Liquid−Liquid Equilibria of (Water + Acetic Acid + Diethyl Succinate or Diethyl Glutarate or Diethyl Adipate) Ternary Systems

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Liquid−liquid equilibrium (LLE) data of the solubility curves and tie-line end compositions were examined for mixtures of water (1) + acetic acid (2) + diethyl succinate or diethyl glutarate or diethyl 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. Distribution coefficients and separation factors were evaluated for the immiscibility region.

Introduction

Acetic acid is manufactured by the fermentation process or synthetic methods. From the fermentation process, dilute aqueous solution of acetic acid is obtained. Therefore, the separation of acetic acid from dilute aqueous solutions is an industrially important problem. The separation of acetic acid and water by distillation is very difficult, requiring a column with many stages and a high reflux ratio, thus incurring high running costs. Because of the lower energy cost, liquid−liquid extraction is an alternative method to distillation. At the same time, liquid−liquid extraction is a technique known to separate acetic acid from aqueous solutions, and many solvents have been tried to improve such recovery.[1−13]

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, in the preparation of pharmaceuticals, in preservative food, or in disinfectant cleaning.[10]

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 environmentally friendly and have low cost, low toxicity, great stability, and rather high boiling temperatures (490 to 518 K), while their viscosity and densities are close to those of water. The dibasic esters are also used as novel solvents in separation techniques.[14] First, Uusi-Penttilä et al. examined LLE data of four different ternary systems.[15] Recently, İnce and Kırbaşlar have examined LLE data of seven different ternary systems.[16−22]

The LLE data in this study were also predicted by the UNIFAC (universal functional group activity coefficient) method.[23] The UNIFAC method is used for predicting the activity coefficients, γ_i. In LLE, the activities of the component i on both phases are equal, and the mole fractions (x_i^E and x_i^R) of conjugate phases can be calculated by using the following equation:

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

where γ_i^E and γ_i^R are the corresponding activity coefficients of component i in solvent (extract) and aqueous (raffinate) phases, respectively. The interaction parameters between each main group are used to calculate activity coefficients of component i. The values of the UNIFAC parameters for LLE predictions were taken from a UNIFAC table.[24]

Table 1. Densities ρ and Refractive Indexes n_D at 20 °C and Boiling Points t_b at 101.33 kPa of Chemicals[25]

	ρ/g·cm^{-3}		n_D		t_b/°C	
compound	expt.	lit.	expt.	lit.	expt.	lit.
water	0.99990	0.9982	1.33240	1.3330	100.05	100.10
acetic acid	1.04430^{25}	1.0446^{25}	1.37201	1.3720	117.95	117.90
diethyl succinate	1.04022	1.0402	1.42014	1.4201	217.65	217.70
diethyl glutarate	1.02204	1.0220	1.42414	1.4241	236.45	236.50
diethyl adipate	1.00763	1.0076	1.42725	1.4272	245.15	245.00

This study is a part of a research program on the recovery of acetic acid from dilute aqueous solutions using organic solvents. The objective of this work is to recover acetic acid from dilute aqueous solutions by using environmentally friendly solvents with high-boiling point. In this paper, LLE results were reported for the three ternary systems (water + acetic acid + diethyl succinate), (water + acetic acid + diethyl glutarate), and (water + acetic acid + diethyl adipate) at 298.15 K, for which no such data have previously been published.

Experimental Section

Materials. Acetic acid, diethyl succinate, diethyl glutarate, and diethyl adipate were purchased from Merck and were of (99, 99, 98, and 99) % mass purity, respectively. The chemicals were used without further purification. GC analysis did not detect any appreciable peaks of impurities. Deionized and redistilled water was used throughout all experiments. Densities and refractive indexes were measured with an Anton Paar densimeter (DMA 4500 model) equipped with a refractometer (RXA 170 model) with accuracies of ± 1·10^{-5} g·cm^{-3} and ± 5·10^{-5}, respectively. Boiling point measurements were obtained by using a Fischer boiling point apparatus. The estimated uncertainty in the boiling point measurements was ± 0.1 °C. The measured physical properties are listed in Table 1 along with literature values.[25]

Procedure. The solubility (binodal) curves were determined by the cloud point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions.[17] The temperature in the cell was kept constant by circulating water from a water bath (NUVE, BS 302 model), which is equipped with a

