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Liquid–Liquid Equilibrium for 2,3-Butanediol + Water + Organic Solvents

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Liquid–liquid equilibrium has been measured for 2,3-butanediol + water + solvents (trichloroethylene, tetrachloroethylene, 2,4-dimethylphenol, 4-nonylphenol, and 4-nonylphenol + toluene) at 25 °C for chlorinated hydrocarbons and at 40 °C for phenolic solvents. The consistency of the results for phenolic solvents was checked with the Othmer–Tobias, Bachman, Hand, and Campbell correlations. UNIQUAC and NRTL equations were used to correlate the results for 2,4-dimethylphenol and the NRTL equation for the results with 4-nonylphenol. The 4-nonylphenol + toluene system gives the best distribution coefficient for the systems tested. Back-extraction of 2,3-butanediol was carried out by contacting the organic phase containing the solvent with NaOH.

Introduction

The production of 2,3-butanediol by fermentation has been considered as a potencial source of fuels (*1*, *2*) or chemical feedstock (*3*) from renewable resources of biomass and waste products. Biomass conversion (hemicellulose, starch, molasses, citrus wastes, etc.) yields xylose as the major product, which can be converted as well as glucose to 2,3-butanediol. Whey is a major byproduct of the dairy industry which is considered a poor substrate for 2,3-butanediol fermentation (*4*), but whey permeate can be fermented to 2,3-butanediol using immobilized cell systems (*5*, *6*).

One of the problems for the production of 2,3-butanediol by fermentation is its economic recovery from the fermentation broth. Distillation is too expensive, as solutions are very dilute and steam distillation is not very efficient because of the low vapor pressure of 2,3-butanediol. An alternative approach for 2,3-butanediol recovery is liquid–liquid extraction, and Othmer (*7*) suggested the use of 1-butanol, butyl acetate, butylene glycol diacetate, and methylvinylcarbinol acetate as extractants. However, solvents with better selectivity and lower solubility in water are desired for more efficient separation.

It has also been suggested that separation of 2,3-butanediol from fermentation broths by reverse osmosis followed by distillation compares economically favorably with respect to other conventional methods (*8*).

In this study two types of solvents were investigated for the extraction of 2,3-butanediol from aqueous solutions. The first were the chlorinated compounds trichloroethylene and tetrachloroethylene, and the second were phenolic compounds 2,4-dimethylphenol, 4-nonylphenol, and a mixture of 4-nonylphenol with toluene as diluent (2:1 in volume). Although typical concentrations of 2,3-butanediol in fermentation broths should be lower than 10 g•dm^{-3} in order to avoid inhibition of the fermenting microorganism, the liquid–liquid equilibrium data have been obtained over the whole range of concentration.

Table 1. Density, ϱ, Refractive Index, n_D, and Solubility, S_3 (Solvent in Water) and S_2 (Water in Solvent), as Mass Fraction

chemical	property	exptl	lit.	ref
2,3-butanediol	ϱ(293.15 K)/(g·cm^{-3})	1.0037	1.0033	19
	n_D(298.15 K)	1.4852	1.4366	19
	S_3(193.15 K)	infinite	infinite	19
	S_2(293.15 K)	infinite		
trichloroethylene	ϱ(293.15 K)/(g·cm^{-3})	1.4642	1.4642	20
	n_D(293.15 K)	1.4773	1.4773	20
	S_3(298.15 K)	0.0017	0.00137	19
	S_2(298.15 K)	0.0038	0.00320	19
tetrachloroethylene	ϱ(293.15 K)/(g·cm^{-3})	1.6230	1.6228	19
	n_D(293.15 K)	1.5058	1.50576	19
	S_3(298.15 K)	0.0002	0.000150	19
	S_2(298.15 K)	0.0001	0.000105	19
toluene	ϱ(198.15 K)/(g·cm^{-3})	0.8623	0.86219	19
	n_D(293.15 K)	1.4969	1.49693	19
	S_3(298.15 K)	0.0005	0.000515	19
	S_2(298.15 K)	0.0003	0.000334	19
4-nonylphenol	ϱ(293.15 K)/(g·cm^{-3})	0.9493		
	n_D(293.15 K)	1.5108		
	S_3(313.15 K)	0.0007		
	S_2(313.15 K)	0.0272		
2,4-dimethylphenol	ϱ(293.15 K)/(g·cm^{-3})	1.0117	0.9650	20
	n_D(287.15 K)		1.5420	20
	n_D(299.15 K)	1.5372		
	S_3(313.15 K)	0.0086		
	S_3(298.15 K)		0.00787	19
	S_2(313.15 K)	0.0833		

Experimental Section

A. Chemicals. 2,3-Butanediol (Merck, synthesis grade), 2,4-dimethylphenol (Merck, synthesis grade), and 4-nonylphenol (Aldrich) were used as supplied by the manufacturers. 2,3-Butanediol was a mixture of the *d*-, *l*- and *meso*-isomers, and chromatographic analysis showed a purity higher than 97 mass %. 2,4-Dimethylphenol had an 8 mass % content of 2,5-dimethylphenol, but no separation by distillation was performed because of the close boiling points of both isomers. 4-Nonylphenol was a mixture of ring and chain isomers with a purity higher than 0.98 mass fraction.

