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Liquid–Liquid Extraction of 2-Butoxyethanol from Aqueous Solution with 2-Octanol and Di-*n*-butyl Ether as Solvents

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Liquid–liquid equilibrium data were determined for ternary systems of 2-butoxyethanol–water with 2-octanol and di-*n*-butyl ether as solvents at 298 K. The equilibrium data were correlated and an estimation of the plait point was made by using some of the more common correlations available in the literature. The experimental data were compared with those predicted by the UNIQUAC method. The two solvents exhibit similar behavior, although, di-*n*-butyl ether shows a higher selectivity.

Introduction

Solvent extraction has been commonly used in the downstream processing of biological materials such as intracellular enzymes and proteins (*1*). Suitable extraction systems for this type of recovery are the aqueous-phase systems, which result from the incompatibility between aqueous polymers (e.g. PEG and dextran) or between a polymer and an appropriate salt (e.g. potassium phosphate (*2*). An alternative to the aqueous-phase systems is the critical solution temperature aqueous systems (CSTAS), where a homogeneous mixture of an organic solvent and water splits into two phases, viz. an organic phase and an aqueous phase, when the homogeneous mixture is heated above its lower critical solution temperature. If a third component is present in the original homogeneous mixture, it will be distributed between the two phases obtained by heating. The 2-butoxyethanol–water system shows a reasonable critical solution temperature (CST) range: 48.9 °C (lower CST) and 128 °C (upper CST). The loop diagram is limited by these temperatures and a composition range of 10–60 wt % 2-butoxyethanol (*3*, *4*). When 2-butoxyethanol is used as solvent in liquid–liquid extraction, the presence of a third component alters the critical solution temperatures. Also, when salts are added, such as alkali-metal halides, the loop expands and the CST falls below 35 °C, precluding the denaturation and or precipitation of biomolecules being separated (*4*, *5*).

When the temperature is raised above the CST, a substantial amount of 2-butoxyethanol still remains dissolved in the aqueous phase upon separation of the two phases. To recover it from the aqueous solution, liquid–liquid extraction using a conventional solvent can be used. The aim of this work was to study an alcohol and an ether as solvents for the recovery of 2-butoxyethanol.

Experimental Section

Chemicals. All the chemicals used, 2-butoxyethanol, 2-octanol, and di-*n*-butyl ether, were of reagent grade and were further purified by distillation. No impurities were detected by gas–liquid chromatography, and good agreement was found between literature values and measured physical properties at 20 °C, as shown in Table I. Bidistilled water was used for the determination of equilibrium data.

Procedure. Mutual solubility isotherms (binodal curves) were determined by using the cloud-point method. The binodal compositions were plotted against density and refractive index and used as calibration curves to determine the tie-line compositions. Heterogeneous mixtures of known compositions were shaken in a jacketed cell and allowed to settle for at least 5 h. The tie-line compositions were obtained from density (U-type 7-cm^3 pycnometer) and refractive index (PAY refractometer, type ABBE) measurements of both phases and by making use of the aforementioned calibration curves. Figure 1 shows densities and refractive indices at 24 °C for the 2-butoxyethanol–water–2–octanol system. Density measurements were used in the vicinity of the plait point, as refractive indices in that composition region cannot be measured accurately enough. The method has been described in detail in former publications (*6*, *7*).

Table I. Physical Properties of the Chemicals at 20 °C

chemical	refractive index exptl	refractive index lit.[a]	density, g/cm^3 exptl	density, g/cm^3 lit.[a]
2-butoxyethanol	1.4198	1.4185	0.9010	0.9019
2-octanol	1.4262	1.4260	0.8200	0.8230
di-*n*-butyl ether	1.3990	1.4010	0.7695	0.7694

[a] Data taken from: *Solvents Guide*; 2nd ed.; Cleaver-Hume: London, 1963.

