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Liquid−Liquid Equilibria for Ternary Systems of Water + Formic Acid + Dibasic Esters

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Liquid−liquid equilibrium (LLE) data including solubility curves and tie-line compositions were measured for mixtures of water (1) + formic acid (2) + dimethyl succinate or dimethyl glutarate or dimethyl adipate (3) at $T = 298.2$ K and atmospheric pressure, $p = (101.3 \pm 0.7)$ kPa. The relative mutual solubility of the formic acid is higher in the aqueous phase than in the dibasic ester phases. 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 and modified UNIFAC methods. Distribution coefficients and separation factors were evaluated for the immiscibility region.

Introduction

Formic acid is an essential chemical industry material. It is widely used in the textile industry, tanning industry, rubber-processing industry, and pharmaceutical industry. In addition, formic acid is used as a preservative and antibacterial agent in livestock feed, and it is used as a miticide against the Varroa mite in the beekeeping industry.[1,2]

In the industrial synthesis of formic acid, for example, by the reaction of methanol and carbon monoxide and hydrolysis of the methyl formate formed, aqueous solutions containing (20 to 50) % acid are always obtained. When concentrated by distillation, these aqueous solutions give an azeotrope, so that the formic acid cannot be obtained directly in an anhydrous form. Distillation under pressure, extractive distillation, and azeotropic distillation are used to concentrate the solutions. These processes are of high-energy consumption. To reduce the cost of concentrating acid solutions, extraction can be applied as an alternative.[3] The extractions of formic acid equilibria have been studied by some researchers.[4−7]

Formic acid is also found in natural gas and crude oil fields. Thus, knowledge of the liquid−liquid phase behavior of formic acid, in general, is of great importance to the chemical and petrochemical industries. A significant amount of formic acid is also produced as a byproduct in the manufacture of other chemicals, especially acetic acid.[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 environmentally friendly and have low cost, low toxicity, great stability, and rather high boiling temperatures, while their viscosity and density is close to those of water. The dibasic esters are also used as novel solvents in separation techniques.[9] First, Uusi-Penttilä et al.[10] examined LLE data of different ternary systems. Recently, İnce and Kırbaşlar[11−17] have examined LLE data of six different ternary systems.

Table 1. Physical Properties of the Pure Components at $T = 293.2$ K and $p = 101.3$ kPa[24]

	$\rho/(\mathrm{kg \cdot m^{-3}})$		n_D		T_b/K	
	density		refractive index		boiling point	
component	exptl	lit.	exptl	lit.	exptl	lit.
water	999.90	998.23	1.33240	1.3330	373.2	373.25
formic acid	1220.04	1220.0	1.37144	1.3714	374.4	374.2
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.

The LLE data were predicted by the UNIFAC (universal functional group activity coefficient) method.[18] The UNIFAC method is used for predicting the activity coefficients, γ_i. In LLE, the activities of the components i on both phases are equal, and the mole fractions x_i^E, x_i^R of conjugate phases can be calculated by 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 the extract and raffinate phases. 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 are obtained from a table.[19]

Nevertheless, the modified UNIFAC model was proposed several years ago.[20] It shows various advantages when compared with the group contribution methods, such as UNIFAC or ASOG. These advantages were attained by using a modified combinatorial part and a large database to fit temperature-dependent group interaction parameters simultaneously to vapor−liquid equilibrium and liquid−liquid equilibrium.[21−23] The values of the modified UNIFAC parameters for LLE predictions are obtained from a table.[20]

This study is part of a research program on the recovery of carboxylic acids from dilute aqueous solutions using organic solvents. The objective of this work is to recover formic acid from dilute aqueous solutions by using environmentally friendly solvents with a high-boiling point. In this paper, LLE results were reported for the three ternary systems water + formic acid + dimethyl succinate, water + formic acid + dimethyl glutarate,

