5 Liquid–Liquid Extraction Applied to the Processing of Vegetable Oil

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CONTENTS

In this chapter, we will discuss the fundamentals of the liquid–liquid extraction process applied to deacidification of vegetable oils with some special attention to the retention of bioactive compounds. Deacidification is the removal of free fatty acids from vegetable oils, and it is the most difficult step in oil refining, mainly because of its impact on productivity. Deacidification of oils is usually performed by chemical, physical, or miscella methods. Liquid–liquid extraction is a quite promising process for deacidification of vegetable oils that minimizes the loss of neutral oil and retains bioactive compounds. In the first part of this chapter, fundamentals of liquid–liquid extraction, the main concepts of the equipment for stagewise and continuous contact types, the liquid–liquid equilibrium diagram for fatty components and short-chain alcohol systems, distribution coefficients and selectivity of the solvent, mass transfer and some graphical methods for solving the equilibrium and mass balances, the most important thermodynamic models for description or prediction of liquid–liquid equilibrium, and the mathematical basis for simulating a stagewise column are presented and discussed. In the second part, a review of the literature in applying liquid–liquid extraction in the food and food-related processes are presented. In the last part of this chapter, we present our own results in the deacidification of vegetable oils and the retention of bioactive compounds.

5.1 FUNDAMENTALS OF LIQUID–LIQUID EXTRACTION

Crude vegetable oils are a mixture of triacylglycerols, partial acylglycerols, free fatty acids, phosphatides, pigments, sterols, and tocopherols. Refining procedures have been developed over decades to make the vegetable oil suitable for edible use. Some of the minor components are valuable and should be retained in the refined oil or recovered from the stream generated in the refining processes.

Fatty acids are almost straight chain aliphatic carboxylic acids. The most natural fatty acids are C4 to C22, varying chain length and unsaturation. Systematic names for fatty acids are complicated for casual use. Two numbers separated by a colon represent the number of carbons and number of double bounds. The position of double bounds could be indicated from carboxyl end of the chain, shown as Δx, where x is the number of carbons from carboxyl end. The double-bound geometry *cis* and *trans* is represented by abbreviation c and t, respectively. Some fatty acids have common names that facilitate their identification. Nomenclatures and formula for some fatty acids are presented in Table 5.1.

Triacylglycerols are triesters of glycerol (1,2,3-trihydroxypropane) with fatty acids. Most of triacylglycerols do not have a random distribution of fatty acids on the glycerol backbone. In vegetable oils, unsaturated fatty acids predominate at position 2 of the glycerol backbone. Simplified structures and abbreviations are used to identify the fatty acids esterified to glycerol; e.g. 1-stearoyl-2-oleoyl-3-stearoyl-*sn*-glycerol is abbreviated to SOS.

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The removal of free fatty acids, deacidification, is the most difficult step in oil refining, mainly because of its impact on the productivity. Deacidification of oils is

TABLE 5.1
Nomenclatures and formulas for some fatty acids

Fatty acid	Common name	Symbol	Formula
8:0	Caprylic		$CH_3(CH_2)_6COOH$
10:0	Capric		$CH_3(CH_2)_8COOH$
12:0	Lauric	La	$CH_3(CH_2)_{10}COOH$
14:0	Myristic	M	$CH_3(CH_2)_{12}COOH$
16:0	Palmitic	P	$CH_3(CH_2)_{14}COOH$
18:0	Stearic	S	$CH_3(CH_2)_{16}COOH$
18:1, 9c	Oleic	O	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
18:2, 9c12c	Linoleic	L	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$
18:3, 9c12c15c	Linolenic	Ln	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$
22:1, 13c	Erucic	E	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$

performed by chemical, physical, and miscella methods. Most edible oils are produced by chemical refining [1] because it is a highly versatile process applicable for all crude oil. However, for oils with high acidity, chemical refining causes high losses of neutral oil as a result of saponification and emulsification. For highly acidic oils, the physical method is also a feasible process for deacidification that results in a lower loss of neutral oil than the chemical method, but more consumption of energy is required, and the refined oil is subject to undesirable alteration in color and to a reduction of stability with regard to resisting oxidation. The miscella method is the deacidification of crude oil prior to solvent stripping. In this process, the neutralization reaction of free fatty acids with sodium hydroxide occurs in the miscella, which is a mixture of 40%–60% oil in hexane. Bhosle and Subramanian [2] present some new approaches that may be used as alternatives to current industrial deacidification, such as biological deacidification, reesterification, supercritical fluid extraction, membrane technology, and liquid–liquid extraction.

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Liquid–liquid extraction is an alternative processes carried out at room temperature and atmospheric pressure. According to Thomopoulos [3], this process is based on the difference in the solubility of free fatty acids and triacylglycerols in the solvent, as well as on the difference of boiling points of triacylglycerols, free fatty acids, and solvent during the subsequent separation.

Currently, cleaner processes have been developed because of environmental issues, and there is a demand for new products retaining minor compounds with bioactive properties. Liquid–liquid extraction is a quite promising process that minimizes the loss of neutral oil and retains bioactive compounds. The streams leaving the extract column, raffinate and extract, will be separated by other unity operations and a nonpolluting stream is generated.

5.1.1 Equipment

5.1.1.1 Equipment for Liquid–Liquid Extraction

The rate of mass transfer between two liquid phases is described by $N = KA\Delta c$, where N is the mass transfer rate, K is the overall mass transfer coefficient, A is

AQ3 the interfacial area, Δc the composition difference driving force. The rate may be increased by dispersing one of the liquids into smaller droplets, which are immersed into the other, with resulting large interfacial area. This favor eddy diffusion rather than molecular diffusion, which is slow.

Equipment for liquid–liquid extraction provides the direct contact of two immiscible liquids that are not in equilibrium, which involves dispersing one liquid in the form of small droplets (the dispersed phase) into the other liquid (continuous phase) in attempting to bring the liquids to equilibrium and these resulting liquids are mechanically separated.

5.1.1.2 Equipment for Stagewise Contact

The typical and oldest extraction equipment is known as mixer-settler, in which each stage presents two well-defined and delimited regions: the first, the mixer, involves dispersing one of the liquids to the other and the second, the settler, involves the mechanical separation. Such an operation may be carried out in batch or continuous flow. If batch, the same vessel will be used for both mixing and settling; if continuous, the mixer and settler usually are in different vessels. The mixing vessel uses some form of rotating impeller placed on its center, which provides an effective dispersion of phases. The simplest settler is a decanter, and a baffle may be used to protect the vessel from the disturbance caused by the flow entering the dispersion. This basic unity of mixer-settler may be connected to form a cascade, for cross-flow or more usually countercurrent flow.

The perforated-plate (sieve-plate) column is similar to a tray distillation column. The plates contain downspouts in their free extremity, which allow the downward flow of the heavy liquid (continuous phase). Below each plate and outside the downspout, the droplets of the light phase (dispersed one) coalesce and accumulate in a liquid layer. This layer of liquid flows through the holes of the plate and is dispersed in a large number of droplets within the continuous phase located above the plate.

5.1.1.3 Equipment for Continuous Contact

In this equipment, two immiscible liquids flow countercurrently in continuous contact as a result of the difference in density of the liquid streams without settling. The force of gravity acts to provide the flows, and the equipment is usually a vertical column, with the light liquid entering at the bottom and the heavy one at the top. The complete separation of phases occurs only in one extremity of the equipment, in the top, if the dispersed phase is the light liquid or in the bottom, if the heavy liquid is dispersed.

The simplest equipment for differential contact is the spray column, which consists basically of an empty shell with provision for introducing and removing the liquids.

If the light liquid is dispersed, the heavy liquid enters at the top through the distributor and fills the column, flows downward as a continuous phase, and leaves at the bottom. The light liquid enters at the bottom of the column by a distributor, which disperses it into small droplets. These droplets flow upward through the continuous phase, coalesce, and form an interface at the top of the column, and the light liquid leaves the equipment. Although this column is easily constructed, its use is not recommended because of its low efficiency in mass transfer as a result of absence of accessories that improve the dispersion or high axial mixture.

In packed columns, the shell of the column may be filled with a random or a structural packing arrangement. In the first case, the packing is constituted of elements one-eighth of the diameter of the column, which is made for a gas–liquid system such as Raschig, Lessing, and Paul rings, and Berl and Intalox saddles, disposed in random arrangement with intermediate support grids. The packing is made of ceramic, metal, or polymeric materials. Structured packing is formed from vertical corrugated thin sheets of ceramic, metal, or plastic with the angle of the corrugations reversed in adjacent sheets to form a very open honeycomb structure with inclined channels and a high surface area. To simplify installation, the packing is found in segments of diameter near to that of the diameter of the column. Liquid distribution is crucial for a proper distribution of the liquids in the column. The material of packing must be chosen to ensure that the continuous phase will wet it preferentially and the droplets will not coalesce.

Extractors could also be mechanically agitated in a fashion somewhat similar to that of the mixer-settler. There is a great variety of mechanically agitated columns for continuous contact.

The first example is the Rotating Disk Contactor column or simply RDC column, which has a number of horizontal stator rings fixed in the shell that divides the extractor into a number of chambers. A series of circular flat disks is fixed on a rotating central shaft and is centered in each chamber. In the literature, we could find modifications of the original RDC column, such as the ones that use perforated disks (PRDC) or columns without stators.

The Khüni column has a rotating shaft with impellers that are fixed in the center of a compartment delimited by two adjacent perforated plates. These plates help to control the volumetric fraction of the dispersed phase held inside the column. In the York–Scheibel column, the agitation is similar to the Khüni column, but each compartment with impellers are separated from each other by packing sections.

Pulsed columns are a variation of agitated columns, where perforated plates move up and down or the liquids are pulsed in a stationary column by an outside mechanism. This type of agitation is compatible with other extractors, like packed or perforated-plate columns.

5.1.1.4 Centrifugal Extractors

The most important centrifugal extractor is the Podbielniak extractor, which has a horizontal shaft that rotates a cylindrical drum rapidly (30–85 rps). There are perforated concentric plates inside the drum. The two liquids are fed into the equipment by the shaft, and the centrifugal force moves the light liquid to the center and the heavy to the wall of the drum countercurrently. Both phases leave the equipment through the shaft in the opposite sides of their feed. These extractors are important when short residence times are necessary and for liquids with a small density difference. Continuous centrifuges can also be used connected to a settler to accelerate the separation of the phases.

More information about equipment for liquid–liquid extraction can be found in Treybal [4] and Godfrey and Slater [5].

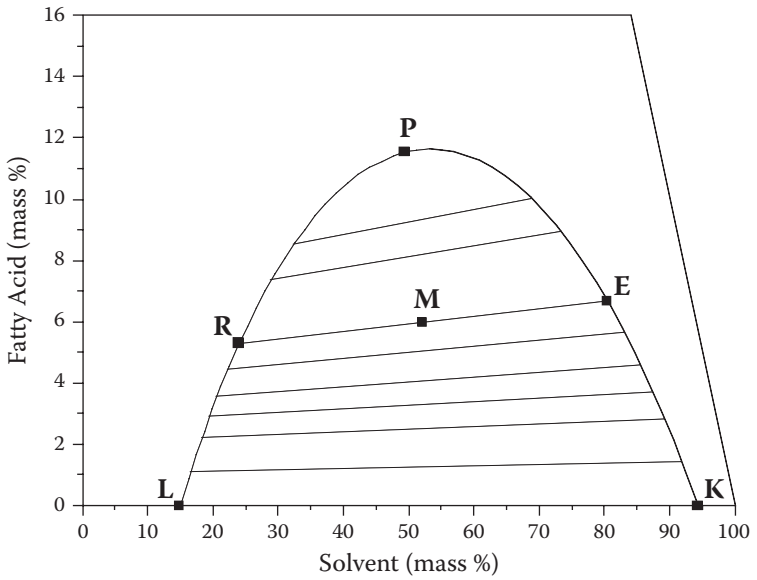


FIGURE 5.1 Liquid–liquid equilibrium diagram (K to L, base line; R to E, tie line; M, overall composition; P, plait point).

5.1.2 Liquid–Liquid Equilibrium Diagram for Fatty System and Short-Chain Alcohol Systems

In the system of vegetable oil (1) + free fatty acids (2) + short-chain alcohol (3), only the pair (1) + (3) is partially soluble. The diagrams in a triangular coordinates are used at constant temperature and pressure. In a rectangular coordinate, abscissa and ordinate present the composition of the short-chain alcohol (component 3) and the free fatty acid (component 2), respectively.

Figure 5.1 presents an example of a liquid–liquid equilibrium diagram of this fatty system, of which the components 1(vegetable oil) and 3 (short-chain alcohols) are partially miscible.

