J. Chem. Eng. Data **2004,** *49,* 1456−1459

Quaternary Liquid−Liquid Equilibrium of Water + Acetic Acid + Propionic Acid + Solvent (Amyl Alcohol, Cyclohexyl Acetate, or Toluene) Systems

Süheyla Çehreli and Mehmet Bilgin*

Istanbul University, Engineering Faculty, Department of Chemical Engineering, 34320 Avcilar, Istanbul, Turkey

Liquid−liquid equilibrium data of water + acetic acid + propionic acid + solvent (amyl alcohol, cyclohexyl acetate, and toluene) quaternary systems were determined. Solubility curves and tie lines were measured at 298.15 K. A comparison of the extracting capabilities of the solvents was made with respect to distribution coefficients, separation factors, and solvent-free selectivity bases. The reliability of the data was ascertained from Othmer−Tobias plots. We conclude that all solvents are suitable separating agents for dilute aqueous acetic and propionic acid mixtures.

Introduction

Carboxylic acid fermentation has long been known and is still a major process for producing some principal carboxylic acids naturally. Acetic and propionic acids are the most important carboxylic acids that are widely used in industry, which makes the biotechnological production of these acids of interest. The efficient separation of organic acids from fermentation broth (aqueous solution) is of economic importance in the chemical industry, and there is a constant need for liquid−liquid equilibrium (LLE) data for the design of the separation equipment. Phase equilibrium data also provide valuable information about the molecular interactions and macroscopic behavior of fluid mixtures.

Many solvents have been tried and tested to improve the recovery of various organic acids from aqueous solutions, and the phase equilibrium data of the related systems are presented in the literature.[1−4] LLE data for the water + acetic acid + cyclohexyl acetate ternary[5] and for water + acetic acid + toluene and water + propionic acid + toluene ternaries[6] has been presented previously. After investigating these studies, it is briefly reported that the (cyclohexyl acetate + cyclohexanol) mixture can be used in various ratios instead of pure solvents for the recovery of acetic acid. Furthermore, it is concluded that methyl butyl ketone and methyl isopropyl ketone are suitable separating agents for dilute aqueous propionic acid and that high-boiling phthalic esters (such as dimethyl and diethyl phthalate), cyclohexyl acetate, and isophorone are suitable separating agents for dilute aqueous acetic acid. The objective of this work is to gather LLE data of water + acetic acid + propionic acid + solvent (amyl alcohol, cyclohexyl acetate, and toluene) quaternary systems at 298.15 K and to show the trend in the distribution coefficients and separation factors for these systems because no such data are available in the literature.

Experimental Section

Chemicals. Acetic acid (100%), propionic acid (99.99%), toluene (99%), cyclohexyl acetate (>98%), and amyl alcohol (>99%) supplied by Merck were used without further purification. GC analysis did not detect any appreciable peaks of impurities. 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 ± 0.20) K and their boiling points at (101.33 ± 0.27) kPa. Refractive indexes were measured with an Abbé-Hilger refractometer to ±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-points measurements are ±0.0001 g 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[7] for comparison.

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

	n_D		ρ/(g·cm^{-3})		t_b/°C	
compound	measured	lit	measured	lit	measured	lit
acetic acid	1.3720	1.3716	1.0495	1.0492	117.7	117.9
propionic acid	1.3811	1.3809	0.9925	0.9930	140.9	141.0
amyl alcohol	1.4104	1.4101	0.8140	0.8144	138.0	$137.3^{99.73}$
cyclohexyl acetate	1.4398	1.4401	0.9692	0.9698	172.6	173.0
toluene	1.4960	1.4961	0.8673	0.8669	110.3	110.6

Apparatus and Procedure. Solubility data for the quaternary systems were determined by the cloud-point method. The data measurements were made in an equilibrium cell equipped with a magnetic stirrer and an isothermal fluid jacketed beaker to keep the temperature of the stock solution constant. The mixture temperature was regulated by a thermostatic certified Fischer thermometer with an accuracy of ±0.2 K. The cell, designed to contain a solution from (50 to 200) cm^3, was filled with homogeneous water + acid mixtures prepared by mass. The acid mixture of acetic and propionic acid, which consists of completely miscible components, was prepared in a 1:1 mass ratio. An electronic Sauter balance with an accuracy of ±0.1 mg was used. The ternary mixtures of known compositions were shaken in the cell at constant temperature. The fourth component (solvent) was progressively added by means of an automatic microburet with an accuracy of ±0.005 cm^3. The endpoint was determined by observing the transition from a homogeneous to a hetero-

---

* To whom correspondence should be addressed. E-mail: mbilgin@istanbul.edu.tr. Fax: +90-212-5911997.

