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"EQUILÍBRIO DE FASES DE SISTEMAS COMPOSTOS POR ÓLEOS VEGETAIS, ÁCIDOS GRAXOS E ETANOL HIDRATADO"

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Aos meus pais...

... Júlio (in memorian) …

..."Aqueles que amamos nunca morrem, apenas
partem antes de nós".
(Amado Nervo)

... e Isold ...

..."O verdadeiro amor não se conhece por aquilo que exige,
mas por aquilo que oferece".
(Jacinto Benavente)

Aos meus irmãos...

... Júlio César e Sérgio...

... Ao meu sobrinho Pedro...

...Aos meus tios e primos queridos...

..."Não pode haver felicidade genuína longe do lar. Nele
encontramos as melhores influências e os
relacionamentos mais doces que a vida pode nos
oferecer".

(Ezra Taft Benson)

...DEDICO.

*"**SABER** que se sabe o que se sabe, e saber que não se sabe o que não se sabe, eis a verdadeira ciência".*
(Confúcio)

*"**APRENDER** é a única coisa de que a mente nunca se cansa, nunca tem medo e nunca se arrepende".*
(Leonardo da Vinci)

*"A consciência do **DEVER** cumprido infunde em nossa alma uma doce alegria"*
(George Herbert)

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RESUMO

Este trabalho de tese de doutoramento teve como objetivo avaliar vários aspectos do processo de extração líquido-líquido (ELL) como uma rota alternativa para a desacidificação de óleos vegetais. O conhecimento do equilíbrio de fases do sistema de interesse é essencial para o bom planejamento e desenvolvimento do processo de ELL. O presente trabalho apresenta dados de equilíbrio para sistemas compostos por óleos vegetais (milho/palma), ácidos graxos (oléico/ palmítico) e solvente (etanol contendo diferentes teores de água, até 18% em massa), e a correlação destes dados empregando os modelos termodinâmicos NRTL e UNIQUAC. O trabalho foi realizado com o objetivo de otimizar a concentração de água no solvente para reduzir a perda de óleo neutro sem afetar de forma significativa o coeficiente de distribuição dos ácidos graxos. Para o óleo de palma, a metodologia de superfície de resposta (MSR) também foi utilizada a fim de avaliar o efeito de algumas variáveis de processo, como teor de água no solvente e razão óleo:solvente, sobre a perda de óleo neutro, transferência de ácidos graxos livres e preservação dos carotenóides. Essa metodologia permitiu otimizar a razão óleo:solvente ao redor de 0,75 e o teor de água no solvente em torno de 6%. Estudou-se, ainda, o processo de desacidificação do óleo de palma por extração líquido-líquido em equipamento contínuo, utilizando condições previamente otimizadas com o auxílio da metodologia de superfície de resposta. O impacto deste tipo de processo sobre a qualidade do produto final também foi avaliado. Os resultados indicaram que é possível obter um óleo de palma refinado com acidez livre menor do que 0,3% (em massa), mantendo um teor considerável de compostos nutracêuticos no produto refinado.

ABSTRACT

This PhD thesis had the aim of evaluating various aspects of the liquid-liquid extraction (LLE) process as an alternative route for the deacidification of vegetable oils. The knowledge of the liquid-liquid equilibrium of the systems of interest is essential for planning and developing a LLE process. The present work reports equilibrium data for systems containing vegetable oils (corn/palm), fatty acids (oleic/ palmitic) and solvents (ethanol containing different water contents up to 18 mass%), and the correlation of these data by the NRTL and UNIQUAC models. This work was performed with the aim of optimizing the water content in the solvent in order to reduce the loss of neutral oil without affecting in a significant way the fatty acid distribution coefficients. For the palm oil, the response surface methodology (RSM) was also utilized to analyze the effect of some process variable, such as water content in the solvent and mass ratio of oil to solvent, on the loss of neutral, on the free fatty acids transfer and on the carotenoids preservation. This methodology allowed to optimize the mass ratio of oil to solvent around 0.75 and the water content in the solvent around 6 mass%. Furthermore, the deacidification of palm oil by liquid-liquid extraction in a continuous equipment was studied using the optimized conditions obtained in the response surface analysis. The impact of this type of process on the final product quality was also evaluated. The experimental results indicated that it is possible to obtain a refined palm oil with free acidity less than 0.3% (in mass), keeping a considerable content of nutraceutical compounds in the refined product.

CAPÍTULO 1 - Introdução

Os óleos vegetais são substâncias que, em seu estado bruto, consistem predominantemente de triacilgliceróis, apresentando também em menor nível mono e diacilgliceróis, ácidos graxos livres (AGL), pigmentos (carotenóides e clorofilas), esteróis, tocoferóis, fosfolipídeos e proteínas. A remoção de ácidos graxos livres (desacidificação) é a etapa mais importante do processo de refino de óleos, principalmente porque o rendimento do óleo neutro nesta operação tem um efeito significativo no custo do processo (Hamm, 1983).

Alguns óleos merecem destaque entre os óleos vegetais comestíveis. São eles: o óleo de milho, que adquiriu grande importância devido às suas excelentes características organolépticas e nutricionais, e pelo seu ótimo desempenho como óleo de fritura e salada (Antoniassi, 1996); e o óleo de palma, que possui vasta aplicação industrial, e é considerado mundialmente como a maior fonte natural de vitamina A. Além disso, é rico em antioxidantes naturais, como os tocoferóis, que apresentam valor de vitamina E (OMB, 1999). No entanto, em ambos os casos, a elevada acidez do óleo bruto dificulta o processo de refino pelos métodos tradicionais (refino químico e refino físico), causando grandes perdas de óleo neutro e de compostos nutracêuticos. Assim, é importante o estudo de um processo alternativo para a desacidificação desses óleos.

A técnica de desacidificação do óleo através da extração líquido-líquido (ELL) usando solventes adequados, tem despertado interesse devido às vantagens que traz em relação aos refinos físico e químico. Como é feita a temperaturas próximas à ambiente, consome menos energia e submete o óleo a tratamentos mais brandos, permitindo a preservação dos compostos nutracêuticos. Além disso, a ELL tem a

vantagem de evitar a produção de poluentes e reduzir as perdas de óleo neutro.

Este trabalho de tese de doutoramento teve como objetivo avaliar vários aspectos do processo de extração líquido-líquido como uma rota alternativa para a desacidificação de óleos vegetais comestíveis. Os resultados foram apresentados e discutidos em artigos publicados ou submetidos em revistas científicas durante o desenvolvimento da pesquisa, e estão apresentados nos Capítulos 3 a 6 deste trabalho.

O artigo apresentado no Capítulo 3, entitulado **"Liquid-Liquid Equilibrium Data for the System Corn Oil + Oleic Acid + Ethanol + Water at 298.15 K"** foi publicado no ***Journal of Chemical and Engineering Data*** e apresenta dados de equilíbrio para o sistema óleo de milho + ácido oléico + etanol + água a 25ºC, e a correlação destes dados empregando os modelos termodinâmicos NRTL e UNIQUAC. Este trabalho foi realizado com o objetivo de otimizar a concentração de água no solvente para reduzir a perda de óleo neutro sem afetar de forma significativa o coeficiente de distribuição dos ácidos graxos.

O Capítulo 4, entitulado **"Liquid-Liquid Equilibrium Data for the System Palm Oil + Fatty Acids + Ethanol + Water at 318.2K"**, aceito para publicação na revista ***Fluid Phase Equilibria***, apresenta dados de equilíbrio líquido-líquido para sistema modelo contendo óleo de palma refinado + ácidos graxos (palmítico/oléico) + etanol + água a 45ºC. Estes dados de equilíbrio também foram correlacionados pelos modelos NRTL e UNIQUAC, sendo os parâmetros ajustados utilizados para predizer o equilíbrio de fases de sistemas reais compostos por óleo de palma branqueado e solventes alcoólicos.

O trabalho apresentado no Capítulo 5, entitulado **"Partition of Nutraceutical Compounds in Deacidification of Palm Oil by**

Solvent Extraction" e submetido ao ***Journal of Food Engineering***, foi realizado com o objetivo de estudar a influência da desacidificação por extração com solvente sobre os compostos nutracêuticos do óleo de palma, como carotenóides e tocoferóis. Para isso foram medidos os coeficientes de partição destes compostos através da determinação do equilíbrio de fases de sistemas contendo óleo de palma + ácidos graxos + etanol + água + compostos nutracêuticos a 45ºC. Os coeficientes de partição também foram correlacionados pelo modelo UNIQUAC.

A última etapa deste trabalho está apresentada no Capítulo 6, entitulado **"Deacidification of Palm Oil by Solvent Extraction"** que será, em breve, submetido ao ***Journal of American Oil Chemists' Society***. Nesta etapa, foi estudada a influência de algumas variáveis do processo sobre a perda/transferência de compostos graxos durante a desacidificação do óleo de palma. A metodologia de planejamento experimental e análise de superfície de resposta foi utilizada como ferramenta para analisar o efeito das variáveis de processo a fim de minimizar a perda de óleo neutro e maximizar a transferência de ácidos graxos e a preservação dos carotenóides. Estudou-se, ainda, o processo de desacidificação do óleo de palma por extração líquido-líquido em equipamento contínuo, utilizando as condições otimizadas na análise de superfície de resposta. Os resultados experimentais indicaram que é possível obter um óleo de palma refinado com acidez livre menor do que 0,3% (em massa), mantendo um teor considerável de compostos nutracêuticos.

Desta forma, pretende-se contribuir para uma melhor avaliação do processo de extração líquido-líquido como técnica alternativa aos métodos tradicionais no refino de óleos vegetais.

CAPÍTULO 2 - Revisão Bibliográfica

2.1 Natureza e Composição dos Óleos Vegetais

Os óleos vegetais são substâncias líquidas insolúveis em água, e que em seu estado bruto consistem predominantemente de triacilgliceróis e ácidos graxos.

Estruturalmente, um triacilglicerol é o produto da esterificação de uma molécula de glicerol com três moléculas de ácidos graxos, gerando três moléculas de água e uma molécula de triacilglicerol. Qualquer ácido graxo não ligado a uma molécula de glicerol é dito ácido graxo livre (Lawson, 1985).

Além de triacilgliceróis e ácidos graxos livres, presentes em menor quantidade, todos os óleos contém uma pequena quantidade de mono e diacilgliceróis, pigmentos, esteróis, tocoferóis, fosfatídeos e proteínas. Segundo Swern (1964), nos óleos vegetais brutos, esses componentes representam menos que 5% da sua composição, e nos óleos vegetais refinados, menos que 2%. Portanto, os óleos vegetais refinados podem ser representados como uma mistura de triacilgliceróis.

2.1.1 Composição do óleo de milho

O óleo de milho bruto, em geral, contém de 3 a 9% de ácidos graxos livres, conteúdo de fósforo de 300 a 1000 ppm e índice de iodo de 110 a 125 gramas de iodo/ 100 gramas de óleo. Contém ainda pigmentos, como xantofilas e carotenos, além de ceras como álcool de miricila e ácido lignocérico (C24:0). Os fosfolipídeos contêm 50% de fosfatidil inositol, sendo o restante constituído de glicerilfosfatidil colina e fitoglicolipídeos (Leibovitz & Ruckenstein, 1983).

A alta estabilidade do óleo de milho se deve à presença de antioxidantes naturais como tocoferóis, ácido ferúlico e ubiquinonas; pela sua composição em ácidos graxos; pela posição 2 dos triacilgliceróis estar ocupada pelos ácidos graxos insaturados e pela ausência de clorofila (Leibovitz & Ruckenstein, 1983; Orthoefer & Sinram, 1987; Strecker et al., 1990).

Cerca de 59% dos ácidos graxos do óleo de milho são polinsaturados, 26% são monoinsaturados e 15% saturados. Os principais ácidos graxos do óleo de milho são o oléico (18:1) e o linoléico (18:2). De acordo com o Codex Alimenarius (1993), as quantidades esperadas desses compostos no óleo de milho são de 24 a 42% para o ácido oléico e de 34 a 62% para o ácido linoléico.

2.1.2 Composição do óleo de palma

A composição típica do óleo de palma bruto é de 87 a 92% de triacilgliceróis, 3 a 8% de diacilgliceróis, 0 a 0,5% de monoacilgliceróis, 1 a 5% de ácidos graxos livres e cerca de 1% de componentes menores que incluem carotenóides (500-850ppm), tocoferóis (500-1000ppm), esteróis (300-600ppm), glicolipídeos (1000 a 3000ppm), fosfolipídeos (20 a 80ppm), álcoois triterpênicos (300-800ppm) e hidrocarbonetos. Esses constituintes menores desempenham um importante papel na estabilidade e no curso do processamento do óleo. Alguns deles, como os carotenóides e os tocoferóis, conferem ao óleo de palma maior valor nutricional (Trujillo-Quijano, 1997).

Os ácidos graxos saturados e insaturados no óleo de palma encontram-se numa relação aproximada de 1:1. Os principais ácidos graxos desse óleo são o palmítico (46,5%), o oléico (37,1%) e o linoléico (9,9%) (Trujillo-Quijano, 1997).

2.2 Aspectos Nutricionais do Óleo de Palma

A presença de certos componentes eleva o valor nutricional do óleo de palma. Os carotenóides, além de apresentar valor de vitamina A, reduzem o risco de certos tipos de câncer e possuem ainda habilidade supressora de oxigênio "singlet", um tipo de oxigênio altamente reativo capaz de ocasionar enormes danos celulares (Trujillo-Quijano, 1999).

Mesmo com seu valor nutricional, os carotenóides são removidos no processo atual de refino para a obtenção de um óleo de cor clara, de melhor aceitação (Trujillo-Quijano, 1997). Assim, todas as valiosas características do óleo de palma são perdidas, e os benefícios nutricionais são somente aproveitados usando o óleo bruto, fato comum no nordeste brasileiro. Os poucos casos de deficiência de vitamina A e xeroftalmia no Estado da Bahia pode ser atribuído ao uso rotineiro de óleo de palma bruto na cozinha baiana (Trujillo-Quijano, 1994).

Além dos carotenóides, o óleo de palma também é rico em tocoferóis, que são antioxidantes naturais e apresentam valor de vitamina E. A presença desses componentes proporciona ao óleo de palma e seus produtos uma longa vida-de-prateleira (Hamid & May, 1997).

2.3 Refino de Óleos Vegetais

Refino é um termo genérico para as etapas de purificação dos óleos vegetais brutos, e que tem como objetivo remover as impurezas presentes nos óleos, tais como: ácidos graxos livres, fosfatídeos, pigmentos e traços de metais. Entretanto, nem todas as impurezas são indesejáveis. Os carotenóides e tocoferóis são componentes nutricionalmente importantes e melhoram também a estabilidade oxidativa do óleo. Portanto, sua presença é altamente desejável em

todos os óleos e gorduras. O mercado desses produtos nutracêuticos vem aumentando e vários processos têm sido desenvolvidos visando sua preservação no óleo (Trujillo-Quijano, 1997).

A remoção dos ácidos graxos livres (desacidificação) é a mais importante das etapas do processo de purificação de óleos, principalmente devido ao rendimento de óleo neutro nesta etapa, que têm um efeito significativo no custo global final (Hamm, 1983). A desacidificação de óleos vegetais tem sido feita por refino químico ou refino físico.

No refino químico, a etapa de desacidificação é efetuada por neutralização com soda cáustica, ocasionando a conversão dos ácidos graxos livres em sabões, que são removidos posteriormente por meio de centrifugação ou decantação (Hartman, 1971).

No entanto, este processo apresenta dificuldades quando aplicado a óleos com um alto teor de ácidos graxos, como os óleos de milho e de palma. Para esses óleos o refino químico não é econômico devido às perdas causadas pela saponificação do óleo neutro e pelo arraste mecânico de óleo neutro nas emulsões. As perdas de óleo neutro, para óleos de milho cru com conteúdos de ácidos graxos livres entre 8 e 14%, podem atingir de 15 a 25%, no refino alcalino, de acordo com Leibovitz e Ruckenstein (1983) e cerca de 14%, em refinarias brasileiras, para óleos com 4% de acidez (Antoniassi et al., 1998).

Já o refino físico consiste na remoção dos ácidos graxos livres por destilação a vácuo com injeção direta de vapor d'água. O método se baseia na diferença considerável entre os pontos de ebulição dos ácidos graxos livres e dos triacilgliceróis à pressão de operação, facilitando a remoção dos primeiros com uma insignificante perda de óleo (Hartman, 1971).

Entretanto, para alguns óleos, as condições necessárias neste processo (altas temperaturas: 200-250ºC; e baixas pressões: 5-10mmHg) têm um grande impacto na qualidade do produto final. Óleos com grande teor de fosfatídeos não podem ser purificados por este método, pois a decomposição térmica destes compostos origina um material de cor escura dificilmente removível, prejudicando a aparência e o sabor do produto final (Antoniassi et al., 1998). Compostos nutracêuticos, como carotenóides e tocoferóis, são eliminados pelo refino físico (Trujillo-Quijano, 1994). Além disso, o grau de desacidificação alcançado não é sempre satisfatório (Maza et al., 1992).

A técnica de desacidificação por extração líquido-líquido (ELL) tem se mostrado como uma rota alternativa na obtenção de óleos vegetais com teores aceitáveis de ácidos graxos livres. O método consiste na extração dos ácidos graxos livres com álcoois ou outros solventes que tenham uma maior afinidade com os ácidos do que com os triacilgliceróis. A razão do potencial deste processo está no fato da perda de óleo neutro no extrato poder ser consideravelmente inferior à perda no refino químico para óleos de acidez elevada, e também por ser um processo alternativo para óleos aos quais a temperatura normalmente requerida para o refino físico (220 a 270^{o}C) não é aceitável. Além disso, em relação ao refino químico, elimina-se o problema de formação e descarte dos sabões produzidos (Hamm, 1983).

Segundo Trujillo-Quijano (1994), deve ser destacado que o óleo refinado por extração líquido-líquido possui sabor e odor brandos, característicos do óleo desodorizado. Assim, pode ser dispensada a desodorização convencional, na qual o óleo é submetido a um severo tratamento térmico. Visando a preservação dos carotenóides e tocoferóis do óleo de palma, este fato é de grande importância.

A escolha dos solventes para a extração dos ácidos graxos livres é governada pela diferença de polaridade entre os ácidos graxos (contendo uma extremidade polar) e os triacilgliceróis (apolares). Um solvente polar é capaz de produzir extratos contendo baixas concentrações de triacilgliceróis. A adição de água ao solvente reduz sua capacidade de extração de triacilgliceróis, mas em menor extensão também para os ácidos graxos (Norris, 1964).

Ensaios realizados para obtenção de dados de equilíbrio líquido-líquido para sistemas ternários de óleos vegetais (milho e canola), ácidos graxos e álcoois de cadeia curta (metanol, etanol, isopropanol, n-propanol) (Batista et al., 1999a; Batista et al., 1999b) têm mostrado que o etanol hidratado é o solvente mais adequado ao processo (Hamm, 1983; Monnerat & Meirelles, 1995; Antoniassi et al., 1995; Antoniassi et al., 1998, Gonçalves et al., 1999). A hidratação do solvente pode diminuir a solubilização de óleo pelo etanol e, consequentemente, minimizar a perda de óleo neutro. Um dos objetivos deste trabalho é otimizar o nível de água no solvente.

2.4 Extração Líquido–Líquido (ELL)

No processo de ELL, duas correntes resultam do contato entre a alimentação (óleo + ácidos graxos) e o solvente: o extrato, que é a solução rica em solvente contendo o soluto (ácidos graxos) extraído, e o refinado, a solução residual da alimentação contendo pouco soluto. Uma certa quantidade de solvente também fica retida no refinado, mas devido à elevada diferença entre os pontos de ebulição do solvente e dos compostos graxos, a recuperação do solvente do óleo refinado pode ser facilmente conduzida por meio de destilação/evaporação.

Estudos com isopropanol hidratado foram realizados por Shah e Venkatesan (1989) e a extração dos AGL com a utilização de etanol hidratado na miscela foi realizada por Türkay e Civelekoglu (1991a, b). Seus resultados mostram que a extração líquido-líquido pode ser um processo promissor na desacidificação de óleos vegetais.

Trujillo-Quijano (1994) realizou o refino do óleo de palma por ELL contracorrente usando etanol aquoso numa coluna empacotada. O processo desenvolvido pode ser aplicado para desacidificar/desodorizar simultaneamente óleos de palma, além de remover os glicerídeos parciais presentes. As baixas temperaturas usadas no processo de refino por ELL preservaram os pigmentos carotenóides, que se concentraram no refinado em cerca de 6 %. Numa coluna empacotada de 3,5 estágios teóricos e com a proporção etanol/óleo de 3,57/1 foi possível extrair mais de 99 % dos AGL, a partir de óleo de palma bruto contendo 3,65 % de AGL.

2.5 Coluna de Discos Rotativos Perfurados (PRDC)

A PRDC consiste de um cilindro vertical equipado com discos perfurados presos a um eixo central ligado a um motor de velocidade variável, visando promover dispersão e o contato entre as fases. As alimentações são introduzidas perpendiculares à direção do escoamento. Para reduzir o efeito do movimento dos líquidos e garantir a separação das fases, duas zonas mortas, uma abaixo e outra acima da região de extração, fazem parte do equipamento. A retirada de amostras da fase refinado é feita no compartimento inferior, e a da fase extrato na saída desta corrente no topo da coluna de extração (Pina, 2001).

Antoniassi (1996) estudou o processo de ELL em coluna de discos rotativos perfurados (PRDC) como técnica de desacidificação do óleo de

milho cru. O etanol hidratado foi selecionado como o solvente mais adequado ao processo e o desempenho da extração a 30°C foi superior do que a 40°C, considerando todos os parâmetros estudados. Foi feito também um estudo sobre o pré-tratamento mais adequado para o óleo de milho bruto. Como o teor de fósforo dos óleos degomados pode variar muito, a matéria-prima mais padronizada para ser utilizada seria o óleo branqueado, que estaria seco e quase livre de fosfatídeos.

Pina & Meirelles (2000) realizaram estudos sobre a desacidificação do óleo de milho por extração líquido-líquido, utilizando etanol a 96% como solvente, em colunas de discos rotativos (RDC) e de discos rotativos perfurados (PRDC). Bons resultados foram obtidos quanto a teores aceitáveis de ácidos graxos livres, menor que 0,3% para óleos com acidez de 3,5% e perdas de óleo neutro de até 4,8%. A perda de óleo neutro pode ser considerada baixa se comparada às perdas em torno de 14% por refino químico, para o mesmo teor de ácido graxo no óleo bruto, obtidas nas refinarias de óleo de milho no Brasil (Antoniassi et al., 1998). Batista et al. (1999a) simularam a desacidificação de óleo de canola utilizando etanol anidro como solvente e obtiveram acidez residual no óleo de 0,29% e perda de óleo neutro de 8%. Esta maior perda de óleo neutro é conseqüência da maior solubilidade do óleo no álcool anidro.

Além de sua aplicação em óleos vegetais, a PRDC também pode ser empregada com sistemas aquosos bifásicos (SAB) para a extração e purificação de proteínas. Cunha (2003) estudou a extração de cutinase com ATPS composto por polietilenoglicol (PEG) e um sal de potássio e comparou um sistema de extração em batelada com a extração contínua em PRDC. A extração contínua proporcionou uma capacidade de separação 2,5 vezes maior do que a extração em batelada.

Os estudos de Carneiro-da-Cunha (1994) demonstraram a eficiência da extração da cutinase com coluna PRDC e sistemas miscelares.

Tambourgi et al. (1999) estudaram a extração das proteínas citocromo b5, protease e ascórbico oxirredutase utilizando o sistema bifásico PEG - fosfato de potássio, com uma coluna PRDC. Porto et al. (2000) trabalharam com a extração de albumina do soro bovino em coluna PRDC.

Sarubbo et al. (2003) também estudaram os mecanismos de transferência de proteína de soro bovino em uma PRDC, usando um sistema aquoso bifásico composto de PEG - polissacarídeo (goma do cajueiro).

2.6 Equilíbrio de fases

Para o bom desenvolvimento e o planejamento de um processo de refino por extração líquido-líquido é essencial o conhecimento do equilíbrio de fases do sistema de interesse. Como a ELL é uma operação de transferência de massa, ela é fortemente afetada por considerações do equilíbrio de fases. Portanto, o conhecimento exato das relações do equilíbrio é vital para as considerações quantitativas dos processos de extração. As quantidades necessárias do solvente são determinadas por estes dados. O parâmetro de equilíbrio fundamental é o coeficiente de distribuição ou partição k_i:

$$k_i = \frac{w_i^{II}}{w_i^{I}} \qquad (2.1)$$

na qual w_i^{II} é a fração mássica do componente i no extrato (II), e w_i^{I} é a fração mássica do componente i no refinado (I), desde que o equilíbrio tenha sido atingido.

O valor de k_i não é necessariamente maior que 1, embora valores elevados sejam desejáveis, uma vez que uma menor quantidade de solvente será necessária para a extração (Pina, 2001).

Considerando o uso de um solvente em particular para separar os componentes de uma solução binária por extração líquido-líquido, emprega-se o conceito de seletividade $S_{i/j}$, definida como:

$$S_{i/j} = \frac{k_i}{k_j} \tag{2.2}$$

na qual $S_{i/j}$ é a seletividade do solvente em relação aos componentes i e j.

O componente i é considerado o soluto a ser removido da alimentação e o componente j é a substância que permanece no refinado. Para a separação com o uso de um solvente ser possível, $S_{i/j}$ deve ser maior que 1,0. Quanto maior esta seletividade, mais efetiva será a operação (Cusack et al., 1991).

No caso da desacidificação de óleo vegetais por ELL, o componente i se refere ao ácido graxo a ser extraído. Já o componente j representa o óleo neutro remanescente na corrente de refinado.

Considerando que o sistema de interesse neste trabalho é composto basicamente por triacilgliceróis, ácidos graxos e solvente, e que os diferentes tipos de triacilgliceróis, por um lado, e os diferentes tipos de ácidos graxos, por outro lado, possuem muitas semelhanças físico-químicas entre si, tal sistema pode ser tratado como um pseudoternário ou pseudoquaternário, compostos respectivamente por:

triacilglicerol equivalente – ácido graxo equivalente – solvente anidro ou triacilglicerol equivalente – ácido graxo equivalente – solvente – água.

O diagrama de equilíbrio para esse tipo de sistema pode ser representado em coordenadas triangulares, como mostra a Figura 2.1 a seguir.

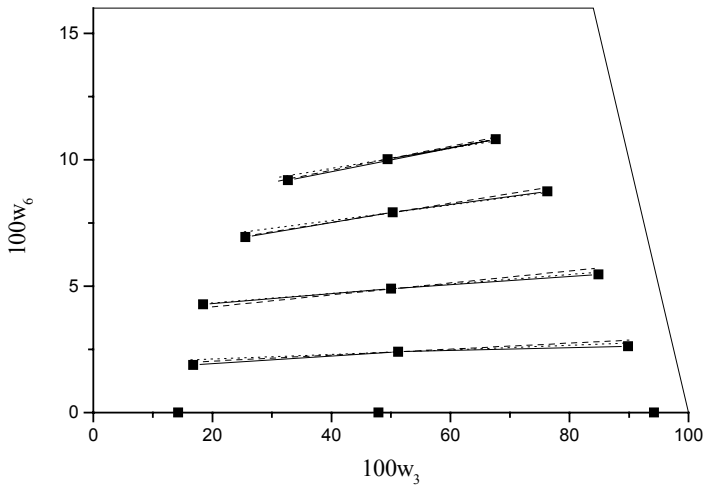

Figura 2.1. Dados de equilíbrio líquido-líquido para o sistema óleo de milho + ácido oléico (6) + etanol anidro (3) a 25°C (■experimental, - - - predição UNIFAC, . . .predição ASOG)*

O tratamento matemático do equilíbrio parte da seguinte relação termodinâmica válida para duas fases líquidas:

$$a_i^I = a_i^{II} = \gamma_i^I \cdot x_i^I = \gamma_i^{II} \cdot x_i^{II} \qquad (2.3)$$

na qual a é a atividade, x é a fração molar, γ o coeficiente de atividade, i representa cada um dos compostos presentes e os sobrescritos I e II se referem às fases oleosa (ou refinado) e alcoólica (ou extrato), respectivamente, em equilíbrio.

*Os dados de equilíbrio apresentados no diagrama acima foram medidos pela autora durante seu trabalho de Iniciação Científica. Dados de equilíbrio para esse sistema também foram medidos a diferentes temperaturas (Gonçalves et al., 1998).

Muitas expressões semi-empíricas têm sido propostas na literatura para relacionar os coeficientes de atividade à composição e temperatura da mistura. Todas estas expressões contêm parâmetros ajustáveis a dados experimentais, sendo que os principais modelos sugeridos para o equilíbrio líquido-líquido são as equações NRTL e UNIQUAC, cuja grande vantagem é permitir a extensão dos parâmetros obtidos pelo ajuste dos modelos a sistemas binários para o cálculo do equilíbrio em sistemas multicomponentes contendo os mesmos constituintes.