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Table 2. Experimental Solubility Curve Data for Water + Formic Acid + Dibasic Ester Ternary Systems at T = 298.2 K

w_1	w_2	w_3
Water (1) + Formic Acid (2) + Dimethyl Succinate (3)		
0.8763	0.0000	0.1237
0.6916	0.0959	0.2125
0.4718	0.1195	0.4087
0.3292	0.1105	0.5603
0.4140	0.1183	0.4677
0.2263	0.0932	0.6805
0.0557	0.0000	0.9443
Water (1) + Formic Acid (2) + Dimethyl Glutarate (3)		
0.9373	0.0000	0.0627
0.7827	0.1092	0.1081
0.6335	0.1678	0.1987
0.5256	0.1767	0.2977
0.3810	0.1671	0.4519
0.2730	0.1479	0.5791
0.1619	0.1013	0.7368
0.0489	0.0000	0.9511
Water (1) + Formic Acid (2) + Dimethyl Adipate (3)		
0.9718	0.0000	0.0282
0.8314	0.1129	0.0557
0.7363	0.1830	0.0807
0.6581	0.2193	0.1226
0.5482	0.2393	0.2125
0.2988	0.2003	0.5009
0.4116	0.2325	0.3559
0.2503	0.1892	0.5605
0.1998	0.1621	0.6381
0.1222	0.1057	0.7721
0.0321	0.0000	0.9679

Table 3. Experimental Tie-Line Data of Water + Formic Acid + Dibasic Ester Ternary Systems at T = 298.2 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) + Formic Acid (2) + Dimethyl Succinate (3)					
0.7540	0.0664	0.1796	0.1292	0.0458	0.8250
0.7340	0.0773	0.1887	0.1454	0.0546	0.8000
0.6550	0.1073	0.2377	0.1990	0.0810	0.7200
Water (1) + Formic Acid (2) + Dimethyl Glutarate (3)					
0.8550	0.0574	0.0876	0.0601	0.0399	0.9000
0.8200	0.0815	0.0985	0.0671	0.0489	0.8840
0.7290	0.1317	0.1393	0.0966	0.0874	0.8160
0.6400	0.1641	0.1959	0.1204	0.1216	0.7580
Water (1) + Formic Acid (2) + Dimethyl Adipate (3)					
0.9030	0.0559	0.0411	0.0603	0.0297	0.9100
0.8000	0.1358	0.0642	0.0919	0.0731	0.8350
0.7250	0.1842	0.0908	0.1274	0.1206	0.7520
0.6430	0.2236	0.1334	0.1688	0.1492	0.6820

and water + formic acid + dimethyl adipate at T = 298.2 K, for which no such data have previously been published.

Experimental

Materials. Formic acid, dimethyl succinate, dimethyl glutarate, and dimethyl adipate were purchased from Merck and were of (> 0.99, 0.98, 0.99, and 0.99) mass fraction purity, respectively. The chemicals were used without further purification. GC analysis did not detect any appreciable peaks of impurities. Distilled water was used throughout all experiments. Refractive indices were measured with an Anton Paar refractometer (RXA 170 model); its stated accuracy is $\pm\ 5 \cdot 10^{-5}$. Densities were measured with an Anton Paar densimeter (DMA 4500 model). Boiling point measurements were obtained by using a Fischer boiling point apparatus. The estimated uncertainties in the density and boiling point measurements were $\pm\ 1 \cdot 10^{-2}$ kg·m^{-3} and ± 0.1 K, respectively. The measured physical properties are listed in Table 1, along with the literature values.[24]

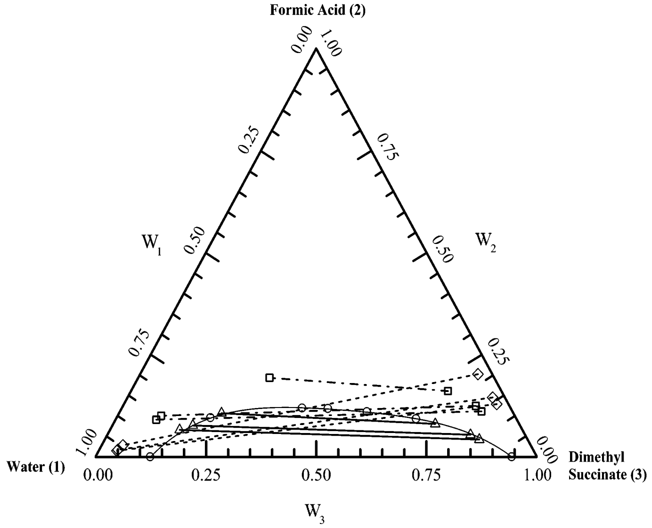

Figure 1. Ternary diagram for LLE of water (1) + formic acid (2) + dimethyl succinate (3) at T = 298.2 K. ○, experimental solubility curve; △, experimental tie-lines; ◇, calculated (UNIFAC) tie-lines; □, calculated (modified UNIFAC) tie-lines.