The component 2, the free fatty acid, dissolves completely in vegetable oil (1) and short-chain alcohol (3), but 1 and 3 dissolve only to a limited extend, and they are represented in the diagram by the saturated liquid binary solutions at L (rich in oil, 1) and at K (rich in short-chain alcohols, 3). Any binary mixture between L and K will separate into two immiscible liquids with composition at L and K. The point L represents the solubility of the short-chain alcohol in the vegetable oil, and the point K, the solubility of the vegetable in the short-chain alcohols.

The LRPEK curve is the binodal curve and represents the change in solubility of the phase rich in the vegetable oil (oil phase) and the phase-rich short-chain alcohol (alcoholic phase). Outside this curve, any ternary mixture will be a solution of one phase. Underneath this curve, any ternary mixture, such as mixture M, will form two immiscible mixtures of equilibrium composition indicated at R (oil phase) and E (alcoholic phase). The line RE is a tie line and must pass necessarily through point M, which represents the overall composition.

The point P, known as the plait point, is the last tie line where the binodal curve converges and the composition of the oil and alcoholic phases are equal.

The distribution coefficient (*ki*) of component *i* is defined as the ratio of its composition in phase II (alcoholic phase) to its composition in phase I (oil phase):

$$k_i = \frac{w_i^{II}}{w_i^{I}}. \tag{5.1}$$

In the example presented in Figure 5.1, the composition of free fatty acid (2) in phase II is larger than in phase I and hence the distribution coefficient will be larger than 1.

The capacity of short-chain alcohols (3) for separating the free fatty acid (2) from vegetable oil (1) is measured by the ratio of the distribution coefficient of the free fatty acid (2) to the distribution coefficient of the vegetable oil (1). This factor of separation is known as selectivity and represents the effectiveness of a short-chain alcohol in extracting the free fatty acid from the vegetable oil. Then the selectivity must exceed unity, and the greater values are the better, that is, the separation is easier:

$$\beta_{ij} = \frac{k_i}{k_j}. \tag{5.2}$$

5.1.3 Mass Transfer: Mass Balance Equations

In this section, we present the mass balances for a extractor of the stagewise type. Each stage is a theoretical stage, such that the extract and raffinate streams that are leaving are in equilibrium. In the next topic, we discuss the lever-arm rule for graphical addition in rectangular coordinates that will be useful for understanding the solutions.

5.1.3.1 Lever-Arm Rule

If a mixture with R kg is added to another E kg, both containing A, B, and C components, a new ternary mixture is generated with M kg. This mixing process is represented in Figure 5.2 and the lever-arm rule in Figure 5.3.

We can write the global mass and mass balance for components B and C as follows:

Global mass balance:

$$R + E = M, \tag{5.3}$$

Mass Balance for component B:

$$Rx_{B,R} + Ey_{B,E} = Mx_{B,M}, \tag{5.4}$$

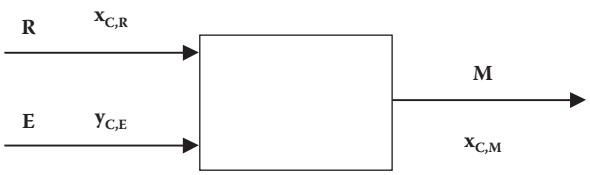


FIGURE 5.2 Mixing process.

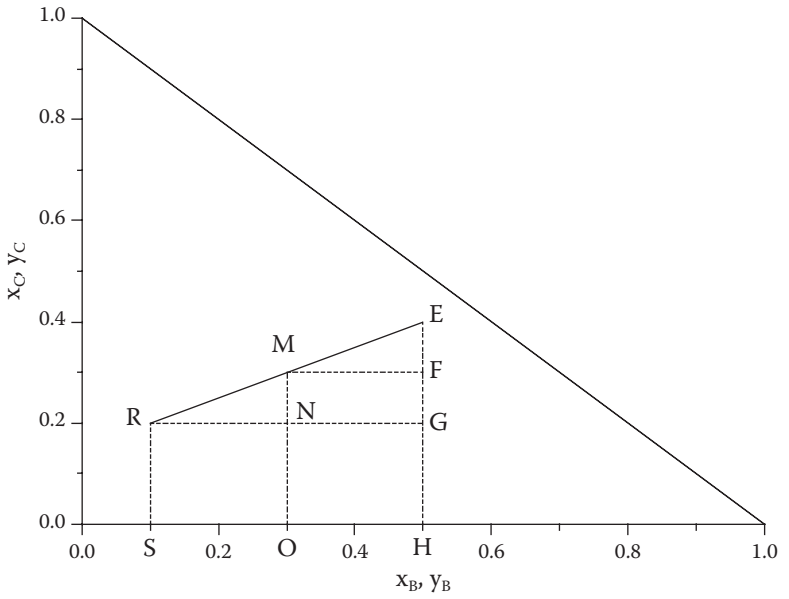


FIGURE 5.3 Lever-arm rule in rectangular coordinates.

Mass Balance for component C:

$$Rx_{C,R} + Ey_{C,E} = Mx_{C,M}, \tag{5.5}$$

substituting Equation 5.3 into 5.4 and rearranging,

$$\frac{R}{E} = \frac{y_{B,E} - x_{B,M}}{x_{B,M} - x_{B,R}}, \tag{5.6}$$

substituting Equation 5.3 into 5.5 and rearranging,

$$\frac{R}{E} = \frac{y_{C,E} - x_{C,M}}{x_{C,M} - x_{C,R}}, \tag{5.7}$$

combining Equations 5.6 and 5.7 and rearranging,

$$\frac{x_{C,M} - x_{C,R}}{x_{B,M} - x_{B,R}} = \frac{y_{C,E} - x_{C,M}}{y_{B,E} - x_{B,M}}. \tag{5.8}$$ AQ7

This shows that the points R, M, and E must be lined up. This straight line is represented in Figure 5.3.

From Figure 5.3, one can see that if

$$x_{C,R} = \text{line RS or } \overline{RS}$$
$$y_{C,E} = \text{line EH or } \overline{EH}$$
$$x_{C,M} = \text{line MO or } \overline{MO},$$

$$\text{then} \quad \frac{R}{E} = \frac{y_{C,E} - x_{C,M}}{x_{C,M} - x_{C,R}} = \frac{\overline{EH} - \overline{FH}}{\overline{MO} - \overline{RS}} = \frac{\overline{EF}}{MN},$$

and by using a similar right angle triangles,

$$\frac{R}{E} = \frac{\overline{EF}}{\overline{MN}} = \frac{\overline{ME}}{\overline{RM}}. \tag{5.9}$$

5.1.3.2 Single-Stage Equilibrium Extraction

Consider the following example: 100 kg/h of vegetable oil with 10 % (mass) of fatty acid and 100 kg/h of pure ethanol enter in a single equilibrium stage. The process is shown in Figure 5.4. The streams are mixed, and the exit streams R_1 and E_1 leave in equilibrium:

Global mass balance:

$$F + S_1 = E_1 + R_1 = M_1 = 200 \text{ kg/h}.$$

Apply lever-arm rule for overall composition:

$$\frac{\overline{FM_1}}{\overline{FS_1}} = \frac{S}{M} = \frac{100}{200} = 0.5,$$

Mass balance for component C:

$$x_{C,M_1} = \frac{x_{C,F}F + y_{C,S_1}S_1}{M_1},$$

Mass balance for component B:

$$x_{C,M_1} = \frac{x_{B,F}F + y_{B,S_1}S_1}{M_1},$$

Mass flows of extract and raffinate by lever-arm rule:

$$\frac{\overline{R_1M_1}}{E_1M_1} = \frac{E_1}{R_1} = 0.9 \Rightarrow E_1 = 0.9R_1$$

$$E_1 = 94.74 \text{ kg/h}$$
$$R_1 = 105.26 \text{ kg/h}$$

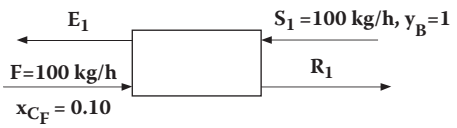


FIGURE 5.4 Single-stage extraction.

Composition of extract (E_1) and raffinate (R_1) Stream from liquid–liquid diagram (Figure 5.5):

E_1	R_1
$y_{C,E1} = 0.052$	$x_{C,R1} = 0.048$
$y_{B,E1} = 0.925$	$x_{B,R1} = 0.120$
$y_{A,E1} = 1 - (y_{B,E1} + y_{C,E1}) =$	$x_{A,R1} = 1 - (x_{B,R1} + x_{C,R1}) =$
$= 1 - (0.052 + 0.925) = 0.023$	$1 - (0.078 + 0.120) = 0.832$

Lever-arm rule for extract (E_1) and raffinate (R_1) Stream:

$$\frac{E_1}{R_1} = \frac{\overline{R_1M_1}}{\overline{E_1M_1}} = 0.9 \Rightarrow E_1 = 0.9R_1$$

$$R_1 = 105.26 \text{ kg / h}$$
$$E_1 = 94.74 \text{ kg / h.}$$

5.1.3.3 Multistage Crosscurrent Extraction

Consider the following example: 100 kg/h of vegetable oil with 10 % (mass) of fatty acid and 100 kg/h of pure ethanol enter in the first stage of a multistage crosscurrent extractor. The process is shown in Figure 5.6. The streams that enter in each stage n are mixed and the exit streams R_n and E_n leave in equilibrium. The raffinate stream R is successively in contact with fresh solvent stream. In this case, we consider that $R_{n-1} = S_n$. The mass fraction of fatty acid in the final raffinate is 0.005.

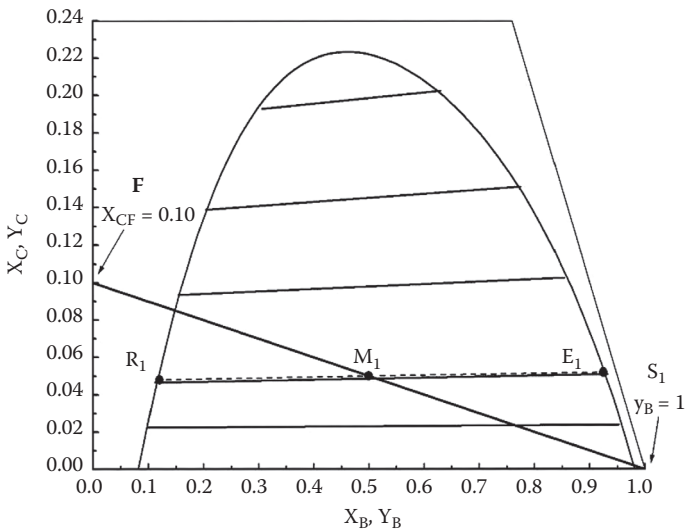


FIGURE 5.5 Phase diagram for single-stage extraction.

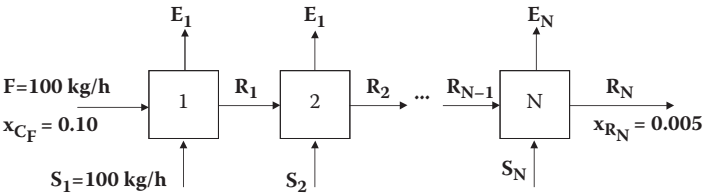


FIGURE 5.6 Flow sheet of crosscurrent extraction.

Mass balance in stage 1:

$$F + S_1 = M_1 = R_1 + E_1$$

Match with a line through the points F and S_1 (Figure 5.7)
Apply lever-arm rule to find point M_1:

$$\frac{\overline{FM_1}}{\overline{FS_1}} = \frac{S_1}{M_1} = \frac{100}{200} = 0.5.$$

$\overline{FS_1}$ is known, and then $\overline{FM_1}$ is found by lever-arm rule or by mass balance for components B and C (left column and right column, respectively):

$$x_{C,M} = \frac{x_{C,F}F + y_{C,S_1}S_1}{M_1} \qquad x_{C,M_1} = 0.5$$

$$x_{B,M} = \frac{x_{B,F}F + y_{B,S_1}S_1}{M_1} \qquad y_{C,M_1} = 0.5$$

If there is no tie line that passes in M_1 in the liquid–liquid diagram, it is necessary to interpolate a tie line to find E_1 and R_1 (Figure 5.7).

Mass balance for the next stage:

$$R_1 + S_2 = M_2 = R_2 + E_2.$$

Match the points R_1 and S_2, applying the lever-arm rule to find M_2 (Figure 5.7).
If $R_{i-1} = S_i$, then $R_1 = S_2$:

$$\frac{\overline{RM_2}}{\overline{RS_2}} = \frac{S_2}{M_2} = 0.5.$$

The segment $\overline{RS_2}$ is known, so $\overline{RM_2}$ is found.

