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Liquid–Liquid Equilibria of Some Water + 2-Propanol + Solvent Ternaries

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Experimental liquid–liquid equilibrium data were obtained at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa for nine water + 2-propanol + solvent systems. An adequate high-boiling solvent, 2-methylbutyl acetate, was proposed for separating 2-propanol from dilute aqueous solutions.

Introduction

The liquid–liquid equilibria (LLE) in water + 2-propanol + solvent systems provide important information in the design of equipment for the extraction of 2-propanol from aqueous mixtures. The main purpose of this study is to report the experimental data on the phase equilibria of some systems containing water, 2-propanol, and solvent at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa. These ternaries are as follows: (1) water + 2-propanol + dichloromethane, (2) water + 2-propanol + 1,2-dichloroethane, (3) water + 2-propanol + 2-methylbutyl acetate, (4) water + 2-propanol + 1-pentanol, (5) water + 2-propanol + phenylmethanol, (6) water + 2-propanol + cyclohexanol, (7) water + 2-propanol + 1-methylcyclohexanol, (8) water + 2-propanol + dibenzyl ether, and (9) water + 2-propanol + octanenitrile.

Solvents with distribution coefficients greater than 0.2 and separation factors greater than 10 are considered potential candidates as extractants. In view of this criterion, some liquids, especially high-boiling ones, were proposed to be chosen as solvents for separating 2-propanol from dilute aqueous solutions.

Experimental Section

Chemicals. The chemicals used in this study, except octanenitrile, were furnished by Merck. The octanenitrile was supplied by Aldrich. Dichloromethane and 1,2-dichloroethane were dried over anhydrous $MgSO_4$. The alcohols and the 2-methylbutyl acetate were dried over anhydrous K_2CO_3. All of the solvents were redistilled under moderate vacuum (chloroalkanes under atmospheric pressure), and then the middle fractions were collected. Impurities detectable by gas chromatography were found: less than 0.1% in dichloromethane, 1,2-dichloroethane, 2-propanol, cyclohexanol, 1-pentanol, and phenylmethanol and less than 0.25% in dibenzyl ether, octanenitrile, and 2-methylbutyl acetate. Purity was better than 99.5% for 1-methylcyclohexanol (ca. 0.4% 2-methylcyclohexanol isomer).

Liquid chromatographic grade acetone from Merck, as an internal substance in gas chromatographic analysis, was used without further purification.

Deionized water was distilled from alkaline $KMnO_4$ and then redistilled.

Mutual Solubilities. Mutual solubilities of partially miscible components of each ternary, except cyclohexanol + water, were determined at 293.16 ± 0.30 K by applying the synthetic method. The cyclohexanol + water experiments were performed at 300.12 ± 0.30 K.

One pure substance was filled into the cell equipped with a magnetic stirrer and a jacket for isothermal fluid circulation. The inner temperature of the cell containing the sample was observed with a certified Fischer mercury thermometer accurate to ±0.1 K. The sample temperature was kept constant at 293.16 ± 0.30 K by means of a thermostated bath. After thermal equilibrium had been reached, the other substance was added from a microburet accurate to ±0.005 mL, until the turbidity appeared. After 5 min, if the cloudiness had disappeared, an extra drop was added to obtain a stable heterogeneity. The overall binary composition was determined by weighing and titrating both together. An electronic Sauter balance accurate to ±0.1 mg was used. The accuracy of the determinations was limited by the difficulty in observing the transition point of the mixture.

Binodal Curves. The experimental solubility isotherms of each ternary were determined at 293.16 ± 0.30 K by the combined application of two different methods.

(a) Synthetic Method. Pure 2-propanol was added from an automatic titrator accurate to ±0.01 mL to the water–solvent mixtures located within the immiscibility range. The end point was determined by observing the disappearance of the heterogeneity. The experiments were carried out in the above-mentioned isothermal apparatus. The quantity of 2-propanol used to obtain a clear and stable solution was determined volumetrically. The initial composition of the titrated binary was measured by weighing.

