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Phase Equilibrium of Water + Formic Acid + Acetic Acid + Solvent (Amyl Acetate or Diisobutyl Ketone or Diisopropyl Ether) Quaternary Liquid Systems

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Liquid−liquid equilibrium data of water + formic acid + acetic acid + solvent (amyl acetate, diisobutyl ketone, and diisopropyl ether) quaternary systems were measured at 298.15 K and atmospheric pressure. Complete phase diagrams were obtained by determining solubility curves and tie-lines. A comparison of the extracting capabilities of the solvents was made with respect to distribution coefficients, separation factors, and solvent-free selectivity bases. Reliability of the data was ascertained from Othmer−Tobias plots. The tie-lines were also predicted using the UNIFAC model. It is concluded that the used solvents can be treated as suitable separating agents for dilute aqueous formic and acetic acid mixtures.

Introduction

More than 20 % of the industrial production of organic intermediates, such as methacrylic acid, phthalic acid, acrylonitrile, and cyclohexanone, is carried out via heterogeneous partial oxidation of hydrocarbons. In addition to the products of total oxidation—carbon dioxide and water—carboxylic acids, and in particular those which are relatively resistant to oxidation, such as formic acid, acetic acid, and adipic acid, are obtained as unwanted byproducts. After the main product has been isolated, these very dilute acids are present in the process effluent (content of carboxylic acids below 10 %).[1]

Recovery of formic and acetic acid from aqueous solutions with other separation processes such as extractive and azeotropic distillation is high-energy consumption.[2] Formic and acetic acid are also found in gas and oil fields. Thus, knowledge of the phase behavior of carboxylic acids, in general, is of great importance to the chemical and petrochemical industries.[3]

The design of liquid−liquid extraction equipment becomes complex when the feed is a mixture of three components or when a mixture of two solvents is used because corresponding quaternary liquid−liquid equilibria (LLE) have to be considered. Although liquid extraction of formic and acetic acids from aqueous solutions with various solvents has been performed and reported by several researchers on a ternary basis,[4–20] the quaternary LLE data on related acids is scarce in the literature.[21–27] In this study, quaternary LLE data of water + formic acid + acetic acid + solvent (amyl acetate, diisobutyl ketone, and diisopropyl ether) systems were determined at 298.15 K and atmospheric pressure, because no such data are available in the literature. Complete phase diagrams were obtained by solubility and tie-line measurements simultaneously for each solvent. The tie-lines predicted using the UNIFAC[28] were compared with the experimental data.

Table 1. Refractive Indexes n_D and Densities ρ at 20 °C and Boiling Points t_b at 101.33 kPa of Chemicals[29]

	n_D		$\rho/(g \cdot cm^{-3})$		$t_b/°C$	
compound	meas'd.	lit.	meas'd.	lit.	meas'd.	lit.
formic acid	1.3711	1.3714	1.2185	1.220	100.9	101.0
acetic acid	1.3721	1.3720	1.0445[a]	1.0446[a]	117.7	117.9
amyl acetate	1.4025	1.4023	0.8759	0.8756	149.1	149.2
diisobutyl ketone	1.4118[b]	1.412[b]	0.8065	0.8062	169.6	169.4
diisopropyl ether	1.3863[a]	1.3865[a]	0.7190[a]	0.7192[a]	68.2	68.4

[a] At 25 °C. [b] At 21 °C.