Batista et al. (1999a) utilizaram as equações NRTL e UNIQUAC para modelar o equilíbrio líquido-líquido de sistemas graxos compostos por óleo de canola/ ácido oléico comercial e diferentes solventes (metanol, etanol, isopropanol). No ajuste desses modelos aos dados de equilíbrio, o óleo de canola foi substituído por um triacilglicerol equivalente de peso molecular igual ao peso molecular médio do óleo. O mesmo tratamento foi dado ao ácido oléico comercial. Desta forma, o sistema ficou composto por um triacilglicerol equivalente, um ácido graxo equivalente e um solvente. Os ajustes obtidos foram excelentes, com baixíssimos desvios entre os valores de concentração experimentais e os calculados.

Neste trabalho, foram utilizados estes mesmos modelos para correlacionar os dados de equilíbrio. No entanto, como a intenção é trabalhar com solvente alcoólico hidratado, o sistema foi tratado como pseudoquaternário. Em função das diferenças físico-químicas significativas entre água e etanol, e a sua provável diferença de distribuição entre as duas fases do sistema, é recomendável que os dois componentes presentes no solvente misto sejam considerados separadamente no tratamento matemático. As equações NRTL e UNIQUAC, em unidade de fração mássica, estão apresentadas no Capítulo 3 adiante.

Vale notar que a equação UNIQUAC dispõe de dois parâmetros ajustáveis para cada par de componentes presentes no sistema, ao invés de três parâmetros, como o modelo NRTL. Outro aspecto a ser mencionado é que tanto a equação UNIQUAC quanto a equação NRTL foram originalmente formuladas em fração molar, mas as equações apresentadas no Capítulo 3 estão devidamente transformadas para unidades de fração mássica. Devido à grande diferença de massa molecular (MM) dos compostos que estarão presentes nos sistema estudados ($MM_{\text{triacilgliceróis}}$ = 833-879g/gmol; $MM_{\text{ácidos graxos}}$ = 256-282g/gmol; MM_{etanol} = 46g/gmol; $MM_{\text{água}}$ =18g/gmol), trabalhar com fração mássica permite um ajuste mais preciso do modelo aos dados experimentais do que empregar fração molar (Oishi & Prausnitz, 1978; Batista et al., 1999a).

2.7 Referências Bibliográficas

Antoniassi, R. Desacidificação de óleo de milho com etanol em Coluna de Discos Rotativos (RDC). Campinas, 1996 - Tese de Doutorado - Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas

Antoniassi, R., Esteves, W., Meirelles, A.J.A. Deacidification of corn oil with ethanol. I- Equilibrium Data. 9th World Congress of Food Science and Technology, Budapeste, Hungria, 1995.

Antoniassi, R., Esteves, W., Meirelles, A.J.A. Pretreatment of corn oil for physical refining. *J. Am Oil Chem. Soc*., v.75, p. 1411-1415, 1998.

Batista, E., Monnerat, S., Kato, K., Stragevitch, L., Meirelles, A.J.A. Liquid-liquid equilibrium for systems of canola oil, oleic acid and short-chain alcohols. *J. Chem. Eng. Data*, v.44, p. 1360-1364, 1999a.

Batista, E., Monnerat, S., Stragevitch, L., Pina, C.G., Gonçalves, C.B., Meirelles, A.J.A. Prediction of Liquid-liquid equilibrium for systems of vegetable oils, fatty acids and ethanol. *J. Chem. Eng. Data*, v.44, p.1365-1369, 1999b.

Carneiro- Da- Cunha, M. G., Aires- Barros, M. R., Tambourgi, E. B., Cabral, J. M. S. Recovery of a recombinant cutinase with reversed

micelles in a continuous perforated rotating disc contactor. *Biotechnology Techniques*, v.8, p.413-418, 1994.

Codex Alimentarius - Fats, oils and related products - volume eight, p.29-32 - Joint FAO/ WHO Food and Agriculture Organization of the United Nations and World Health Organization, Rome, 1993.

Cunha, M. T.; Costa, M.J.L.; Calado C.R.C.; Fonseca L.P; Aires-Barros M.R.; Cabral J.M.S. Integration of production and aqueous two-phase systems extraction of extracellular Fusarium solani pisi cutinase fusion proteins. *Journal of Biotechnology*, v.100, p. 55-64, 2003.

Cusack, R. W.; Fremeaux, P.; Glatz, D. A Fresh Look at Liquid-Liquid Extraction Part 1: Extraction Systems, *Chem. Eng*., v.2, p. 66-76, 1991.

Gonçalves, C. B.; Pina, C. G.; Meirelles, A. J. A. Dados de equilíbrio do sistema óleo de milho/ ácido oléico/ etanol. In CD-ROM do XIV Congresso Brasileiro de Ciência e Tecnologia de Alimentos, Rio de Janeiro, julho/1998.

Gonçalves, C.B., Pina, C.G., Meirelles, A.J.A. Liquid-liquid equilibrium data for the system corn oil/oleic acid/ethanol. 10th World Congress of Food Science & Technology, 3-8 outubro de 1999, Sydney, Australia, p.119.

Hamid, H. A.; May, C. Y.; Natural Antioxidants from Palm Oil. *Palm Oil Technical Bulletin*, v.3, n.4, Aug-Out 1997.

Hamm, W. Liquid-liquid extraction in the food industry. In: Lo, T.C., Baird, M.H., Hanson, C. Handbook of Solvent Extraction, p.593-597, John Wiley and Sons, New York, 1983.

Hartman, L. Tecnologia Moderna da indústria de óleos vegetais. Fundação Centro Tropical de Pesquisas e Tecnologia de Alimentos, 330p., Campinas, 1971.

Lawson, H.W. Standards for Fats and Oils. Westport: Avi Publishing Company, 1985.

Leibovitz, Z. & Ruckenstein, C. Our experiences in processing maize (corn) germ oil. *J. Am Oil Chem. Soc*., v.60, p.347A-351A, 1983.

Maza, A.;Ormsbee, R.A.; Strecler, L.R. Effects of deodorization and Steam, refining parameters on finished oil quality. *J. Am Oil Chem. Soc.*, v.69, p. 1003-1008, 1992.

Monnerat,S & Meirelles, A.J.A. Liquid-liquid equilibrium data for canola oil, oleic acid and short-chain alcohols systems. 9th World Congress of Food Science and Technology, Budapeste, Hungria, p.52, 1995.

Norris, F.A. Refining and Bleaching. In: Mattil, K.F.;Norris, F.A.; Stirton, A.J.;Swern,D. Bailey's Industrial Oil and Fat Products 3. ed. New York: John Wiley & Sons, 719-768, 1964.

Oishi, T; Prausnitz, J. M. Estimation of Solvent Activities in Polymer Solutions Using a Group-Contribution Method. *Ind. Eng. Chem. Process Des. Dev.*, v.17, p. 333-339, 1978.

OMB; Referência bibliográfica de documento eletrônico. Disponível na Internet: http://www.omb.com.br/dendeicultura/produtos 16 Dez. 1999.

Orthoefer, F.T. & Sinram, R.D. Corn oil: composition, processing and utilization. In: Watson, S.A. & Ramstad, P.E. Corn: Chemistry and Technology, St. Paul, Minnesota: *American Association of Cereal Chemists*, Inc., p.535-551, 1987.

Pina, C. G. Desempenho de uma coluna de discos rotativos na desacidificação do óleo de milho. 115p, Tese de Doutorado – Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas, 2001.

Pina, C.G. & Meirelles, A.J.A Deacidification of corn oil by solvent extraction in a perforated rotating disc column. *J. Am Oil Chem. Soc.,* v.77, p. 553-559, 2000.

Porto, A. L. F.; Sarubbo, L. A.; Lima-Filho, J. L.; Aires-Barros, M. R.; Cabral, J. M. S.; Tambourgi, E. B. Hydrodynamics and mass transfer in aqueous two-phase protein extraction using a continuous perforated rotating disc contactor. *Bioprocess Engineering*, v.22, p 215-218, 2000.

Sarubbo, L. A., Tambourgi, E. B., Porto, A. L. F., Oliveira L.A., Vieira, L. F.D. F., Lima- Filho, J. L., Campos- Takaki, G. M.; Performance of a perforated rotating disc contactor in the continuous extraction of a protein using the PEG–cashew-nut tree gum aqueous two-phase system. *Biochemical Engineering Journal*, 3721, p.1–7, 2003.

Shah, K. J.; Venkatesan, T. K. Aqueous Isopropyl Alcohol for Extraction of Free Fatty Acids from Oils. *J. Am. Oil Chem. Soc*., v.66, p.783-787, 1989.

Strecker, L.R.; Maza, A.; Winnie, G.F. Corn Oil - composition, processing and utilization. In: World Conference Proceedings. Edible fats and oils processing: Basic principles and modern practices. American Oil Chemists' Society. Proceedings, p.309-323, 1990.

Swern, D. Composition and Characteristics of Individual Fats and Oils. In: Mattil, K.F.; Norris, F.A.; Stirton, A.J. Bailey's Industrial Oil and Fat Products. 3 ed., New York: John Wiley & Sons, 165-247, 1964.

Tambourgi, E. B., Porto, A. L. F., Sarubbo, L. A., Oliveira L.A., Vieira, L. F.D. F., Lima-Filho, J. L., Behaviour of Proteins in Continuous Extraction

with Aqueous two- phase system. IcheaP-4, The Fourth Italian Conference on Chemical and Process Engineering, Florence- Italy, 2-5 May, 1999, p507-510.

Trujillo-Quijano, J.A. Óleo de Palma: Um Produto Natural. Revista Óleos & Grãos, p.19-23, Mar/Abr 1997.

Trujillo-Quijano, J.A. Óleo de Palma: Um Produto Premium. Revista Óleos & Grãos, p.30-39, Jul/Ago 1999.

Trujillo-Quijano, J.A. Aproveitamento Integral do Óleo de Palma. Tese de Doutorado - Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas, 1994.

Türkay, S. & Civelekoglu, H. Deacidification of sulfur olive oil. I. Single-stage liquid-liquid extraction of miscella with ethyl alcohol. *J. Am. Oil Chem. Soc.*, v.68, p.83-86, 1991a.

Türkay, S. & Civelekoglu, H. Deacidification of sulfur olive oil. II. Multi-stage liquid-liquid extraction of miscella with ethyl alcohol. *J. Am. Oil Chem. Soc.*, v.68, p.818-821, 1991b.

CAPÍTULO 3 - Liquid-Liquid Equilibrium Data for the System Corn Oil + Oleic Acid + Ethanol + Water at 298.15K

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Abstract

Deacidification of vegetable oils can be performed by liquid-liquid extraction. The present paper reports experimental data for the system corn oil + oleic acid + ethanol + water at 298.15 K and different water contents. The addition of water to the solvent reduces the loss of neutral oil in the alcoholic phase and improves the solvent selectivity. The experimental data were correlated by the NRTL and UNIQUAC models, with a global deviation of 0.89% and 0.92%, respectively.

3.1 Introduction

Crude vegetable oils consist predominantly of triacylglycerols and free fatty acids, with mono and diacylglycerols also present in lower level. They are obtained mainly by solid-liquid extraction from oil seeds using hexane petroleum fractions as solvent.[1,2] The refining processes of crude vegetable oils involve solvent stripping, degummimg, bleaching, deacidification and deodorization.[3,4] The removal of free fatty acids (FFA) is the most important stage of the purification process of oils, mainly because the yield of neutral oil in this operation has a significant effect in the cost of refining.[5] Besides, the presence of these compounds can adversely affect oil quality and stability to oxidation.

Deacidification of oils is usually performed by chemical or physical refining. However, for oils with high acidity, chemical refining causes high losses of neutral oil due to saponification and emulsification. Physical refining is also a feasible process for deacidification of highly acidic oils, since it results in less loss of neutral oil than the traditional process, but more energy is consumed. Moreover, in some cases, the refined oil is subject to undesirable alterations in color and a reduction

of stability to oxidation.[6] Thus, it is important to develop alternative processes for the deacidification of edible oils.

The deacidification of oils by liquid-liquid extraction using an appropriate solvent has been receiving attention due to its advantages in comparison to the physical and chemical refining. Kale et al.[7] studied the deacidification of crude rice bran oil by extraction with methanol. Turkay and Civelekoglu[8] investigated the liquid-liquid extraction of sulfur olive oil miscella in hexane with aqueous ethanol solutions. As this process is carried out at room temperature and atmospheric pressure, less energy is consumed and the oil is submitted to softer treatments. Besides, the liquid-liquid extraction has the advantages of avoiding the formation of waste products and reducing the loss of neutral oil. Furthermore, solvent stripping from refined oil and solvent recovery from extract stream can be easily carried out, because of the high difference between the boiling points of the solvent, fatty acids, and triacylglycerols. In fact, these operations can be accomplished by evaporation or distillation at relatively low temperatures, in most cases lower than 353.15K.[9]

Liquid-liquid equilibrium data for systems containing vegetable oils and fatty acids are relatively scarce in the literature, yet such information is essential for studying the deacidification of edible oils by solvent extraction. The present paper reports liquid-liquid equilibrium data for the system corn oil + oleic acid + ethanol + water at 298.15 K and different water contents. The addition of water to the solvent reduces the loss of neutral oil and improves the solvent selectivity.[9] The experimental data set was used for adjusting the parameters of the NRTL and UNIQUAC models.

3.2 Material

Refined corn oil of the Mazzola brand (Brazil) was utilized as a source of triacylglycerols, and commercial oleic acid of Riedel-deHaen as the source of fatty acids. The chemical composition of these reagents was determined by gas chromatography of fatty acid methyl esters (these data are published in BATISTA e*t al.*[10]) [†]. Corn oil contains 12 different isomer sets with molecular weights varying in the range (831.35 to 887.46) g/gmol. The commercial oleic acid contains 83.13 mass% oleic acid, 5.82 mass% palmitoleic acid, 5.05 mass% linoleic acid, 4.05 mass% palmitic acid and linolenic, stearic and myristic acids as minor components. The average molecular weight was 872.61 g/gmol for the corn oil, and 278.59 g/gmol for the commercial oleic acid.

The solvent used was ethanol, from Merck, with purity greater than 99.5%. Distilled water was used to obtain the aqueous solvent at different water contents (5, 8, 12, 18 wt%).

3.3 Experimental Procedure

Equilibrium cells similar to those of Silva et al.[11] were used for the determination of liquid-liquid equilibrium data. The cell temperature was controlled with a thermostatic bath (Cole-Parmer, Model 12101-15, accurate to 0.1K). Thermometers (Cole-Parmer Instrument Co) with subdivisions of 0.1K were used for monitoring the cell temperature. The component quantity was determined by weighing on a Sartorius analytical balance (Model A200 S, accurate to 0.0001 g). The mixture was stirred vigorously with a magnetic stirrer (FISATOM, Model 752A) for 20 min and left to rest for 12 h at least. This led to the formation of two clear and transparent phases, with a well-defined interface.

[†] As composições do ácido oléico e do óleo de milho, obtidas de Batista et al. (10), estão reproduzidas nas Tabelas A.1 e A.2 no anexo A

The oleic acid concentration was determined using potentiometric titration (Modified AOCS Method Ca 5a-40)[12] with an automatic burette (METROHM, Model Dosimat 715); the solvent was determined by evaporation in a vacuum oven (Model EIV-1). The water concentration was determined by Karl Fisher titration, according to AOCS method Ca 23-55.[13] Having determined the fatty acids concentration, solvent and water, the tryacylglicerols concentration was obtained by difference. The uncertainties of the concentrations varied within the following ranges: (0.02 to 0.24)% for oleic acid, (0.02 to 0.11) % for ethanol, (0.02 to 0.18)% for water and (0.03 to 0.24)% for corn oil, being the lowest figures obtained for the lowest concentrations.

3.4 Results

The overall experimental composition of the mixtures and the corresponding tie lines for the systems of interest are presented in Table 3.1. All concentrations are expressed as mass percentage.

Table 3.1. Quaternary Liquid-Liquid Equilibrium Data for the System Corn Oil (1) + Commercial Oleic Acid (2) + Solvent [Ethanol (3) + Water (4)] at 298.15K

Water conc. in solvent	Overall composition				alcohol phase (II)				oil phase (I)			
	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$
5 wt%	47.98	0	49.40	2.63	1.61	0	92.39	5.99	91.63	0	8.07	0.30
	47.21	2.53	47.72	2.54	2.33	2.40	89.93	5.34	87.79	2.24	9.65	0.33
	43.46	4.91	49.02	2.61	1.61	5.11	87.91	5.37	84.23	4.64	10.74	0.39
	39.25	9.87	48.32	2.57	4.33	10.26	80.39	5.03	75.20	9.35	14.89	0.56
	35.65	14.52	47.32	2.51	7.35	15.11	73.06	4.48	65.77	13.87	19.70	0.67
	29.85	19.99	47.62	2.53	16.72	20.25	59.17	3.86	50.11	19.29	28.51	2.09
8 wt%	49.97	0	46.03	4.00	0.66	0	88.38	10.96	93.76	0	5.64	0.60
	44.97	5.39	45.67	3.97	1.34	4.54	83.36	10.76	85.34	5.64	8.36	0.66
	39.78	9.81	46.38	4.03	1.71	8.73	79.45	10.11	77.96	10.39	10.88	0.76
	35.49	14.59	45.93	3.99	2.57	13.82	73.76	9.86	69.63	15.34	13.91	1.11
	30.99	19.77	45.30	3.94	5.14	19.33	66.49	9.03	58.97	20.97	18.40	1.66
12 wt%	50.07	0	43.94	5.99	0.44	0	85.59	13.97	94.57	0	5.10	0.34
	47.94	2.40	43.70	5.96	0.67	1.81	83.73	13.80	90.56	2.71	6.08	0.65
	45.85	4.92	43.32	5.91	0.82	3.80	81.62	13.76	86.09	5.65	7.59	0.66
	41.49	9.65	43.26	5.90	1.21	7.86	77.73	13.21	78.14	10.97	10.13	0.77
	34.15	14.79	44.93	6.13	2.03	12.99	72.49	12.49	69.08	16.54	13.37	1.01
	30.04	19.99	43.97	5.99	3.98	18.34	66.19	11.48	59.72	21.67	17.08	1.53
	24.59	25.06	44.30	6.04	8.31	24.04	57.41	10.24	48.27	26.35	22.83	2.55
18 wt%	50.35	0	40.72	8.94	0.20	0	79.52	20.28	95.71	0	3.68	0.61
	48.27	2.42	40.44	8.88	0.19	1.43	77.88	20.49	91.12	3.20	5.05	0.63
	44.10	4.91	41.81	9.18	0.21	2.84	76.69	20.26	86.36	6.63	6.24	0.77
	39.94	9.80	41.22	9.05	0.12	6.08	73.56	20.24	77.07	13.27	8.72	0.94
	34.70	15.08	41.18	9.04	0.07	10.30	69.60	20.03	66.88	20.10	11.60	1.43
	29.66	20.15	41.16	9.03	0.64	14.94	65.56	18.86	57,37	25.80	14,89	1.94
	25.22	24.89	40.91	8.97	3.23	19.77	59.94	17.07	48.58	29.92	18.56	2.94

3.5 Modeling

The experimental equilibrium data determined in this work and the data for corn oil + oleic acid + anhydrous ethanol reported by Batista et al.[10] were used together to adjust the parameters of the NRTL and UNIQUAC models. Due to the large difference in molecular weights of the components, mass fractions were used as unity of concentration.[14] In the NRTL model, the activity coefficient (γ_i) assumes the following form[‡]:

$$\ln\gamma_i = \frac{\sum_{j=1}^{K}\frac{\tau_{ji}G_{ji}w_j}{\overline{M}_j}}{\sum_{j=1}^{K}\frac{G_{ji}w_j}{\overline{M}_j}} + \sum_{j=1}^{K}\left[\frac{w_j G_{ji}}{\overline{M}_j\sum_{\ell=1}^{n}\frac{G_{\ell j}w_\ell}{\overline{M}_\ell}}\left(\tau_{ij} - \frac{\sum_{\ell=1}^{K}\frac{\tau_{\ell j}G_{\ell j}w_\ell}{\overline{M}_\ell}}{\sum_{\ell=1}^{K}\frac{G_{\ell j}w_\ell}{\overline{M}_\ell}}\right)\right] \tag{3.1}$$

where

$$G_{ij} = exp\left(-\alpha_{ij}\tau_{ij}\right) \tag{3.2}$$

$$\tau_{ij} = A_{ij}/T \tag{3.3}$$

$$\alpha_{ij} = \alpha_{ji} \tag{3.4}$$

In the equations above, A_{ij} and α_{ij} are the interaction parameters of the NRTL model, w is the mass fraction, $\overline{M}$ is the molecular weight of the compounds or pseudo-compounds, K is the number of compounds or pseudo-compounds and T is the equilibrium temperature (K).

The equations for the UNIQUAC model are given below:

$$\ln\gamma_i = \ln\gamma_i^{Comb} + \ln\gamma_i^{Res} \tag{3.5}$$

$$\ln\gamma_i^{Comb} = \frac{\ln\Psi_i'}{\ln\left(w_i/\zeta\,\overline{M}_i\right)} + 1 - \frac{\zeta\,\overline{M}_i\Psi_i'}{w_i} + \frac{z}{2}\overline{M}_i\,q_i'\ln\frac{\theta_i'}{\Psi_i'} - \frac{z}{2}\overline{M}_i\,q_i'\left(1-\frac{\Psi_i'}{\theta_i'}\right) \tag{3.6}$$

[‡] Em unidades de fração mássica: $a_i = \gamma_i \cdot w_i$

where $$\zeta = \sum_{j=1}^{K} \frac{w_j}{\overline{M}_j} \tag{3.7}$$

$$\theta_i' = \frac{q_i' w_i}{\sum_{j=1}^{K} q_j' w_j}; \quad \Psi_i' = \frac{r_i' w_i}{\sum_{j=1}^{K} r_j' w_j} \tag{3.8}$$

and

$$\ln\gamma_i^{Res} = \overline{M}_i \, q_i' \left[1 - \ln\left(\sum_{j=1}^{K} \theta_j' \tau_{ji} \right) - \sum_{j=1}^{K} \left(\theta_i' \tau_{ij} \Big/ \sum_{k=1}^{K} \theta_k' \tau_{kj} \right) \right] \tag{3.9}$$

where $$\tau_{ij} = \exp\left(-\frac{A_{ij}}{T} \right) \tag{3.10}$$

In eqs 3.5 to 3.10, $\ln\gamma_i^{Comb}$ and $\ln\gamma_i^{Res}$ represent the combinatorial and residual contributions, respectively, and $\overline{M}_i$ is the average molecular weight of the corn oil or the commercial fatty acid. As usual in the UNIQUAC model, the lattice coordination number z was assumed to be equal to 10. A_{ij} and A_{ji} are the adjustable parameters. The adjustments were made by treating the system as a pseudoquaternary one, composed by a single triacylglycerol having the corn oil average molecular weight, a representative fatty acid with the molecular weight of the commercial oleic acid, ethanol and water. The values of r_i' and q_i' for the UNIQUAC model were calculated via eq 3.11:

$$r_i' = \frac{1}{\overline{M}_i} \sum_{j}^{C} x_j \sum_{k}^{G} v_k^{(j)} R_k; \qquad q_i' = \frac{1}{\overline{M}_i} \sum_{j}^{C} x_j \sum_{k}^{G} v_k^{(j)} Q_k \tag{3.11}$$

where x_j is the molar fraction of the triacylglycerols of the corn oil or the fatty acids of the commercial oleic acid and $v_k^{(j)}$ is the number of groups k in molecule j. C is the number of components in the oil or in the commercial fatty acid and G the number of groups. As already mentioned, the compositions of the corn oil and the commercial oleic

acid used in the present paper are reported by Batista et al.[10] The parameters R_k and Q_k were obtained from Magnussen et al.[15] The calculated r_i' and q_i' values are furnished in Table 3.2.

Table 3.2. Parameters r_i' e q_i' for Corn Oil, Riedel-deHaen Oleic Acid, Ethanol and Water

compound	r_i'	q_i'
corn oil (1)	0.044023	0.035675
commercial oleic acid (2)	0.045142	0.037157
ethanol (3)	0.055905	0.056177
water (4)	0.051069	0.077713

The parameter estimation was based on the minimization of the objective function of composition, following the procedure developed by Stragevitch and d'Avila.[16]

$$S = \sum_{m}^{D} \sum_{n}^{N} \sum_{i}^{K-1} \left[\left(\frac{w_{inm}^{I,ex} - w_{inm}^{I,calc}}{\sigma_{w_{inm}^{I}}} \right)^2 + \left(\frac{w_{inm}^{II,ex} - w_{inm}^{II,calc}}{\sigma_{w_{inm}^{II}}} \right)^2 \right] \qquad (3.12)$$

where D is the total number of groups of data, N is the total number of tie lines, and K is the total number of compounds or pseudo-compounds in the group of data m. The subscripts i, n and m are compound, tie line and group number, respectively, and the superscripts I and II are the phases; ex and $calc$ refer to experimental and calculated concentrations. $\sigma_{w_{inm}^{I}}$ and $\sigma_{w_{inm}^{II}}$ are the standard deviations observed in the compositions of the two liquid phases. Adjusted parameters of the NRTL and UNIQUAC models are shown in Tables 3.3 and 3.4, respectively.

Table 3.3. NRTL Parameters for the System Corn Oil (1) + Commercial Oleic Acid (2) + Ethanol (3) + Water (4) at 298.15K

pair ij	A_{ij}/K	A_{ji}/K	α_{ij}
12	198.39	-289.66	0.37020
13	-166.14	1620.9	0.40115
14	17.625	2911.2	0.17723
23	-652.55	778.64	0.33541
24	3500.0	3483.4	0.25428
34	-10.984	-173.64	0.15018

Table 3.4. UNIQUAC Parameters for the System Corn Oil (1) + Commercial Oleic Acid (2) + Ethanol (3) + Water (4) at 298.15K

pair ij	A_{ij}/K	A_{ji}/K
12	273.64	-212.27
13	246.94	-54.214
14	3032.0	-148.81
23	56.468	-80.240
24	235.76	49.931
34	337.46	-279.92

The deviations between experimental and calculated compositions in both phases for each system can be found in Table 3.5. These deviations are calculated according to eq 3.13:

$$\Delta w = 100\sqrt{\frac{\sum_{n}^{N}\sum_{i}^{K}\left[\left(w_{i,n}^{I,ex}-w_{i,n}^{I,calc}\right)^2+\left(w_{i,n}^{II,ex}-w_{i,n}^{II,calc}\right)^2\right]}{2\,N\,K}} \qquad (3.13)$$

Table 3.5. Mean Deviations in Phase Compositions

	Δw (%)	
system	NRTL	UNIQUAC
corn oil + oleic acid + anhydrous ethanol	0.82	0.84
corn oil + oleic acid + 5% aqueous ethanol	1.27	1.39
corn oil + oleic acid + 8% aqueous ethanol	0.82	0.79
corn oil + oleic acid + 12% aqueous ethanol	0.71	0.79
corn oil + oleic acid + 18% aqueous ethanol	0.81	0.79
Global Deviation	0.89	0.92

Figures 3.1 and 3.2 show the experimental points and calculated tie-lines for the systems corn oil/ oleic acid/ 5% aqueous ethanol and corn oil/ oleic acid/ 8% aqueous ethanol. The equilibrium diagrams were plotted in triangular coordinates. For representing the pseudoquaternary systems in triangular coordinates, ethanol + water was admitted as a mixed solvent. Figures 3.1 and 3.2 indicate that both models provided a good representation of phase compositions, but the NRTL model allowed a better estimation of the fatty acid concentration in both phases.