10.1021/je049848j CCC: $27.50

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

w_1	w_2	w_3
	Amyl Alcohol	
0.0874	0.0000	0.0000
0.0908	0.0315	0.0315
0.1123	0.0952	0.0952
0.1941	0.1427	0.1426
0.2808	0.1593	0.1591
0.3841	0.1621	0.1619
0.4203	0.1591	0.1589
0.5192	0.1505	0.1503
0.5640	0.1445	0.1444
0.6182	0.1360	0.1358
0.6802	0.1233	0.1233
0.7994	0.0803	0.0802
0.9014	0.0356	0.0355
0.9740	0.0000	0.0000
	Cyclohexyl Acetate	
0.0215	0.0000	0.0000
0.0247	0.0602	0.0609
0.0682	0.1258	0.1273
0.1130	0.1686	0.1705
0.1621	0.1939	0.1962
0.2321	0.2131	0.2156
0.3280	0.2198	0.2223
0.3892	0.2202	0.2227
0.4998	0.2063	0.2088
0.6167	0.1735	0.1755
0.7078	0.1402	0.1418
0.8690	0.0622	0.0629
0.9969	0.0000	0.0000
	Toluene	
0.0030	0.0000	0.0000
0.0079	0.0851	0.0861
0.0100	0.1340	0.1355
0.0236	0.2033	0.2057
0.0397	0.2297	0.2324
0.0713	0.2643	0.2674
0.1195	0.2983	0.3017
0.1848	0.3199	0.3236
0.2273	0.3239	0.3276
0.3274	0.3019	0.3054
0.4264	0.2709	0.2740
0.6369	0.1779	0.1799
0.7729	0.1118	0.1132
0.9993	0.0000	0.0000

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

aqueous phase			solvent phase		
w_1	w_2	w_3	w_1	w_2	w_3
		Amyl Alcohol			
0.9292	0.0278	0.0159	0.0914	0.0365	0.0494
0.9072	0.0431	0.0218	0.0962	0.0590	0.0815
0.8746	0.0617	0.0322	0.1331	0.0879	0.1149
0.8348	0.0863	0.0449	0.1505	0.1064	0.1363
0.7923	0.1064	0.0587	0.2129	0.1270	0.1511
0.6732	0.1561	0.0957	0.2671	0.1520	0.1645
		Cyclohexyl Acetate			
0.9242	0.0446	0.0267	0.0224	0.0201	0.0423
0.8839	0.0690	0.0427	0.0303	0.0326	0.0693
0.8429	0.0952	0.0562	0.0397	0.0508	0.0986
0.7965	0.1230	0.0729	0.0479	0.0696	0.1273
0.7454	0.1504	0.0920	0.0670	0.0901	0.1527
0.6712	0.1900	0.1202	0.0792	0.1174	0.1835
0.6003	0.2166	0.1476	0.1093	0.1403	0.2060
0.5240	0.2352	0.1710	0.1588	0.1706	0.2147
		Toluene			
0.9114	0.0486	0.0397	0.0055	0.0032	0.0149
0.8282	0.0971	0.0743	0.0052	0.0114	0.0446
0.7559	0.1399	0.1037	0.0061	0.0202	0.0697
0.6992	0.1718	0.1280	0.0118	0.0288	0.0847
0.6343	0.2064	0.1575	0.0134	0.0384	0.1120
0.5874	0.2309	0.1786	0.0199	0.0493	0.1296
0.5469	0.2494	0.1982	0.0199	0.0606	0.1490
0.4837	0.2782	0.2282	0.0242	0.0750	0.1633