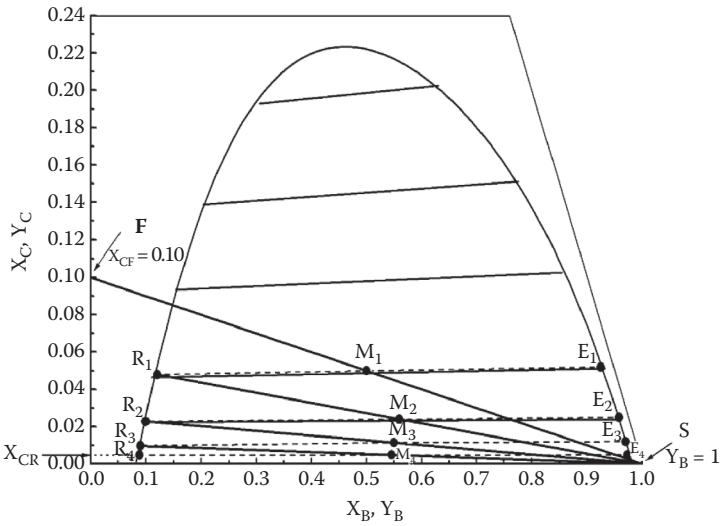


FIGURE 5.7 Phase diagram for crosscurrent extraction.

A new tie line passing through M_2 is traced, and the points E_2 and R_2 are found. This procedure must go on until $x_{C,R_N} \leq 0.005$. In this example, the extractor has four stages (Figure 5.7).

Stage 1:

$$S_1 = 100 \text{ kg/h}$$

$$R_1 + E_1 = M_1 = 200 \text{ kg/h}$$

$$\frac{E_1}{R_1} = \frac{\overline{R_1 M_1}}{\overline{E_1 M_1}} = 0.9 \Rightarrow E_1 = 0.9 R_1$$

$$R_1 = 105.26 \text{ kg/h}$$

$$E_1 = 94.74 \text{ kg/h}$$

Stage 2:

If $R_{i-1} = S_i$, then $R_1 = S_2$.

$$S_2 = 105.26 \text{ kg/h}$$

$$R_1 + S_2 = M_2 = R_2 + E_2$$

$$R_2 + E_2 = 210.52 \text{ kg/h}$$

$$\frac{E_2}{R_2} = \frac{\overline{R_2M_2}}{\overline{E_2M_2}} = 1.16 \Rightarrow E_2 = 1.16R_2$$

$$R_2 = 97.46 \text{ kg/h}$$
$$E_2 = 113.06 \text{ kg/h}.$$

Stage 3:
If $R_{i-1} = S_i$, then $R_2 = S_3$.

$$S_3 = 97.46 \text{ kg/h}$$

$$R_2 + S_3 = M_3 = R_3 + E_3$$

$$R_3 + E_3 = 194.92 \text{ kg/h}$$

$$\frac{E_3}{R_3} = \frac{\overline{R_3M_3}}{\overline{E_3M_3}} = 1.10 \Rightarrow E_3 = 1.10R_3$$

$$R_3 = 92.82 \text{ kg/h}$$
$$E_3 = 102.10 \text{ kg/h}.$$

Stage 4:1
If $R_{i-1} = S_i$, then $R_3 = S_4$.

$$S_4 = 92.82 \text{ kg/h}$$

$$R_3 + S_4 = M_4 = R_4 + E_4$$

$$R_4 + E_4 = 185.64 \text{ kg/h}$$

$$\frac{E_4}{R_4} = \frac{\overline{R_4M_4}}{\overline{E_4M_{43}}} = 1.07 \Rightarrow E_3 = 1.07R_3$$

$$R_3 = 89.68 \text{ kg/h}$$
$$E_3 = 95.96 \text{ kg/h}.$$

The total mass flow of extract:

$$E = E_1 + E_2 + E_3 + E_4 = 405.86 \text{ kg/h}.$$

From the liquid–liquid diagram:

$$y_{C,E_1} = 0.052$$
$$y_{C,E_2} = 0.025$$
$$y_{C,E_3} = 0.012$$
$$y_{C,E_4} = 0.005$$

and

$$y_{C,E} = \frac{\sum_{i=1}^{4} E_i y_{C,E_i}}{E} = 0.023 \cdot$$

5.1.3.4 Continuous Multistage Countercurrent Extractor

In this case, 100 kg/h of vegetable oil with 10% (mass) of fatty acid enters in the first stage and 300 kg/h of pure ethanol in the opposite side of the extractor. Extract and raffinate streams flow in a countercurrent arrangement. Figure 5.8 shows the flow sheet of the process. Each of the raffinate and extract streams that leave any of the stages are in equilibrium. In this case, the mass fraction of fatty acid in the final raffinate stream must be less than or equal to 0.005.

Global mass balance for the extractor:

$$F + S = M = R_N + S_1 .$$

Mass balance for each stage:

Stage 1: $E_1 + R_1 = F + E_2 \Rightarrow E_1 - F = E_2 - R_1$

Stage 2: $E_2 + R_2 = R_1 + E_3 \Rightarrow E_2 - R_1 = E_3 - R_2$

…

Stage N: $E_N + R_N = R_{N-1} + S \Rightarrow E_N - R_{N-1} = S - R_N$

$$E_1 - F = E_2 - R_1 = E_3 - R_2 = ... = E_N - R_{N-1} = S - R_N = \Delta .$$

Global mass balance for the extractor:

$$F + S = M = R_N + S_1 = 400 \text{ kg/h} .$$

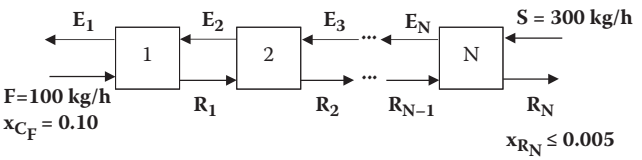


FIGURE 5.8 Flow sheet of countercurrent extraction.

Match the points F and S and applying the lever-arm rule (Figure 5.9):

$$\frac{\overline{FM}}{FS} = \frac{S}{M} = \frac{300}{400} = \frac{3}{4}.$$

And from mass balance:

$$x_{C,M} = \frac{x_{C,F}F + y_{C,S}S}{M} \qquad x_{C,M} = 0.025$$

$$x_{B,M} = \frac{x_{B,F}F + y_{B,S}S}{M} \qquad x_{B,M} = 0.750.$$

Match the point R_N to M and find point E_1 in the binodal curve. The points R_N and E_1 are lined up by mass balance.

To find the point Δ, trace the lines $\overline{FE_1}$ and $\overline{R_N S}$, the interception of the two lines is the point Δ.

By mass balance the points F, E_1, and Δ and the points R_N, S, and Δ are lined up:

$$E_1 - F = S - R_N = \Delta$$

Match the point R_1 to Δ and find the point E_2 in the binodal curve:

$$E_2 - R_1 = \Delta.$$

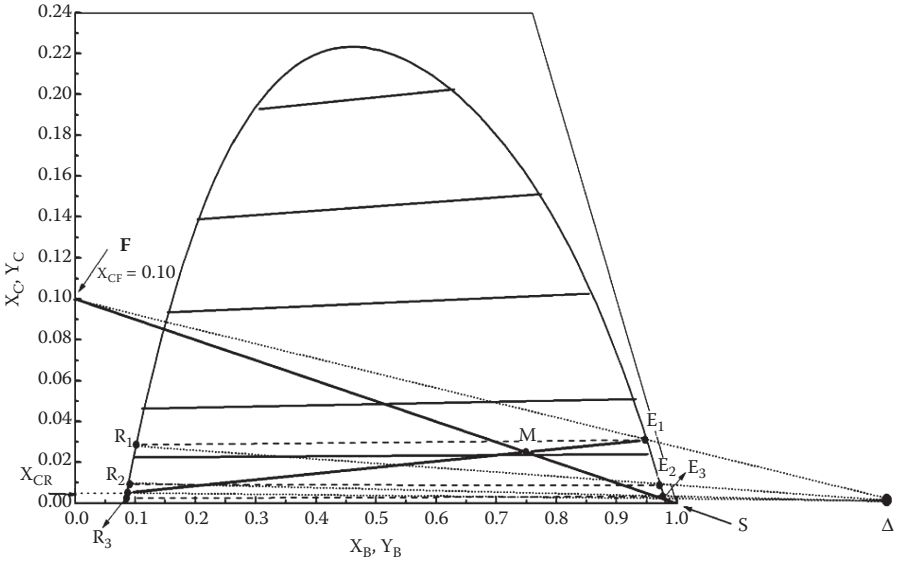


FIGURE 5.9 Phase diagram for countercurrent extraction.

Use this procedure until $x_{C,R_N} \leq 0.005$. In this example, three stages are necessary to reach this composition of component C in the raffinate stream.

The mass flows of raffinate and extract, the lever-arm rule is applied:

$$\frac{\overline{R_N M}}{\overline{E_1 M}} = \frac{E_1}{R_N} = 3.3 \Rightarrow E_1 = 3.3 R_N$$

$$E_1 + R_N = 400 \text{ kg / h}$$
$$R_N = 93.02 \text{ kg / h}$$
$$E_1 = 306.98 \text{ kg / h}.$$

5.1.4 Thermodynamic: Phase Equilibrium

Design of chemical separation, such as liquid–liquid extraction, requires quantitative partial equilibrium properties of fluid mixture. When it is not possible to obtain all data for the desirable mixture in temperature and pressure conditions of interest, it is necessary to correlate the available experimental data to obtain the best interpolation.

The thermodynamic equilibrium condition for each component *i* in the mixture is given by the following:

$$f_i^I = f_i^{II} \tag{5.10}$$

using the definition of the activity coefficient we have

$$\gamma_i^I x_i^I f_i = \gamma_i^{II} x_i^{II} f_i, \tag{5.11}$$

where

$$\gamma_i^I x_i^I = a_i^I \quad \text{and} \quad \gamma_i^{II} x_i^{II} = a_i^{II}. \tag{5.12}$$

Many semi-empirical expressions have been proposed in literature to correlate excess Gibbs energy, mainly to the composition of the mixture. All these expressions contain adjustable parameters to fit experimental data in order to calculate the activity coefficient. The main molecular models suggested for description of phase equilibrium are the NRTL (Non-Random Two-Liquid) [6] and the UNIQUAC (Universal Quasi Chemical) [7] models. When the molecular weights of the components in the mixture are very different, such as in the fatty systems containing short-chain alcohols, it is preferable to use the mass fraction as a composition unit. Oishi and Prausnitz [8] had already used this procedure for calculating solvent activity with the UNIQUAC and the UNIFAC models in polymeric solutions.

In this case, activity should be rewritten as follows:

$$a_i = \gamma_i^x x_i = \gamma_i^w w_i, \tag{5.13}$$

where

$$\gamma_i^x = \gamma_i^w M_i \sum_j^n w_j / M_j. \tag{5.14}$$

In the NRTL model, the activity coefficient using composition expressed in mass fraction takes the following form:

$$\ln\gamma_i = \frac{\sum_j^C \frac{\tau_{ji} G_{ji} w_j}{M_j}}{\sum_j^C \frac{G_{ji} w_j}{M_j}} + \sum_{j=1}^C \left[\frac{w_j G_{ij}}{M_j \sum_k^n \frac{G_{kj} w_k}{M_k}} \left(\tau_{ij} - \frac{\sum_k^C \frac{\tau_{kj} G_{kj} w_k}{M_k}}{\sum_k^C \frac{G_{kj} w_k}{M_k}} \right) \right], \tag{5.15}$$

where

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \tag{5.16}$$

$$\tau_{ij} = A_{ij}/T \tag{5.17}$$

$$\alpha_{ij} = \alpha_{ji}. \tag{5.18}$$

For the UNIQUAC model, it has the following form:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{5.19}$$

$$\ln\gamma_i^C = \ln\left(\frac{\phi_i'}{w_i/\zeta M_i}\right) + 1 - \frac{\zeta M_i \phi_i'}{w_i} + \frac{z}{2} M_i q_i' \ln\frac{\theta_i'}{\phi_i'} - \frac{z}{2} M_i q_i' \left(1 - \frac{\phi_i'}{\theta_i'}\right), \tag{5.20}$$

where

$$\zeta = \sum_j^C \frac{w_j}{M_j} \tag{5.21}$$

$$\theta_i' = \frac{q_i' w_i}{\sum_j^C q_j' w_j}; \; \phi_i' = \frac{r_i' w_i}{\sum_j^C r_j' w_j} \tag{5.22}$$

and

$$r_i' = \frac{1}{M_i} \sum_k^G v_k^{(i)} R_k; \;\; q_i' = \frac{1}{M_i} \sum_k^G v_k^{(i)} Q_k \tag{5.23}$$

$$\ln\gamma_i^R = M_i q_i' \left[1 - \ln\left(\sum_j^C \theta_j' \tau_{ji} \right) - \sum_j \left(\theta_i' \tau_{ij} \Big/ \sum_k^C \theta_k' \tau_{kj} \right) \right]. \tag{5.24}$$

The adjustable parameters τ_{ij} and τ_{ji} are defined as follows:

$$\tau_{ij} = \exp\left[-\left(\frac{u_{ij} - u_{jj}}{RT} \right) \right] = \exp\left[-\left(\frac{A_{ij}}{T} \right) \right] \tag{5.25}$$

$$\tau_{ji} = \exp\left[-\left(\frac{u_{ji} - u_{ii}}{RT} \right) \right] = \exp\left[-\left(\frac{A_{ji}}{T} \right) \right]. \tag{5.26}$$

Due to the similarity of the triacylglycerols, the vegetable oil can be represented by a single triacylglycerol having the average molecular weight of all triacylglycerols of the oil. The same reasoning can be extended to a mixture of fatty acids. Then the values of r_i' and q_i' for the UNIQUAC model can be calculated by Equation 5.23, which considers the composition of triacylglycerols and fatty acids of any vegetable oil and any mixture of fatty acids, respectively. The parameters R_k and Q_k can be taken from Magnussen et al. [9]:

$$r_i' = \frac{1}{\overline{M}_i} \sum_j^C x_j \sum_k^G \nu_k^{(i)} R_k; \; q_i' = \frac{1}{\overline{M}_i} \sum_j^C x_j \sum_k^G \nu_k^{(i)} Q_k, \tag{5.27}$$

where x_j is the molar fraction of the triacylglycerols of the vegetable oil or fatty acids of a mixture of fatty acids and $\overline{M}_i$ is the average molecular weight of the vegetable oil or a mixture of fatty acids.