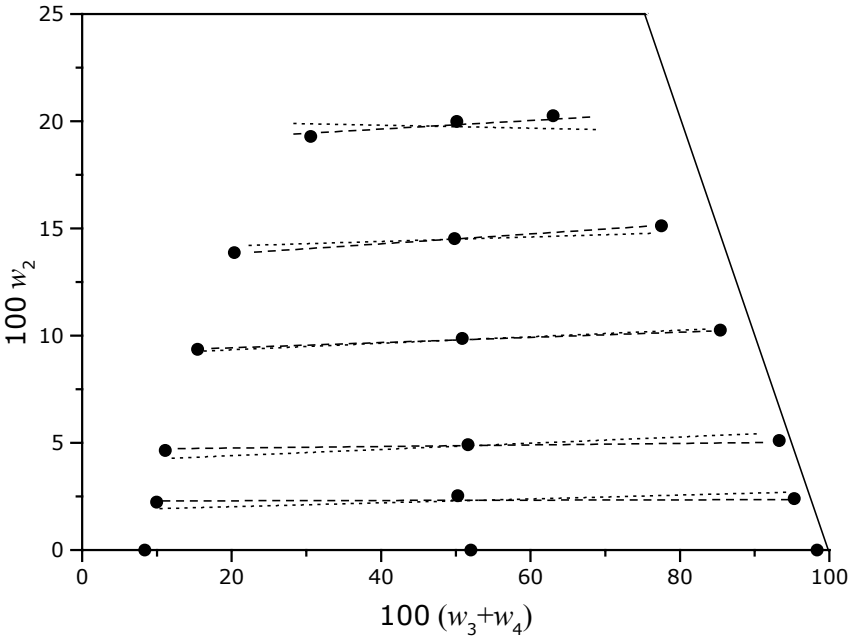

Figure 3.1. System of corn oil (1) + oleic acid (2) + 5% aqueous solvent [ethanol (3) + water (4)] at 298.15 K: experimental (●); (- - -) NRTL; (·····) UNIQUAC

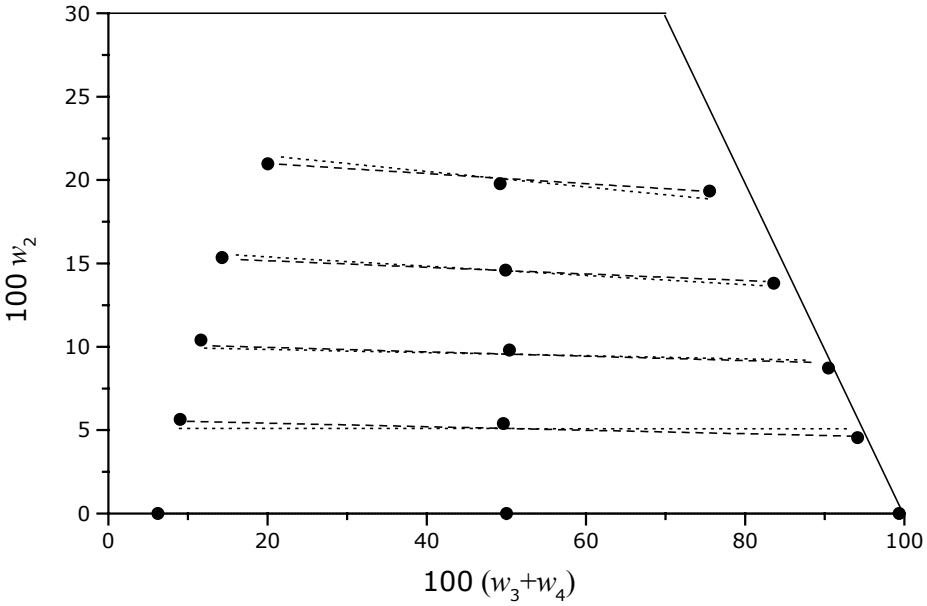

Figure 3.2. System of corn oil (1) + oleic acid (2) + 8% aqueous solvent [ethanol (3) + water (4)] at 298.15 K: experimental (●); (- - -) NRTL; (·····) UNIQUAC

Figure 3.3 presents the distribution coefficient at 298.15K for the systems studied in the present work. As can be observed, the addition of water in the solvent decreases fatty acid distribution coefficient, which is calculated according to eq 3.14 below. These results indicate that aqueous ethanol has a lower capacity for extraction of fatty acids. Otherwise, the addition of water increases the solvent selectivity and consequently reduces the loss of neutral oil in solvent extraction. Solvent selectivity can be calculated by eq 3.15 below.

$$k_i = \frac{w_i^{II}}{w_i^{I}} \tag{3.14}$$

$$S = \frac{k_2}{k_1} \tag{3.15}$$

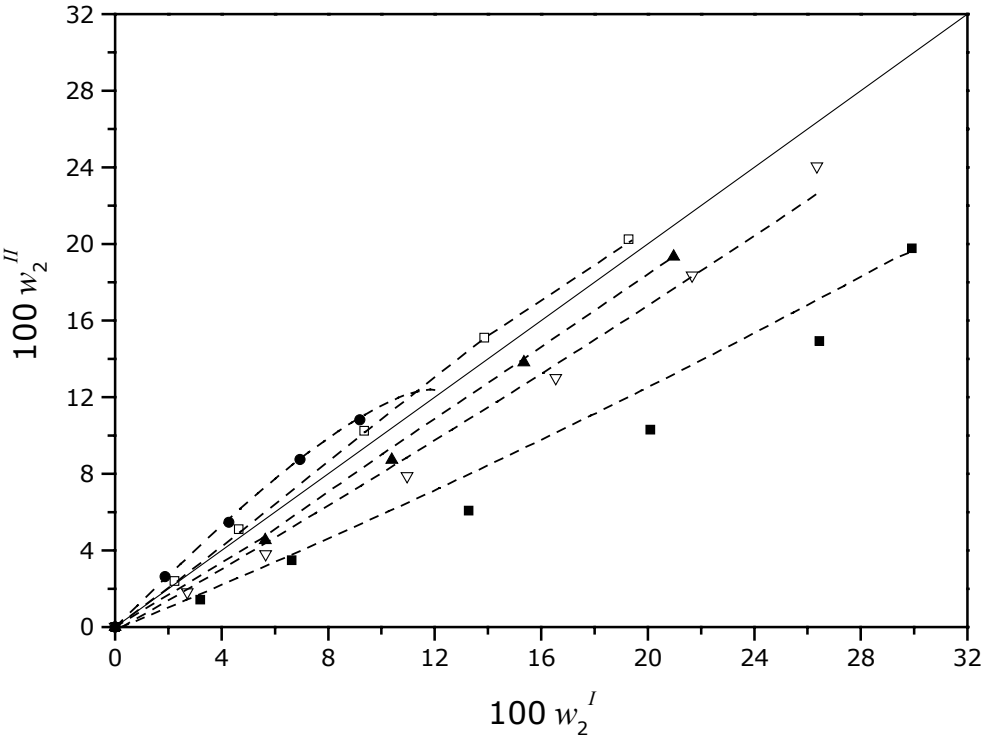

Figure 3.3. Distribution diagram at 298.15 K for systems of corn oil (1) + oleic acid (2) + ethanol (3) + water (4): (●) anhydrous ethanol; (□) 5wt% aqueous ethanol; (▲) 8wt% aqueous ethanol; (▽) 12wt% aqueous ethanol; (■) 18wt% aqueous ethanol; (- - -) NRTL[§]

[§] A Figura A.1 no anexo A apresenta o desempenho do modelo UNIQUAC.

Figure 3.3 also shows that the NRTL model reproduces very well the experimental distribution coefficients, except for the system with 18% aqueous ethanol.

In order to have a better insight about the influence of the water content on the performance of the solvent, flash calculations were performed for a crude oil containing 5wt% of FFA and different water concentrations in the solvent. The mass ratio between crude oil and aqueous solvent was fixed at the value 1:1, corresponding to a concentration of 2.5wt%. of FFA in the overall mixture. The results were presented in Figure 3.4.

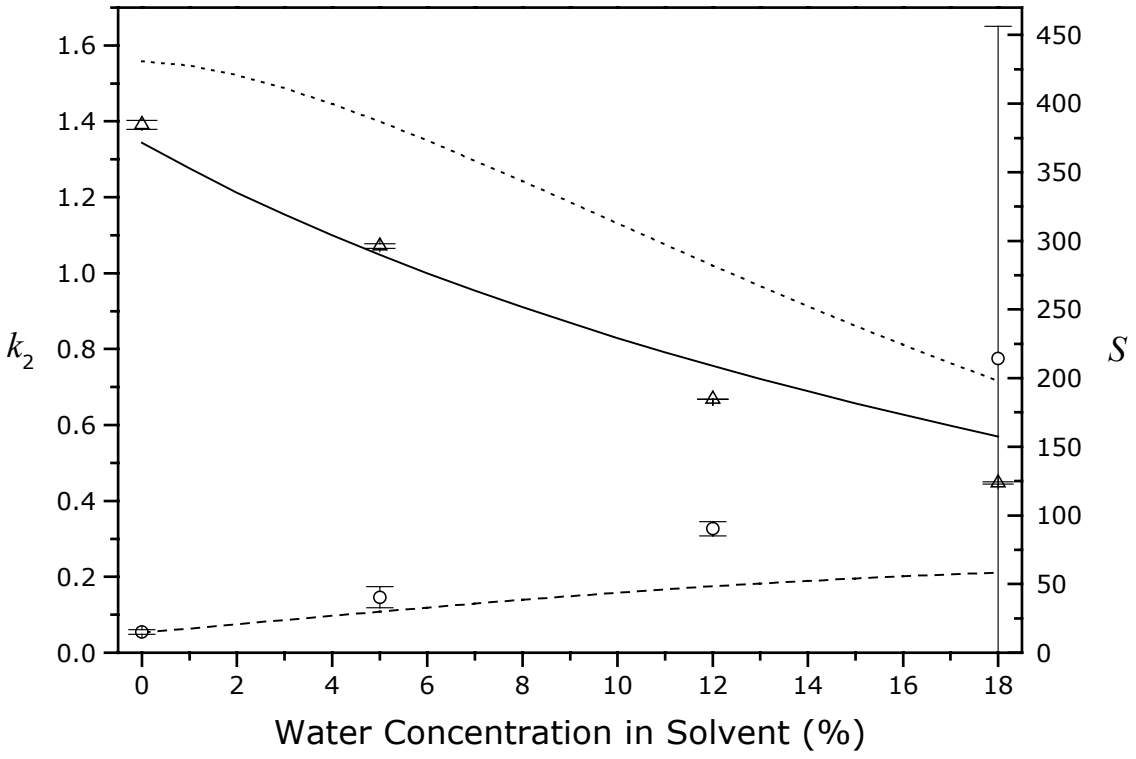

Figure 3.4. Fatty acid distribution coefficient and selectivities for systems of corn oil (1) + oleic acid (2) + ethanol (3) + water (4): (—) calculated k_2 by the NRTL model; (·····) calculated k_2 by the UNIQUAC model; (- - -) calculated S by the NRTL model; (△) experimental k_2; (○) experimental S.

As can be seen, the addition of water causes a significant increase in the solvent selectivity. In spite of the small difference between the global deviations obtained for the two models (see Table 3.5), their estimations of the fatty acid distribution coefficient are significantly different (Figure 3.4). Such result confirms that the NRTL model provided a better description of the fatty acid concentrations. The selectivity values estimated by the NRTL model are close to the experimental results, except for aqueous ethanol containing 18wt% of water. In this last case, the uncertainty of the experimental selectivity, calculated by error propagation, is very high (see the error bars in Figure 3.4). In fact, for such system (18wt% of water in the solvent), the oil concentration in the alcoholic phase is very low and exhibits a relative high experimental uncertainty, which influences the uncertainties of the oil distribution coefficient and the solvent selectivity.

3.6 Conclusion

Liquid-liquid equilibrium data for systems containing corn oil + oleic acid + ethanol + water were experimentally determinated at 298.15 K. The addition of water in the solvent causes a decrease in the fatty acid distribution coefficient and an increase in the selectivity.

Despite the complexity of the studied systems, the estimated parameters for the NRTL and UNIQUAC models are representative, since the description of the liquid-liquid equilibrium for all the systems had presented mean deviations lower than 1.39% in relation to the experimental data. These parameters enable the modeling and simulation of liquid-liquid extractors using the proposed solvents.

Moreover, the results obtained allow one to conclude that a water content in the range of 4-6 wt% in the aqueous ethanol is appropriate

for deacidification by solvent extraction, as it still provides values of fatty acid distribution coefficient around unity, and high values for the solvent selectivity (larger than 25).

3.7 Literature Cited

(1) Fornari, T.; Bottini, S; Brignole, E. A Application of UNIFAC to Vegetable Oil-Alkane Mixtures. *J. Am. Oil Chem. Soc*. **1994**, 71, 391-395.

(2) González, C.; Resa, J. M.; Ruiz, A.; Gutiérrez, J. I. Densities of Mixtures Containing *n*-Alkanes with Sunflower Seed Oil at Different Temperatures. *J. Chem. Eng. Data*. **1996**, 41, 796-798.

(3) Leibovitz, Z.; Ruckenstein, C. Our Experiences in Processing Maize (Corn) Germ Oil. *J. Am. Oil Chem. Soc*. **1983**, 60, 347A-351A.

(4) Cvengros, J. Physical Refining of Edible Oils. *J. Am. Oil Chem. Soc*. **1995**, 72, 1193-1196.

(5) Lo, T. C.; Baird, M. H.; Hanson, C. Handbook of Solvent Extraction New York: John Wiley & Sons, 1983, p.980.

(6) Antoniassi, R.; Esteves, W.; Meirelles, A. J. A. Pretreatment of Corn Oil for Physical Refining. *J. Am. Oil Chem. Soc*. **1998**, 75, 1411-1415.

(7) Kale, V.; Katikaneni, S. P. R.; Cheryan, M. Deacidifying Rice Brain Oil by Solvent Extraction and Membrane Technology. *J. Am. Oil Chem. Soc*. **1999**, 76, 723-727.

(8) Turkay, S.; Civelekoglu, H. Deacidification of Sulfur Olive Oil. l. Single Stage Liquid-Liquid Extraction of Miscella with Ethyl Alcohol. *J. Am. Oil Chem. Soc*. **1991**, 68, 83-86.

(9) Pina, C. G.; Meirelles, A. J. A. Deacidification of Corn Oil by Solvent Extraction in a Perforated Rotating Disc Column. *J. Am. Oil Chem. Soc*. **2000**, 77, 553-559.

(10). Batista, E.; Monnerat, S.; Stragevitch, L.; Pina, C. G.; Gonçalves, C. B.; Meirelles, A.J.A. Prediction of liquid-liquid equilibrium for systems of vegetable oils, fatty acids, and ethanol. *J. Chem. Eng. Data*. **1999**, 44, 1365-1369.

(11) Silva, L. H. M.; Coimbra, J. S.; Meirelles, A. J. A. Equilibrium Phase Behavior of Poly(ethylene glycol) + Potassium Phosphate + Water Two Phase Systems at Various pH and Temperatures. *J. Chem. Eng. Data*. **1997**, 42, 398-401.

(12) A.O.C.S. *Official and Tentative Methods of the American Oil Chemists' Society,* Press, 3 ed., Champaign, v.1, 1993.

(13) A.O.C.S. *Official methods and recommended practices of the American Oil Chemists' Society*, Press, 3 ed., Champaign, v. 1-2, 1988.

(14) Batista, E.; Monnerat, S.; Kato, K.; Stragevitch, L.; Meirelles, A. J. A. Liquid-Liquid Equilibrium for Systems of Canola Oil, Oleic Acid and Short-Chain Alcohols. *J. Chem. Eng. Data*. **1999**, 44, 1360-1364.

(15) Magnussen, T.; Rasmussen, P.; Fredenslund, A. Unifac Parameter Table for Prediction of Liquid-Liquid Equilibria. *Ind. Eng. Chem. Process Des*. *Dev*. **1981**, 20, 331-339.

(16) Stragevitch, L.; d'Avila, S. G. Application of a Generalized Maximum Likelihood Method in the Reduction of Multicomponent Liquid-Liquid Equilibrium Data. *Braz. J. Chem. Eng.* **1997**, 14, 41-52.

3.8 Acknowledgements

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CAPÍTULO 4 - Liquid-Liquid Equilibrium Data for the System Palm Oil + Fatty Acids + Ethanol + Water at 318.2K

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Abstract

Deacidification of vegetable oils can be easily performed by liquid-liquid extraction using appropriate solvents like ethanol. This paper reports experimental data for systems containing palm oil + palmitic/ oleic acid + ethanol + water at 318.2 K and different water contents. The addition of water to the solvent reduces the loss of neutral oil in the alcoholic phase and improves the solvent selectivity. The experimental data were correlated by the NRTL and UNIQUAC models. For systems with palmitic acid, the global deviations between experimental and calculated concentrations were 0.75% for the NRTL model and 0.61% for the UNIQUAC equation. For systems with oleic acid, the corresponding values were 1.05% and 0.84%. The adjusted interaction parameters were used to predict the equilibrium of bleached palm oil + aqueous ethanol at 318.2 K, with deviation between calculated and experimental mass percentages not higher than 1.60%.

Keywords: Liquid-liquid equilibria; Experimental Data; Solvent extraction; Deacidification; Palm oil; Fatty acids; Aqueous ethanol

4.1 Introduction

In the last decades, the production of palm oil showed a huge increase, as it plays an important role in the international market of oils and fats, covering several sectors of chemical and food industries [1]. Another important characteristic of palm oil is its stability, which is due to the presence of natural antioxidant substances, such as carotenoids and tocopherols, and its balanced ratio (1:1) between saturated (mainly palmitic) and unsaturated (mainly oleic) fatty acids [2]. However, palm oil is still susceptible to factors that can harm its quality. For instance,

the action of the enzymes in the palm fruit and of the microbial lipases induces hydrolysis and forms high levels of free fatty acids (FFAs) [3]. Although this free acidity is usually expressed as palmitic acid mass%, data on literature [4] indicate that palm oil contains considerable concentrations of triacylglycerols with oleic acid in position 1 or 3 (very susceptible to hydrolysis), such as POO, SOO, OOO, suggesting a significant presence of free oleic acid in crude oil.

This high acidity in crude oil complicates the refining process by traditional methods. Chemical refining is responsible for great losses of neutral oil in the soapstock after alkali neutralization. Physical refining, generally used for palm oil, involves a degummimg pretreatment, a bleaching step, and a high-temperature (513.2-533.2 K), low-pressure (1-3mmHg) deodorization/ deacidification step. This last stage is responsible for great losses of nutraceutical compounds, such as the carotenoids (destroyed by the high temperature) and the tocopherols (partially steam stripped) [5]. In this way, it is important to study alternative processes for the deacidification of palm oil.

Liquid-liquid extraction is a separation process that takes advantage of the relative solubilities of solutes in immiscible solvents. A partial separation occurs when the components of the original mixture have different relative solubilities in the selected solvent phase [6]. The deacidification of oils by liquid-liquid extraction by means of an appropriate solvent is receiving attention because of the low energy and reagent consumption, avoiding pollution and submitting the oil to softer treatments. Moreover, such process reduces the loss of neutral oil and may preserve the nutraceutical compounds. Kim et al. [7] and Kale et al. [8] studied the deacidification of crude rice bran oil by extraction with methanol. Turkay and Civelekoglu [9] investigated the liquid-liquid extraction of sulfur olive oil micelle in hexane with aqueous ethanol

solutions. Bhatacharyya et al. [10] and Shah and Venkatesan [11] studied the deacidification of rice bran and groundnut oils using aqueous isopropanol as solvent. All these studies confirmed a reduction in the acidic value of the oil.

Information on liquid-liquid equilibrium data for systems containing vegetable oils and fatty acids is essential for studying the deacidification of edible oils by solvent extraction. Batista et al. [12] reported liquid-liquid equilibrium data for the systems containing canola oil, oleic acid and short chain alcohols (such as methanol, anhydrous ethanol, isopropanol, n-propanol and aqueous ethanol) at different temperatures. Gonçalves et al. [13] and Rodrigues et al. [14] measured liquid-liquid equilibrium data for the systems containing corn and rice bran oils, respectively, oleic acid, ethanol and water at 298.2 K.

The present paper reports liquid-liquid equilibrium data for model systems containing palm oil + palmitic acid + ethanol + water and palm oil + oleic acid + ethanol + water at 318.2 K and with different water contents. The addition of water to the solvent reduces the loss of neutral oil and improves the solvent selectivity [13,14,15]. The experimental data set was used to adjust the parameters of the NRTL and UNIQUAC models. The adjusted interaction parameters were used to predict the liquid–liquid equilibrium of real systems containing bleached palm oil + aqueous ethanol.

4.2 Material

Refined and bleached palm oils were provided by Agropalma (Brazil), and palmitic and oleic acids were purchased from Acròs and Merck, respectively. The bleached palm oil (BPO) was previously pretreated by Agropalma until the bleached step of its conventional

refining process. The BPO sample had a high free acidity, since the oil had not yet been submitted to the final deodorization/deacidification step. The fatty acid composition of all these fatty reagents was determined by gas chromatography of fatty acid methyl esters, according to the official method (1-62) of the AOCS [16]. Samples were prepared in the form of fatty acid methyl esters, according to the official method (2-66) of the AOCS [17]. An HP 5890 gas chromatograph with a flame ionization detector and an integrator was used under the following experimental conditions: capillary fused silica column of cyanopropylsiloxane (60 m x 0.25 μm x 0.32mm), hydrogen as the carrier gas at a rate of 2.5 ml/min, an injection temperature of 523.2 K, a column temperature of 423.2 – 473.2 K (1.3K/min), and a detector temperature of 553.2 K. The fatty acid methyl esters were identified by comparison with the retention times of the NU CHECK Inc. standards (Elysian, IL) and the quantification was accomplished by internal normalization.

The statistical methodology suggested by Antoniosi Filho et al. [18] was used to obtain the probable triacylglycerol composition of the refined and bleached palm oils, starting from the fatty acid composition.

In order to determine the fatty acid composition of the free acidity and to compute its average molecular mass, it was necessary to separate the FFAs from the bleached oil. For this, the oil (previously heated at 343.2 K) was submitted to alkali neutralization with sodium hydroxide (NaOH) 18 ºBe (12.69% in water w/w), i.e., a saponification reaction, in which NaOH reacted with FFAs producing fatty acids salts (also called soap) and water. This reaction was carefully performed in order to guarantee that all the free fatty acids were consumed by the sodium hydroxide. For this reason, the FFA concentration was previously

determined by titration, and an amount of sodium hydroxide 10% above the stoichiometric requirement was added to the bleached oil.

The mixture formed by bleached oil at 343.2 K + NaOH solution was vigorously stirred for 15 minutes and, after that, centrifuged at 8825 *g* (corresponding to 7000 rpm) for 10 minutes to promote the soap separation. In order to avoid that the soap dragged neutral oil, the mixture was further washed with petroleum ether (which only solubilizes the oil), followed by centrifugation, for at least five times. The fatty acids salts obtained were esterified and then analyzed by gas chromatography, using the methodology described above.

The solvents used were anhydrous ethanol, from Merck, with purity greater than 99.5%, and alcoholic solutions containing 3.11±0.03, 5.76±0.02, 6.10±0.02, 10.20±0.05 and 12.41±0.01 mass% water, prepared by the addition of deionized water (Milli-Q, Millipore) to the anhydrous ethanol.

The refined palm oil had a residual acidity of 0.030±0.003 mass%, and the bleached oil used in this work presented 3.88±0.01 mass%. These acidity values were calculated considering all the free fatty acids (FFAs) composition, determined as described above.

4.3 Experimental Procedure

The liquid-liquid equilibrium experiments were accomplished following the same methodology described in Gonçalves et al. [13]. Model fatty systems containing free fatty acids and triacylglycerols were prepared by the addition of known quantities of palmitic or oleic acid to refined palm oil, with the free fatty acids in oil, w_{2O}, varying within the range of 0 to 0.36 mass fraction. The model fatty systems were mixed with the ethanolic solvents, in the mass ratio 1:1 of oil to solvent, at

318.2±0.1 K, in order to determine the liquid-liquid equilibrium data necessary to adjust the NRTL and the UNIQUAC parameters. Bleached palm oil was mixed with aqueous ethanol containing 3.11±0.03, 5.76±0.02, 10.20±0.05 or 12.41±0.01 mass% water, in mass ratios of 2:1, 1:1 and 1:2. These data were used to test the prediction capacity of the adjusted NRTL and UNIQUAC parameters.

With the systems in equilibrium, the compositions of both phases were measured. The palmitic/ oleic acid concentration was determined by titration (official method 2201 of the IUPAC [19]) with an automatic burette (METROHM, Model Dosimat 715); the solvent was determined by evaporation in a vacuum oven (Napco model 5831). The water concentration was determined by Karl Fisher titration, according to AOCS method Ca 23-55 [20]. Having determined the fatty acid concentration, the solvent and the water, the triacylglycerol concentration was obtained by difference. All measurements were performed at least in triplicate, and the standard deviations varied within the following ranges: $(0.04 \cdot 10^{-2}$ to 0.13)% for fatty acids, $(0.05 \cdot 10^{-2}$ to 0.98)% for ethanol, $(0.06 \cdot 10^{-1}$ to 0.07)% for water and $(0.07 \cdot 10^{-1}$ to 0.98)% for palm oil.

In order to have an insight about the free fatty acids composition in the phases in equilibrium of a real system, a single experimental datum was measured mixing bleached palm oil and 6.39±0.03 mass% aqueous ethanol, in a mass ratio 1:1 of oil to solvent. The alcoholic and oil phases were evaporated in a vacuum oven, and the free fatty acids were separated from remaining oils of each phase and analyzed following the same methodology adopted for the FFAs from bleached oil and described above.

4.4 Results

The fatty acid compositions of refined palm oil (RPO), bleached palm oil (BPO) and Acròs palmitic acid are presented in Table 4.1. The corresponding data for commercial oleic acid from Merck are published in Rodrigues et al. [14].

Table 4.1. Fatty Acid Composition of Refined Palm Oil (RPO), Bleached Palm Oil (BPO) and Acròs Palmitic Acid

Symbol	Fatty Acid		*MM*[b] (g.gmol^{-1})	RPO		BPO		Palmitic Acid	
				% Molar	% Mass	% Molar	% Mass	% Molar	% Mass
L	lauric	C12:0[a]	200.32	0.65	0.49	0.90	0.67	0.23	0.18
M	myristic	C14:0	228.38	1.10	0.93	2.01	1.70	2.61	2.33
P	palmitic	C16:0	256.43	44.69	42.49	42.15	40.07	96.22	96.44
Po	palmitoleic	C16:1	254.42	0.08	0.07	0.50	0.48	---	---
S	stearic	C18:0	284.49	4.66	4.91	4.02	4.23	0.94	1.05
O	oleic	C18:1	282.47	39.56	41.44	33.69	35.28	---	---
Li	linoleic	C18:2	280.45	8.86	9.22	14.69	15.27	---	---
Le	linolenic	C18:3	278.43	---	---	0.76	0.79	---	---
A	arachidic	C20:0	312.54	0.40	0.46	1.30	1.51	---	---

[a] In CX:Y, X=number of carbons, Y=number of double bonds
[b] *MM* = molecular mass.

As Table 4.1 shows, palmitic and oleic acids are the most important fatty acids present in both oils. The Acròs palmitic acid contains 96.44 mass% palmitic acid, 2.61 mass% myristic acid and linolenic and stearic acids as minor components. The commercial oleic acid from Merck contains 78.02 mass% oleic acid, 11.97 mass% linoleic acid, 5.36 mass% palmitic acid, 1.42 mass% stearic acid, 1.13 mass% lauric acid and myristic, palmitoleic, linolenic and arachidic acids as minor components.

The probable triacylglycerol compositions of the refined and bleached palm oils, obtained from the fatty acid compositions and shown in Table 1, are indicated in Table 4.2.

Table 4.2. Probable Triacylglycerol Composition of Palm Oil

Group	Main Triacyl-glycerol	*MM*[b] (g.gmol^{-1})	RPO		BPO	
			% Molar	% Mass	% Molar	% Mass
46:0[a]	MPP	779.29	---	---	0.82	0.76
46:1	LOP	777.28	0.85	0.78	0.99	0.90
48:0	PPP	807.35	5.91	5.63	5.43	5.17
48:1	MOP	805.33	1.55	1.47	2.43	2.31
48:2	OOL/MLiP[c]	803.31	0.66	0.62	1.27	1.21
50:0	PPS	835.40	1.83	1.80	1.56	1.54
50:1	POP	833.38	28.75	28.27	21.50	21.15
50:2	PLiP	831.37	7.06	6.92	10.53	10.33
50:3	MOLi	829.35	---	---	1.32	1.29
52:0	PPA	863.45	---	---	0.63	0.65
52:1	POS	861.44	5.98	6.07	4.13	4.20
52:2	POO	859.42	23.42	23.74	17.15	17.39
52:3	POLi	857.41	9.91	10.02	13.60	13.76
52:4	PLiLi	855.39	1.12	1.13	3.72	3.76
54:1	POA	889.49	0.82	0.86	1.50	1.58
54:2	SOO	887.48	2.49	2.60	2.13	2.23
54:3	OOO	885.46	5.70	5.96	4.39	4.59
54:4	OOLi	883.44	3.25	3.39	4.37	4.55
54:5	OLiLi	881.43	0.70	0.73	1.99	2.07
56:2	OOA	915.53	---	---	0.53	0.57

[a] In X:Y. X=number of carbons (except carbons of glycerol), Y=number of double bonds

[b] *MM* = molecular mass

[c] In case of refined palm oil OOL is the main triacylglycerol in the isomer set 48:2. For bleached palm oil the main triacylglycerol in this isomer set is MLiP.

In Table 4.2, the main triacylglycerol represents the component of greatest concentration in the isomer set with x carbons and y double bonds. Refined and bleached palm oils contain 16 and 20 different isomer sets, respectively, with molecular masses varying in the range of 777.28 to 915.53 g/gmol.