(b) Analytical Method. Samples of ternary mixtures within the heterogeneous gap were prepared by mass and then charged into the isothermal equilibrium unit. The samples were strongly stirred for 30 min. The content was allowed to settle under isothermal conditions until the phases separated. Complete separation was enforced by a periodical rotating movement of ±45° in opposite directions, applied to the vertical settler. Then the adhesional forces preventing the migration of the droplets were wholly overcome. After the phase equilibrium had been reached, an appropriate amount of each conjugate layer was withdrawn for quantitative analysis.

After a known amount of acetone as an internal substance had been added to the weighted sample, the 2-propanol content was determined by gas chromatography using a flame ionization detector (Aerograph Hydrogen-Flame, Model 600-C; column, Supelco Carbopack-C 0.2% CW-1500 60/80; entrainer, N_2; temperature, 110–120 °C). The determinations were performed by using a standard calibration curve (peak area ratios versus weight fraction ratios).

The water content of each sample was determined by means of the Karl-Fischer method using a KF automatic titrator set. Sampling was done at least twice for each layer to obtain a mean value. The weight fraction of the third component was obtained by back-calculation.

Results

According to the analytical method, relatively larger uncertainties in the experimental data could occur near the plait-point region. In order to eliminate these inaccuracies, a synthetic method was also used to perform the plait-point arc of the equilibrium curve. Then the resulting experimental binodal curve was reproduced with respect to both analytical and synthetic methods together.

The experimental tie lines and the binodal curves of each investigated system are plotted in Figures 1–9. The water +

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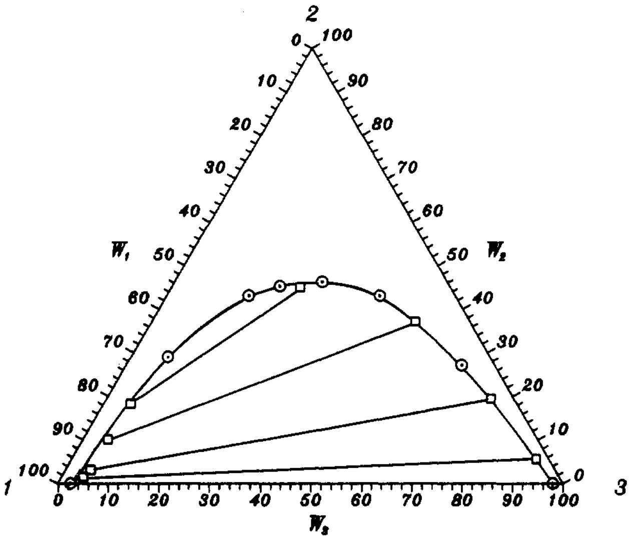

Figure 1. Ternary diagram for experimental LLE of water (1) + 2-propanol (2) + dichloromethane (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa: ⊙, synthetic data; ☐, analytical data (concentrations expressed in wt %, W_i).

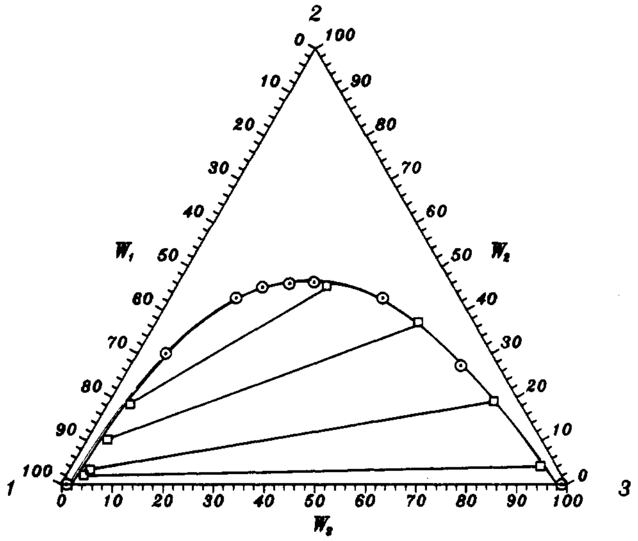

Figure 2. Ternary diagram for experimental LLE of water (1) + 2-propanol (2) 1,2-dichloroethane (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa: ⊙, synthetic data; ☐, analytical data (concentrations expressed in wt %, W_i).