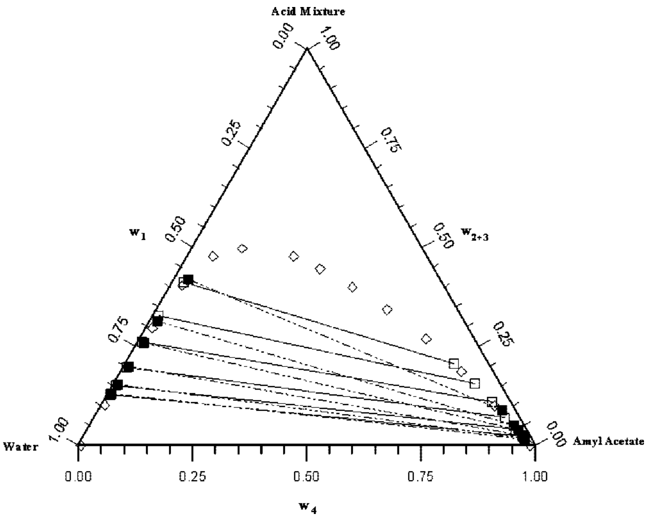

Figure 1. Phase equilibrium of the water (1) + acid mixture (2 + 3) + amyl acetate (4) system at 298.15 K: ◇, solubility data; □, experimental tie-line data; ■, UNIFAC tie-line data.

Experimental

Chemicals. Formic acid (≥ 99 %), acetic acid (100 %), amyl acetate (98 %), diisobutyl ketone (~75 % 2,6-dimethyl-4-heptanone + ~25 % 2,4-dimethyl-6-heptanone), and diisopropyl ether (≥ 99 %) were supplied by Merck and used without further purification. Deionized water was used during the experiments. The purity of the chemicals was checked on the basis of their refractive indexes and densities at (293.00 ± 0.20) K and their

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Table 2. Solubility Data for Water (1) + Formic Acid (2) + Acetic Acid (3) + Solvent (4) Quaternary Systems at 298.15 K

w_1	w_2	w_3	w_4
standard deviation = 0.029	Amyl Acetate		
0.9950	0.0000	0.0000	0.0050
0.8928	0.0509	0.0511	0.0052
0.7934	0.0989	0.0992	0.0085
0.6910	0.1482	0.1483	0.0125
0.5714	0.2016	0.2022	0.0248
0.4670	0.2388	0.2391	0.0551
0.3937	0.2486	0.2491	0.1086
0.2901	0.2389	0.2393	0.2317
0.2482	0.2234	0.2237	0.3047
0.2010	0.1996	0.1999	0.3995
0.1526	0.1716	0.1718	0.5040
0.1048	0.1344	0.1346	0.6262
0.0682	0.0932	0.0935	0.7451
0.0390	0.0505	0.0508	0.8597
0.0108	0.0000	0.0000	0.9892
standard deviation = 0.031	Diisobutyl Ketone		
0.9960	0.0000	0.0000	0.0040
0.9009	0.0460	0.0475	0.0056
0.8121	0.0893	0.0901	0.0085
0.7211	0.1343	0.1356	0.0090
0.6310	0.1785	0.1803	0.0102
0.5341	0.2260	0.2282	0.0117
0.4447	0.2651	0.2677	0.0225
0.3646	0.2886	0.2942	0.0526
0.2785	0.3082	0.3113	0.1020
0.1788	0.2855	0.2883	0.2474
0.1608	0.2701	0.2749	0.2942
0.1467	0.2556	0.2587	0.3390
0.1202	0.2216	0.2238	0.4344
0.0968	0.1872	0.1891	0.5269
0.0633	0.1391	0.1404	0.6572
0.0414	0.0962	0.0972	0.7652
0.0270	0.0533	0.0539	0.8658
0.0105	0.0000	0.0000	0.9895
standard deviation = 0.039	Diisopropyl Ether		
0.9717	0.0000	0.0000	0.0283
0.8732	0.0489	0.0493	0.0286
0.7956	0.0869	0.0877	0.0298
0.7234	0.1206	0.1219	0.0341
0.5711	0.1881	0.1900	0.0508
0.4347	0.2324	0.2347	0.0982
0.3509	0.2419	0.2443	0.1629
0.2374	0.2247	0.2270	0.3109
0.1813	0.2044	0.2065	0.4078
0.1316	0.1749	0.1767	0.5168
0.0877	0.1379	0.1393	0.6351
0.0619	0.1114	0.1126	0.7141
0.0331	0.0486	0.0497	0.8686
0.0056	0.0000	0.0000	0.9944

boiling points at (101.33 ± 0.27) kPa. Refractive indexes were measured with an Abbé-Hilger refractometer in ± 0.0005 accuracy. Densities were obtained with an Anton Paar (model DMA 4500) density meter. Boiling points were measured with a Fischer boiling point apparatus. Estimations of the uncertainties in density and boiling point measurements are ± 0.0001 $g\cdot cm^{-3}$ and ± 0.1 K, respectively. The physical properties measured are in good agreement with published values, and they are listed in Table 1 along with literature values[29] for comparison.

