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Liquid−Liquid Equilibria for 2,3-Butanediol + Water + 4-(1-Methylpropyl)phenol + Toluene at 25 °C

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Liquid−liquid equilibria were measured at 25 °C for 2,3-butanediol + water + 4-(1-methylpropyl)phenol + toluene. The consistency of the results was checked with the Othmer−Tobias, Bachman, Hand, and Campbell correlations. Results show that distribution coefficients increase with an increase in the concentration of 4-(1-methylpropyl)phenol in toluene, but selectivity remains almost constant. A qualitative interpretation of the quaternary system 2,3-butanediol + water + 4-(1-methylpropyl)phenol + toluene is presented, as at certain concentrations a third phase is formed.

Introduction

2,3-Butanediol is a starting chemical for the production of solvents, polyurethane, synthetic fibers, and diacetyl, and is used as a foodstuff additive. Hydrogenation of 2,3-butanediol yields 1,3-butadiene, but this compound is usually produced more cheaply by the petrochemical route.

Glycols are chemicals with low volatility and strong hydrophilic characteristics, due to hydrogen bonds with water molecules, and hence, their recovery from aqueous solutions is difficult. Several routes have been attempted in order to remove glycols from aqueous solutions: (a) distillation and multiple-effect evaporation, which are very energy-intensive processes (b) physical extraction, which is not a very efficient method because of the low distribution coefficients (Othmer et al., 1945), (c) hybrid processes, involving reverse osmosis and distillation, which compare favorably with other methods (Sridhar, 1989), (d) salting-out with potassium carbonate (Afschar et al., 1993), and (e) reversible chemical complexation; organoboronates and aldehydes have been used recently as complexing agents (Randel et al., 1994; Broekhuis et al., 1994).

In previous work 2,4-dimethylphenol and 4-nonylphenol showed promising results as extractants for the recovery of 2,3-butanediol from aqueous solutions (Escudero et al., 1994). The low solubility of phenols in water, their acidic characteristics, and their low cost make them attractive as glycol extractants (Robbins, 1979). A rough estimation of the activity coefficients at infinite dilution for the system 2,3-butanediol + phenols, using the MOSCED model (Thomas and Eckert, 1984), shows that they are on the order of 0.24, a value well below those for other conventional solvents, which show a very poor extraction efficiency for 2,3-butanediol. However, many of these phenols have a high viscosity or are solid at room temperature, and hence a diluent is needed to dissolve the extractant.

In this work 4-(1-methylpropyl)phenol has been tested for the recovery of 2,3-butanediol from aqueous solutions at 25 °C. Because 4-(1-methylpropyl)phenol is a solid, it was dissolved in toluene at three different concentrations (200, 500, and 700 g·dm^{-3}).

Table 1. Physical Properties of the Chemicals: Density, ρ, Refractive Index, n_D, Solubility, S_{iw}, Solvent in Water, and S_{wi}, Water in Solvent, as Mass Fraction

chemical	property	exptl	lit.
2,3-butanediol (b)	ρ(293.15 K)/(g·cm^{-3})	1.0037	1.0033[a]
	n_D(298.15 K)	1.4352	1.4366[a]
	S_{bw}(293.15 K)	infinite	infinite[a]
	S_{wb}(293.15 K)	infinite	
4-(1-methylpropyl)phenol	ρ(293.15 K)/(g·cm^{-3})		0.9883[b]
	n_D(294.15 K)		1.5182[b]
	mp (K)		334.15−335.15[b]
toluene (t)	ρ(298.15 K)/(g·cm^{-3})	0.8623	0.86219[a]
	n_D(293.15 K)	1.4969	1.49693[a]
	S_{tw}(298.15 K)	0.0005	0.000515[a]
	S_{wt}(298.15 K)	0.0003	0.000334[a]

[a] Riddick et al. (1986). [b] Weast (1983).