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Table 2. Experimental Solubility Curve Data for (Water + Acetic Acid + Dibasic Ester) Ternary Systems at 298.15 K

w_1	w_2	w_3	w_1	w_2	w_3
Water (1) + Acetic Acid (2) + Diethyl Succinate (3)					
0.9781	0.0000	0.0219	0.3412	0.2967	0.3621
0.8477	0.1193	0.0330	0.2882	0.2850	0.4268
0.7584	0.1886	0.0530	0.2792	0.2809	0.4399
0.6902	0.2329	0.0769	0.1904	0.2447	0.5649
0.6299	0.2707	0.0994	0.1206	0.1807	0.6987
0.5486	0.2989	0.1525	0.0798	0.1061	0.8141
0.4537	0.3076	0.2387	0.0250	0.0000	0.9750
Water (1) + Acetic Acid (2) + Diethyl Glutarate (3)					
0.9847	0.0000	0.0153	0.2826	0.3228	0.3946
0.7705	0.1965	0.0330	0.2340	0.3045	0.4615
0.6600	0.2799	0.0601	0.1633	0.2560	0.5807
0.5023	0.3420	0.1557	0.1017	0.1819	0.7164
0.4195	0.3437	0.2368	0.0248	0.0000	0.9752
0.3313	0.3343	0.3344			
Water (1) + Acetic Acid (2) + Diethyl Adipate (3)					
0.9910	0.0000	0.0090	0.3125	0.3548	0.3327
0.7856	0.1968	0.0176	0.2483	0.3398	0.4119
0.6710	0.2913	0.0377	0.2106	0.3215	0.4679
0.5403	0.3628	0.0969	0.1403	0.2589	0.6008
0.4748	0.3778	0.1474	0.0898	0.1824	0.7278
0.3678	0.3693	0.2629	0.0183	0.0000	0.9817

Table 3. Experimental Tie-Line Data of (Water + Acetic Acid + Dibasic Ester) Ternary Systems at 298.15 K

water-rich phase (mass fraction)			solvent-rich phase (mass fraction)		
w_{11}	w_{21}	w_{31}	w_{13}	w_{23}	w_{33}
Water (1) + Acetic Acid (2) + Diethyl Succinate (3)					
0.9206	0.0505	0.0289	0.0409	0.0346	0.9245
0.8573	0.1132	0.0295	0.0502	0.0585	0.8913
0.7682	0.1809	0.0509	0.0829	0.1143	0.8028
0.6713	0.2462	0.0825	0.1269	0.1839	0.6892
Water (1) + Acetic Acid (2) + Diethyl Glutarate (3)					
0.8887	0.0894	0.0219	0.0378	0.0576	0.9046
0.7916	0.1779	0.0305	0.0598	0.1037	0.8365
0.6925	0.2560	0.0515	0.0979	0.1694	0.7327
0.6111	0.3045	0.0844	0.1419	0.2270	0.6311
Water (1) + Acetic Acid (2) + Diethyl Adipate (3)					
0.9313	0.0578	0.0109	0.0245	0.0259	0.9496
0.8549	0.1300	0.0151	0.0389	0.0608	0.9003
0.7830	0.1989	0.0181	0.0511	0.0982	0.8507
0.6955	0.2741	0.0304	0.0815	0.1720	0.7465

temperature controller capable of maintaining the temperature within ± 0.1 °C. The major central part of the solubility curves was obtained by titrating heterogeneous mixtures of water + dibasic ester with acetic acid until the turbidity had disappeared. For the water-side and solvent-side, binary mixtures of either (water + acid) or (dibasic ester + acid) were titrated against the third component until the transition from homogeneity to heterogeneity was observed. All mixtures were prepared by weighing with a Mettler scale accurate to within $\pm 1 \cdot 10^{-4}$ g.

Mutual solubility values of the binary mixture (water + dibasic ester) were measured using the method also 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 microburette, with an accuracy of $\pm 3 \cdot 10^{-3}$ cm^3 and is limited by visual inspection of the transition across the apparatus. The accuracy of the visual inspection of the transition is achieved by waiting for about 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.

