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Solvent Selection for Extraction from Dilute Solution

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Abstract

An improved strategy for the selection of solvents for recovery of chemicals from dilute solution is presented. Low solvent losses and a high solute distribution coefficient are primary goals for solvent selection. High relative volatility of the solvent also is an important property if the solute is to be recovered from the extract by distillation. Low solvent losses will ensure adequate selectivity and the formation of two phases. High solute-solvent boiling point difference will increase the relative volatility and reduce the chance of azeotrope formation. The dependence of these properties on solvent structure is examined in some detail, and this indicates guidelines for the selection of solvents with the desired properties. The strategy is illustrated with the example of 1-butanol recovery.

1. INTRODUCTION

We have shown in a previous paper (*1*) that the cost of recovery of potentially valuable products from dilute solution tends to be dominated by materials handling costs in the early stages of the overall separation process. Thus, rapid volume reduction is almost always important. An economic and effective volume reduction can be obtained by extraction or sorption using a specific separating agent with high affinity for the desired solute and a method for readily separating the solute from the separating agent. Selection of a separating agent requires screening a very large number of potential systems at low cost. A relatively small number of the more promising agents then can be studied in more detail.

1.1. Goals and Scope

We are concerned here with improving the efficiency of this preliminary screening process. We will restrict our discussion to solvent extraction of dilute aqueous feed streams followed by distillation of the extract to give the desired concentrated product. Many process flow sheets are possible, for example:

(a) Extraction followed by distillation of the extract to give an overhead solute–water mixture and a bottoms of purified solvent which may be recycled. The overhead goes to a second distillation for water–solute separation.
(b) Extraction followed by extractive distillation to give an overhead of water and a bottoms solute–solute mixture. In this case the bottoms goes to a second still for solute–solvent separation.

In each case the entire volume of extract must be processed in at least one distillation.

We develop and illustrate our solvent screening strategy with data, predictions, and process design examples involving the classes, general examples, and specific examples of solvents listed in Table 1. We are specifically interested in the recovery of polar organic solutes from dilute

TABLE 1
Compound Classes and Examples Considered in This Work

Solvent class		General examples		Specific examples	
A	Aliphatic hydrocarbons	a	*n*-Alkanes	*a*	Octane
B	Halide hydrocarbons	b1	1,1,*N*,*N*-Tetrachloroalkanes		
		b2	1,1,1-Trichloroalkanes		
C	Ethers	c	Ethylethers		
D	Esters				
E	Ketones	e	2-*n*-Ketones		
				e	furfural
F	Aldehydes			*f*	Heptanal
G	Amines	g1	Primary *n*-amines		
		g2	Tertiary amines	*g*	Tributylamine
H	Aliphatic alcohols	h	1-*n*-Alcohols	*h*	Dodecanol
I	Phenols	i	4-*n*-Alkylphenols	*i*	*o*-Ethylphenol
J	Organic acids	j	1-*n*-Aliphatic acids	*j1*	Heptanoic acid
				j2	Palmitic acid
K	Aliphatic diols	k1	1,*N*-Aliphatic diols	*k1*	Hexylene glycol
		k2	1,2-Aliphatic diols		

aqueous solution, important in recovery from both waste streams and fermentation broths (*2*). We choose as a case study the recovery of 1-butanol, and focus on solvents with boiling points greater than that of 1-butanol.

1.2. Approach

To improve the efficiency of solvent screening, we start by identifying which system properties have a primary influence on process cost. We then seek to reduce the number of system properties to be considered explicitly by finding property interrelationships. Finally, we identify relationships between the reduced set of system properties and solvent structure in order to guide solvent selection.

1.3. Review of Solvent Selection Methods

Attempts to identify improved solvents for recovery of oxychemicals such as ethanol or 1-butanol from dilute aqueous solution are numerous (e.g., *2–12*).

Busche (*2*) noted for recovery from dilute aqueous solution that if the boiling point of the product is less than that of water, then distillation is relatively easy. However, if the product is a high boiler, then the water must be boiled away from the product, which results in an energy intensive process. For the example of acetic acid recovery, solvent extraction followed by azeotropic distillation uses 1/20th of the equivalent steam energy of simple distillation and ½ of the energy of melt crystallization. Electrodialysis required the least energy of the processes consdiered by Busche. However, this process is not applicable to the recovery of neutral solvents.

Dadgar and Foutch (*5*) listed 16 criteria for screening for solvents for recovery of acetone, butanol, and ethanol from dilute aqueous solution. They reported experimental distribution coefficients and selectivities for each of 47 test solvents from 11 different solvent classes. They tabulated literature data for density, viscosity, boiling and freezing points, surface tension, enthalpy of vaporization, toxicity, flammability, solubility in water, and cost. Chemical stability was also discussed. Their major screening goal was high selectivity. We shall show below that selectivity often is unimportant, the number of variables to be considered explicitly can be reduced, and predictive techniques and available data can be used to reduce the amount of experimental work needed to find better solvents.

Zacchi et al. (*12*) determined steam use, but not overall costs, for ethanol recovery from aqueous solution. He considered both a conventional distillation or extraction followed by distillation, using a solvent with a boiling point either higher or lower than that of the solute. Extraction with a low boiling solvent required a high distribution coefficient, K_D, absence of an ethanol–solvent azeotrope, a high relative volatility of solvent relative to ethanol, and a solvent easily stripped from the raffinate. They suggested that if extraction is to reduce energy costs relative to conventional distillation, then a $K_D > 7.5$ is required for a 4-wt% ethanol feed, and a $K_D > 5.7$ for an 8-wt% feed. A high K_D is required to reduce the quantity of volatile solvent to be distilled for this process to be competitive with conventional distillation.

Zacchi et al. (*12*) also considered ethanol extraction with high boiling solvents, followed by one distillation to separate the ethanol/water mixture from the solvent and a second distillation to separate the ethanol from the water. They suggested that this process requires the absence of an ethanol–solvent azeotrope, an ethanol–water relative volatility comparable in the presence and the absence of solvent, a high selectivity to minimize the size and energy requirements of the second distillation, and a K_D of about 1. However, we note that the size of the second still could be kept small if the solvent has a high K_D and a selectivity of at least 1.

For either high-boiling or low-boiling solvents (relative to the solute), specific solvent–solute interactions are required for a high K_D. However, solvent–water interactions must not be strong enough to give high solvent losses or miscibility. This means that extractive distillation followed by a second distillation for solute–solvent separation [such as flow sheet (b) described above] may be the favored configuration for solvents with high K_D.

Munson and King (*9*) noted for ethanol extraction that within a given class of solvents there is a trade-off between K_D and β, the selectivity. Branching within a given class increases selectivity. However, branching also increases solvent losses, as we shall see later.

Some authors have suggested that selectivity is important for extraction of ethanol from dilute aqueous solution (e.g., *8*, *10*), while others have not. For example, Ishii et al. (*7*) suggested the following solvent property criteria for solvent selection for extraction from fermentation broths: nontoxic, immiscible with feed, high K_D, low viscosity, high density difference, sterilizable and autoclavable, and low cost. They did not mention selectivity.