There are many adjusted parameters of the NRTL and the UNIQUAC models that describe the liquid–liquid equilibrium of these fatty systems in the literature [10–19].

5.1.5 Group Contribution Models

In a group contribution method, the basic idea is that the number of functional group is much smaller than the chemical compounds of interest in chemical technology. If the physical properties can be calculated by summing group contribution, it is possible to obtain a large number of these properties in terms of a much smaller number of parameters that characterize the contribution of functional groups in the mixture.

For calculating phase equilibrium in the simulation of deacidification of vegetable oils through liquid–liquid extraction, the group contribution models, the UNIFAC [20] and the ASOG [21], are more appropriate, because they avoid to expand the pseudo-ternary systems vegetable oil + fatty acids + short-chain alcohols in a multicomponent system with a small number of structural groups, and consequently, a small number of binary interaction parameters is required.

Both the UNIFAC and the ASOG models assume the following forms when compositions are expressed in mass fractions.

5.1.5.1 UNIFAC Model

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R. \tag{5.28}$$

In this model, the combinatorial part is taken directly from the UNIQUAC model. The residual part is as follows:

$$\ln \gamma_i^R = \sum_k^C \nu_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right], \tag{5.29}$$

where $\Gamma_k^{(i)}$ is the group activity coefficient of the group k in the reference solution containing only molecules of the same type i:

$$r_i' = \frac{1}{M_i} \sum_k^G \nu_k^{(i)} R_k; \quad q_i' = \frac{1}{M_i} \sum_k^G \nu_k^{(i)} Q_k \tag{5.30}$$

$$\theta_i' = \frac{q_i' w_i}{\sum_j^C q_j' w_j}; \ \phi_i' = \frac{r_i' w_i}{\sum_j^C r_j' w_j} \tag{5.31}$$

$$\ln \Gamma_k = M_k Q_k' \left[1 - \ln \left(\sum_m^G \Theta_m' \Psi_{mk} \right) - \sum_m^G \left(\Theta_m' \Psi_{km} \Big/ \sum_n^G \Theta_n' \Psi_{nm} \right) \right] \tag{5.32}$$

$$\Theta_m = \frac{Q_m' W_m}{\sum_n^G Q_n' W_n}; \ W_m = \frac{\sum_j^C \nu_m^{(j)} w_j}{\sum_j^C \sum_n^G \nu_n^{(j)} w_j} \tag{5.33}$$

$$\Psi_{mn} = \exp\left[-\left(\frac{U_{mn} - U_{nn}}{RT} \right) \right] = \exp\left[-\left(a_{mn}/T \right) \right]. \tag{5.34}$$

5.1.5.2 ASOG Model

$$\ln \gamma_i = \ln \gamma_i^{FH} + \ln \gamma_i^G \tag{5.35}$$

$$\ln \gamma_i^{FH} = \ln \left(\frac{\zeta \nu_i^{FH}}{\sum_j^C \frac{w_j}{M_j} \nu_j^{FH}} \right) + 1 - \frac{\zeta \nu_i^{FH}}{\sum_j^C \frac{w_j}{M_j} \nu_j^{FH}}, \tag{5.36}$$

where

$$\zeta = \sum_{j}^{C} \frac{w_j}{M_j} \tag{5.37}$$

$$\ln \gamma_i^G = \sum_{k}^{G} \nu_{ki} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \tag{5.38}$$

$$\ln \Gamma_k = -\ln \sum_{l}^{G} W_l a_{k,l} + 1 - \sum_{l}^{G} \left(W_l a_{l,k} \Big/ \sum_{m}^{G} W_m a_{l,m} \right), \tag{5.39}$$

where W is the mass fraction of the group, calculated from Equation 5.33:

$$a_{k,l} = \exp\left(m_{k,l} + \frac{n_{k,l}}{T} \right). \tag{5.40}$$

The functional groups of fatty systems in alcoholic solutions for the UNIFAC model are as follows: CH_3, CH_2, CH, CH_2COO, CH=CH, COOH, and OH and for the ASOG model areCH_2, COO, C=C, COOH, and OH. The UNIFAC parameters for LLE were published by Magnussen et al. [9] and the ASOG parameters by Tochigi et al. [22]. Batista et al. [23] adjusted some of the UNIFAC and the ASOG parameters for fatty systems, and the results in the prediction of the liquid–liquid equilibrium of these systems were better than those using original parameters.

5.1.5.3 Minor Component

Binary interaction parameters of the UNIQUAC or the NRTL models between minor component and any other component in the fatty system (triacylglycerols, free fatty acids, ethanol, water) can be determined, assuming that the minor component are at infinite (∞) dilution in the liquid–liquid equilibrium system. In this case, distribution coefficient, calculated according to Equation 5.41 below, can be approached by the distribution coefficient at infinite dilution k_i^{∞}. Using the isoactivity criterion this distribution coefficient for minor component, k_i^{∞}, can be calculated by Equation 5.42:

$$k_i = w_i^{II} \Big/ w_i^{I} \tag{5.41}$$

$$k_i^{\infty} = \left(\gamma_i^{w,I} \right)^{\infty} \Big/ \left(\gamma_i^{w,II} \right)^{\infty}. \tag{5.42}$$

To calculate γ_i^{∞}, the composition of both phases are required. Since the minor component is present in a very low composition, the phase compositions can be estimated taking in account only the major components (triacylglycerols, free fatty acids, ethanol, water). The binary interaction parameters between the major components are used to perform liquid–liquid flash calculations for the estimation of phase compositions on the basis of the overall experimental composition of the mixtures.

The infinite dilution activity coefficient (γ_i^{∞}) is obtained applying the limit in the UNIQUAC or the NRTL models, keeping constant the mass fractions of the other components of the mixture and making the minor component compositions tend to zero.

For the adjustment of interaction parameters between minor components and any other components, the estimation was based on the minimization of the distribution coefficient objective function, Equation 5.43 below, following the procedure developed by Pessôa Filho and described in Rodrigues et al. [13, 16] and Gonçalves [18]. In Equation 5.43, the additional term is a penalty function suggested by Kang and Sandler [24] and used to preclude interaction parameters with too large absolute values:

$$OF(k_i) = \left(\sum_{n=1}^{N} \left(k_i^{ex} - k_i^{calc} \right)^2 \Big/ N \right)^{1/2} + Q \sum_{l=1}^{L} (p_l^2) / L, \tag{5.43}$$

where n is the tie line index, N is the total number of tie lines, ki is the minor compounds' distribution coefficient, ex and $calc$ refer to experimental and calculated values, Q is a small value that does not alter significantly the function residue, l is the UNIQUAC or NRTL parameter index, L is the total number of adjustable parameters, and p_l is the UNIQUAC or NRTL parameter.

5.1.6 Simulation of a Liquid–Liquid Extraction Column

The schematic representation of a stagewise column is shown in Figure 5.10. The vegetable oil with free fatty acids stream (F) enters the column in stage 1 and the solvent stream (S) in the opposite side of the column. Extract and raffinate streams flow from stage to stage countercurrently and provide the formation of two product streams, the final extract ($E1$) and final raffinate (RN) streams. Extract (en) and raffinate (rn) streams leave stage n in equilibrium.

In the vegetable oil deacidification process, the final raffinate stream (RN) contains refined vegetable oil and a residual fraction of the solvent, and the final extract stream ($E1$) contains the solvent with the free fatty acids extracted and a residual fraction of vegetable oil.

The algorithm, suggested by Naphtali and Sandholm [25] and developed for simulation of distillation column, is suitable to simulate the liquid–liquid extraction with the modifications of mass balance and equilibrium equations.

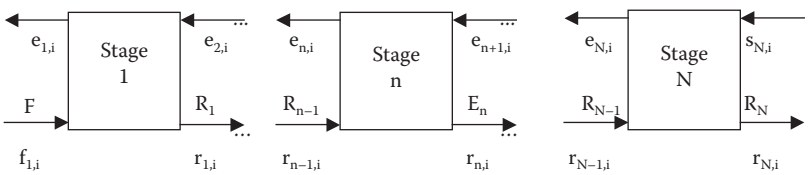


FIGURE 5.10 Schematic representation of a liquid–liquid extraction column.

The mass balance and liquid–liquid equilibrium equation are grouped for each component and each stage. The resultant group of equation has structure of a tridiagonal block that permits a rapid solution with Newton–Raphson method.

For each stage n, a set of dependent relationships (test functions $F_{k(n,i)}$) must be satisfied:

Mass balances of component i:

$$F_{1(n,1)} = r_{n,i} - r_{n-1,i} + e_n y_{n,i} - e_{n+1,i} \quad n = 2, 3, \ldots, N-1 \tag{5.44}$$

$$i = 1, 2, \ldots, \mathrm{C}$$

$$F_{1(1,i)} = r_{1,i} - f_{1,i} + e_{1,i} - e_{2,i} \quad i = 1, 2, \ldots, \mathrm{C} \tag{5.45}$$

$$F_{1(N,i)} = r_{N,i} - r_{N-1,i} + e_{N,i} - s_{N,i} \quad i = 1, 2, \ldots, \mathrm{C}. \tag{5.46}$$

Equilibrium conditions:

$$F_{2(n,i)} = k_{n,i} E_n r_{n,i} / R_n - e_{n,i} \quad n = 2, 3, \ldots, N-1 \tag{5.47}$$

$$i = 1, 2, \ldots, \mathrm{C},$$

where

$$k_{n,i} = \gamma_{n,i}^{w,I} / \gamma_{n,i}^{w,II} = w_{n,i}^{II} / w_{n,i}^{I} \tag{5.48}$$

$$F_{2(1,i)} = k_{1,i} E_1 r_{1,i} / R_1 - e_{1,i} \quad i = 1, 2, \ldots, \mathrm{C} \tag{5.49}$$

$$F_{2(N,i)} = k_{N,i} E_N r_{N,i} / R_N - e_{N,i} \quad i = 1, 2, \ldots, \mathrm{C}. \tag{5.50}$$

The above relationships comprise a vector of the test function:

$$F(x) = \begin{Bmatrix} F_1 \\ F_2 \end{Bmatrix} = 0 \tag{5.51}$$

which contains 2NC elements and which may be solved for equally many unknowns:

$$x = \begin{Bmatrix} e \\ r \end{Bmatrix}. \tag{5.52}$$

The iterative Newton–Raphson method solves Equation 5.51 using the prior set of values of the independent variables. In Newton–Raphson's interaction a new group of values, x_r, is generated from a previous estimation, x_{r-1}:

$$x_r = x_{r-1} - F_{r-1}(x_{r-1}) \Big/ \left(\partial F/\partial x\right)\Big|_{x_{r-1}}, \tag{5.53}$$

when $|x_r - x_{r-1}|$ is enough small, the correct group of x was found and the iteration stops.

5.2 STATE OF THE ART—MINI REVIEW OF LITERATURE

For the success of the commercial production of enzymes and proteins, there is a need for efficient downstream processing techniques. The downstream process for these biological materials requires purification techniques that are delicate enough to preserve the biological activity [26]. The purification protocols involve several steps, which increase the cost of the process and reduce the yield. The conventional procedures include ammonium sulphate precipitation, chromatography, dialysis, and filtration. Simpler and more efficient purification processes are needed.

Aqueous two-phase systems (ATPS) could be a good alternative to a first purification step because such systems allow removal of several contaminants by a simple and economic process. ATPS are formed by adding to water, either two structurally different hydrophilic polymers, such as dextran and polyethylene glycol (PEG) [27], or maltodextrin and PEG [28, 29], or a polymer and salt, such as PEG and potassium phosphate or PEG and sodium sulphate [30–32].

