Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Cockrem, M. C. M. , Meyer, R. A. and Lightfoot Jr., E. N.(1986) 'Recovery of *n*-Butanol from Dilute Solution by Extraction', Separation Science and Technology, 21: 10, 1059 — 1074
To link to this Article: DOI: 10.1080/01496398608058397
URL: http://dx.doi.org/10.1080/01496398608058397

SEPARATION SCIENCE AND TECHNOLOGY, 21(10), pp. 1059-1074, 1986

Recovery of *n*-Butanol from Dilute Solution by Extraction

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Abstract

A simple but effective strategy is suggested to seek extraction agents for recovery of oxychemicals from dilute aqueous solution. Application of this strategy, which is based on specialization of UNIFAC and UNIFAP, to *n*-butanol identified highly effective solvents as well as a promising polymer. The best solvent identified, 4-*n*-butylphenol, has an *n*-butanol mass distribution coefficient relative to water of up to 25 and selectivities of about 200. The polymer, poly(*p*-vinylphenol), is somewhat less effective, but there is a good probability of finding related compounds of practical interest.

INTRODUCTION

A. Scope and Motivation

The dominant costs in recovery from dilute solutions are related to materials handling, and it is therefore critically important to obtain rapid volume reduction (*1*). Improved equipment design and control will lower separation costs, but improved separation chemistry is the most important consideration. Extraction with solid sorbents is particularly attractive since they permit efficient contacting of large volumes of a dilute stream with small volumes of extractant (i.e., highly unbalanced stream rates) in available equipment.

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0149-6395/86/2110-1059$3.50/0

Our goal is to search systematically for improved extractants to recover chemicals from dilute aqueous solutions such as fermentation broths and waste streams.

An effective extractant must have both high capacity for the solute (i.e., a high distribution coefficient from dilute solution) and a high selectivity against water. The activity coefficient of the solute in the extractant must be low and the activity coefficient of water (the major contaminant) high.

In addition, the solute must be easily released. Either the activity coefficient of the solute in the extractant must be easily changed from low (for sorption) to high (for desorption) or a secondary recovery system used.

In this paper we propose a systematic method to search for liquid solvents and simple polymers with high distribution coefficients, capacity, and selectivity. We do not examine reversibility or extractant losses and cost here, as our ultimate goal is to develop readily reversible crosslinked polymeric gels.

Even though our primary interest is in solid sorbents, we chose to begin our search with the prediction of liquid-phase activity coefficients: prediction methods are more highly developed and more extensive data are available. If a solvent and a sorbent are chemically similar, then we expect the intermolecular forces to be similar. The additional entropic, size, and shape effects which are important in sorbents will be considered later.

We choose this approach in part because it permits a rapid and efficient search for sorbents. Also, liquid solvents are easier to prepare and test.

We consider as a useful test case the recovery of *n*-butanol from dilute aqueous solution at 1 to 10 g/L, typical of concentrations in fermentation broth where continuous removal of the *n*-butanol is desirable to reduce inhibition of the fermenting organism, *Clostridum acetobutylicum* (*2, 3*).

B. Solvents and Sorbents for *n*-Butanol

Available liquid–liquid equilibrium data follow the general trends shown in Table 1: high distribution coefficients for *n*-butanol are associated with poor selectivity against water and vice versa.

Extractive acetone–butanol fermentation has been demonstrated successfully, using as the extracting solvent corn oil (*4*) or dibutylphthalate (*9*). Experimental screening by Hashimoto (*6*) of potential *n*-butanol solvents costing less than $0.88/kg suggested a best extractant of 2-octanol

TABLE 1
Selectivity and Distribution Coefficient of *n*-Butanol from Aqueous Solution into Some Solvents as Reported in the Literature

Solvent	Selectivity	Distribution coefficient	Refs.
Vegetable oil	High	Low	*4*
Benzene			*5*
Halocarbons			*5*
Ethyl acetate			*5*
Dibutylphthalate			*6*
Acetone			*5, 7*
Methyl butyl ketone			*8*
n-Alcohols			*7*
Glycerol	Low	High	*5*

(*6*). None of these solvents has distribution coefficients high enough to provide a large volume reduction.

A solute–solvent interaction classification (*10*) can be used to screen solvents empirically. Acids or aromatic hydroxyl compounds are indicated as both good *n*-butanol solvents and good water solvents, suggesting poor selectivity.