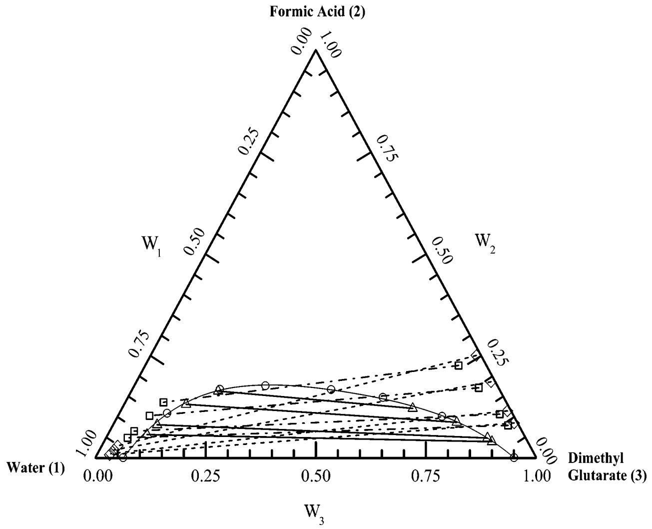

Figure 2. Ternary diagram for LLE of water (1) + formic acid (2) + dimethyl glutarate (3) at T = 298.2 K. ○, experimental solubility curve; △, experimental tie-lines; ◇, calculated (UNIFAC) tie-lines; □, calculated (modified UNIFAC) tie-lines.

Experimental Procedures. The solubility curves were determined by the cloud point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions.[12] 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 titrating heterogeneous mixtures of water + dibasic ester with formic acid until the turbidity had disappeared. For the water-side and solvent-side, binary mixtures of either water + formic acid or dibasic ester + formic acid were titrated against the third component until the transition from homogeneity to heterogeneity was observed. All mixtures were prepared by weighing with a Sartorious scale (CP 224S model) accurate to within $\pm\ 1 \cdot 10^{-7}$ kg.

Mutual solubility values of the water + dibasic ester 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

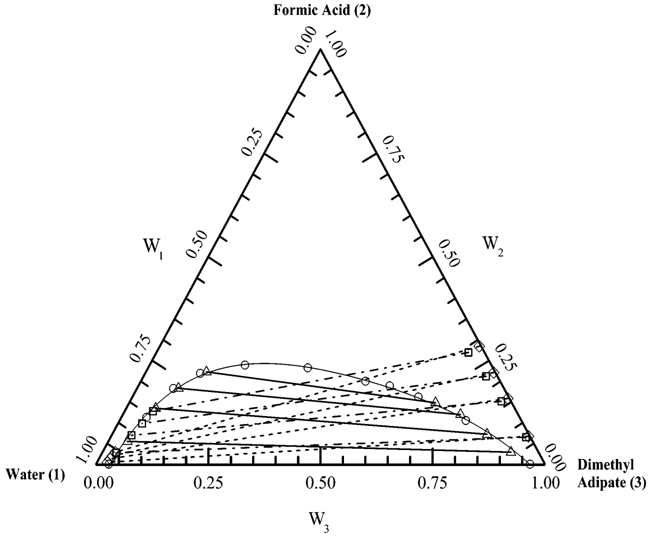

Figure 3. Ternary diagram for LLE of water (1) + formic acid (2) + dimethyl adipate (3) at $T = 298.2$ K. ○, experimental solubility curve; △, experimental tie-lines; ◇, calculated (UNIFAC) tie-lines; □, calculated (modified UNIFAC) tie-lines.

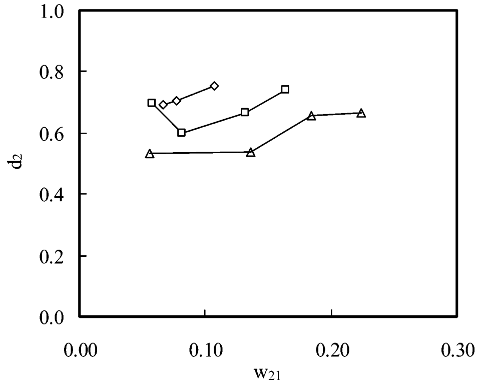

Figure 4. Distribution coefficient of formic acid, d_2, plotted against the mass fraction of formic acid in the aqueous phase, w_{21}. ◇, dimethyl succinate; □, dimethyl glutarate; △, dimethyl adipate.