Table I. Liquid–Liquid Equilibria for Water (1) + 2-Propanol (2) + Dichloromethane (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa

A. Analytical Method (Tie-Line Data)

	aqueous phase			solvent phase		
	w_1	w_2	w_3	w_1	w_2	w_3
1	0.942	0.016	0.042	0.024	0.057	0.919
2	0.919	0.032	0.049	0.046	0.195	0.759
3	0.850	0.102	0.048	0.108	0.372	0.520
4	0.762	0.185	0.053	0.297	0.450	0.253

B. Synthetic Method (Equilibrium Curve Data)

	w_1	w_2	w_3		w_1	w_2	w_3
1	0.976		0.024 (ms)[a]	5	0.337	0.452	0.211
2	0.021		0.979 (ms)[a]	6	0.248	0.462	0.290
3	0.638	0.290	0.072	7	0.150	0.430	0.420
4	0.409	0.430	0.161	8	0.066	0.272	0.662

[a] ms = mutual solubility data.

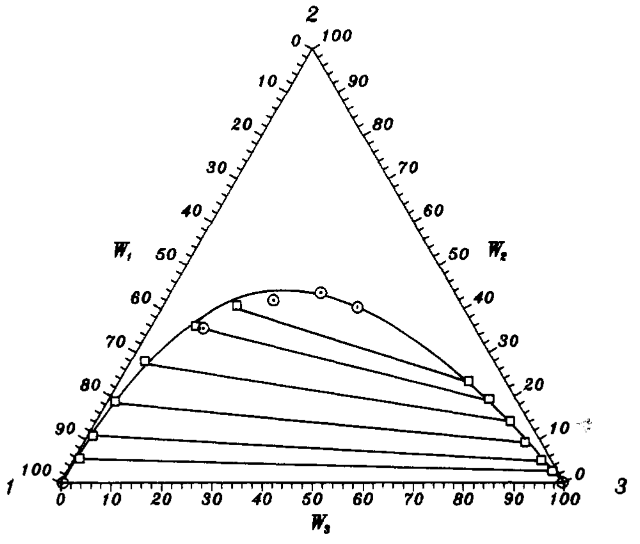

Figure 3. Ternary diagram for experimental LLE of water (1) + 2-propanol (2) + 2-methylbutyl acetate (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa: ⊙, synthetic data; ☐, analytical data (concentrations expressed in wt %, W_i).

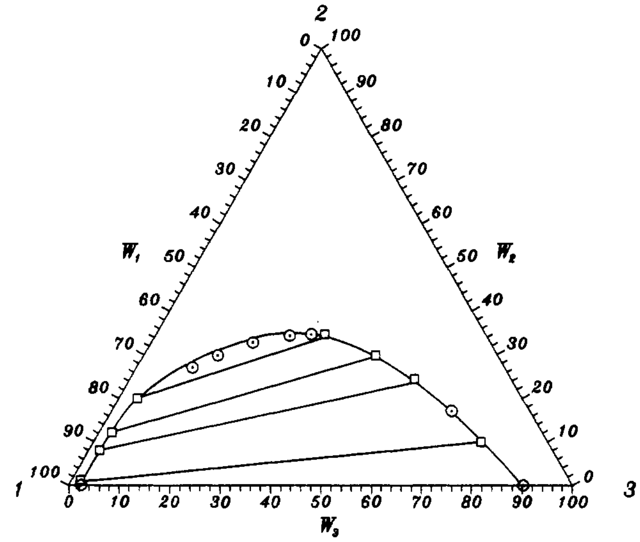

Figure 4. Ternary diagram for experimental LLE of water (1) + 2-propanol (2) + 1-pentanol (3) at 293.16 ± 0.30 K and 0.1013 + 0.0020 MPa: ⊙, synthetic data; ☐, analytical data (concentrations expressed in wt %, W_i).

