Fluid Phase Equilibria 442 (2017) 87–95

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Solubility behavior of mixtures containing refined soybean oil and low-toxic solvents at different temperatures

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ARTICLE INFO

Article history:
Received 19 December 2016
Received in revised form
14 March 2017
Accepted 15 March 2017
Available online 18 March 2017

Keywords:
Liquid-liquid extraction
Low-toxic solvent
Deodorization
Refined soybean oil

ABSTRACT

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

1. Introduction

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

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

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

Qualitative tools, such as the method of Cusack et al. [25], comprise initial solvent-selection methods, and are used as a guide

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http://dx.doi.org/10.1016/j.fluid.2017.03.013

for preselecting a limited group of candidates (substances) to act as solvents for a certain solute-diluent system. Cusack et al. [25] method chooses a solvent that lowers the value of the solute activity coefficient relative to its value in the solute-diluent mixture (initial mixture) [21]. Group contribution methods, such as the UNIQUAC Functional-group Activity Coefficients (UNIFAC) method [26], can be used for estimating activity coefficients of compounds within the mixture, based on their functional groups. Particularly, in the case of fatty systems, poorly predictive capacity of the UNIFAC method, in its different versions, has been pointed out in the literature [6,27,28]. Efforts have been made toward suiting the UNIFAC parameter matrix for selected branches of mixtures [27,28] based on available experimental data.

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

2. Solvent screening for liquid-liquid extraction

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

3. Experimental section

3.1. Material

Refined soybean oil (Liza™, Cargill, Brazil) was purchased in a local market. Official AOCS methods Ce 1f-96 and Ce 1–62 [40] were applied for determining its fatty acids profile, which is presented in Table S1 (*Supplementary Material*). Results in Table S1 show that RSO is rich in polyunsaturated fatty acids (54% m/m, mainly linoleic acid), followed by monounsaturated fatty acids (22.9% m/m, mainly oleic acid). Fatty acids with 18 carbons sum up 85% m/m, approx., distributed among stearic, oleic, linoleic and linolenic acids, with presence of a small content of *trans* isomers.

From Table S1, a probable triacylglycerol (TAG) profile (Table S2) of RSO was estimated using the statistical procedure of Antoniosi Filho et al. [41]. An equivalent TAG for this probable profile is formed by two linoleic acids and one oleic acid (LiLiO), named {3-[(9Z)-9-Octadecenoyloxy]-1,2-propanediyl-(9Z,12Z,9′Z, 12′Z)bis(-9,12-octadecadienoate)}, with a molecular weight of 874.5 g.gmol^{-1}. Since RSO is a multicomponent mixture containing mainly TAGs with 18 carbons, it was possible to represent RSO as a pseudocomponent (LiLiO) both in modeling and prediction of LLE data [6,7,15,42–45].

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

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

3.2. Solubility behavior of RSO and preselected solvents

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

3.3. Determination of phase diagrams

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

Binodal curves, presented as T–w diagrams, in which w is the mutual solubilities in mass fraction, were measured by cloud point detection following two different procedures, according to Treybal [29]. In the case of temperatures located far from the region of the upper critical solution temperature (UCST), the constant-temperature method was used. On the contrary, the constant-composition method was successfully applied. These methods