Table II. Binodal Curve and Tie-Line Data for 2-Butoxyethanol (1)–Water (2)–2-Octanol (3) at 298 K

(a) Binodal Curve Data, wt %

(1)	(2)	(3)	(1)	(2)	(3)
0.00	4.31	95.69	56.00	28.28	15.69
6.82	5.36	87.83	54.22	33.90	11.88
16.31	6.69	76.99	49.32	43.33	7.30
23.91	8.04	68.05	43.34	52.34	4.31
31.24	9.38	59.38	36.41	60.70	2.89
37.70	10.86	51.44	29.51	68.88	1.61
43.03	13.02	43.95	22.23	76.62	1.15
49.15	15.81	35.03	14.49	84.72	0.79
53.10	19.35	27.55	7.25	92.23	0.52
54.72	21.93	23.35	0.00	99.36	0.65
55.61	24.65	19.75			

(b) Tie-Line Data, wt %

aqueous phase (1)	aqueous phase (2)	aqueous phase (3)	organic phase (1)	organic phase (2)	organic phase (3)
13.44	85.93	0.62	48.00	45.50	6.50
12.00	87.37	0.62	53.00	36.75	10.25
10.50	89.00	0.50	56.00	28.75	15.25
10.33	89.17	0.50	55.88	25.12	19.00
9.75	89.75	0.50	54.50	21.25	24.25
9.63	89.87	0.50	54.00	20.25	25.75
9.50	90.00	0.50	51.50	17.75	30.75
7.50	92.00	0.50	44.00	13.25	42.75
7.25	92.25	0.50	43.00	12.75	44.25
5.00	94.50	0.50	37.75	11.00	51.25
4.75	94.75	0.50	35.75	10.75	53.50
3.75	95.75	0.50	27.50	9.00	63.50
1.87	97.38	0.75	15.00	6.75	78.25

Results

Liquid–liquid equilibrium data of the two systems with 2-butoxyethanol at 298 K are given in Tables II and III. Figure

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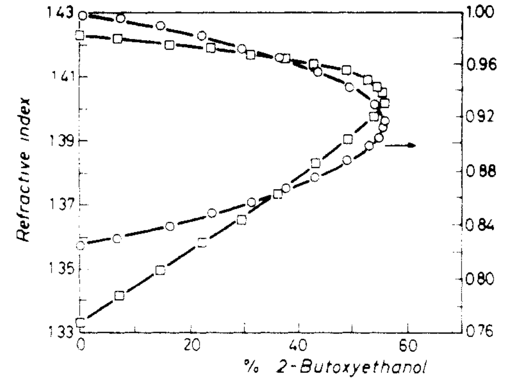

Figure 1. Densities and refractive indices for the system 2-butoxyethanol–water–2-octanol at 24 °C.