Table II. Liquid–Liquid Equilibria for Water (1) + 2-Propanol (2) + 1,2-Dichloroethane (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa

A. Analytical Method (Tie-Line Data)

	aqueous phase			solvent phase		
	w_1	w_2	w_3	w_1	w_2	w_3
1	0.945	0.022	0.033	0.031	0.042	0.927
2	0.926	0.034	0.040	0.050	0.191	0.759
3	0.858	0.103	0.039	0.110	0.372	0.518
4	0.773	0.184	0.043	0.249	0.456	0.295

B. Synthetic Method (Equilibrium Curve Data)

	w_1	w_2	w_3		w_1	w_2	w_3
1	0.990		0.010 (ms)[a]	6	0.320	0.460	0.220
2	0.011		0.989 (ms)[a]	7	0.271	0.463	0.266
3	0.645	0.300	0.055	8	0.153	0.427	0.420
4	0.442	0.427	0.131	9	0.076	0.272	0.652
5	0.378	0.452	0.170				

[a] ms = mutual solubility data.

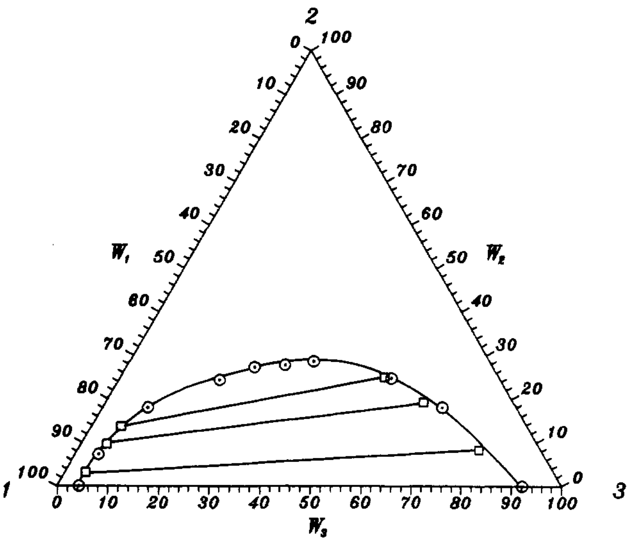

Figure 5. Ternary diagram for experimental LLE of water (1) + 2-propanol (2) + phenylmethanol (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa: ⊙, synthetic data; ☐, analytical data (concentrations expressed in wt %, W_i).

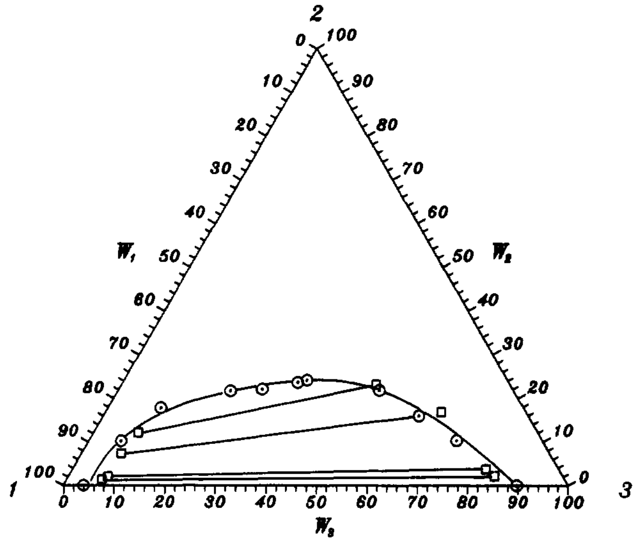

Figure 6. Ternary diagram for experimental LLE of water (1) + 2-propanol (2) + cyclohexanol (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa: ⊙, synthetic data; ☐, analytical data (concentrations expressed in wt %, W_i).