The calculated average molecular masses were 847.78 g/gmol for the refined palm oil, 847.44 g/gmol for the bleached palm oil, 255.84 g/gmol for the palmitic acid and 278.96 g/gmol for the oleic acid.

Table 4.3 shows the fatty acids composition of the free acidity in bleached palm oil, as well as the results obtained by analyzes of the phases in equilibrium of the system bleached palm oil + 6.39 mass% aqueous ethanol.

Table 4.3. Fatty Acid Composition of FFAs in BPO, FFAs in Oil Phase (*I*), FFAs in Alcoholic Phase (*II*)

Symbol	Fatty Acid	*MM*[b] (g.gmol^{-1})	FFAs in BPO		FFAs in *I*[c]		FFAs in *II*[c]	
			% Molar	% Mass	% Molar	% Mass	% Molar	% Mass
L	C12:0[a]	200.32	1.12	0.83	0.42	0.31	0.43	0.32
P	C16:0	256.43	46.81	44.58	47.75	45.4	44.64	42.33
S	C18:0	284.49	3.56	3.76	4.76	5.02	3.87	4.07
O	C18:1	282.47	39.19	41.11	37.38	39.15	39.61	41.38
Li	C18:2	280.45	9.17	9.55	9.38	9.75	11.22	11.64
A	C20:0	312.54	0.16	0.18	0.32	0.37	0.22	0.26

[a] In CX:Y, X=number of carbons, Y=number of double bonds
[b] *MM* = molecular mass
[c] System bleached palm oil + 6.39 mass% aqueous ethanol, mass ratio oil to solvent equal to 1:1

In Table 4.3, the composition of FFAs in BPO shows that oleic acid is present in a concentration very close to that of palmitic acid (in mass %). Also, both equilibrium phases for the system bleached palm oil + 6.39 mass% aqueous ethanol present similar FFAs compositions among themselves and to the free acidity of the bleached oil. The molecular masses obtained were 269.70 g/gmol for fatty acids in the oil phase and 270.41 g/gmol for fatty acids in the alcoholic phase. Such values are close to the molecular mass calculated for FFAs from bleached oil, 269.30 g/gmol, indicating that is reasonable to assume this value for all the acidity calculations in the phases.

The overall experimental composition of the mixtures and the corresponding tie-lines for the pseudo-ternary model systems, composed by refined palm oil + palmitic or oleic acid + anhydrous ethanol, and pseudo-quaternary ones, composed by refined palm oil + palmitic or oleic acid + ethanol + water, are presented in Tables 4.4 and 4.5, respectively.

Table 4.6 shows the overall experimental composition of the mixtures and the corresponding tie-lines for the systems composed by bleached palm oil + ethanolic solution. All concentrations are expressed as mass percentage.

Table 4.4. Liquid-Liquid Equilibrium Data for the Systems Refined Palm Oil (1) + Palmitic Acid (2) + Anhydrous Ethanol (4) and Refined Palm Oil (1) + Oleic Acid (3) + Anhydrous Ethanol (4) at 318.2K

Overall Composition			Alcohol Phase (*II*)			Oil Phase (*I*)		
$100w_1$	$100w_2$	$100w_4$	$100w^{II}_1$	$100w^{II}_2$	$100w^{II}_4$	$100w^{I}_1$	$100w^{I}_2$	$100w^{I}_4$
48.40	0.00	49.97	11.64	0.00	88.36	75.00	0.00	25.00
48.40	1.50	50.10	14.81	1.62	83.57	71.53	1.42	27.05
46.94	3.00	50.07	18.42	3.39	78.18	65.72	2.72	31.56
45.41	4.49	50.10	24.37	5.02	70.61	58.20	4.23	37.58
$100w_1$	$100\ w_3$	$100\ w_4$	$100w^{II}_1$	$100w^{II}_3$	$100w^{II}_4$	$100w^{I}_1$	$100w^{I}_3$	$100w^{I}_4$
48.63	1.50	49.87	14.04	1.58	84.39	71.70	1.48	26.82
46.92	3.01	50.06	17.86	3.20	78.63	66.28	2.94	30.78
45.51	4.54	49.95	24.17	4.85	70.98	58.89	4.40	36.71

Table 4.5. Liquid-Liquid Equilibrium Data for the Systems Refined Palm Oil (1) + Palmitic Acid (2) + Solvent [Ethanol (4) + Water (5)] and Refined Palm Oil (1) + Oleic Acid (3) + Solvent [Ethanol (4) + Water (5)] at 318.2K

$100w_{5S}$[a]	Overall Composition				Alcohol Phase (*II*)				Oil Phase (*I*)			
	$100w_1$	$100w_2$	$100w_4$	$100w_5$	$100w^{II}{}_1$	$100w^{II}{}_2$	$100w^{II}{}_4$	$100w^{II}{}_5$	$100w^{I}{}_1$	$100w^{I}{}_2$	$100w^{I}{}_4$	$100w^{I}{}_5$
6.10	49.90	0.00	47.04	3.06	2.85	0.00	90.79	6.36	88.12	0.00	11.30	0.58
	47.94	2.00	47.01	3.06	3.19	2.23	88.32	6.25	84.93	1.75	12.68	0.64
	45.91	3.99	47.03	3.07	3.97	4.24	85.73	6.06	80.71	3.64	14.87	0.77
	43.90	6.00	47.05	3.05	5.08	6.18	83.10	5.64	77.12	5.78	16.28	0.83
	41.88	8.02	47.05	3.05	6.33	8.21	80.02	5.44	73.22	7.71	18.00	1.07
	39.97	9.93	47.03	3.07	8.03	10.04	76.60	5.33	67.80	9.58	21.43	1.19
12.41	50.15	0.00	43.67	6.19	0.72	0.00	86.50	12.78	91.66	0.00	7.71	0.62
	48.01	2.00	43.79	6.20	0.90	1.76	85.31	12.03	87.70	2.55	8.91	0.84
	46.15	4.02	43.65	6.18	1.42	3.27	83.55	11.75	84.30	4.63	10.11	0.96
	43.56	5.94	44.23	6.26	1.40	5.40	81.80	11.40	80.86	6.78	11.25	1.11
	39.67	9.92	44.16	6.25	2.19	9.31	77.55	10.94	73.19	11.03	14.20	1.59
	35.85	13.94	43.98	6.23	4.14	13.00	72.17	10.69	65.55	15.03	17.32	2.10
	31.96	17.97	43.85	6.21	7.75	16.92	65.07	10.27	55.85	19.13	22.29	2.73

Table 4.5. (Continued)

	$100w_1$	$100w_3$	$100w_4$	$100w_5$	$100w^{II}{}_1$	$100w^{II}{}_3$	$100w^{II}{}_4$	$100w^{II}{}_5$	$100w^{I}{}_1$	$100w^{I}{}_3$	$100w^{I}{}_4$	$100w^{I}{}_5$
6.10	48.97	1.07	46.91	3.04	2.67	1.06	90.28	5.99	86.84	1.11	11.66	0.39
	45.96	3.99	47.00	3.05	3.97	4.24	86.16	5.63	80.71	3.64	15.01	0.63
	44.26	4.93	47.72	3.09	4.34	5.07	85.05	5.54	79.83	4.85	14.63	0.71
	42.21	8.02	46.46	3.31	6.33	8.21	80.19	5.27	73.22	7.71	18.26	0.81
12.41	47.90	2.00	43.88	6.22	0.69	1.76	86.51	11.04	88.15	2.36	8.50	0.99
	45.95	4.00	43.84	6.21	0.86	3.49	84.74	10.92	84.78	4.72	9.28	1.23
	43.98	6.01	43.80	6.21	0.76	5.33	83.06	10.85	80.68	6.95	10.99	1.38
	40.03	10.01	43.76	6.20	0.58	9.03	80.56	9.83	73.91	11.33	13.22	1.53
	35.94	13.97	43.87	6.22	2.41	12.81	75.35	9.43	64.63	15.55	17.74	2.08
	32.49	17.51	43.80	6.21	3.85	16.43	71.44	8.28	58.88	19.07	20.79	2.26

[a] $100w_{5S}$ = water mass percentage in the solvent

Table 4.6. Liquid-liquid Equilibrium Data for the System Bleached Palm Oil [Oil (1) + Free Fatty Acids (2+3)] + Solvent [Ethanol (4) + Water (5)] at 318.2K

$100w_{5S}$[a]	Overall Composition				Alcohol Phase (*II*)				Oil Phase (*I*)			
	$100w_1$	$100w_{2+3}$[b]	$100w_4$	$100w_5$	$100w^{II}_1$	$100w^{II}_{2+3}$[b]	$100w^{II}_4$	$100w^{II}_5$	$100w^{I}_1$	$100w^{I}_{2+3}$[b]	$100w^{I}_4$	$100w^{II}_5$
3.11	31.83	1.28	64.81	2.08	5.66	1.39	90.34	2.61	80.68	1.12	17.52	0.68
	48.04	1.94	48.47	1.55	6.78	2.27	87.94	3.01	78.34	1.76	19.09	0.81
	63.91	2.58	32.47	1.04	6.91	3.15	87.07	2.87	77.05	2.48	19.55	0.92
5.76	30.89	1.25	63.95	3.91	3.04	1.31	90.11	5.54	85.64	1.19	12.16	1.01
	47.43	1.91	47.74	2.92	3.09	2.07	89.27	5.57	84.15	1.78	12.95	1.12
	62.92	2.54	32.55	1.99	2.88	2.82	87.49	6.81	83.27	2.41	12.82	1.50
6.39	47.83	1.98	46.98	3.21	3.56	2.02	88.29	6.13	84.34	1.79	12.74	1.13
10.20	32.53	1.31	59.41	6.75	1.73	1.24	86.74	10.29	88.03	1.48	9.49	1.00
	48.00	1.94	44.95	5.11	1.76	1.73	85.43	11.08	86.90	2.15	9.83	1.12
	64.19	2.59	29.83	3.39	1.68	2.32	83.93	12.07	86.35	2.71	9.70	1.24
12.41	31.83	1.29	58.58	8.30	0.86	1.22	87.44	10.48	88.67	1.56	8.88	0.89
	47.46	1.92	44.34	6.28	0.76	1.71	86.35	11.18	88.04	2.18	8.64	1.14
	63.64	2.57	29.60	4.19	0.72	2.30	86.49	10.49	87.54	2.71	8.68	1.07

[a] $100w_{5S}$ = water mass percentage in the solvent
[b] 2+3 represents the total acidity, considering the composition given in Table 4.3, in which the main fatty acids are palmitic (2) and oleic (3)

The tie-lines based on the experimental data were determined by linear regression of each corresponding set of overall, oil and alcoholic phase concentrations. Correlation coefficients around 99% were obtained for all tie-lines, indicating a good alignment between the experimental data, relative to both overall and phase concentrations.

4.5 Modeling

The experimental equilibrium data obtained for the model systems were used to adjust the parameters of the NRTL and UNIQUAC models. These equations were originally formulated in molar fraction, but, due to the large difference in molecular masses of the components, mass fractions were used as unity of concentration [12,21]. The NRTL and UNIQUAC equations for the activity coefficients, with concentrations in mass fraction, can be found in Gonçalves et al. [13].

The parameter adjustments were made by treating the model systems refined palm oil + palmitic acid + anhydrous ethanol and refined palm oil + oleic acid + anhydrous ethanol as pseudo-ternary ones. The model systems refined palm oil + palmitic acid + ethanol + water and the model systems refined palm oil + oleic acid + ethanol + water were treated as pseudo-quaternary ones.

For the adjustment process, the palm oil was treated as a single triacylglycerol with the oil's average molecular mass. The same supposition was extended to the fatty acids (palmitic and oleic) and assuming that the different components within each fatty compound class behave in a very similar way in the liquid-liquid system under analysis. In this case, a pseudo-compound having the corresponding average physical-chemical properties can adequately replace such components. Such hypothesis will be tested by the adjustment of the

parameters to the model systems and the subsequent use of these parameters in the equilibrium prediction for systems containing bleached palm oil.

The values of r_i' and q_i' for the UNIQUAC model, given in Table 4.7, were calculated using equation 4.1:

$$r_i' = \frac{1}{\overline{M}_i}\sum_j^C x_j \sum_k^G v_k^{(j)} R_k; \qquad q_i' = \frac{1}{\overline{M}_i}\sum_j^C x_j \sum_k^G v_k^{(j)} Q_k \tag{4.1}$$

where x_j is the molar fraction of the triacylglycerols of the palm oil or the fatty acids of the palmitic/oleic acid, and $v_k^{(j)}$ is the number of groups k in the molecule j. $\overline{M}_i$ is the average molecular mass of the palm oil or the fatty acid, C is the number of components in the oil or in the fatty acid and G is the number of groups in molecule j. The parameters R_k and Q_k were obtained from Magnussen et al. [22].

Table 4.7. Parameters r_i' e q_i' for Refined Palm Oil, Acròs Palmitic Acid, Ethanol, Water, Bleached Palm Oil and Free Fatty Acids in Bleached Palm Oil

compound	r_i'	q_i'
Refined palm oil	0.044186	0.035894
Palmitic acid	0.045401	0.037559
Oleic acid	0.045127	0.037140
Ethanol	0.055905	0.056177
Water	0.051069	0.077713
Bleached palm oil	0.044101	0.035819
FFAs in bleached palm oil	0.045247	0.037317

The parameter estimation was based on the minimization of the objective function of composition, ($OF(w)$, equation 4.2 below), following the procedure developed by Stragevitch and d'Avila [23].

$$OF(w) = \sum_{m}^{D} \sum_{n}^{N} \sum_{i}^{K-1} \left[\left(\frac{w_{inm}^{I,ex} - w_{inm}^{I,calc}}{\sigma_{w_{inm}^{I}}} \right)^2 + \left(\frac{w_{inm}^{II,ex} - w_{inm}^{II,calc}}{\sigma_{w_{inm}^{II}}} \right)^2 \right] \quad (4.2)$$

where D is the total number of groups of data, N is the total number of tie-lines, and K is the total number of compounds or pseudo-compounds in the group of data m. The subscripts i, n and m are pseudo-compound, tie-line and group number, respectively, and the superscripts I and II are the phases; ex and $calc$ refer to experimental and calculated concentrations. $\sigma_{w_{inm}^{I}}$ and $\sigma_{w_{inm}^{II}}$ are the standard deviations observed in the compositions of the two liquid phases. The values adopted for these deviations were 0.075 for systems containing palmitic acid and 0.080 for systems containing oleic acid, which represent the average values of the standard deviations observed in the experimental data. The adjusted parameters of the NRTL and UNIQUAC models are shown in Table 4.8.

Table 4.8. NRTL and UNIQUAC Interaction Parameters between Refined Palm Oil (1), Palmitic Acid (2), Oleic Acid (3) + Ethanol (4) + Water (5) at 318.2 ± 0.1K

pair ij	Thermodynamic Model				
	NRTL			UNIQUAC	
	A_{ij}/K	A_{ji}/K	α_{ij}	A_{ij}/K	A_{ji}/K
12	194.78	-301.89	0.20562	289.00	-229.39
13	10.282	-153.22	0.50603	225.43	-198.39
14	-338.36	1583.7	0.45078	215.60	-44.697
15	52.665	3122.5	0.18914	4147.1	-171.86
24	-791.09	709.02	0.24280	31.404	-99.657
25	3195.9	1865.6	0.26666	127.95	294.36
34	-376.26	172.46	0.57000	180.18	-220.29
35	6962.8	7922.6	0.10000	486.37	513.48
45	-67.100	-255.04	0.47000	332.23	-330.34

The deviations between experimental and calculated compositions for each system can be found in Table 4.9. These deviations are calculated according to equation 4.3:

$$\Delta w = 100 \sqrt{\frac{\sum_{n}^{N}\sum_{i}^{K}\left[\left(w_{in}^{I,ex} - w_{in}^{I,calc}\right)^2 + \left(w_{in}^{II,ex} - w_{in}^{II,calc}\right)^2\right]}{2\,N\,K}} \qquad (4.3)$$

Table 4.9. Mean Deviations in Phase Compositions

	System	Δw (%)	
		NRTL	UNIQUAC
Correlation	Refined palm oil + palmitic acid + anhydrous ethanol	0.25	0.35
	Refined palm oil + palmitic acid + 6.10 mass% aqueous ethanol	0.81	0.42
	Refined palm oil + palmitic acid + 12.41 mass% aqueous ethanol	1.24	0.84
	Global Deviation	0.75	0.61
	Refined palm oil + oleic acid + anhydrous ethanol	0.79	0.71
	Refined palm oil + oleic acid + 6.10 mass % aqueous ethanol	0.99	0.55
	Refined palm oil + oleic acid + 12.41 mass% aqueous ethanol	1.17	1.02
	Global Deviation	1.05	0.84
Prediction[a]	Bleached palm oil + 3.11 mass % aqueous ethanol	0.73	1.16
	Bleached palm oil + 5.76 mass %aqueous ethanol	1.06	0.63
	Bleached palm oil + 6.39 mass % aqueous ethanol	0.48	0.43
	Bleached palm oil + 10.20 mass % aqueous ethanol	0.71	0.52
	Bleached palm oil + 12.41 mass % aqueous ethanol	1.52	1.60
	Global Deviation	1.02	1.03

[a] The interaction parameters between palmitic (2) and oleic (3) acids were assumed to be zero

Figures 4.1 and 4.2 show the experimental points and calculated tie-lines for the systems palm oil/ palmitic acid/ 6.10 mass% aqueous ethanol and palm oil/ oleic acid/ 6.10 mass% aqueous ethanol, respectively. The equilibrium diagrams are plotted in triangular coordinates. In order to represent the pseudo-quaternary systems in triangular coordinates, ethanol + water was admitted as a mixed solvent. Figures 4.1 and 4.2 indicate that both thermodynamic models provided a good representation of the phase concentrations.

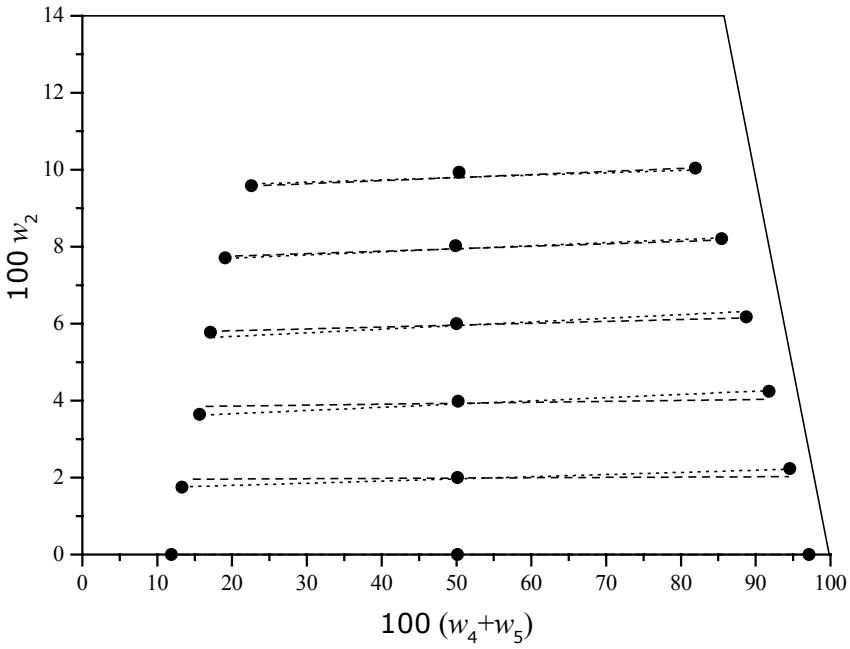

Figure 4.1. System of refined palm oil (1) + palmitic acid (2) + 6.10±0.02 mass% aqueous solvent [ethanol (4) + water (5)] at 318.2 K: experimental (●); (- - -) NRTL; (·····) UNIQUAC

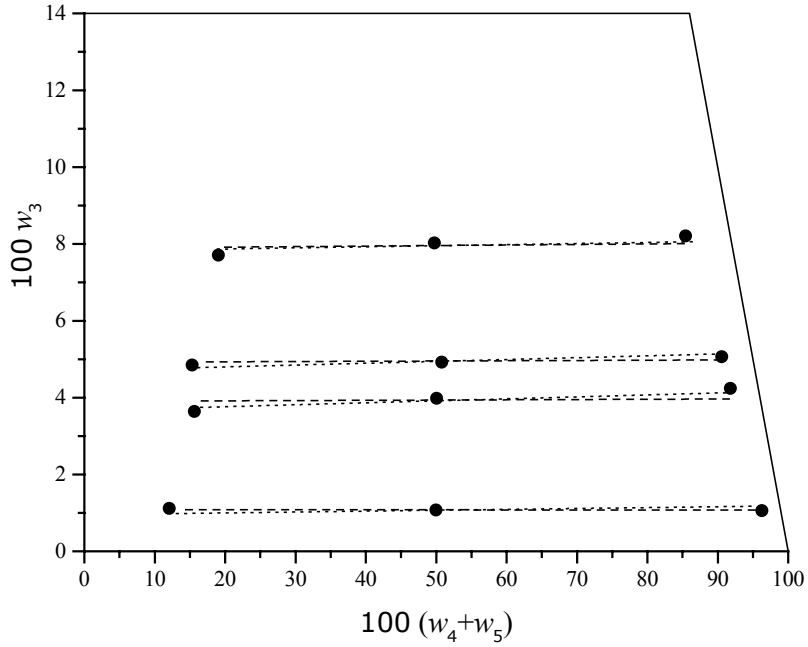

Figure 4.2. System of refined palm oil (1) + oleic acid (3) + 6.10±0.02 mass% aqueous solvent [ethanol (4) + water (5)] at 318.2 K: experimental (●); (- - -) NRTL; (·····) UNIQUAC

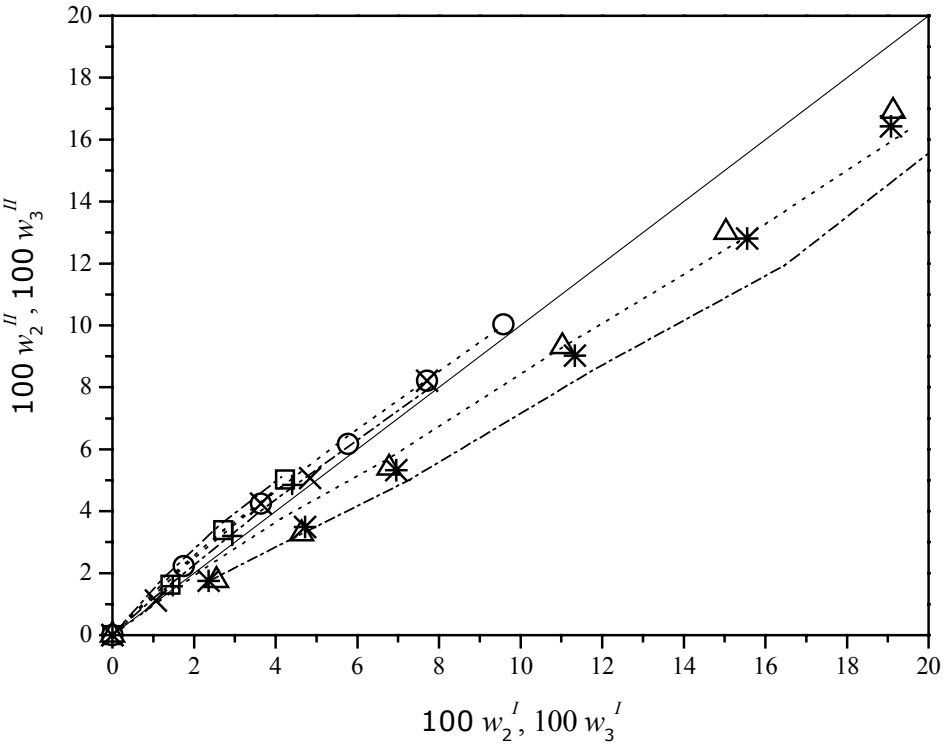

Figure 4.3. Distribution diagram at 318.2K for systems of refined palm oil (1) + palmitic acid (2) + ethanol (4) + water (5): (□) anhydrous ethanol; (○) 6.10 mass% aqueous ethanol; (△) 12.41 mass% aqueous ethanol; (·····) UNIQUAC; and refined palm oil (1) + oleic acid (3) + ethanol (4) + water (5): (+) anhydrous ethanol; (×) 6.10 mass% aqueous ethanol; (✳) 12.41 mass% aqueous ethanol; (-·-·-) UNIQUAC

Figure 4.3 presents the distribution of palmitic and oleic acids between the phases for the model systems. It shows that the addition of water in the solvent decreases the fatty acid distribution coefficients, which is calculated according to equation 4.4 below. Moreover, it should be noted that both fatty acids are distributed in a very similar way between the phases. The curves obtained for the systems with anhydrous ethanol and 6.10 mass% aqueous ethanol are located above the diagonal, indicating that the distribution coefficient for these systems is larger than 1. On the other hand, the system with 12.41 mass% water presents distribution coefficients smaller than 1. This

means that the larger the concentration of water, the smaller the solvent capacity for extracting the fatty acids. However, this effect is not significant in the range of water concentrations between 0 and 6 mass%, becoming more effective only for water content higher than 6 mass%. Although it is not necessary that for distribution coefficient to be larger than 1, high values are desirable, since either a smaller amount of solvent or a lower number of equilibrium stages can be used for the extraction. Figure 4.3 also shows that the UNIQUAC model provides a good representation of the experimental fatty acid distribution coefficients, except for the system with 12.41 mass% aqueous ethanol. In this case, the UNIQUAC model overestimates the palmitic acid distribution coefficients for low levels of free acidity and underestimates the oleic acid distribution coefficients for high levels of acidity.

$$k_i = w_i^{II} / w_i^{I} \tag{4.4}$$

Although the effect of the water content on the fatty acid distribution coefficient is not significant, its effect is very expressive in relation to the size of the phase splitting region. In fact, the addition of water increases the solvent selectivity (calculated by equation 4.5 below), i.e., it allows the solvent to distinguish the fatty acids and the triacylglycerols in a better way, therefore removing the FFAs without extracting the neutral oil. The solvent concentration in the refined oil also decreases with the addition of water, facilitating its removal. The effect of the water content in the solvent selectivity can be better visualized in the Figure 4.4.

$$S_{i/j} = k_i / k_j \tag{4.5}$$

where, in this case, i represents the fatty acid and j the oil.

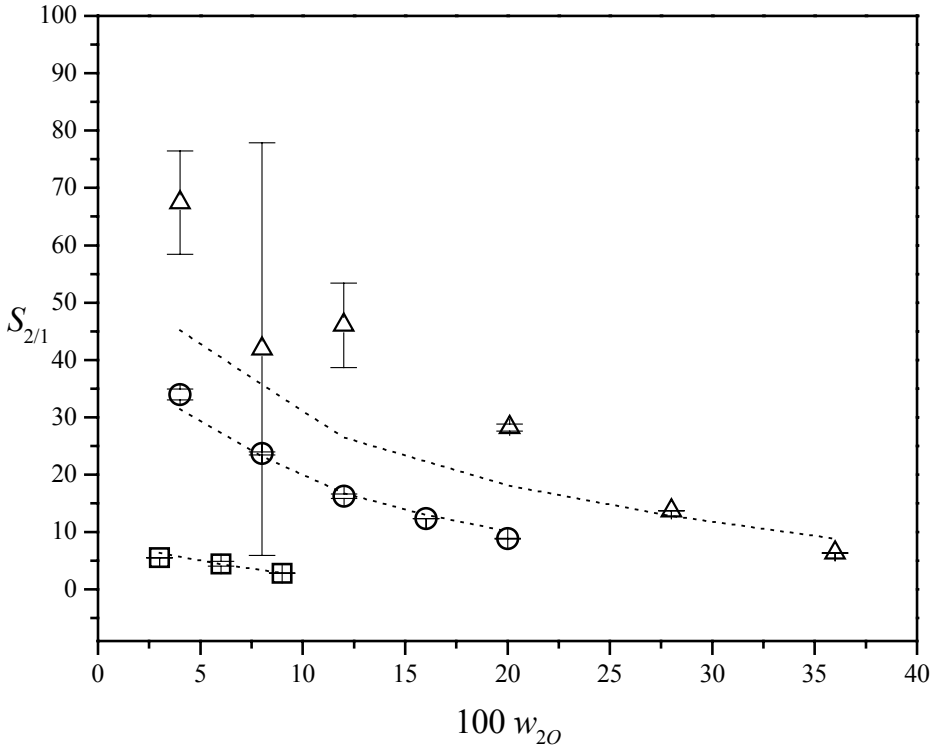

Figure 4.4. Selectivity ($S_{2/1}$) for different solvents: (□) anhydrous ethanol; (○) 6.10 mass% aqueous ethanol; (△) 12.41 mass% aqueous ethanol; (·····) UNIQUAC[**]

As can be seen in Figure 4.4, the solvent selectivity, $S_{2/1}$, decreases with the increase of the free palmitic acid in crude oil, w_{2O}, but in general it is much larger for solvents with higher water concentrations. It should be noted that w_{2O} in Figure 4.4 indicates the free fatty acid content in the systems refined palm oil + palmitic acid. As in all experiments a mass ratio 1:1 of oil to solvent was used, the w_{2O}–values are approximately twice that of the fatty acid concentration in the overall system, w_2, given in Tables 4.4 and 4.5. The error bars indicated in Figure 4 were calculated by error propagation, using equation 4.4 and 4.5 and the uncertainties of the concentrations in the phases in equilibrium. The error bars were very small for the systems with 0 and

[**] A Figura A.2 no anexo A apresenta o desempenho do modelo NRTL

6.10 mass% water content in the solvent, but they were large for the system with 12.41 mass% water content in the solvent, specially for low levels of free fatty acids in the oil. In fact, an increase of water content in the solvent and a reduction of free acidity in the oil promote a significant decrease of both the water concentration in the oil phase (w^{I}_{4}) and of the loss of neutral oil in the alcoholic phase (w^{II}_{1}). In these situations, w^{II}_{1} exhibits a relatively high experimental uncertainty, which influences the uncertainties of the oil distribution coefficient and the experimental solvent selectivity. This is especially valid for the system with 12.41 mass% of water and acidity lower than 12.5 mass%. Furthermore, in the case of the experimental datum with 8 mass% of palmitic acid in the oil, the fatty acid concentration in the oil phase presented a relatively higher uncertainty (around 0.13 mass%), which resulted in a high uncertainty for the respective distribution coefficient and consequently for the selectivity. Figure 4.4 also shows that the UNIQUAC model reproduces very well the solvent selectivity, except for the system with 12.41 mass% water content in the solvent. For such system, the oil concentration in the alcoholic phase is very low and it exhibits a relatively high experimental uncertainty, which influences the uncertainties of the oil distribution coefficient and the experimental solvent selectivity.