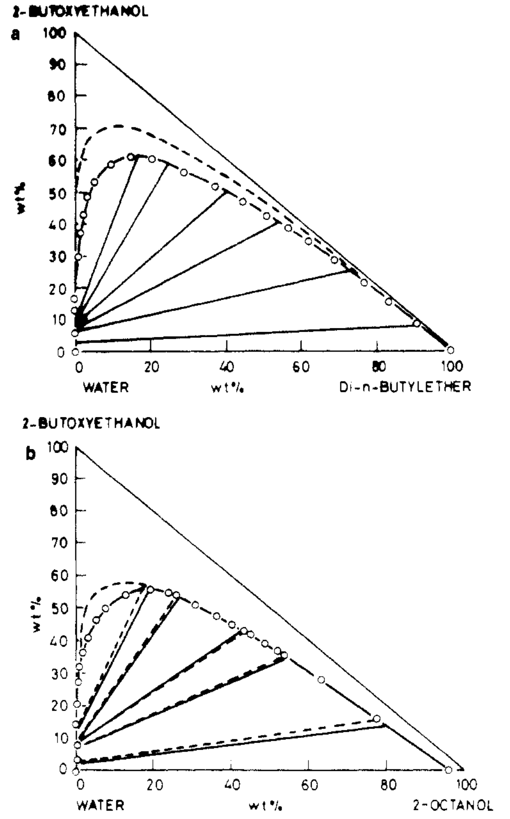

Figure 2. Liquid–liquid equilibrium data at 298 K for the systems (a) 2-butoxyethanol–water–2-octanol and (b) 2-butoxyethanol–water–di-*n*-butyl ether. Continuous lines, experimental data; dashed lines, UNIQUAC predictions. Tie lines were not predicted for the system 2-butoxyethanol–water–di-*n*-butyl ether by UNIQUAC method.

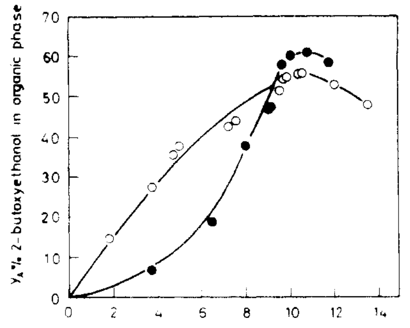

Figure 3. Equilibrium distribution diagram at 298 K with solvents (●) di-*n*-butyl ether and (○) 2-octanol.

Table III. Binodal Curve and Tie-Line Data for 2-Butoxyethanol (1)–Water (2)–Di-*n*-butyl Ether (3) at 298 K

(a) Binodal Curve Data, wt %

(1)	(2)	(3)	(1)	(2)	(3)
0.00	0.28	99.72	60.81	26.45	12.74
9.75	0.60	89.65	59.39	31.01	9.60
18.01	1.30	80.69	57.31	35.32	7.37
26.01	2.20	71.79	50.93	44.79	4.28
34.90	3.17	61.92	43.94	35.01	3.05
41.71	5.00	53.29	36.44	61.46	2.10
48.41	6.45	45.14	29.18	69.36	1.46
54.05	9.50	36.10	21.66	77.56	0.77
57.79	13.60	28.60	14.53	84.88	0.59
60.52	18.68	20.79	6.79	92.96	0.25
61.40	21.88	16.71	0.00	99.93	0.06

(b) Tie-Line Data, wt %

aqueous phase			organic phase		
(1)	(2)	(3)	(1)	(2)	(3)
15.50	84.00	0.50	50.00	46.00	4.00
11.75	87.95	0.30	59.50	30.50	10.00
10.60	89.15	0.25	61.30	23.70	15.00
10.00	89.75	0.25	60.75	18.75	20.50
9.75	90.00	0.25	58.00	13.75	28.25
9.00	90.75	0.25	47.25	6.25	46.50
8.00	91.81	0.19	35.00	3.50	61.50
6.50	93.37	0.13	19.00	1.75	79.25
3.75	96.17	0.08	7.00	0.50	92.50

Table IV. Correlation of Equilibrium Data for the 2-Butoxyethanol–Water–Solvent Systems at 298 K

	solvent	
equation	2-octanol	di-*n*-butyl ether
Bachman–Brown (*8*) $y_S/x_W = My_S + N$	$M = 0.0102$ $N = 0.0201$ ($r = 0.9995$)	$M = 0.0105$ $N = 0.0139$ ($r = 0.9995$)
Hand (*9*) $\log (y_A/y_S) = C \log (x_A/x_W) + D$	$C = 3.2535$ $D = 3.5122$ ($r = 0.9831$)	$C = 2.7351$ $D = 3.1222$ ($r = 0.9897$)
Othmer–Tobias (*10*) $\log [(100 - y_S)/y_S] =$ $E \log [(100 - x_W)/x_W] + F$	$E = 4.1890$ $F = 4.4665$ ($r = 0.9878$)	$E = 3.4308$ $F = 3.8699$ ($r = 0.9924$)
Ishida (*11*) $\log [(y_Ax_S)/(x_Ay_S)] =$ $G \log [(y_Wx_S)/(x_Wy_S)] + H$	$G = 0.4872$ $H = 0.1869$ ($r = 0.9981$)	$G = 0.5258$ $H = 0.2255$ ($r = 0.9993$)
Hirata–Fujita (*12*) $\log [y_A/(100 - y_A)] =$ $I \log [x_A/(100 - x_A)] + J$	$I = 1.0300$ $J = 1.0440$ ($r = 0.9909$)	
Major–Swenson (*13*) $\log [(100 - y_A)/y_A] =$ $K \log [(100 - x_A)/x_A] + L$	$K = 1.0300$ $L = -1.0440$ ($r = 0.9909$)	