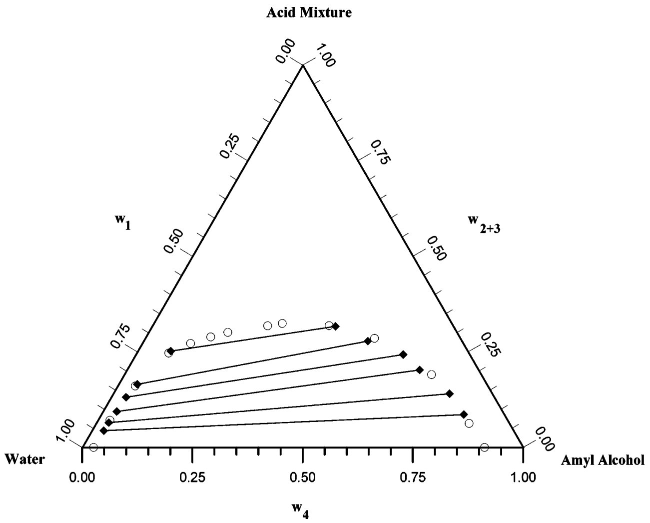

Figure 1. Phase equilibrium of a water (1) + acid mixture (2 + 3) + amyl alcohol (4) system at 298.15 K: ○, solubility data; ◆, tie-line data.

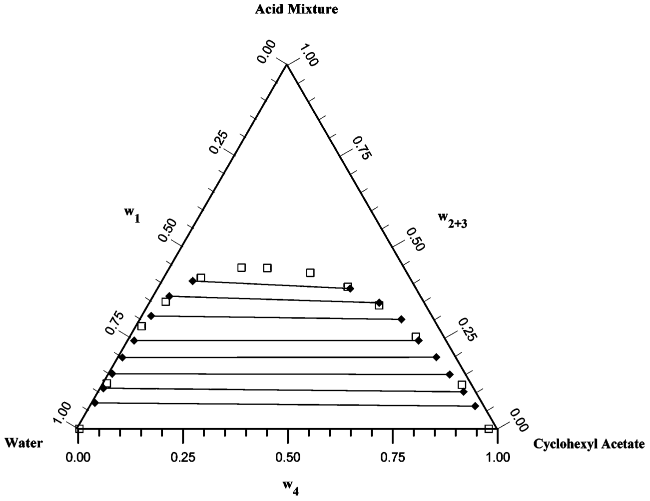

Figure 2. Phase equilibrium of a water (1) + acid mixture (2 + 3) + cyclohexyl acetate (4) system at 298.15 K: □, solubility data; ◆, tie-line data.

geneous mixture. This pattern was convenient for providing the water-rich side of the curves. The data for the solvent-rich side of the curves were therefore obtained by titrating the homogeneous acid mixture + solvent with water until turbidity appeared.

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

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 and being allowed to reach equilibrium, samples were carefully taken from each phase and analyzed. The analysis for the determination of the acetic acid, propionic acid, and solvent content of the two layers was performed by gas chromatography (HP 6890), and water was analyzed with a Karl Fischer titrator (Mettler Toledo DL38). The uncertainty of the mass fraction measurements for the overall composition determination was ±0.002.

Results and Discussion

The experimental solubility curve data and the experimental mutual solubilities for the water (1) + acetic acid

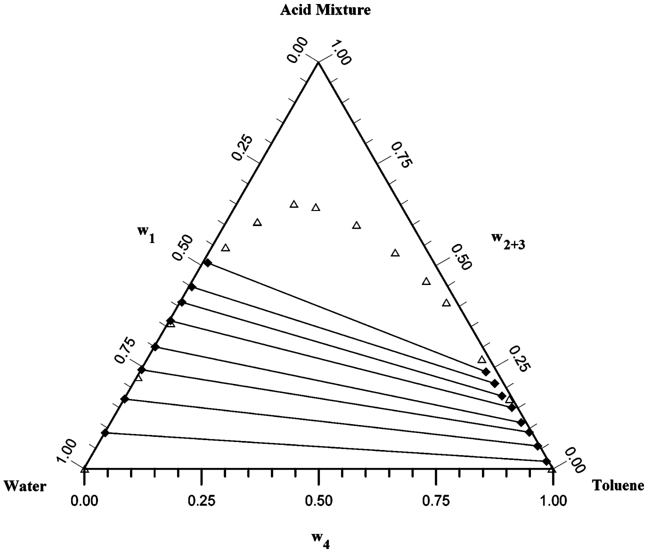

Figure 3. Phase equilibrium of a water (1) + acid mixture (2 + 3) + toluene (4) system at 298.15 K: △, solubility data; ◆, tie-line data.