Table III. Liquid–Liquid Equilibria for Water (1) + 2-Propanol (2) + 2-Methylbutyl Acetate (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa

A. Analytical Method (Tie-Line Data)

	aqueous phase			solvent phase		
	w_1	w_2	w_3	w_1	w_2	w_3
1	0.933	0.057	0.010	0.010	0.027	0.963
2	0.881	0.109	0.010	0.020	0.052	0.928
3	0.798	0.188	0.014	0.031	0.094	0.875
4	0.693	0.280	0.027	0.037	0.142	0.821
5	0.552	0.361	0.087	0.054	0.193	0.753
6	0.446	0.408	0.146	0.073	0.234	0.693

B. Synthetic Method (Equilibrium Curve Data)

	w_1	w_2	w_3		w_1	w_2	w_3
1	0.996		0.004 (ms)[a]	4	0.368	0.419	0.213
2	0.004		0.996 (ms)[a]	5	0.266	0.436	0.298
3	0.540	0.355	0.105	6	0.211	0.402	0.387

[a] ms = mutual solubility data.

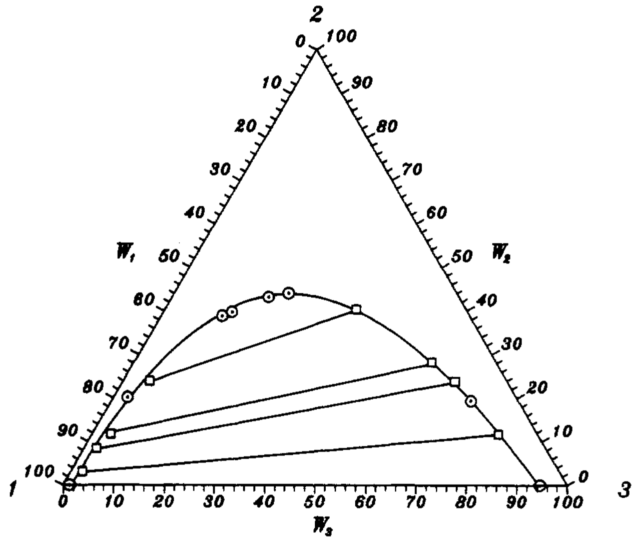

Figure 7. Ternary diagram for experimental LLE of water (1) + 2-propanol (2) + 1-methylcyclohexanol (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa: ⊙, synthetic data; ☐, analytical data (concentrations expressed in wt %, W_i).

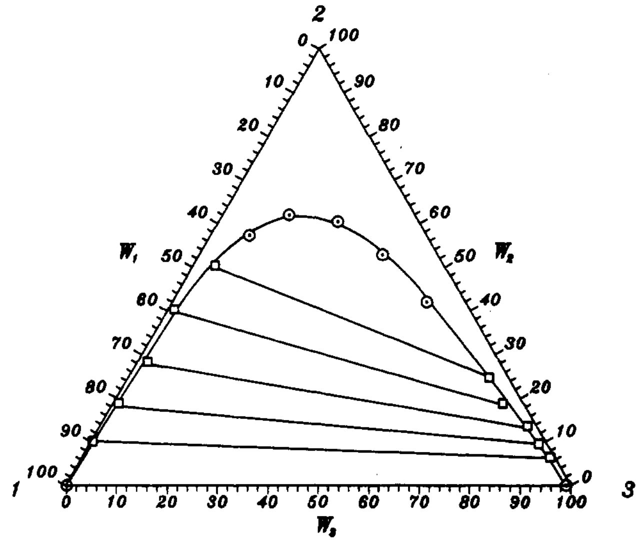

Figure 8. Ternary diagram for experimental LLE of water (1) + 2-propanol (2) + dibenzyl ether (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa: ⊙, synthetic data; ☐, analytical data (concentrations expressed in wt %, W_i).