In this paper we consider solvent selection for the general problem of recovery of polar organics from dilute aqueous solution. We consider the entire cost picture and attempt to show general approaches and strategies where possible. We find that selectivity is important only if the K_D is low, and suggest that a solvent meeting the requirements of immiscibility (and low solvent losses) will most likely have a high selectivity anyway.

2. SYSTEM PROPERTIES AND PROCESS COSTS

We consider here a process consisting of extraction followed by distillation to produce a solute–water mixture overhead and a solvent bottoms, which is recycled to the extractor. The water in the overhead is then removed by either a second distillation or by sorption. Similar analyses, not shown here, reveal similar trends but have different details for other flow sheets.

Rapid reduction in the volume of material to be handled is the primary task for recovery from dilute solution. This may reduce both capital and operating costs for the extractor, distillation column, reboiler and condenser, solute drying equipment, and solvent inventory. *Low solvent losses* are critical for economic recovery; otherwise one dilute solution separation problem will be replaced by another. *Easy reversibility* in this case means low distillation energy requirements and small column size. A question we address later is whether using a solvent which permits a large volume reduction for extraction will make distillation more difficult. *Low cost for solute drying* or removal of water from the extract is also important. This generally means that the total quantity of water in the extract should be a small fraction of the quantity of water in the feed. If the volume reduction in the extraction is large, then the total quantity of extract and hence the quantity of water in the extract are both small. We now address these factors individually.

Volume and mass reduction are related by phase densities, which for liquid systems near atmospheric pressure fall in a relatively narrow range. Thus, for initial solvent screening we shall use mass reduction, which is more convenient. The solute distribution coefficient, K_D, is the ratio of the weight fraction of solute in the solvent phase to the weight fraction of solute in the aqueous phase. The water distribution coefficient, K_W, is defined similarly. The selectivity, β, is the ratio K_D/K_W. Mole-fraction-based terms can be misleading as the solvent and aqueous phase often have widely differing molecular weights.

2.1. Rapid Volume Reduction

First, we examine the sensitivity of mass reduction and water contamination of the solvent-rich extract to both the solute distribution coefficient and the selectivity. We consider some representative process design examples, using countercurrent liquid-liquid extraction for the series of specific solvent examples listed in Table 1, and specifying 90% removal of 1-butanol from a 1% weight aqueous feed, with 32 equilibrium stages. The equilibrium data used here, generated with UNIFAC with the VLE parameter set, are accurate enough to reveal trends important for solvent selection.

K_D is the primary indicator of mass reduction as shown in Fig. 1. The amount of extract phase per unit mass of feed (which is the reciprocal of the mass reduction) for the extraction step alone is nearly directly predicted by the mass fraction K_D alone. in these cases, selecting a solvent with a higher distribution coefficient will reduce the mass of extract

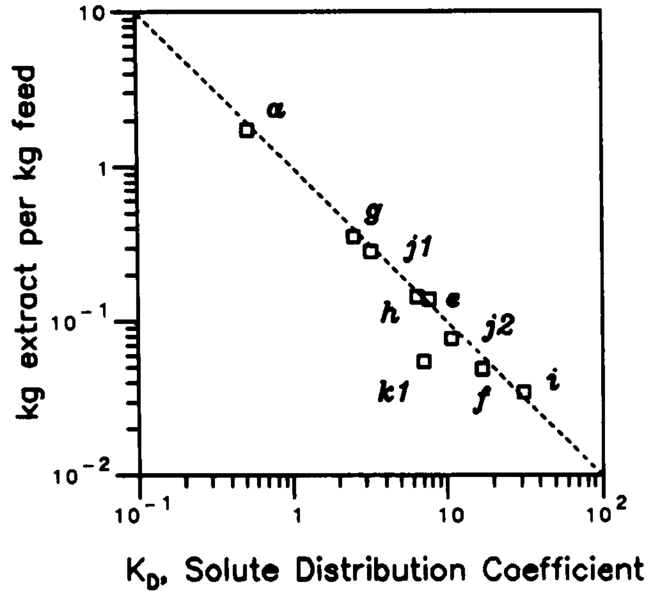

FIG. 1. Process design calculations for solvent-1-butanol-water: amount of extract versus concentration distribution coefficient for 1-butanol. Results are shown for rigorous design calculations for eight specific examples of solvents for extraction of 1-butanol from 1% weight aqueous solution, using 32 equilibrium stages. Equilibrium data are determined using UNIFAC with VLE parameters.

produced. The effect of increasing the selectivity is less clear, and a plot of the reciprocal of the mass reduction versus selectivity, shown in Fig. 2, has consdierable scatter. In fact, it appears that a higher selectivity might lead to a greater mass of extract in some cases. This is because there tends to be a trade-off between the selectivity and the distribution coefficient for the extraction of polar compounds from dilute aqueous solution. These results can be put in terms of the sensitivities

$$\frac{\partial \ln(\text{mass reduction})}{\partial \ln(K_D)} \doteq -1$$

with high precision and

$$\frac{\partial \ln(\text{mass reduction})}{\partial \ln(\beta)} \doteq 0$$

with low precision.

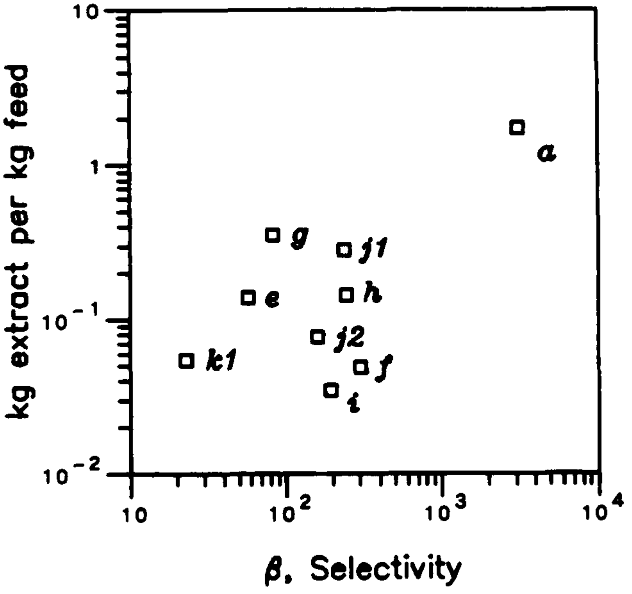

FIG. 2. Process design calaculations for solvent-1-butanol-water: amount of extract phase versus selectivity for 1-butanol. Results are for calculations as in Fig. 1.

However, the selectivity, β, is very good for estimating the water contamination of the solvent phase. The amount of water in the extract phase after the extraction step alone clearly decreases as the selectivity increases for these case studies, as shown in Fig. 3.

The benefits of early mass reduction are cumulative to all subsequent unit operations due to reduced flow rates of undesired material. In the extraction step it is desirable both to reduce the overall mass rapidly and to minimize the amount of water in the extract. The distribution coefficient is the primary determining factor in extraction mass reduction. At K_D's large enough to be economically interesting, we shall show that β has little economic effect.

A high solvent distribution coefficient in the extractor provides two benefits for the distillation step:

1. There is a higher concentration of solute in the extract stream fed to the distillation. This reduces the concentration span between the feed plate and the purified solute.