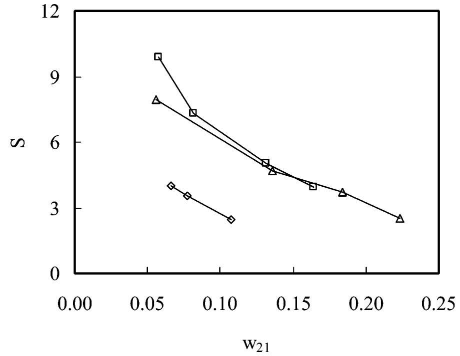

Figure 5. Separation factor, S, plotted against the mass fraction of formic acid in the aqueous phase, w_{21}. ◇, dimethyl succinate; □, dimethyl glutarate; △, dimethyl adipate.

of the method depends on the precision of the Metrohm microburette, with an accuracy of $\pm 3 \cdot 10^{-9}$ 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 by waiting for about 5 min in the transition point and observing the heterogeneity. All visual experiments were repeated at least three times to acquire high accuracy.

End-point determinations of the tie-lines were carried out through the independent analysis of the conjugate phases that were regarded as being in equilibrium. Mixtures of known masses of water, formic acid, and dibasic ester lying within the immiscibility region 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 raffinate and extract layers.

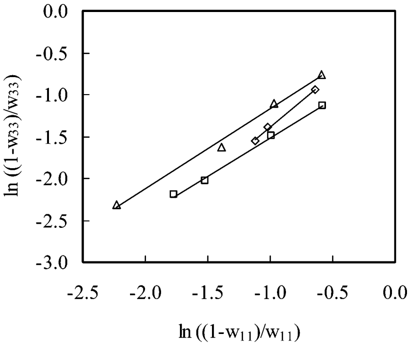

Figure 6. Othmer−Tobias plots of the water (1) + formic acid (2) + dibasic ester (3) ternary systems at $T = 298.2$ K. ◇, dimethyl succinate; □, dimethyl glutarate; △, dimethyl adipate.

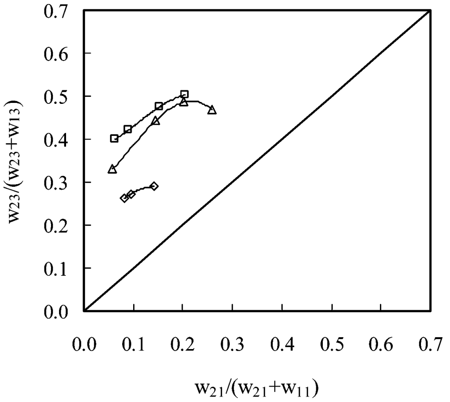

Figure 7. Selectivity diagram of the water (1) + formic acid (2) + dibasic ester (3) ternary systems at $T = 298.2$ K. ◇, dimethyl succinate; □, dimethyl glutarate; △, dimethyl adipate.

Table 4. UNIFAC R_k and Q_k Parameters[19]

group	main group no.	R_k	Q_k
CH_2	1	0.6744	0.54
CH_3COO	14	1.9031	1.728
HCOOH	13	1.528	1.532
H_2O	8	0.92	1.4

Table 5. UNIFAC Group Interaction Parameters for Prediction[19]

M	n	a_{mn}, K	a_{nm}, K
CH_2	CH_3COO	−320.1	972.4
CH_3COO	HCOOH	−117.6	1417
HCOOH	CH_2	139.4	1744
H_2O	CH_2	1300	342.4
H_2O	CH_3COO	385.9	−6.32
H_2O	HCOOH	652.3	−465.7

Table 6. Modified UNIFAC (Dortmund) R_k and Q_k Parameters[20]

group	main group no.	R_k	Q_k
CH_2	1	0.6325	0.7081
CH_3COO	11	1.27	1.6286
HCOOH	44	0.8	1.2742
H_2O	7	1.7334	2.4561

Analysis. The liquid samples were analyzed by a gas chromatograph HP 6890 model, directly connected to a ChemStation (HP G2070 AA) and equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) for the quantitative determination of water, formic acid, and dibasic esters. An HP-Plot Q column (15 m × 0.32 mm × 0.02 mm)

Table 7. Modified UNIFAC (Dortmund) Group Interaction Parameters for Prediction[20]

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	44	1935.7	0	0	−21.23	0	0
7	11	−675.5	3.609	0	322.3	−1.305	0
11	44	745.4	0	0	−447.04	0	0
44	7	594.45	−2.2535	0	−804.28	2.828	0

