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Liquid−Liquid Equilibria of Water + Acetic Acid + Dimethyl Glutarate Ternary System

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Liquid−liquid equilibrium (LLE) data of water + acetic acid + dimethyl glutarate were measured at T = (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. UNIFAC and modified UNIFAC models were used to predict the phase equilibrium data in the ternary system. Distribution coefficients and separation factors were evaluated for the immiscibility region.

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.[2−4]

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 that is used to separate the acetic acid from aqueous solutions, and in this respect, many solvents have been tried to improve recovery efficiency.[5−11]

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 and have low cost, low toxicity, great stability, and rather high boiling temperatures T = (463 to 573) K, while their viscosity and density are close to those of water.[12−15]

The real behavior of 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.[16] A special UNIFAC version for the prediction of liquid−liquid equilibria was published by Magnussen et al.[17] 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. The mole fractions x_i^{E} and x_i^{R} of LLE phases can be calculated using the following equation:

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

where E is the extract (solvent) phase, R is the raffinate (aqueous) phase, and γ is the activity coefficient of the component i.

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 reached 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.[18−22] 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.[21]

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 glutarate ternary system, for which no such data have previously been published.

Experimental Section

Materials. Acetic acid and dimethyl glutarate were purchased from Merck Company and were both received with a quoted purity of 99.8 % and >99 %, 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 $2 \cdot 10^{-3}$ and $4 \cdot 10^{-4}$ mass fractions, respectively. Distilled water was used throughout all experiments. Refractive indices were measured with Abbé−Hilger refractometer; its stated accuracy is $\pm\ 5 \cdot 10^{-4}$. 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 the literature.[23]

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Table 1. Densities (ρ), Refractive Indices (n_D), and Boiling Temperatures (T_b) of the Pure Components[23]

	ρ (298.2 K)/kg·m^{-3}		n_D (298.2 K)		T_b (101325 Pa)/K	
component	exp	lit	exp	lit	exp	lit
water	997.08	997.0	1.3324	1.3325	373.2	373.15
acetic acid	1047.22	1044.6	1.3719^a	1.3720^a	391.2	391.05
dimethyl glutarate	1087.74^a	1087.6^a	1.4242	1.4242	487.2	487.15

^{a} Indicate that the temperature was at 293.2 K.

Table 2. Experimental Tie Line Data for Water (1) + Acetic Acid (2) + Dimethyl Glutarate (3) Ternary System at Each Temperature

water-rich phase			solvent-rich phase		
x_1	x_2	x_3	x_1	x_2	x_3
		T = 298.2 K			
0.9803	0.0123	0.0074	0.2978	0.0509	0.6513
0.9678	0.0229	0.0093	0.3785	0.0904	0.5310
0.9560	0.0335	0.0104	0.4545	0.1197	0.4258
0.9432	0.0437	0.0131	0.5268	0.1346	0.3386
0.9279	0.0548	0.0173	0.6248	0.1407	0.2345
		T = 308.2 K			
0.9794	0.0127	0.0080	0.3511	0.0447	0.6042
0.9660	0.0241	0.0099	0.4017	0.0858	0.5126
0.9536	0.0350	0.0114	0.4586	0.1134	0.4281
0.9327	0.0513	0.0160	0.5284	0.1306	0.3409
0.9084	0.0671	0.0245	0.6065	0.1403	0.2532
		T = 318.2 K			
0.9803	0.0116	0.0081	0.4071	0.0437	0.5492
0.9667	0.0234	0.0099	0.3973	0.0871	0.5155
0.9525	0.0355	0.0119	0.4994	0.1104	0.3901
0.9290	0.0521	0.0189	0.5718	0.1271	0.3012
0.8861	0.0755	0.0384	0.6530	0.1347	0.2123