Trichloroethylene (Fluka, >99%, GC), tetrachloroethylene (Fluka, >99%, GC), and toluene (Panreac, >98%, GC)

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Table 2. Mutual Solubility and Tie Lines for 2,3-Butanediol (1) + Water (2) + Tetrachloroethylene (3) at 25 °C as Mass Fraction *w*

Mutual Solubility

aqueous phase			organic phase		
w_1	w_3	w_2	w_1	w_3	w_2
0.0000	0.0002	0.9998	0.0066	0.9934	0.0000
0.1574	0.0002	0.8424	0.7789	0.2211	0.0000
0.2582	0.0008	0.7410	0.0000	0.9998	0.0002
0.3724	0.0038	0.6238			
0.5229	0.0051	0.4720			
0.5724	0.0075	0.4201			
0.6666	0.0126	0.3208			
0.7362	0.0241	0.2397			
0.7715	0.0376	0.1909			
0.8153	0.0625	0.1222			
0.8257	0.0863	0.0880			
0.8271	0.1334	0.0395			
0.8115	0.1706	0.0179			

Tie Lines

aqueous phase			organic phase		
w_1	w_3	w_2	w_1	w_3	w_2
0.0750	0.0002	0.9248	0.0000	0.9999	0.0001
0.2250	0.0004	0.7746	0.0000	0.9999	0.0001
0.3250	0.0025	0.6725	0.0000	0.9999	0.0001
0.4300	0.0040	0.5660	0.0000	0.9999	0.0001
0.6000	0.0075	0.3925	0.0000	0.9999	0.0001
0.7250	0.0230	0.2520	0.0000	0.9999	0.0001

were further purified by vacuum distillation in a packed Oldershaw-type column. The physical properties of the chemicals are given in Table 1.

B. Methods. Mutual solubility for 2,3-butanediol + water + solvent was determined at 25 ± 0.05 °C for trichloroethylene and tetrachloroethylene and at 40 ± 0.05 °C for 2,4-dimethylphenol and 4-nonylphenol. When toluene was used as the diluent of 4-nonylphenol, the solvent mixture consisted of 68.57 mass % 4-nonylphenol and 31.43 mass % toluene. Mutual solubility results were obtained by titration of binary mixtures of known composition with the third component until the onset of turbidity. The mass of the saturated mixture allowed the mass of the third component to be determined. A chromatographic analysis of the samples was made, and refractive indices were determined at 26 ± 0.05 °C for the chlorinated solvents and at 41 ± 0.05 °C for 2,4-dimethylphenol as solvent. With 4-nonylphenol a density and refractometry analysis at 41 ± 0.05 °C was carried out, and with the mixture 4-nonylphenol + toluene only a refractometry analysis at this temperature was made.

Equilibrium results were determined by preparing ternary mixtures with a known composition located within the two-phase region. The samples were shaken in thermostated settling cells, and kept for 12 h (24 h in the case of the 4-nonylphenol) to reach equilibrium between the two phases. After settling, both phases were sampled and equilibrium compositions determined by gas–liquid chromatography (Perkin-Elmer Model 990 gas chromatograph with flame ionization detector), refractometry (PZO-RL2 Abbe-type refractometer, 0.0002 division), and/or densitometry (Ostwald picnometer, 3.9461 cm^3 volume, absolute error 0.0002). The chromatographic column was of stainless steel (3 m × 1/8 in.) and packed with Carbowax 1500, 15 mass %, on Chromosorb WHP (50–80 mesh) as the stationary phase. The column temperature was 130 °C for chlorinated solvents and 170 °C for 2,4-dimethylphenol. The standard deviation for chromatographic composition was estimated as 0.001 mass fraction of 2,3-butanediol.