Table IV. Liquid–Liquid Equilibria for Water (1) + 2-Propanol (2) + 1-Pentanol (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa

A. Analytical Method (Tie-Line Data)

	aqueous phase			solvent phase		
	w_1	w_2	w_3	w_1	w_2	w_3
1	0.971	0.012	0.017	0.132	0.100	0.768
2	0.898	0.081	0.021	0.191	0.244	0.565
3	0.853	0.122	0.025	0.242	0.298	0.460
4	0.765	0.199	0.036	0.320	0.346	0.334

B. Synthetic Method (Equilibrium Curve Data)

	w_1	w_2	w_3		w_1	w_2	w_3
1	0.976		0.024 (ms)[a]	5	0.472	0.327	0.201
2	0.098		0.902 (ms)[a]	6	0.391	0.343	0.266
3	0.620	0.270	0.110	7	0.347	0.346	0.307
4	0.556	0.298	0.146	8	0.155	0.171	0.674

[a] ms = mutual solubility data.

Table V. Liquid–Liquid Equilibria for Water (1) + 2-Propanol (2) + Phenylmethanol (3) at 293.16 - 0.30 K and 0.1013 ± 0.0020 MPa

A. Analytical Method (Tie-Line Data)

	aqueous phase			solvent phase		
	w_1	w_2	w_3	w_1	w_2	w_3
1	0.928	0.032	0.040	0.122	0.084	0.794
2	0.853	0.097	0.050	0.179	0.193	0.628
3	0.805	0.137	0.058	0.228	0.251	0.521

B. Synthetic Method (Equilibrium Curve Data)

	w_1	w_2	w_3		w_1	w_2	w_3
1	0.958		0.024 (ms)[a]	6	0.474	0.273	0.253
2	0.079		0.921 (ms)[a]	7	0.411	0.278	0.311
3	0.882	0.073	0.045	8	0.350	0.287	0.363
4	0.733	0.179	0.088	9	0.216	0.248	0.536
5	0.559	0.243	0.198	10	0.148	0.181	0.671

[a] ms = mutual solubility data.

Table VI. Liquid–Liquid Equilibria for Water (1) + 2-Propanol (2) + Cyclohexanol (3) at 300.16 ± 0.30 K and 0.1013 ± 0.0020 MPa

A. Analytical Method (Tie-Line Data)

	aqueous phase			solvent phase		
	w_1	w_2	w_3	w_1	w_2	w_3
1	0.917	0.014	0.069	0.136	0.022	0.842
2	0.902	0.021	0.077	0.145	0.038	0.817
3	0.848	0.074	0.078	0.168	0.169	0.663
4	0.791	0.122	0.087	0.266	0.232	0.502

B. Synthetic Method (Equilibrium Curve Data)

	w_1	w_2	w_3		w_1	w_2	w_3
1	0.961		0.039 (ms)[a]	7	0.420	0.236	0.344
2	0.103		0.897 (ms)[a]	8	0.399	0.241	0.360
3	0.835	0.102	0.063	9	0.267	0.218	0.515
4	0.719	0.178	0.103	10	0.218	0.159	0.623
5	0.562	0.217	0.221	11	0.171	0.103	0.726
6	0.498	0.220	0.282				

[a] ms = mutual solubility data.

Table VII. Liquid–Liquid Equilibria for Water (1) + 2-Propanol (2) + 1-Methylcyclohexanol (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa

A. Analytical Method (Tie-Line Data)

	aqueous phase			solvent phase		
	w_1	w_2	w_3	w_1	w_2	w_3
1	0.946	0.032	0.022	0.078	0.117	0.805
2	0.891	0.085	0.024	0.104	0.239	0.657
3	0.846	0.118	0.036	0.127	0.283	0.590
4	0.709	0.240	0.051	0.218	0.404	0.378

B. Synthetic Method (Equilibrium Curve Data)

	w_1	w_2	w_3		w_1	w_2	w_3
1	0.988		0.012 (ms)[a]	5	0.467	0.397	0.136
2	0.055		0.945 (ms)[a]	6	0.378	0.431	0.191
3	0.773	0.201	0.026	7	0.334	0.440	0.226
4	0.491	0.388	0.121	8	0.096	0.193	0.711

[a] ms = mutual solubility data.

