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Ternary (liquid–liquid) equilibrium data of furfuryl alcohol with organic solvents at $T = 298.2$ K: Experimental results and thermodynamic models

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ABSTRACT

Basing on the importance of liquid–liquid equilibrium (LLE) data for the chemical industry, ternary LLE systems of water + furfuryl alcohol + (MIBK, ethyl acetate, furfural or *n*-butanol) were investigated at $T = 298.2$ K and atmospheric pressure. Solubility and tie-line data of these ternary LLE systems were determined by a direct measurement method. An uncertainty propagation calculation was used to validate the reliability of LLE results. Distribution coefficients (D) and separation factors (S) were calculated to evaluate the capability of selective organic solvents for separation of furfuryl alcohol from water. The correlations of experimental results with results obtained by using NRTL, UNIQUAC and UNIFAC models were presented and confirmed by *rmsd* values which were less than 5%.

1. Introduction

Furfuryl alcohol is a toxic component which may cause adverse health effects by the following exposures: inhalation, ingestion or eyes/dermal contact. The National Institute for Occupational Safety and Health (NIOSH) listed furfuryl alcohol as a carcinogen [1,2]. However, furfuryl alcohol has been widely applied in the chemical and polymer industries. Nowadays, the major applications of furfuryl alcohol are production of resins, acid proof bricks as well as corrosion resistant fiber glass and polymer concrete. In addition, furfuryl alcohol is also an intermediate chemical for the synthesis of dispersing agents, lubricants, lysine, plasticizers, tetrahydrofurfuryl alcohol and vitamin C [3,4]. In these productions, furfuryl alcohol may contaminate industrial wastewaters. Due to the toxicity of furfuryl alcohol and considering also its adverse environmental impact, separation of furfuryl alcohol from wastewaters before their discharge should be highly important.

Liquid–liquid extraction has long been used in chemical engineering processes and wastewater treatment due to its industrially applicable and economical method. In the development and design of separation processes liquid–liquid equilibrium (LLE) data are mainly required. In particular, the LLE data of ternary systems have a fundamental and important role in the industrial units [5,6]. The ternary LLE data are usually determined by direct measurement or by cloud-point titration methods. For the method of direct measurement, a ternary mixture is separated into two liquid phases. The compositions of these phases in equilibrium state are obtained by analysis. The method of cloud-point titration has been used in many measurements to obtain the concentration of components in liquid phases. The type of measurement was selected based on the property of the ternary mixture e.g. density, pH, viscosity, sound velocity and refractive index. Again, refractive index measurements have been used extensively [7].

In addition, in the design of separation processes for the industries, thermodynamic models are also required. Many authors have reported in the literature the activity coefficient models for prediction of different ternary liquid–liquid systems, e.g. the non-random two liquid (NRTL) model [8–11], the universal quasi chemical (UNIQUAC) model [12–14] and the universal functional activity coefficient (UNIFAC) model [15–17]. These models involve

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Table 1
Source and mass fraction purity of materials.

Material name	Source	Purity/% mass	Analysis method
Furfuryl alcohol	Sigma-Aldrich	99.0	GC
Furfural	Sigma-Aldrich	99.0	GC
n-Butanol	Erba Lachema	99.5	GC
Methyl isobutyl ketone	MicroChem	99.5	GC
Ethyl acetate	MicroChem	99.8	HPLC

the binary interaction parameters which can be obtained by a software program and regression with experimental data. However, no attempt has been made for correlating LLE data of furfuryl alcohol with the above mentioned NRTL, UNIQUAC and UNIFAC models.

The main purpose of this work was to provide a new series of LLE data. The ternary systems of furfuryl alcohol with efficient organic solvents were investigated at a temperature of 298.2 K and atmospheric pressure. Methyl isobutyl ketone (MIBK), ethyl acetate, furfural and *n*-butanol were selected as organic solvents. MIBK is highly selective, non-toxic and relatively less miscible in aqueous solutions [18]. Ethyl acetate is a good solvent and safe for the environment [19]. In addition, furfural and *n*-butanol are the preferable solvents for use in industry [20,21]. For each ternary system, the solubility and tie-line data were determined by a direct measurement method. The reliability of experimental results was validated with the uncertainty propagation calculation. Distribution coefficients (D) and separation factors (S) were obtained from the tie-line data to present the separation capability of the selective organic solvents. The LLE data were correlated using NRTL, UNIQUAC and UNIFAC models. The values of binary interaction parameters for these equilibrium models were obtained by the Aspen Plus v. 2006.5 simulation program (AspenTech, Burlington, MA, USA) and regressed with the experimental data.