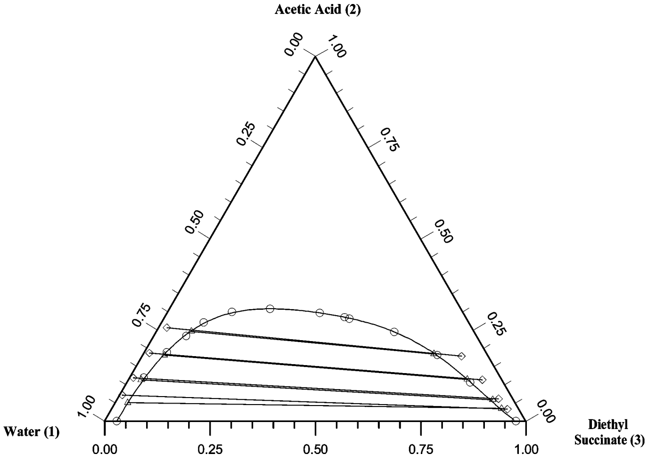

Figure 1. Ternary diagram for LLE of water (1) + acetic acid (2) + diethyl succinate (3) at 298.15 K: ○, experimental solubility curve; △, experimental tie-lines; ◇, calculated (UNIFAC) tie-lines.

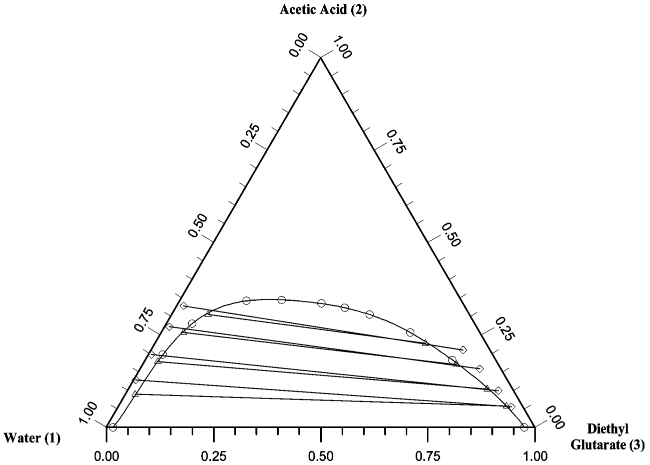

Figure 2. Ternary diagram for LLE of water (1) + acetic acid (2) + diethyl glutarate (3) at 298.15 K: ○, experimental solubility curve; △, experimental tie-lines; ◇, calculated (UNIFAC) tie-lines.

End-point determinations of the tie-lines were carried out with independent analysis of the conjugate phases that were regarded as being in equilibrium. Mixtures of known masses of water, acid, and dibasic ester 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 aqueous and solvent layers.

Analysis. The liquid samples were analyzed by a gas chromatograph, HP 6890 model, equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). A HP Plot Q column (15 m × 0.32 mm × 0.2 μm) for TCD and HP-Innowax polyethylene glycol capillary column (30 m × 0.32 mm × 0.5 μm) for FID were utilized to separate water and organic components of samples, respectively. The standard compound for the analysis was ethanol. Oven temperature was regulated to perform a temperature from (343.15 to 443.15) K at 20 $K \cdot min^{-1}$ and from (443.15 to 523.15) K at 40 $K \cdot min^{-1}$. The detector temperature was kept at 523.15 K, while the injection port temperature was held at 573.15 K. Injections were performed on the split 1/100 mode. Nitrogen was used as a carrier gas with a flow rate of 8 $cm^3 \cdot min^{-1}$. Injection volumes of the liquid samples were 0.3 μL. The uncertainty of the mass fraction measurements for the overall composition determination was 0.002.

Results and Discussion

The compositions of mixture on the solubility curve as well as the mutual binary solubility of water and dibasic esters at 298.15 K are given in Table 2, in which w_i denotes the mass

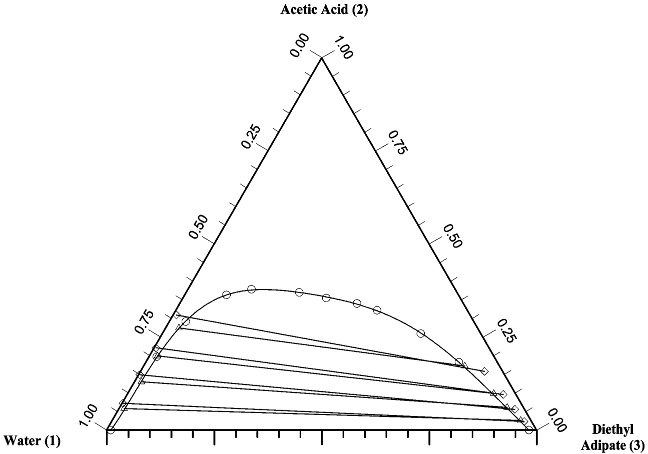

Figure 3. Ternary diagram for LLE of water (1) + acetic acid (2) + diethyl adipate (3) at 298.15 K: ○, experimental solubility curve; △, experimental tie-lines; ◇, calculated (UNIFAC) tie-lines.

