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Liquid–liquid equilibria of the ternary system water + acetic acid + dimethyl succinate

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Abstract

Liquid–liquid equilibrium (LLE) data of water + acetic acid + dimethyl succinate were measured at 298.2, 308.2, and 318.2 K. Complete phase diagrams were obtained by determining binodal curves and tie lines. The reliability of the experimental tie line data was confirmed by using the Othmer–Tobias correlation. The UNIFAC and modified UNIFAC model were used to predict the phase equilibrium data in the ternary system. Distribution coefficients and separation factors were evaluated for the immiscibility region.

Keywords: Liquid–liquid equilibria; Acetic acid; Dimethyl succinate; UNIFAC; Modified UNIFAC

1. Introduction

Acetic acid is one of the most widely used carboxylic acids. It is used in many reactions, such as, the synthesis of acetic esters, and also it can be used as a solvent, for example, in the manufacture of various acetate esters or in the preparation of pharmaceuticals. It can also be used as a fungicide [1].

Acetic acid is manufactured by synthetic methods or fermentation process. Both of these methods give dilute aqueous solutions. Thus, the separation of acetic acid from dilute aqueous solutions is of industrial importance [2–7].

The separation of acetic acid and water by distillation is very difficult; this separation requires a column with many stages and a high reflux ratio, thus incurring high running costs. Because of the lower energy cost of extraction process, liquid–liquid extraction is an alternative to distillation. At the same time, liquid–liquid extraction is a technique, which is used to separate the acetic acid from aqueous solutions and, in this respect, many solvents have been tried to improve recovery efficiency [8–15].

In the scope of investigating more benign solvents as potential replacements for chlorocarbons or aromatic hydrocarbons and as new solvents for separations, we concentrated on the dibasic esters, which have excellent properties for industrial applications. They are environmentally friendly, low cost, low toxicity, great stability and with rather high boiling temperatures $T = 463–573$ K, while their viscosity and density are close to those of water [16–20].

The behavior of non-ideal fluid mixtures can be calculated with the help of activity coefficients. The correct description of multicomponent systems requires reliable thermodynamic models. The UNIFAC model was developed by Fredenslund et al. [21]. A special UNIFAC version for the prediction of liquid–liquid equilibria was published by Magnussen et al. [22]. The UNIFAC model for the estimation of activity coefficients works on the concept that a liquid mixture may be considered as a solution of structural units.

Nevertheless, the modified UNIFAC model was proposed several years ago. It presents various advantages when compared with the group contribution methods, UNIFAC or ASOG. These advantages were achieved by using a modified combinatorial part and by using a large database to fit temperature dependent group interaction parameters simultaneously to vapor–liquid equilibria and liquid–liquid equilibria [23–27]. The main advantages of the modified UNIFAC method are better descriptions of the temperature dependence (residual part) and the real behavior in the dilute solution (combinatorial part). It can be applied more reliably for systems involving molecules with different sizes [26].

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The aim of this study is to recover acetic acid from aqueous solutions using environmentally friendly solvent with high-boiling point. In this paper, LLE results were reported for the water + acetic acid + dimethyl succinate ternary system, for which no such data have previously been published.

2. Experimental

2.1. Materials

Acetic acid and dimethyl succinate were purchased from Merck Company and were both received with a quoted purity of 99.8 and >98%, respectively. The purity of these substances was checked by gas chromatography and used without further purification. Water contents were measured with a Mettler Toledo DL38 Karl Fischer Titrator as 2×10^{-3} and 5×10^{-4} mass fractions, respectively. Distilled water was used throughout all experiments. Refractive indices were measured with Abbé-Hilger refractometer; its stated accuracy is $\pm 5 \times 10^{-4}$. Densities were measured using an Anton Paar DMA 4500 density meter. Boiling temperature measurements were obtained by using a Fischer boiling temperature apparatus. The estimated uncertainties in the density and boiling point measurements were $\pm 10^{-2}$ kg m^{-3} and ±0.1 K, respectively. The measured physical properties are listed in Table 1, along with some values from literature [28].