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

Table 3. Mutual Solubility and Tie Lines for 2,3-Butanediol (1) + Water (2) + Trichloroethylene at 25 °C as Mass Fraction *w*

Mutual Solubility

aqueous phase			organic phase		
w_1	w_3	w_2	w_1	w_3	w_2
0.0000	0.0017	0.9983	0.6904	0.2155	0.0941
0.2008	0.0053	0.7939	0.6741	0.2540	0.0719
0.3112	0.0070	0.6818	0.6105	0.3481	0.0414
0.4048	0.0076	0.5876	0.5786	0.3876	0.0338
0.5086	0.0113	0.4801	0.5226	0.4531	0.0243
0.6186	0.0315	0.3499	0.4372	0.5503	0.0125
0.6812	0.0580	0.2608	0.4067	0.5820	0.0113
0.7130	0.1435	0.1435	0.3292	0.6640	0.0068
0.7057	0.0976	0.1967	0.2986	0.6959	0.0055
			0.2699	0.7182	0.0119
			0.2164	0.7794	0.0042
			0.1982	0.8010	0.0008
			0.1148	0.8834	0.0018
			0.0000	0.9962	0.0038

Tie Lines

aqueous phase			organic phase		
w_1	w_3	w_2	w_1	w_3	w_2
0.0700	0.0045	0.9255	0.0000	0.9962	0.0038
0.0950	0.0050	0.9000	0.0000	0.9962	0.0038
0.4775	0.0080	0.5145	0.0050	0.9930	0.0020
0.5250	0.0140	0.4610	0.0080	0.9900	0.0020
0.7150	0.1250	0.1600	0.0175	0.9770	0.0055

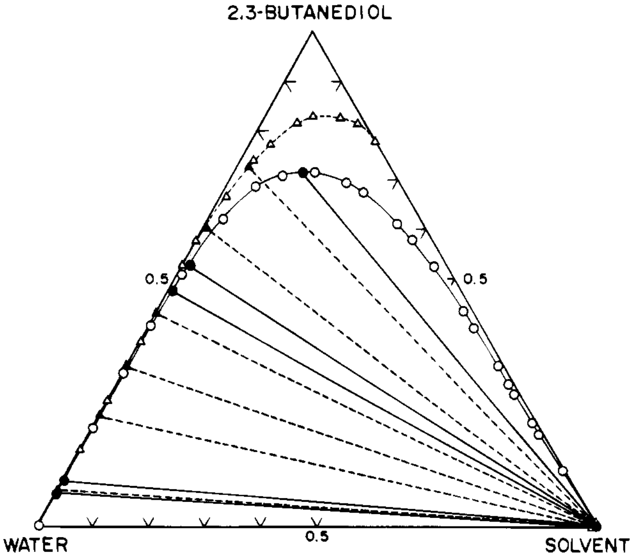

Figure 1. Liquid–liquid equilibria for the systems 2,3-butanediol + water + chlorinated solvents at 25 °C as mass fraction: (△) experimental binodal curve with tetrachloroethylene, (○) experimental binodal curve with trichloroethylene, (▲) experimental tie line with tetrachloroethylene, (●) experimental tie line with trichloroethylene.

Results and Discussion

A. Solvent Selection. A suitable solvent of a fermentation product must have a high capacity for the solute and a high selectivity against water. The solvent cost and other solvent properties are also of paramount importance (*9*).

Empirical solvent selection is usually based on solute–solvent interactions based on the possibility of a liquid being able to form hydrogen bonds. 2,3-Butanediol forms hydrogen bonds and is very hygroscopic, which suggests a strong interaction with water, typical of the diol compounds. Following Robbins' solute–solvent classification (*10*), acids and aromatic hydroxyl compounds are potential solvents for 2,3-butanediol. Other Lewis acids such as chlorinated hydrocarbons could also extract 2,3-butanediol

Table 4. Mutual Solubility and Tie Lines for 2,3-Butanediol (1) + Water (2) + 2,4-Dimethylphenol (3) as Mass Fraction *w*, Distribution Coefficient (K_D), and Selectivity (β) at 40 °C

Mutual Solubility

aqueous phase			organic phase		
w_1	w_3	w_2	w_1	w_3	w_2
0.0000	0.0086	0.9914	0.3080	0.3516	0.3404
0.0596	0.0093	0.9311	0.3053	0.3763	0.3184
0.0754	0.0100	0.9146	0.2948	0.4190	0.2862
0.1016	0.0118	0.8866	0.2560	0.5288	0.2152
0.1732	0.0157	0.8111	0.1995	0.6367	0.1638
0.2370	0.0238	0.7392	0.1279	0.7461	0.1260
0.2978	0.0607	0.6415	0.1019	0.7832	0.1149
0.3068	0.1056	0.5876	0.0607	0.8360	0.1033
0.3152	0.1836	0.5012	0.0000	0.9107	0.0893
0.3149	0.2476	0.4375			

