Partition coefficients of refined soybean oil (RSO) (k_1, Eq.4.3-1) for pseudobinary systems composed of refined soybean oil (1) + organic solvents under atmospheric pressure: (A) anhydrous ethanol (2), (B) acetic acid (3), (C) ethyl lactate (4) and (D) dimethyl sulfoxide (5). Legend: (●) experimental data; (×) NRTL; (+) UNIQUAC; (△) UNIFAC-LL; (▷) UNIFAC-HIR; (□) UNIFAC-Dortmund; (◁) NIST-modified UNIFAC; (▽) UNIFAC-Lyngby.

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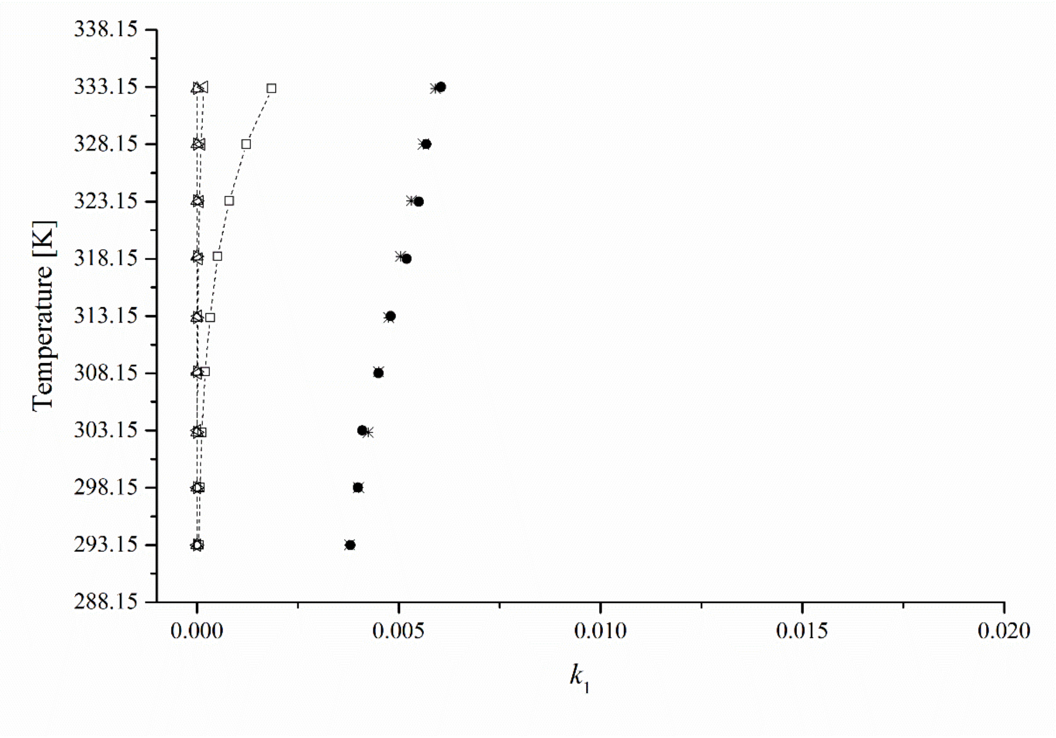
k_1

(C)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323.15
318.15
313.15
308.15
303.15
298.15
293.15
288.15
Temperature [K]
0.000
0.005
0.010
0.015
0.020
k_1

(D)

APÊNDICE A.3

Material suplementar do artigo “Phase equilibria for systems containing refined soybean oil plus cosolvents at different temperatures”.

Table A.3.1. Liquid-liquid equilibrium (mass fractions w) predicted by the UNIFAC versions for the system refined soybean oil (1) + anhydrous ethanol (2) + water (5).[a]

	UNIFAC-LL				**UNIFAC-DMD**				**UNIFAC-LBY**				**UNIFAC-HIR**				**NIST-UNIFAC**			
	Raffinate phase		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**	
T/K	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5
293.15	0.947	0.001	0.000	0.105	0.960	0.001	0.000	0.103	0.981	0.001	0.000	0.101	0.945	0.001	0.007	0.105	0.962	0.001	0.000	0.103
298.15	0.945	0.001	0.000	0.105	0.958	0.001	0.000	0.103	0.980	0.001	0.000	0.101	0.942	0.001	0.007	0.105	0.960	0.001	0.000	0.103
303.15	0.943	0.001	0.000	0.105	0.955	0.001	0.000	0.104	0.979	0.001	0.000	0.102	0.939	0.001	0.007	0.105	0.957	0.001	0.000	0.103
308.15	0.941	0.001	0.000	0.105	0.953	0.001	0.000	0.104	0.978	0.001	0.000	0.102	0.935	0.001	0.007	0.106	0.954	0.001	0.000	0.103
313.15	0.939	0.001	0.000	0.106	0.950	0.001	0.000	0.104	0.977	0.001	0.000	0.102	0.932	0.001	0.007	0.106	0.951	0.002	0.000	0.104
318.15	0.937	0.001	0.000	0.106	0.947	0.001	0.000	0.104	0.976	0.001	0.000	0.102	0.928	0.001	0.008	0.106	0.948	0.002	0.000	0.104
323.15	0.935	0.001	0.000	0.106	0.944	0.002	0.000	0.105	0.974	0.001	0.000	0.102	0.925	0.001	0.008	0.107	0.945	0.002	0.000	0.104
328.15	0.933	0.001	0.000	0.106	0.941	0.002	0.000	0.105	0.973	0.001	0.000	0.102	0.921	0.001	0.008	0.107	0.941	0.002	0.000	0.104
333.15	0.931	0.001	0.000	0.106	0.938	0.002	0.000	0.105	0.972	0.001	0.000	0.102	0.917	0.001	0.008	0.107	0.937	0.002	0.000	0.104

[a] Mass ratio of the cosolvent anhydrous ethanol plus water (9:1).

Table A.3.2. Liquid-liquid equilibrium (mass fractions *w*) predicted by the UNIFAC versions for the systems refined soybean oil (1) + ethyl lactate (3) + water (5) or + formic acid (6). [a]

	UNIFAC-LL				**UNIFAC-DMD**				**UNIFAC-LBY**				**UNIFAC-HIR**				**NIST-UNIFAC**			
	Raffinate phase		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**	
T/*K*	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5
293.15	0.978	0.001	0.000	0.102	0.521	0.011	0.000	0.975	0.973	0.001	0.000	0.102	0.509	0.034	0.000	1.000	0.906	0.003	0.000	0.108
298.15	0.977	0.001	0.000	0.102	0.521	0.011	0.000	0.974	0.972	0.001	0.000	0.102	0.509	0.033	0.000	1.000	0.901	0.003	0.000	0.109
303.15	0.976	0.001	0.000	0.102	0.521	0.011	0.000	0.973	0.971	0.001	0.000	0.102	0.509	0.032	0.000	1.000	0.896	0.003	0.000	0.109
308.15	0.975	0.001	0.000	0.102	0.521	0.012	0.000	0.971	0.970	0.001	0.000	0.102	0.510	0.031	0.000	1.000	0.890	0.004	0.000	0.109
313.15	0.974	0.001	0.000	0.102	0.521	0.012	0.000	0.970	0.968	0.001	0.000	0.102	0.510	0.031	0.000	1.000	0.885	0.004	0.000	0.110
318.15	0.973	0.001	0.000	0.102	0.520	0.013	0.000	0.969	0.967	0.001	0.000	0.102	0.511	0.030	0.000	1.000	0.878	0.004	0.001	0.110
323.15	0.972	0.001	0.000	0.102	0.520	0.013	0.000	0.967	0.966	0.001	0.000	0.102	0.511	0.029	0.000	1.000	0.872	0.005	0.001	0.111
328.15	0.970	0.001	0.000	0.102	0.520	0.014	0.000	0.965	0.964	0.001	0.000	0.102	0.511	0.029	0.000	1.000	0.864	0.005	0.001	0.111
333.15	0.969	0.001	0.000	0.102	0.520	0.014	0.000	0.963	0.963	0.001	0.000	0.103	0.512	0.028	0.000	1.000	0.857	0.006	0.001	0.112
	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6
293.15	0.957	0.009	0.000	0.095	0.708	0.041	0.035	0.070	0.968	0.000	0.000	0.103	0.563	0.044	0.117	0.086	0.745	0.027	0.068	0.090
298.15	0.954	0.009	0.000	0.095	0.702	0.041	0.039	0.070	0.967	0.001	0.000	0.103	0.566	0.044	0.110	0.086	0.730	0.028	0.067	0.091
303.15	0.952	0.009	0.000	0.095	0.690	0.042	0.044	0.070	0.965	0.001	0.000	0.103	0.569	0.044	0.105	0.086	0.719	0.029	0.067	0.092
308.15	0.950	0.010	0.000	0.095	0.677	0.042	0.050	0.070	0.964	0.001	0.000	0.103	0.572	0.043	0.101	0.086	0.727	0.028	0.069	0.093
313.15	0.947	0.010	0.001	0.094	0.663	0.042	0.057	0.071	0.962	0.001	0.000	0.103	0.573	0.043	0.098	0.086	0.719	0.028	0.070	0.093
318.15	0.945	0.011	0.001	0.094	0.646	0.043	0.065	0.071	0.960	0.001	0.000	0.103	0.573	0.043	0.095	0.086	0.710	0.029	0.072	0.094
323.15	0.943	0.011	0.001	0.094	0.628	0.044	0.074	0.071	0.959	0.001	0.000	0.104	0.573	0.044	0.094	0.086	0.700	0.029	0.074	0.094
328.15	0.940	0.012	0.001	0.094	0.606	0.045	0.085	0.070	0.957	0.001	0.000	0.104	0.572	0.044	0.093	0.086	0.689	0.030	0.077	0.094
333.15	0.937	0.012	0.001	0.093	0.582	0.046	0.097	0.070	0.955	0.001	0.000	0.104	0.570	0.044	0.092	0.086	0.677	0.031	0.081	0.094