A number of *n*-butanol sorbents have been suggested (see Table 2), and Silicalite (*12*) is the most promising: it exhibits a volumetric distribution coefficient of the order of 50 for a 0.2% weight feed and a selectivity of about 1000 (*14*). Silicalite will sorb *n*-butanol from fermentation broth (*16*). However, desorption, for instance with hot gases, appears to be difficult (*15*). Montmorillonite clays also exhibit high distribution coefficients (*17, 18*) but low selectivities.

EXPLORATORY SOLVENT SELECTION

A. Available Methods of Predicting Solvent Properties

Many thermodynamic correlations of solvent properties require that specific data be available for each compound to be examined. For example, the Modified Cohesive Energy Density model (*26*) for solvent activity coefficients at infinite dilution gives relatively accurate predictions but insufficient flexibility to examine untested possibilities.

TABLE 2
Capacity for *n*-Butanol and Selectivity Against Water of Some Potential Sorbents as Reported in the Literature

Sorbent	Selectivity	Capacity	Refs.
Zeolite ZSM-5	High	Very high	*11*
Silicalite	High	High	*12-16*
Montmorillonite clays	Low	High	*17-20*
Sephadex G-10		Moderate	*21*
Non-ionic polystyrene		Moderate	*22*
Strong acid ion exchangers	Low	Low	*23*
Active carbon		Low	*24*
Controlled pore glass		Low	*25*

Group contribution methods can predict activity coefficients in untested systems, subject to certain assumptions being met (*27*), and perhaps the best available is UNIFAC (*28*). Parameters necessary to apply UNIFAC are evaluated from vapor-liquid (VLE) or liquid-liquid (LLE) equilibrium data (*28*, *29*) or gas-liquid chromatography (GLC) data (*30*, *31*). The VLE parameter set can, in theory, be used for predicting LLE. In practice, however, two different parameter sets are used for the two different types of equilibria in order to improve the overall accuracy of the predicted activity coefficients (*29*). Further, a modified combinatorial term is used to obtain parameters from GLC data (*32*). This modification improved predictions of activity coefficients at infinite dilution for alcohols in hexadecane, 1-octadecane, and 2-dodecanone (*33*). We test this modification for dilute solution below.

It has been proposed to use UNIFAC with a LLE parameter set to provide guidelines for liquid solvent selection (*33*, *34*). It has been reported that UNIFAC or UNIQUAC may give estimates of solvent properties which would be useful in a qualitative screening of solvents for ethanol recovery (*35*).

B. Our Approach

In our initial search for solvents, we are not concerned with high accuracy, but only with reliable and rapid qualitative screening. We assume that:

(1) Any ternary system of practical interest to us can be represented as two conjugate binary phases: for high selectivity, the solvent and

water must be relatively immiscible, and we can assume that the mutual solubility of these two components has a negligible effect on the activity of the solute for low solute concentrations (*36*).

(2) Activity coefficients can be adequately predicted using UNIFAC with the larger and more accurate VLE parameter set. The number and accuracy of predictions based on LLE parameters are limited (*37*) since only a relatively small set of LLE ternary data is available and thermodynamic consistency tests cannot be performed. On the other hand, VLE parameters are based on binary VLE or mutual solubility data, which can be checked for thermodynamic consistency, and they are also easier to obtain.

To identify a high distribution coefficient and high capacity, we use data for the water/*n*-butanol binary pair and UNIFAC predictions for the *n*-butanol/solvent binary pair. Selectivity against water is then identified using solubility data for the water/solvent pair. If necessary, modified solvent structures are examined to find high selectivity. Some of the best candidate solvents thus identified are then experimentally tested to confirm the predictions.

Capacities, distribution coefficients, and selectivities are calculated using the equations shown in the Appendix.

1. Characterization of the n-Butanol-Water System

Figure 1 shows data for *n*-butanol activity coefficients in aqueous solution (*38*) compared with predictions using either UNIFAC, UNIFAC with a modified combinatorial term, or the Wilson equation (*39*). All predictions use VLE parameters. The modified UNIFAC is poor for this system involving strong interactions. The simple UNIFAC prediction agrees best with the data, and as it covers a wider concentration range than the data, it is deemed adequate to supplement data for screening purposes.