Tie Lines

aqueous phase			organic phase				
w_1	w_3	w_2	w_1	w_3	w_2	K_D	β
0.0180	0.0086	0.9734	0.0340	0.8680	0.0980	1.89	18.77
0.0550	0.0080	0.9370	0.0700	0.8230	0.1070	1.27	11.12
0.0635	0.0090	0.9275	0.0780	0.8145	0.1075	1.23	10.61
0.0960	0.0100	0.8940	0.1060	0.7745	0.1195	1.10	8.23
0.1430	0.0130	0.8440	0.1475	0.7160	0.1365	1.03	6.37
0.2660	0.0360	0.6980	0.2675	0.4980	0.2345	1.01	3.01
0.2998	0.0615	0.6303	0.3010	0.4025	0.2965	1.01	2.17

(*11*). On the basis of the former considerations and reported data on 1-butanol extraction (*12*, *13*), the following solvents were selected: trichloroethylene, tetrachloroethylene, 2,4-dimethylphenol, and 4-nonylphenol. 4-Nonylphenol has a rather high viscosity to be used as the extraction solvent, and hence, experiments were also carried out with 4-nonylphenol dissolved in toluene as diluent.

B. Equilibrium Measurements. Mutual solubility and tie-line results for aqueous solutions of 2,3-butanediol with trichloroethylene and tetrachloroethylene at 25 °C are listed in Tables 2 and 3, respectively, and shown in Figure 1.

Mutual solubility and tie-line results for aqueous solutions of 2,3-butanediol with 2,4-dimethylphenol, 4-nonylphenol, and 4-nonylphenol + toluene at 40 °C are listed in Tables 4–6, respectively, and shown in Figures 2–4.

The chlorinated solvents show a practically null capacity as extractants for 2,3-butanediol, as could be expected from their very low polarity. Trichloroethylene shows a very slight capacity probably because of its small polarity (μ = 1.10 D). These results follow the same trend when chlorinated compounds are used for the extraction of ethanol: they show high selectivities (β = 50–150) but very poor distribution coefficients (K_D = 0.02–0.12) (*14*).

For the phenolic extractants of 2,3-butanediol from dilute solutions, the distribution coefficients follow the order 2,4-dimethylphenol > 4-nonylphenol > 4-nonylphenol + toluene. Selectivities are in the order 4-nonylphenol > 4-nonylphenol + toluene > 2,4-dimethylphenol, but at higher concentrations of 2,3-butanediol, the solvent nonylphenol + toluene shows higher selectivities than 4-nonylphenol, as shown in Figure 5.

The consistency of the data was tested by the Bachman, Campbell, Hand, and Othmer–Tobias (*15*) methods. All methods gave good correlations for the equilibrium distribution data, the largest deviations being found for the system 2,3-butanediol + water + 4-nonylphenol with the Bachman method. Plait points were determined by Treybal's method (*15*); the following values given in 2,3-butanediol mass fraction for the three solvents were obtained: 2,4-dimethylphenol, 0.295; 4-nonylphenol, 0.473; 4-nonylphenol + toluene, 0.516.

Table 5. Mutual Solubility and Tie Lines for 2,3-Butanediol (1) + Water (2) + 4-Nonylphenol (3) as Mass Fraction *w*, Distribution Coefficient (K_D), and Selectivity (β) at 40 °C

Mutual Solubility

aqueous phase			organic phase		
w_1	w_3	w_2	w_1	w_3	w_2
0.0000	0.0007	0.9993	0.4777	0.2750	0.2473
0.0356	0.0025	0.9619	0.4657	0.3031	0.2312
0.0505	0.0036	0.9459	0.4355	0.3691	0.1954
0.1041	0.0040	0.8919	0.4280	0.3823	0.1897
0.1417	0.0041	0.8542	0.3969	0.4344	0.1687
0.1711	0.0042	0.8247	0.3884	0.4501	0.1615
0.2339	0.0044	0.7617	0.3753	0.4750	0.1498
0.2868	0.0048	0.7084	0.3441	0.5249	0.1310
0.3231	0.0047	0.6722	0.3208	0.5570	0.1222
0.3861	0.0051	0.6088	0.2963	0.5920	0.1117
0.4127	0.0051	0.5822	0.2643	0.6373	0.0984
0.4684	0.0052	0.5264	0.2232	0.7011	0.0756
0.5210	0.0054	0.4736	0.1885	0.7469	0.0664
0.5425	0.0111	0.4464	0.1497	0.7987	0.0516
0.5509	0.0322	0.4169	0.1173	0.8404	0.0423
0.5543	0.0462	0.3995	0.0900	0.8719	0.0381
0.5531	0.0623	0.3846	0.0445	0.9260	0.0295
0.5543	0.0798	0.3659	0.0000	0.9728	0.0272
0.5300	0.1497	0.3203			
0.5128	0.1934	0.2938			
0.4924	0.2386	0.2690			