Experimental Section

A. Chemicals. 2,3-Butanediol (Merck, synthesis grade) and 4-(1-methylpropyl)phenol (Aldrich, 4-*sec*-butylphenol in catalog, synthesis grade) were used as supplied by the manufacturers. Toluene (Probus, reagent grade) was further purified by vacuum distillation in a packed Oldershaw-type column, and water was bidistilled in an all-glass apparatus. 2,3-Butanediol was a mixture of the D-, L-, and meso-isomers. GLC analysis of the chemicals was done to test their purities using a gas chromatograph (Perkin-Elmer Model 990) equipped with a flame ionization detector. The chromatographic column was of stainless steel (2 m × 1/8 in.) and packed with Carbowax 20M (10% mass) on Chromosorb WHP (50/100 mesh) as the stationary phase. The operative conditions were injection temperature 250 °C, detector temperature 250 °C, column temperature 80 °C for toluene, 130 °C for 2,3-butanediol, and 160 °C for 4-(1-methylpropyl)phenol dissolved in toluene, and carrier gas N_2, 25 cm^3/min. Analysis showed a purity higher than 99% for 2,3-butanediol with a composition of about 14% for the DL-form and 85% for the meso-form, 93% for 4-(1-methylpropyl)phenol, and 99.99% for toluene. The accuracy in the estimation of the chemicals in mass fraction

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Table 2. Mutual-Solubility and Tie-Line Data for 2,3-Butanediol (1) + Water (2) + (4-(1-Methylpropyl)phenol + Toluene, 200 g·dm^{-3}) (3) at 25 °C as Mass Fraction, *w*

aqueous phase			organic phase		
w_{x1}	w_{x3}	w_{x2}	w_{y1}	w_{y3}	w_{y2}
Mutual-Solubility Data					
0.0000	0.0016	0.9984	0.0000	0.9942	0.0058
0.1019	0.0020	0.8961	0.1199	0.8617	0.0184
0.1948	0.0028	0.8024	0.1894	0.7831	0.0275
0.2929	0.0028	0.7043	0.2805	0.6891	0.0304
0.3983	0.0050	0.5967	0.3771	0.5996	0.0233
0.4880	0.0073	0.5047	0.4850	0.5003	0.0147
0.5858	0.0110	0.4032	0.5868	0.4025	0.0107
0.6805	0.0246	0.2949	0.6445	0.3436	0.0119
0.7855	0.0800	0.1345	0.7248	0.2508	0.0244
0.7903	0.0835	0.1262	0.7602	0.2011	0.0387
			0.7742	0.1816	0.0442
			0.7870	0.1538	0.0592
			0.7914	0.1378	0.0708
Tie-Line Data					
0.0200	0.0016	0.9784	0.0000	0.9942	0.0058
0.0470	0.0016	0.9514	0.0060	0.9880	0.0060
0.0950	0.0020	0.9030	0.0075	0.9860	0.0065
0.1200	0.0028	0.8772	0.0080	0.9850	0.0070
0.1800	0.0028	0.8172	0.0150	0.9800	0.0050
0.2400	0.0028	0.7572	0.0175	0.9760	0.0065
0.3530	0.0048	0.6422	0.0325	0.9590	0.0085
0.4400	0.0063	0.5537	0.0500	0.9400	0.0100
0.6550	0.0215	0.3235	0.0570	0.9300	0.0130
0.7700	0.0625	0.1675	0.0675	0.9175	0.0150