2.2. Experimental procedures

The binodal curve for water + acetic acid + dimethyl succinate ternary system was determined by cloud-point method [19]. Binary mixtures of known compositions were shaken in a glass stoppered cell equipped with a magnetic stirrer and jacketed for circulating water from a constant temperature bath at $T = 298.2 \pm 0.1$, 308.2 ± 0.1 and 318.2 ± 0.1 K. The third component was progressively added until the transition point was reached. The end point was determined by usually observing the transition from a homogenous to a heterogeneous mixture.

The mutual solubilities of water + dimethyl succinate system were also determined by using cloud-point method. A weighted amount of one component was placed in the cell; then the other component was added until a permanent heterogeneity was observed.

Temperature was controlled using circulating water from water bath (NUVE, BS 302 model) and the water temperature was kept constant by a PID controller within ±0.1 K. All mixtures were prepared by weighing with a Sartorious (CP 224S model) scale accurate within $\pm 10^{-7}$ kg. The solvent was added by a microburet (Metrohm) with an accuracy of $\pm 3 \times 10^{-9}$ m^3.

Tie line data were obtained by preparing water + acetic acid + dimethyl succinate ternary mixtures of known overall compositions lying within the two phase region and after being stirred vigorously for at least 2 h in jacked cell [11] and then left to stand for at least 4 h. After the complete separation of the phases, samples were carefully taken from each phase and analyzed to obtain the tie lines.

2.3. Analysis

The liquid samples were analyzed by a Gas Chromatograph (Hewlett Packard GC, Model 6890 Series) equipped with a Thermal Conductivity Detector (TCD) for the quantitative determination of water, acetic acid and dimethyl succinate. A 15 m long HP-Plot Q column (320 μm diameter with a 20 μm film thickness) was used with a temperature-programmed analysis. Column temperature, 383 K (5 min) to 403 K at 10 K min^{-1}; and to 523 K (2 min) by 25 K min^{-1} ramp rate and injection mode, split ratio 100/1; detector, TCD; injector temperature, 523 K and detector temperature, 473 K; carrier gas, nitrogen 6 mL min^{-1}; injected volume of 1 μL of liquid sample. Samples with known compositions were used to calibrate the instrument in the composition range of interest. Three or four analyses were performed for each sample in order to obtain a mean mass fraction value with repeatability better than 1%.

3. Results and discussion

The experimental tie line data of water + acetic acid + dimethyl succinate ternary system at $T = 298.2$, 308.2 and 318.2 K are given in Table 2. The experimental binodal curve, experimental and predicted tie lines at each temperature were shown in Figs. 1–3. As it can be seen in Figs. 1–3, it was found that dimethyl succinate was little soluble in water and water was also little soluble in dimethyl succinate (on average 8% as mass fraction at each temperature), but miscible with acetic acid. The selectivity and strength of the solvent to extract the acetic acid were calculated as distribution coefficient and separation factor [29]. In addition, the separation factors and distribution coefficients are given in Table 3.

The extraction power of the solvent at each temperature, plots of D_2 versus w_{21} are shown in Fig. 4.

The effectiveness of extraction of acetic acid by dimethyl succinate is given by its separation factor (S), which is a measure of dimethyl succinate to separate acetic acid from water. This

Table 1
Densities, ρ, refractive indices, n_D, and boiling temperatures, T_b of pure components [28]

Component	ρ (293.2 K)/kg m^{-3}		n_D (298.2 K)		T_b (101.325 kPa)/K	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Water	998.21	997.0^a	1.3324	1.3325	373.2	373.15
Acetic acid	1049.42	1044.6^a	1.3713	1.3720^b	391.2	391.05
Dimethyl succinate	1114.18	1119.8	1.4196	1.4197	469.8	469.55

Superscripts (a, b) of density and refractive index indicated the temperature at 298.2 and 293.2 K, respectively.