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Liquid–Liquid Equilibria for Water + Ethanol + 2-Methylpropyl Ethanoate and Water + Ethanol + 1,2-Dibromoethane at 298.15 K

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Liquid–liquid equilibrium, distribution coefficients, and selectivities of the systems water + ethanol + 2-methylpropyl ethanoate or + 1,2-dibromoethane have been determined at 298.15 K in order to evaluate their suitability in preferentially extracting ethanol from aqueous solution. Tie-line data were satisfactorily correlated by the Othmer and Tobias method, and the plait point coordinates for the two systems were estimated. The experimental data were compared with the values calculated by the NRTL and UNIQUAC models. The water + ethanol + 2-methylpropyl ethanoate system was also compared with the values predicted by the UNIFAC model. Poor qualitative agreement was obtained with these models. From the experimental results, we can conclude that both solvents are inappropriate for ethanol extraction processes from aqueous solutions.

Introduction

The feasibility of recovering ethanol from fermentation broths as economically as possible is gaining in importance due to the increased attraction of using ethanol as a substitute for conventional liquid fuels. Consequently, there is a need for new energy-efficient separation methods for recovering ethanol because of the high energy requirements for traditional distillation methods. When applied to recovery from dilute solutions, these last processes require 30–60% of the product combustion energy to separate the ethanol from the water. Then alternative separative processes, including liquid–liquid extraction, must be considered.

If solvent extraction should be used for ethanol recovery, a low volatility of the solvent is convenient because the evaporative purification of ethanol would be simpler with considerable energy savings. Other requirements are a high distribution coefficient for ethanol, a high selectivity for ethanol over water, and a high separation factor.

The aim of this work was to investigate the possibility to extract the ethanol from water with 2-methylpropyl ethanoate and with 1,2-dibromoethane at 298.15 K. To evaluate the potential of these solvents, complete phase diagrams at 298.15 K were obtained. The binodal curves, tie lines, and plait point coordinates were also fitted using the NRTL (*1*) and UNIQUAC (*2*) activity coefficient models. Only the water + ethanol + 2-methylpropyl ethanoate system, was reasonably predicted using the UNIFAC group contribution activity coefficient method (*3*), because some main group interaction parameters for the other system are not available at present. We cannot find LLE experimental results for these systems in the available literature.

This paper is a continuation of our investigation on ternary liquid–liquid systems containing water + ethanol + solvents (*4–6*).

Experimental Section

Materials. Anhydrous ethanol (Merck, reagent grade) was dried with magnesium activated with iodine under reflux. The product was then fractionally distilled and the midle fraction collected. The last traces of water were removed by circulating the ethanol through a glass column (0.03 × 2 m) packed with 0.3-nm molecular sieves. 2-Methylpropyl ethanoate (Carlo Erba, RP) was stored over anhydrous $MgSO_4$ for 24 h and fractionally distilled. The middle portion boiling to 115.5–116.5 °C at normal pressure was collected. 1,2-Dibromoethane (May & Becker, pa) was used without further purification (purity minimum 99.6%, GC). Water was bidistilled in an all-glass apparatus. All organic purified chemicals were stored over activated molecular sieves to prevent water absorption.

The binodal curves were determined by the cloud-point method. Binaries of known compositions were shaken in an equilibrium cell equipped with a magnetic stirrer and a jacket for circulating the isothermal water at the desired temperature (±0.05 K). The third component was added from a microburet until the transition point was reached. The contents of the three components were determined by mass, yielding a complete binodal curve. The uncertainty in the observed values was determined by the accuracy of the observation of the transition point since the quantities of the titrating component were accurately determined by mass. The estimated error through the whole curve was less than ±0.0005 of the mass fraction of ethanol.

After equilibrium was reached, the refractive indexes of the ternary systems were measured with a Jena Abbe refractometer at 298.15 K with an accuracy of ±0.0001, and with these values a calibrating curve, refractive index against the mass fraction of ethanol, was drawn.