Apparatus and Procedure. Solubility data for the quaternary systems were determined by the cloud point method. The apparatus and experimental procedure were described in detail previously.[23]

The mutual solubilities of water and solvent were determined by applying a synthetic method. A known mass of first substance was introduced into the cell, and the other was added until a permanent heterogeneity had been observed. An automatic burette with an accuracy of ± 0.001 cm^3 was used.

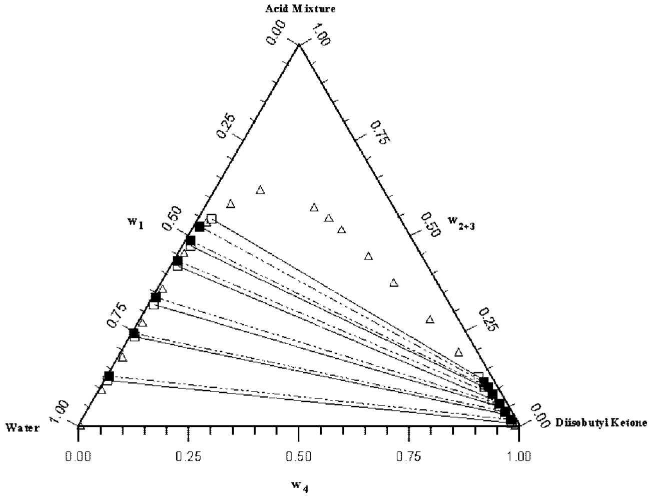

Figure 2. Phase equilibrium of the water (1) + acid mixture (2 + 3) + diisobutyl ketone (4) system at 298.15 K: Δ, solubility data; □, experimental tie-line data; ■, UNIFAC tie-line data.

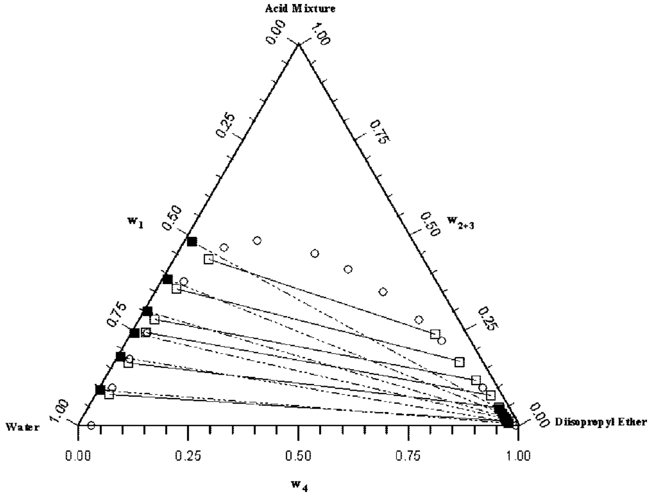

Figure 3. Phase equilibrium of the water (1) + acid mixture (2 + 3) + diisopropyl ether (4) system at 298.15 K: ○, solubility data; □, experimental tie-line data; ■, UNIFAC tie-line data.

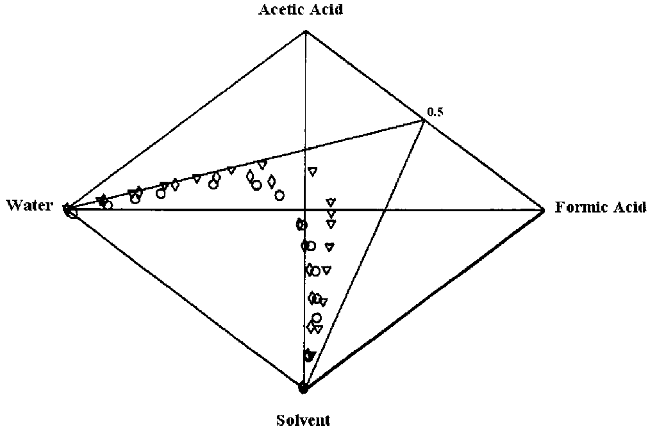

Figure 4. Tetrahedral representation of the solubility surface of the water (1) + formic acid (2) + acetic acid (3) + solvent (4) quaternary system: ◇, amyl acetate; Δ, diisobutyl ketone; ○, diisopropyl ether.