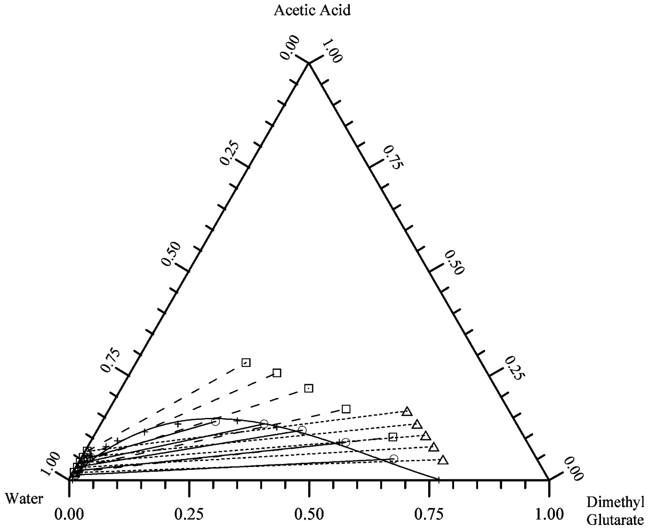

Figure 1. Ternary diagram for LLE of water (1) + acetic acid (2) + dimethyl glutarate (3) at 298.2 K as mole fraction. − + −, experimental binodal curve; − ○ −, experimental tie lines; − − □ − −, UNIFAC tie lines; --△--, modified UNIFAC tie lines.

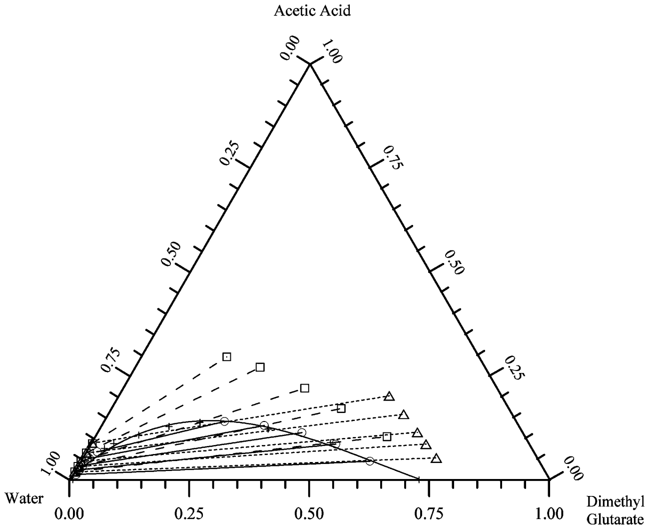

Figure 2. Ternary diagram for LLE of water (1) + acetic acid (2) + dimethyl glutarate (3) at 308.2 K as mole fraction. − + −, experimental binodal curve; − ○ −, experimental tie lines; − − □ − −, UNIFAC tie lines; --△--, modified UNIFAC tie lines.

Experimental Procedure. The binodal curve for water + acetic acid + dimethyl glutarate ternary system was determined by cloud-point method.[14] 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 ± 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 observing the transition from a homogeneous to a heterogeneous mixture.

The mutual solubilities of water + dimethyl glutarate 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 platinum resistance thermometer of Pt-100 type with a precision of ± 0.1 K controlled by PID controller. All mixtures were prepared by weighing with a Mettler scale accurate within $\pm\ 10^{-7}$ kg. The solvent was added by a microburet (Metrohm) with an accuracy of $\pm\ 3\cdot10^{-9}$ m^3.

Tie line data were obtained by preparing water + acetic acid + dimethyl glutarate 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 6 h. After the complete separation of the phases, samples were carefully taken from each phase and analyzed to obtain the tie lines.

Analysis. The liquid samples were analyzed by a gas chromatograph (Hewlett-Packard GC, model 6890 series) directly connected to a ChemStation (HP G2070 AA) and equipped with a thermal conductivity detector (TCD) for the quantitative determination of water, acetic acid, and dimethyl glutarate. A 15 m long HP-Plot Q column (320 μm diameter with a 20 μm film thickness) was used with a temperature-programmed analysis. The oven temperature was fixed at 523 K. The detector temperature was kept at 523 K, while injection-port temperature was held at 473 K. The flow rate of carrier gas, nitrogen, was kept 6 mL·min.$^{-1}$ Samples with known compositions were used to calibrate the instrument in the composition range of interest.

Results and Discussion

The experimental tie line data of water + acetic acid + dimethyl glutarate ternary system at T = (298.2, 308.2, and 318.2) K are given in Table 2. The experimental binodal curve and experimental and predicted tie lines at each temperature were shown in Figures 1 to 3. As it can be seen in Figures 1 to 3, it was found that dimethyl