PEG + salt systems have been used in large-scale protein separation because of larger droplet sizes, a higher density difference between the phases, and lower viscosity, leading to a much faster separation than PEG + dextran systems. Industrial applications of the PEG + salt systems could be improved by the availability of commercial separators, which allow faster continuous protein separations [33–35].

The most common polymer + polymer system is composed of polyethylene glycol and dextran [36, 37]. Polypropylene glycol (PPG) is a polymer that is structurally closely related to PEG. PPGs of low molecular weight are soluble in water, whereas high molecular mass ones are only partially soluble [38]. Some recent purification techniques employing ATPS suggest the use of thermo-separating polymers, such as copolymers of ethylene oxide (EO) and propylene oxide (PO) units, to reduce the cost of polymer recovery [39, 40]. Dextran is a high-cost polymer that makes difficult the use of ATPS in large-scale processes. Maltodextrin (MD) can be used as a lower cost substitute for dextran [28, 30]. MD is a commercial polymer of D-glucose units linked primarily by $\alpha(1\rightarrow4)$ bonds. This polymer is obtained by acidic and enzymatic hydrolysis of starch. Low-molecular-mass saccharides, such as glucose, maltose, and sucrose, can also be used for dextran replacement, with the advantage that such compounds are of common occurrence in the food industry [41].

Phase equilibrium data for such systems are mainly found in the works of Albertsson [36] and Zaslavsky [37]. However, these data are not yet complete, particularly regarding the behavior of such systems at different experimental conditions, for example, temperature and pH.

Silva et al. [31] studied the effect of temperature, pH, and polymer molecular weight changes on the binodal curve and tie lines of the phase equilibrium diagrams for PEG + potassium phosphate + water systems. The equilibrium phase behavior of MD and PEG systems at 298.2 K and atmospheric pressure, under several conditions of concentrations and molecular weights of the polymers, was studied by Silva and Meirelles [28].

There are many reports in the literature concerning the partition of different enzymes and proteins in ATPS [26].

The behavior of the partition coefficients of bovine serum albumin (BSA), α-lactoalbumin (α-La), and β-lactoglobulin (β-Lg) in PEG/MD systems at 298.2 K, with several PEG/MD polymer concentrations and different polymer molecular weights were published by Silva and Meirelles [29].

Alves et al. [42] performed an experimental study of the partitioning of different proteins, cheese whey α-La, β-Lg, and BSA, and porcine insulin in ATPS containing PEG (1500, 600, 1450, and 3350) and salt (potassium phosphate, and sodium citrate), and PEG (1450, 8000, and 10,000) and MD (2000 and 4000). The results showed the feasibility of α-LA and β-Lg purification. Partition coefficients of the BSA, α-LA, and β-Lg were also studied by Silva and Meirelles [30] in systems containing PPG 400 and MD at 25ºC. Lima et al. [26] investigated the partitioning of four pectinolytic enzymes from a commercial pectinase preparation (Pectinex-3XL) in ATPS composed of PEG and potassium phosphate.

Another important application of liquid–liquid extraction is the organic acids purification such as citric, tartaric, lactic, and phosphoric acids. The recovery of carboxylic acids by liquid–liquid extraction with aliphatic tertiary amines dissolved in organic diluents has been studied by several authors [43–48].

The worldwide production of citric acid exceeds 500,000 ton/yr. In contrast with a lot of products that previously were obtained by microbiological methods and nowadays are obtained by synthetic methods, this acid continues to be manufactured, mainly by fermentation. Seventy percent of all citric acid produced is used by the food industry, and 18% is used by the pharmaceutical industry. Its use in the food industry represents 55%–65% of the total acidulants' market, in which 20%–25% corresponds to phosphoric acid and 5% to malic acid. The fermentation process technology for the industrial production of organic acids has been known for more than a century. Citric acid is one of the macro-fermentation processes of greater success within the bioproduct industries.

The classical method for recovering citric acid is based on the precipitation of calcium salts, by addition of calcium hydroxide in the fermentation broth. The solid is filtrated and treated with sulfuric acid (H2SO4) for the preferential precipitation of sulfate calcium. The free organic acid in the filtrate is purified using activated carbon or ion exchange and is concentrated by evaporation. The acid crystallizes with great difficulty and very low efficiency. Compared to the usual separation processes, liquid–liquid extraction seems to be a very promising alternative [49].

In relation to phosphoric acid, several publications deal with the modeling of the extraction of phosphoric acid from water by tri-*n*-butyl phosphate [50, 51]. In fact, the phosphoric acid is an important raw material for fertilizer applications, as well as for products with higher purity standards [52].

The success of a liquid–liquid extraction process relies on solvent selection. Mixed solvents composed of tertiary amines and alcohol are suggested as appropriated solvents [43, 53]. The disadvantage of their use is their great toxicity and, consequently, higher purification costs. Welsh and Williams [54] studied several kinds of vegetable oils, as solvents to the recovery of organic compounds from aqueous solutions, such as corn oil, canola oil, olive oil, and others. The authors verified that short-chain alcohols and organic acids presented low recovery and small distribution coefficients, when the vegetable oils are used as single solvents. Therefore, there is great appeal to the search for new solvents, mainly combinations of solvents. The main difficulty is the analysis of mixed solvents because of the lack of equilibrium data.

Lintomen et al. [49] studied new solvents for the recovery of citric acid by liquid–liquid extraction using the following systems: water/citric acid/short-chain alcohol (2-butanol or 1-butanol) and water/citric acid/short-chain alcohol/tricaprylin.

Recently, Uslu [55] published a study of tartaric acid recovery from aqueous solutions using tertiary amine. Batch extraction experiments were performed with Alamine 336 dissolved in the diluents of various types—ketone (methyl isobutyl ketone), aromatic (toluene), different alkanes (hexane, cyclohexane), and alcohol (butan-1-ol).

Similar to that of citric acid, the interest toward lactic acid recovery from fermentation broth has been increased. This interest is caused by the increase in the demand of pure, naturally produced lactic acid, mainly for the food (as food additive and preservative) and pharmaceutical industries or for production of biodegradable polymers. Yankov et al. [56] investigated the lactic acid extraction from aqueous solutions and synthetic fermentation broth by means of a system composed of trioctylamine and an active (decanol) and an inactive (dodecane) diluent.

Essential volatile oils are vegetable products, which are basically a mixture of terpenic hydrocarbons and oxygenated derivatives such as aldehydes, alcohols and esters. Citrus essential oil is used as a flavoring agent in pharmaceuticals as well as a fragrant ingredient in soaps, detergents, creams, lotions, and perfumes. From its components, oxygenated compounds are mainly responsible for the aroma and flavor, and their content has become a definitive parameter in establishing the price of the volatile oil and representing a reference of quality [57].

Citrus oils are obtained from the small balloon-shaped glands or vesicles located in the flavedo or colored portion of the citrus peel. The quality of these oils depends on factors such as soil, climate, extraction method of the oil, weather, maturity, and the variety of the fruit. Citrus oils are complex mixtures of over 200 chemical compounds, of which more than 100 have been identified. These include highly volatile components such as terpenes, sesquiterpenes, and oxygenated compounds and nonvolatile compounds such as pigments and waxes. The terpene fraction can constitute from 50% up to more than 95% of the oil. However, this fraction gives little contribution to the flavor and fragrance of the oil. Because terpenes are mostly unsaturated compounds, they are easily decomposed by heat, light, and oxygen to unpleasant off flavors and aromas. Therefore, it is common industrial practice to remove some of the terpenes and, as a consequence, to concentrate the oxygenated compounds, which are mainly responsible for the characteristic citrus flavor and fragrance. This

procedure is known as "deterpenation" or "folding" and is carried out to improve oil stability, increase oil solubility, and reduce storage and transport costs [58–60].

Table 5.2 presents the main volatile compounds of citrus essential oils.

Deterpenation is currently done by distillation, solvent extraction, supercritical fluid extraction, or chromatographic separation [70–75]. The main drawbacks of these conventional processes are low yields, formation of thermally degraded undesirable byproducts, and/or solvent contamination of the products [58, 73]. Solvent extraction is probably the most common process used by industry. The solvents most often used are hexane and chloroform, because of their intrinsic characteristics of selectivity related to terpenes and oxygenated compounds [76].

Alternative solvents have been suggested as substitutes of hexane and chloroform, such as acetonitrile, nitromethane, and dimethylformamide [77], diethylene glycol [78], 1,2-propanediol and 1,3-propanediol [79], aminoethanol [80], methanol [81], 2-butene-1,4-diol, ethylene glycol, and ionic liquids (1-ethyl-3-methylimidazolium methanesulfonate) [82].

In view of a possible future food, cosmetic, or pharmaceutical application of the extract, it is necessary to use solvents such as ethanol or water [57, 58, 83, 84].

The light components of the essential oil mixtures are completely soluble in ethanol but not completely soluble in water. The solution obtained by adding ethanol to water maintains the polar characteristics of water, but its polarity is lowered by the presence of the alcohol. Alcoholic extracts of citrus essential oils are particularly requested by the industry for the following reasons [83, 85, 86]:

1. They are highly soluble in aqueous solutions and can therefore be used to make drinks and perfumes;
2. They enhance the aromatic strength of the mixture; and
3. Oxidation reactions are reduced in the presence of alcohol [58].

Studies about essential oils deterpenation by liquid–liquid extraction are scarce in the literature. Massaldi and King [87] published an article concerning a simple technique for the determination of solubilities and activity coefficients of *d*-limonene, *n*-butylbenzene, and *n*-hexyl acetate in water and sucrose.

TABLE 5.2
Volatile compounds present in essential oils

Orange[a,b]	Mandarin[a,c]	Grapefruit[a,d,e]	Lemon[a,f,g,h]	Bergamot[f,i]
Etanal	Etanal	Etanal	Neral	Linalool
Octanal	Octanal	Decanal	Geranial	Linalyl acetate
Nonanal	Decanal	Ethyl acetate	β-Pinene	γ-Terpinene
Citral	α-Sinensal	*d*-Limonene	Geraniol	β-Pinene
d-Limonene	Thymol	Nootkatone	Geranyl acetate	*d*-Limonene
α-Pinene	γ-Terpinene		Neryl acetate	
	β-Pinene		Bergamoptene	

[a] l[61]; [b]l[62]; [c]l[63]; [d]l[64]; [e]l65]; [f]l[66]; [g]l[67]; [h]l[68]; [i]l[69].

Ternary liquid–liquid equilibria for α-pinene + Δ_3-carene + polar compound (acetonitrile, nitromethane, and dimethylformamide) systems were determined by Antosik and Stryjek [77], at the temperature 298.2 K.

Thermodynamic behavior related to systems composed of essential oil compounds plus ethanol and water was firstly published by Gironi et al. [83]. The authors reported solubilities for the binary systems of water + limonene and water + citral at atmospheric pressure and at 293 K. Equilibrium data of ternary systems of water + ethanol + limonene and water + ethanol + citral were also determined.

Tamura and Li [81] tested methanol plus water as solvent for the deterpenation process. In this chapter, the authors measured the mutual solubilities of the terpenes dissolved in water or methanol and their multicomponent liquid–liquid equilibria.

Cháfer et al. studied the influence of the temperature on phase equilibrium of systems composed of limonene, ethanol, and water [88], and of linalool, ethanol, and water [58], respectively.

An ample study related to solvent choice for deterpenation of essential oils has been developed by Arce et al. [57, 78–80, 82, 84]. First, the authors evaluated the performance of diethylene glycol as solvent for systems containing limonene plus linalool at three different temperatures: 298.2, 308.2, and 318.2K [78]. Subsequently, the following solvents were tested for the same oil systems: 1,2-propanediol e 1,3-propanediol [79], ethanol plus water [57, 84], 2-aminoethanol [80], 2-butene-1,4-diol, ethylene glycol, and 1-ethyl-3-methylimidazolium methanesulfonate [82].

Deacidification of vegetable oils can also be performed by liquid–liquid extraction. Oilseeds are the major source for the production of edible oils, which are regarded as an important component of the diet, being an important source of energy, of essential fatty acids (such as linoleic acid), and of fat-soluble vitamins (such as vitamins A and E). Crude vegetable oils are predominantly composed of triacylglycerols and free fatty acids, with mono- and diacylglycerols also present at lower levels. The refining of vegetable oils consists of several steps, including its extraction from solid matrix by pressing and/or using organic solvents [89, 90], degumming, bleaching, deacidification, and deodorization [91, 92].

The removal of free fatty acids (deacidification) is the most difficult step of the oil purification process, mainly because it has the maximum economic impact on oil production. Deacidification of oils is performed industrially by chemical, physical, or miscella methods. However, for oils with high acidity, chemical refining causes high losses of neutral oil as a result of saponification and emulsification. Physical refining is also a feasible process for deacidification of highly acidic oils, because it results in lower losses 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 with regard to resisting to oxidation [1].