4.6 Prediction of Liquid-Liquid Equilibrium

The adjusted parameters for the NRTL and UNIQUAC models were tested in the prediction of liquid-liquid equilibrium (LLE) for the system bleached palm oil + ethanol + water at 318.2 K. Liquid-liquid flash calculations for the estimation of phase compositions were performed based on the overall experimental composition of the mixtures. The r_i'

and q_i' values for bleached palm oil and free fatty acids are given in Table 4.7.

Since equilibrium data for model systems containing the two main fatty acids together were not determined, the interaction parameters between them were fixed at zero (A_{23}=0 and A_{32}=0, for both thermodynamic models, and α_{23}=0 for the NRTL model) for the LLE prediction. Indeed, considering that the two compounds are very similar, the activity coefficient (γ) of a solution containing only palmitic and oleic acid is very close to one.

The deviations between experimental and estimated compositions in both phases were calculated according to equation 4.3 and are shown in Table 4.9. Figures 4.5 and 4.6 show the experimental points and the predicted tie-lines for the systems bleached palm oil + 3.11 mass% aqueous ethanol and bleached palm oil + 10.20 mass% aqueous ethanol, respectively. As the phases of these systems were not analyzed in relation to the composition of their free acidity, the results of the predictions (palmitic + oleic acids) were compared with the total acidity in the phases.

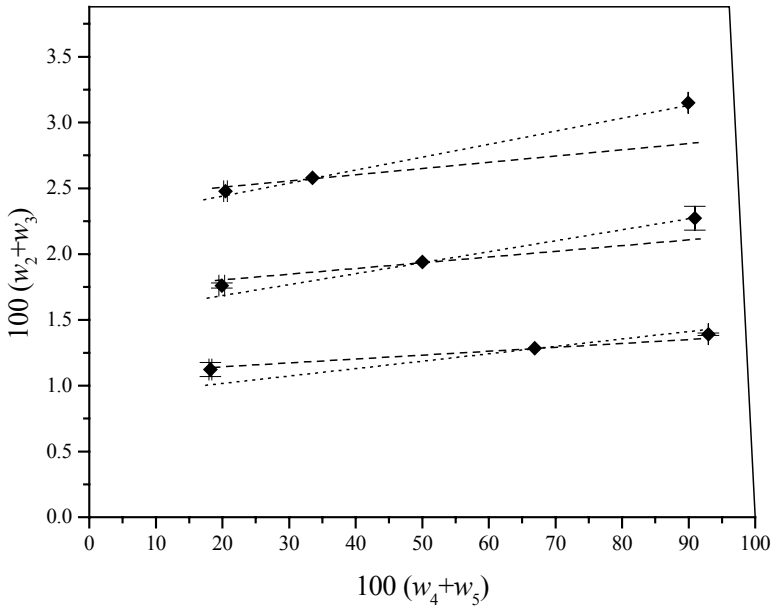

Figure 4.5. Prediction of the liquid-liquid equilibrium for the system of bleached palm oil [palm oil (1) + palmitic acid (2)+ oleic acid (3)] + 3.11 mass% aqueous solvent [ethanol (4) + water (5)] at 318.2 K: experimental (◆); (- - -) NRTL; (·····) UNIQUAC

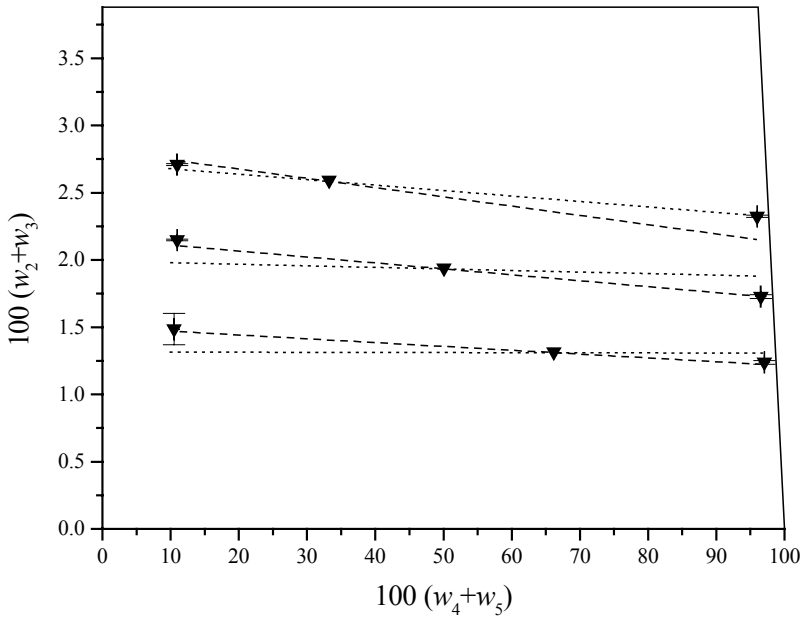

Figure 4.6. Prediction of the liquid-liquid equilibrium for the system of bleached palm oil [palm oil (1) + palmitic acid (2)+ oleic acid (3)] + 10.20 mass% aqueous solvent [ethanol (4) + water (5)] at 318.2 K: experimental (▼); (- - -) NRTL; (·····) UNIQUAC

Despite the differences between the compositions of the refined and bleached palm oils, the parameters adjusted to the model systems allow a good prediction of phase equilibrium for systems containing bleached palm oil, and both thermodynamic models presented practically the same global deviation.

Although the UNIQUAC model presented a deviation higher than the NRTL model for the system with 3.11 mass% aqueous ethanol (see Table 4.9), the former provided a better estimation of the fatty acid concentration in both phases (see Figure 4.5), but at the same time it overestimated the extraction of free fatty acids for the system with 10.20 mass% aqueous ethanol (see Figure 4.6). On the other hand, the fatty acid concentrations for such system were well described by the NRTL model.

Concerning the system with 3.11 mass% of water in the solvent, the UNIQUAC model underestimates the solvent concentration in the oil phase, which justifies the higher deviation obtained in this case. In the case of the system with 10.20 mass% aqueous ethanol, the NRTL model slightly overestimates the solvent concentration in the oil phase, resulting in the higher global deviation.

These results indicate that it is a reasonable approach to consider the interaction parameters between the fatty acids as equal to zero, since the predicted values of the concentrations were close to the experimental ones.

Such statement can be corroborated by combining the results presented in Tables 4.3 and 4.6 for the system with 6.39 mass% aqueous ethanol, which allowed the calculation of the experimental distribution coefficients (k_i) for all the free fatty acids present in the phases in equilibrium. Such k_i values varied in the range 0.79 = $k_{C20:0}$ <

$k_{C18:0} < k_{C16:0} < k_{C12:0} = 1.16$, for the saturated fatty acids, indicating that the increase of the carbon chain decreases the fatty acid distribution coefficients, once a reduction of the solubility in ethanol occurs. Comparing the results for stearic ($k_{C18:0} = 0.91$), oleic ($k_{C18:1} = 1.19$), and linoleic acids ($k_{C18:2} = 1.35$), it was possible to observe the effect of the double bonds on k values.

It is important to emphasize that the main fatty acids (palmitic and oleic) presented experimental distribution coefficients close to one (1.05 and 1.19, respectively), and the corresponding predicted values were equal to 1.30 and 1.10 for the UNIQUAC model, and 1.03 and 0.97 for the NRTL model. Such results show that the first model predicted the oleic acid distribution coefficient in a better way, while the second provided a better result for the palmitic acid.

In order to have a better insight about the distribution coefficient and the selectivity predictions, flash calculations were performed for a bleached oil containing 3.88 mass% of FFA and different water concentrations in the solvent. The mass ratio between crude oil and aqueous solvent was fixed at the value 1:1, and the results are presented in Figure 4.7.

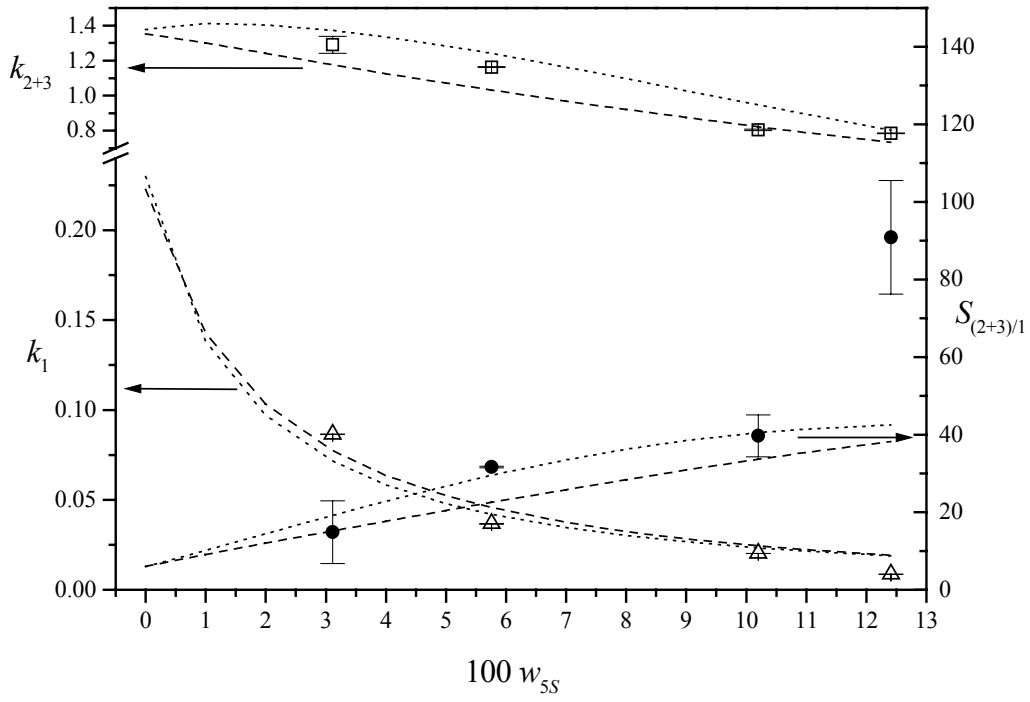

Figure 4.7. Prediction of oil (1) and fatty acids (2) distribution coefficients (k_i) for different solvents at 318.2 K: (△) k_1 experimental; (□) k_{2+3} experimental; (●) $S_{(2+3)/1}$ experimental; (- - -) NRTL; (·····) UNIQUAC

As can be seen in Figure 4.7, the UNIQUAC model allowed a good prediction of the fatty acid distribution coefficient (k_{2+3}) for systems with lower water concentration in the solvent, while the NRTL model presented better results for the systems containing the highest water levels in ethanol. It can also be observed that, in general, both models described the oil distribution coefficient (k_1) accurately. Consequently, the solvent selectivity ($S_{(2+3)/1}$) was well described as well, except for the system with 12.41 mass% aqueous ethanol, a result similar to that already described for the model systems (see Figure 4.4).

4.7 Conclusion

Liquid-liquid equilibrium data for systems containing palm oil + palmitic/ oleic acid + ethanol + water were experimentally determined at 318.2 K. The water addition to the solvent causes a considerable increase in the selectivity and a slight decrease of the fatty acid distribution coefficient in the range of 0 to 6 mass%. Only for values above 6 mass% of water in solvent such effect is more evident.

Despite the complexity of the studied systems, the estimated parameters for the NRTL and UNIQUAC models are representative, since the description of the liquid-liquid equilibrium for all the systems presented deviations lower than 1.25% in relation to the experimental data. These parameters enabled the prediction of liquid-liquid equilibrium for systems containing bleached oil and aqueous ethanol, making possible the modeling and simulation of liquid-liquid extractors using the proposed solvents.

Moreover, the results obtained allows the conclusion that water contents around 6 mass% in the aqueous ethanol are appropriate for deacidification by solvent extraction, as it still provides high values of fatty acid distribution coefficients, low values of oil distribution coefficients, and, consequently, high values for the solvent selectivity.

4.8 List of Symbols

A_{ij}, A_{ji} NRTL or UNIQUAC interaction parameters
C total number of different components in the pseudocompounds
D total number of groups of data
G total number of groups
k_i distribution coefficient of compound i
K total number of components or pseudocompounds in the data group m
M_i average molecular mass of the pseudocompound i

N total number of the tie-lines
$OF(w)$ objective function of composition
q_i' area parameter of component i
Q_k Van der Waals area of group k
r_i' volume parameter of component i
R_k Van der Waals volume of group k
$S_{i/j}$ selectivity of compound i in relation to compound j
T temperature (K)
$v_k^{(i)}$ number of group k in molecule i
x_i molar fraction of compound or pseudocompound i
w_i mass fraction of compound or pseudocompound i
Δw phase composition global deviation

Greek symbol
α_{ij} NRTL interaction parameter
γ_i activity coefficient of compound i
$\sigma_{w_{inm}^{OP}}$ e $\sigma_{w_{inm}^{AP}}$ standard deviations observed in the compositions of the two liquid phases

Subscripts
i, j component or pseudocomponent
k group
m group number
n tie-line
S solvent
O oil

Superscripts
I oil phase
II alcoholic phase
ex experimental value
$calc$ calculated value

4.9 Acknowledgements

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4.10 Literature Cited

[1] J. A. Truillo-Quijano, Revista Óleos & Grãos, Jul/Aug (1999) 30-38.

[2] Y. M. Choo, 22 (1989) pp. 1-6. In: B.S. Baharin, Y.B. Man and R. A. Rahman, J. Am. Oil Chem. Soc., 78 (2001), 851-855.

[3] Y. B. Man, M. H. Moh and F. R. Van deVoort, J. Am. Oil Chem. Soc., 76 (1999) 485-489.

[4] A. E. Bailey, Vol. 2, 5 ed., New York. John Wiley & Sons, 1995.

[5] M. Rossi, M. Gianazza, C. Alamprese and F. Stanga, J. Am. Oil Chem. Soc., 78 (2001) 1051-1055.

[6] C. Thomopoulos, Rev. Fran. des Corps Gras, 18 (1971) 143-150.

[7] S. Kim, C. Kim, H. Cheigh and S. Yoon, J. Am. Oil Chem. Soc., 62 (1985) 1492-1495.

[8] V. Kale, S. P. R. Katikaneni and M. Cheryan, J. Am. Oil Chem. Soc., 76 (1999) 723-727.

[9] S. Turkay and H. Civelekoglu, J. Am. Oil Chem. Soc. 68 (1991) 83-86.

[10] A. C. Bhattacharyya, S. Majumdar and D. K. Bhattacharyya, Oléagineaux, 42 (1987) 431-433.

[11] K.J. Shah and T.K. Venkatesan, J. Am. Oil Chem. Soc., 66 (1989) 783-787.

[12] E. Batista, S. Monnerat, K. Kato, L. Stragevitch and A. J. A. Meirelles, J. Chem. Eng. Data, 44 (1999) 1360-1364.

[13] C. B. Gonçalves; E. Batista and A. J. A. Meirelles, J. Chem. Eng. Data, 47 (2002) 416-420.

[14] C. E. C. Rodrigues; R. Antoniassi and A. J. A. Meirelles, J. Chem. Eng. Data, 48 (2003) 367-373.

[15] C. G. Pina and A. J. A. Meirelles, J. Am. Oil Chem. Soc., 77 (2000) 553-559.

[16] A.O.C.S. Official methods and recommended practices of the American Oil Chemists' Society, Press, 3 ed., Champaign, v. 1-2, 1988.

[17] A.O.C.S. Official methods and recommended practices of the American Oil Chemists' Society, Press, 5 ed., Champaign, 1998.

[18] N. R. Antoniosi Filho, O. L. Mendes and F. M. Lanças, Chromatographia, 40 (1995) 557-562.

[19] IUPAC Standard methods for the analysis of oils, fats and derivatives. 6 th edition, part 1 (sections I and II). PAQUOT, C. editor, Pergamon Press, 1979.

[20] A.O.C.S. Official and Tentative Methods of the American Oil Chemists' Society, Press, 3 ed., Champaign, v.1, 1993.

[21] E. Batista, S. Monnerat, L. Stragevitch, C. G. Pina, C. B. Gonçalves and A. J. A. Meirelles, J. Chem. Eng. Data, 44 (1999) 1365-1369.

[22] T. Magnussen, P. Rasmussen and A. Fredenslund, Ind. Eng. Chem. Process Des. Dev., 20 (1981) 331-339.

[23] L. Stragevitch and S. G. d'Avila, Braz. J. Chem. Eng., 14 (1997) 41-52.

CAPÍTULO 5 – Partition of Nutraceutical Compounds in Deacidification of Palm Oil by Solvent Extraction

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Trabalho submetido ao *Jounal of Food Engineering*, 2004.

Abstract

The aim of the present work was to study the influence of the deacidification by solvent extraction on partition coefficients of carotenoids and tocopherols, by measuring the equilibrium data for the system palm oil + fatty acids + ethanol + water + nutraceutical compounds at 318.2 K. Partition coefficients of carotenoids and tocopherols were also correlated by the UNIQUAC model.

Keywords: Palm Oil, Liquid-liquid Extraction, Solvent Extraction, Tocopherols, Carotenoids, UNIQUAC

5.1 Introduction

The world production of palm oil had a huge increase in the last decades due to its vast industrial application. It also plays an important role among the vegetable oils for being considered the world's richest source of natural plant carotenoids in term of retinal (pro-vitamin A) equivalent (Choo, 1989). Moreover, palm oil contains a considerable amount of tocopherols (including tocotrienols), which are natural antioxidants that present vitamin E value (Bailey, 1995; Hamid & May, 1997).

Besides presenting vitamin A value, carotenoids reduce the risk of certain types of cancer and possess the ability of suppressing singlet oxygen (Wrona, Korytowski, Roznowska, Sarna & Truscott, 2003). Despite its nutritional value, carotenoids are removed in the physical refining process (generally used for oils with high acidity, such as palm oil) in order to obtain a clear colour oil, which has better acceptance for industrial purposes (Rossi, Gianazza, Alamprese & Stanga, 2001). Thus,

some valuable characteristics of palm oil are lost during its processing, and the corresponding nutritional benefits remains available only in the crude oil (Bailey, 1995).

In fact, the physical refining is responsible for great losses of nutraceutical compounds from palm oil. The carotenoids concentration (around 500-700 ppm in crude palm oil) is reduced to the half during the bleached step of the physical refining process, being these components completely destroyed during the high-temperature (240-260ºC) and low-pressure (1-3 mmHg) deacidification/deodorization step. Also, during this stage of the refining process, tocopherols are partially steam stripped, being their levels reduced from 600-1000 ppm to 356-630 ppm (Goh, Choo & Ong, 1985; Rossi et al., 2001).

Liquid-liquid extraction using appropriate solvents, such as ethanol, can be an alternative technique for refining palm oil. As this process is carried out at room temperature and atmospheric pressure, less energy is consumed and the oil is subjected to milder conditions, potentially preserving the nutraceutical compounds (carotenoids and tocopherols) (Thomopoulos, 1971).

In order to investigate the deacidification of edible oils by solvent extraction, it is essential to have information on liquid-liquid equilibrium for systems containing vegetable oils, fatty acids and the selected solvent. Some of these equilibrium data have already been reported on the literature: Batista, Monnerat, Kato, Stragevitch & Meirelles (1999) measured liquid-liquid equilibrium data for the systems containing canola oil, oleic acid and short chain alcohols at different temperatures; Gonçalves, Batista & Meirelles (2002) and Rodrigues, Antoniassi & Meirelles (2003) determined liquid-liquid equilibrium data for the systems containing corn and rice bran oils, respectively, oleic acid, and aqueous ethanol at 25ºC. In our prior work (Gonçalves & Meirelles,

2004), liquid-liquid equilibrium data systems containing palm oil, fatty acids (palmitic and oleic acids) and aqueous ethanol were reported. All these works indicated that the liquid-liquid extraction, using aqueous ethanol as solvent, allows oil deacidification without a great loss of neutral oil.

Rodrigues, Pessôa Filho & Meirelles (2004) studied the partition coefficients of γ-orizanol and tocopherols in systems containing rice bran oil, fatty acids and aqueous ethanol. Their results show that most of the nutraceutical compounds from rice bran oil can be kept on the refined oil after solvent extraction.

The present paper reports carotenoids and tocopherols partition coefficients in systems containing palm oil + fatty acids + aqueous ethanol at 45ºC and with different water contents and mass ratios of oil to solvent. The UNIQUAC model was used to correlate the partition coefficients of carotenoids and tocopherols.

5.2 Material

Refined palm oil (RPO) and bleached palm oil (BPO) were provided by Agropalma (Brazil), being the last one pretreated by Agropalma until the bleached step of its conventional refining process. The palmitic acid was purchased from Acròs and the oleic acid was purchased from Merck. The chemical composition of these reagents was determined by gas chromatography of fatty acid methyl esters. Such data for palm oils (RPO and BPO) and palmitic acid are reported in Gonçalves & Meirelles (2004), and for oleic acid in Rodrigues et al. (2003). The Acròs palmitic acid contains 96.44 mass% palmitic acid, 2.61 mass% myristic acid and linolenic and stearic acids as minor components. The commercial oleic acid from Merck contains 78.02 mass% oleic acid, 11.97 mass% linoleic

acid, 5.36 mass% palmitic acid, 1.42 mass% stearic acid, 1.13 mass% lauric acid and myristic, palmitoleic, linolenic and arachidic acids as minor components.

The calculated molecular masses were 847.78 g/gmol for the refined palm oil, 847.44 g/gmol for the bleached palm oil, 255.84 g/gmol for the palmitic acid and 278.96 g/gmol for the commercial oleic acid.

Anhydrous ethanol with purity greater than 99.5% was obtained from Merck and deionized water (Milli-Q, Millipore) was used throughout.

The β-carotene and the α-tocopherol were purchased from Sigma, with purity greater than 99%.

5.3 Experimental Procedure

Alcoholic solutions containing 1.65±0.03, 1.84±0.01, 1.91±0.02, 2.57±0.02, 3.10±0.03, 3.76±0.05, 4.12±0.04, 4.39±0.01, 5.62±0.01, 5.76±0.02, 8.45±0.04, 9.89±0.09, 12.03±0.07 and 19.99±0.06 mass% of water were previously prepared. The water concentration in the solvent was determined by Karl Fisher titration, according to AOCS method Ca 23-55 (1993).

For measuring the partition coefficients of carotenes, bleached palm oil containing 3.88±0.01 mass% of free acidity and 255±1 ppm of carotenes was mixed with ethanolic solvents in the mass ratios of oil to solvent (O:S) 1:2, 1:1 and 2:1, at 45.0±0.1ºC.

Due to the analytical difficulty of determining tocopherols content on the presence of carotenes (Wong, Timms & Goh, 1988), model fatty systems containing free fatty acids and triacylglycerols were prepared

by the addition of known quantities of palmitic and oleic acids (ratio 1:1) to refined palm oil (carotene free), totalizing 4.28 ± 0.03 mass% free fatty acids in oil. Also, α-tocopherol was added to such model fatty system, generating an oil with 1254 ± 12 ppm of total tocopherols. The model fatty system was mixed with each ethanolic solvent, in the mass ratios of oil to solvent 1:2, 1:1 and 2:1, at 45.0±0.1ºC.

The components were weighed on an analytical balance (Adam model A200), accurate to 0.0001g, and placed in polypropylene centrifuge tubes (15 ml) (Corning Inc.). The tubes were vigorously stirred for at least 15 min and left to rest for 24 h in a thermostatic bath at 45.0±0.1ºC (Cole Parmer, model 12101-05).

After phase equilibrium was obtained, samples of both phases were taken and the corresponding concentrations of nutraceutical compounds measured. The quantification of total carotenoids was preformed at 450 nm according to Porim Test Methods (1990). The total tocopherols concentration was determined at 520 nm according to the methodology developed by Emmerie-Engel (Parrish, 1980). β-Carotene and α-Tocopherol (both 99%, purchased from Sigma) were used as standards in their respective analyses and the solvents used were hexane and toluene (both from Em Science), respectively. All measurements were performed at least in triplicate.

5.4 Modeling

In our prior work (Gonçalves & Meirelles, 2004), liquid-liquid equilibrium data were used to obtain UNIQUAC interaction parameters for systems containing palm oil, fatty acids (palmitic/ oleic), ethanol and water at 45ºC. The adjustments were made treating the model systems palm oil + palmitic acid + anhydrous ethanol and palm oil + oleic acid +

anhydrous ethanol as pseudoternary ones, and the model systems palm oil + palmitic acid + ethanol + water and palm oil + oleic acid + ethanol + water as pseudoquaternary ones.

In the present work a set of experiments was performed to measure the partition coefficients of minor compounds (carotenoids and tocopherols). Such data were used to adjust UNIQUAC interaction parameters between these nutraceutical compounds and the other components or pseudo-components (palm oil (1), palmitic acid (2), oleic acid (3), ethanol (4) and water (5)). The nutraceutical distribution coefficients (k_i), are given by eq 5.1 below.

$$k_i = w_i^{II} / w_i^{I} \qquad [5.1]$$

In eq 5.1, w is the mass fraction, i is the minor compound (carotenoid, i=6 or tocopherol, i=7) and the superscripts II and I are alcoholic and oil phases, respectively. Since the concentrations of both nutraceutical pseudocompounds are very low, it can be assumed that they are present in the liquid-liquid equilibrium system at infinite dilution (∞). Using the iso-activity criterion for phase equilibrium, k_i can be approached by the distribution coefficient at infinite dilution (k_i^{∞}), calculated according to eq 5.2:

$$k_i^{\infty} = \left(\hat{\gamma}_i^{II}\right)^{\infty} / \left(\hat{\gamma}_i^{I}\right)^{\infty} \qquad [5.2]$$

where $\hat{\gamma}$ is the mass fraction-scale activity coefficient, which is related to the molar fraction-scale activity coefficient γ by the following equation:

$$\left(\hat{\gamma}_i\right)^{\infty} = \left(\gamma_i\right)^{\infty} / M_i \left(\sum_{j=1}^{K} w_j / M_j \right) \qquad [5.3]$$

In eq 5.3, *M* is the pseudocompound average molecular mass and *K* is the total number of pseudocompounds that compose the fatty system. Equation 5.3 was used to convert the molar fraction-scale

activity coefficient, used in the UNIQUAC model, in to mass fraction-scale ones, employed in eq 5.2 for calculating the distribution coefficients. The UNIQUAC equation expressed in mass fraction-scale is presented in Appendix A. The infinite dilution activity coefficient was obtained applying the limit to the UNIQUAC model, as the minor compound concentration tends to zero.

The adjustment process was accomplished for each nutraceutical compound separately. Carotenoids and tocopherols present in palm oil were treated as single components with their correspondent average molecular masses. This approach was already used in our prior work (Gonçalves & Meirelles, 2004), for other pseudocompounds, such as palm oil (triacylglycerols mixture), and palmitic and commercial oleic acids (fatty acids mixtures), and assumes that the different components within each fatty compound class behave in a very similar way in the liquid-liquid system under analysis.

Each average molecular mass was calculated considering the carotenoids and tocopherols composition data for palm oil obtained from literature (Yap, Choo, Ooi & Goh, 1991; Mordret & Laurent, 1978)[††].

For carotenoids, the calculated average molecular mass was 536.87 g/gmol, and for tocopherols, the average molecular mass was 414.37 g/gmol.