[a] Mass ratio of the cosolvents ethyl lactate plus water or plus formic acid (9:1).

Table A.3.3.. Liquid-liquid equilibrium (mass fractions w) predicted by the UNIFAC versions[a] for the systems refined soybean oil (1) + dimethyl sulfoxide (4) + water (5) or + formic acid (6).[b]

	UNIFAC-LL				**UNIFAC-DMD**				**UNIFAC-HIR**				**NIST-UNIFAC**			
	Raffinate phase		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**	
T/*K*	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5	w_1	w_5
293.15	0.998	0.000	0.000	0.250	0.986	0.001	0.000	0.253	0.997	0.000	0.000	0.251	0.986	0.001	0.000	0.253
298.15	0.998	0.000	0.000	0.250	0.985	0.001	0.000	0.253	0.997	0.000	0.000	0.251	0.985	0.001	0.000	0.253
303.15	0.998	0.000	0.000	0.250	0.984	0.001	0.000	0.253	0.997	0.000	0.000	0.251	0.984	0.001	0.000	0.253
308.15	0.998	0.000	0.000	0.250	0.983	0.001	0.000	0.254	0.996	0.000	0.000	0.251	0.983	0.001	0.000	0.253
313.15	0.998	0.000	0.000	0.250	0.982	0.001	0.000	0.254	0.996	0.000	0.000	0.251	0.982	0.001	0.000	0.254
318.15	0.998	0.000	0.000	0.250	0.981	0.001	0.000	0.254	0.996	0.000	0.000	0.251	0.981	0.001	0.000	0.254
323.15	0.998	0.000	0.000	0.250	0.980	0.001	0.000	0.254	0.996	0.000	0.000	0.251	0.979	0.001	0.000	0.254
328.15	0.997	0.000	0.000	0.250	0.978	0.001	0.000	0.255	0.995	0.000	0.000	0.251	0.978	0.001	0.000	0.254
333.15	0.997	0.001	0.000	0.250	0.977	0.001	0.000	0.255	0.995	0.000	0.000	0.251	0.976	0.002	0.000	0.255
	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6	w_1	w_6
293.15	0.996	0.000	0.000	0.100	0.876	0.039	0.000	0.064	0.991	0.000	0.000	0.100	0.892	0.027	0.000	0.079
298.15	0.996	0.000	0.000	0.100	0.870	0.039	0.000	0.065	0.991	0.001	0.000	0.100	0.887	0.027	0.000	0.080
303.15	0.996	0.000	0.000	0.100	0.863	0.039	0.000	0.066	0.990	0.001	0.000	0.100	0.881	0.027	0.000	0.081
308.15	0.995	0.000	0.000	0.100	0.854	0.038	0.000	0.066	0.989	0.001	0.000	0.100	0.874	0.027	0.000	0.081
313.15	0.995	0.000	0.000	0.100	0.845	0.038	0.001	0.067	0.989	0.001	0.000	0.100	0.866	0.027	0.000	0.082
318.15	0.995	0.000	0.000	0.100	0.833	0.039	0.001	0.067	0.988	0.001	0.000	0.100	0.856	0.027	0.001	0.082
323.15	0.994	0.000	0.000	0.100	0.820	0.039	0.002	0.067	0.987	0.001	0.000	0.100	0.845	0.028	0.001	0.082
328.15	0.994	0.000	0.000	0.100	0.804	0.039	0.003	0.067	0.986	0.001	0.000	0.100	0.833	0.028	0.002	0.082
333.15	0.994	0.000	0.000	0.100	0.786	0.040	0.004	0.067	0.986	0.001	0.000	0.101	0.818	0.029	0.002	0.082

[a] UNIFAC-LBY was not applied due to lack of group-group interaction parameters for the DMSO group. [b] Mass ratio of the cosolvents dimethyl sulfoxide plus water (7.5:2.5) or plus formic acid: (9:1)

APÊNDICE A.4

Material suplementar do artigo "Liquid-liquid equilibria and density data for pseudoternary systems of refined soybean oil + (hexanal, or heptanal, or butyric acid, or valeric acid, or caproic acid, or caprylic acid) + dimethyl sulfoxide at 298.15 K".

Table A.4.1. Composition of refined soybean oil in terms of its fatty acid profile.

Symbol	**Fatty acid**	**C*X*:*Y*** [a]	**MW/g·mol^{-1}** [b]	**% mass**	**% molar**
M	Myristic	14:0	228.38	0.09	0.11
P	Palmitic	16:0	256.43	11.06	12.02
Po	Palmitoleic (ω 7)	16:1	254.41	0.08	0.09
S	Stearic	18:0	284.48	3.50	3.43
O	Oleic (ω 9)	18:1	282.47	24.10	23.78
t–L	*Trans* Linoleic (ω 6)	18:2	328.45	0.36	0.30
L	Linoleic (ω 6)	18:2	280.45	53.72	53.38
A	Arachidic	20:0	312.54	0.39	0.35
t–Ln	*Trans* Linolenic (ω 3)	18:3	278.44	0.00	0.00
Ln	Linolenic (ω 3)	18:3	278.44	5.78	5.78
Ga	Cis–11–Eicosenoic (ω 11)	20:1	310.51	0.22	0.20
Be	Behenic	22:0	340.59	0.52	0.42
Lg	Lignoceric	24:0	368.63	0.19	0.14

[a] *X* = number of carbons, *Y* = number of double bonds. [b] Molecular weight.

Table A.4.2. Probable triacylglycerol (TAG) profile of refined soybean oil.

TAG	**C*X*:*Y*** [a]	**MW/g·gmol^{-1}** [b]	**% mass**	**% molar**
PLP	50:2	831.35	2.09	2.20
OOP	52:2	859.41	3.39	3.69
PLO	52:3	857.39	10.05	10.92
SLO	54:3	885.44	4.14	4.64
LLP	52:4	855.38	12.29	13.31
OOL	54:4	883.43	12.35	13.83
LLO	54:5	881.41	21.64	24.17
LLL	54:6	879.40	19.38	21.58
LLLn	54:7	877.38	5.10	5.67

[a] *X* = number of carbons, *Y* = number of double bonds. [b] Molecular weight.

Figure A.4.1. Analytical curve of hexanal in 2-propanol.

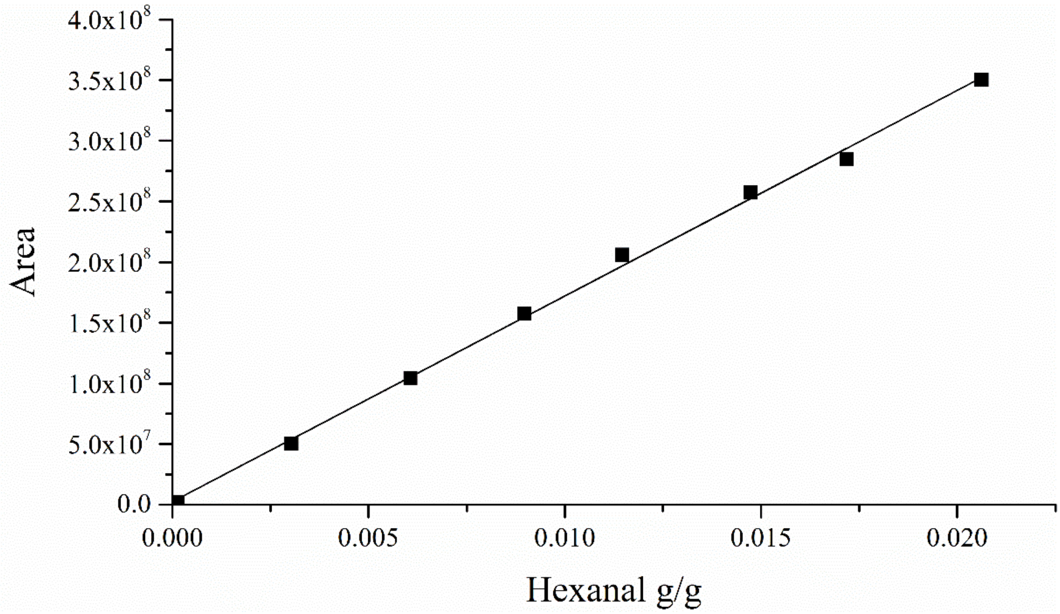


Figure A.4.2. Analytical curve of heptanal in 2-propanol.