AQ8

New approaches for deacidification of vegetable oils have been proposed in the literature, such as biological deacidification, chemical reesterification, supercritical fluid extraction, membrane processing, and solvent (or liquid–liquid) extraction.

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 [3]. The deacidification of oils by liquid–liquid extraction by

means of an appropriate solvent is receiving attention because of its advantages in comparison to physical and chemical refining. As this process is normally carried out at room temperature and atmospheric pressure, less energy is consumed and the oil is submitted to softer treatments. Besides, liquid–liquid extraction has the advantages of avoiding the formation of waste products, but still reduces the loss of neutral oil and may preserve the nutraceutical compounds. Furthermore, solvent stripping from refined oil and solvent recovery from extract stream can be easily carried out because of the great 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 K [3, 93, 94].

The use of solvent extraction for deacidification of vegetable oils was first proposed by Bollmann [95]. In this patent the author suggests the use of methyl alcohol, ethyl alcohol, amyl alcohol, acetone or acetic ester not diluted or diluted with water. van Dijck [96] suggested a process combining liquid–liquid extraction and alkali refining. Free fatty acids from fats and oils were neutralized by adding a base, such as ammonia, and subsequently the soaps were removed by countercurrent extraction with a suitable solvent, such as ethanol.

Another study based on liquid–liquid extraction associated with alkali refining was patented by Nestlé Co. [97]. According to the inventors, free fatty acids are removed by controlled neutralization in an aqueous medium containing an alcohol or a polyol.

Swoboda [98] reports a process for refining palm oil and palm oil fractions, using as solvent mixtures of ethanol and water or isopropanol and water, preferably with a composition near the azeotropic one. According to the author, azeotropic mixtures are preferred because of the advantages of recycling the solvent.

Bhatacharyya et al. [99] and Shah and Venkatesan [100] studied the deacidification of rice bran and groundnut oils using aqueous 2-propanol as solvent. Kim et al. [101] and Kale et al. [102] tested methanol in the refining of RBO. All these studies showed a decrease in the oil acidic value. Turkay and Civelekoglu [103] investigated the liquid–liquid extraction of sulfur olive oil miscella in hexane with aqueous ethanol solutions. Apelblat et al. [93] published an article that reports phase diagrams for soybean oil or jojoba oil plus oleic acid and several solvents (1,2-butanediol, dimethyl sulfoxide, *cis*-2-butene-1,4-diol, formamide, and *n*-methylformamide), at 298.2 K.

The extraction of free fatty acids from fatty materials using solvents has a long history, and several studies have already shown that this process is, in principle, feasible using short-chain alcohols, especially ethanol, as solvent [3, 93, 99, 100, 102, 104–110]. Ethanol has low toxicity, ease recovery in the process, good values of selectivity and of the distribution coefficient for free fatty acids [10, 11, 14, 15, 17, 106], and low losses of nutraceutical compounds [12, 13, 16, 18].

AQ9

In the last years, equilibrium data for systems composed of several vegetable oils (canola, corn, palm, rice bran, Brazil nut, macadamia nut, grape seed, sesame seed, garlic, soybean, and cottonseed oils) plus saturated, monounsaturated, or diunsaturated free fatty acids, such as stearic, palmitic, oleic, and linoleic acids plus solvent (ethanol + water) have been published [10–19, 23, 111]. This set of works emphasizes that the mixture ethanol + water is more often recommended to be used as solvent for

deacidification of vegetable oils. In fact, this new technique may produce vegetable oils with low acidic levels and simultaneously minimize the loss of neutral oil and nutraceutical compounds.

5.3 APPLICATIONS

5.3.1 Deacidification of Vegetable Oils

In this section we discuss some effects in the liquid–liquid equilibrium for fatty systems using short-chain alcohols. This information is useful in the choice of solvent or temperature for deacidification of vegetable oils by liquid–liquid extraction.

5.3.1.1 Effect of Temperature

The information about mutual solubility of the oil and solvent is contained in the
AQ10 base line of liquid–liquid diagram (Figure 5.1). The mutual solubility for vegetable oil and short-chain alcohols increases with an increase in temperature, and above some temperatures, this binary mixture is totally soluble. The increase in mutual solubility with increasing temperatures affects the liquid–liquid equilibrium. The area underneath binodal decreases at higher temperatures, and the slopes of the tie line or distribution coefficients may change.

Batista et al. [10] presented the liquid–liquid equilibrium for the system containing refined canola oil + commercial oleic acid and short-chain alcohols at different temperatures. For systems with anhydrous methanol and anhydrous ethanol, the heterogeneous region decreases with the increasing in temperature from 293 to 303 K, and only a slight change in the distribution coefficient of oleic acid is observed. The increasing of mutual solubility of canola oil and anhydrous methanol or anhydrous ethanol with almost no impact on the slope of tie lines causes a decrease in the selectivity of the solvents with increasing temperatures.

Figure 5.11 shows the tie lines and binodal curves for the systems of refined canola oil + commercial oleic acid + methanol at 293 and 303 K.

5.3.1.2 Length Chain of Alcohols

Figure 5.12 represents the binodal curves for the system of refined canola oil + commercial oleic acid + anhydrous methanol or anhydrous ethanol. It can be seen that the heterogeneous region for the system with methanol is higher than for the system with ethanol, because the mutual solubility of refined canola oil with methanol is lower than that with ethanol, which can be explained by the higher polarity of the methanol chain in relation to that of ethanol.

The results proved that the distribution coefficient of oleic acid with anhydrous ethanol is somewhat larger than 1, whereas that for anhydrous methanol is somewhat smaller, which suggests that methanol has a somewhat lower capacity for extraction of fatty acids oil, thus presenting less selectivity than methanol.

As expected, the system of canola oil + oleic acid + anhydrous isopropanol at 293 K and canola oil + oleic acid + anhydrous *n*-propanol at 283 K formed only a minimum heterogeneous area.

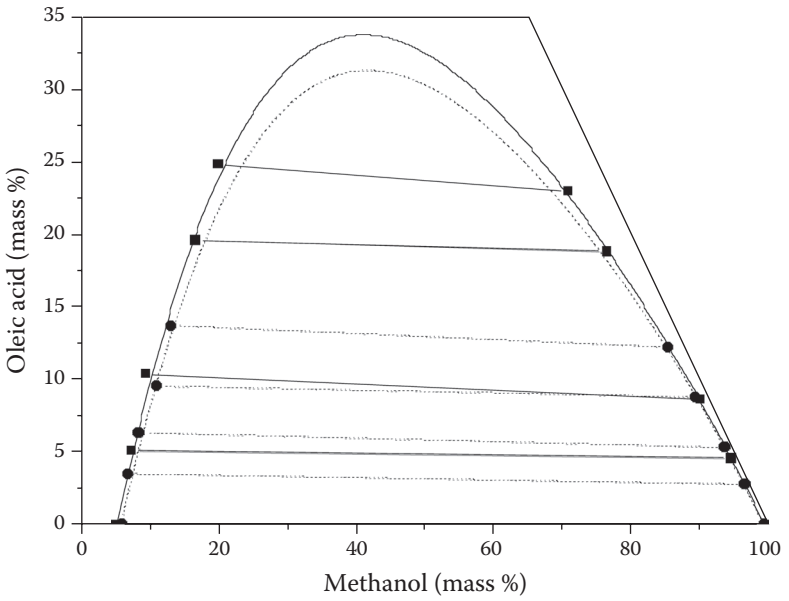


FIGURE 5.11 Experimental tie lines and binodal curves for the systems of refined canola oil + commercial oleic acid + anhydrous methanol at 293.2 K (—■—) and at 303.2 K (···●···).

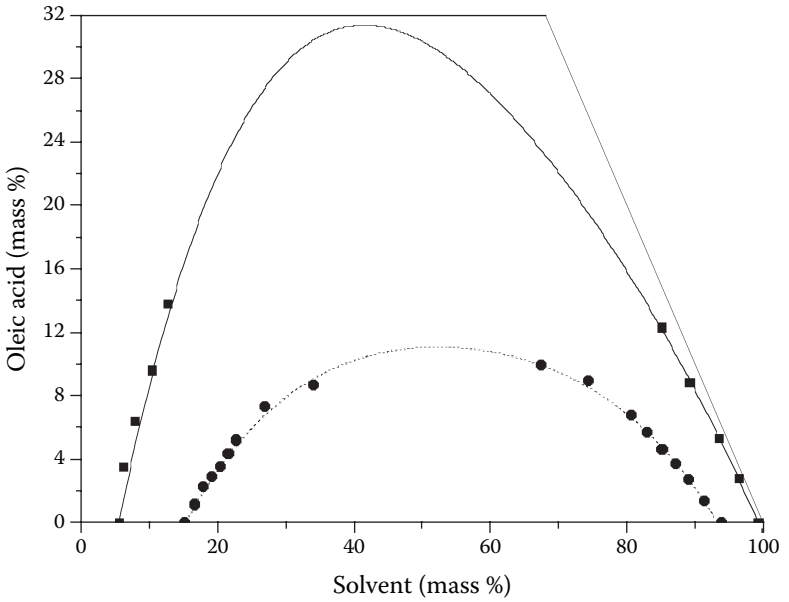


FIGURE 5.12 Binodal curves for the system refined canola oil + commercial oleic acid + solvents: anhydrous methanol (—■—) and anhydrous ethanol (···●···) at 303.2 K.

5.3.1.3 Addition of Water in the Solvent

The addition of water in ethanol increases its polarity and consequently decreases the mutual solubility of aqueous ethanol and vegetable oil. In Figure 5.13, one can seen that the heterogeneous area at 303 K for the system of canola oil + oleic acid + anhydrous ethanol is lower than that for that fatty system with aqueous ethanol as solvent.

The addition of water in ethanol also decreases the distribution coefficient of the free fatty acid and in a stronger way the distribution coefficient of the vegetable oil. This effect represents that aqueous ethanol has lower capacity of extraction of free fatty acids, but the selectivity of the solvent increases and consequently reduces the loss of neutral oil in solvent extraction (see Figures 5.14 and 5.15).

Some articles [11, 12, 14] concluded that water content about 6% mass in the aqueous ethanol is appropriate for deacidification by solvent extraction, as it still provides distribution coefficients of the free fatty acid around unity and high selectivity of the solvent.

5.3.2 Deacidification of Vegetable Oils Retaining Bioactive Compounds

The majority of chemical compounds in human and animal organisms have clearly defined functions, and some of them are indispensable for maintaining the correct metabolism. Among these compounds there are polyunsaturated fatty acids, essential unsaturated fatty acids (EFAs)—linoleic, linolenic, and substances that protect them with antioxidant or other beneficial physiological properties—tocopherols, and tocotrienols belonging to the group of vitamin E, γ-oryzanol, and carotenoids [112].

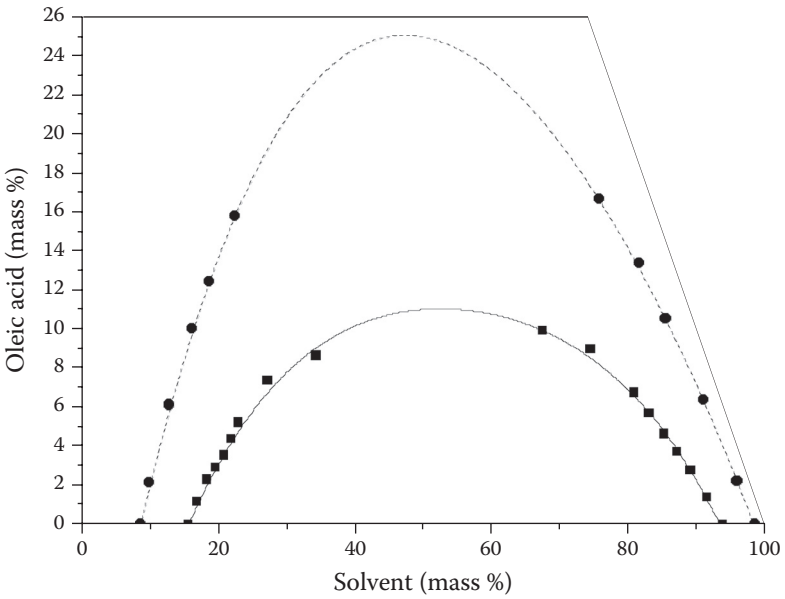


FIGURE 5.13 Binodal curves for the system refined canola oil + commercial oleic acid + solvents: anhydrous ethanol (—■—) and aqueous ethanol (···●···) at 303.2 K.