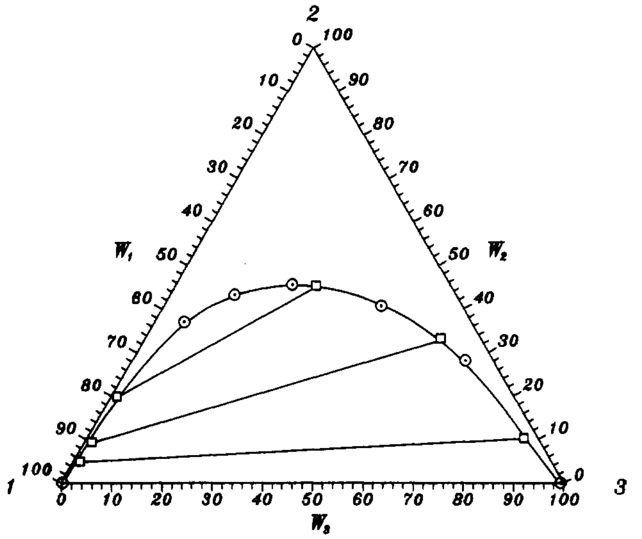

Figure 9. Ternary diagram for experimental LLE of water (1) + 2-propanol (2) + octanenitrile (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa: ⊙, synthetic data; □, analytical data (concentrations expressed in wt %, W_i).

Table VIII. Liquid–Liquid Equilibria for Water (1) + 2-Propanol (2) + Dibenzyl Ether (3) at 293.16 ± 0.30 K and 0.1013 ± 0.0020 MPa

A. Analytical Method (Tie-Line Data)

	aqueous phase			solvent phase		
	w_1	w_2	w_3	w_1	w_2	w_3
1	0.896	0.101	0.003	0.009	0.065	0.926
2	0.802	0.188	0.010	0.015	0.096	0.889
3	0.697	0.284	0.019	0.018	0.137	0.845
4	0.575	0.403	0.022	0.031	0.188	0.781
5	0.453	0.504	0.043	0.039	0.247	0.714

B. Synthetic Method (Equilibrium Curve Data)

	w_1	w_2	w_3		w_1	w_2	w_3
1	0.999		0.001 (ms)[a]	5	0.161	0.604	0.235
2	0.010		0.990 (ms)[a]	6	0.109	0.528	0.363
3	0.352	0.572	0.076	7	0.077	0.420	0.503
4	0.250	0.619	0.131				

[a] ms = mutual solubility data.

Table IX. Liquid–Liquid Equilibria for Water (1) + 2-Propanol + Octanenitrile (3) at 293.16 ± 0.30 K for 0.1013 ± 0.0020 MPa

A. Analytical Method (Tie-Line Data)

	aqueous phase			solvent phase		
	w_1	w_2	w_3	w_1	w_2	w_3
1	0.936	0.051	0.013	0.028	0.103	0.869
2	0.892	0.095	0.013	0.080	0.332	0.588
3	0.790	0.195	0.015	0.267	0.453	0.280

B. Synthetic Method (Equilibrium Curve Data)

	w_1	w_2	w_3		w_1	w_2	w_3
1	0.998		0.002 (ms)[a]	5	0.314	0.455	0.231
2	0.007		0.993 (ms)[a]	6	0.162	0.406	0.432
3	0.572	0.370	0.058	7	0.057	0.281	0.662
4	0.441	0.432	0.127				

[a] ms = mutual solubility data.

2-propanol + solvent LLE data are listed in Tables I–IX. The concentrations are expressed in weight fractions, w_i.