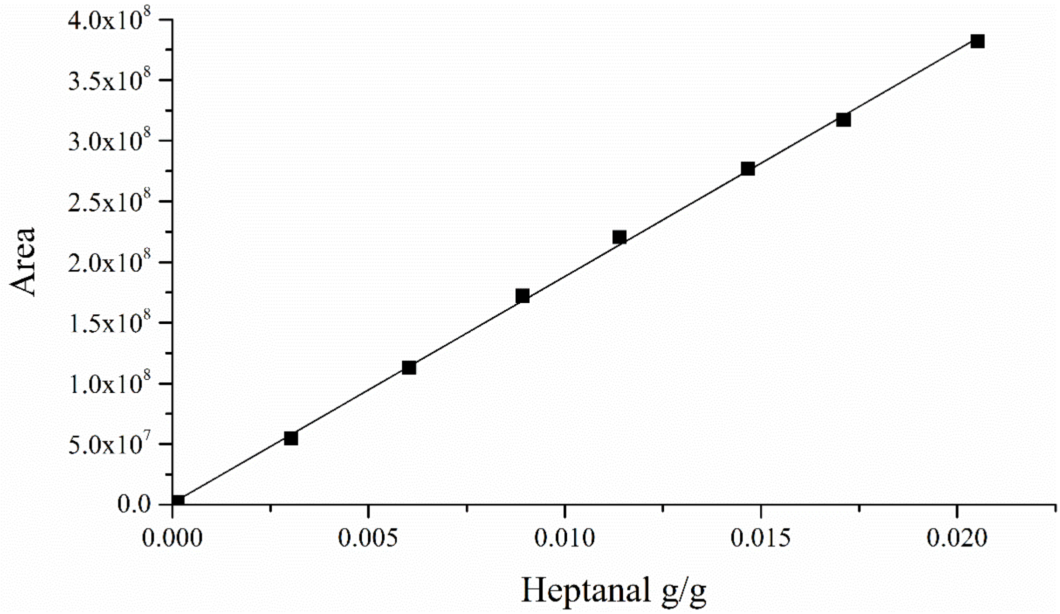


Table A.4.3. Parameters of analytical calibration, their standard error and limits of detection (LOD) and quantification (LOQ).

Parameter	Hexanal		Heptanal	
	Value	Standard error (s)	Value	Standard error (s)
Slope (S)	16957800000	330212000	18690000000	207931000
Intercept	2420990	4036090	1246260	2529460
Limit of detection (LD) [g/g][a]	0.00079		0.00045	
Limit of quantification (LQ) [g/g][a]	0.00238		0.00135	

[a] Limits of detection (LD) and quantification (LQ) are calculated as: $LD = 3.3\,s/S$ and $LQ = 10\,s/S$.

Table A.4.4. Sub-division of refined soybean oil, solutes, and dimethyl sulfoxide into functional groups.

Main group	1			2	3	4	5	6
	CH_2			C=C	COOC	CHO	COOH	DMSO
Sub-group	1	2	3	4	5	6	7	8
	CH_3	CH_2	CH	CH=CH	CH_2COO	CHO	COOH	DMSO
Refined Soybean Oil (LLO)	3	37	1	5	3			
Hexanal	1	4				1		
Heptanal	1	5				1		
Butyric acid	1	2					1	
Valeric acid	1	3					1	
Caproic acid	1	4					1	
Caprylic acid	1	6					1	
Dimethyl sulfoxide								1

Table A.4.5. Group volume (R_k) and surface area (Q_k) parameters.

Group		UNIFAC version			
		UNIFAC-LL and UNIFAC-HIR		UNIFAC-DMD and NIST-UNIFAC	
Main group	Sub-group	R_k	Q_k	R_k	Q_k
(1) CH_2	(1) CH_3	0.9011	0.8480	0.6325	1.0608
	(2) CH_2	0.6744	0.5400	0.6325	0.7081
	(3) CH	0.4469	0.2280	0.6325	0.3554
(2) C=C	(4) CH=CH	1.1167	0.8670	1.2832	1.2489
(3) COOC	(5) CH_2COO	1.6764	1.4200	1.2700	1.4228
(4) CHO	(6) CHO	0.9980	0.9480	0.7173	0.7710
(5) COOH	(7) COOH	1.3013	1.2240	0.8000	0.9215
(6) DMSO	(8) DMSO	2.8266	2.4720	3.6000	2.6920

Table A.4.6. Structural parameters *q* (surface area of component *i*) and *r* (volume of component *i*) of refined soybean oil, odoriferous compounds and dimethyl sulfoxide.

Compound	**UNIFAC version**			
	UNIFAC-LL and UNIFAC-HIR		**UNIFAC-DMD and NIST-UNIFAC**	
	r	*q*	*r*	*q*
Refined Soybean Oil (LLO)	38.7157	31.3470	36.1585	40.2504
Hexanal	4.5967	3.9560	3.8798	4.6642
Heptanal	5.2711	4.4960	4.5123	5.3723
Butyric acid	3.5512	3.1520	2.6975	3.3985
Valeric acid	4.2256	3.6920	3.3300	4.1066
Caproic acid	4.9000	4.2320	3.9625	4.8147
Caprylic acid	6.2488	5.3120	5.2275	6.2309
Dimethyl sulfoxide	2.8266	2.4720	3.6000	2.9189

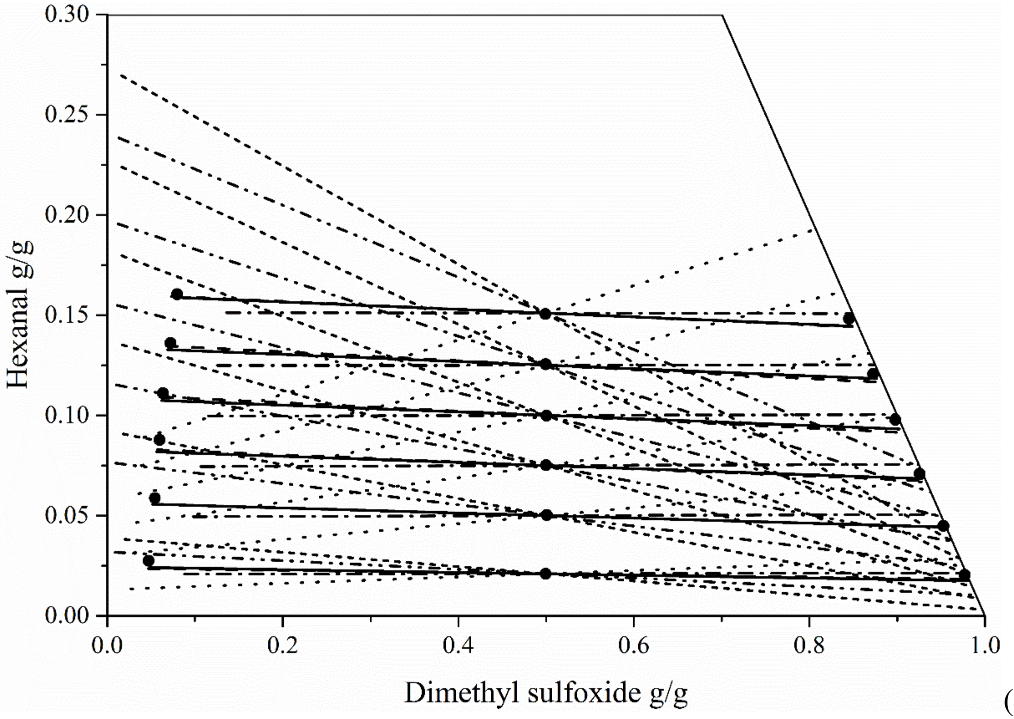
Table A.4.7 (part 1). Predicted liquid-liquid equilibrium data (mass fractions *w*) for pseudoternary systems composed of refined soybean oil (1) plus odoriferous compounds (*x*) plus dimethyl sulfoxide (8) at T = 298.15 K.