Table 3. Mutual-Solubility and Tie-Line Data for 2,3-Butanediol (1) + Water (2) + (4-(1-Methylpropyl)phenol + Toluene, 500 g·dm^{-3}) (3) at 25 °C as Mass Fraction, *w*

aqueous phase			organic phase		
w_{x1}	w_{x3}	w_{x2}	w_{y1}	w_{y3}	w_{y2}
Mutual-Solubility Data					
0.0000	0.0001	0.9999	0.0000	0.9898	0.0102
0.1018	0.0001	0.8981	0.0977	0.8836	0.0187
0.2430	0.0003	0.7567	0.1698	0.7890	0.0412
0.3317	0.0105	0.6578	0.2354	0.7065	0.0581
0.4643	0.0133	0.5224	0.3105	0.6095	0.0800
0.5254	0.0164	0.4582	0.3658	0.5244	0.1098
0.6119	0.0221	0.3660	0.4346	0.4441	0.1213
0.6619	0.0318	0.3063	0.4522	0.4249	0.1229
0.7005	0.0536	0.2459	0.4948	0.3897	0.1155
0.7231	0.0675	0.2094	0.5354	0.3661	0.0985
			0.5650	0.3457	0.0893
			0.5995	0.3062	0.0943
			0.6458	0.2644	0.0898
			0.6796	0.2238	0.0966
			0.7155	0.1758	0.1087
			0.7320	0.1455	0.1225
			0.7371	0.1141	0.1488
Tie-Line Data					
0.0450	0.0001	0.9549	0.0090	0.9800	0.0110
0.0700	0.0001	0.9299	0.0200	0.9700	0.0100
0.1250	0.0001	0.8749	0.0250	0.9620	0.0130
0.1460	0.0003	0.8537	0.0350	0.9540	0.0110
0.1700	0.0003	0.8297	0.0400	0.9475	0.0125
0.2100	0.0005	0.7895	0.0500	0.9350	0.0150
0.3375	0.0110	0.6515	0.1050	0.8730	0.0220
0.5100	0.0160	0.4740	0.1850	0.7730	0.0420
0.7070	0.0520	0.2410	0.2050	0.7450	0.0500

was ±1 × 10^{-4}. Physical properties of the chemicals are given in Table 1, along with literature values published by Riddick et al. (1986) or Weast (1983).

B. Methods. The extraction solvents consisted of a mixture of 4-(1-methylpropyl)phenol with toluene at concentrations of 200, 500, and 700 g·dm^{-3}. Mutual solubility data for the 2,3-butanediol + water + solvent systems were determined at (25 ± 0.05) °C by titration of a binary mixture of know composition with the third component until the onset of turbidity. The saturated mixture was weighted to determine the mass of component added. Analysis of the samples was made by measuring densities (Ostwald pycnometer, 3.9461 cm^3 volume, absolute error 0.0002 g·cm^{-3}) and refractive indices (PZO-RL2 Abbe type refractometer, 0.0002 division) at (26.00 ± 0.05) °C. Equilibrium data were determined by preparing ternary mixtures with a composition located within the two-phase region. Samples were shaken vigorously in thermostated settling cells, and kept for 12 h to ensure equilibrium was established. After settling, both phases were sampled and equilibrium compositions determined by refractometry and pycnometry.

Table 4. Mutual-Solubility and Tie-Line Data for 2,3-Butanediol (1) + Water (2) + (4-(1-Methylpropyl)phenol + Toluene, 700 g·dm^{-3}) (3) at 25 °C as Mass Fraction, *w*