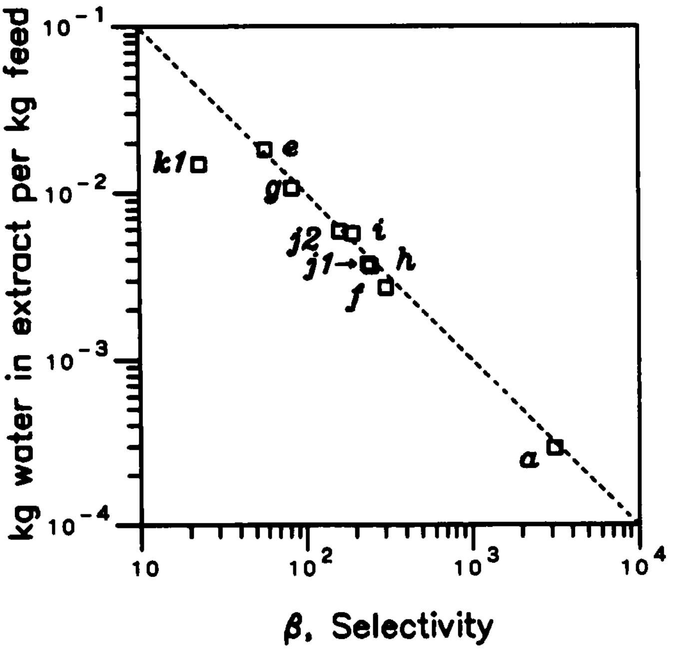

FIG. 3. Process design calculations for solvent-1-butanol-water: amount of water in the extract phase versus selectivity for 1-butanol. Results are for calculations as in Fig. 1.

2. There will be fewer stages needed since the residual solute concentration in the stripped solvent can be higher. This is because there can be higher solute concentration in the solvent entering the extractor for a given raffinate concentration. The concentration span in the still from the feed plate to the reboiler should remain proportional to the concentration range from the extractor feed to the raffinate.

Water removal from the extract is the only step in which the selectivity affects equipment size in a major way.

2.2. Reduction of Solvent Losses

It is critical that either the amount of solvent lost in the raffinate phase is small or that recovery of lost solvent from the raffinate is cheaper and simpler than the original task of solute recovery. The former requires that the value of lost solvent must be much less than the value of the solute.

> For example, given a 1% w/w feed and a solvent cost per kilogram of 10 times that of the solute, then solvent losses must be less than 0.005% w/w in order to achieve the requirement that solvent losses be less than 5% of the solute value.

Thus, minimizing solvent losses is clearly a major constraint on solvent extraction from dilute solution.

For a dilute feed and good yield, there will be little if any solute remaining in the raffinate. Thus, the solubility of the solvent in water will be an excellent measure of the expected solvent losses.

2.3. Easy Reversibility

Reversibility involves two related tasks: rectifying to produce a solvent-free stream containing concentrated solute and water, and stripping to produce a solute-free solvent which can be recycled to the extractor. A high volatility of the solute relative to the solvent will reduce both the number of distillation stages required for each task and the heat load for the distillation. A low latent heat of vaporization of the solvent will reduce the reboiler heat load. It is desirable that the solvent–solute–solvent system does not form an azeotrope.

3. PROBLEM SIMPLIFICATION BY USING INTERELATIONSHIPS BETWEEN SYSTEM PROPERTIES

In this section we seek to reduce the number of system properties to be considered explicitly by identifying property interrelationships.

3.1. Miscibility, Selectivity, and Solvent Losses

3.1.1. Miscibility and Mutual Solubility

Two liquid phases are required for liquid-liquid extraction, unless a membrane or other means is used to separate the phases. Whether two phases are miscible depends on intermolecular interactions, as does the mutual solubility of the phases. Here we examine data for a variety of solvent-water binary pairs, but note that the presence of a solute affects the mutual solubility of the other solvent and water.

The critical solution temperature is the temperature at which the transition between two phases and one phase occurs. Mutual solubility data from Ref. *13* for 10°C below the critical solution temperature are shown in Fig. 4, representing close to the borderline condition for the two phases to become one. The critical solution temperature is greater than 100°C for each of the solvent-water pairs shown, except for phenol-water. This plot shows that even at the edge of the two-phase region, where a single phase is about to form, the solubility of water in the solvent is less than 60 wt%. This means that K_W will be less than 0.6, and that the selectivity will be at least 1.6 times greater than the distribution coefficient. Thus, despite a large fraction of water in the solvent phase, two immiscible phases can still exist. The requirement of solvent-water immiscibility does not constrain selectivity or solvent losses. The solubility of the solvent in water is greater than 10 wt% for all cases. This suggests that if losses of a polar organic solvent into water are less than 10 wt%, then two phases will be formed rather than one.

Conclusion: If we search for a solvent (and operating temperature for extraction) which provides for low solvent losses, then we need not be concerned about immiscibility.

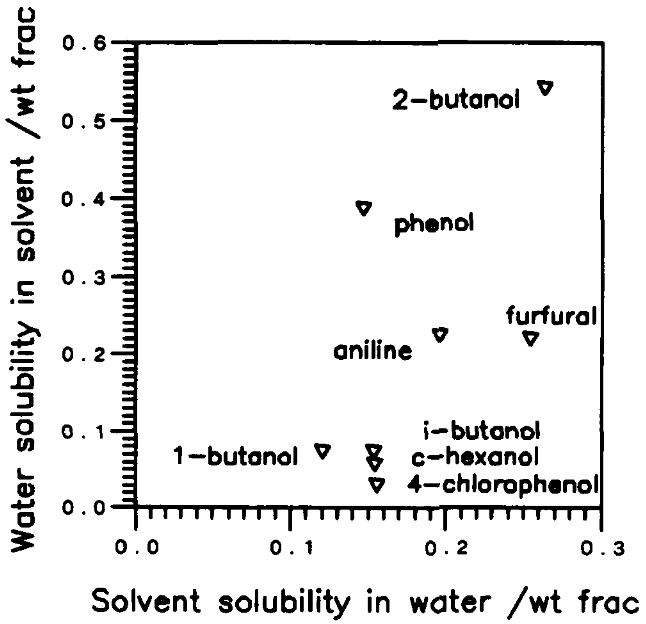

FIG. 4. Data for solvent-water: miscibility limits at 10°C below the critical solution temperature. Shown is the solubility of solvent in water versus solubility of water in solvent. Data are from Ref. *13*.

3.1.2. Selectivity and Solvent Losses

The distribution of water into the solvent depends on two major factors: the solubility of water in pure solvent, and the coextraction of water into the solvent associated with the presence of the solute. The latter effect depends on the type and amount of solute present, and to a lesser extent on specific solvent-solute-water complexing. Thus, one expects that the solubility of water in a solvent is a good indication of water distribution into the solvent, at least for comparison of different solvents.