Different compositions prepared by mass within the heterogeneous region were shaken vigorously for at least 2 h at constant temperature for tie-line determinations. Preliminary experiments indicated that this period was sufficient to reach equilibrium. Then the magnetic stirrer was turned off, samples of each phase were removed and analyzed by refractive indexes, and the compositions were obtained with the aid of the calibrating curve. In this way, the two end points of a tie line were obtained. An independent material balance of an equilibrium mixture must lie on the straight line joining the equilibrium values.

Splitting due to cooling was avoided by using warm hypodermic syringes to remove the equilibrium phases for tie-line determinations.

Results and Discussion

The densities and refractive indexes of the pure liquids and the mutual solubilities of 2-methylpropyl ethanoate and 1,2-dibromoethane with water at 298.15 K are in good

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Table I. Density (ρ) and Refractive Index (n_D) of Pure Components and Mutual Solubilities at 298.15 K

compound	ρ/(kg m^{-3}) exptl	ρ/(kg m^{-3}) lit.	n_D exptl	n_D lit.
anhydrous ethanol	785.1	785.06^{a}	1.3594	1.3584^{e}
2-methylpropyl ethanoate	867.6	867.7^{b}	1.3885	1.3880^{b}
1,2-dibromoethane	2167.4	2168.7^{b}	1.5356	1.5360^{b}
water	997.0	997.07^{e}	1.3326	1.3325^{e}

Mutual Solubilities

system	water in solvents		solvents in water	
water + 2-methylpropyl ethanoate	1.10	1.02^{b,c}	0.68	0.63^{b,c}
water + 1,2-dibromoethane	0.08	0.071^{b}	0.49	0.429^{b,d}

[a] Blas, L. *Agenda del Químico*; Aguilar S. A.: Madrid, 1954; p 816. [b] Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley & Sons: New York, Chichester, Brisbane, Toronto, and Singapore, 1986; pp 404–405 and 541–542. [c] Measured at 293.15 K. [d] Measured at 303.15 K. [e] Weast, R. C. *CRC Handbook of Chemistry and Physics*, 69th ed.; CRC Press: Boca Raton, FL, 1988–1989; pp F10 and E382.

Table II. Experimental Binodal Compositions in Mass Fraction, w, and Refractive Index, n_D, for Water (1) + Ethanol (2) + 2-Methylpropyl Ethanoate (3) at 298.15 K

water-rich layer			2-methylpropyl ethanoate-rich layer		
$100w_1$	$100w_2$	n_D	$100w_1$	$100w_2$	n_D
99.32	0.00	1.3329	39.18	35.25	1.3650
94.66	4.55	1.3365	35.99	34.85	1.3657
88.91	10.17	1.3402	31.03	34.87	1.3687
85.38	13.62	1.3429	25.97	33.43	1.3712
81.37	17.49	1.3456	23.85	33.27	1.3721
75.88	22.46	1.3493	19.89	31.33	1.3738
70.93	26.42	1.3522	18.04	29.84	1.3753
66.05	29.96	1.3545	15.97	28.87	1.3757
59.76	33.26	1.3570	13.89	27.28	1.3762
55.09	34.95	1.3580	11.10	24.67	1.3781
49.89	35.86	1.3605	8.80	21.21	1.3796
45.32	35.54	1.3629	7.45	18.47	1.3810
41.63	35.14	1.3645	5.05	13.74	1.3828
41.34^{a}	35.34^{a}		3.73	10.08	1.3840
			2.24	5.59	1.3854
			1.10	0.00	1.3878

[a] Estimated plait point.

Table III. Experimental Binodal Compositions in Mass Fraction, w, and Refractive Index, n_D, for water (1) + ethanol (2) + 1,2-dibromoethane (3) at 298.15 K

water-rich layer			1,2-dibromoethane-rich layer		
$100w_1$	$100w_2$	n_D	$100w_1$	$100w_2$	n_D
99.51	0.00	1.3321	2.22	15.00	1.4812
89.18	9.70	1.3389	1.56	10.80	1.5008
78.64	19.65	1.3461	1.30	7.70	1.5100
68.88	29.50	1.3523	1.02	4.55	1.5205
57.67	38.69	1.3573	0.08	0.00	1.5354
48.69	45.74	1.3602			
39.01	50.71	1.3661			
31.88	54.08	1.3702			
29.92	53.89	1.3720			
26.51	54.17	1.3745			
22.64	53.65	1.3787			
19.27	53.87	1.3811			
14.87	51.86	1.3872			
11.84	48.55	1.3948			
10.22	44.96	1.3994			
6.82	37.94	1.4105			
6.48	37.46	1.4120			
4.47	28.25	1.4149			
2.73	19.68	1.4189			
2.44^{a}	18.06^{a}				

[a] Estimated plait point.