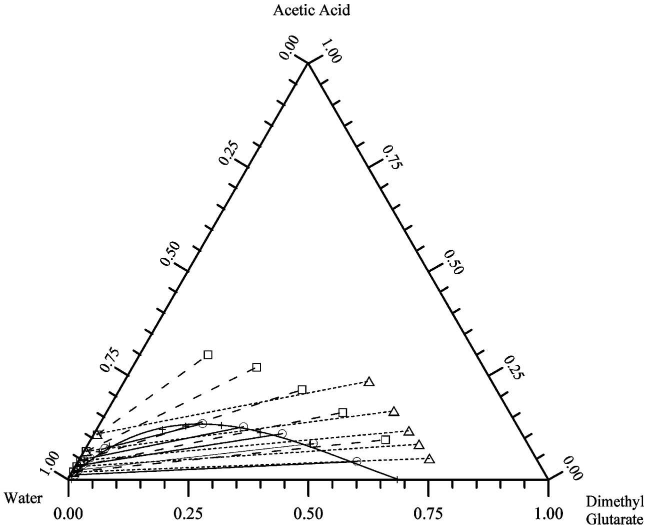

Figure 3. Ternary diagram for LLE of water (1) + acetic acid (2) + dimethyl glutarate (3) at 318.2 K as mole fraction. − + −, experimental binodal curve; − ○ −, experimental tie lines; − − □ − −, UNIFAC tie lines; --△--, modified UNIFAC tie lines.

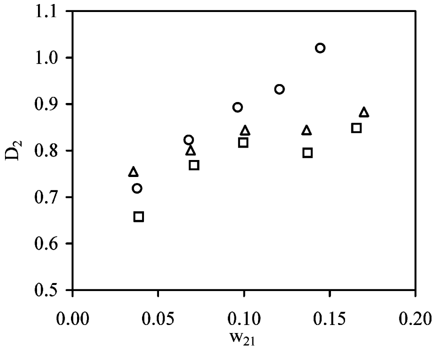

Figure 4. Distribution coefficient (D_2) of acetic acid as a function of the mass fraction, w_{21} of acetic acid in water-rich phase. T = ○, 298.2 K; □, 308.2 K; △, 318.2 K.

Table 3. Distribution Coefficients (D_i) of Water (1) + Acetic Acid (2) and Separation Factors (S)

D_1	D_2	S	D_1	D_2	S	D_1	D_2	S
T = 298.2 K			T = 308.2 K			T = 318.2 K		
0.0528	0.7188	13.62	0.0667	0.6580	9.86	0.0833	0.7549	9.06
0.0816	0.8230	10.08	0.0899	0.7687	8.55	0.0883	0.8009	9.07
0.1190	0.8930	7.51	0.1214	0.8173	6.73	0.1424	0.8439	5.93
0.1690	0.9321	5.52	0.1768	0.7950	4.50	0.2130	0.8447	3.97
0.2678	1.0208	3.81	0.2711	0.8485	3.13	0.3647	0.8835	2.42

glutarate was little soluble in water and water was also little soluble in dimethyl glutarate (on average 5 % 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 separation factor and distribution coefficient.[24] 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 Figure 4.

The effectiveness of extraction of acetic acid by dimethyl glutarate is given by its separation factor (S), which is a measure of dimethyl glutarate to separate acetic acid from water. This quantity is found to be greater than 1 (separating factor varying between 2.42 and 13.62) reported here, which means that the extraction of acetic acid by dimethyl glutarate is possible.

Tie Line Correlation. The reliability of experimentally measured tie line data can be ascertained by applying the following Othmer−Tobias correlation equation:[25]

$$\ln [(1 - w_{33})/w_{33}] = a + b \ln[(1 - w_{11})/w_{11}] \qquad (2)$$

where w_{11} is the mass fraction of water (1) in the water-rich phase; w_{33} is the mass fraction of dimethyl glutarate (3) in the solvent-rich phase; a and b are constant and slope of the eq 2, respectively.

The linearity of the plot indicates the degree of consistency of the data. Othmer−Tobias plot is shown in Figure 5 for only at 298.2 K. The parameters of Othmer−Tobias correlations are given in Table 4. The approach of the correlation factor (r^2) to 1 indicates the degree of consistency of related data.

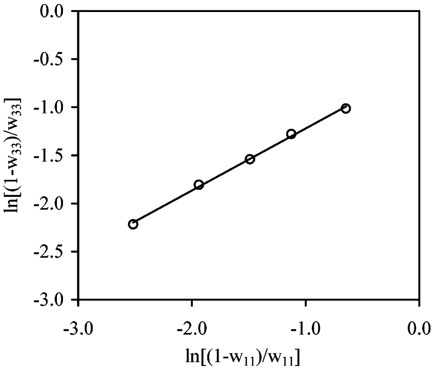

Figure 5. Othmer−Tobias plot of water (1) + acetic acid (2) + dimethyl glutarate (3) system at 298.2 K.