The tie-lines were obtained by preparing quaternary mixtures of known overall compositions lying within the two-phase region and after being shaken thoroughly at constant temperature. The acid mixture of formic acid and acetic acid, which consists of completely miscible components, was prepared in a 1:1 mass

Table 3. Tie-Line Compositions for Water (1) + Formic Acid (2) + Acetic Acid (3) + Solvent (4) Quaternary Systems at 298.15 K

overall composition				aqueous phase				solvent phase			
w_1	w_2	w_3	w_4	w_1	w_2	w_3	w_4	w_1	w_2	w_3	w_4
	standard deviation = 0.032							Amyl Acetate			
0.4806	0.0390	0.0394	0.4410	0.8661	0.0228	0.1063	0.0048	0.0148	0.0031	0.0205	0.9616
0.4585	0.0502	0.0505	0.4408	0.8431	0.0328	0.1189	0.0052	0.0239	0.0067	0.034	0.9354
0.4233	0.0681	0.0685	0.4401	0.7975	0.0420	0.1550	0.0055	0.0310	0.0111	0.0594	0.8985
0.3757	0.0920	0.0926	0.4397	0.7310	0.0560	0.2066	0.0064	0.0406	0.0177	0.0925	0.8492
0.3343	0.1147	0.1155	0.4355	0.6622	0.0692	0.2586	0.0100	0.0545	0.0246	0.1311	0.7898
0.2843	0.1489	0.1499	0.4169	0.5639	0.0850	0.3276	0.0235	0.0741	0.0319	0.1748	0.7192
	standard deviation = 0.036							Diisobutyl Ketone			
0.5237	0.0372	0.0374	0.4017	0.8736	0.0267	0.0957	0.0040	0.0119	0.0021	0.0080	0.9780
0.4403	0.0756	0.0762	0.4079	0.7557	0.0608	0.1760	0.0075	0.0186	0.0050	0.0267	0.9497
0.4121	0.1052	0.1059	0.3768	0.6693	0.0813	0.2405	0.0089	0.0197	0.0077	0.0449	0.9277
0.3286	0.1296	0.1306	0.4112	0.5665	0.1034	0.3176	0.0125	0.0252	0.0108	0.0612	0.9028
0.2993	0.1547	0.1558	0.3902	0.5088	0.1111	0.3645	0.0156	0.0275	0.0147	0.0887	0.8691
0.2308	0.1789	0.1801	0.4102	0.4256	0.1256	0.4193	0.0295	0.0286	0.0222	0.1085	0.8407
	standard deviation = 0.027							Diisopropyl Ether			
0.5665	0.0268	0.0269	0.3798	0.8901	0.015	0.0671	0.0278	0.0104	0.0021	0.0091	0.9784
0.4990	0.0615	0.0619	0.3776	0.8039	0.0326	0.1335	0.030	0.0224	0.0098	0.0411	0.9267
0.4564	0.0908	0.0914	0.3614	0.725	0.0575	0.1872	0.0303	0.0228	0.018	0.062	0.8972
0.4271	0.1069	0.1077	0.3583	0.6871	0.0653	0.2156	0.0320	0.0375	0.0202	0.1005	0.8418
0.3775	0.1404	0.1414	0.3407	0.5979	0.0793	0.2805	0.0423	0.0488	0.0371	0.1331	0.7810
0.3176	0.1795	0.1808	0.3221	0.486	0.0962	0.3428	0.0750	0.0709	0.0414	0.1987	0.6890

ratio. The mixture was allowed to reach equilibrium for 4 h at constant temperature and then left for 4 h to settle down into raffinate (aqueous) and extract (solvent) layers. The samples were carefully taken from each phase and analyzed.