Table IV. Experimental Tie-Line Data for Water (1) + Ethanol (2) + Solvent (3) Systems at 298.15 K

water-rich layer		solvent-rich layer	
$100w_1$	$100w_2$	$100w_1$	$100w_2$
2-Methylpropyl Ethanoate			
90.90	8.25	1.40	2.50
85.00	14.00	2.25	5.25
79.50	19.50	3.50	10.00
74.30	23.75	5.05	14.25
68.25	28.25	8.30	20.50
62.70	32.00	14.55	27.75
58.40	34.00	18.55	30.25
55.00	35.00	22.55	32.75
1,2-Dibromoethane			
91.90	7.58	0.49	0.61
78.40	20.15	0.48	1.52
67.80	30.30	0.58	2.12
61.10	36.36	0.67	2.73
49.50	45.15	0.77	3.03
42.50	49.39	0.97	3.63
33.30	53.18	1.06	4.24
31.30	53.64	0.95	4.85
19.60	53.64	1.04	5.76

agreement with published values, and they are listed in Table I along with literature values for comparison.

The experimental values for the binodal curve for water + ethanol + 2-methylpropyl ethanoate and water + ethanol + 1,2-dibromoethane at 298.15 K are given in Tables II and III, respectively. The experimental tie-line data for both ternary systems at 298.15 K are given in Table IV.

Figure 1 shows the experimental liquid–liquid equilibrium (LLE) diagram and predicted LLE by the UNIFAC method (broken lines) for the water + ethanol + 2-methylpropyl ethanoate system at 298.15 K. Figure 2 shows the experimental LLE diagram for the water + ethanol + 1,2-dibromoethane system at the same temperature. The smoothing curves connecting the experimental data points are hand-drawn; no attempt to fit the data by an empirical equation was made.

The tie-line data are satisfactorily correlated by the method of Othmer and Tobias (7) for both systems. An empirical equation

$$\log[(1 - w_1)/w_1] = m \log[(1 - w_3)/w_3] + b \qquad (1)$$

can represent all tie-line data with adequate precision for the Othmer and Tobias method, where w_1 is the mass fraction of water in the water-rich layer and w_3 is the mass fraction of solvent in the solvent-rich layer. In our case, the best values of the parameters of eq 1, m and b, are given in Table V for the two systems with the corresponding linear correlation coefficients. Table V also lists the experimental and calculated plait points (UNIFAC, NRTL, and UNIQUAC methods) for both systems at 298.15 K.

In selecting solvents, it is necessary to take into account the effect of the aqueous ethanol concentration on the ethanol distribution coefficients and the selectivity for ethanol over water. As shown in Table VI, the ethanol distribution coefficients (D_e) defined as the ratio of the ethanol mass fraction in the organic phase to that in the aqueous phase are not constant, and they have a tendency to increase as the ethanol concentration is increased. A similar conclusion can be derived from the water distribution coefficient (D_w) defined as the equilibrium water content in the solvent phase. The ratio of the ethanol distribution coefficient to the water distribution coefficient yields the separation factor (S_w^{EtOH}) shown in the same table.