2. Search for Low n-Butanol Activity Coefficients

Table 3 shows activity coefficients predicted using UNIFAC or modified UNIFAC for *n*-butanol in representative potential solvents. Candidates were selected heuristically using our literature search, empirical guidelines (*10*), heat of mixing data (*40*), solubility parameter data (*41*), MOSCED model predictions (*26*), and our general knowledge

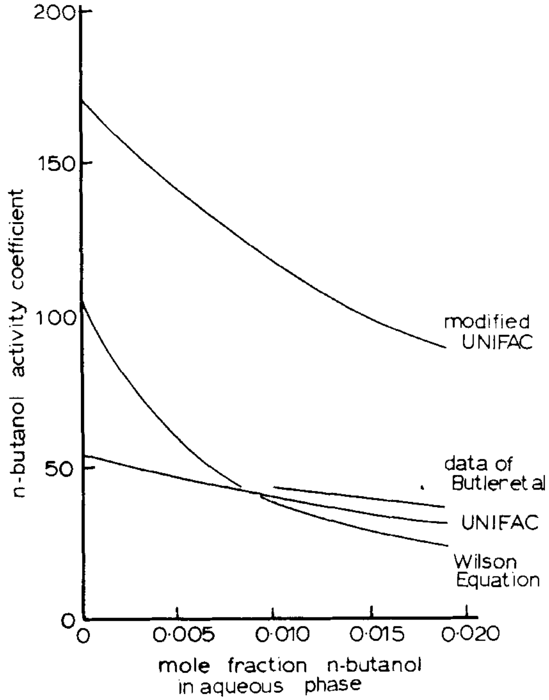

FIG. 1. Activity coefficients of *n*-butanol in dilute solution in water at 25°C and 1 atm.

of physical chemistry. Compounds capable of hydrogen bonding were considered to be likely candidates. *n*-Butanol is amphoteric since it can donate or accept hydrogen bonds.

Little difference is seen between UNIFAC and modified UNIFAC for these binary solvent/butanol systems. Many promising solvents with low activity coefficients for *n*-butanol were found. The most promising are phenols and naphthalenediols.

Note that there are no UNIFAC calculation results for several classes of compounds since parameters are not available. Organic acids are expected to be good *n*-butanol solvents under conditions not favoring esterification. Other Lewis acids, compounds with *d*-shell electrons, and phenols with electron-withdrawing groups may also be worth testing.

TABLE 3
Screening for Solvents with High Affinity for *n*-butanol, Where the Order of Predicted Activity Coefficients Using UNIFAC ("UNMOD") and the Dilute Solution Modification ("MOD") Differ as Indicated by an Arrow

Solvent	Activity coefficients for *n*-butanol in solvent at 25°C: Mole fraction *n*-butanol			
	0.10		0.01	
	UNMOD	MOD	UNMOD	MOD
Tetrahydronaphthalene	5.79	5.94	11.02	11.33 ←
n-Butylbromide	4.41	4.41	11.14	11.14
Nitrobenzene	5.95	5.95	10.20	10.20
1-Nitrooctane	3.09	3.09	4.05	4.05
Isobutylene glycol	1.09	1.10	1.08	1.09
1-Butanolamine	1.01	1.01	1.02	1.02
Ethylbutylamine	0.94	0.95	0.93	0.95
Pyridine	0.72	0.73	0.74	0.75
Dimethylformamide	0.72	0.73	0.69	0.70
3-Methylpyridine	0.66	0.66	0.64	0.64
n-Butylamine	0.63	0.63	0.59	0.59
N,N-Dimethylaniline	0.74	0.74	0.56	0.58
Methylamine	0.45	0.57	0.39	0.53 ←
n-Butylnitrile	0.54	0.54	0.50	0.50
Naphthalene-1,4-diol	0.23	0.23	0.12	0.12
Phenol	0.18	0.18	0.09	0.09

3. Search for Selectivity

Table 4 shows the expected relative order of the selectivity for *n*-butanol against water of some promising solvents. This is based on the assumption that for high selectivity the solubility of water in the extractant must be low. We measured the solubility of water in 4-*n*-butylphenol at 25°C using the Karl-Fischer method to determine the water content of the 4-*n*-butylphenol phase (*42*). The other solubility data were readily available in the literature. Table 4 also shows that data for the solubility of the extractant in water only provide an indication of possible selectivity.