The liquid samples were analyzed by gas chromatography (HP 6890), equipped with flame ionization (FI) and thermal conductivity (TC) detectors. A 50 m long SGE B1 column (0.32 mm i.d., 0.5 μm film thickness) was utilized to separate samples at tailorized oven programs. Column temperature was held at 343 K (1 min) and rose to 473 K by a 12 $\text{K}\cdot\text{min}^{-1}$ ramp rate. The detector temperature was kept at 473.15 K, while the injection port temperature was held at 523.15 K. Injections were performed on the split 70/1 mode. Nitrogen was used as a carrier at a rate of 2.6 $\text{cm}^3\cdot\text{min}^{-1}$. Ethanol was used as an internal standard. Injection volumes of the liquid samples were 0.3 μL. The compositions of water and formic acid were determined by means of a thermal conductivity detector (TCD). Acetic acid and solvent contents of samples were detected by a flame ionization detector (FID). The uncertainty of the mass fraction measurements for overall composition determination was ± 0.002.

Results and Discussion

The experimental solubility curve data and the experimental mutual solubilities for the water (1) + formic acid (2) + acetic acid (3) + solvent (4) quaternary systems are reported in Table 2. The tie-line compositions for the systems are given in Table 3. All measurements were replicated at least three times and standard deviation values were denoted in Table 2 and 3.

The experimental data were compared with the value predicted by the UNIFAC method. The structural and interaction parameters of related systems were taken from the literature.[30] The root-mean-square deviations (rmsd) were calculated from the difference between the experimental data and the predictions of the UNIFAC method according to the following equation

$$\text{rmsd} = \left[\frac{\sum_k^N \left[\sum_j \sum_i (w_{ijk} - w_{ijk}^{\text{calcd}})^2\right]}{6N}\right]^{1/2} \qquad (1)$$

where w_{ijk} is the composition of component i in phase j on tie-line k. N is the number of tie-lines.

The experimental tie-line compositions and solubility values of the water + acid mixture + amyl acetate, water + acid mixture + diisobutyl ketone, and water + acid mixture + diisopropyl ether systems are plotted in Figures 1 to 3, respectively, along with the predicted values. The UNIFAC method correlated the experimental data for amyl acetate, diisobutyl ketone, and diisopropyl ether with rmsd values of 0.0512, 0.0119, and 0.0731, respectively. It is concluded that the solvents studied show low solubilities against water and can be used to extract the acid mixture from dilute aqueous solutions. The tetrahedral representation of the solubility surface of the quaternary system obtained from the experimental data is shown in Figure 4.

Reliability of measured tie-line compositions was ascertained by making Othmer–Tobias plots[31] for each system. The plots are presented in Figure 5. The linear correlation coefficients for the systems with amyl acetate, diisobutyl ketone, and diisopropyl ether as solvent are 0.9715, 0.9957, and 0.9814, respectively. The linearity of the plots (a correlation factor close to 1) indicates the consistency degree of the related data.

To study the capacity and selectivity of the solvents to extract the acid mixture, distribution coefficients D_i for the formic acid

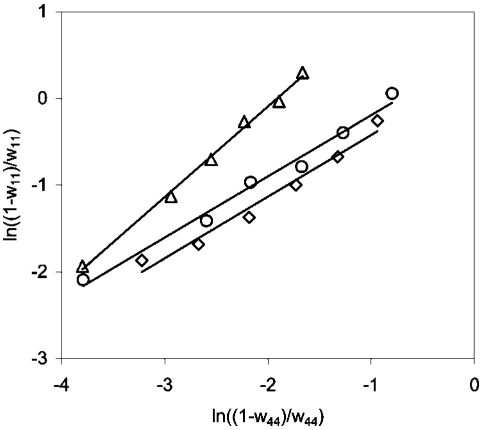

Figure 5. Othmer–Tobias plots of water (1) + formic acid (2) + acetic acid (3) + solvent (4) systems at 298.15 K: ◇, amyl acetate; Δ, diisobutyl ketone; ○, diisopropyl ether.