UNIFAC-LL				**UNIFAC-DMD**				**UNIFAC-HIR**				**NIST-UNIFAC**			
Raffinate phase		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**	
w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x
Refined soybean oil (1) + hexanal (2) + dimethyl sulfoxide (8)															
0.960	0.032	0.000	0.010	0.891	0.021	0.000	0.021	0.942	0.038	0.000	0.003	0.959	0.013	0.000	0.029
0.914	0.076	0.000	0.025	0.853	0.049	0.000	0.051	0.891	0.091	0.000	0.009	0.938	0.031	0.000	0.067
0.874	0.115	0.000	0.037	0.819	0.074	0.000	0.076	0.848	0.135	0.000	0.014	0.920	0.046	0.000	0.099
0.834	0.155	0.000	0.049	0.785	0.100	0.000	0.100	0.804	0.180	0.000	0.021	0.903	0.061	0.000	0.131
0.792	0.195	0.000	0.062	0.750	0.125	0.001	0.125	0.760	0.224	0.000	0.029	0.886	0.075	0.000	0.162
0.748	0.238	0.000	0.074	0.713	0.151	0.001	0.151	0.714	0.269	0.000	0.037	0.869	0.089	0.000	0.193
Refined soybean oil (1) + heptanal (3) + dimethyl sulfoxide (8)															
0.957	0.034	0.000	0.008	0.889	0.023	0.000	0.018	0.941	0.039	0.000	0.002	0.886	0.022	0.000	0.020
0.909	0.082	0.000	0.019	0.846	0.056	0.000	0.043	0.889	0.093	0.000	0.006	0.846	0.052	0.000	0.048
0.866	0.124	0.000	0.028	0.809	0.084	0.000	0.065	0.844	0.139	0.000	0.010	0.811	0.078	0.000	0.072
0.822	0.167	0.000	0.037	0.771	0.113	0.000	0.086	0.798	0.185	0.000	0.014	0.775	0.105	0.000	0.095
0.778	0.210	0.000	0.045	0.732	0.142	0.000	0.108	0.753	0.231	0.000	0.019	0.739	0.132	0.000	0.118
0.731	0.256	0.000	0.054	0.692	0.172	0.001	0.130	0.706	0.279	0.000	0.025	0.700	0.160	0.001	0.142
Refined soybean oil (1) + butyric acid (4) + dimethyl sulfoxide (8)															
0.973	0.018	0.000	0.037	0.893	0.019	0.000	0.038	0.927	0.054	0.000	0.001	0.920	0.001	0.000	0.057
0.957	0.034	0.000	0.068	0.871	0.035	0.000	0.071	0.883	0.100	0.000	0.002	0.925	0.002	0.000	0.100
0.942	0.049	0.000	0.097	0.851	0.050	0.000	0.100	0.838	0.144	0.000	0.004	0.929	0.003	0.000	0.136
0.925	0.065	0.000	0.128	0.827	0.067	0.001	0.133	0.789	0.194	0.000	0.006	0.933	0.004	0.000	0.174
0.908	0.082	0.000	0.159	0.803	0.084	0.001	0.164	0.740	0.243	0.000	0.008	0.936	0.005	0.000	0.208
0.893	0.096	0.000	0.185	0.782	0.100	0.001	0.191	0.695	0.287	0.000	0.011	0.939	0.006	0.000	0.235

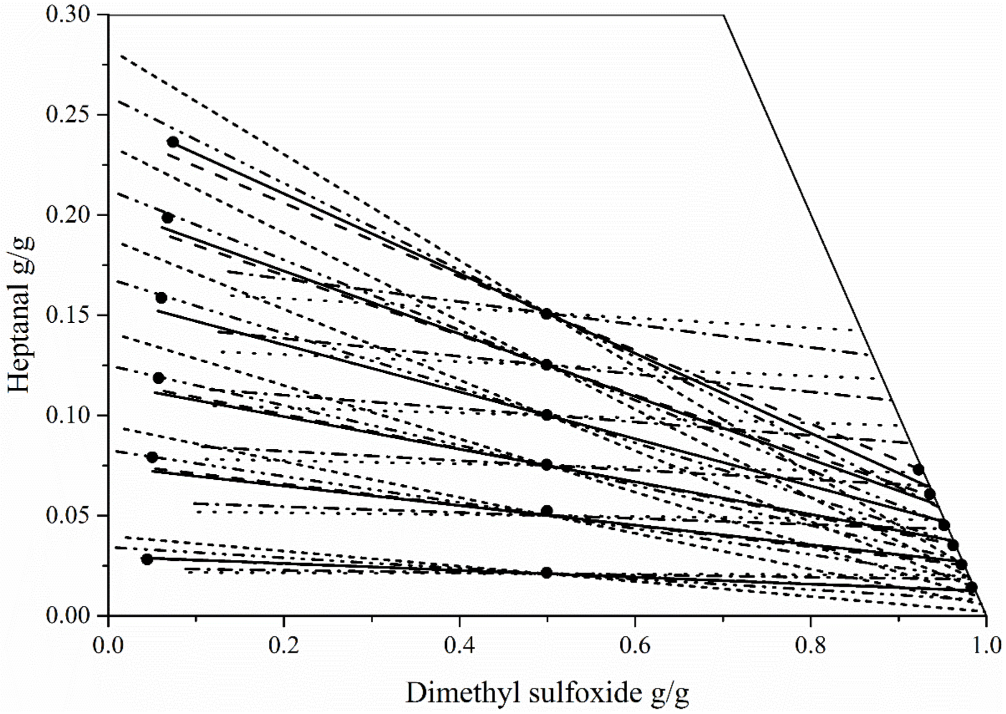
Table A.4.7 (part 2). Predicted liquid-liquid equilibrium data (mass fractions w) for pseudoternary systems composed of refined soybean oil (1) plus odoriferous compounds (x) plus dimethyl sulfoxide (8) at T = 298.15 K.

UNIFAC-LL				**UNIFAC-DMD**				**UNIFAC-HIR**				**NIST-UNIFAC**			
Raffinate phase		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**		**Raffinate phase**		**Extract phase**	
w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x	w_1	w_x
Refined soybean oil (1) + valeric acid (5) + dimethyl sulfoxide (8)															
0.971	0.020	0.000	0.030	0.892	0.020	0.000	0.031	0.932	0.049	0.000	0.000	0.918	0.001	0.000	0.051
0.948	0.042	0.000	0.061	0.863	0.041	0.000	0.064	0.881	0.101	0.000	0.001	0.922	0.002	0.000	0.099
0.929	0.061	0.000	0.087	0.839	0.059	0.000	0.091	0.838	0.146	0.000	0.002	0.925	0.003	0.000	0.136
0.907	0.082	0.000	0.116	0.810	0.080	0.001	0.122	0.788	0.196	0.000	0.003	0.928	0.005	0.000	0.174
0.886	0.102	0.000	0.143	0.783	0.100	0.001	0.150	0.740	0.244	0.000	0.005	0.930	0.006	0.000	0.207
0.866	0.123	0.000	0.170	0.755	0.120	0.001	0.178	0.691	0.294	0.000	0.006	0.932	0.008	0.000	0.236
Refined soybean oil (1) + caproic acid (6) + dimethyl sulfoxide (8)															
0.967	0.024	0.000	0.026	0.888	0.023	0.000	0.027	0.926	0.055	0.000	0.000	0.917	0.001	0.000	0.056
0.941	0.049	0.000	0.051	0.858	0.046	0.000	0.054	0.882	0.101	0.000	0.001	0.919	0.003	0.000	0.100
0.916	0.074	0.000	0.076	0.827	0.069	0.000	0.081	0.837	0.147	0.000	0.001	0.921	0.004	0.000	0.136
0.890	0.100	0.000	0.100	0.795	0.092	0.000	0.108	0.788	0.197	0.000	0.002	0.923	0.006	0.000	0.174
0.863	0.125	0.000	0.125	0.763	0.116	0.001	0.134	0.737	0.248	0.000	0.003	0.925	0.008	0.000	0.208
0.836	0.151	0.000	0.149	0.730	0.139	0.001	0.160	0.692	0.293	0.000	0.004	0.926	0.009	0.001	0.235
Refined soybean oil (1) + caprylic acid (7) + dimethyl sulfoxide (8)															
0.964	0.028	0.000	0.015	0.888	0.025	0.000	0.017	0.939	0.041	0.000	0.000	0.914	0.002	0.000	0.042
0.921	0.069	0.000	0.036	0.841	0.061	0.000	0.042	0.881	0.102	0.000	0.000	0.914	0.004	0.000	0.098
0.889	0.101	0.000	0.051	0.805	0.089	0.000	0.060	0.837	0.147	0.000	0.001	0.914	0.006	0.000	0.135
0.852	0.137	0.000	0.067	0.766	0.119	0.000	0.079	0.789	0.196	0.000	0.001	0.914	0.009	0.000	0.171
0.813	0.175	0.000	0.084	0.724	0.151	0.000	0.100	0.739	0.247	0.000	0.001	0.914	0.011	0.001	0.206
0.774	0.213	0.000	0.100	0.683	0.182	0.000	0.119	0.689	0.298	0.000	0.001	0.913	0.013	0.001	0.236

Figure A.4.3. Predicted liquid-liquid equilibrium data for pseudoternary systems composed of refined soybean oil plus odoriferous compounds plus dimethyl sulfoxide (8) at 298.15 K and under atmospheric pressure: (A) hexanal, (B) heptanal, (C) butyric acid, (D) valeric acid, (E) caproic acid and (F) caprylic acid. Legend: (●) experimental data; (solid) NRTL; (dash) UNIQUAC; (dash dot dot) UNIFAC-LL; (short dash) UNIFAC-HIR; (dash dot) UNIFAC-Dortmund; (dot) NIST-modified UNIFAC.