Neither UNIFAC nor the modified UNIFAC represented the water/solvent system well. Predicted activity coefficients suggested that the

TABLE 4
The Search for Selectivity: Solvents Are Arranged in the Order of Increasing Solubility of Water in the Solvent

		Literature solubility data			
Solvent	Expected selectivity	Water in solvent (g/L)	Solvent in water (g/L)	Temperature (°C)	Ref.
Phenol	High	2.0	87.1	25	*44*
m-Chloroaniline		11.5		36	*46*
m-Chloroaniline			3.00	25	*48*
Ethylhexanoic acid		12.6	2.5	20	*43*
1-Dodecanol		13	<0.2	20	*44*
n-Butyronitrile		25	35	20	*43*
1-Octanol		45	0.6	20	*44*
1-Hexanol		72	5.9	20	*44*
p-Butylphenol	Moderate	86		25	This work
p-Butylphenol			0.4	25	*47*
1-Butanol		238	73.1	25	*44*

concentration of water in a solvent phase in contact with water would be as much as two orders of magnitude greater than reported solubility limits.

4. Experimental Confirmation

To test our screening procedure and assumptions, we selected three different solvents for experimental testing: 4-*n*-butylphenol (Kodak, Rochester, New York), *n*-dodecanol (Aldrich, Milwaukee, Wisconsin), and *m*-chloroaniline (Aldrich). The first of these is an excellent *n*-butanol solvent and the other two are indifferent.

Distribution coefficient predictions were tested experimentally via batch equilibrium contacting of 0.3 mL *n*-butanol/water solution with 0.3 mL solvent in a 1-mL Reacti-vial (Pierce Chemical Co., Rockford, Illinois) with a Teflon–silicone septum. The sample was shaken vigorously and allowed to stand for 12 h, then shaken and settled a second time. *n*-Butanol concentrations in both phases were then determined using a Perkin-Elmer Sigma 3B gas chromatograph with a 3% OV-101 column, temperature programming from 100 to 260°C and FID detection, coupled to a Sigma 15 data station. *n*-Butanol mass balance closure was 95% or better in all cases except one, in which it was only 71%.

5. Results and Discussion

Figure 2 shows the predicted and measured distribution coefficients for *n*-butanol from aqueous solution into the three solvents tested. Both sets of results indicate that 4-*n*-butylphenol has a high distribution coefficient for *n*-butanol, and that both *m*-chloroaniline and *n*-dodecanol provide lower and less useful distribution coefficients.

The distribution coefficient for 4-*n*-butylphenol is particularly high at low concentrations and does not become constant until much lower concentrations (results not shown here). This is due to concentration dependence of the *n*-butanol activity coefficient in 4-*n*-butylphenol, the activity coefficient in the aqueous phase being approximately constant in this dilute range.

The selectivity against water for each of these solvents is expected to be high due to the low solubility of water in each of these solvents, as indicated in Table 4, and to their high distribution coefficients for *n*-butanol. For the solvent 4-*n*-butylphenol, these data suggest a selectivity of up to 290.

Table 5 shows that for the solvent 4-*n*-butylphenol both predictions using our binary model and predictions using UNIFAC only for the full ternary two-phase system give similar results. For the purposes of screening solvents, our simplifying assumptions appear to be justified, at least for this case.

Table 6 shows predicted solvent behavior of 4-*n*-butylphenol for three solutes. Our double binary model is used in each case. The distribution coefficient and capacity are predicted to be high for *n*-butanol, and moderate for ethanol or acetone. Selectivity is predicted to be high in each case.

After we had completed our search, we found that the use of alkylated phenols and related compounds for extraction and extractive distillation of low molecular weight alcohols, in particular for ethanol, had been previously reported (*49*) and patented (*50*), and that some results of King's group at Berkeley concerning the use of phenols as solvents for the four isomers of butanol are to be presented later this year (*51*).