2. Experimental

2.1. Materials

Materials consisting of furfuryl alcohol ($C_5H_6O_2$, MW 98.10 g/mol), furfural ($C_5H_4O_2$, MW 96.08 g/mol), *n*-butanol (C_4H_9OH, MW 74.12 g/mol), methyl isobutyl ketone ($C_6H_{12}O$, MW 100.16 g/mol) and ethyl acetate ($C_4H_8O_2$, MW 88.11 g/mol) were used in this work. The source and mass fraction purity of materials are listed in Table 1. All materials were used without further purification. Distilled water was used in all experiments.

2.2. Apparatus and procedure

The solubility data for the ternary systems were determined by the direct measurement method in organic-rich and aqueous-rich phases at equilibrium. A digital analytical balance—Mettler Toledo AE200 (with an accuracy of ±0.0001 g) was used to obtain the weights of all components. The temperature of the systems was controlled by a water jacket that was checked using a digital thermometer (with an accuracy of ±0.1 K). The binary mixtures of known compositions of furfuryl alcohol and organic solvents were prepared in closed glass vessels. The binary mixtures were continually titrated with water until they became turbid. The end point of titration was achieved when the mixtures remained turbid for 15 min. During this time the glass vessels were agitated periodically to observe the turbidity. These procedures were used to determine the solubility curve of the organic-rich phase. To repeat all measurements at least three times, the known quantity of furfuryl alcohol was then added into the mixtures for back transparent. The mixtures were again titrated with water until they became turbid, and the same end point of titration was taken. The solubility curve of aqueous-rich phase was determined using the binary mixtures of furfuryl alcohol and water in the same manner. The organic solvents were added to titration.

The tie-line data were obtained from the ternary mixtures after reaching equilibrium compositions. More water was successively added until transition from homogeneous to heterogeneous state appeared in the mixtures. Thereafter, the mixtures were agitated vigorously at 200 rpm for 2 h, then centrifugated and left to complete separation for 14 h. These periods were long enough for samples reaching two equilibrium liquid layers. The organic-rich phase was carefully withdrawn from the top layer of the glass vessel by syringe and then weighed. The remaining aqueous-rich sample was also weighed and analyzed by gas chromatography. The compositions of all components were calculated directly basing on the analytical results and the mass balance equation. The ProSim program was used to plot triangular phase diagrams for all ternary LLE data.

2.3. Analysis

The separated phases were analyzed by gas chromatography (Hewlett Packard 5890 Series II, with FID detector) using a 1.4 m × 3 mm glass column packed with 5% C20M + 5% SE. The quantitative determination of the reaction samples was done by the external standard method using an aqueous solution of each sample with known concentration and response factor.

2.4. Reliability of LLE results

The reliability of LLE results was validated by the uncertainty propagation calculation as according to the GUM and NIST [22,23]. In this work, the standard uncertainties ($u(x_i)$), as shown in the respective footnote tables, were calculated based on Eqs. (1) and (2).

$$u(x_i) = \sqrt{\frac{1}{n(n-1)}\sum_{k=1}^{n}\left(X_{i,k} - \overline{X_i}\right)^2} \tag{1}$$

$$\overline{X_i} = \frac{1}{n}\sum_{k=1}^{n} X_{i,k} \tag{2}$$

where n is the number of independent observations, $X_{i,k}$ is the input quantity as obtained under the same conditions of measurement and $k = 1, 2, \ldots, n$.

3. Results and discussion

3.1. Experimental solubility and tie-line data

Experimental solubility data from the binodal curve diagrams (Fig. 1) of four ternary systems (water + furfuryl alcohol + organic solvents) at $T = 298.2$ K and atmospheric pressure are shown in Table 2 and Fig. 1. As can be seen in Fig. 1, only one liquid pair (water + organic solvents) is partially miscible and two liquid pairs (furfuryl alcohol + water or organic solvents) are completely miscible. It indicates that all four ternary systems exhibit the type-1 behavior of LLE [24]. The area of the two-phase region decreased in the following order of organic solvents: MIBK > ethyl acetate > furfural > *n*-butanol. This area depends on the mutual solubility of water and the organic solvents. Thus, the type of organic