aqueous phase			organic phase		
w_{x1}	w_{x3}	w_{x2}	w_{y1}	w_{y3}	w_{y2}
Mutual-Solubility Data					
0.0000	0.0014	0.9986	0.0000	0.9925	0.0075
0.0886	0.0015	0.9099	0.0991	0.8699	0.0310
0.1016	0.0016	0.8968	0.1880	0.7617	0.0503
0.1985	0.0017	0.7998	0.2821	0.6396	0.0783
0.3012	0.0026	0.6962	0.3206	0.5744	0.1050
0.3838	0.0057	0.6105	0.3551	0.5258	0.1191
0.4460	0.0068	0.5472	0.3729	0.4915	0.1356
0.4893	0.0100	0.5007	0.4021	0.4499	0.1480
0.5577	0.0130	0.4293	0.4380	0.3943	0.1677
0.6101	0.0210	0.3689	0.4710	0.3501	0.1789
0.6267	0.0322	0.3411	0.4918	0.3231	0.1851
0.6646	0.0371	0.2983	0.5169	0.3009	0.1822
0.6711	0.0494	0.2795	0.5448	0.2845	0.1707
			0.5824	0.2645	0.1531
			0.6014	0.2539	0.1447
			0.6366	0.2199	0.1435
			0.6704	0.1722	0.1574
			0.7015	0.1251	0.1734
			0.7019	0.0725	0.2256
Tie-Line Data					
0.0250	0.0014	0.9736	0.0040	0.9900	0.0060
0.0350	0.0014	0.9636	0.0050	0.9890	0.0060
0.0650	0.0014	0.9336	0.0150	0.9750	0.0100
0.1150	0.0016	0.8834	0.0330	0.9530	0.0140
0.2150	0.0020	0.7830	0.0750	0.9020	0.0230
0.3550	0.0040	0.6410	0.1400	0.8200	0.0400
0.5050	0.0100	0.4850	0.2300	0.7100	0.0600
0.6150	0.0230	0.3620	0.3040	0.6050	0.0910

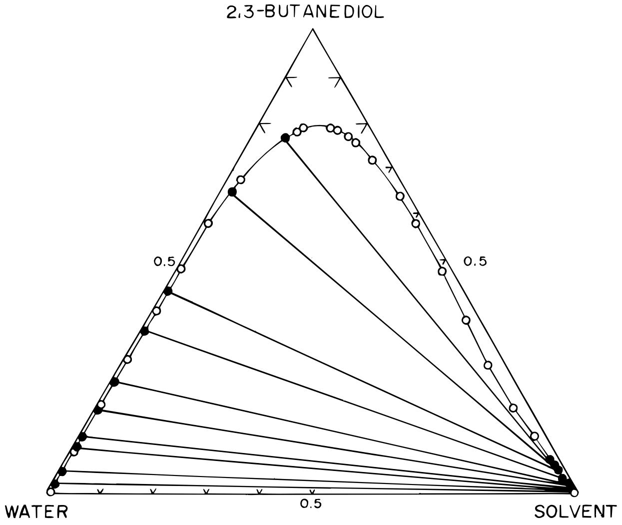

Figure 1. Binodal curve (○) and tie lines (●) for the system 2,3-butanediol + water + (4-(1-methylpropyl)phenol + toluene, 200 g·dm^{-3}) at 25 °C, as mass fraction.

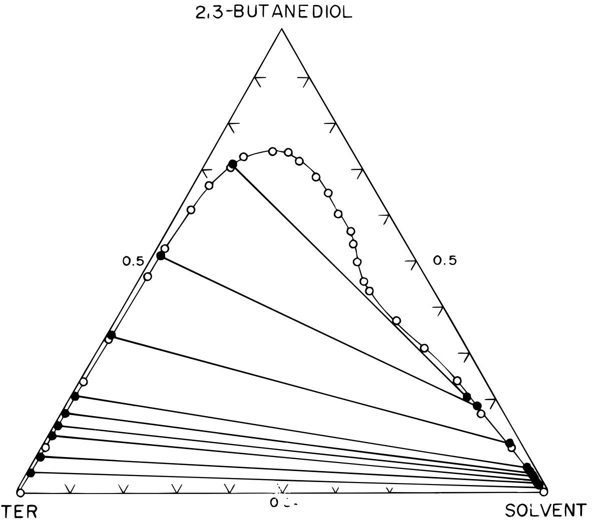

Figure 2. Binodal curve (○) and tie lines (●) for the system 2,3-butanediol + water + (4-(1-methylpropyl)phenol + toluene, 500 g·dm^{-3}) at 25 °C, as mass fraction.