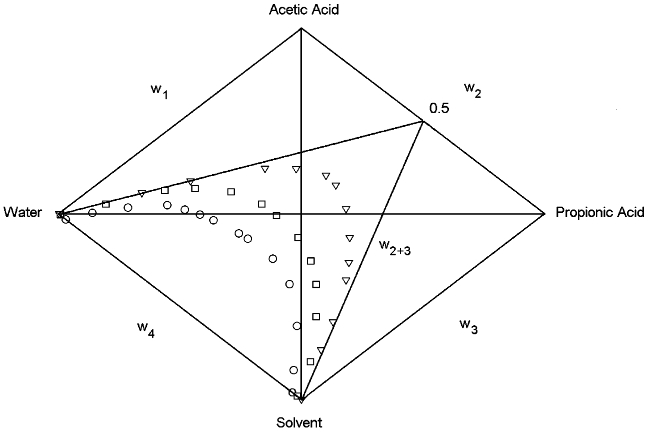

Figure 4. Tetrahedral representation of the solubility surface of a water (1) + acetic acid (2) + propionic acid (3) + solvent (4) quaternary system: ○, amyl alcohol; □, cyclohexyl acetate; ▽, toluene.

(2) + propionic acid (3) + solvent (4) quaternary systems are reported in Table 2. The tie-line compositions for the systems are given in Table 3. The experimental tie-line compositions and solubility values of the water + acid mixture + amyl alcohol, water + acid mixture + cyclohexyl acetate, and water + acid mixture + toluene systems are plotted in Figures 1 to 3, respectively. The concentrations in the phase diagrams were given in mass fraction (w). We conclude that all solvents show low solubility against water and can be used to extract the acid mixture from dilute aqueous solutions. The results indicate that the solubility of the solvents is high enough in acid mixtures. The tetrahedral representation of the solubility surface of the quaternary system obtained from the experimental data is shown in Figure 4.

The reliability of measured tie-line compositions was ascertained by making Othmer−Tobias plots[8] for each system. The plots are presented in Figure 5. The linear correlation coefficients for the systems with amyl alcohol, cyclohexyl acetate, and toluene as solvent are 0.9769, 0.9987, and 0.9962, respectively. The linearity of the plots (a correlation factor close to 1) indicates the degree of consistency of the related data. The standard deviation for tie-line composition data was 0.0029.

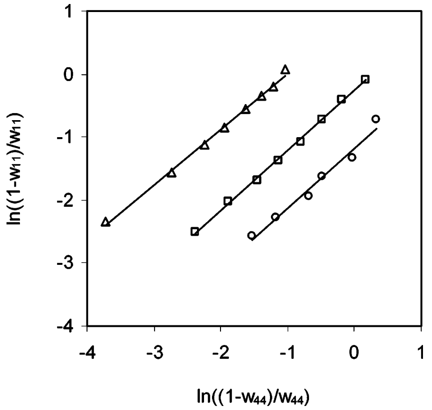

Figure 5. Othmer−Tobias plots of water (1) + acetic acid (2) + propionic acid (3) + solvent (4) systems at 298.15 K: ○, amyl alcohol; □, cyclohexyl acetate; △, toluene.

Table 4. Experimental Distribution Coefficients D_i and Separation Factors S_i at 298.15 K

D_1	D_2	D_3	S_2	S_3
		Amyl Alcohol		
0.0984	1.3129	3.1069	13.35	31.59
0.1060	1.3689	3.7385	12.91	35.26
0.1522	1.4246	3.5683	9.36	23.45
0.1683	1.2329	3.0356	7.33	18.04
0.2687	1.1936	2.5741	4.44	9.58
0.3968	0.9737	1.7189	2.45	4.33
		Cyclohexyl Acetate		
0.0242	0.4514	1.5846	18.66	65.51
0.0342	0.4724	1.6252	13.79	47.45
0.0471	0.5338	1.7533	11.34	37.24
0.0601	0.5653	1.7464	9.40	29.05
0.0899	0.5987	1.6599	6.66	18.47
0.1180	0.6179	1.5267	5.24	12.93
0.1820	0.6476	1.3956	3.56	7.67
0.3030	0.7255	1.2556	2.39	4.14
		Toluene		
0.0060	0.0658	0.3753	10.91	62.19
0.0063	0.1174	0.6003	18.70	95.60
0.0081	0.1444	0.6721	17.89	83.29
0.0169	0.1676	0.6617	9.93	39.21
0.0211	0.1860	0.7111	8.81	33.66
0.0339	0.2135	0.7256	6.30	21.42
0.0364	0.2430	0.7518	6.68	20.66
0.0500	0.2696	0.7156	5.39	14.30