Tie Lines

aqueous phase			organic phase				
w_1	w_3	w_2	w_1	w_3	w_2	K_D	β
0.0250	0.0020	0.9730	0.0150	0.9570	0.0280	0.60	20.85
0.0700	0.0037	0.9263	0.0450	0.9250	0.0300	0.64	19.85
0.1225	0.0040	0.8735	0.0750	0.8900	0.0350	0.61	15.27
0.1800	0.0042	0.8158	0.1100	0.8500	0.0400	0.61	12.46
0.2350	0.0045	0.7605	0.1400	0.8125	0.0475	0.60	9.54
0.3130	0.0046	0.6824	0.1750	0.7650	0.0600	0.56	6.36
0.3700	0.0050	0.6250	0.2230	0.7000	0.0770	0.60	4.89
0.4400	0.0052	0.5548	0.2770	0.6230	0.1000	0.63	3.49
0.4925	0.0053	0.5022	0.3460	0.5240	0.1300	0.70	2.71

Liquid–liquid equilibrium data were also correlated by the multicomponent expressions for the activity coefficient NRTL equation (*16*) for the systems with 2,4-dimethylphenol and 4-nonylphenol, and the UNIQUAC equation (*17*) for the system with 2,4-dimethylphenol. The NRTL and UNIQUAC equations contain six binary parameters which were estimated by a nonlinear regression method based on the maximum-likelihood principle (*18*) from the equilibrium data. The nonrandomness parameter in the NRTL equation was kept constant, α_{12} = 0.2, in all cases. The size parameter, *r*, and surface parameter, *q*, used in the UNIQUAC model are the following: for water r = 0.9200, q = 1.400; for 2,3-butanediol r = 3.7560, q = 3.320; for 2,4-dimethylphenol r = 5.0217, q = 3.816.

The goodness of fit was measured by the root-mean-squared deviation or residual function, *F* (mol %):

$$F = 100[\sum_k \min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2/6M]^{1/2}$$

where x and $\hat{x}$ are the experimental mole fraction of the liquid phase and the mole fraction of the predicted tie line lying close to the considered experimental tie line, respectively, and M is the number of tie lines. Table 7 shows the interaction parameter values and their root-mean-squared deviation. There is good agreement between the correlated and experimental data as shown in Figures 6 and 7.

Distribution coefficients and selectivities are in a range similar to that reported for the extraction of ethanol with

Table 6. Mutual Solubility and Tie Lines for 2,3-Butanediol (1) + Water (2) + (4-Nonylphenol + Toluene) (3) as Mass Fraction w, Distribution Coefficient (K_D), and Selectivity (β) at 40 °C

Mutual Solubility

aqueous phase			organic phase		
w_1	w_3	w_2	w_1	w_3	w_2
0.0000	0.0017	0.9983	0.5210	0.2616	0.2174
0.0997	0.0021	0.8982	0.5116	0.2813	0.2071
0.1559	0.0021	0.8420	0.4997	0.3053	0.1950
0.1911	0.0025	0.8064	0.4791	0.3389	0.1820
0.2235	0.0030	0.7735	0.4371	0.4169	0.1460
0.2816	0.0030	0.7154	0.4104	0.4510	0.1386
0.3200	0.0031	0.6769	0.3931	0.4785	0.1284
0.3902	0.0031	0.6067	0.3825	0.5014	0.1161
0.4584	0.0043	0.5373	0.3337	0.5709	0.0954
0.4744	0.0046	0.5210	0.3078	0.6083	0.0839
0.5215	0.0062	0.4723	0.2865	0.6379	0.0756
0.5461	0.0086	0.4453	0.2774	0.6500	0.0726
0.5638	0.0096	0.4266	0.2371	0.6987	0.0642
0.5737	0.0146	0.4117	0.1969	0.7555	0.0476
0.5985	0.0153	0.3862	0.1519	0.8066	0.0415
0.6044	0.0868	0.3088	0.1428	0.8167	0.0405
0.5667	0.1762	0.2571	0.1189	0.8528	0.0283
			0.0899	0.8846	0.0255
			0.0564	0.9149	0.0287
			0.0468	0.9322	0.0210
			0.0221	0.9555	0.0224
			0.0000	0.9804	0.0196