The behavior of the separation factor is dissimilar for the two systems, since this property for the system with 2-me-

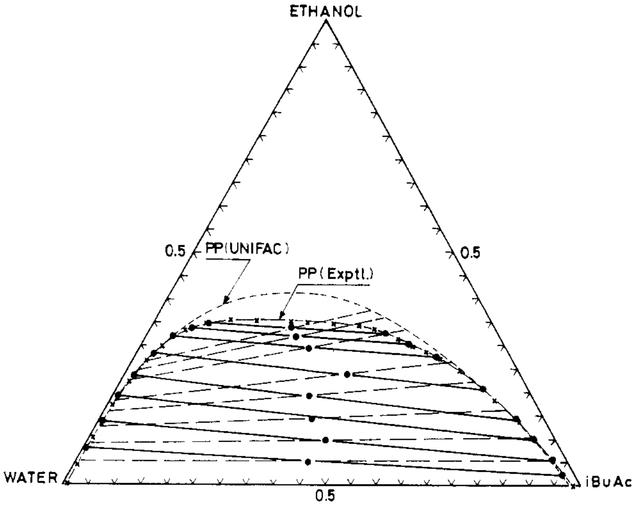

Figure 1. Binodal curves and tie lines for the system water + ethanol + 2-methylpropyl ethanoate (iBuAc) at 298.15 K: (●—●) experimental tie lines, (×) experimental binodal curve, (- - -) UNIFAC predictions, (●) overall composition for tie lines. PP = Plait point.

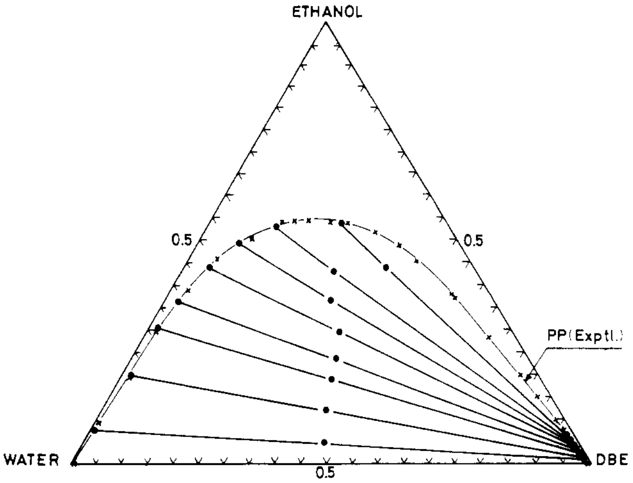

Figure 2. Binodal curve and tie lines for the system water + ethanol + 1,2-dibromoethane (DBE) at 298.15 K: (●—●) experimental tie lines, (×) experimental binodal curve, (●) overall composition for tie lines. PP = Plait point.

Table V. Experimental and Calculated Plait Point, Parameters of Equation 1 and Linear Correlation Coefficients (LCC) in the Othmer and Tobias Correlation for the Systems Water (1) + Ethanol (2) + 2-Methylpropyl Ethanoate (3) and Water (1) + Ethanol (2) + 1,2-Dibromoethane (3) at 298.15 K

		Plait points and parameters of eq 1			
solvent	w_i	exptl	NRTL	UNIQUAC	UNIFAC
2-methylpropyl ethanoate	w_1	0.4143	0.3898	0.3741	0.4712
	w_2	0.3534	0.3738	0.3754	0.3973
	w_3	0.2332	0.2364	0.2505	0.1315
	m	0.5571			
	b	−0.1330			
	LCC	0.9983			
1,2-dibromoethane	w_1	0.0244	0.0014	0.0080	
	w_2	0.1806	0.4750	0.4887	
	w_3	0.7950	0.5235	0.5033	
	m	2.7613			
	b	1.9724			
	LCC	0.9899			

thylpropyl ethanoate decreases monotonically when the ethanol concentration increases, while the separation factor for the system with 1,2-dibromoethane presents a minimum as can be seen in Table VI.

Table VI. Ethanol Extraction Properties at 298.15 K

solvent	D_e	D_w	w_{23}[a]	S_w^{EtOH}
2-methylpropyl ethanoate	0.3030	0.0140	0.0250	21.6
	0.3750	0.0225	0.0525	16.7
	0.5130	0.0350	0.1000	14.7
	0.6000	0.0510	0.1425	11.8
	0.7260	0.0830	0.2050	8.7
	0.8670	0.1460	0.2775	5.9
	0.8900	0.1860	0.3025	4.8
	0.9540	0.2260	0.3275	4.2
1,2-dibromoethane	0.0805	0.0049	0.0061	16.4
	0.0754	0.0048	0.0152	15.7
	0.0699	0.0058	0.0212	12.1
	0.0751	0.0067	0.0273	11.2
	0.0671	0.0070	0.0303	8.7
	0.0735	0.0097	0.0363	7.6
	0.0797	0.0106	0.0424	7.5
	0.0904	0.0095	0.0485	9.5
	0.1074	0.0104	0.0576	10.3

[a] Mass fraction of ethanol in the solvent-rich layer.