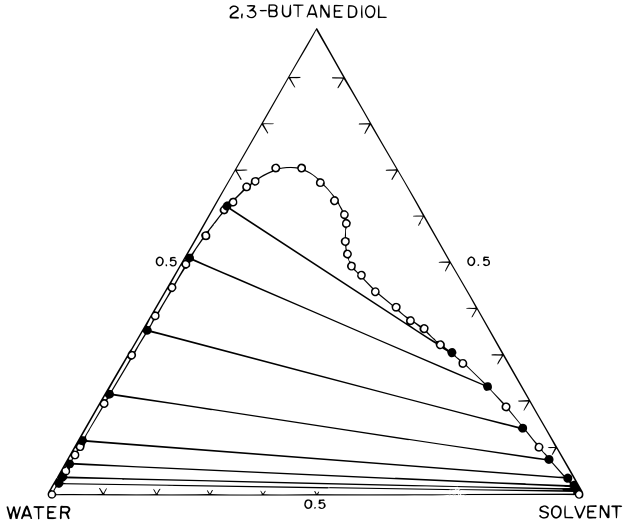

Figure 3. Binodal curve (○) and tie lines (●) for the system 2,3-butanediol + water + (4-(1-methylpropyl)phenol + toluene, 700 g·dm^{-3}) at 25 °C, as mass fraction.

The estimated error in the final tie-line data from mass balance was less than 0.001 mass fraction.

Results and Discussion

Mutual solubillity and tie-line results for water + 2,3-butanediol + 4-(1-methylpropyl)phenol + toluene at 25 °C are listed in Tables 2−4 for concentrations of 200, 500, and 700 g·dm^{-3} toluene, and the ternary diagrams are shown in Figures 1−3.

The mixture 4-(1-methylpropyl)phenol + toluene shows a rather low capacity as an extractant for 2,3-butanediol,

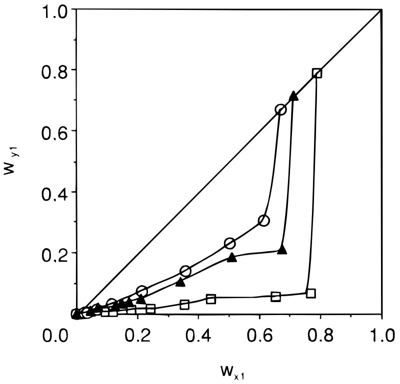

Figure 4. Equilibrium distribution diagrams for 2,3-butanediol + water + (4-(1-methylpropyl)phenol + toluene) for the solvent concentrations (□) 200 g·dm^{-3}, (▲) 500 g·dm^{-3}, and (○) 700 g·dm^{-3}, at 25 °C.

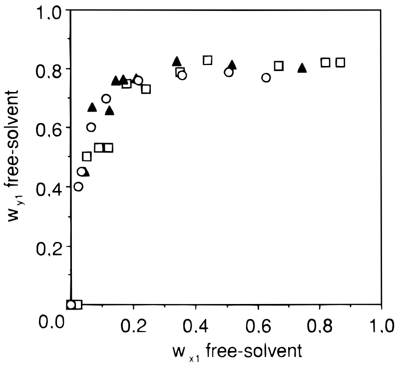

Figure 5. Selectivity diagram on solvent-free basis for the system 2,3-butanediol + water + (4-(1-methylpropyl)phenol + toluene) for the solvent concentrations (□) 200 g·dm^{-3}, (▲) 500 g·dm^{-3}, and (○) 700 g·dm^{-3}, at 25 °C.

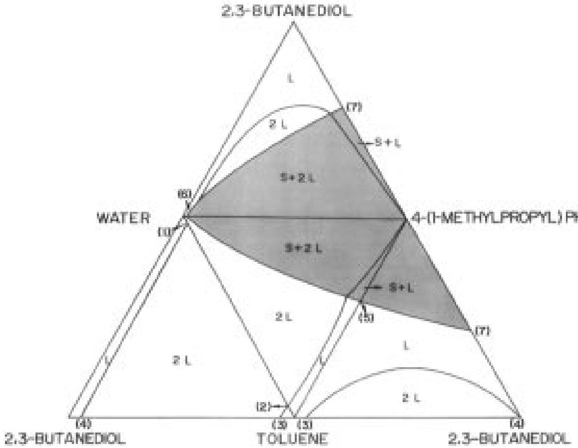

Figure 6. Ternary equilibria (estimated) for the quaternary system 2,3-butanediol + water + 4-(1-methylpropyl)phenol + toluene and experimental mutual solubility data at 25 °C: S, solid phase; L, liquid phase; 2, two phases.