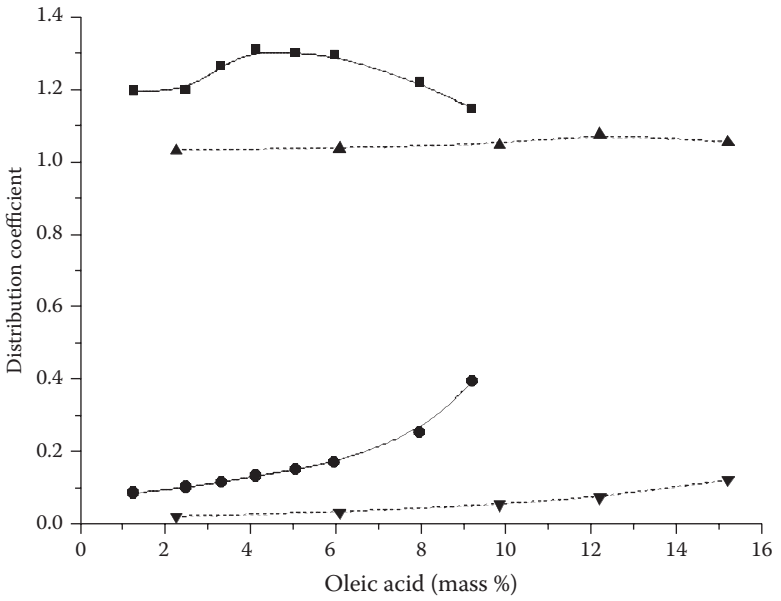


FIGURE 5.14 Distribution coefficient of: oleic acid (—■—) and canola oil (—●—) at 303.2 K in anhydrous ethanol and oleic acid (···▼···) and canola oil (···▲···) at 303.2 K in aqueous ethanol.

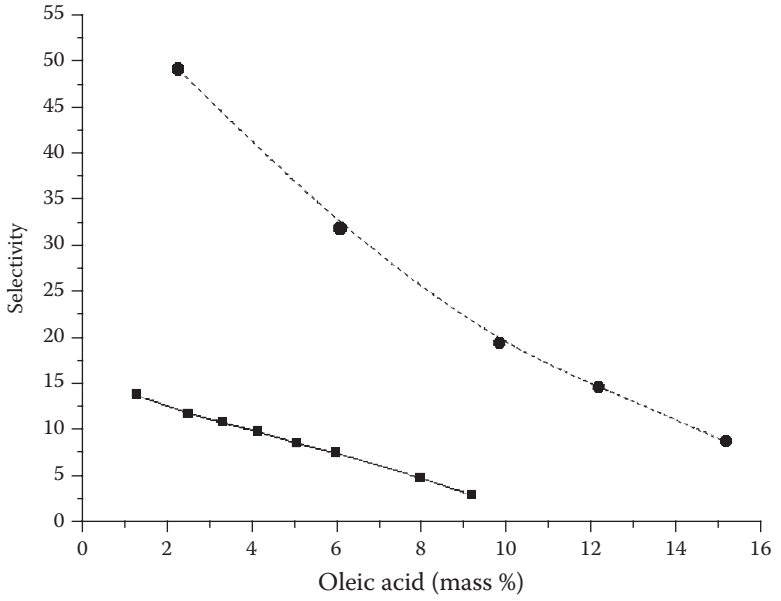
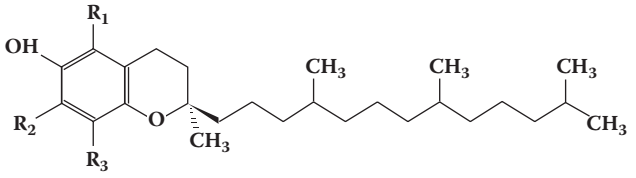


FIGURE 5.15 Selectivity of anhydrous ethanol (—■—) and aqueous ethanol (···●···) at 303.2 K.

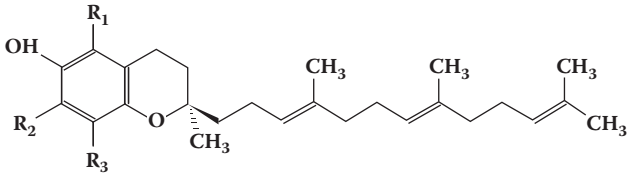
These singular compounds are not synthesized by human or animal organisms, and so they have to be supplied in due time and in appropriate quantities [112]. Vitamin E and EFAs are substances of particular physiologic significance, and it is important to maintain their proper proportions [112–114].

Vitamin E (Figure 5.16) is a fat-soluble vitamin that comprises two major homologous series of compounds (tocochromanols), known as tocopherols and tocotrienols. The tocopherols are structurally characterized by a saturated side chain in the chroman ring, whereas the tocotrienols possess an unsaturated phytyl side chain. Four homologs of each type are known to exist in nature and have different degrees of antioxidant and vitamin E activity.

Gogolewski et al. [115] proposed a division of oils into three groups according to their nutritive value and contribution to the human organism's daily demand for fat, tocochromanols, and EFAs. The first group includes, e.g., the coconut, and olive oils; the quantity of EFAs and tocopherols in them is not sufficient for their protection from oxidation. The second group is formed by oils of which 100 g contains 30–32 g EFAs and 30–35 mg vitamin E. The third group is constituted of oils capable of supplementing the diet with vitamin E and the EFAs; among other oils there are those obtained from the wheat and maize germs with the highest content of EFAs and tocopherols and/or tocotrienols, such as rice bran, cottonseed, soybean, sunflower seed, and corn oils. Some authors suggest the optimum quantitative ratio of 0.5 mg of vitamin E equivalent to 1 g EFAs in the human organism [116–118].



A



B

	R_1	R_2	R_3
α	methyl	methyl	methyl
β	methyl	hydrogen	methyl
γ	hydrogen	methyl	methyl
δ	hydrogen	hydrogen	methyl

FIGURE 5.16 Chemical structure of Vitamin E (A: tocopherols; B: tocotrienols).

TABLE 5.3
Tocopherol contents of principal edible oils

Edible oil	Total tocopherols (mg/kg)
Palm oil	360–560
Rice bran oil	900
Cottonseed oil	830–900
Corn oil	870–2500
Olive oil	30–300
Soybean oil	900–1400
Peanut oil	330–480
Sunflower oil	630–700
Canola oil	690–695
Sesame seed oil	531–1000

In a general way, tocopherols and tocotrienols prevent formation of free radicals. They also take over the energy of the latter, inhibiting further metabolic transformations of polyunsaturated fatty acids during storage of oils, and after consumption, they also participate in many physiologic processes in human organisms. In relation to the tocotrienol isomers, they present antioxidant and antitumor activities [119–123].

As can be seen in Table 5.3, vegetable oils are rich sources of tocopherols. Vitamin E has traditionally been extracted from the residues of the soybean refining industry. Tocotrienols, on the other hand, are predominantly found in palm oil and in cereal oils such as barley and RBOs. With the emergence of palm oil as the first largest edible oil in the world markets [124], technological advances have been made enabling the extraction of tocotrienols from palm oil, which is currently available commercially.

Table 5.4 shows a typical tocols composition in crude palm and RBOs. Both vegetable oils present predominantly α-tocopherol and γ-tocotrienol.

TABLE 5.4
Tocols composition in crude palm and rice bran oils

Tocols	Crude palm oil (%)	Crude rice bran oil (%)
α-Tocopherols	21.5	23.2
β-Tocopherols	3.7	3.3
γ-Tocopherols	3.2	11.8
δ-Tocopherols	1.6	0.7
α-Tocotrienols	7.3	14.0
β-Tocotrienols	7.3	—
γ-Tocotrienols	43.7	44.3
δ-Tocotrienols	11.7	2.6

Refining of oils comprises several physical and chemical processes that aim at eliminating the unnecessary substances. During refining process, substances with biological activity, such as tocopherols and tocotrienols, are also removed [125–128].

The contents of total and individual tocopherols and tocotrienols of vegetable oils at different stages of industrial chemical and physical refining processes gradually decrease until the end of the refining processes. The average losses of total tocopherol content in sunflower seed oil during the chemical and physical refining processes were found to be 30.2 and 35.5%, respectively [129].

The steam distillation (stripping) stage of the physical refining process causes greatest overall reduction (average 24.6%) in total tocopherol content in sunflower seed oil. In contrast to the physical refining process, the degumming–neutralizing stage in the chemical refining process causes greatest overall reduction (average 14.7%) in total tocopherol content. An additional average loss of 11.0 % occurs during deodorizing in the chemical refining process. In both chemical and physical refining, the bleaching stage causes similar effects. The physical refining process promotes a greater loss in the total and individual tocopherol contents when compared with the chemical refining process [116, 129, 130].

It has been reported that refined bleached deodorized (RBD) palm oil, palm olein, and palm stearin retain approximately 69, 72, and 76% of the original level of vitamin E in the crude oils, respectively. During the deodorization step refining process of RBO, a significant portion, about 25%, of vitamin E is stripped away with the distillate [131, 132].

Palm oil 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 [133]. Figure 5.17 presents the chemical structure of the main carotenoid in palm oil (β-carotene). The typical composition of carotenoids in this oil is shown in Table 5.5.

Besides presenting vitamin A value, carotenoids reduce the risk of certain types of cancer and possess the ability of suppressing singlet oxygen [134]. 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 color oil, which has better acceptance for industrial purposes [135]. Thus, some valuable characteristics of palm oil are lost during its processing, and the corresponding nutritional benefits remain available only in the crude oil [136].

In fact, the physical refining is responsible for great losses of nutraceutical compounds from palm oil. The carotenoid concentration (about 500–700 mg/kg in crude palm oil) is reduced to the half during the bleached step of the physical refining

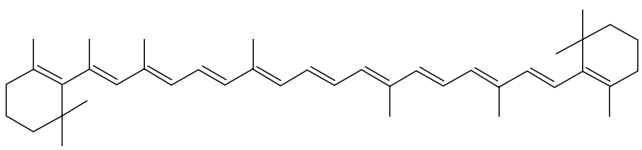


FIGURE 5.17 Chemical structure of β-carotene.

TABLE 5.5
Typical carotenoid composition of palm oil

Carotenoid	Percentage
β-Carotene	56.0
α-Carotene	35.2
cis–α-Carotene	2.5
Other carotenes (<2%)	6.3

process, because these components are completely destroyed during the high-temperature (240ºC–260ºC) and low-pressure (1–3 mmHg) deacidification–deodorization step.

In comparison with most vegetable oils, rice bran oil (RBO) has a qualitatively different composition of bioactive minor components, such as γ-oryzanol, tocotrienols, and phytosterols [131]. γ-Oryzanol derivatives, in particular, are found in only a very limited number of oils. γ-Oryzanol covers the whole group of ferulic acid esters of triterpene alcohols and phytosterols [137]. The four major components of γ-oryzanol in RBO have already been identified as 24-methylenecycloartanol

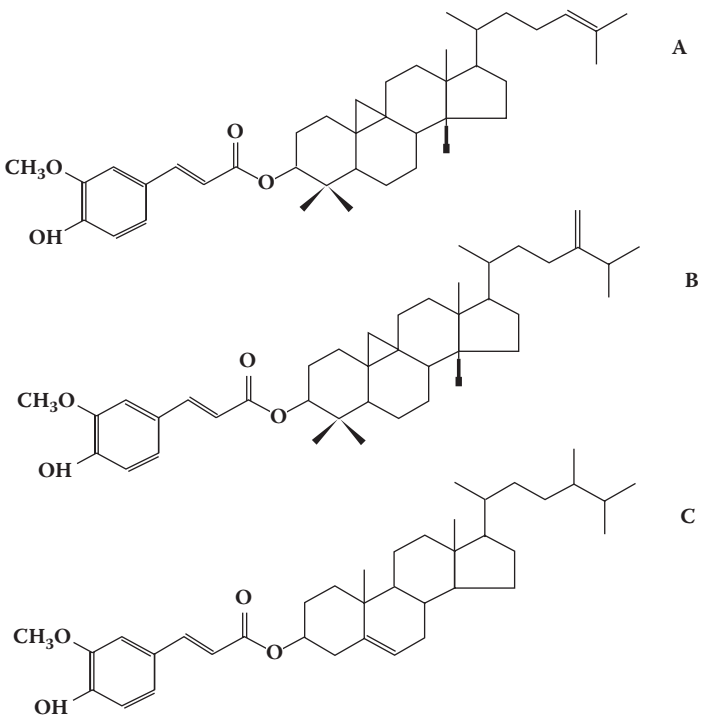


FIGURE 5.18 Chemical structure of γ-oryzanol (A: cycloartenylferulate; B: 24-methylencycloartanylferulate; C: campesterylferulate).

TABLE 5.6
Components of γ-oryzanol

Component	Molecular weight	Formula
Campesterylferulate	576.9	$C_{38}H_{56}O_4$
Campestanylferulate	578.9	$C_{38}H_{58}O_4$
b-Sitosterylferulate	590.9	$C_{39}H_{58}O_4$
Cycloartenylferulate	602.9	$C_{40}H_{58}O_4$
Cycloartanylferulate	604.9	$C_{40}H_{60}O_4$
24-Methylencycloartanylferulate	616.9	$C_{41}H_{60}O_4$

ferulate, campesterol ferulate, cycloartenol ferulate, and sitosterol ferulate [121, 123, 138]. Figure 5.18 shows the three major components in γ-oryzanol, and Table 5.6 shows the six main components in γ-oryzanol.