Tie Lines

aqueous phase			organic phase				
w_1	w_3	w_2	w_1	w_3	w_2	K_D	β
0.0600	0.0020	0.9380	0.0125	0.9700	0.0175	0.21	11.17
0.1710	0.0025	0.8265	0.0400	0.9400	0.0200	0.23	9.67
0.3030	0.0031	0.6939	0.1030	0.8685	0.0285	0.34	8.28
0.4100	0.0040	0.5860	0.1600	0.8000	0.0400	0.39	5.71
0.4900	0.0049	0.5051	0.2200	0.7250	0.0550	0.45	4.12
0.5630	0.0096	0.4274	0.3100	0.6050	0.0850	0.55	2.77
0.6070	0.0450	0.3480	0.3950	0.4760	0.1290	0.65	1.76

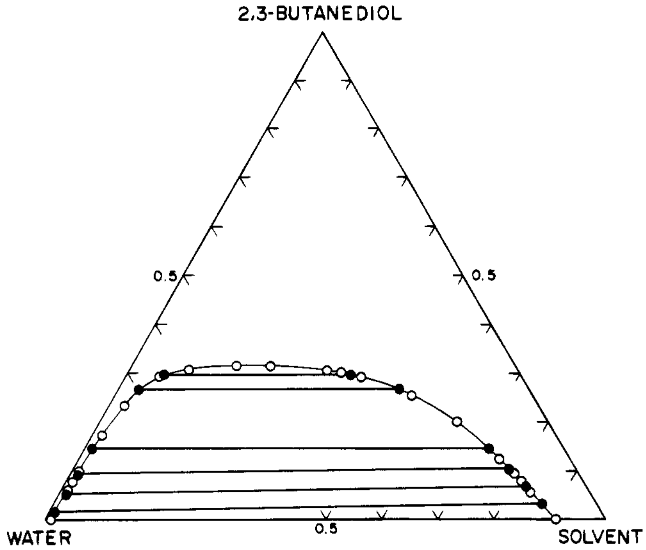

Figure 2. Binodal curve (○) and and tie lines (●) for the system 2,3-butanediol + water + 2,4-dimethylphenol at 40 °C as mass fraction.

alcohols (*11*), but are much lower than those reported for the extraction of 1-butanol with *p*-butylphenol (*13*). The results reported here were obtained at 40 °C, while the results for *p*-butylphenol were reported at 18 °C.

2,4-Dimethylphenol and 4-nonylphenol showed a tendency to form emulsions when contacted with aqueous solutions of 2,3-butanediol. For 2,4-dimethylphenol, emulsions were quite stable in the range of 0.15–0.25 mass fraction of 2,3-butanediol in the aqueous phase, and therefore extraction was not possible in that range of concentration. Furthermore, this system showed an isopicnic tie line for 0.20 mass fraction of 2,3-butanediol in the aqueous phase.

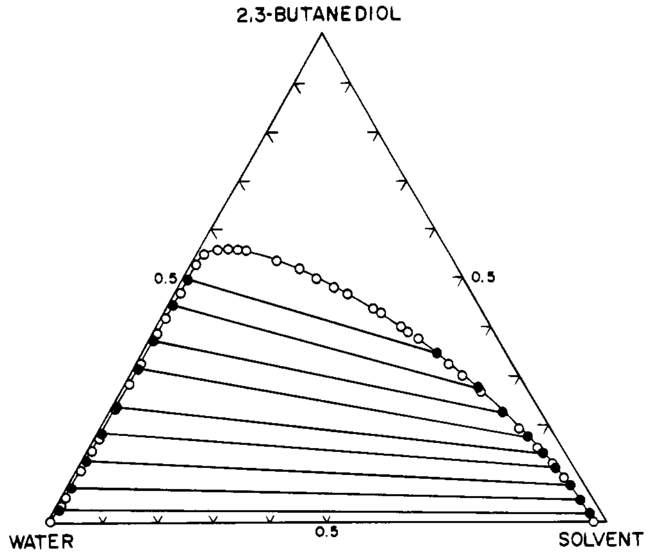

Figure 3. Binodal curve (○) and tie lines (●) for the system 2,3-butanediol + water + 4-nonylphenol at 40 °C as mass fraction.