The parameters $r_i^{'}$ and $q_i^{'}$ for the UNIQUAC model were calculated via eq 5.4 below.

$$r_i^{'} = \frac{1}{\overline{M}_i}\sum_j^C x_j \sum_k^G v_k^{(j)} R_k; \qquad q_i^{'} = \frac{1}{\overline{M}_i}\sum_j^C x_j \sum_k^G v_k^{(j)} Q_k \qquad [5.4]$$

The values of $r_i^{'}$ and $q_i^{'}$ were 0.043931 and 0.035164, respectively, for the carotenoids, and 0.043501 and 0.034375 for the tocopherols.

[4] As composições dos carotenóides e tocoferóis estão apresentadas nas Tabelas A.3 e A.4 no Anexo A.

In eq. 5.4, x_j is the molar fraction of each component present in the carotenoids or tocopherol mixture and $v_k^{(j)}$ is the number of groups k in molecule j. $\overline{M}_i$ is the average molecular mass of the carotenoids or the tocopherols, C is the number of components in each nutraceutical mixture and G the number of groups in molecule j. The parameters R_k and Q_k were obtained from Magnussen, Rasmussen & Fredenslund (1981).

The adjustments of the UNIQUAC interaction parameters between the minor (carotenoids or tocopherols) and major (palm oil, fatty acids, ethanol and water) components were accomplished according to the same procedure presented in Rodrigues et al. (2004), which is based on the minimization of the distribution coefficient objective function, $OF(k_i)$, given by eq 5.5 below.

$$OF(k_i) = \sqrt{\frac{\sum_{n=1}^{N} [k_i^{exp} - k_i^{calc}]^2}{N}} \qquad [5.5]$$

where n is the tie line index, N is the total number of tie lines, k_i is nutraceutical compound distribution coefficient, and the superscripts ex and $calc$ refer to experimental and calculated values, respectively.

Equilibrium phase compositions were calculated on the basis of the overall experimental composition of the mixtures. The interaction parameters between the major pseudocompounds were obtained from Gonçalves and Meirelles (2004). Afterwards, the interaction parameters between the minor and major pseudocompounds were adjusted in order to minimize eq 5.5 above.

5.5 Results

Tables 5.1 and 5.2 present the experimental and calculated partition coefficients of carotenoids and tocopherols, respectively.

Table 5.1. Experimental and calculated distribution coefficients of carotenoids (k_6)

$100w_{5S}$[a]	Overall Composition					k_6	
	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_5$	*exp*	*calc*
0	31.82	0.67	0.62	66.89	0.00	0.1350	0.1366
	48.05	1.01	0.93	50.01	0.00	0.1301	0.1236
	63.82	1.34	1.24	33.60	0.00	0.1106	0.1140
1.65	31.79	0.69	0.63	65.78	1.11	0.0930	0.0936
	48.39	1.05	0.97	48.78	0.81	0.0805	0.0752
	62.65	1.35	1.25	34.18	0.57	0.0367	0.0441
1.91	32.03	0.67	0.62	65.40	1.28	0.0539	0.0760
	63.77	1.34	1.24	33.01	0.64	0.0214	0.0311
2.57	31.18	0.67	0.62	65.79	1.74	0.0438	0.0457
	48.44	1.05	0.97	48.27	1.27	0.0439	0.0326
3.76	31.64	0.68	0.63	64.52	2.53	0.0200	0.0218
	48.09	1.04	0.96	48.04	1.87	0.0177	0.0140
	59.00	1.28	1.18	37.09	1.45	0.0082	0.0082
4.39	30.40	0.66	0.61	65.33	3.00	0.0173	0.0174
	46.80	1.01	0.93	49.00	2.26	0.0160	0.0107
	58.91	1.27	1.18	36.94	1.70	0.0027	0.0059
5.76	25.49	0.54	0.49	69.25	4.23	0.0173	0.0195
	47.42	1.00	0.92	47.74	2.92	0.0090	0.0108
						$OF(k_6)$ = 0.0071	

[a] $100w_{5S}$ = water mass percentage in the solvent

Table 5.2. Experimental and calculated distribution coefficients of tocopherols (k_7)

$100w_{5S}$[a]	Overall Composition					k_7	
	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_5$	*exp*	*calc*
0	32.45	0.75	0.70	66.10	0.00	0.66	0.67
	47.63	1.11	1.02	50.24	0.00	0.75	0.75
1.84	32.95	0.77	0.71	64.37	1.20	0.56	0.54
	45.69	1.07	0.98	51.31	0.95	0.59	0.58
	60.52	1.41	1.30	36.09	0.68	0.60	0.60
4.12	32.46	0.75	0.70	63.36	2.73	0.36	0.38
	47.87	1.11	1.03	47.93	2.06	0.37	0.39
	61.09	1.42	1.31	34.68	1.50	0.37	0.37
5.62	34.28	0.80	0.73	60.57	3.62	0.29	0.30
	47.79	1.11	1.03	47.26	2.81	0.28	0.30
	60.93	1.42	1.31	34.30	2.04	0.28	0.28
8.45	32.89	0.76	0.71	60.10	5.54	0.22	0.20
	46.12	1.07	0.99	47.43	4.39	0.22	0.19
	61.82	1.44	1.33	32.42	2.99	0.20	0.18
9.89	32.59	0.76	0.70	59.42	6.53	0.19	0.17
	47.12	1.10	1.01	45.75	5.02	0.16	0.16
	62.01	1.45	1.33	31.73	3.48	0.14	0.14
12.03	34.89	0.81	0.75	55.90	7.65	0.11	0.13
	47.79	1.11	1.03	44.05	6.02	0.11	0.12
	61.59	1.44	1.32	31.36	4.29	0.11	0.11
13.26	33.90	0.79	0.73	56.02	8.56	0.11	0.11
	47.62	1.11	1.02	43.58	6.67	0.10	0.10
19.99	33.92	0.79	0.73	51.66	12.91	0.04	0.06
	47.40	1.10	1.02	40.39	10.09	0.03	0.05
						$OF(k_7)$ = 0.014	

[a] $100w_{5S}$ = water mass percentage in the solvent

Table 5.3 presents the adjusted UNIQUAC interaction parameters between the major pseudocompounds (obtained from Gonçalves and Meirelles, 2004) and between the nutraceutical and the major compounds of the fatty system.

Table 5.3. UNIQUAC Parameters for the System Refined Palm Oil (1) + Palmitic Acid (2) Oleic Acid (3) + Ethanol (4) + Water (5) + Carotenoids (6) or Tocopherol (7) at 45ºC

pair ij	A_{ij}/K	A_{ji}/K	pair ij	A_{ij}/K	A_{ji}/K
12	289.00	-229.39	16	-2270.58	-1100.05
13	225.43	-198.39	26	2169.99	-141.09
14	215.60	-44.697	36	-2137.64	2501.33
15	4147.1	-171.86	46	-1180.38	-1193.97
24	31.404	-99.657	56	-2544.04	-1086.18
25	127.95	294.36	17	-184.92	-67.766
34	180.18	-220.29	27	677.64	736.30
35	486.37	513.48	37	-18.948	946.98
45	332.23	-330.34	47	138.67	-306.04
			57	-338.19	37.528

Figures 5.1 and 5.2 show the distribution coefficients of carotenoids and tocopherols, respectively, for different water content in solvent and different mass ratios of oil to solvent (O:S).

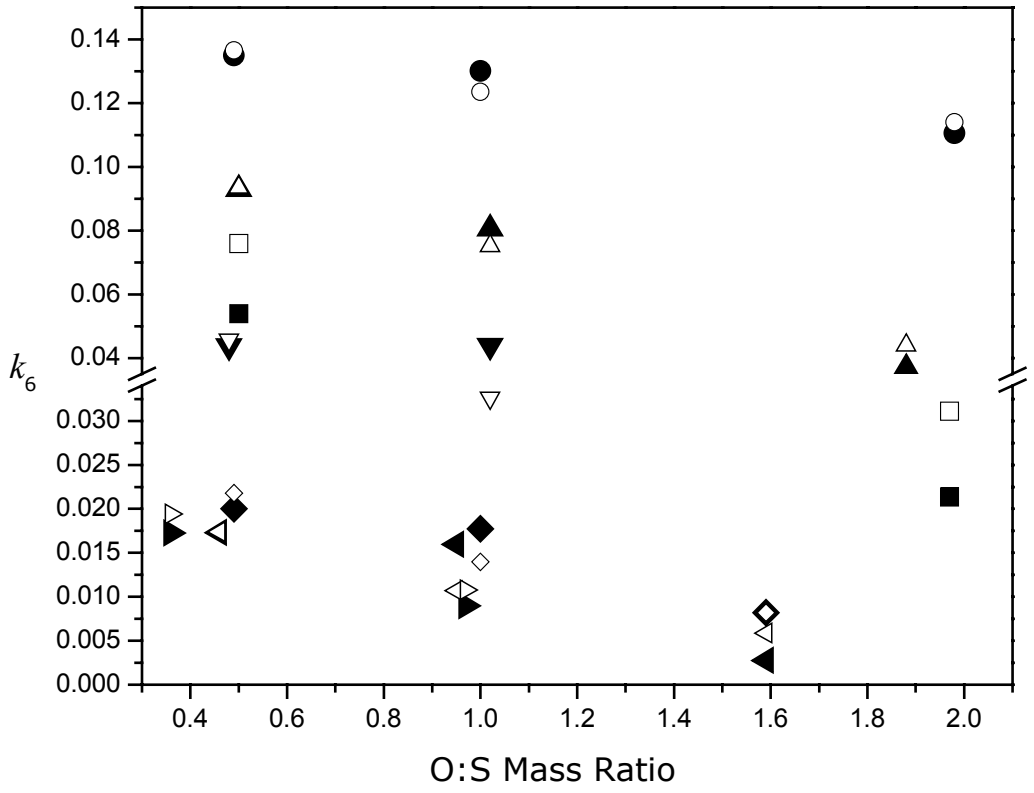

Figure 5.1. Carotenoids (6) distribution coefficients at 45ºC: experimental, full symbol; UNIQUAC, empty symbol: (●) anhydrous ethanol; (▲) 1.65 water mass% in the solvent; (■) 1.91 water mass% in the solvent; (▼) 2.57 water mass% in the solvent; (♦) 3.76 water mass% in the solvent; (◀) 4.39 water mass% in the solvent; (▶) 5.76 water mass% in the solvent

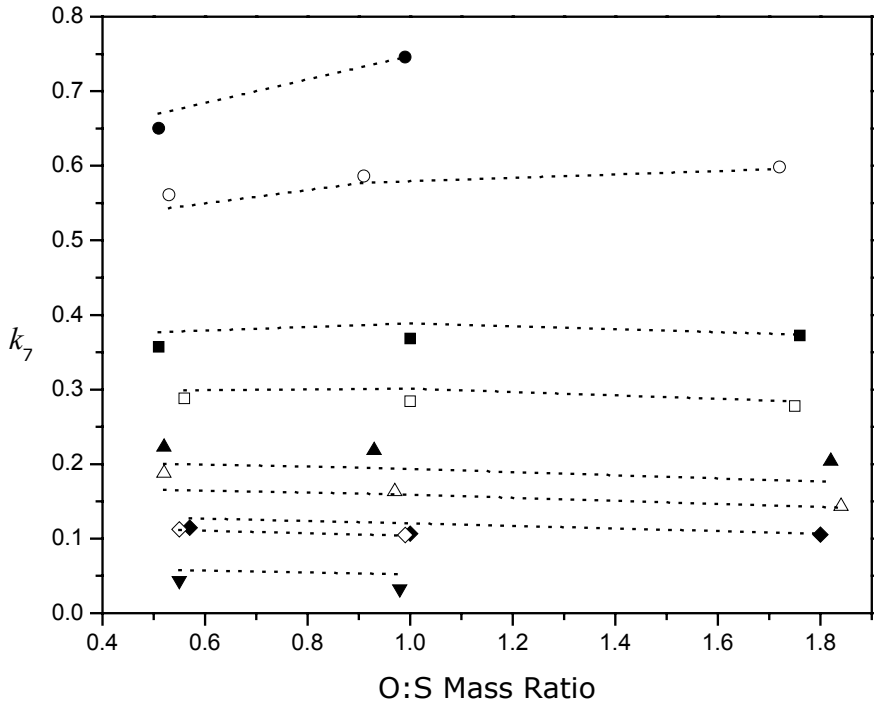

Figure 5.2. Tocopherols (7) distribution coefficients at 45ºC: (●) anhydrous ethanol; (○) 1.84 water mass% in the solvent; (■) 4.12 water mass% in the solvent; (□) 5.62 water mass% in the solvent; (▲) 8.45 water mass% in the solvent; (△) 9.89 water mass% in the solvent; (♦) 12.03 water mass% in the solvent; (◊) 13.26 water mass% in the solvent; (▼) 19.99% water mass% in the solvent; (·····) UNIQUAC

As can be seen in Figure 5.1 and 5.2, the addition of water in the solvent decreases both nutraceutical compounds distribution coefficients. This means that the larger the concentration of water, the smaller the solvent capacity for extracting the carotenoids and the tocopherols. It can also be observed that for all the aqueous solvents studied, the distribution coefficients of minor compounds were smaller than unity, indicating their preference for the oil phase. It is important to emphasize that this effect is desirable, once it demonstrates that most of such compounds remain in the oil refined by liquid-liquid extraction. It is also noticed that the tocopherols are extracted to the alcoholic phase in a larger quantity than the carotenoids. This behavior was already expected due to the structural differences between the two molecules. In fact, tocopherols and carotenoids are insoluble in water, because they have an apolar long chain (what turns them liposoluble). However, the OH group linked to the tocopherol aromatic ring enhances its solubility in ethanol.

In relation to the mass ratio of oil to solvent, it was observed that when the ratio increases the distribution coefficients of carotenoids decreases. In the case of tocopherols, this effect was not observed.

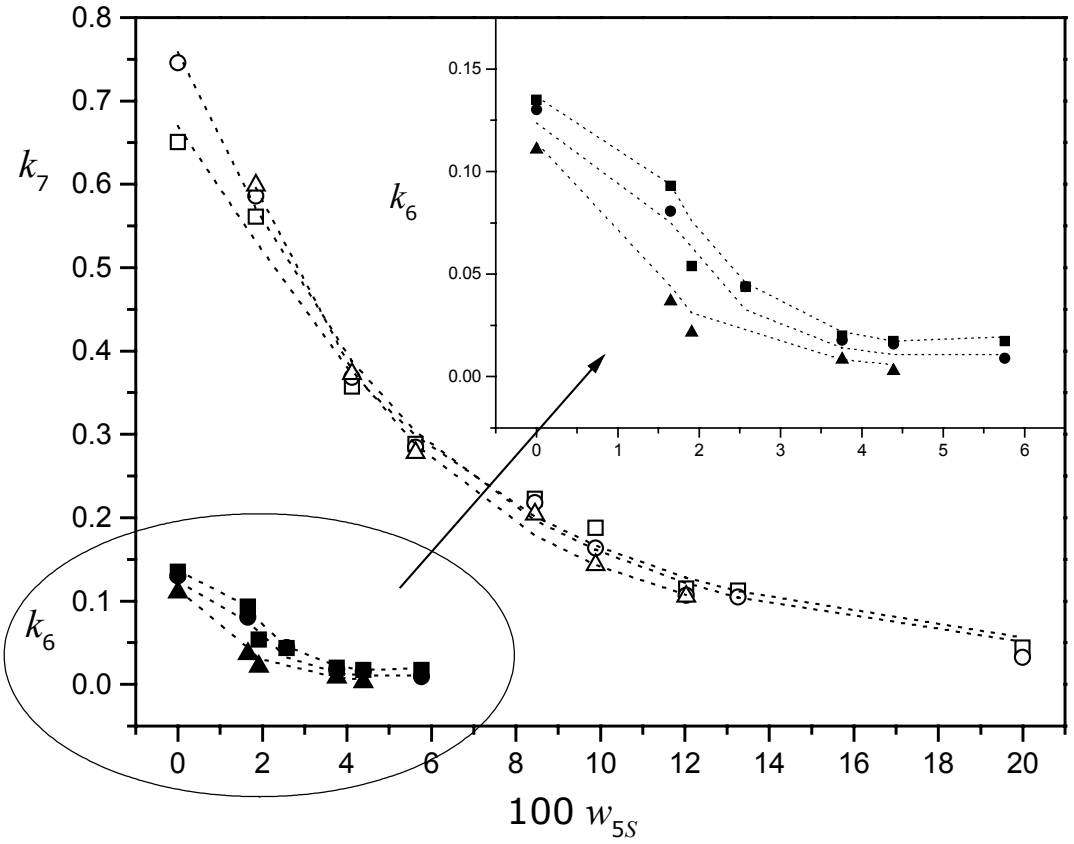

Figure 5.3. Carotenoids (6) and Tocopherols (7) distribution coefficients at 45ºC: ratio O:S 1:2 (■ k_6, □ k_7); ratio O:S 1:1 (● k_6, ○ k_7); ratio O:S 2:1 (▲ k_6, △ k_7); (·····) UNIQUAC

The larger influence of the water content in solvent can be better visualized in Figure 5.3. Figures 5.1 to 5.3 also show that the UNIQUAC model provides a good representation of the experimental distribution coefficients, being the objective function $OF(k_i)$ equal to 0.0071 for carotenoids and 0.0144 for tocopherols.

5.6 Conclusion

Deacidification of palm oil by liquid-liquid extraction, using aqueous ethanol as solvent, allowed the retention of nutraceutical compounds in refined oil. The estimated interaction parameters obtained

for the UNIQUAC model were representative, making possible the modeling and simulation of liquid-liquid extractors for palm oil deacidification, as well as the estimation of the losses of nutraceutical compounds during this refining process.

5.7 References

A.O.C.S. (1993). Official and Tentative Methods of the American Oil Chemists' Society, Press, 3 ed., Champaign, v.1.

Bailey, A. E. (1995). *Bailey's Industrial Oil and Fat Products - Volume 2*, 5ºed. New York. John Wiley & Sons.

Batista, E., Monnerat, S., Kato, K., Stragevitch, L., Meirelles, A.J.A. (1999). Liquid-liquid Equilibrium for Systems of Canola Oil, Oleic Acid and Short-chain Alcohols. *J. Chem. Eng. Data*, *44,* 1360-1364.

Choo, Y. M. (1989). Carotenoids from Palm Oil, PORIM Palm Oil Developments No. 22, (pp. 1-6). In: Baharin, B.S.; Man, Y.B.; Rahman, R. A. (2001). The Effect of Carotene Extraction System on Crude Palm Oil Quality, Carotene Composition, and Carotene Stability During Storage. *J. Am. Oil Chem. Soc*., 78, 851-855.

Goh, S. H.; Choo, Y. M.; Ong, S. H. (1985). Minor Constituents of Palm Oil. *J. Am. Oil Chem. Soc*., 62, 237-240.

Gonçalves, C. B; Batista, E.; Meirelles, A. J. A. (2002). Liquid-Liquid Equilibrium Data for the System Corn Oil + Oleic Acid + Ethanol + Water at 298.15K. *J. Chem. Eng. Data*, *47,* 416-420.

Gonçalves, C. B; Meirelles, A. J. A. (2004). Liquid-liquid Equilibrium Data for the System Palm Oil + Fatty Acids + Ethanol + Water at 318.2 K. Fluid Phase Equilibria. In press.

Hamid, H. A.; May, C. Y. (1997). Natural Antioxidants from Palm Oil. *Palm Oil Technical Bulletin*, v.3, n.4, Aug-Oct.

Magnussen, T.; Rasmussen, P.; Fredenslund, A. (1981). Unifac Parameter Table for Prediction of Liquid-Liquid Equilibria. *Ind. Eng. Chem. Process Des*. *Dev*., 20, 331-339.

Mordret, F. & Laurent, A. M.; *Rev. Fr. des Corps Gras* 25, 245 (1978). In Bailey, A. E. (1995). *Bailey's Industrial Oil and Fat Products - Volume 2*, 5ºed. New York. John Wiley & Sons.

Parrish, D. B. (1980). CRC Crit. Rev. Food Sci. Nutr. 13:161.

Porim Test Methods (1990). Caroten Content. *Palm Oil Research Institute of Malaysia*.

Rodrigues, C. E. C., Pessôa Filho, P. A., & Meirelles, A. J. A. (2004). Phase Equilibrium for the System Rice Bran Oil + Fatty Acids + Ethanol + Water + γ-Oryzanol + Tocols. *Fluid Phase Equilibria*, 216 (2), 271-283.

Rodrigues, C. E. C.; Antoniassi, R.; Meirelles, A. J. A. (2003). Equilibrium Data for the System Rice Bran Oil + Fatty Acids + Ethanol + Water at 298.2K. *J. Chem. Eng. Data*, *48*, 367-373.

Rossi, M.; Gianazza, M.; Alamprese, C.; Stanga, F. (2001). The Effect of Bleaching and Physical Refining on Color and Minor Components of Palm Oil. *J. Am. Oil Chem. Soc*., 78 (10), 1051-1055.

Thomopoulos, C. Méthode de Desacidification des Huiles par Solvant Sélectif. (1971). *Rev. Fran. des Corps Gras*, *18,* 143-150.

Wong, M.L.; Timms, R.E.; Goh, E. M. (1988). Colorimetric determination of total tocopherols in palm oil, olein and stearin. *Journal of American Oil Chemists' Society*, v 65, p.258-261.

Wrona, M.; Korytowski, W.; Roznowska, M.; Sarna, T.; Truscott, T.G. (2003). Cooperation of antioxidants in protection against photosensitized oxidation. Free Radical Biology and Medicine, 35 (10), 1319-1329.

Yap, S. C.; Choo, C. K. Ooi, A. S. H.; Goh, S. H. (1991). *Elaeis* 3 (2) (12), 375. In Bailey, A. E. (1995). *Bailey's Industrial Oil and Fat Products - Volume 2*, 5ºed. New York. John Wiley & Sons.

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Appendix A

Activity coefficient (γ_i) for the UNIQUAC model using mass-fractions as unity of concentration:

$$\ln\gamma_i = \ln\gamma_i^{Comb} + \ln\gamma_i^{Res} \qquad [A.1]$$

$$\ln\gamma_i^{Comb} = \frac{\ln\Psi_i'}{\ln\left(w_i/\zeta\,\overline{M}_i\right)} + 1 - \frac{\zeta\,\overline{M}_i\Psi_i'}{w_i} + \frac{z}{2}\overline{M}_i\,q_i'\ln\frac{\theta_i'}{\Psi_i'} - \frac{z}{2}\overline{M}_i\,q_i'\left(1-\frac{\Psi_i'}{\theta_i'}\right) \qquad [A.2]$$

where $\zeta = \sum_{j=1}^{K}\frac{w_j}{\overline{M}_j}$ [A.3]

$$\theta_i' = \frac{q_i' w_i}{\sum_{j=1}^{K} q_j' w_j}; \qquad \Psi_i' = \frac{r_i' w_i}{\sum_{j=1}^{K} r_j' w_j} \qquad [A.4]$$

and

$$\ln\gamma_i^{Res} = \overline{M}_i\,q_i'\left[1-\ln\left(\sum_{j=1}^{K}\theta_j'\tau_{ji}\right) - \sum_{j=1}^{K}\left(\theta_i'\tau_{ij}\Big/\sum_{k=1}^{K}\theta_k'\tau_{kj}\right)\right] \qquad [A.5]$$

where $\tau_{ij} = \exp\left(-\frac{A_{ij}}{T}\right)$ [A.6]

CAPÍTULO 6 – Deacidification of Palm Oil by Solvent Extraction

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Trabalho a ser submetido ao *JAOCS*, 2004.

Abstract

In the present work, the influence of process variable on the losses/transfer of fatty compounds during the deacidification of palm oil by liquid-liquid extraction is reported. The response surface methodology (RSM) was used to analyze the effect of process variables, aiming to minimize the losses of neutral oil and maximize the transfer of free fatty acids plus carotenoids preservation. By using the optimized conditions observed in RSM analysis, the deacidification of palm oil by continuous liquid-liquid extraction was performed in a perforated rotating disc contactor (PRDC). The experimental results indicate that it is possible to obtain refined palm oil with a free acidity lower than 0.1 mass % by continuous liquid-liquid extraction.

Keywords: Palm oil, Liquid-liquid extraction, Deacidification, Carotenoids, RSM, UNIQUAC, PRDC

6.1 Introduction

The rapid expansion in world production of palm oil over the last decades has attracted the attention of the oils and fat industry. Crude palm oil is extracted from the fresh mesocarp of the palm fruit and contains a small amount of undesirable components and impurities, such as mesocarp fibers, free fatty acids (FFAs), phospholipids, trace metals, oxidation products, and odoriferous substances. As a result, palm oil is normally refined to a bland, stable product before it is used for direct consumption or for formulation of edible products (1).

Two methods are available for refining crude palm oil: physical and chemical. They differ basically in the manner in which the free fatty acids are removed. As the chemical refining is not recommended for oils with high acidity, such as palm oil, physical refining has become the

major processing route because of its efficiency and simple effluent treatment. However, the drastic conditions in which this process is carried out (temperature: 240-260ºC; pressure: 1-3 mmHg) led to the complete destruction of carotenoids and to a significant reduction of tocopherols, both important components that confer to palm oil a high nutritional value (1).

The deacidification of oils by liquid-liquid extraction using an appropriate solvent, such as ethanol, can be an alternative technique for refining palm oil. As this process is carried out at room temperature and atmospheric pressure, less energy is consumed and the oil is submitted to softer treatments, potentially preserving the nutraceutical compounds. This technique is based on the difference of solubility of FFA and neutral triacylglycerols in an appropriate solvent (2). Several results reported in the literature indicate the decrease of FFA content in the oil submitted to solvent extraction (3-6). The losses of neutral oil and nutraceutical compounds during this process were also reported (7-9). Some liquid-liquid equilibrium data for systems containing triacylglycerols (TAGs), free fatty acids (FFAs) and short chain alcohols, essential to planning and developing liquid-liquid extraction process, were determined, correlated and predicted, and are available in the literature (10-14). In our prior works (15,16), liquid-liquid equilibrium data systems containing palm oil, fatty acids (palmitic and oleic acids), aqueous ethanol and nutraceutical compounds were measured and correlated by thermodynamic models.

The present work reports the influence of process variables on the losses of neutral oil, the transfer of free fatty acids and the preservation of carotenoids during the deacidification of palm oil by liquid-liquid extraction. The response surface methodology was used to analyze the effect of process variables, such as mass ratio of oil to solvent and water

content in the solvent, aiming to minimize the losses of neutral oil and maximize the transfer of free fatty acids plus carotenoids preservation. By using the optimized conditions observed in RSM analysis, the deacidification of palm oil by continuous liquid-liquid extraction was performed in a perforated rotating disc contactor (PRDC). The experimental results indicate that it is possible to obtain refined palm oil with a free acidity lower than 0.1 mass % by liquid-liquid extraction.

6.2 Material and Methods

In this study, two different samples of bleached palm oil (kindly supplied by the Agropalma brand, Brazil) were used. Both oils were analyzed by gas chromatography of fatty acid methyl esters, according to the official method (1-62) of the AOCS (17). Samples were prepared in the form of fatty acid methyl esters according to the official method (2-66) of the AOCS (18). An HP 5890 gas chromatograph with a flame ionization detector and an integrator was used under the following experimental conditions: capillary fused silica column of cyanopropylsiloxane (60 m x 0.25 μm x 0.32 mm), hydrogen as the carrier gas at a rate of 2.5 ml/min, an injection temperature of 548.2 K, a column temperature of 448.2 – 498.2 K (1.3K/min), and a detection temperature of 578.2 K. The fatty acid methyl esters were identified by comparison with the retention times of NU CHECK Inc. standards (Elysian, IL) and the quantification was accomplished by internal normalization.

Fatty acid composition of the bleached palm oil used in the liquid-liquid equilibrium experiments (for composing the experimental design) has already been reported by Gonçalves & Meirelles (15). Such sample presented an acidity of 3.88±0.01 mass%, determined by titration (19)

with an automatic burette (Metrohm, model Dosimat 215) and 255±0.01 ppm of total carotenes, determined by spectrophotometry (Perkin Elmer, model Lambda 40) at 450 nm, according to Porim Test Methods (19), using hexane (Em Science) as solvent and β-carotene 99% (Sigma) as standard. The solvents used were anhydrous ethanol, from Merck, with purity greater than 99.5%, and alcoholic solutions containing 1.91±0.03, 5.76±0.02, 10.00±0.05 and 12.41±0.01 mass% water, prepared by the addition of deionized water (Milli-Q, Millipore) to anhydrous ethanol. The water concentration in the solvent was determined by Karl Fisher titration, according to AOCS method Ca 23-55 (21).