Solvent solubility in water versus water solubility in solvent data is shown in Fig. 5 for a variety of solvent classes with differing isomers and

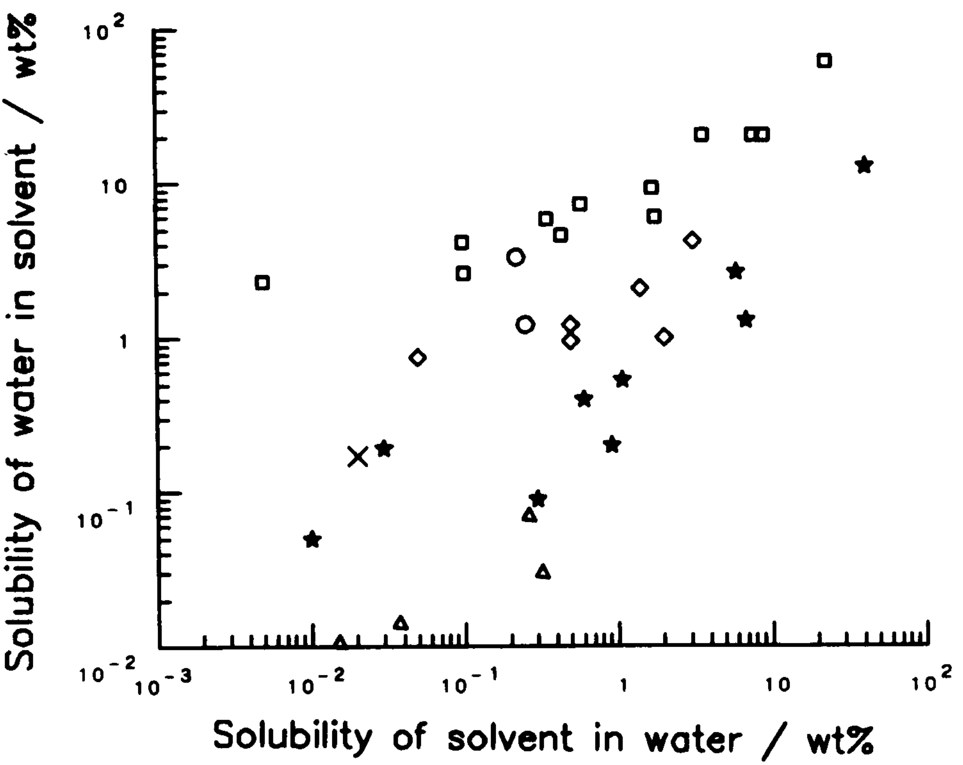

FIG. 5. Data for solvent-water: solubility of solvent in water versus solubility of water in solvent. All points shown are binary data from Flick (*14*) for a variety of isomers and molecular weights within each general class of compounds.

molecular solvents within each class. Similar data and UNIFAC-based predictions only for homologous series of solvents are shown in Fig. 6. All data listed in Fig. 5, taken from Flick (*14*), are for binary mutual solubilities at either 25 or 20°C. The predictions use UNIFAC predictions of liquid phase activity coefficients, using the LLE parameter set from Ghemling et al. (*15*). As the number of aliphatic CH_2 groups increases for a given solvent functional group, the solubility in water decreases. The trend present in both these plots is clear: as the number of aliphatic groups increases, the solubility of the solvent in water decreases much more rapidly than the solubility of water in the solvent phase decreases. The solubility of water in the solvent phase is rather insensitive to the number of CH_2 groups present in the molecule.

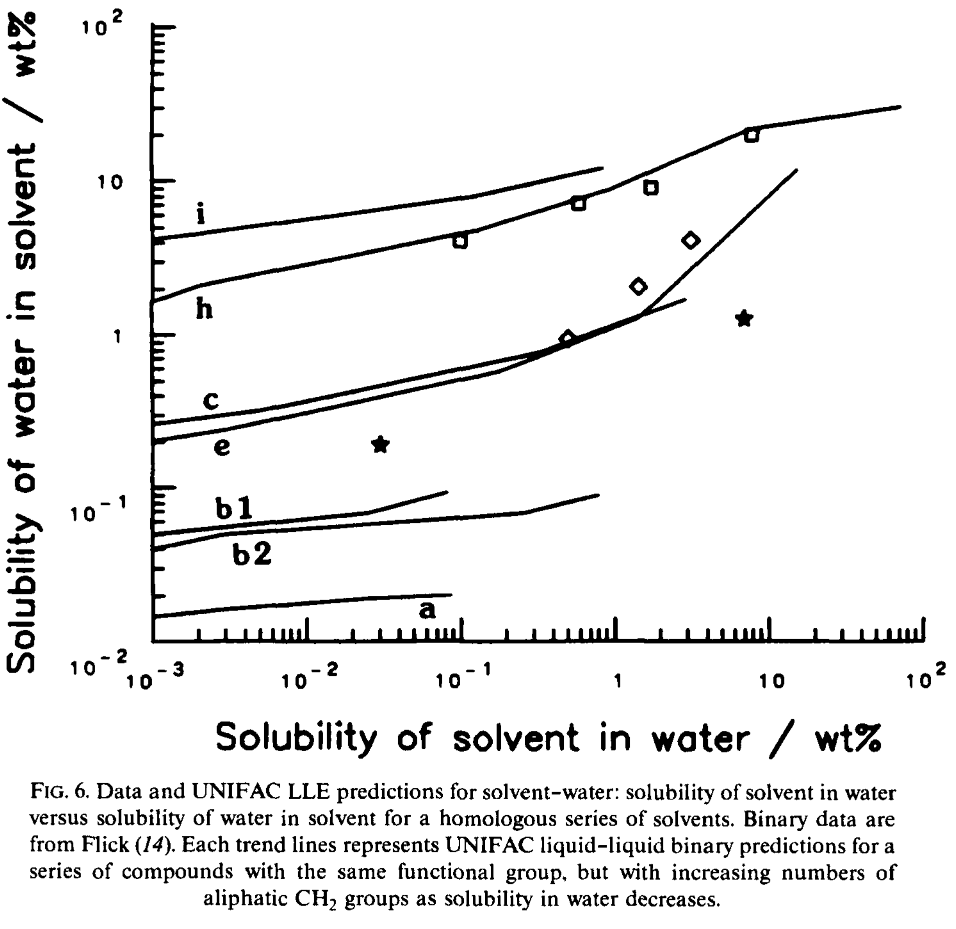

FIG. 6. Data and UNIFAC LLE predictions for solvent-water: solubility of solvent in water versus solubility of water in solvent for a homologous series of solvents. Binary data are from Flick (*14*). Each trend lines represents UNIFAC liquid-liquid binary predictions for a series of compounds with the same functional group, but with increasing numbers of aliphatic CH_2 groups as solubility in water decreases.

We know that low solvent losses are desirable, and thus we search for solvents with a low solubility in water. This is equivalent to moving toward the left-hand side of Fig. 5 or Fig. 6. In this region the magnitude of the solubility of water in the solvent is low and fairly constant for any given solvent functional group. The distribution coefficient for water, K_W, is less than 0.1 for all the solvents shown in these figures. Thus, screening for low solvent losses leads to solvents with low K_W. Now, as we found earlier, as long as K_D is large and K_W is less than 0.1, then we need not be concerned about the selectivity.

3.1.3. Summary

If losses of solvent into the aqueous phase are small, then selectivity of the solvent for the solute versus water will be adequate. In addition, the aqueous and organic phases will be immiscible.

3.2. Relative Volatility, Azeotropes, and Boiling Point

A high relative volatility is desirable if the solute is to be recovered from the solvent by distillation. Several alternate distillation flow sheets are possible, but in each case a high relative volatility between the solute and the solvent will reduce the difficulty of separating these two components. In addition, it is desirable to avoid the formation of azeotropes between any of the three pairs of components in the system.