(A)



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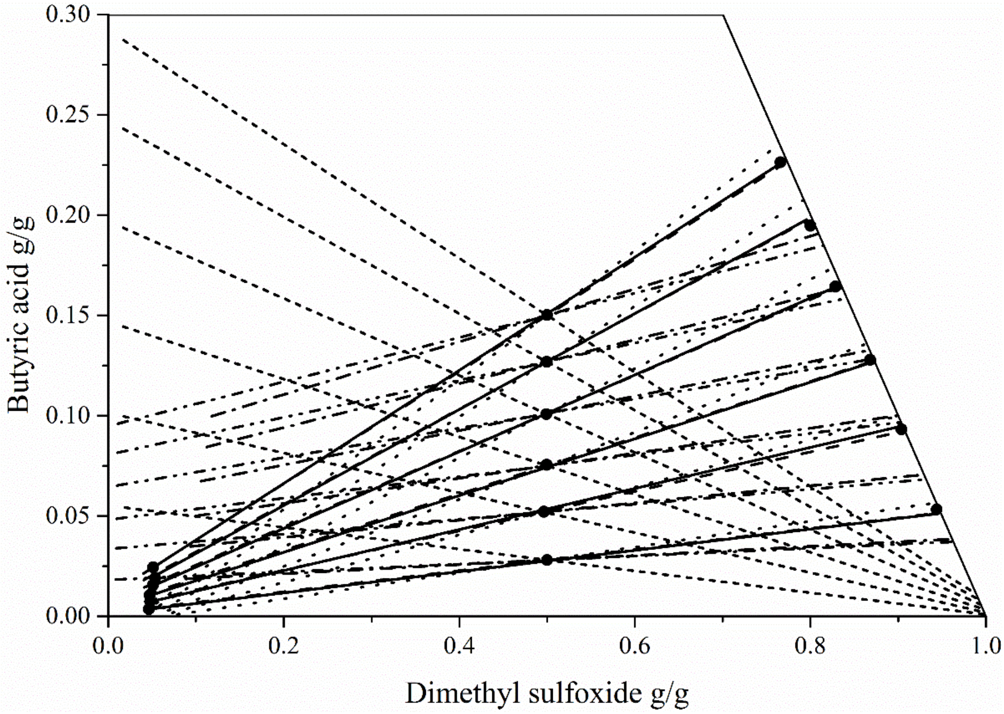
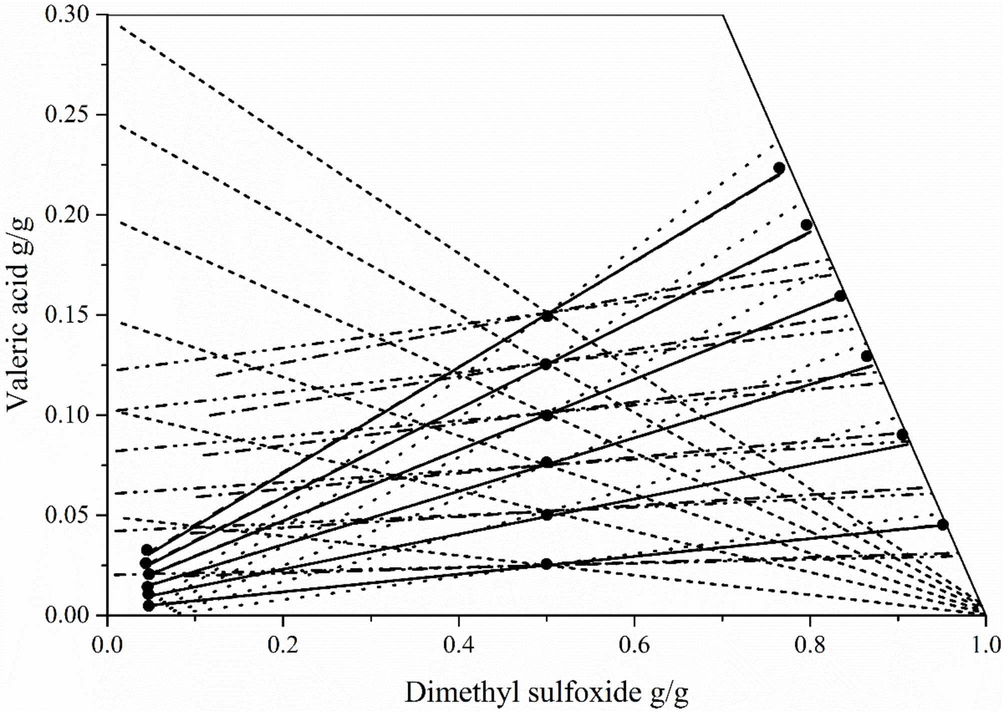
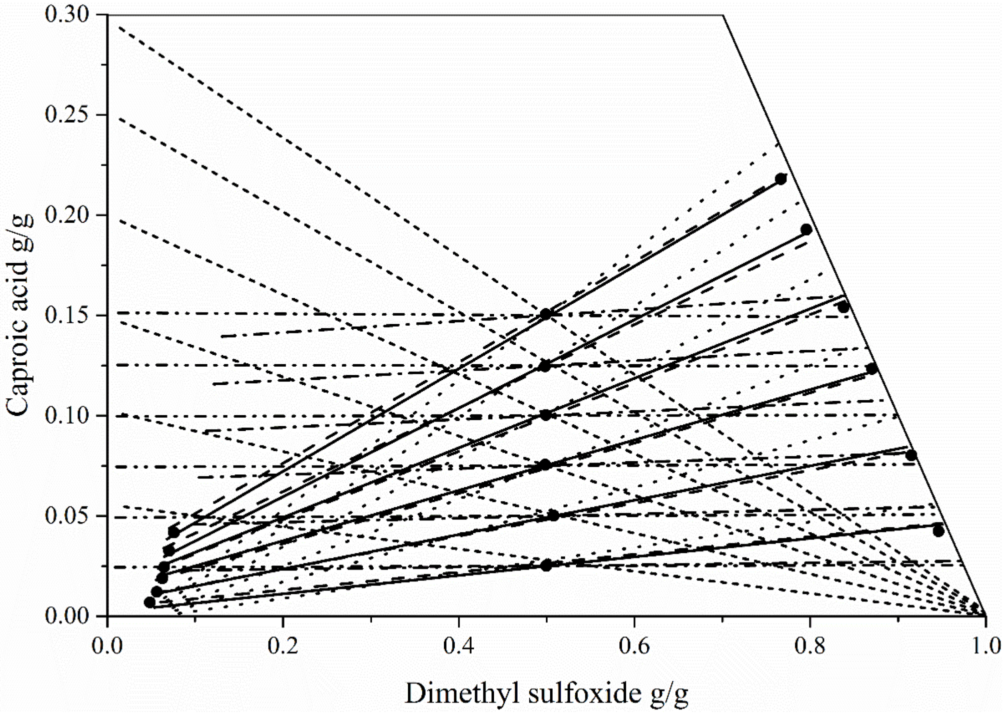

0.30
0.25
0.20
0.15
0.10
0.05
0.00
Butyric acid g/g
0.0
0.2
0.4
0.6
0.8
1.0
Dimethyl sulfoxide g/g