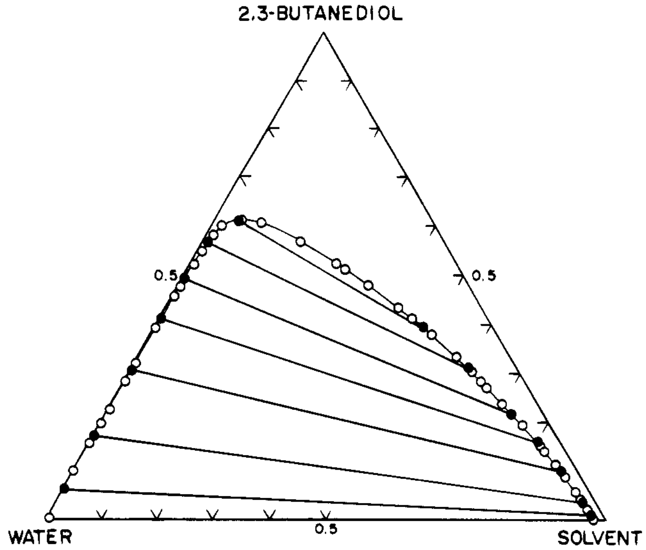

Figure 4. Binodal curve (○) and tie lines (●) for the system 2,3-butanediol + water + (4-nonylphenol + toluene) at 40 °C as mass fraction.

Densities and viscosities of the extraction streams are useful for the design and operation of an extractor. In order to decrease the 4-nonylphenol viscosity, toluene was used as the diluent and measurements were made at 40 °C. Densities, viscosities, and mutual solubilities in water for some of the extraction mixtures are reported in Table 8.

Toluene has a very low capacity for extracting 2,3-butanediol, and as the diluent of 4-nonylphenol, in a volume ratio of 2:1, it decreases the extraction capacity of 4-nonylphenol. The extraction of 2,3-butanediol by 4-nonylphenol can probably be attributed to the solvation of the solute with the carbon-bonded oxygen donor extractant; the presence of toluene, a nonpolar compound, weakens the strong hydrogen bonding properties of the phenol and favors the $\pi-\pi$ interaction, characteristic of aromatic compounds.

C. Solvent Recovery. Solvent recovery is an integral part of the extraction process, which in some cases presents serious difficulties. One of the advantages of phenolic extractants is that they can easily be recovered from the

Table 7. UNIQUAC and NRTL Interaction Parameter Values and Root-Mean-Squared Deviation

		UNIQUAC		NRTL	
component *I*	component *J*	*A*(*IJ*)	*A*(*JI*)	*A*(*IJ*)	*A*(*JI*)
water	2,3-butandeiol	−326.58	83.555	−2952.7307	49.1826
water	2,4-dimethylphenol	590.59	−119.250	1968.5306	−246.8879
2,3-butanediol	2,4-dimethylphenol	−167.47	21.255	−694.5640	−2917.6688

room-mean-squared deviation for UNIQUAC 0.3971

root-mean-squared deviation for NRTL 0.8340

component *I*	component *J*	*A*(*IJ*)	*A*(*JI*)
water	2,3-butanediol	742.0784	−887.4262
water	4-nonylphenol	1686.4289	27.9391
2,3-butanediol	4-nonylphenol	36064.8239	−1616.3369

root-mean-squared deviation for NRTL 1.8186

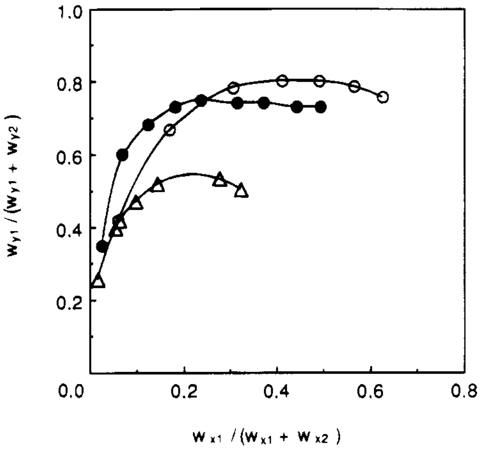

Figure 5. Selectivity diagram on a free-solvent basis for the systems 2,3-butanediol (1) + water (2) + phenolic solvents (3) at 40 °C as mass fraction. Solvents: (△) 2,4-dimethylphenol, (●) 4-nonylphenol, and (○) 4-nonylphenol + toluene.