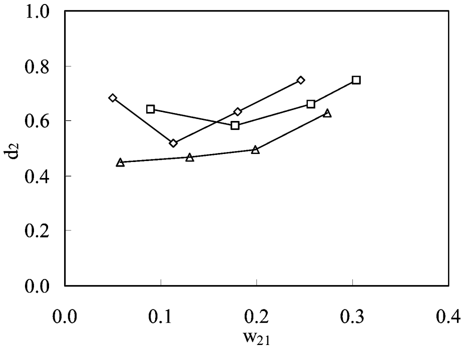

Figure 4. Distribution coefficient of acetic acid, D_2, plotted against the mass fraction of acetic acid in aqueous phase, w_{21}: ◇, diethyl succinate; □, diethyl glutarate; △, diethyl adipate.

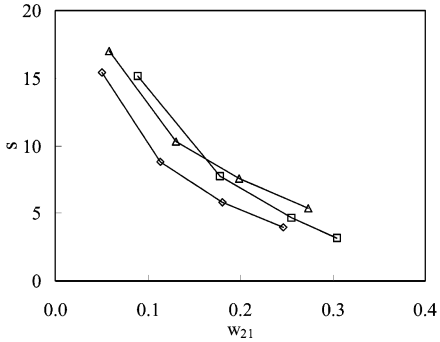

Figure 5. Separation factor, *S*, plotted against the mass fraction of acetic acid in the aqueous phase, w_{21}: ◇, diethyl succinate; □, diethyl glutarate; △, diethyl adipate.

fraction of the *i*th component. Table 3 shows the experimental tie-line compositions of the equilibrium phases, for which w_{i1} and w_{i3} refer to the mass fractions of the *i*th component in the aqueous and solvent phases, respectively. The solubility curves and tie-lines are shown in Figures 1 to 3. Referring to Figures 1 to 3, the mutual solubility of water in dibasic esters depends on the carbon number of dibasic esters. Figures 1 to 3 show that the area of the two-phase heterogeneous region changes in the order of diethyl succinate < diethyl glutarate < diethyl adipate. This explains that the solubility of water in dibasic esters decreases with increasing carbon chain length of the dibasic esters and also that water is the most soluble in diethyl succinate and the least soluble in diethyl adipate. The slopes of the tie-lines obtained in this work show that acetic acid is more soluble in water than in dibasic esters.

Table 4. Distribution Coefficients for Water (D_1) and Acetic Acid (D_2) and Separation Factors (S) at 298 K

D_1	D_2	S
Water (1) + Acetic Acid (2) + Diethyl Succinate (3)		
0.044	0.69	15.42
0.059	0.52	8.83
0.108	0.63	5.86
0.189	0.75	3.95
Water (1) + Acetic Acid (2) + Diethyl Glutarate (3)		
0.043	0.64	15.15
0.076	0.58	7.72
0.141	0.66	4.68
0.232	0.75	3.21
Water (1) + Acetic Acid (2) + Diethyl Adipate (3)		
0.026	0.45	17.03
0.046	0.47	10.28
0.065	0.49	7.57
0.117	0.63	5.35

Distribution coefficients, D_i, for water ($i = 1$) and acetic acid ($i = 2$) and separation factors, S, were calculated as follows:

$$D_i = w_{i3}/w_{i1} \tag{2}$$

$$S = \frac{\text{distribution coefficient of acetic acid}}{\text{distribution coefficient of water}}$$

$$S = (w_{23}/w_{21})/(w_{13}/w_{11}) \tag{3}$$

where w_{23} and w_{21} are the mass fractions of acetic acid in solvent-rich and water-rich phases, respectively. w_{13} and w_{11} are the water mass fractions in solvent-rich and water-rich phases, respectively.

The distribution coefficients and separation factors for each dibasic ester are given in Table 4. The effectiveness of extraction of acetic acid through solvent is given by its separation factor, which is an indication of the ability of solvent to separate acetic acid from water. This quantity is found to be greater than 1 (separation factors varying between 3.21 and 17.03) for the systems reported here, which means that extraction of acetic acid by dibasic esters are possible. The separation factors and distribution coefficients are not constant over the whole two-phase region. The extracting power of the solvents is shown in Figures 4 and 5.