Table 8. Root-Mean-Square Deviations (rmsd's) of the UNIFAC and Modified UNIFAC Models for Prediction of Ternary Systems at $T = 298.2$ K

system	UNIFAC	modified UNIFAC
water + formic acid + dimethyl succinate	0.3623	0.2587
water + formic acid + dimethyl glutarate	0.3558	0.1987
water + formic acid + dimethyl adipate	0.3994	0.2260

for TCD and an HP-Innowax polyethylene glycol capillary column (30 m × 0.32 mm × 0.05 mm) for FID were utilized to separate water and formic acid and dibasic esters of samples with a temperature-programmed analysis. Column temperature was held at $T = 293.2$ K (3 min) and rose to $T = 503.2$ K (10 min) at a 30 $K \cdot min^{-1}$ ramp rate and injection mode (split ratio 100:1; detectors, TCD and FID; injector temperature $T = 543.2$ K and detector temperature $T = 473.2$ K). Nitrogen was used as a carrier gas (8 $cm^3 \cdot min^{-1}$) and with an injected volume of 0.0003 cm^3 (0.3 μL) of the liquid sample. Concentration determinations were accurate to ± 0.001 mass fraction.

Results and Discussion

The compositions of mixtures on the binodal curve, including the mutual binary solubility of water and dibasic esters at $T = 298.2$ K, are given in Table 2. 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 ith component in the aqueous and solvent phases, respectively. The binodal 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 dimethyl succinate < dimethyl glutarate < dimethyl adipate. This explains that the solubility of water in dibasic esters decreases due to the increase of carbon chain length of the dibasic esters. The slopes of the tie-lines obtained in this work show that formic acid is more soluble in water than in dibasic esters because of its low molecular weight and high affinity for water.

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

$$d_i = w_{i3}/w_{i1} \qquad (2)$$

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

where w_{23} and w_{21} are the mass fractions of formic acid in solvent-rich and water-rich phases, respectively, and 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 Figures 4 to 5. The effectiveness of extraction of formic acid through solvent is given by its separation factor, which is an indication of the ability of the solvent to separate formic acid from water. This quantity is found to be greater than 1 (separation factors varying between 2.48 and 9.89) for the systems reported here, which means that extraction of formic acid by dibasic esters is possible. The separation factors and distribution coefficients are not constant over the complete two-phase region.

Tie-Line Correlation. The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer−Tobias correlation for each solvent[25]

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

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; and a and b are constants of eq 4.

Othmer−Tobias plots were constructed presenting $\ln[(1 - w_{33})/w_{33}]$ against $\ln[(1 - w_{11})/w_{11}]$. The correlations are shown in Figure 6 at $T = 298.2$ K. The linearity of correlation indicates the degree of consistency of the related data.

Theoretical Methods. The equilibrium data of the ternary system are predicted by UNIFAC and modified UNIFAC methods using the interaction parameters of CH_2, CH_3COO, HCOOH, and H_2O functional groups obtained by Magnussen et al.[19] and Gmehling et al.[20] The values of the UNIFAC and modified UNIFAC parameters for LLE predictions are summarized in Tables 4 to 7. The calculated tie-lines are presented in Figures 1 to 3.

The root-mean-square deviations (rmsd's) are calculated from the difference between the experimental data and the predictions of the UNIFAC and modified UNIFAC methods for each ternary system according to the following equation

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

where n is the number of tie-lines; $w_{i,\text{exptl}}$ is the experimental mass fraction; $w_{i,\text{calcd}}$ is the calculated mass fraction of component i; j refers to phases; and $k = 1, 2, 3, \ldots n$ (tie-lines). The rmsd values of the UNIFAC and modified UNIFAC method are given in Table 8.

Selectivity diagrams on a solvent-free basis are obtained by plotting $w_{23}/(w_{23} + w_{13})$ against $w_{21}/(w_{21} + w_{11})$ for each dibasic ester in Figure 7. The selectivity of the dibasic esters increases in the order dimethyl succinate < dimethyl adipate < dimethyl glutarate.

Conclusions

The LLE data for the ternary systems of water + formic acid + dimethyl succinate, water + formic acid + dimethyl glutarate, and water + formic acid + dimethyl adipate at $T = 298.2$ K are reported. The LLE data are also predicted by UNIFAC and modified UNIFAC methods, which have not fitted the experimental data adequately. It is concluded that the dibasic esters used in this study may serve as suitable solvents to extract formic acid from its dilute aqueous solutions because they show slight solubility in water. The solubility of water in dibasic esters decreases with an increase of carbon chain length. It is shown that formic acid is more soluble in the water phase than in the dibasic ester phase. 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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