Table 4. Constants of Othmer−Tobias Equation for the Ternary System

T/K	a	b	r^2
298.2	0.6438	−0.5781	0.9979
308.2	1.0502	0.1393	0.9946
318.2	1.0776	0.1125	0.9931

Table 5. UNIFAC Group Interaction Parameters for Prediction[17]

	CH_2	CH_3COO	CH_3	COOH	H_2O	R_k	Q_k
CH_2	0	−320.1	0	1744	342.4	0.6744	0.54
CH_3COO	972.4	0	972.4	−117.6	−6.32	1.9031	1.728
CH_3	0	−320.1	0	1744	342.4	0.9011	0.848
COOH	139.4	1417	139.4	0	−465.7	1.3013	1.224
H_2O	1300	385.9	1300	652.3	0	0.92	1.40

Table 6. Modified UNIFAC(Dortmund) R_k and Q_k Parameters[21]

group	main group number	R_k	Q_k
CH_2	1	0.6325	0.7081
CH_3COO	11	1.27	1.6286
CH_3	1	0.6325	1.0608
COOH	20	0.8	0.9215
H_2O	7	1.7334	2.4561

Theoretical Methods. The equilibrium data of the ternary system were predicted by UNIFAC and modified UNIFAC methods using the interaction parameters between CH_3, CH_2, COOH, CH_3COO, and H_2O functional groups obtained by Magnussen et al.[17] and Gmehling et al.[21] The values of the UNIFAC and modified UNIFAC parameters for LLE predictions are summarized in Tables 5 to 7. As shown in Figures 1 to 3, LLE relations predicted by the UNIFAC and modified UNIFAC methods do not adequately fit to the experimental LLE data. The discrepancy between the experimental and predicted solubilities changed slightly with temperature. UNIFAC model was predicted LLE data better than modified UNIFAC model as shown in Figures 1 to 3.

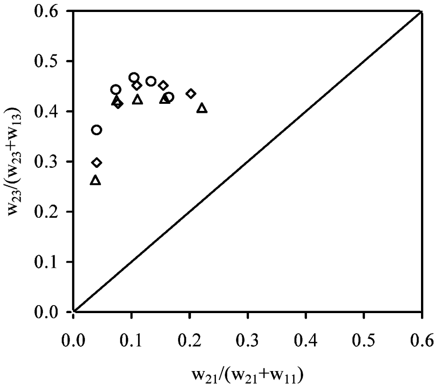

Figure 6. Selectivity diagram at each temperature (free-solvent basis), *T* = ○, 298.2 K; □, 308.2 K; △, 318.2 K.

Table 7. Modified UNIFAC (Dortmund) Group Interaction Parameters for Prediction[21]

n	*m*	a_{nm}/K	b_{nm}	c_{nm}/K^{-1}	a_{mn}/K	b_{mn}	c_{mn}/K^{-1}
1	7	1391.3	−3.6156	$0.1144 \cdot 10^{-2}$	−17.253	0.8389	$0.9021 \cdot 10^{-3}$
1	11	98.656	1.9294	$-0.3133 \cdot 10^{-2}$	632.22	−3.3912	$0.3928 \cdot 10^{-2}$
1	20	1182.2	−3.2647	$0.9198 \cdot 10^{-2}$	2017.7	−9.0933	$0.1024 \cdot 10^{-1}$
7	11	−675.50	3.6090	0.0	322.3	−1.3050	0.0
11	20	62.031	1.0567	0.0	59.594	−0.7120	0.0
20	7	624.97	−4.6878	$0.5237 \cdot 10^{-2}$	−1795.2	12.708	$-0.1546 \cdot 10^{-1}$

Selectivity diagrams on a solvent-free basis are plotted at each temperature in Figure 6. The effect of temperature change on the selectivity values was found to be insignificant.

Conclusions

The temperature has practically no effect on the size of immiscibility region at the temperatures considered. The tie lines in Figures 1 to 3 show that acetic acid is more readily soluble in water-rich phase than in the solvent-rich phase. Separation factors are decreased by the increase of acetic acid concentration, as can be seen from Table 4. It was found that the UNIFAC and modified UNIFAC methods do not fitted satisfactorily to the experimental data, but the UNIFAC model fitted to the experimental data better than modified UNIFAC model.

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