The accuracy of the synthetic method is ±0.002 in weight fraction of 2-propanol. In the case of the analytical method the composition measurements were generally accurate to ±0.005 and ±0.003 weight fractions for 2-propanol and water, respectively. The accuracy estimations were performed by using standard mixtures. In order to estimate the performance of the investigated solvents, their distribution coefficients D_i for 2-propanol (i = 2) and water (i = 1) and their separation factors S were determined:

$$D_i = \frac{\text{concentration in solvent phase}}{\text{concentration in aqueous phase}} \tag{1}$$

$$S = \frac{\text{distribution coefficient of 2-propanol } (D_2)}{\text{distribution coefficient of water } (D_1)} \tag{2}$$

Table X. Experimental Distribution Coefficients D_i of Water (i = 1) and 2-Propanol (i = 2) and Separation Factors ($S = D_2/D_1$)[a]

system no.	D_2	D_1	S
1	3.647	0.127	28.72
2	3.612	0.128	28.20
3	0.477	0.023	20.74
4	2.442	0.284	8.60
5	1.832	0.283	6.47
6	2.535	0.134	11.53
7	2.398	0.150	15.97
8	0.510	0.019	26.84
9	3.495	0.089	39.27

[a] Composition range: 10 – 20 wt % of 2-propanol in water.

The results are listed in Table X.

Conclusions

A survey of the literature indicates that no LLE data are available for the present ternaries, except the water + 2-propanol + 1,2-dichloroethane system. Our tie-line data are in fair agreement, but the binodal curve compares well with those reported by Izmailov and Franke (*1*).

It appears that ternaries 4–7 represent type IC systems, whereas 1, 2, and 8 are considered type IB systems. Besides, ternaries 3 and 9 seem to be in the IC category rather than IB (*2*).

Unfortunately, in the determination of mutual solubilities for IC systems there is some loss of accuracy up to 50% in weight fraction of dissolved component.

It can be mentioned that no solutropic system was observed among the studied ternaries.

Industrial purposes usually require D_i values higher than 0.2 and separation factors higher than 10 (*3*, *4*). Therefore, the studied solvents may serve as separating agents for 2-propanol, except phenylmethanol, cyclohexanol, and 1-pentanol. The best results were obtained with dibenzyl ether and octanenitrile. Unfortunately, these are toxic and expensive solvents. Outstanding advantages of high-boiling solvents in separating substances from dilute aqueous solutions have recently been reported by some researchers (*5–8*). The solute will be the only overhead product if the solvent has a higher boiling point. With higher solvent/solute ratios, the energy consumption of stripping or distillation operations will be quite high if the solvent has a lower boiling point. Therefore, high-boiling solvents like 2-methylbutyl acetate and 1-methylcyclohexanol, showing very low solubility against water, are considered adequate separating agents for 2-propanol.

Glossary

W_i	weight percent of ith component
w_i	weight fraction of ith component
D_i	distribution coefficient of ith component, eq 1
S	separation factor, eq 2

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Equilibrium Diagrams at 20 °C of Water–Tartaric Acid–2-Methyl-1-propanol, Water–Tartaric Acid–1-Pentanol, and Water–Tartaric Acid–3-Methyl-1-butanol Ternary Systems

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The purpose of this work is to study the tartaric acid recovering possibilities from wine distillery wastewater through a liquid–liquid extracting process. 2-Methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol may be suitable as extracting solvents. Water–tartaric acid–alcohol ternary system solubility diagrams and tie lines were established at the temperature of 20 °C. Partition coefficients are comprised between 0.07 and 0.42. 1-Pentanol seems to be the best solvent to extract tartaric acid from regeneration of ion-exchanging resins.

Introduction

Tartaric acid is extracted from natural substances. It is an organic acid used as an acidulant in the food processing and pharmaceutical industries (*1*). In order to recover tartaric acid from wine distillery wastewater, which is present with a concentration of about 3.4 g/L (*2*, *3*), we considered the possibility of using the liquid–liquid extracting process.

The solvation character of oxygen atoms tied to the carbon chain lends especially to alcohols extracting properties with regard to acids. Thus we have selected 2-methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol.

Experimental Section

Chemicals. The solvents have been obtained with a purity of 98% (mass %) and the tartaric acid with a purity of 99% (mass %). The analysis by the high-performance liquid chromatography method bears out these purities.

Experimental Procedures. Solubility isotherms and tie-line data were determined with an experimental device comprising separatory funnels maintained at the constant temperature of 20 ± 0.1 °C in a thermostated vessel. Several tartaric acid solutions at different concentrations were prepared to determine the tie lines.

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