Table 5. Mutual Solubility of Binary Systems at 25 °C as Mass Fraction

binary system	exptl	lit.	point in Figure 6
toluene (t) + water (w)		$S_{tw} = 0.0005^a$	1
		$S_{wt} = 0.0003^a$	2
2,3-butanediol (b) + toluene (t)	$S_{bt} = 0.0076$		3
	$S_{tb} = 0.0096$		4
4-(1-methylpropyl)phenol (p) = toluene (t)	$S_{pt} = 0.6525$		5
4-(1-methylpropyl)phenol (p) + water (w)	$S_{pw} = 0.0004$		6
2,3-butanediol (b) + water (w)		S_{bw} = infinite^a	
4-(1-methylpropyl)phenol (p) + 2,3-butanediol (b)	$S_{pb} = 0.3928$		7

[a] Weast (1983).

and the capacity increases as the concentration of 4-(1-methylpropyl)phenol increases, as shown in Figure 4. Selectivities are practically the same for the three systems on a solvent-free basis, as shown in Figure 5. Emulsions formed by the ternary system tend to be more stable as the concentratrion of phenol increases in the extractant mixture.

The consistency of equilibrium data was tested by the Bachman, Campbell, Hand, and Othmer−Tobias methods (Laddha and Degaleesan, 1978). All methods gave good correlations for the equilibrium distribution data; the largest deviations were found for the lower extractant concentration, i.e., 200 g·dm^{-3}. Plait points were determined by Treybal's method (Laddha and Degaleesan, 1978); their values given in mass fraction of 2,3-butanediol for the three 4-(1-methylpropyl)phenol + toluene systems were the following: 200 g·dm^{-3}, 0.7890; 500 g·dm^{-3}, 0.7150; 700 g·dm^{-3}, 0.6700.

The binodal curves show a warp which is relatively slight for the less concentrated solvent but increases strongly at higher concentrations of phenol. This warp moves toward higher concentrations of 2,3-butanediol as the concentration of extractant in the diluent increases, as shown in Figures 1−3. The convex region could result from the presence of solid 4-(1-methylpropyl)phenol in the system, but this was not observed visually in the concentration range investigated.

It is possible from the reported equilibrium data and mutual solubilities of the binary mixtures involved in the extraction system, Table 5, to obtain a qualitative quaternary solubility diagram, which is shown in Figure 6.

Distribution coefficients and selectivities for the system 2,3-butanediol + water + 4-(1-methylpropyl)phenol + toluene are in the range of values reported for the extraction of alcohols and acids with alcohols (Cabral, 1991) but are lower than those obtained at 40 °C for 2,4-dimethylphenol ($K_D = 1.89-1.01$), nonylphenol ($K_D = 0.60-0.70$), and 4-nonylphenol + toluene (2:1 volume ratio) ($K_D = 0.21-0.65$) (Escudero et al., 1994).

Nomenclature

K_D = distribution coefficient, W_{y1}/W_{x1}
W_x = mass fraction in the aqueous phase
W_y = mass fraction in the organic phase
n_D = refractive indice
m_p = melting point
S_{ij} = mutual solubility of component i in component j, as mass fraction

Subscripts

1 = 2,3-butanediol
2 = water
3 = solvent (mixtures of 4-(1-methylpropyl)phenol + toluene)

Registry Numbers Supplied by the Authors. 2,3-Butanediol, 513-85-9; 4-(1-methylpropyl)phenol, 99-71-8; toluene, 108-88-3.

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