EXPLORATORY SORBENT SELECTION

We next examined the sorbent poly(4-vinylphenol) (PVP), which is similar chemically to the solvent 4-*n*-butylphenol. For predictions, we again assumed our system to be represented by a double binary. Activity of *n*-butanol in the sorbent was predicted using UNIFAP (*52*), a modified

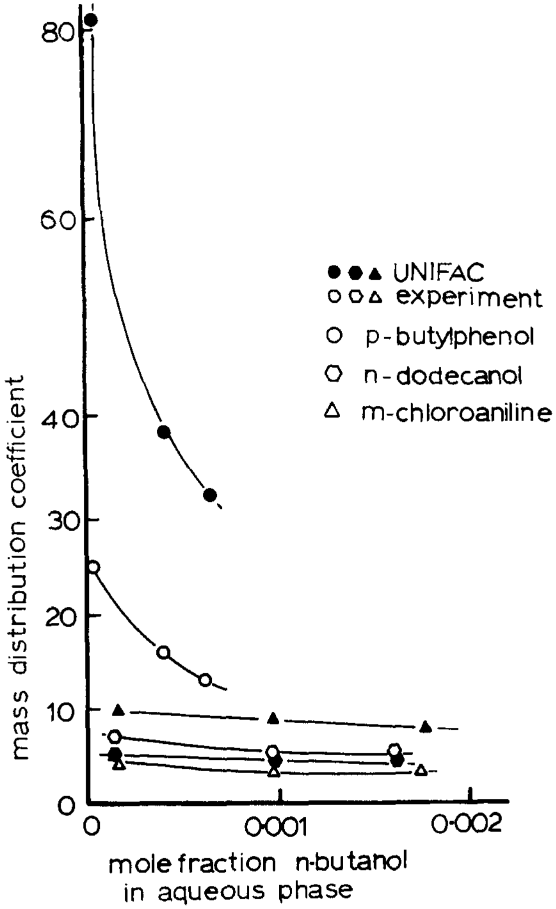

FIG. 2. Comparison of experimental and predicted distribution coefficients for three *n*-butanol solvents: *p*-butylphenol and *n*-dodecanol data are for 18°C, *m*-chloroaniline data are for 30°C. Predicted distribution coefficients are calculated using our double binary model. All distribution coefficients are calculated on a basis of water-free solvents.

TABLE 5
Comparison of Predictions for Double Binary Model and Ternary System for the Case of *p*-Butylphenol as a Solvent for Extracting *n*-Butanol from Water

	Model used	
	Ternary system	Binary model
Equilibrium *n*-butanol concn in aqueous phase (g/L)	6.58	6.58
Mass distribution coefficient	24.6	21.4
Capacity for *n*-butanol (g butanol/kg butylphenol)	162	141
Selectivity	236	264

TABLE 6
Three Examples of *p*-Butylphenol as a Solvent for Extraction of Solute from Dilute Aqueous Solution Using Our Double Binary Model Predictions

	Solute		
	Acetone	*n*-Butanol	Ethanol
Mass distribution coefficient	10.7	21.4	8.4
Capacity (g solute/kg butylphenol)	34.4	141	10.7
Selectivity (approximately)	120	250	100
Equilibrium solute concentration in the aqueous phase (g/L)	3.22	6.58	1.28

form of UNIFAC including a free volume term. We also experimentally tested PVP for *n*-butanol sorption and compared observed results with predictions.

A. Experimental Procedure

A feed of 0.9 ml *n*-butanol (Mallinkrodt AR) in aqueous solution at either 23.89 or 10.44 g/L initial concentration was contacted with between 30 and 300 mg of PVP (nominal molecular weight, 30,000; Polysciences, Warrington, Pennsylvania; used as supplied) in a 1-mL Microvial (Pierce, Rockford, Illinois). The vial was rotated end-over-end at about 1 rps in a water bath at 25.0 ± 0.2°C for 2 days, followed by 3 days of settling. *n*-Butanol concentration was determined using a Carle 9500 Basic Gas Chromatograph with FID detector, a Chromabsorb W-HP column with

20% SP2100 and 0.1% CW1500 at 90°C, and an isopropanol internal standard. Experimental capacities for duplicate experiments agreed within 12%.

B. Results and Discussion

Experimental and predicted capacities of poly(*p*-vinylphenol) are compared in Fig. 3. As in the case of the 4-*n*-butylphenol solvent, the predicted result is higher than the experimental result.

The selectivity of PVP was not measured; however, we expect it to be high. Predictions using UNIFAP suggest that water is totally insoluble in PVP, and we found experimentally that PVP is insoluble in water.

SUMMARY AND CONCLUSIONS

We have used UNIFAC to screen potential solvents, assuming that the ternary system of interest can be modeled as a double binary. This assumption was found to be adequate for the case study presented here, a search for better *n*-butanol solvents. Minimal experimental work was required to confirm that 4-*n*-butylphenol is indeed an excellent *n*-butanol solvent.

