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Phase equilibria of (water + levulinic acid + dibasic esters) ternary systems

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ABSTRACT

Liquid–liquid equilibrium (LLE) data of the solubility (binodal) curves and tie-line end compositions were examined for mixtures of {(water (1) + levulinic acid (2) + dimethyl succinate or dimethyl glutarate or dimethyl adipate (3)} at 298.15 K and 101.3 ± 0.7 kPa. The reliability of the experimental tie-line data was confirmed by using the Othmer–Tobias correlation. The LLE data of the ternary systems were predicted by UNIFAC method. The LLE data were correlated fairly well with UNIQUAC and NRTL models, indicating the reliability of the UNIQUAC and NRTL equations for these ternary systems. The best results were achieved with the NRTL equation, using non-randomness parameter ($\alpha = 0.3$) for the correlation. Distribution coefficients and separation factors were measured to evaluate the extracting capability of the solvents.

1. Introduction

Levulinic acid, a carboxylic acid containing ketone structure, is a clear to brownish semi-solid melting at 310 K soluble in ethanol, ethyl ether and chloroform. It is used to manufacture perfumery, food additives, fuel additives, herbicides, solder flux, stabilizers and printing inks. Levulinic acid and its esters are also used as plasticizers and solvents in polymer, textiles and coatings. Therefore, it is important to separate and purify levulinic acid [1].

The efficient separation of carboxylic acids from aqueous solutions is an important concept in the chemical fermentation industry where many solvents have been tested to improve such recovery [2–8].

In the scope of investigating more benign solvents as potential replacements for chlorocarbons or aromatic hydrocarbons and as new solvents for separations, we have concentrated on the dibasic esters, which have excellent properties for industrial applications. They are environmental friendly, low cost, low toxicity, great stability and with rather high-boiling point (388–469.2 K), while the values of viscosity and density are close to those of water. The dibasic esters are also used as novel solvents in separation techniques [9]. Firstly, Uusi-Penttilä et al. [10] examined liquid–liquid equilibrium (LLE) data of some different ternary systems. Recently, Kırbaşlar et al. [11–15] examined LLE data of some different ternary systems.

In LLE, the activities of the component *i* on both phases are equal and the mole fractions x_i^E, x_i^R of conjugate phases can be calculated using the following equation

$$\gamma_i^E x_i^E = \gamma_i^R x_i^R, \tag{1}$$

where γ_i^E and γ_i^R are the corresponding activity coefficients of component *i* in extract and raffinate phases. The liquid phase activity coefficient is represented as follows:

$$\ln\gamma_i = \ln\gamma_i\,(\text{combinatorial}) + \ln\gamma_i\,(\text{residual}) \tag{2}$$

The combinatorial and residual parts of the activity coefficient are due to the difference in shape and energy of the molecules, respectively.

The LLE data were predicted and correlated with the universal functional group activity coefficient (UNIFAC) [16], quasi-chemical model (UNIQUAC) [17] and non-random two liquid equation (NRTL) models [18]. The UNIFAC method depends on the optimised interaction parameters between each pair of main groups present the system, whereas the UNIQUAC and NRTL models depend on the optimised interaction parameters between the compounds in the system.

In this work, dimethyl succinate, dimethyl glutarate and dimethyl adipate were used as solvents in the separation of

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Table 1
Physical properties of the pure components at $T = 293.15$ K and $p = 101.325$ kPa [22].

Compound	ρ (kg m^{-3})		n_D		T_b (K)	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Water	999.90	998.23	1.33240	1.3330	373.2	373.25
Levulinic acid	1133.50	1133.7	1.43950	1.4396	518.2	518
Dimethyl succinate	1119.13	1119.8	1.41969	1.4197	469.2	469.4
Dimethyl glutarate	1087.67	1087.6	1.42454	1.4242	487.3	487.2
Dimethyl adipate	1061.72	1060.0	1.42825	1.4283	388.0[a]	388.2[a]

[a] At 1.733 kPa.

levulinic acid from water. Several studies have been carried out to present LLE data to extract levulinic acid from its dilute aqueous solutions [19–21]. In this paper, we report the LLE results for the three ternary system (water + levulinic acid + dimethyl succinate), (water + levulinic acid + dimethyl glutarate) and (water + levulinic acid + dimethyl adipate) at $T = 298.15$ K, for which no such data were available.

2. Experimental

2.1. Materials

Levulinic acid, dimethyl succinate, dimethyl glutarate and dimethyl adipate were purchased from Merck and were of 0.98, 0.98, 0.99 and 0.99 mass fraction purity, respectively. The chemicals were used without further purification. Deionized and redistilled water was used throughout all experiments.