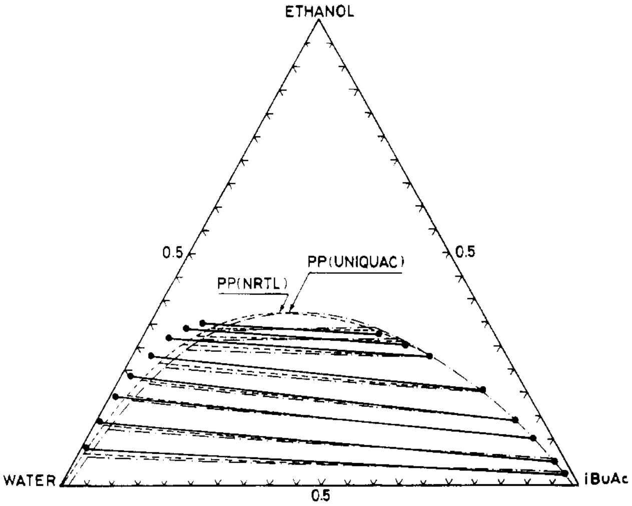

Figure 3. Binodal curves and tie lines calculated for the system water + ethanol + 2-methylpropyl ethanoate (iBuAc) at 298.15 K using the equations (- - -) NRTL and (• • •) UNIQUAC, together with the corresponding experimental tie lines (●—●).

Zane Egan et al. (*8*) conclude that solvents with experimental distribution coefficients for ethanol greater than 0.15 and a separation factor greater than 10 are potential candidates for the extraction process. From the analysis of Table VI, we can conclude that these extraction properties are exceeded by the 2-methylpropyl ethanoate at low ethanol concentrations (which is the most important region for ethanol extraction from fermentation broth), but the separation factor is smaller than this minimum value at high ethanol concentrations. For the 1,2-dibromoethane neither the distribution coefficient nor the separation factor appears as appropriate for extraction processes. Then, we conclude that both solvents are inappropriate for the ethanol extraction process from aqueous solutions.

Correlation of the Experimental Data

Thermodynamic models, such as the NRTL (*1*) and UNIQUAC (*2*) activity coefficient models, were used to correlate the LLE for these systems, with the help of an iterative computer program developed by Sørensen (*9*). In order to minimize the values of the two objective functions in terms of activity and molar fractions, a penalty term, designed to reduce the risk of multiple solutions associated with high parameter values, was included. Figures 3 and 4 show the LLE calculations using these models for water +

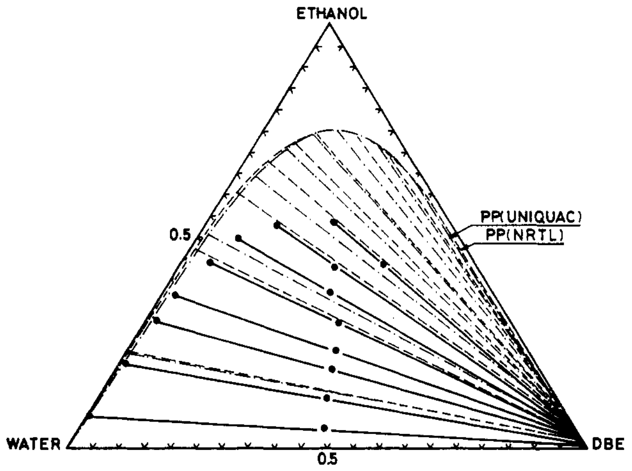

Figure 4. Binodal curves and tie lines calculated for the system water + ethanol + 1,2-dibromoethane (DBE) at 298.15 K using the equations (- - -) NRTL and (· · ·) UNIQUAC, together with the corresponding experimental tie lines (●—●).