We have also found that poly(4-vinylphenol), a sorbent incorporating free phenolic groups, has a high capacity for *n*-butanol, and that this result may be predicted using UNIFAP.

We note that both UNIFAP and a form of UNIFAC with a modified combinatorial term are inadequate for predicting behavior in aqueous systems. This is support for our simplifying assumption, as we can use more readily available binary data to characterize the solute in the aqueous phase, or water in the solvent or sorbent phase, rather than attempting to predict ternary behavior in these phases.

APPENDIX

Calculation Methods

1. Calculate activity of B in B/W model aqueous phase. Available data are supplemented by UNIFAC at low concentrations.
2. Use UNIFAC to determine the mole fraction B in B/S model

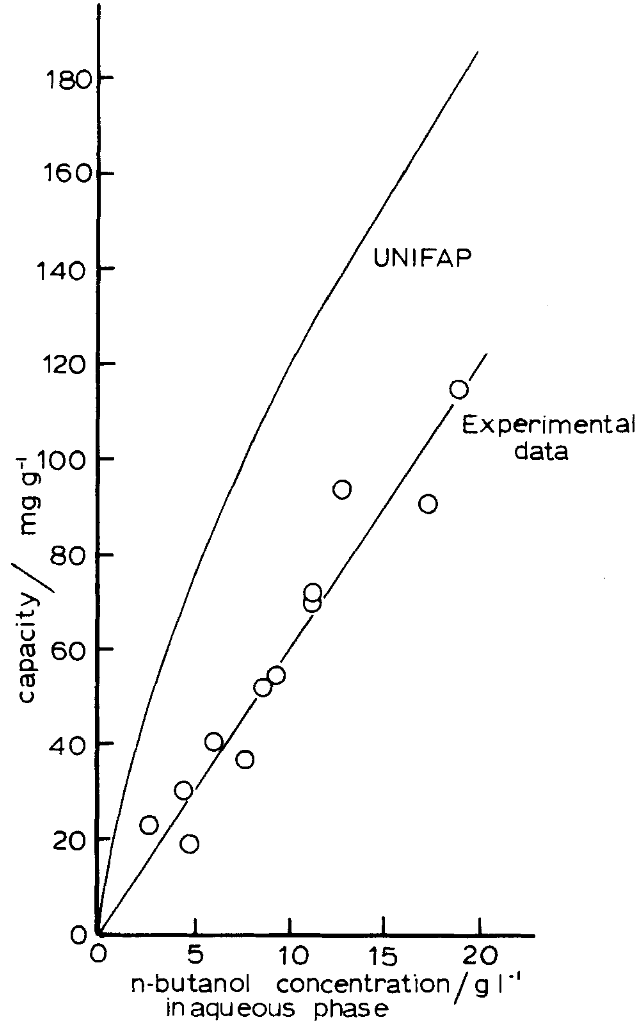

FIG. 3. Comparison of experimental and predicted capacities for poly(*p*-vinylphenol) at 25°C and 1 atm. Predicted capacities are determined from activities calculated using UNIFAP.

extractant phase, such that the activity of B equals that of B in the model aqueous phase. Hence, determine the weight fraction of B in the extractant phase.

3. The weight fraction of W in the aqueous phase is about 1.
4. The solvent phase will be saturated with water; use data for the W/S model solvent phase.
5. For polymers, use UNIFAP. Then mass distribution coefficients, K_a, are given by

$$K_a(\text{solute}) = \frac{(\text{g solute/kg extractant phase})}{(\text{g solute/kg aqueous phase})} \qquad \begin{matrix}\text{Method 2}\\ \text{Method 1}\end{matrix}$$

$$K_a(\text{water}) = \frac{(\text{g water/kg extractant phase})}{(\text{g water/kg aqueous phase})} \qquad \begin{matrix}\text{Method 4}\\ \text{Method 3}\end{matrix}$$

and

$$\text{selectivity} = \frac{K_a(\text{solute})}{K_a(\text{water})}$$

and

$$\text{capacity} = (\text{g solute/kg extractant phase})$$

where B = n-butanol
W = water
S = solvent

Acknowledgments

Listings of the UNIFAC and UNIFAP programs and parameter sets were kindly sent to us by John Prausnitz, University of California-Berkeley, and by Aage Fredenslund, Instituttet for Kemiteknik, Danmarks Tekniske Højskole, Lyngby, Denmark.

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Received by editor April 22, 1986