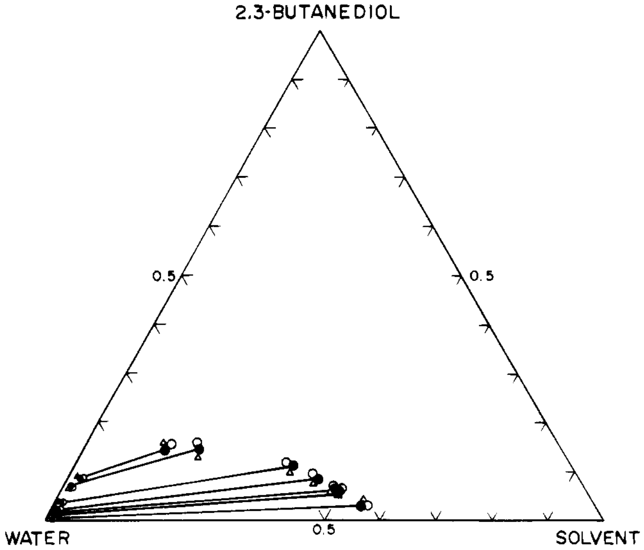

Figure 6. Liquid−liquid equilibrium data for the system 2,3-butanediol + water + 2,4-dimethylphenol at 40 °C in mole fraction: (●) experimental data, (○) calculated with the NRTL equation, (△) calculated with the UNIQUAC equation.

extract phase by addition of a NaOH concentrated solution. The phenolic compound forms solid sodium phenolate which is filtered off, and the solvent is recovered by treating the filter cake with sulfuric acid. When toluene is used as the diluent and the extractant mixture is treated with NaOH, two liquid phases are formed, besides the solid phenolate. 4-Nonylphenol is easily recovered as the solubility of sodium 4-nonylphenolate in toluene is lower than 0.005 mass fraction at 20 °C.

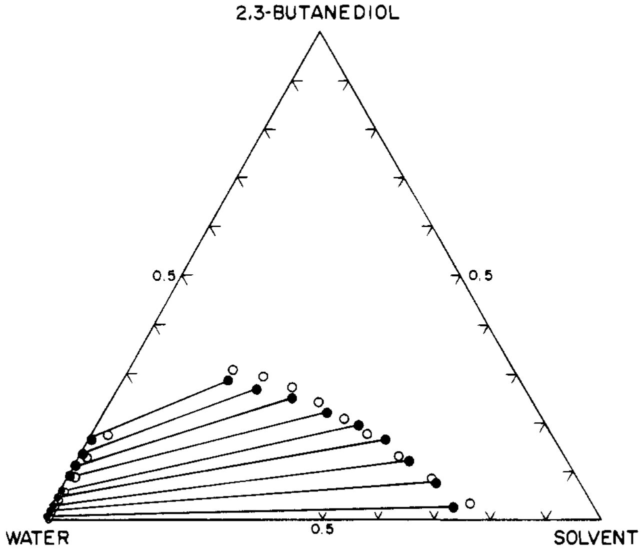

Figure 7. Liquid−liquid equilibrium data for the system 2,3-butanediol + water + 4-nonylphenol at 40 °C in mole fraction: (●) experimental data, (○) calculated with the NRTL equation.

Table 8. Experimental Values of Density ϱ, Viscosity η, and Mutual Solubility *S* in Mass Fraction for Some of the Extraction Mixtures

chemical	*T*/K	ϱ/ (g·cm^{-3})	$10^3\eta$/ (Pa·s)	*S* (solvent in water)	*S* (water in solvent)
nonylphenol	293.15	0.9493	1832.681	0.0007	0.0272
	313.15	0.9357	155.825		
	333.15	0.9220	22.842		
2,3-butanediol	293.15	1.0037	122.101	infinite	infinite
	313.15	0.9919	23.552		
	333.15	0.9758	6.466		
4-nonylphenol (3) + 2,3-butanediol (1) (w_1 = 0.5139)	293.15	0.9760	356.418		
	313.15	0.9611	46.463		
	333.15	0.9453	11.788		
4-nonylphenol (3) + toluene (4) (w_3 = 0.6857)	293.15		3.955	0.0006	0.0171
	313.15			0.0017	0.0196
	314.15	0.9068			

Acknowledgment

We thank Dr. Sagrario Beltrán for her help in the thermodynamic data treatment.

List of Symbols

K_D	solute distribution coefficient, W_{y_1}/W_{x_1}
W_x	mass fraction in the aqueous phase
W_y	mass fraction in the organic phase
β	selectivity, $W_{y_1}W_{x_2}/W_{y_2}W_{x_1}$
A(*IJ*)	binary parameters in the NRTL and UNIQUAC equations

Subscripts

1	2,3-butanediol
2	water
3	solvent

Registry Numbers Supplied by the Authors. 2,3-Butanediol, 513-85-9; 4-nonylphenol, 25154-52-3; 2,4-dimethylphenol. 105-67-9; toluene, 108-88-3; tetrachloroethylene, 127-18-4; trichloroethylene, 79-01-6.

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