2.2. Apparatus and procedure

Refractive indexes were measured with Anton Paar refractometer (RXA 170 model) with stated accuracy of $\pm 5 \times 10^{-5}$. Densities were measured with Anton Paar densimeter (Model 4500). Boiling point measurements were obtained by using a Fischer boiling point apparatus. The estimated uncertainties in the density and boiling point measurements were $\pm 1 \times 10^{-2}$ kg m^{-3} and 0.1 K, respectively. The measured physical properties are listed in Table 1, along with literature values [22].

The solubility curves were determined by the cloud point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions. The temperature in the cell was kept constant by circulating water from a water bath (NUVE, BS 302 Model), which is equipped with a temperature controller capable of maintaining the temperature within ±0.1 K. The major central part of the solubility curves was obtained by titration heterogeneous mixtures of water + dibasic ester with levulinic acid until the turbidity had disappeared. Binary mixtures of either (water + levulinic acid) or (dibasic ester + levulinic acid) were titrated against the third component until the transition from homogeneity to cloudiness was observed. All mixtures were prepared by weighing with a Mettler scale accurate to within $\pm 10^{-4}$ g. Mutual solubility values of the (water + dibasic ester) binary were measured using the method based on the detection of the cloud point. The transition point between the homogeneous and heterogeneous zones was determined visually. The reliability of the method depends on the precision of the Metrohm micro burette with an accuracy of $\pm 3 \times 10^{-9}$ m^3, and is limited by the visual inspection of the transition across the apparatus. The accuracy of the visual inspection of the transition is achieved with waiting approximately 5 min in the transition point and observing the heterogeneity. All visual experiments were repeated at least three times in order to acquire high accuracy. Concentration determinations were accurate to ±0.001 mass fraction.

End-point determinations of the tie lines were based upon the independent analysis of the conjugate phases that were regarded as being in equilibrium. Mixtures of known masses of water, levulinic acid, and dibasic esters lying within the heterogeneous gap were introduced into the extraction cell and were stirred vigorously for at least 4 h, and then left for 6 h (the time necessary to attain equilibrium was established in preliminary experiments) to settle down into water and dibasic esters layers.

The liquid samples were analyzed by a Gas Chromatograph (HP6890 model), equipped with flame ionization detector (FID) and thermal conductivity detector (TCD). A 15 m long HP Plot Q column (0.32 mm i.d., 0.2 μm film thickness) for TCD, and an HP-Innowax polyethylene glycol capillary column (30 m × 0.32 mm × 0.5 μm) for FID were utilized to separate organic components and water of samples at tailorized oven programs suitable for each ternary. The detector temperature was kept $T = 473.15$ K, while the injection port temperature was held at $T = 523.15$ K. Injections were performed on the split 70:1 mode. Nitrogen was used as a carrier gas at a rate of 8 cm^3 min^{-1}. Injection volumes of the liquid samples were 0.3 μL. The greatest errors in the determination of mole fraction composition using the calibration curves were $\pm 2\ 10^{-3}$ in water-rich phase and in dibasic ester-rich phase.

3. Results and discussion

3.1. LLE measurements

The experimental binodal curves of the water (1) + levulinic acid (2) + dibasic ester (3) systems are plotted in Figs. 1–3, and the numerical data are presented in Table 2. Table 3 shows the experimental tie-line compositions of the equilibrium phases, for

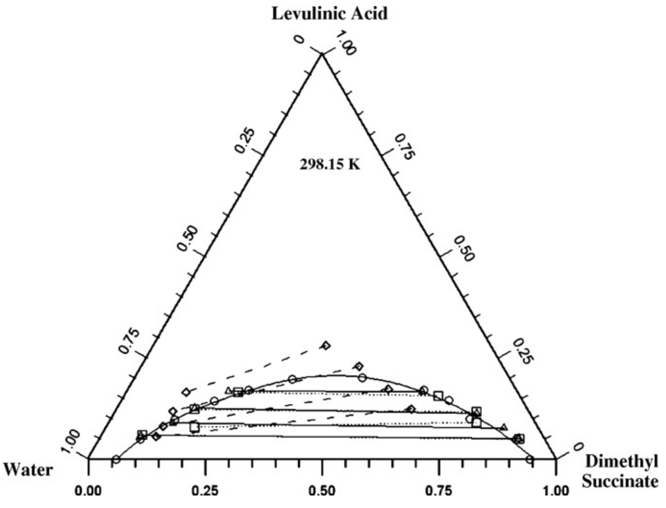

Fig. 1. Ternary diagram for LLE of {water (1) + levulinic acid (2) + dimethyl succinate (3)} at $T = 298.15$ K; –○– experimental solubility curve; –Δ– experimental tie-line data; –◇– calculated (UNIFAC) tie-line data; –□– correlated (UNIQUAC) tie-line data.