Table 4. Experimental Distribution Coefficients D_i and Separation Factors S_i for Water (1) + Formic Acid (2) + Acetic Acid (3) + Solvent (4) Quaternary Systems at 298.15 K

D_1	D_2	D_3	S_2	S_3
		Amyl Acetate		
0.0171	0.136	0.1929	7.95	11.28
0.0283	0.2043	0.286	7.22	10.11
0.0389	0.2643	0.3832	6.79	9.85
0.0555	0.3161	0.4477	5.70	8.07
0.0823	0.3555	0.507	4.32	6.16
0.1314	0.3753	0.5336	2.86	4.06
		Diisobutyl Ketone		
0.0136	0.0787	0.0836	5.79	6.15
0.0246	0.0822	0.1517	3.34	6.17
0.0294	0.0947	0.1867	3.22	6.35
0.0445	0.1044	0.1927	2.35	4.33
0.054	0.1323	0.2433	2.45	4.51
0.0672	0.1768	0.2588	2.63	3.85
		Diisopropyl Ether		
0.0117	0.1333	0.1356	11.39	11.59
0.0279	0.3006	0.3079	10.77	11.04
0.0314	0.3130	0.3312	9.97	10.55
0.0546	0.3093	0.4661	5.66	8.54
0.0816	0.4678	0.4745	5.73	5.81
0.1459	0.4304	0.5796	2.95	3.97

($i = 2$) and acetic acid ($i = 3$) and the separation factors S_i are determined as follows

$$D_i = w_{i4}/w_{i1} \tag{2}$$

$$S_i = D_i/D_1 \tag{3}$$

where w_{i4} and w_{i1} are the mass fractions of component i in the solvent and aqueous phase, respectively. The results for the water (1) + formic acid (2) + acetic acid (3) + solvent (4) systems at 298.15 K are listed in Table 4. Although the initial composition of the acid mixture was in 1:1 mass ratio, it is noticeable that the used solvents show higher distribution coefficients and separation factors for acetic acid than formic acid. To compare the selectivity advantages of amyl acetate, diisobutyl ketone, and diisopropyl ether, solvent-free based selectivity diagrams were plot in Figure 6. The selectivity diagram indicated that the performance of the solvents increases in diisobutyl ketone, amyl acetate, and diisopropyl ether order.

Conclusion

Phase equilibrium data of water + formic acid + acetic acid + solvent (amyl acetate, diisobutyl ketone, and diisopropyl ether) quaternary systems at 298.15 K were measured, and the trend of the distribution coefficients and separation factors for these systems were calculated. The experimental tie-lines of these systems were compared with the predicted data of the UNIFAC method. Although the used solvents have distribution coefficients lower than 1, they are concluded as adequate solvents to extract the formic and acetic acid mixture from its dilute aqueous solutions since they show low solubilities against water and high separation factors. It is observed that the solvents used in this study show higher distribution coefficients and separation factors for acetic acid than formic acid.

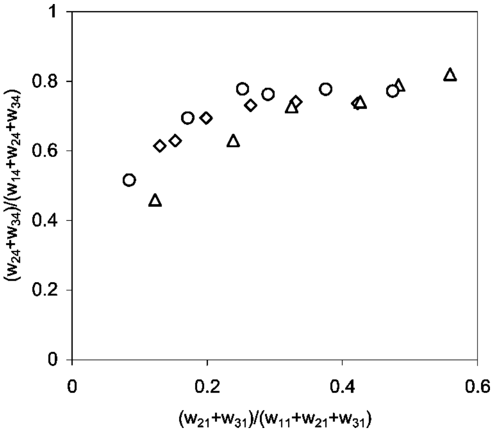

Figure 6. Selectivity diagrams of water (1) + formic acid (2) + acetic acid (3) + solvent (4) systems at 298.15 K: ◇, amyl acetate; Δ, diisobutyl ketone; ○, diisopropyl ether.

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