We seek a predictive relationship for the key distillation property, relative volatility. We are concerned with distilling a ternary mixture of solvent, extracted solute, and coextracted water. This ternary distillation for polar solute recovery can be usefully represented as a pseudobinary distillation of the solute from the solvent. To simplify the discussion, we shall consider here only solutes with boiling points greater than that of water, the so-called "high-boiling" solutes. For the case of extractive distillation, the water is removed in a first distillation unit prior to the solute–solvent separation. For the case of regular distillation, the water will be more volatile than the solute and thus the key components will be solute and solvent.

3.2.1. Relative Volatility and Boiling Point

Many different relationships have been proposed which relate the (assumed constant) relative volatility of binary pairs of nonpolar compounds to their boiling points (e.g., *16–18*). Relative volatilities can also be calculated from vapor-pressure data (e.g., *19*). Here we determine if either vapor pressure or boiling point data can be useful for screening polar solvents with high relative volatilities.

The relative volatility for the strongly interacting binary pair of solute and solvent depends on the mixture composition and may vary by an order-of-magnitude within a single distillation tower. Some convenient yet useful average relative volatility is needed, and we use a binary, liquid phase, mole fraction arithmetic average relative volatility $\bar{\alpha}_{Bin_x}$, determined by averaging the relative volatility at evenly spaced liquid mole fractions, 0.1, 0.2, 0.3, . . . , 0.9. Either an arithmetic ($\alpha_{Ter,tray}$) or geometric average of the relative volatilities for the ternary system at conditions at each tray in a distillation column design is more likely to be appropriate for actual design.

We checked the validity using the binary liquid mole fraction average relative volatility with the results of rigorous multistage distillation calculations using real ternary feed streams of 1-butanol extracted from dilute aqueous solution with the specific test solvents listed in Table 1. For each solvent the distillation tower height differs. The relative volatility averaged over all the trays, $\bar{\alpha}_{Ter,tray}$, is plotted versus the binary liquid mole fraction average, $\bar{\alpha}_{Bin,x}$ in Fig. 7. The correlation is excellent

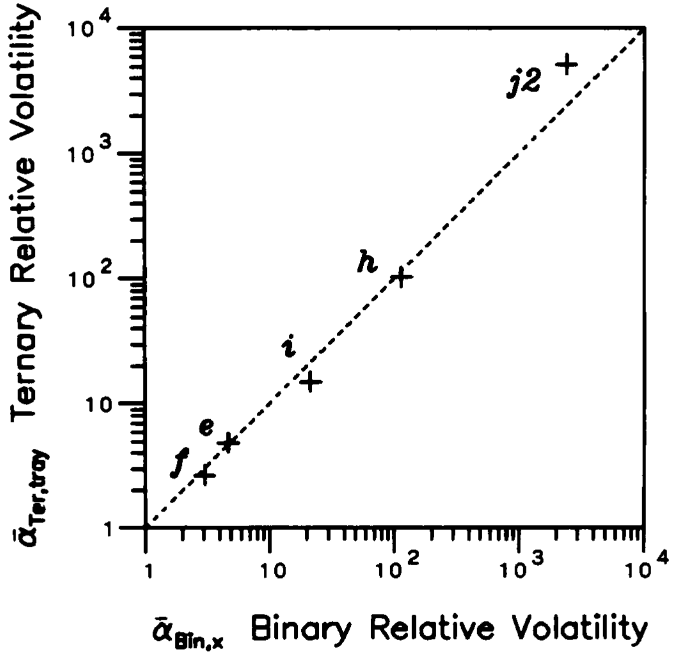

FIG. 7. UNIFAC VLE predictions for solvent-1-butanol and process design calculations for solvent-solute-water: binary liquid composition weighted average relative volatility versus ternary system distillation tower tray weighted average relative volatility. The binary data were calculated simply using UNIFAC VLE predictions, and averaging the relative volatility at each liquid mole fraction evenly spaced from 0.0 to 1.0. The ternary data were calculated using a extract produced in a 32-stage liquid-liquid extractor as a feed to a distillation tower. The number of trays and tray compositions in the distillation tower were then determined using rigorous calculations. The average was taken over the relative volatility for all trays.

for the wide range of solvent classes considered here, indicating that using the simpler measure of the relative volatility, $\bar{\alpha}_{Bin,x}$, is sufficient for solvent screening. The basis for this behavior is outlined in Appendix A.3. We now proceed to search for higher relative volatilities.

For a wide range of binary pairs, $\bar{\alpha}_{Bin,x}$ is related to the difference in boiling point between the two components, as shown in Fig. 8. The points here are calculated from vapor–liquid equilibrium data given in Ref. *20*.

We now consider examples of binary pairs involving 1-butanol plus each of the specific solvent examples in Table 1, and examine different predictions of $\bar{\alpha}_{Bin,x}$ as a function of the boiling point difference, ΔT^b,

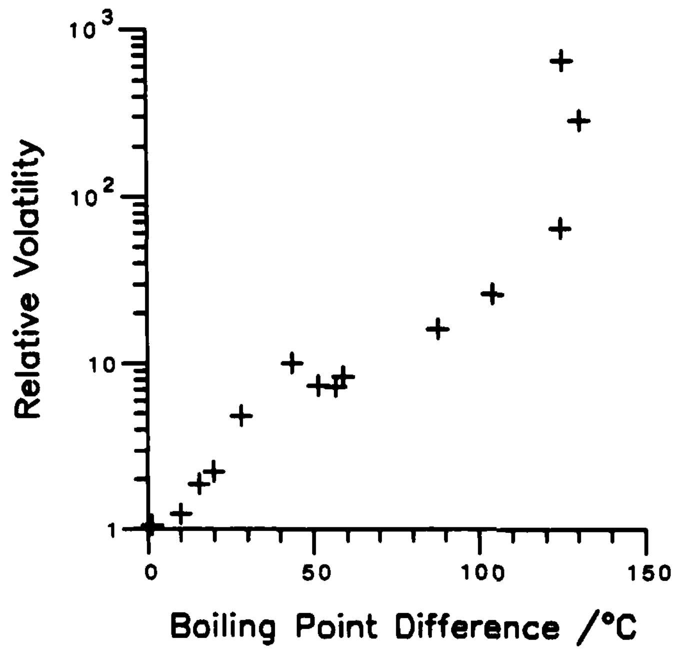

FIG. 8. Results derived from binary data: average relative volatility for various polar compound–other compound pairs as a function of the boiling point difference between the pair. The other compound may or may not be polar. All data are for atmospheric pressure and are taken from Ref. *20*. The average is calculated giving equal weighting to the relative volatility at evenly spaced liquid compositions from 0.1 to 1.0 mole fraction. The binary pairs considered, in increasing order of boiling point difference, are ethyl acetate–ethanol, *n*-ethylbutylamine–butanol, tetrahydrofuran–isopropanol, acetone–ethanol, hexane–1-propanol, diethyl ether–ethanol, chloroform–butanol, acetic acid–*c*-hexyl acetate, ethanol–pentanol, hexane–hexanol, acetone–furfural, acetone–phenol, benzene–benzyl alcohol, and tetrahydrofuran–ethylene glycol.