To study the capacity and selectivity of the solvents used to extract the acid mixture, distribution coefficients D_i for acetic acid ($i = 2$) and propionic acid ($i = 3$) and the separation factors S_i are determined as follows:

$$D_i = \frac{w_{i4}}{w_{i1}} \tag{1}$$

$$S_i = \frac{D_i}{D_1} \tag{2}$$

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) + acetic acid (2) + propionic acid (3) + solvent (4) systems at 298.15 K are listed in Table 4. The results for the distribution values and the separation factors make the solvents good candidates for separating agents. Although the initial concentration of the acid mixture was a 1:1 mass ratio, it is noticeable that all solvents show higher distribution coefficients and separation factors for propionic acid than acetic acid. To compare the selectivity advantages of amyl alcohol, cyclohexyl acetate, and toluene, we plotted solvent-free-based selectivity diagrams in Figure 6. The selectivity diagram indicated

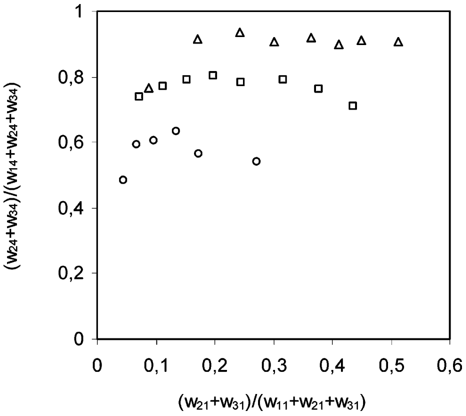

Figure 6. Selectivity diagrams of water (1) + acetic acid (2) + propionic acid (3) + solvent (4) systems at 298.15 K: ○, amyl alcohol; □, cyclohexyl acetate; △, toluene.

that the performance of the solvents increases in the order of amyl alcohol, cyclohexyl acetate, and toluene.

Conclusions

LLE data of water + acetic acid + propionic acid + solvent (amyl alcohol, cyclohexyl acetate, and toluene) quaternary systems at 298.15 K were measured, and the trends in the distribution coefficients and separation factors for these systems were calculated. We conclude that all solvents, showing low solubilities against water, may serve as adequate solvents for the extraction of acetic and propionic acid mixtures from dilute aqueous solutions. It is observed that all solvents used in this study show higher distribution coefficients and separation factors for propionic acid than acetic acid.

Literature Cited

(1) Cehreli, S. Liquid-Liquid Equilibria of the Acetic Acid - Water - Mixed Solvent (Cyclohexyl Acetate-Cyclohexanol) System. *Braz. J. Chem. Eng.* **2002**, *19*, 45−53.

(2) Taghikhani, V.; Vakili-Nezhaad, G. R.; Khoshkbarchi, M. K.; Shariaty-Niassar, M. Liquid−Liquid Equilibria of Water + Propionic Acid + Methyl Butyl Ketone and of Water + Propionic Acid + Methyl Isopropyl Ketone. *J. Chem. Eng. Data* **2001**, *46*, 1107−1109.

(3) Colombo, A.; Battilana, P.; Ragaini, V.; Bianchi, C. L.; Carvoli, G. Liquid−Liquid Equilibria of the Ternary Systems Water + Acetic Acid + Ethyl Acetate and Water + Acetic Acid + Isophorone (3,5,5-Trimethyl-2-cyclohexen-1-one). *J. Chem. Eng. Data* **1999**, *44*, 35−39.

(4) Dramur, U.; Tatli, B. Liquid−Liquid Equilibria of Water + Acetic Acid + Phthalic Esters (Dimethyl Phthlate and Diethyl Phthalate) Ternaries. *J. Chem. Eng. Data* **1993**, *38*, 23−25.

(5) Sayar, A. A.; Tatli, B.; Dramur, U. Liquid−Liquid Equilibria of Water + Acetic Acid + Cyclohexyl Acetate Ternary. *J. Chem. Eng. Data* **1991**, *36*, 378−382.

(6) Badakhsan, A.; Chowdhury, A. I.; Leung, R. Effect of Temperature on Liquid−Liquid Equilibria for Three Systems Containing Acetic Acid−Water−Toluene, Propionic Acid−Water−Cyclohexane, Propionic Acid−Water−Toluene at Atmospheric Pressure. *J. Chem. Eng. Data* **1985**, *30*, 416−421.

(7) Weast, R. C. *Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL, 1989−1990.

(8) Othmer, D. F.; Tobias, P. E. Tie Line Correlation. *Ind. Eng. Chem.* **1942**, *34*, 693−696.

Received for review April 16, 2004. Accepted June 21, 2004.

JE049848J