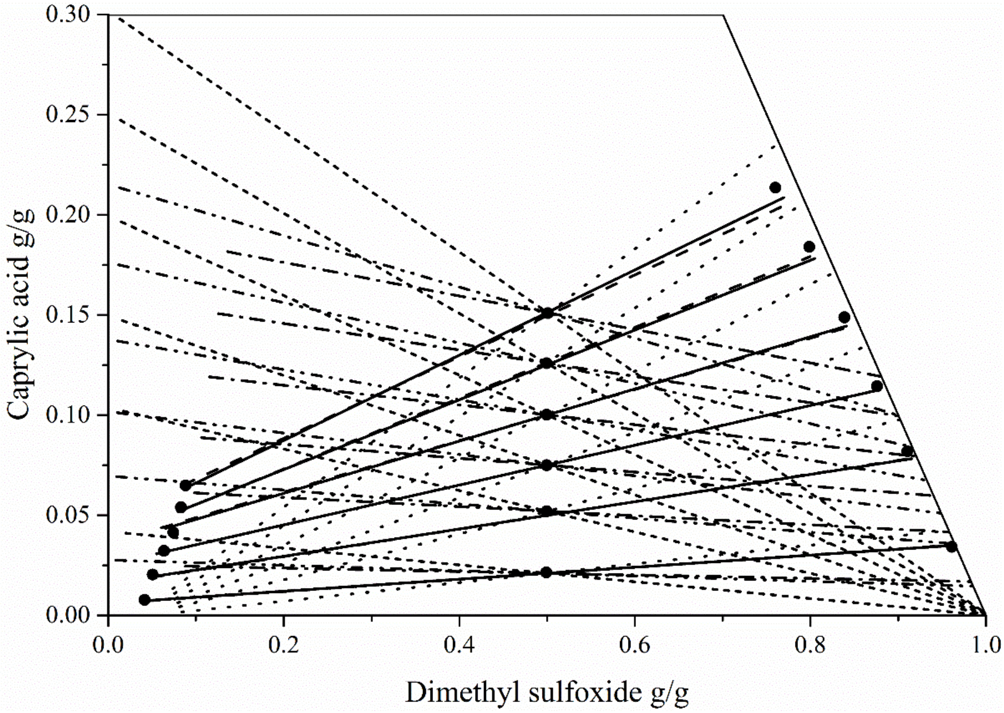
(C)


0.30
0.25
0.20
0.15
0.10
0.05
0.00
Valeric acid g/g
0.0
0.2
0.4
0.6
0.8
1.0
Dimethyl sulfoxide g/g

(D)

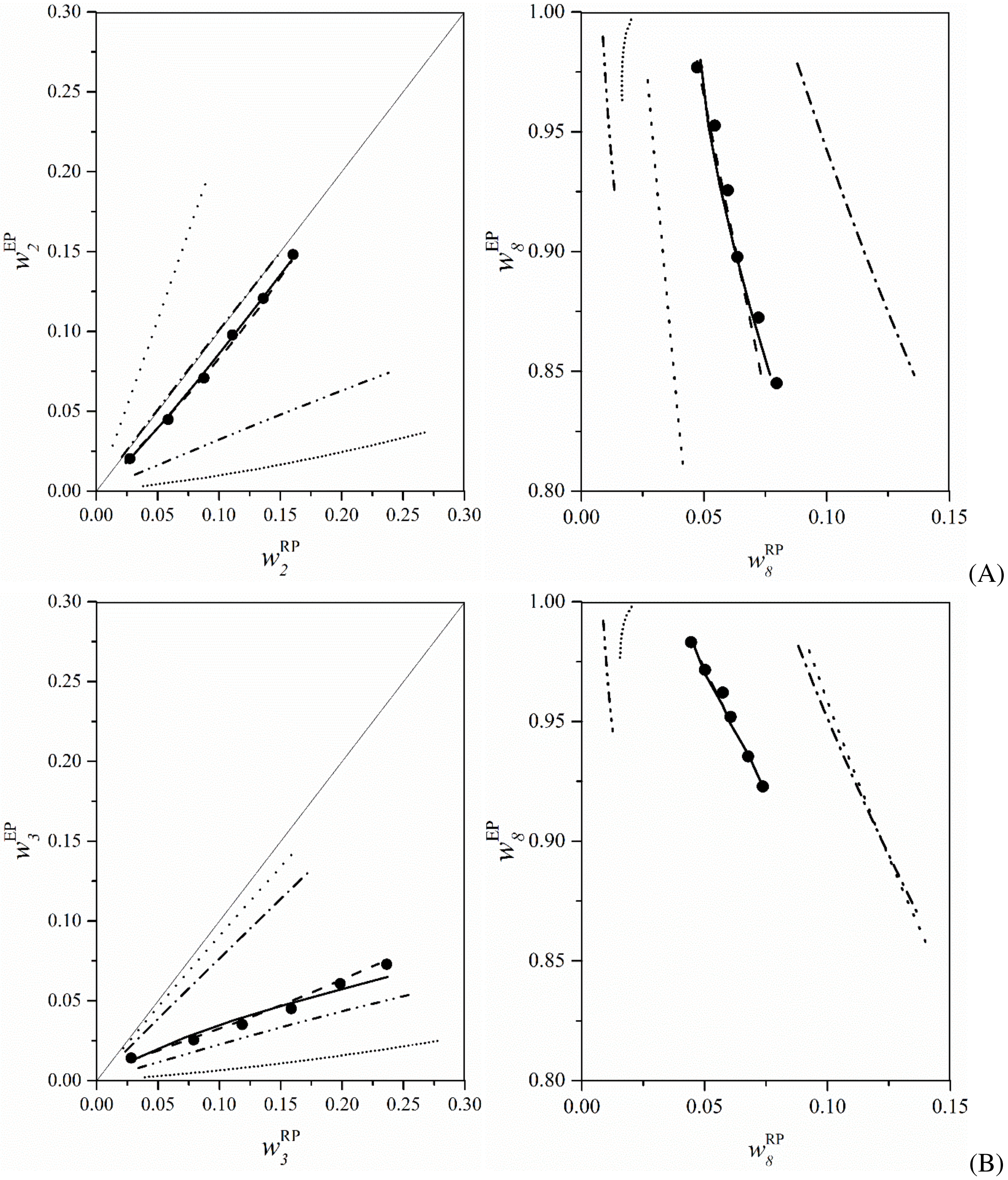

0.30
0.25
0.20
0.15
0.10
0.05
0.00
Caproic acid g/g
0.0
0.2
0.4
0.6
0.8
1.0
Dimethyl sulfoxide g/g

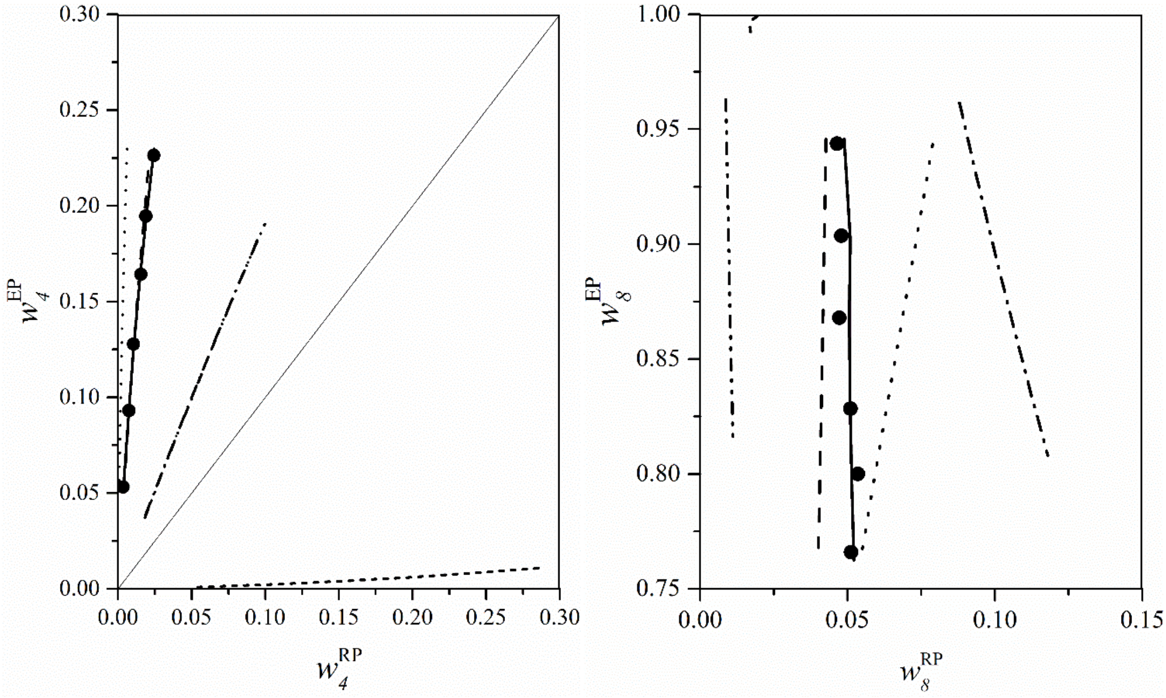
(E)


0.30
0.25
0.20
0.15
0.10
0.05
0.00
Caprylic acid g/g
0.0
0.2
0.4
0.6
0.8
1.0
Dimethyl sulfoxide g/g