between the solvent and 1-butanol as shown in Fig. 9. All predictions and data on this plot are specific for binary pairs involving 1-butanol as one of the components. The $\bar{\alpha}_{Bin,x}$ calculated using UNIFAC with the vapor-liquid equilibrium (VLE) parameter set is almost directly proportional to ΔT^b for $\bar{\alpha}_{Bin,x}$ ranging from 1 to over 100. Also shown are two data points from Fig. 8 which are for 1-butanol systems, which suggest that the UNIFAC predictions are reasoanble, at least for the lower values of these data. Also shown in Fig. 9 are two rule-of-thumb predictions of the relative volatility: one based (see *16*, *18*) on the Pictet-Trouton rule plus the Clausius-Clapeyron equation, and the other based on the Ramsay-Young rule plus a correlation for the vapor pressure of 1-butanol as a function of temperature. The derivations of and assumptions required for

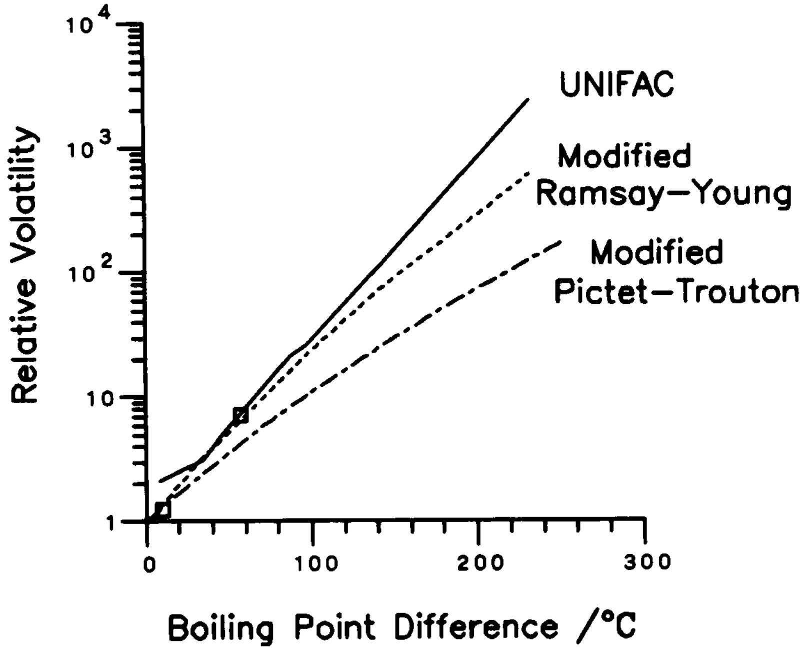

FIG. 9. Results derived from binary data, binary UNIFAC VLE predictions, and rules-of-thumb: average relative volatility for various 1-butanol-solvent pairs as a function of the boiling point difference between the components. Data points are for 1-butanol–solvent pairs, with data from Ref. *20*. Relative volatility predicted using UNIFAC VLE for each of seven 1-butanol-solvent pairs is shown. Also shown are rule-of-thumb predictions, specific here for any 1-butanol–solvent system, based either on the Ramsay-Young rule plus a 1-butanol vapor pressure correlation or based on the Pictet-Trouton rule. Details and assumptions for both predictions are given in Appendix A.

these two rules-of-thumb are given in Appendix A. All three relationships show similar behavior: relative volatility increases exponentially as the difference in solute–solvent boiling points increases.

3.2.2. Azeotropes and Boiling Point

Choice of a solvent with a large boiling point difference from that of the solute has a second advantage: the chance of azeotrope formation is significantly reduced. Horsley (*22*) presented plots, each summarizing considerable data on azeotrope composition from Ref. *23*, to aid prediction of azeotrope formation for a large variety of systems. For any class of binary system the risk of azeotrope formation decreases dramatically as the boiling point difference between components increases. For example, we show here six of these plots involving either alcohols or butanols as one of the binary components, replotted together as Fig. 10. Binary azeotrope compositions are shown as a function of the boiling point difference between the binary components. For the six different groups of systems involving alcohols, azeotrope formation is unlikely for a boiling point difference of about 50°C. We also show individual data points, taken from Ref. *23* for a variety of systems involving *n*-butanol as one of the components, in Fig. 11. It can be seen that the scatter is not large, apart from the outlying point for 1-butanol–water.

3.2.3. Other Considerations

Note that the viscosity in the distillation tower is, to a first approximation, independent of the boiling point of the solvent or solute or the mixture present in the column, as for many liquids at their boiling point the viscosity is about 0.3×10^{-2} Pa · s.

3.2.4. Summary

The benefits of selecting a solvent with a sufficiently large boiling point difference from the solute include:

1. The relative volatility of the solute relative to the solvent will be high.

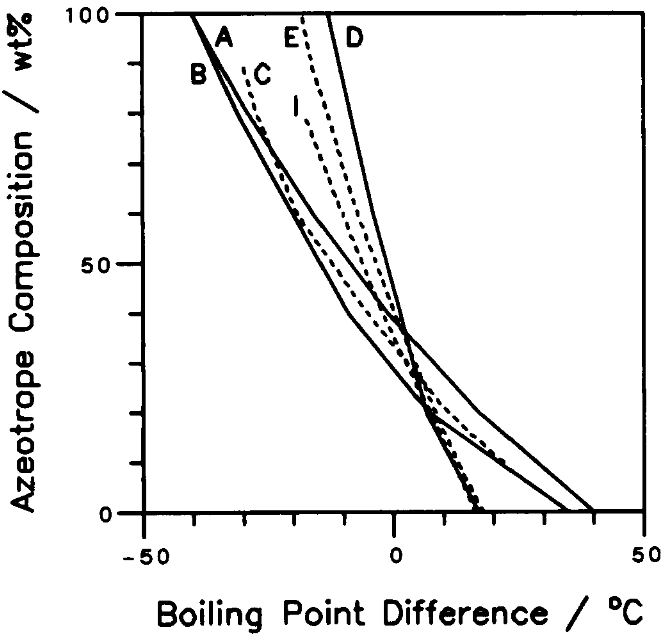

FIG. 10. Trend lines from data for solvent–alcohol: binary azeotrope composition (wt% of alcohol) versus boiling point difference (alcohol boiling point minus boiling point of second component). Each line represents the trend for many azeotropes: the actual data show scatter about each line. The solid lines are systems with one component being any of the butanol isomers. The dashed lines are systems with one component being an alcohol. This plot is an overlay of six plots taken from the 51 such plots presented in Horsley (*22*).

2. The solute–solvent system will not form an azeotrope.
3. Heat recovery may be enhanced or vapor recompression used, as there is a higher temperature difference across the column.

However, the choice of a high boiling point solvent must be tempered by some potential drawbacks which include:

1. Increased heat requirements due to higher latent heat of vaporization.
2. Higher temperature stream requirements due to the higher reboiler temperature.
3. Increased heat loss from the column due to the higher column operating temperature.