For the PRDC experiments, a bleached oil containing 4.23±0.01 mass% of free fatty acids (FFAs) and 225±0.01 ppm of total carotenes was utilized, being its fatty acid composition present in Table 6.4. In addition, such sample was characterized in terms of mono-, di-, triacylglycerols and polymerized triacylglycerols by gel permeation HPLC according to AOCS Cd 22-91 (18) (HPLC system Perkin Elmer model 250, refractive index detector Sicon Analytic, columns Jordi Gel DVB 300 mm x 7.8 mm id, 0.01 and 0.05 μm, mobile phase tetrahydrofurane, sample solution 1% (w/v) in tetrahydrofurane); peroxide value, according to method AOCS Cd 8b-90 (18); iodine and saponification values calculated from fatty acid composition, following AOCS methods Cd 1c-85 and Cd 3a-94, respectively (18); determination of total tocopherols (tocopherols and tocotrienols) by HPLC (AOCS official method Ce 8-89 (18); HPLC system Perkin Elmer model 250, fluorescence detector Shimadzu RF-10 AXL with excitation wavelength at 290 nm and emission wavelength at 330 nm, column Merck Li Chrosorb Si 60, 5 μm, 250 mm x 4 mm id, mobile phase isopropanol in hexane 1:99 (v/v)); concentration of total carotenoids; and Lovibond

color read in a Lovibond Tintometer model E in a 5.25'' cell and expressed in units of yellow (Y), red (R) and blue (B). For the experiments in the PRDC, neutral ethanol (containing 5.8 mass% of water), food grade, purchased from Usina Ester (Brazil) was used as solvent.

Physical properties of the oils samples at 45ºC were also measured. The density measurements were performed using DMA 58 Density Meter (Anton Paar). The viscosity data were obtained by an AMV 200 Viscometer (Anton Paar).

The analysis described above were also performed in a crude palm oil (CPO) and a refined palm oil (RPO), both supplied by Agropalma brand (Brazil), and in the palm oil deacidified by liquid-liquid extraction (RPO-LLE), in order to compare the characteristics of such oils submitted to different steps of refining process.

6.2.1 Response Surface Methodology

Liquid-liquid equilibrium experiments were accomplished by mixing bleached palm oil with ethanolic solvents (water content in solvent varying from 0 to 12 mass%) at different mass ratios of oil to solvent (O:S) mass ratios (1:2, 1:1 or 2:1). The components were weighed on an analytical balance (Adam, model A250), accurate to 0.0001g, and placed in polypropylene tubes (15 ml, Corning Inc). The tubes were vigorously stirred for at least 15 min and left to rest for 24h in a thermostatic bath at 45ºC (Cole-Parmer, model 12101-05).

After phase equilibrium was obtained, samples of both phases were taken and analyzed. The concentration of free fatty acids was determined by titration (19) with an automatic burette (Metrohm, model Dosimat 715). The total solvent concentration was determined by

evaporation at 60.0 ºC in a vacuum oven (Napco, model 5831). The water concentration was determined by Karl Fischer titration, according to AOCS method Ca 23-55 (21), with a KF Titrino (Metrohm, model 701). The quantification of total carotenoids was determined at 450 nm according to Porim Test Methods (20). The neutral oil concentration was determined by difference. All measures were performed at least in triplicate.

The response surface methodology was used to investigate the effect of the mass ratio of oil to solvent and the water content in solvent on the carotenoids preservation, losses of neutral oil (NO) and on the FFA transfer during an equilibrium stage of the deacidification process by liquid-liquid extraction.

The $\%FFA\ transfer$ and the $\%NO\ loss$ were calculated by eq 6.1.

$$\%(Transfer/Loss) = 100 \cdot \frac{m^{AP} \cdot w_i^{AP}}{m^{Oil} \cdot w_i^{Oil}} \qquad [6.1]$$

where m is mass, w is mass fraction, AP is alcohol phase, Oil is the palm oil and i is FFA or TAG, being m^{AP} calculated by mass balance.

The carotenoids preservation was expressed as the respective content remaining in oil ($Carotene^{oil}$, in ppm) after one stage of equilibrium (eq 6.2).

$$Carotene^{Oil}(ppm) = \left(1 - w_{solv}^{OP}\right) \cdot Carotene^{OP}(ppm) \qquad [6.2]$$

where $solv$ is the solvent (ethanol plus water) and OP is oil phase.

The experimental set was planned to obtain a quadratic model, consisting of 2^2 trials plus a star configuration with three repetitions in central point (22,23). Surfaces were built using the quadratic model for the statistically significant variables. The software Statistica (Statsoft, v. 5.0) was used to analyze the results by non-linear multiple regression.

6.2.2 Deacidification in Continuous Equipment

Palm oil deacidification experiments were performed in a perforated rotating disc contactor (PRDC), a continuous equipment that consists of a column equipped with a central rotating shaft carrying equally spaced perforated discs (total of 33), whose dimensions (in cm) are as follows: column inside diameter, 5; disc diameter, 4.7; column height, 130; extraction zone height, 100; distance between adjacent discs, 2.5. The flow free area in the discs was 20%, containing holes of 3 mm diameter.

The experiments were accomplished at 45ºC and atmospheric pressure, being the column temperature controlled by a thermostatic bath (Cole-Parmer, Model 12101-15, accurate to 0.1ºC) connected to the column jacket. On the basis of the results obtained using the response surface methodology, a mass ratio of oil to solvent equal to 0.74 and a water content in ethanol of approximately 6 mass% were selected. The equipment was filled with the aqueous ethanol through the bottom of the column and its flow rate was maintained at the desired constant value (24.85 g/min). The rotor was started and the rotating speed was measured by a digital tachometer 1726 (Ametek, Largo, FL) and fixed at 150ppm. Subsequently, the bleached oil was fed to the top of the column with the flow rate at the desired value (18.39 g/min), being both feed streams (oil and ethanol) pumped into the column by peristaltic pumps (Cole Parmer, Chicago, IL). After a waiting time of 120 min for attaining the steady state, samples of the outlet streams, extract and raffinate, were taken during the following 120 min and analyzed to determine the solvent, fatty acids and carotenoids concentrations. This procedure was repeated using the raffinate stream of the prior experiment and fresh solvent as feeds until the free acidity in refined oil was less than 0.3 mass %, totalizing three experiments (or

steps) in the PRDC column. Each processing step is a countercurrent contact while the global process, i.e., the set of three steps, is a crosscurrent configuration, once fresh solvent is introduced in each one.

The operational and equilibrium concentrations of free fatty acids in the raffinate stream allowed to calculate the number of ideal equilibrium stages required in each step (eq. 6.3 below). This approach is valid when the operating and equilibrium lines are both straight over a given concentration range, and when just one compound (in this case, FFA) is transferred from one phase to another. For this, it is necessary to use streams concentrations in a acid free-basis (6,24).

$$N = \frac{\log\left[\left(w_{R,2}{}' - w_{R,2}^{*}{}'\right) \Big/ \left(w_{F,2}{}' - w_{E,2}^{*}{}'\right)\right]}{\log\left[\left(w_{E,2}^{*}{}' - w_{R,2}^{*}{}'\right) \Big/ \left(w_{F,2}{}' - w_{R,2}{}'\right)\right]} \qquad [6.3]$$

where N is the number of stages, $w'_{F,2}$ $w'_{E,2}$ and $w'_{R,2}$ are the concentration of fatty acids in the feed, extract and raffinate streams, respectively; the superscripts ‘ and * denote, acid free-basis and equilibrium concentration, respectively (25). The equilibrium curve used in the calculations was obtained from equilibrium data reported in Gonçalves & Meirelles (15) for systems containing bleached palm oil, free fatty acids, ethanol and water, and it presents a correlation coefficient of 0.99. This line is given in eq. 6.4.

$$w_{E,2}^{*}{}' = 1.1627 \cdot w_{R,2}^{*}{}' \qquad [6.4]$$

It should be noted that the approach mentioned above requires a one-component mass transfer system. For this reason its use in the present case is a first approximation, since other fatty compound classes are also transferred during the process. Nevertheless, the fatty acids are the major components to be transferred and the main fatty acids

present in bleached palm oil, palmitic and oleic acids, can be approximately replaced by an equivalent pseudo-fatty acid for equilibrium calculations, as already shown by Gonçalves et al. (12), Rodrigues et al. (13), Rodrigues et al. (14) and Gonçalves & Meirelles (15). Furthermore, this approach allows a first estimation of the number of ideal stages required for the deacidification process, an information that can be helpful in the evaluation of this refining technology.

6.3 Results

Table 6.1 presents all combinations of the studied variables in the statistical analysis and the correspondent responses for both experimental designs studied.

Table 6.1. Experimental Design: 2^2 + star configuration + central points

Coded Variables		Real Variables		Responses		
O:S Ratio	*Water*	*O:S Ratio*	*Water*	*FFA transfer*	*NO loss*	*Carotene^{Oil}*
+1	+1	2	10.00	30.76	0.46	189.43
+1	-1	2	1.91	39.04	3.89	158.65
-1	+1	0.5	10.00	62.98	2.66	203.24
-1	-1	0.5	1.91	71.03	14.30	175.35
0	0	1	5.76	54.82	3.30	195.23
0	0	1	5.76	53.91	3.15	186.07
0	0	1	5.76	53.83	3.17	184.53
-1.41	0	0.36	5.76	65.97	7.66	198.71
0	-1.41	1	0	55.75	14.36	157.92
+1.41	0	2.77	5.76	29.61	0.67	179.59
0	+1.41	1	12.41	45.08	0.81	228.11

The statistical analysis of the experimental results allowed to formulate models representing the percentage of FFA transfer, NO loss and Carotene content in oil, given by eq 6.5 to 6.7, respectively.

$$\%FFA\,transfer = 47.33 - 18.90\cdot(O:S^{*}) - 2.49\cdot(O:S^{*})^{2} + \\ -2.60\cdot(\%Water^{*}) + 2.60\cdot(\%Water^{*})\cdot(O:S^{*}) \quad [6.5]$$

$$\%NO\,loss = 2.86 - 3.05\cdot(O:S^{*}) + 0.46\cdot(O:S^{*})^{2} - 3.84\cdot(\%Water^{*}) + \\ +1.83\cdot(\%Water^{*})^{2} + 2.43\cdot(O:S^{*})\cdot(\%Water^{*}) \quad [6.6]$$

$$Carotene^{Oil}(\text{in ppm}) = 191.21 + 20.36\cdot(\%Water^{*}) \quad [6.7]$$

where *%Water** and *O:S** are coded variables.

Table 6.2 shows the analysis of variance (ANOVA) for the responses at 95.0% of confidence.

As can be observed in Table 6.2, the responses *FFA transfer* and *NO loss* presented high correlation coefficients and the F-test shows that the respective models are reliable since the calculated F values are at least 12 times greater than the values obtained from Box et al. (22). Although for the response $Carotene^{Oil}$ the correlation coefficient be not very high, the F value is 7 times greater than tabled one at a level of 95% confidence.

Figures 6.1 to 6.3 present the surfaces generated by the models obtained in eq 6.5 to 6.7, representing the influence of the mass ratio of oil to solvent (*O:S*) and of the water content in solvent (*% Water*) on the responses studied.

Table 6.2. Analysis of Variance (ANOVA)

Source of Variation	*FFA transfer*				*NO loss*				*Carotene^{Oil}*			
	SS[a]	MS[b]	DF[c]	F[d]	SS[a]	MS[b]	DF[c]	F[e]	SS[a]	MS[b]	DF[c]	F[f]
Regression	2967.5	741.88	4		235.52	46.90	5		3304.9	3304.9	1	
Residual	47.97	7.99	6	92.79	3.70	0.74	5	63.41	796.8	88.53	9	37.33
Total	3015.5		10		238.22		10		4101.6		10	
Correlation coefficient	0.98				0.98				0.81			

[a] Sum of squares; [b] Mean square; [c] Degrees of freedom;
[d] F calc = $F_{0.95;\ 4;\ 6}$ = 4.53; [e] F calc = $F_{0.95;\ 5;\ 5}$ = 5.05; [f] F calc = $F_{0.95;\ 1;\ 9}$ = 5.12

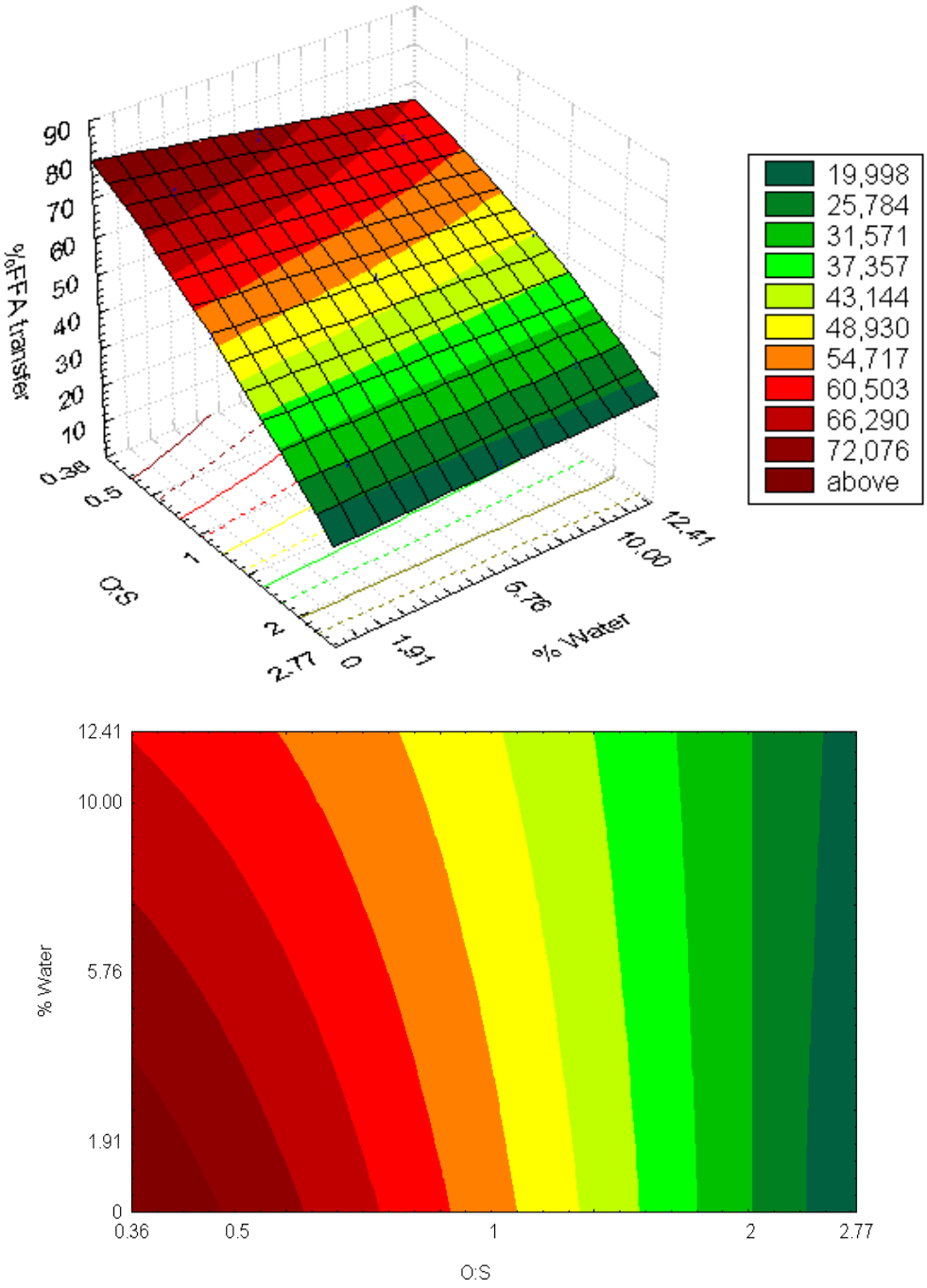

Figure 6.1. Response surface and contour curves of FFA transfer expressed as function of O:S mass ratio and water in solvent

As can be observed in Figure 6.1, lower O:S mass ratios and lower water contents in the solvent provide a better transference of the free fatty acids to the solvent. However, this effect is more pronunciated in the case of the variable O:S mass ratio.

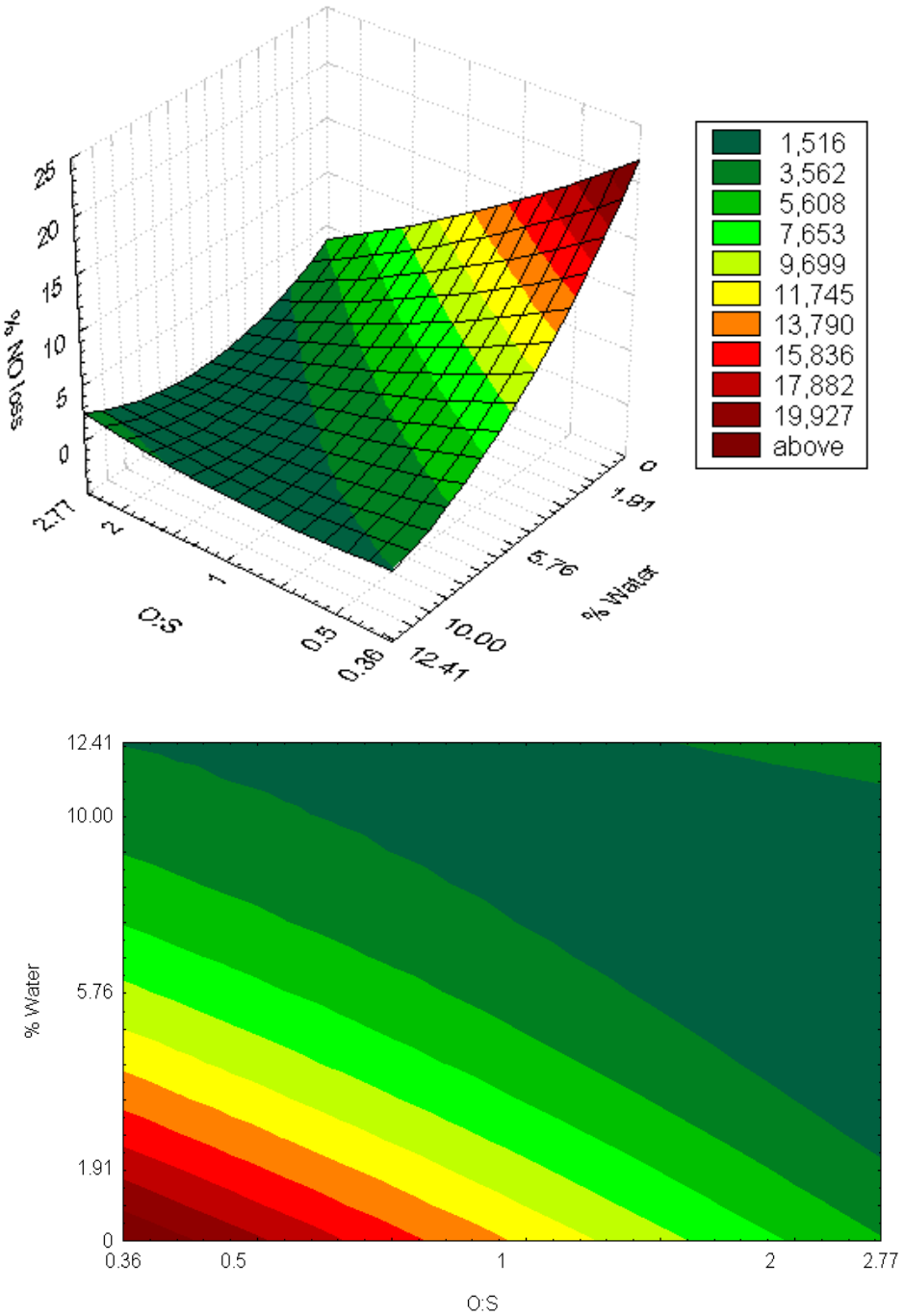

Figure 6.2. Response surface and contour curves of NO loss expressed as function of O:S mass ratio and water in solvent

Figure 6.2 shows that the losses of neutral oil are minimized with the increase of the water content in the solvent. The reduction of the mass ratio O:S only exerts a more significant influence on the %NO loss when solvents with lower water contents are used.

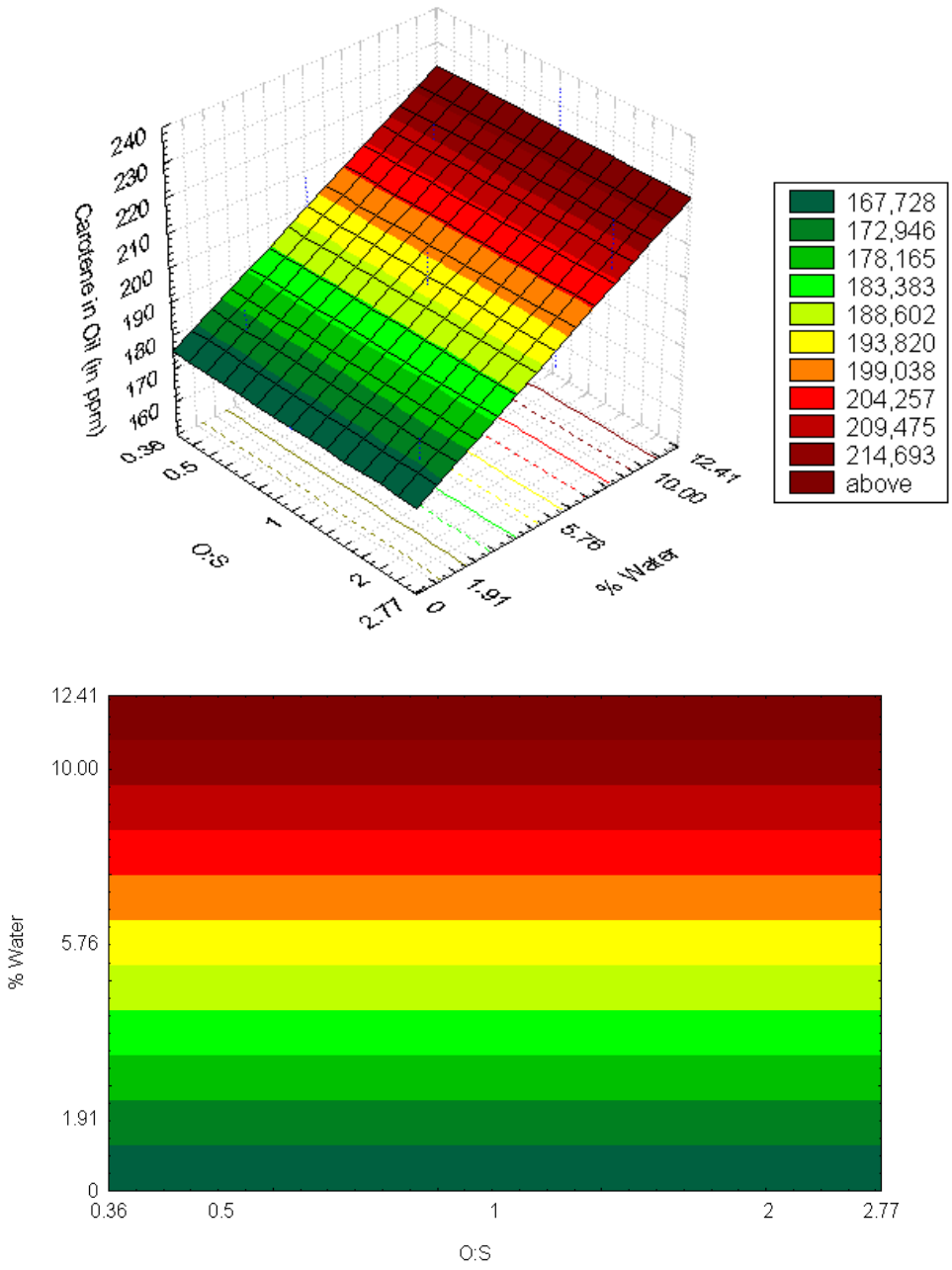

Figure 6.3 Response surface and contour curves of carotenes remaining in refined oil expressed as function of O:S mass ratio and water in solvent

In Figure 6.3, it can be observed that the water content in the solvent is the main effect on the carotene concentration in the oil. As higher the water concentration in the solvent, larger the carotene concentration remaining in the oil after one stage of equilibrium in the

deacidification process. However, even if solvents with low concentrations of water are used, it is possible to retain 65 mass% of the total of carotenoids present in bleached oil, i.e., all the range of variables studied provides o good preservation of the carotenoids in oil. On the other hand, for FFA transference and NO loss such variables exert a significant and opposing influence, as can be observed in Figures 6.1 and 6.2. Thus, it is important to specify a optimized region in which it is possible to obtain a good transference of the FFA without great loss of neutral oil.

As the loss of neutral oil has a significant effect on the total cost of refining process, it is important to establish an acceptable maximum limit. According to Bailey (26), many suppliers of physical refining systems offers loss warranties based on the amount of fatty acids in the feed. They usually claim a minimum loss ranging between 0.2 and 0.4 % plus 1.05-1.2 times the FFA content in the feed. Applying these limits to the bleached palm oil (with 4.23 mass% of FFA) that was used in the perforated rotating disc contactor experiments, it was considered that a loss of neutral oil less than 4.64-5.48% would be acceptable for liquid-liquid extraction.

Analyzing Figures 6.2, it can be observed that several combinations of mass ratio of oil to solvent and water content in solvent turn possible the deacidification of palm oil with losses of neutral oil less than the stipulated value, in one stage of equilibrium. Considering Figure 6.1, it can be seen that high values of FFA transfer (> than 50%) were obtained for mass ratios of oil to solvent less than 1.0. Applying this restriction in Figure 6.2, the range of water concentration in the solvent is also limited for values higher than 4%. However, it is not reasonable to choose of high values water concentration (> than 7 mass%, for example), once more equilibrium stages would be necessary to obtain a

palm oil containing less than 0.3 mass% of FFA. This statement will be corroborated ahead through calculations.

Values within this optimized range (mass ratio O:S = 0.74 and water content in solvent = 5.8 mass%) were used to accomplish the experiments in the perforated rotating disc contactor (PRDC). Concerning the experimental conditions of mass ratio O:S (0.74) and water content in solvent (5.8 mass%) in eq. 6.5 and 6.6, it was possible to obtain, for one equilibrium stage, a % FFA transfer equal to 56.24% and a % TAG loss equal to 4.27%. Three experimental steps in the PRDC were necessary to obtain a refined oil with a final acidity required by the Codex Alimentarius (27) for refined vegetable oils.

Using the fatty acid concentrations obtained after each experimental step, eq. 6.3 provides the following number of ideal equilibrium stages: step 1 – N=2.5; step 2 – N=1.0; step 3 – N=1.0. Table 6.3 presents the experimental results of FFA transfer and NO loss for each processing step and for the whole process.

Table 6.3. Experimental %FFA transfer and %NO loss

Transfer/loss	Step 1 N=2.5	Step 2 N =1.0	Step 3 N =1.0	Whole process
% FFA transfer	81.24	70.71	26.41	95.95
% NO loss	4.95	4.02	1.49	10.67

As observed in Table 6.3 most part of FFA content in BPO was transferred in the first step, but the following two steps were necessary to attain the required final acidity. The NO loss was also large in the first step; the reason for the observed behaviour relies on the higher solubility of the neutral oil in the alcoholic phase when FFA concentration in this phase is high. In fact, the equilibrium data indicate that neutral

oil has a limited solubility in aqueous ethanol, whose value is enhanced by the presence of FFAs (15). The NO loss is also significant in the other two steps, since fresh solvent was used in the last two ones.

If it would be possible to operate the whole process in a countercurrent way, with fresh solvent being fed just once, the NO loss would be lower, since the neutral oil solubility limit in the alcoholic phase would be attained. In this case, the NO loss value would be not higher than 4.95%, a value near the estimated by the response surface methodology. Concerning the number of ideal stages in a countercurrent configuration for the whole process, it can be estimated by eq. 6.3 using FFA concentrations in the feed stream of first step and in the output stream of the third step. This calculation results in a number of equilibrium stages equal to 7.5, higher than the sum of stages estimated for each experimental step. With the purpose of confirming the previous statement (as higher the water content in solvent, higher the number of equilibrium stages), the calculations described above were also performed using the equilibrium data for the system palm oil, fatty acids and 12.41 mass % aqueous ethanol taken from Gonçalves & Meirelles (15). It resulted in a number of ideal stages equal to 32, much higher than 7.5.

In order to evaluate the impact of the deacidification by liquid-liquid extraction on the quality of refined oil, several analyses were accomplished in the bleached palm oil used in the experiments (BPO) and in the refined palm oil deacidified by liquid-liquid extraction (RPO-LLE). Such analyses were also performed in further two different palm oil samples, the first one of crude palm oil (CPO) and the second one industrially refined palm oil (RPO).

Tables 6.4 and 6.5 show, respectively, the fatty acid composition and the physical-chemical properties of CPO, BPO, RPO and RPO-LLE.