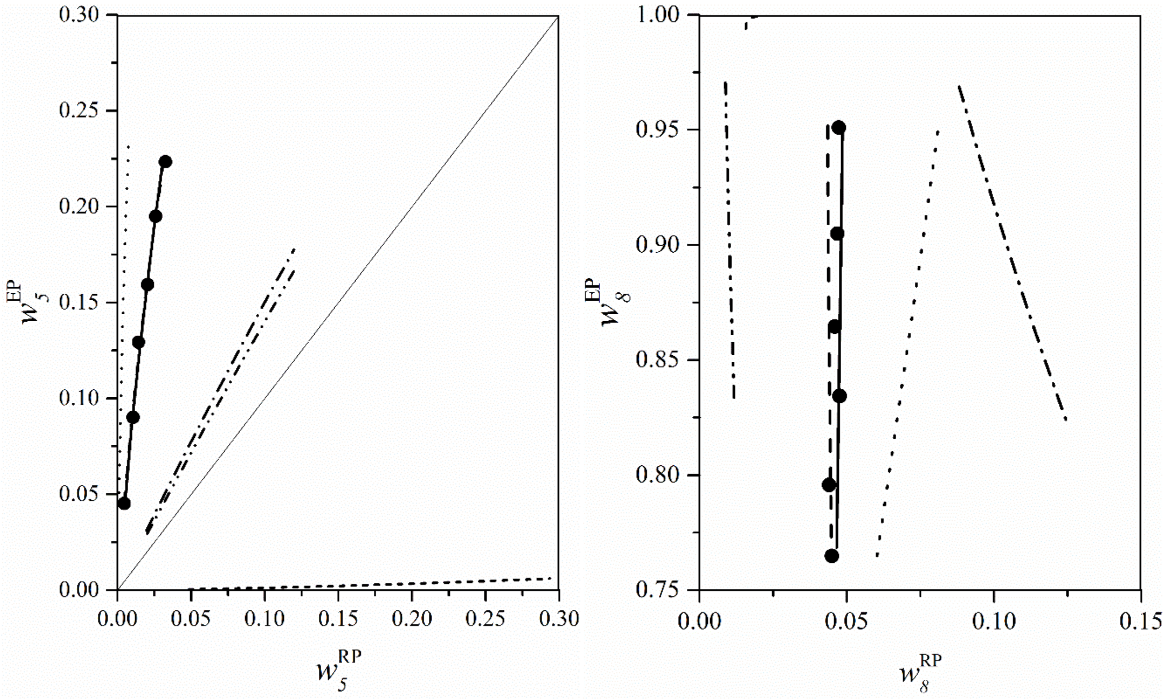
(F)

Figure A.4.4. Distribution of compounds between equilibrium raffinate (RP) and extract (EP) phases for systems containing refined soybean oil (1), solutes (*x*), and dimethyl sulfoxide (8) at 298.15 K and under atmospheric pressure. Solutes *x*: (A) hexanal (2), (B) heptanal (3), (C) butyric acid (4), (D) valeric acid (5), (E) caproic acid (6) and (F) caprylic acid (7). Legend: (●) experimental data; (solid) NRTL; (dash) UNIQUAC; (dash dot dot) UNIFAC-LL; (short dash) UNIFAC-HIR; (dash dot) UNIFAC-Dortmund; (dot) NIST-modified UNIFAC

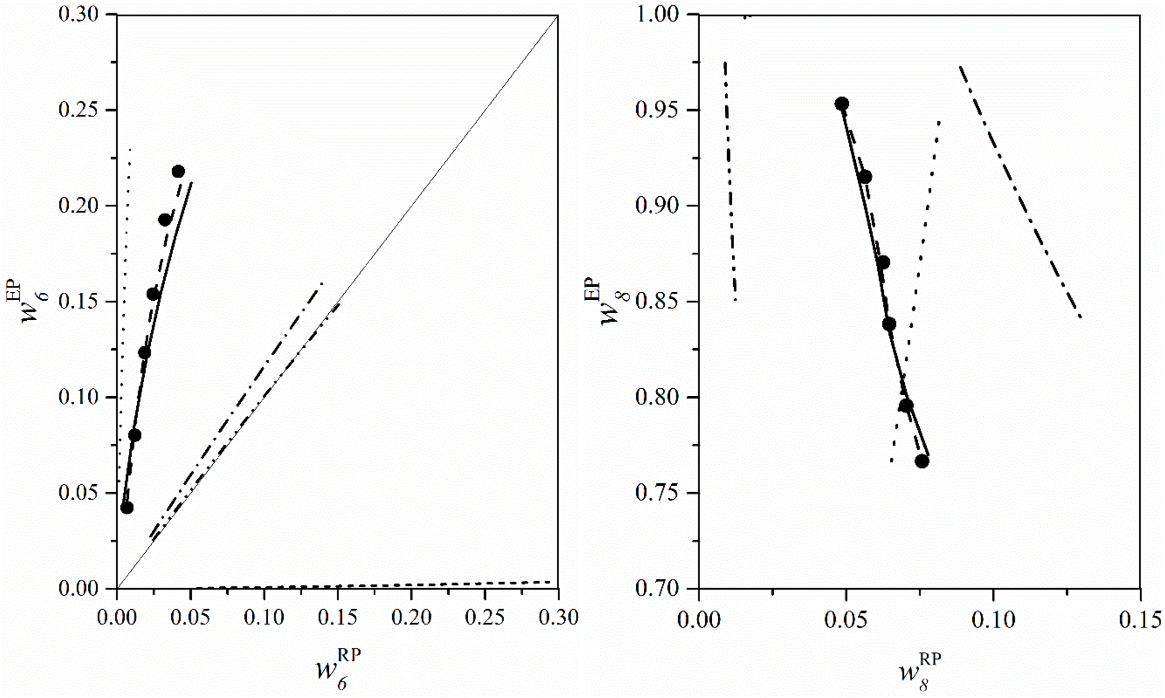



w_4^{EP}
0.00
0.05
0.10
0.15
0.20
0.25
0.30
w_4^{RP}
0.00
0.05
0.10
0.15
0.20
0.25
0.30
w_8^{EP}
0.75
0.80
0.85
0.90
0.95
1.00
w_8^{RP}
0.00
0.05
0.10
0.15

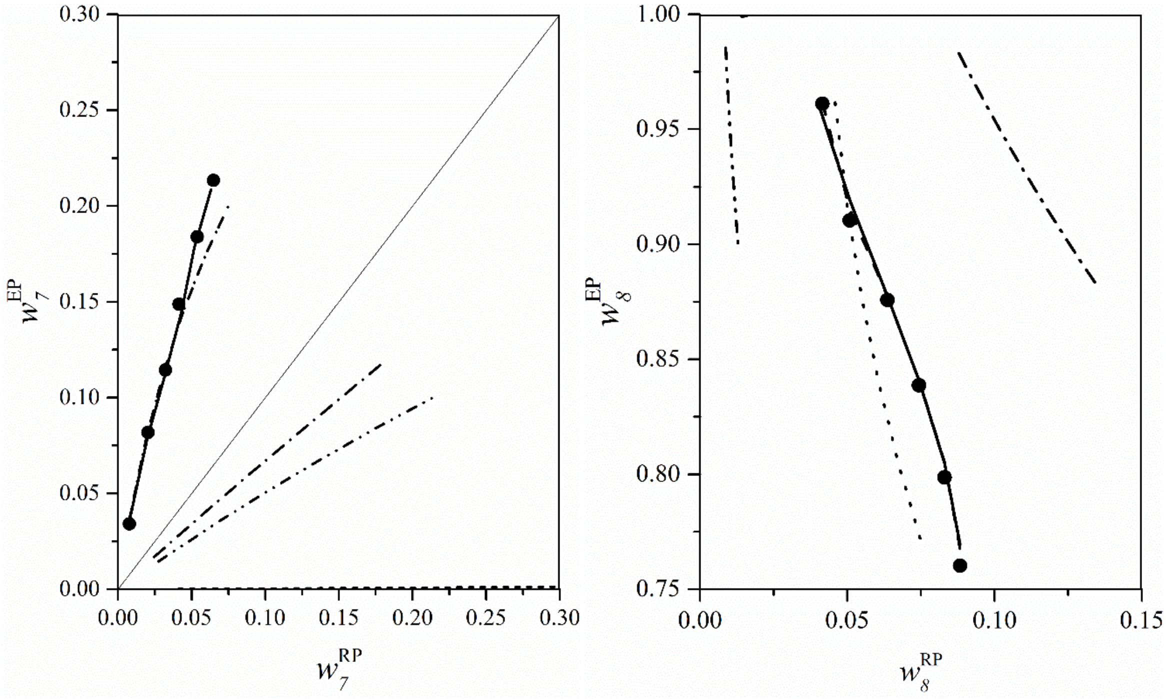
(C)


w_5^{EP}
0.00
0.05
0.10
0.15
0.20
0.25
0.30
w_5^{RP}
0.00
0.05
0.10
0.15
0.20
0.25
0.30
w_8^{EP}
0.75
0.80
0.85
0.90
0.95
1.00
w_8^{RP}
0.00
0.05
0.10
0.15