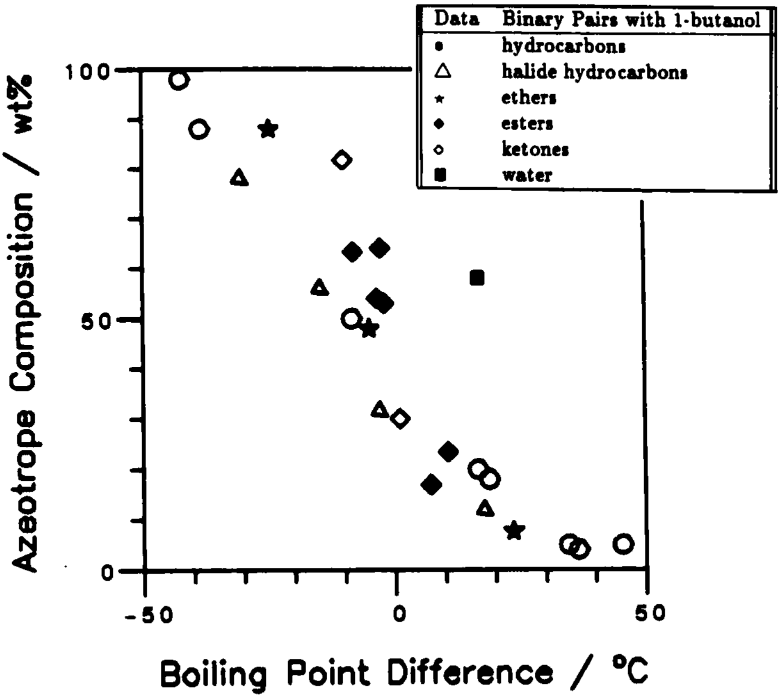

FIG. 11. Data for solvent-1-butanol: binary azeotrope composition (wt% 1-butanol) versus boiling point difference (boiling point of 1-butanol minus boiling point of the second component). Data are shown for hydrocarbons (saturated and unsaturated, linear and cyclic), halide hydrocarbons (aromatic and aliphatic), ethers, esters (aliphatic and aromatic), ketones, and water. The data are from Ref. *23*.

4. Possible solute or solvent decomposition, or the need for vacuum operation.
5. Problems associated with a higher viscosity solvent such as less efficient mass transfer and increased pumping costs.

3.3. System Properties Selected for Solvent Screening

The solvent selection problem has been reduced to a few important criteria:

1. Find a high distribution coefficient for the solute into the solvent (high volume reduction).

2. Minimize solvent losses (need not consider selectivity and immiscibility).
3. Use a high-boiling solvent (high relative volatility, low chance of azeotrope formation) which does not boil at too high of a temperature (solvent decomposition, high viscosity in extractor, higher enthalpy of vaporization, higher heat losses from distillation column).

A good solvent will provide a cost-effective balance between these properties.

4. RELATIONSHIPS BETWEEN SYSTEM PROPERTIES AND SOLVENT STRUCTURE

In this section we show how changing solvent structure affects system properties. The aspects of solvent structure we consider here, in approximate order of importance, are:

1. The nature of the functional group.
2. The number of hydrocarbon moieties (both aliphatic, such as CH_2, and aromatic, such as ACH).
3. The effect of having more than one functional group (multiple substituents).
4. The location of the functional group (such as primary, secondary, or tertiary).
5. The type of hydrocarbon moiety (aliphatic versus aromatic).
6. The branching of the aliphatic hydrocarbon portion of the molecule.

The desirable properties for the solvent–solute–water system are a high distribution coefficient, K_D, for the solute into the solvent, low solvent losses, and a high relative volatility, α.

We illustrate the discussion with the example of 1-butanol recovery from dilute aqueous solution.

4.1. Distribution Coefficient

It is difficult to generalize the complex interactions which occur in the solvent phase, which may contain significant amounts of all three components. Self-association, interactions between pairs of components, and synergistic effects involving all three components can occur. Nevertheless, a simple guideline is that solvent–solute intermolecular interactions must be stronger than those of solute–water for a high distribution coefficient of the solute into the solvent phase from an aqueous phase. It might also be expected that any strong solvent–water interactions will reduce the amount of solvent available for solute–solvent interactions. Real behavior is best determined by experiment, but a significant prescreening of potential candidates is possible (e.g., *3*).

Consider, for example, the distribution coefficient of 1-butanol into various solvents from dilute aqueous solution. Results are shown in Fig. 12 of predictions of the separation into two equilibrium phases of a mixture of 29 mol% solvent, 1 mol% 1-butanol, and 70 mol% water. This mixture is typical of 1-butanol concentrations found in fermentation broths. UNIFAC LLE parameters were used. The choice of functional group is seen to have a significant influence on the K_D, as does the aromatic or aliphatic nature of the backbone. Of those tested here, the

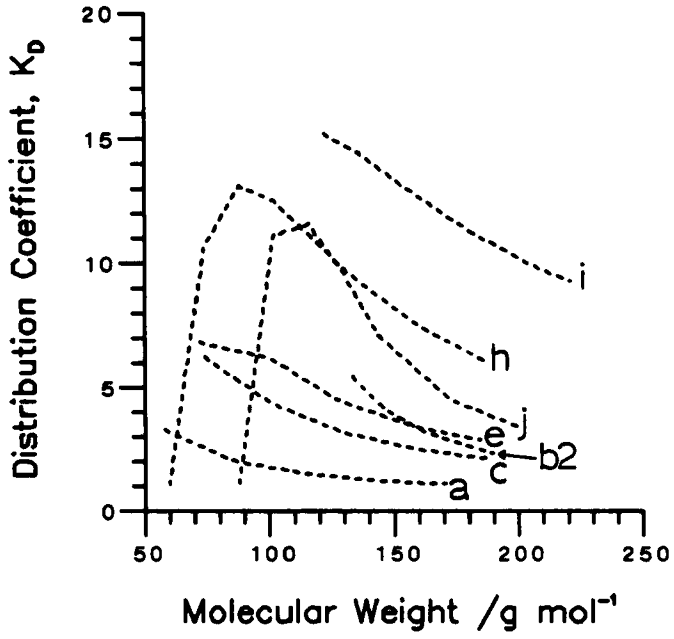

FIG. 12. UNIFAC LLE predictions for solvent–1-butanol–water: distribution coefficient, K_D, as a function of molecular weight for various homologous series. K_D was calculated using UNIFAC with LLE parameters, in each case for the two-phase split of a ternary mixture of the following composition: solvent 29 mol%, 1-butanol 1 mol%, water 70 mol%.

hydroxyl functional group gives the highest K_D, and the aromatic hydroxyl, phenol, is better than the aliphatic hydroxyl in normal alcohols. Note that in this work we restricted our analysis to mainly oxygenated solvents, for which adequate data were available. In an earlier work we reported that a high K_D for 1-butanol extraction could be expected for nitrogen-containing solvents such as anilines, amines, pyridines, and nitriles (see Table 3 in Ref. *3*). The K_D is roughly inversely linearly related to the number of CH_2 groups or the molecular weight of a compound in a homologous series, except for acids and alcohols at lower molecular weights, which exhibit K_D maxima.

It is difficult to predict the effect on K_D of branching of the aliphatic side chain, location of the functional group, or of multiple substitution. Experimental techniques are most useful. For example, we have found in our lab that 3-bromophenol has a higher K_D for 1-butanol from aqueous solution than does 2-bromophenol, which, in turn, has a higher K_D than aliphatic-substituted phenols (*4*).