The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer−Tobias correlation[26] for each solvent as shown in the following equation:

$$\ln(1 - w_{11})/w_{11} = a + b \ln(1 - w_{33})/w_{33} \tag{4}$$

where w_{11} is the mass fraction of water in the water-rich phase; w_{33} is the mass fraction of dibasic esters in the solvent-rich phase; *a* and *b* are the constant and the slope of eq 4.

Othmer−Tobias plots were constructed of $\ln\{(1 - w_{11})/w_{11}\}$ versus $\ln\{(1 - w_{33})/w_{33}\}$. The correlations are shown in Figure 6 at 298.15 K. The correlation being linear indicates the degree of consistency of the related data.

The equilibrium data of the ternary system were predicted by the UNIFAC method and a method using the interaction parameters of CH_2, CH_3, CH_2COO, COOH, and H_2O functional groups obtained by Poling et al.[24] The calculated tie-lines (dashed lines) are presented in Figures 1 to 3.

The root-mean-square deviations (rmsd) were calculated from the difference between the experimental data and the predictions of the UNIFAC method for each ternary system according to the following equation:

$$\text{rmsd} = \{\sum_k [\sum_i \sum_j (w_{i,\text{exp}} - w_{i,\text{calcd}})^2]/6n\}^{1/2} \tag{5}$$

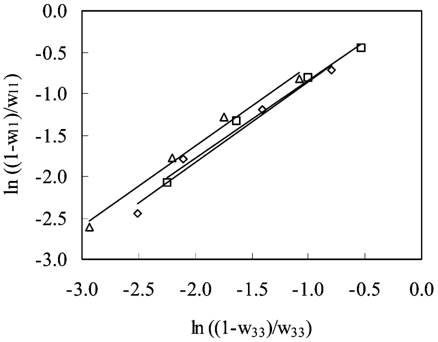

Figure 6. Othmer−Tobias plots of the water (1) + acetic acid (2) + dibasic ester (3) ternary systems at 298.15 K: ◇, diethyl succinate; □, diethyl glutarate; △, diethyl adipate.

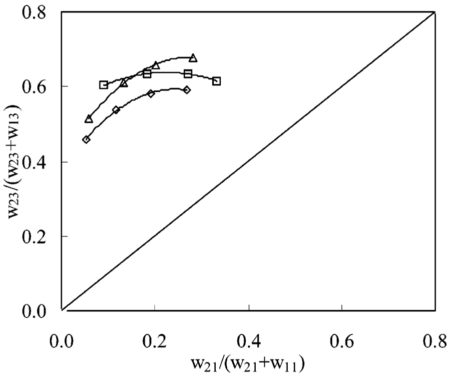

Figure 7. Selectivity diagram of the water (1) + acetic acid (2) + dibasic ester (3) ternary systems at 298.15 K: ◇, diethyl succinate; □, diethyl glutarate; △, diethyl adipate.

where n is the number of tie-lines, $w_{i,\mathrm{exp}}$ is the experimental mass fraction, $w_{i,\mathrm{calcd}}$ is the calculated mass fraction of component i, j refers to phases, and $k = 1, 2, 3, 4, ... n$ (tie-lines). The UNIFAC method correlated the experimental data for the systems with diethyl succinate, diethyl glutarate, and diethyl adipate at 298.15 K with rmsd values of 0.0310, 0.0390, and 0.0202, respectively.

Selectivity diagrams on a solvent-free basis are obtained by plotting $w_{23}/(w_{23} + w_{13})$ versus $w_{21}/(w_{21} + w_{11})$ for each ester in Figure 7. The selectivities of diethyl succinate and diethyl adipate were found to be similar in slopes, but the selectivity of diethyl adipate has hardly changed.

Conclusions

The LLE data for the ternary systems of (water + acetic acid + diethyl succinate), (water + acetic acid + diethyl glutarate), and (water + acetic acid + diethyl adipate) at 298.15 K are reported. The LLE data were also predicted by the UNIFAC method, which was in agreement with the experimental data qualitatively but not quantitatively. It is concluded that the dibasic esters used in this study may serve as suitable solvents to extract acetic acid from its dilute aqueous solutions since they show very little solubility in water. The solubility of water in dibasic esters decreases with increasing carbon chain length, which affects the solubility of water in dibasic esters negatively. It is apparent from the distribution and selectivity data (Table 4) that the separation of acetic acid from water by extraction with dibasic esters is feasible. Another noteworthy observation is that the complete break of conjugate phases was not hindered by density, viscosity, and/or interfacial tension related phenomena during the settling process.

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