(D)


0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00 0.05 0.10 0.15 0.20 0.25 0.30
w_6^{EP}
w_6^{RP}
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.00 0.05 0.10 0.15
w_8^{EP}
w_8^{RP}

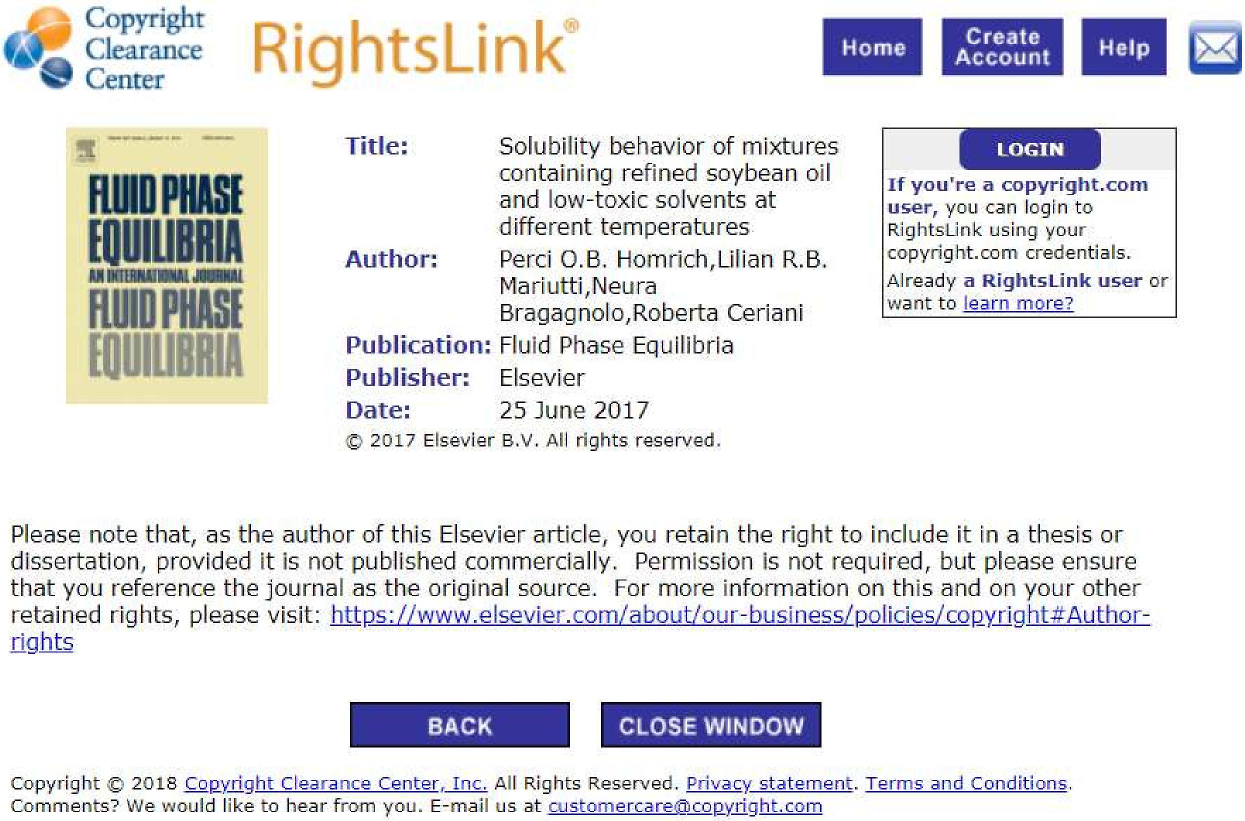
(E)


0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00 0.05 0.10 0.15 0.20 0.25 0.30
w_7^{EP}
w_7^{RP}
1.00
0.95
0.90
0.85
0.80
0.75
0.00 0.05 0.10 0.15
w_8^{EP}
w_8^{RP}

(F)

ANEXO A.1

DIREITO AUTORAL CAPÍTULO 4



Title: Solubility behavior of mixtures containing refined soybean oil and low-toxic solvents at different temperatures
Author: Perci O.B. Homrich,Lilian R.B. Mariutti,Neura Bragagnolo,Roberta Ceriani
Publication: Fluid Phase Equilibria
Publisher: Elsevier
Date: 25 June 2017

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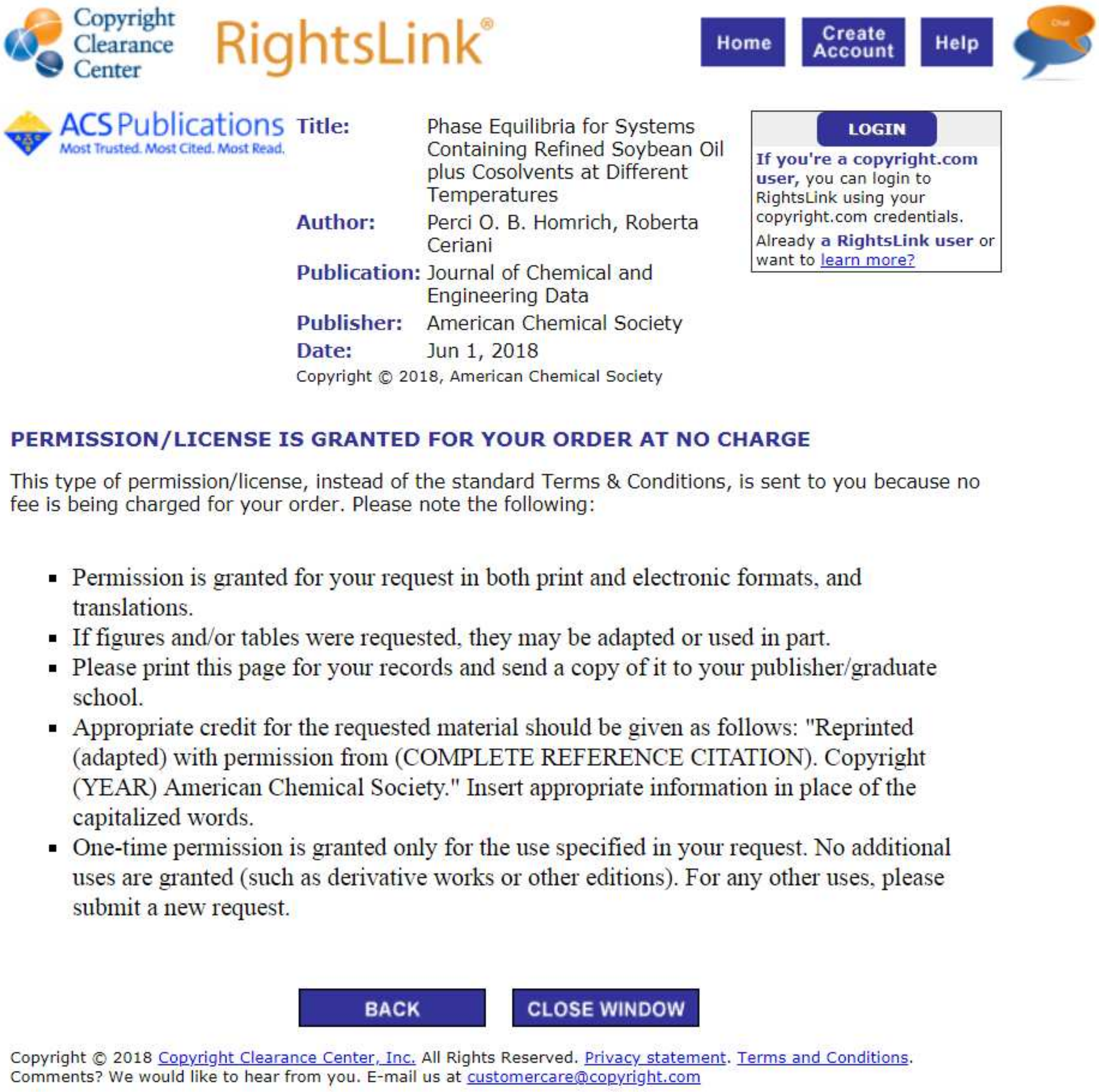
ANEXO A.2

DIREITO AUTORAL CAPÍTULO 6



Title: Phase Equilibria for Systems Containing Refined Soybean Oil plus Cosolvents at Different Temperatures
Author: Perci O. B. Homrich, Roberta Ceriani
Publication: Journal of Chemical and Engineering Data
Publisher: American Chemical Society
Date: Jun 1, 2018
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