Medical studies indicate the hypocholesterolemic effect of RBO in humans and animals. The majority of such studies suggests that RBO is more effective in decreasing serum and liver cholesterol concentrations than oils with similar fatty acid composition, such as groundnut oil [119, 131, 139, 140]. The lowering of cholesterol levels by rice oil may be attributed to its high level of unsaponifiable matter [119, 131, 139].

Crude RBO may contain up to 5% of unsaponifiable matter. In fact, the majority of crude vegetable oils contain 1–5 g kg^{-1} of phytosterols, but RBO can contain up to 30 g kg^{-1} of phytosterols [132]. This level is reduced to values up to 1.5% in the refined RBO. In contrast, most refined vegetable oils contains only 0.3%–0.9% of unsaponifiable matter [141]. In addition to the hypocholesterolemic activity of these rice oil minor compounds, the isolated ingestion of γ-oryzanol may decrease early atherosclerosis [140] and may treat nerve imbalance disorders of menopause [142] and inflammatory processes [143].

Tocotrienols and γ-oryzanol are known as powerful antioxidants, which is associated with the prevention of cardiovascular diseases and some cancers [131, 144, 145]. Because of these beneficial effects, RBO has a high nutritional value and is therefore very appealing as a specialty oil in niche markets [131].

Refining processes have been optimized to obtain high-quality RBO for human consumption [131]. However, refining RBO is more complicated than refining other oils because of the difference in its composition of minor components [146]. The influence of refining processes on RBO has rarely been investigated. Yoon and Kim [147] briefly mentioned the effect of different chemical refining steps on the content of phosphorous, free fatty acids, total sterols, total tocopherols, and γ-oryzanol. That report mainly described the oxidative stability of RBO. Krishna et al. [148] studied the effect of refining on the retention of γ-oryzanol in chemically and physically refined oil.

van Hoed et al. [132] published an article that gives an overview of the effects of each individual step of the chemical refining process on the major and minor components of RBO. The total loss of γ-oryzanol in the whole process of refining is about

83%, being that 77% of the loss is related to the neutralization step [132, 140, 149]. In relation to physical refining, it is reported that most of the oryzanol (66%) can be retained in the refined oil [149].

As mentioned above, traditional methods of refining cause a significant decreasing of nutraceutical compound levels in edible oils. In this context, liquid–liquid extraction using appropriate solvents, such as short-chain alcohols, can be an alternative technique for refining nutritional oils.

Swoboda [98] reports a process for refining palm oil and palm oil fractions using as solvent mixtures ethanol and water or isopropanol and water, preferably with a composition near the azeotropic one. Crude palm oil subjected to solvent extraction may produce a raffinate containing a concentration of carotenoids similar to, or even larger than, the concentration of carotenoids in original source.

With the purpose of obtaining RBO enriched with high levels of tocols—tocopherols and tocotrienols—and γ-oryzanol, Cherukuri et al. [150] suggested a liquid–liquid extraction process using lower aliphatic alcohols (C1 to C6, preferably methanol, ethanol, or isopropanol). The process involves mixing RBO and alcohol, separating the alcohol layer and subsequently distilling this layer in order to recover enriched RBO.

A study of the process variable influence on the losses of γ-oryzanol and tocols during the deacidification process of RBO by liquid–liquid extraction was also reported by Rodrigues et al. [112]. The influence of process variables such as acidity content in the oil, water content in the ethanolic solvent, and oil–solvent ratio, were analyzed using the response surface methodology. The results indicate that the increasing of the acidity level in the oil increases the loss of γ-oryzanol. The addition of water to the solvent reduces the solvent's capacity to extract this minor compound. In relation to tocols' losses the effect of the oil–solvent mass ratio is larger than the effect of water content in the solvent. The tocols' losses increase when the mass ratio oil–solvent ratio is low.

Rodrigues et al. [12, 13] studied the partition coefficients of γ-oryzanol and tocopherols and tocotrienols in systems containing RBO, fatty acids, and aqueous ethanol. Their results show that most of the nutraceutical compounds from RBO can be kept on the refined oil after solvent extraction. These data were correlated by thermodynamic models, such as NRTL and UNIQUAC [13]. These models quantitatively described the systems.

In Rodrigues et al. [16], the equilibrium data for the systems containing cottonseed oil + commercial linoleic acid + ethanol +water + tocopherols were reported. The experimental data, obtained at 298.2 K, were correlated by the NRTL and UNIQUAC equations. These models quantitatively described the systems.

Recently, Gonçalves et al. [18] reported partition coefficients of carotenoids and tocopherols in systems containing palm oil + fatty acids + aqueous ethanol at 318.2 K and different water contents and oil–solvent mass ratios. The UNIQUAC model was used to correlate the partition coefficients of carotenoids and tocopherols.

Figures 5.19 and 5.20 show experimental and calculated data of nutraceutical compound partition coefficients commonly found in edible oils. The distribution coefficients are presented as a function of the water level in the ethanolic solvent [12, 13, 16, 18].

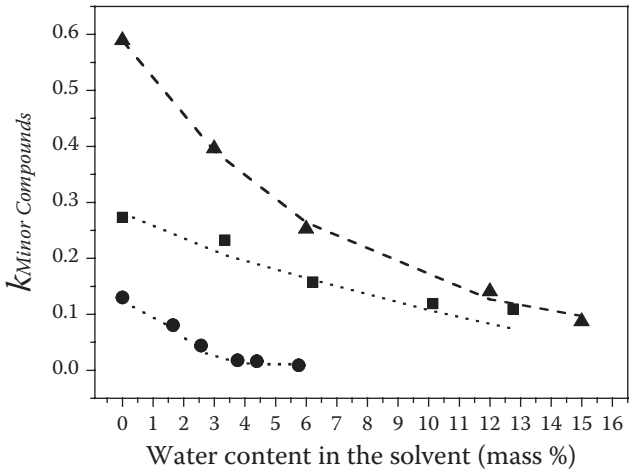


FIGURE 5.19 Minor compounds distribution coefficients (k) as a function of the water content in the solvent: (●) carotenoids in palm oil; (■) γ-oryzanol in rice bran oil; (▲) tocols in cottonseed oil; (·····) UNIQUAC model; (–––) NRTL model.

As can be seen in Figures 5.19 and 5.20, the addition of water in the solvent decreases nutraceutical compound distribution coefficients. This means that the larger the concentration of water, the smaller the solvent capacity for extracting the carotenoids, γ-oryzanol, and the tocols. 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.

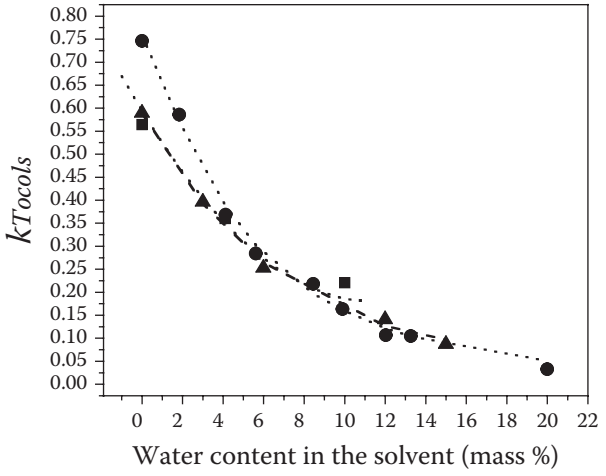


FIGURE 5.20 Tocols distribution coefficients (k) as a function of the water content in the solvent: (●) palm oil; (■) rice bran oil; (▲) cottonseed oil; (·····) UNIQUAC model; (–––) NRTL model.

Despite the same behavior, it can be observed that the tocols are transferred to the alcoholic phase in a major extension than γ-oryzanol. This can be attributed to structural differences between the molecules. Tocols are less hydrophobic than γ-oryzanol [151]. They are composed of smaller molecules that contain an unsaturated side chain in the tocotrienol series and a lower number of methyl substitutions than the oryzanol molecules.

AQ11 It is also noticed that the tocols are extracted to the alcoholic phase in a larger quantity than the carotenoids. In fact, tocols and carotenoids are insoluble in water, because they have an apolar long chain (what makes them liposoluble). However, the OH group linked to the tocopherol aromatic ring enhances its solubility in ethanol.

In relation to the tocols' family, it can be seen in Figure 5.15 that the values of partition coefficients are independent of oil's chemical composition. It is possible to express the unsaturation level of fatty compounds by the iodine value. This can be calculated directly from fatty acid composition of oil according to method Cd 1c-85 AOCS [152]. Palm oil used by Gonçalves et al. [18] showed an iodine value of 55.0, whereas RBO and cottonseed oil studied by Rodrigues et al. [13, 16] presented values that equal 102.3 and 112.9, respectively.

The results showed that deacidification of vegetable oils by liquid–liquid extraction, using aqueous ethanol as solvent, allowed the retention of nutraceutical compounds in refined oil. For example, traditional physical refining usually provides a refined palm oil with approximately 0.03 mass % of tocopherols and exempt of carotenoids. In contrast, the solvent extraction process performed by using solvents containing about 6 mass % of water allows the maintenance of up to 99 mass % of carotenoids and about 80 mass % of tocopherols in refined palm oil.

5.4 NOMENCLATURE

Symbols	Description	Units in SI system	Dimension in M, N, L, T, and θ
a	UNIFAC or ASOG parameter	K	θ
A	NRTL or UNIQUAC parameter	K	θ
C	Number of components	—	—
D	Number of groups of data	—	—
E	Total mass flow of extract	$kg{\cdot}s^{-1}$	$M{\bullet}T^{-1}$
e	Mass flow of a component in extract	$kg{\bullet}s^{-1}$	$M{\bullet}T^{-1}$
F	Total mass flow of feed	$kg{\bullet}s^{-1}$	$M{\bullet}T^{-1}$
f	Mass flow of a component in feed	$kg{\bullet}s^{-1}$	$M{\bullet}T^{-1}$
G	Number of groups	—	—
G	NRTL parameter	—	—
k	Distribution coefficient	—	—
m	Group interaction parameter	—	—
M	Molecular weight	$kg{\bullet}kgmol^{-1}$	$M{\bullet}N^{-1}$
n	Group interaction parameter	—	—
N	Number of stage	—	—
Q	Group area parameter	—	—
q'	Area parameter	$kgmol{\bullet}kg$	$N{\bullet}M^{-1}$
R	Group volume parameter	—	—
R	Total mass flow of raffinate	$kg{\bullet}s^{-1}$	$M{\bullet}T^{-1}$

Symbols	Description	Units in SI system	Dimension in M, N, L, T, and θ
R	Mass flow of a component in raffinate	$kg•s^{-1}$	$M•T^{-1}$
r′	Volume parameter	kgmol/kg	$N•M^{-1}$
S	Total mass flow of solvent	$kg•s^{-1}$	$M•T^{-1}$
S	Mass flow of a component in solvent	$kg•s^{-1}$	$M•T^{-1}$
T	Temperature	K	θ
U	Interaction energy	$kg•m^2•s^{-2}•kgmol^{-1}$	$M•L^2•T^{-2}•N^{-1}$
u	Potential energy	$kg•m^2•s^{-2}•kgmol^{-1}$	$M•L^2•T^{-2}•N^{-1}$
w	Mass fraction	—	—
W	Group mass fraction	—	—
Superscript/Subscript			
C	Combinatorial part	—	—
calc	Calculated	—	—
ex	Experimental	—	—
FH	Size contribution	—	—
G	Group contribution	—	—
I	Oil phase	—	—
II	Alcoholic phase	—	—
i,j,k	Component	—	—
m,n,k,l	Group	—	—
R	Residual	—	—
	Greek letters		
α	NRTL parameter	—	—
β	Selectivity	—	—
ϕ′	Volume fraction	—	—
γ	Activity coefficient	—	—
σ	Standard deviation	—	—
τ	NRTL or UNIQUAC parameter	—	—
θ′	Area fraction	—	—

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AUTHOR QUERIES

AQ1: Is "position 2" correct here?
AQ2: Please confirm sentence change.
AQ3: Variables have been made italic throughout.
AQ4: Is "system" correct here? If not, please change to another noun.
AQ5: Do you mean "composed"?
AQ6: Please confirm change to adjective.
AQ7: Please confirm Equation 5.8 meant here.
AQ8: Please confirm sentence change.
AQ9: References 107 through 153 were renumbered in text and in the list because refs 107 and 108 were duplicated. Ref 108 was deleted. Is it OK to include the (new) Reference 110 here (your Ref 111); citation could not be located in text.
AQ10: Is Figure 5.1 cite here correct?
AQ11: Do you mean "extracted from the alcoholic phase"?
AQ12: Please spell out journal name.
AQ13: Please provide article title.
AQ14: Volume number?
AQ15: Please spell out journal name.