Table 6.4. Fatty Acid Composition of Crude Palm Oil (CPO), Bleached Palm Oil (BPO), Refined Palm Oil (RPO), and Refined Palm Oil Deacidified by Liquid-Liquid Extraction (RPO-LLE)

Fatty Acid	*MM*[b] (g.gmol^{-1})	CPO		BPO		RPO-LLE		RPO	
		% Molar	% Mass	% Molar	% Mass	% Molar	% Mass	% Molar	% Mass
Lauric (C12:0[a])	200.32	0.00	0.00	0.34	0.25	0.00	0.00	0.00	0.00
Myristic (C14:0)	228.38	1.09	0.92	1.25	1.06	1.03	0.87	1.10	0.93
Palmitic (C16:0)	256.43	44.16	41.89	42.73	40.53	42.93	40.66	44.41	42.13
Palmitoleic (C16:1)	254.42	0.18	0.17	0.33	0.31	0.18	0.17	0.16	0.15
Stearic (C18:0)	284.49	4.76	5.01	4.71	4.96	4.83	5.08	4.74	4.99
Oleic (C18:1)	282.47	39.00	40.75	39.71	41.49	40.28	42.03	39.00	40.76
Linoleic (C18:2)	280.45	10.01	10.38	10.11	10.49	9.94	10.30	9.94	10.31
Linolenic (C18:3)	278.43	0.30	0.31	0.31	0.32	0.27	0.28	0.17	0.18
Arachidic (C20:0)	312.54	0.35	0.41	0.35	0.41	0.37	0.43	0.35	0.40
Gadoleic (C20:1)	310.52	0.14	0.16	0.16	0.18	0.16	0.18	0.13	0.15

[a] In CX:Y, X=number of carbons, Y=number of double bonds
[b] *MM* = molecular mass.

Table 6.5. Physical Chemical Properties of Palm Oils

Characteristic		CPO	BPO	RPO-LLE	RPO	Codex (27)
Acidity Level (mass %)		4.14	4.23	0.14	0.14	< 0.3 mass %
Carotenoids (ppm)		647.3	224.5	184.6	nd [f]	na [g]
Tocopherols (ppm)		691.6	718.1	218.8	322.3	150-1500
DAG [a] + MAG [b] (mass %)		6.97	8.14	0.81	8.46	na [g]
IV [c]		54.1	55.1	55.0	53.6	50-55
SV [d] (mg KOH/g oil)		197.7	198.0	197.4	197.7	190-209
PV [e] (mEq/kg)		6.76	11.49	7.48	1.08	< 10
Lovibond Color	Red (R)	29	11	10	4	na [g]
	Yellow (Y)	21	20	20	20	na [g]
Density (kg/m^3) at 45ºC		899.6	896.6	896.32	900.85	891-899
Viscosity (mPa s) at 45ºC		37.16	30.29	30.96	40.01	na [g]

[a] diacylglicerol; [b] monoacylglicerol; [c] iodine value; [d] saponification value; [e] peroxide value;
[f] not detected; [g] not avaiable

As can be observed in Table 6.4, the fatty acid composition of the palm oil are not affected by liquid-liquid extraction, presenting not significant differences in comparison with the palm oil industrially refined, the bleached palm oil used in the experiments and the crude palm oil.

Table 6.5 shows that liquid-liquid extraction process allowed the deacidification, promoting the attainment of a refined palm oil containing a free acidity of 0.14 mass % in solvent free-basis, and maintaining a significant level of carotenoids.

As also presented in Table 6.5, liquid-liquid extraction reduced the peroxide value (PV) from 11.49 measured in BPO to 7.48 in RPO-LLE, but in comparison with the traditionally refined palm oil (RPO), such value is high. Analyzing the Lovibond color results, it can be observed that yellow factor (Y) remained the same along traditional refining

process and after liquid-liquid extraction. On the other hand, the red factor (R) decreased after traditional deacidification steps, probably due to reduction of carotenoids content, but in the case of palm oil processed by liquid-liquid extraction the red factors has almost the same value measured for the bleached oil. In relation to MAG and DAG, the results show that LLE promotes a considerable reduction of these compounds. It is important to note that great part of losses of neutral oil showed in Table 6.4 can be a consequence of the reduction of MAG and DAG. This result is positive, once these partial acylglycerols may cause foaming and bitter taste in oil (28). In addition, the gel permeation HPLC analysis showed that polymeric acylglycerols were not detected in any samples studied. The results also show that the iodine and saponification values did not suffer significant changes after liquid-liquid extraction, indicating that RPO-LLE maintains the same characteristics of the RPO.

6.4 Conclusions

The response surface methodology analysis allowed the selection of better process conditions that maximize de FFAs transfer, minimize the loss of neutral oil (NO), and preserve the carotenoids.

The deacidification of palm oil by solvent extraction using the optimized conditions obtained in RSM were accomplished successfully, permitting the attainment of a refined oil (%FFA < 0.3 mass%) with high concentration of carotenoids, so maintaining its nutritional value.

6.5 Acknowledgements

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6.6 References

1. Bailey, A. E.. *Bailey's Industrial Oil and Fat Products - Volume 2*, 5ºed. Edited by Y. H. Hui, John Wiley & Sons, New York, 1995, pp. 313-320.
2. Thomopoulos, C. Méthod de Desacidification des Huiles par Solvant Sélectif. *Rev. Fran. des Corps Gras*, 18, 143-150 (1971).
3. Bhattacharyya, A. C., Majumdar, S.; Bhattacharyya, D. K. Refining of FFA Rice Bran Oil by Isopropanol Extraction and Alkali Neutralization. *Oléagineaux*, 42: 431-433 (1987).
4. Shah, K. J. Venkatesan, T. K. Aqueous Isopropyl Alcohol for Extraction of Free Fatty Acids from Oils. *J. Am. Oil Chem. Soc*. 66:783-787 (1989).
5. Kale, V. Katikaneni, S. P. R. Cheryan, M. Deacidifying Rice Brain Oil by Solvent Extraction and Membrane Technology. *Ibid*. 76:723-727 (1999).
6. Pina, C. G. & Meirelles, A. J. A Deacidification of corn oil by solvent extraction in a perforated rotating disc column. *Ibid.* 77:553-559, (2000).
7. Kim, S. Kim, C. Cheigh, H. Yoon, S. Effect of Caustic Refining, Solvent Refining and Steam Refining on the Deacidification and Color of Rice Bran Oil. *Ibid.* 62:1492-1495 (1985).
8. Türkay, S. & Civelekoglu, H. Deacidification of sulfur olive oil. I. Single-stage liquid-liquid extraction of miscella with ethyl alcohol. *Ibid.* 68:83-86 (1991a).
9. Türkay, S. & Civelekoglu, H. Deacidification of sulfur olive oil. II. Multi-stage liquid-liquid extraction of miscella with ethyl alcohol. *Ibid.* 68:818-821 (1991b).
10. Batista, E., Monnerat, S., Kato, K., Stragevitch, L., Meirelles, A. J. A. Liquid-liquid equilibrium for systems of canola oil, oleic acid and short-chain alcohols. *J. Chem. Eng. Data* 44:1360-1364 (1999a).

11. Batista, E., Monnerat, S., Stragevitch, L., Pina, C. G., Gonçalves, C. B., Meirelles, A. J. A. Prediction of Liquid-liquid equilibrium for systems of vegetable oils, fatty acids and ethanol. *Ibid.*44:1365-1369 (1999b).

12. Gonçalves, C. B; Batista, E.; Meirelles, A. J. A. Liquid-Liquid Equilibrium Data for the System Corn Oil + Oleic Acid + Ethanol + Water at 298.15K. *Ibid.* 47:416-420 (2002).

13. Rodrigues, C. E. C.; Antoniassi, R.; Meirelles, A. J. A. Equilibrium Data for the System Rice Bran Oil + Fatty Acids + Ethanol + Water at 298.2K. *Ibid.* 48:367-373 (2003).

14. Rodrigues, C. E. C., Pessôa Filho, P. A., Meirelles, A. J. A. Phase Equilibrium for the System Rice Bran Oil + Fatty Acids + Ethanol + Water + γ-Oryzanol + Tocols. *Fluid Phase Equilibria* 216:271-283 (2004).

15. Gonçalves, C. B & Meirelles, A. J. A. Liquid-liquid Equilibrium Data for the System Palm Oil + Fatty Acids + Ethanol + Water at 318.2 K. *Ibid*. (2004), In press.

16. Gonçalves, C. B, Pessôa Filho, P. A., Meirelles, A. J. A. Partition of Nutraceutical Compounds in Liquid-Liquid Systems. *J. Food Eng.* (2004), Submitted.

17. A.O.C.S. *Official methods and recommended practices of the American Oil Chemists' Society*, Press, 3 ed., Champaign, v. 1-2, 1988.

18. A.O.C.S. *Official methods and recommended practices of the American Oil Chemists' Society*, Press, 5 ed., Champaign, 1998.

19. IUPAC *Standard methods for the analysis of oils, fats and derivatives.* 6th edition, part 1 (sections I and II). PAQUOT, C. editor, Pergamon Press, 1979.

20. Porim Test Methods Caroten Content. *Palm Oil Research Institute of Malaysia*, 1990.

21. A.O.C.S. *Official and Tentative Methods of the American Oil Chemists' Society*, Press, 3 ed., Champaign, v.1, 1993.

22. Box, G. E. P.; Hunter, W. G.; Hunter, J. S. *Statistic for Experimenters – An Introduction to Design, Data Analysis and Model Building*. John Wiley & Sons, New York, 1978.

23. Khuri, A. I.; Cornell, J. A. *Response Surface-Design and Analysis*. ASQC Quality Press, New York, 1987.

24. Treybal, R. E. *Mass Transfer Operations*. 3 ed. McGraw-Hill, New York, 1980.

25. McCabe, W. L.; Smith, J. C. *Unit Operations of Chemical Engineering*. 3rd ed. McGraw-Hill Book, New York, 1976.
26. Bailey, A. E.. *Bailey's Industrial Oil and Fat Products - Volume 3*, 5ºed. Edited by Y. H. Hui, John Wiley & Sons, New York, 1995, pp. 350-352.
27. Codex Alimentarius - *Fats, oils and related products* - volume 8, p.29-32 - Joint FAO/ WHO Food and Agriculture Organization of the United Nations and World Health Organization, Rome, 1993.
28. Stuchlík, M; Žák, S. Lipid-Based Vehicle for Oral Drug Delivery. *Biomed. Papers* 145:17–26 (2001).

CAPÍTULO 7 -CONCLUSÕES GERAIS

Os resultados obtidos neste trabalho nos permitem concluir que dados de equilíbrio líquido-líquido para sistemas do tipo óleo/ ácido graxo/ álcool, podem ser facilmente determinados utilizando a metodologia adotada.

Para os dados medidos com o óleo de milho e o ácido oléico, observou-se que a presença de água causa um aumento da região bifásica contra uma diminuição do coeficiente de distribuição. Além disso, o etanol hidratado é mais seletivo do que o anidro, sendo, portanto o melhor solvente a ser utilizado, principalmente contendo um teor de água na faixa de 4 a 6%. Com relação aos dados de equilíbrio com óleo de palma e ácidos graxos (palmítico e oléico), observou-se que a adição de água no solvente causa um aumento considerável na região de separação, mas diminui pouco o coeficiente de distribuição dos ácidos graxos na faixa de 0 a 6%. Somente para valores acima de 6% de água no solvente tal efeito é um pouco mais pronunciado.

Apesar da complexidade dos sistemas estudados, os parâmetros estimados pelos modelos NRTL e UNIQUAC são representativos, uma vez que a descrição do equilíbrio líquido-líquido para todos os sistemas estudados apresentou desvios menores que 1,4% em relação aos dados experimentais.

Para o óleo de palma, os resultados apresentados permitem concluir também que é possível predizer o equilíbrio de fases de sistemas reais e complexos, contendo um óleo ácido pré-tratado e solvente alcoólico, utilizando parâmetros ajustados a sistemas modelo, mesmo considerando a presença de mais um ácido graxo nos sistemas. Estes parâmetros tornam possível a modelagem e simulação de extratores líquido-líquido utilizando os solventes propostos.

Apesar da baixa concentração de carotenóides e tocoferóis nos sistemas estudados, o uso do conceito de diluição infinita para o cálculo do coeficiente de partição foi realizado com sucesso, viabilizando o uso dos parâmetros obtidos para uma futura predição.

A metodologia de planejamento experimental e análise de superfície de resposta permitiu uma avaliação do processo de desacidificação por extração líquido-líquido de uma forma mais ampla, permitindo concluir que utilizando uma razão O:S ao redor de 0,75 e um teor de água no solvente em torno de 6%, é possível desacidificar o óleo de palma sem grandes perdas de óleo neutro e preservando os carotenóides.

O estudo da desacidificação na coluna de extração líquido-líquido indicou o sucesso do processo na extração dos ácidos graxos livres do óleo de palma, permitindo a obtenção de um óleo refinado com características muito próximas ao óleo obtido pelo refino tradicional, preservando os carotenóides. Este resultado é de extrema importância, uma vez que a presença destes compostos eleva o valor nutricional do óleo, tornando-o um alimento funcional.

CAPÍTULO 8 – SUGESTÕES PARA TRABALHOS FUTUROS

- Estudar o desempenho da coluna de extração em óleos com características distintas, como por exemplo, o óleo de coco, rico em ácidos graxos de cadeia curta e saturada (C12:0), e o óleo de algodão, rico em ácidos graxos de cadeia longa polinsaturados (C18:2);
- Fazer o scale-up do processo de extração líquido-líquido aplicado a desacidificação de óleos vegetais;
- Estudar a possibilidade de tratamento das correntes de saída do equipamento de extração;

ANEXO A

A.1. Caracterização da matéria-prima referente ao Capítulo 3

Tabela A.1. Composição em ácidos graxos do Ácido Oléico

Ácido Graxo	%molar	%massa
M	1,5889	1,3025
P	4,3945	4,0450
Po	6,3728	5,8197
S	0,5951	0,6077
O	81,9848	83,1276
Li	5,0178	5,0514
Le	0,0461	0,0461

Fonte: Batista et al. (1999)

Tabela A.2. Composição em ácidos graxos do Óleo de Milho

Símbolo	Ácido Graxo		M (g/gmol)	%molar	%massa
M	mirístico	C14:0[a]	228,38	0,0200	0,0164
P	palmítico	C16:0	256,43	12,8500	11,8457
Po	palmitoléico	C16:1	254,41	0,1300	0,1189
S	esteárico	C18:0	284,48	2,1500	2,1988
O	oléico	C18:1	282,47	34,3200	34,8506
Li	linoléico	C18:2	280,45	49,4400	49,8454
Le	linolênico	C18:3	278,44	0,2700	0,3034
A	araquídico	C20:0	312,54	0,8200	0,8208

[a] Em Cx:y, x é o número de carbonos e y é o número de ligações duplas

A.2. Figura referente a dados de equilíbrio apresentados no Capítulo 3

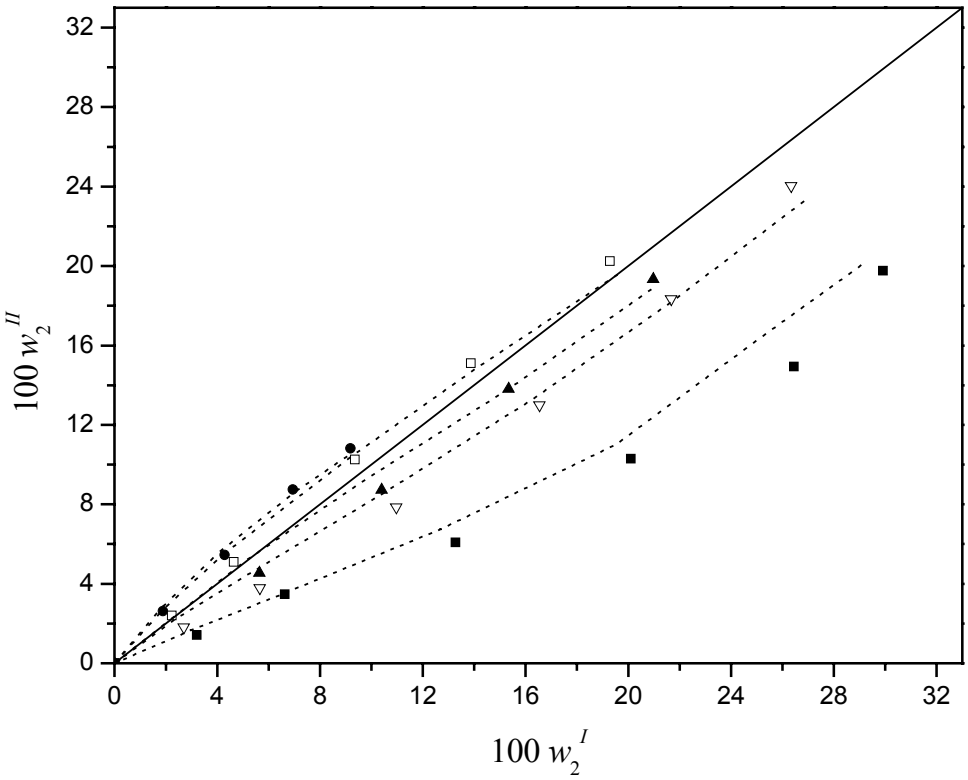


Figura A.1. Diagrama de distribuição a 298.15 K para o sistema óleo de milho (1) + ácido oléico (2) + etanol (3) + água (4): (●) etanol anidro; (□) etanol 5% hidratado; (▲) etanol 8% hidratado; (▽) etanol 12% hidratado; (■) etanol 18% hidratado; (- - -) UNIQUAC

A.3. Figura referente a dados de equilíbrio apresentados no Capítulo 4

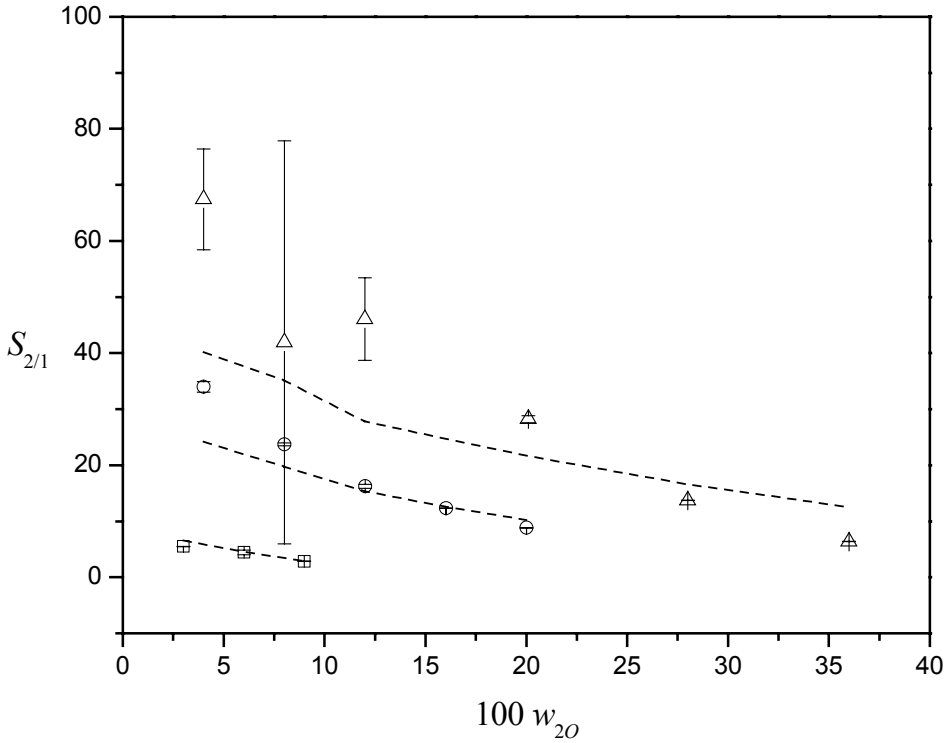


Figura A.2. Seletividade ($S_{2/1}$) para diferentes solventes: (□) etanol anidro; (○) etanol 6,10% hidratado; (△) etanol 12,41% hidratado; (·····) NRTL

A.4. Tabelas da composição dos compostos nutracêuticos referentes ao Capítulo 4

Tabela A.3. Composição em carotenóides do óleo de palma

Carotenóides	% mássica do total de carotenóides
Fitoeno	1,27
cis-β-Caroteno	0,68
Fitoflueno	0,06
β-Caroteno	56,02
α-Caroteno	35,16
cis-α-Caroteno	2,49
ξ-Caroteno	0,69
γ-Caroteno	0,33
δ-Caroteno	0,83
Neurosporeno	0,29
β-Zeacaroteno	0,74
α-Zeacaroteno	0,23
Licopeno	1,30

Tabela A.4. Composição em tocoferóis e tocotrienóis do óleo de palma

Tocoferóis	% mássica do total de tocoferóis
α-Tocoferol	21,5
β-Tocoferol	3,7
γ-Tocoferol	3,2
δ-Tocoferol	1,6
α-Tocotrienol	7,3
β-Tocotrienol	7,3
γ-Tocotrienol	43,7
δ-Tocotrienol	11,7

ANEXO B

B.1. Experimentos Preliminares na Coluna de Extração Líquido-Líquido

B.1.1. Descrição dos experimentos realizados

Com a finalidade de investigar as possíveis dificuldades de se realizar experimentos na coluna de extração, mantendo o óleo de palma aquecido a 45ºC (para que o mesmo não se solidificasse), foram realizados dois experimentos exploratórios:

Experimentos 1 e 2: Utilizou-se óleo de palma refinado com a adição de ácido oléico e ácido palmítico na proporção 1:1, obtendo-se uma acidez livre igual a 3,86% em massa. Devido ao que foi observado em testes com o óleo de farelo de arroz[‡‡], que mostraram a dificuldade de se trabalhar em rotações acima de 200 rpm (problemas de inundação), para o óleo de palma foram realizados testes em rotações mais baixas: 50 rpm (experimento 1) e 150 rpm (experimento 2).

Experimento 3: Utilizou-se óleo de palma branqueado com 3,32% de acidez livre. O teste foi realizado apenas na melhor rotação observada entre os experimentos 1 e 2 (150 rpm).

Após analisar as dificuldades e solucionar os problemas encontrados nos experimentos 1, 2 e 3, foram realizados experimentos finais com o óleo branqueado:

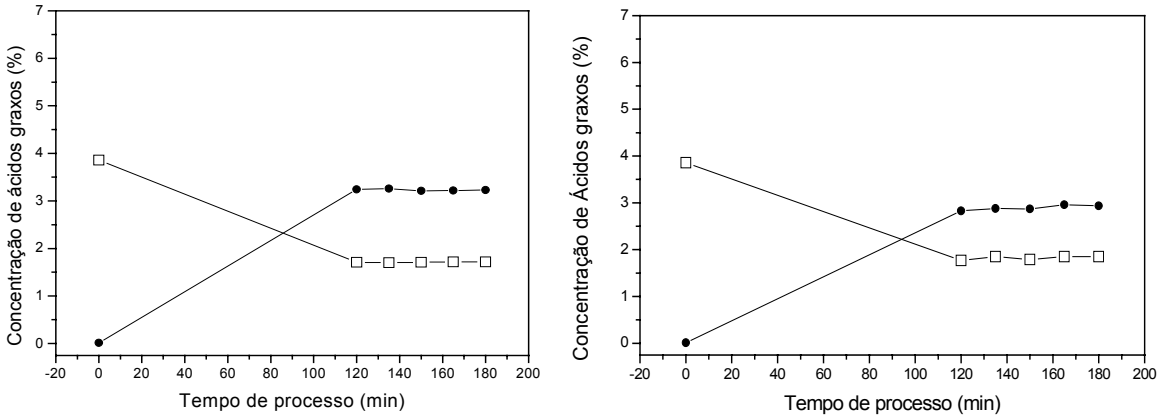
Experimentos 4, 5 e 6: Utilizou-se óleo de palma branqueado com 4,23% de acidez livre, sendo os experimentos realizados na rotação de 150rpm. Esses experimentos estão reportados no Capítulo 6 deste trabalho.

[‡‡] Rodrigues, C. E. C. Desacidificação do óleo de farelo de arroz por extração líquido-líquido. Campinas, 2004, Tese de Doutorado – Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas.

B.1.2. Resultados observados

Experimentos 1 e 2

Esses experimentos, realizados com um sistema modelo (óleo de palma refinado + ácido palmítico + ácido oléico), permitiram conhecer o comportamento da coluna de extração na desacidificação do óleo, variando a velocidade de rotação dos discos, como pode ser observado na Figura B.1 a seguir.



(a) experimento 1 (b) experimento 2

Figura B.1. Variação na concentração de ácidos graxos em PRDC a 150 rpm (a) e a 50 rpm (b) para a desacidificação de óleo de palma com 3,86% de ácidos graxos livres: (●) Concentração de ácidos graxos no extrato; (□) Concentração de ácidos graxos no refinado

Pela Figura B.1, observa-se que partindo de um óleo com 3,68% de acidez livre, e utilizando-se uma razão óleo:solvente igual a 1,07, foi possível obter um refinado com 1,7% de acidez a 150rpm. O extrato, nesta mesma rotação, apresentou cerca de 3,2 % de ácidos graxos livres (AGL). Pôde-se concluir também que a extração foi mais eficiente com velocidade de rotação de discos igual 150 rpm.

Experimento 3:

Esse experimento foi realizado com a melhor rotação encontrada entre os experimentos 1 e 2, e teve como objetivo conhecer o comportamento da coluna com o óleo de palma branqueado. A razão óleo:solvente (O:S) utilizada neste experimento foi igual a 1,26.

Apesar de apresentar boa eficiência na extração, a configuração da coluna para esse óleo não se mostrou satisfatória. Após um certo tempo de operação, houve falha na manutenção da temperatura nas mangueiras de entrada e saída, e por isso, o óleo solidificou-se parcialmente, causando variações nas correntes de refinado, como ser observado na Tabela B.1. Tal fato também causou variação nas concentrações de ácidos graxos livres nas correntes de extrato e refinado, como pode ser observado na Figura B.2.

Tabela B.1. Vazões de refinado medidas após atingido o regime, em uma PRDC para desacidificação de óleo de palma branqueado com 3,32% de AGL

Tempo de Regime (min)	Vazão de Refinado (g/min)
0	25,27
15	31,82
30	30,86
45	19,19
60	10,03
Média	*24,52*

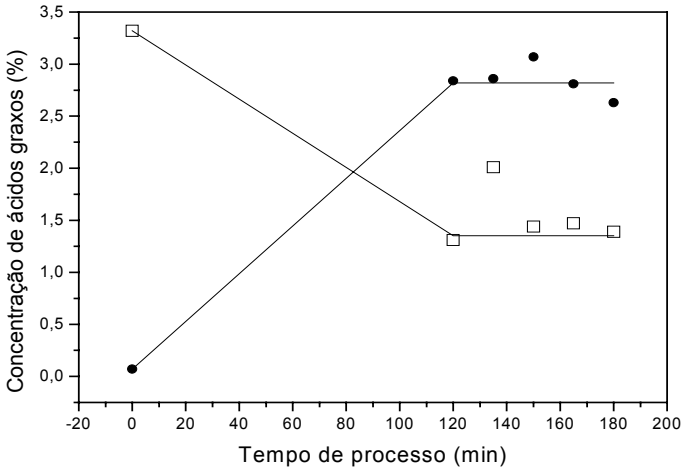


Figura B.2. Variação na concentração de ácidos graxos em PRDC a 150 rpm para a desacidificação de óleo de palma com 3,32 % de AGL: (●) Concentração de AGL no extrato; (□) Concentração de AGL no refinado; (—) Concentração de AGL global

A solidificação do óleo ao longo do experimento ocorreu porque o óleo de palma é constituído por uma quantidade significante (aproximadamente 50%) de estearina (fração saturada), que só é líquida a temperaturas superiores a 45ºC. Assim, foi necessário

reconfigurar toda a linha de extração para que isto não ocorresse nos próximos experimentos.

Experimentos 4,5 e 6:

Devido ao observado nos experimentos anteriores (1, 2 e 3), providências foram tomadas para evitar a solidificação do óleo durante os experimentos 4, 5 e 6, que visavam a desacidificação de um óleo branqueado até um valor menor ou igual ao exigido pela legislação (<0,3 %). Neste caso, o tamanho das mangueiras foi reduzido e o número de conexões diminuído, a fim de evitar pontos de acúmulo de óleo. Além disso, aumentou-se o número de fontes de ar quente nas regiões não encamisadas da coluna. Os resultados destes experimentos estão reportados no Capítulo 6 deste trabalho.

Vale ressaltar que apesar de todo o controle de temperatura realizado na coluna de extração, foram observadas algumas dificuldades de homogeneização das amostras depois de retiradas da coluna para análise. Normalmente, quando as amostras entram em contato com a temperatura ambiente (menor que a da coluna), estas tendem a ficar heterogêneas muito rápido. Este fato pode refletir diretamente nos erros do balanço de massa, e ressalta o problema de controlar a temperatura das amostras fora da coluna, onde a temperatura é a ambiente.