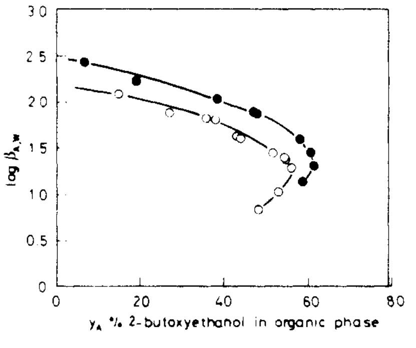

Figure 4. Selectivity diagram at 298 K with solvents (●) di-*n*-butyl ether and (○) 2-octanol.

Table V. Estimated Plait-Point Data in 2-Butoxyethanol–Water–Solvent Systems at 298 K[a]

	correlation		
solvent	Hand (*9*)	Othmer–Tobias (*10*)	Mato–Bueno (*15*)
2-octanol	17.13	19.38	24.21
di-*n*-butyl ether	19.20	21.41	25.56

[a] Values given in wt % 2-butoxyethanol.

2 shows the liquid–liquid equilibrium diagrams along with predicted data by the UNIQUAC method.

The equilibrium distribution diagram and selectivity diagram for both systems are shown in Figures 3 and 4.

The tie-line data for the two systems were correlated by the most common methods available in the literature. The parameters for the different equations along with the correlation coefficients are presented in Table IV.

The plait point has been determined by using the method proposed by Treybal, Weber, and Daley (*14*) and by making use of the Hand (*9*), Othmer–Tobias (*10*), and Mato–Bueno (*15*) correlations. The last one involves log (y_A/x_A) being plotted against x_A; at the plait point, log $(y_A/x_A) = 0$. The estimated plait-point values are given in Table V. It is apparent from Table V that plait-point compositions determined by the Mato–Bueno method are higher than those determined by Treybal's method. The values obtained by the Mato–Bueno method are more realistic as more tie-line compositions are needed in the vicinity of the plait point to obtain its value.

The binodal curves estimated by the UNIQUAC method (*16*, *17*), using the University of Dortmund data bank, fit the data best for 2-octanol, except for high solute concentrations in the vicinity of the plait point. The equilibrium data from the UNIQUAC method show poor agreement with experimental data for di-*n*-butyl ether. The method seems appropriate for calculating liquid–liquid equilibrium with molecules that have OH groups, one of the drawbacks of the UNIFAC method for liquid-phase systems (*18*, *19*).

It can be observed from the equilibrium and selectivity diagrams that 2-octanol shows a higher distribution coefficient than di-*n*-butyl ether for almost the whole range of compositions, though its selectivity is lower. The behavior of both solvents is rather similar, so that solvent selection for the extraction of 2-butoxyethanol would have to be based on their solubility in water and how easily the final separation by distillation can be effected.

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Glossary

x	weight percent in the aqueous phase
y	weight percent in the organic phase
r	correlation coefficient
β	selectivity, $\beta_{A,W} = (y_A/y_W)/(x_A/x_W)$

Subscripts

A	solute
S	solvent
W	water

Registry No. 2-Butoxyethanol, 111-76-2; 2-octanol, 123-96-6; di-*n*-butyl ether, 142-96-1.

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