Table VII. Residual *F* and ΔD_e, Optimized Parameters of the NRTL and UNIQUAC Equations Fitted to LLE Data, and Nonrandomness Parameters of the NRTL Equation (α_{ij}) for the Water + Ethanol + 2-Methylpropyl Ethanoate and Water + Ethanol + 1,2-Dibromoethane Systems at 298.15 K

solvent	F/%	ΔD_e/%	i–j	a_{ij}[a]	a_{ji}[a]	α_{ij}
			NRTL			
2-methylpropyl ethanoate			1–2	2188.8	−1176.3	
	38.65	13.5	1–3	2247.7	−178.43	0.10
			2–3	−839.16	1449.9	
1,2-dibromoethane			1–2	700.17	−259.47	
	41.50	7.0	1–3	2216.3	731.68	0.25
			2–3	514.50	205.33	
			UNIQUAC			
2-methylpropyl ethanoate			1–2	454.77	−187.15	
	60.80	17.1	1–3	68.694	654.59	
			2–3	−127.49	448.22	
1,2-dibromoethane			1–2	286.78	−143.62	
	55.11	8.0	1–3	463.90	384.41	
			2–3	200.30	24.080	

[a] $a_{ij} = (g_{ij} - g_{jj})/R$, K for NRTL equation, where g_{ij} is the energy of interaction between an i–j pair of molecules (cal mol^{-1}). $a_{ji} = (u_{ij} - u_{jj})/R$, K for UNIQUAC equation, where u_{ij} is the UNIQUAC binary interaction parameter (cal mol^{-1}).

ethanol + 2-methylpropyl ethanoate and water + ethanol + 1,2-dibromoethane, respectively.

The nonrandomness of the liquid mixture, which is represented by the optimized third parameter in the NRTL equation (α_{ij}), is shown in Table VII.

The values of the residual function, F (mol %), and the mean error of the ethanol distribution coefficient, ΔD_e, give an idea of the goodness of fit.

$$F = 100[\sum^{k} \min \sum^{i} \sum^{j} (x_{ijk} - \hat{x}_{ijk})^2/6M]^{1/2} \qquad (2)$$

$$\Delta D_e = 100[\sum^{k} [(\hat{D}_e^{\,k} - D_e^{\,k})/D_e^{\,k}]^2/M]^{1/2} \qquad (3)$$

where D_e and $\hat{D}_e$ are the experimental and calculated ethanol distribution coefficients, respectively, 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.

The UNIFAC group contribution method (*3*) was employed by using the group interaction parameters obtained by Magnussen et al. (*10*). The equilibrium compositions were calculated by using a program written by Fredenslund et al. (*3*) for water + ethanol + 2-methylpropyl ethanoate. Figure 1, in which the predicted binodal curve and tie lines are displayed in broken lines, shows that the UNIFAC method predicts an immiscibility region much larger than that experimentally observed.

Conclusions

LLE data for the ternary mixtures water + ethanol + 2-methylpropyl ethanoate and water + ethanol + 1,2-dibromoethane were determined at 298.15 K.

From the experimental results it is evident that neither solvent is appropriate for ethanol extraction processes, since the ethanol extraction properties for both systems are smaller than the ones fixed by Zane Egan et al. (*8*), except for the system with 2-methylpropyl ethanoate at low ethanol concentrations (see Table VI).

On the other hand, the high density of 1,2-dibromoethane is an additional problem because this fact produces a difficult contact between the two phases. If water should be reused in the fermentation process, the relatively high solubility of 1,2-dibromoethane is another problem due to its toxicity to ethanol-producing microorganisms. This problem could be solved by making a barrier to solvent molecules as a protection against solvent toxicity (*11*).

Poor qualitative agreement was obtained with the NRTL and UNIQUAC models. However, the NRTL equation, fitted to the experimental data by using an iterative computing programming developed by Sørensen, is considerably more accurate than the UNIQUAC equation for these systems, as can be seen from the analysis of the residual F and ΔD_e (see Table VII).

The UNIFAC method was applied only for the water + ethanol + 2-methylpropyl ethanoate system, which predicts an immiscibility region larger than that experimentally observed.

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