4.2. Solvent Losses

It is easier to generalize solvent loss behavior than distribution coefficient behavior for extraction from dilute aqueous solution. This is because the concentration of solute in the aqueous phase after extraction is very low, and thus solvent losses are primarily related to the nature of the solvent–water binary pair (pp. 1062–1063 and Ref. 36 in Ref. *3*). Admittedly, the association of solute with the solvent in the aqueous phase may increase solvent losses and reduce the distribution coefficient, but this is of secondary importance for solvent screening.

We shall illustrate our discussion here with the same ternary UNIFAC predictions used for the distribution coefficient examples above. In these examples we found that the predicted concentration of 1-butanol in the aqueous phase is typically 0.1 wt% and at most 1 wt%, indicating that the aqueous phase is reasonably represented by a solvent–water binary mixture. The data and predictions shown in Fig. 6 suggest that the accuracy of these UNIFAC predictions are adequate for solvent screening, but not for design or even final solvent selection which requires experimental data. Note that the UNIFAC predictions for solubility of unsubstituted alkanes in water must be treated with some caution, as the UNIFAC LLE method used here has some difficulty predicting both alcohol and alkane solubilities in water. A choice is made in the derivation of interaction parameters to favor accurate prediction of alcohol solubilities at the expense of alkane solubilities (*15*).

Data and predictions in Figs. 5 and 6 show that the solubility of solvent in water (and hence expected solvent losses) depends on the choice of functional group. The predictions in Fig. 13 show that for the oxygenated compounds and trichloralkanes considered here, the losses for a given solvent molecular weight vary by over one order-of-magnitude and are highest for acids and phenols. Losses of phenols are over double those of alcohols of a similar molecular weight. Losses of each solvent class shown vary in a similar way as the number of aliphatic CH_2 groups, and thus the molecular weight is increased. The most important and striking feature of Fig. 13 is that the solvent losses decrease exponentially with increasing solvent molecular weight. This is in dramatic contrast to the distribution coefficient which decreases linearly with increasing molecular weight (see Fig. 12).

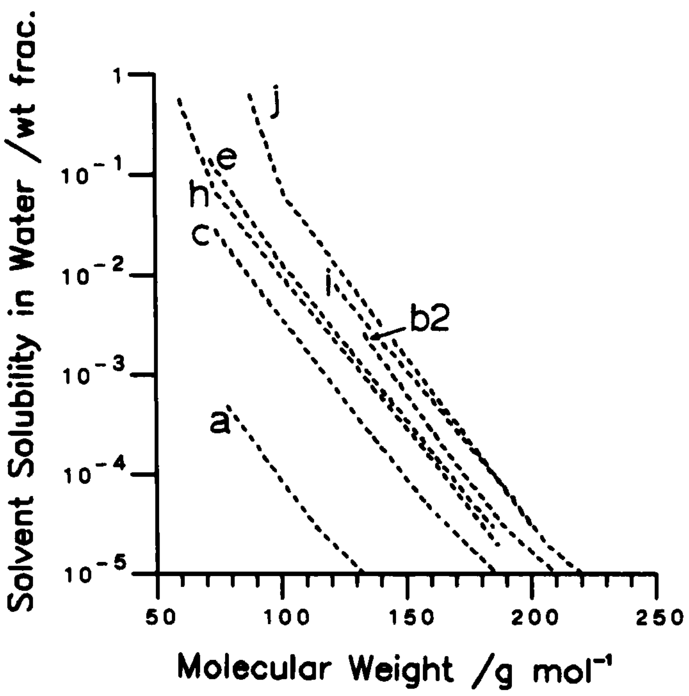

FIG. 13. UNIFAC LLE predictions for solvent-1-butanol-water: solvent losses as a function of molecular weight for various homologous series. The losses shown here are the concentration of solvent in the aqueous phase of a two-phase split of a ternary mixture, predicted using UNIFAC as in Fig. 12.

The functional group location (primary, secondary, or tertiary) may affect solvent losses by as much as one order-of-magnitude. It is difficult to predict these effects, and thus we show data for the examples of 4-, 6-, and 7-carbon alcohols in water (Table 2). For each alcohol molecular weight horizontal lines divide primary, secondary, and tertiary alcohols. For example, 1-heptanol is about 10 times less soluble than any of the tertiary 7-carbon alcohols, 2-methyl-2-hexanol, . . . , 3-ethyl-3-pentanol. This is only one example, and these results need to be extended for other systems. Nevertheless, the data do indicate that this effect can be important, and they suggest that solvent losses are lowest for primary alcohols, amines, etc. Conversely, the data also suggest that tertiary alcohols will be harder to recover from aqueous solution.

Branching of the aliphatic CH_2 chain may reduce or increase solubility of a polar solvent in water. For alcohols the effect of branching is shown *within* each divided section of Table 2. For example, three 6-carbon secondary alcohols with the hydroxyl located at the 2nd carbon have the following solubilities in water: (+−)-2-hexanol 1.37 wt%, 4-methyl-2-pentanol 1.69 wt%, and 3-methyl-2-pentanol 1.94 wt%. Other examples can be found in this table where increased branching also increases solubility in water by less than a factor of 2. A similar effect is seen for ketones in Table 3. The two organic acids shown exhibit a larger and opposite effect: 2-ethylbutyric acid is almost 5 times less soluble in water than hexanoic acid. This shows that while branching of the aliphatic side chain is a secondary effect, it nevertheless should be considered later in solvent screening if reduced losses are needed.

Aromatic compounds are more soluble in water than aliphatic compounds of a similar molecular weight. The magnitude of the difference depends on the extent of substitution, as suggested by Table 4. For *m*-methylphenol and 1-hexanol, the difference is a factor of 4. As the aliphatic character of the alkylphenol increases further, the magnitude of the difference decreases only gradually, as shown in Fig. 13.

4.3. Relative Volatility

The extract mixture can be separated into solvent, solute, and water by distillation. We are concerned here with predicting solute–solvent relative volatility. We have already found that the logarithm of the relative volatility can be predicted to a first approximation from the difference in boiling point between the two components. We now examine how solvent structure affects solvent boiling point.

TABLE 2
Effect of Primary, Secondary, and Tertiary Location of Functional Group on Solvent. For Each Carbon Number, the Primary Alcohols Are Presented First, Then Secondary, Then Tertiary, Divided by Horizontal Lines. Data Are from Refs. *13* and *21*.

Compound	Boiling point (°C)	Solubility in water (wt%)	Molecular weight (g/mol)
	4-Carbon Alcohols		
1-Butanol	117.7	7.8	74.12
2-Methyl-1-propanol	108	8.8	74.12
(+−)-2-Butanol	100	22.5	74.12
2-Methyl-2-propanol	83	miscible	74.12
	6-Carbon Alcohols		
1-Hexanol	158	0.587	102.18
(+−)-2-Hexanol	140	1.37	102.18
4-Methyl-2-pentanol	133	1.69	102.18
3-Hexanol	135	1.75	102.18
3-Methyl-2-pentanol	134.3	1.94	102.18
2-Methyl-3-pentanol	126.7	2.01	102.18
2-Methyl-2-pentanol	121	3.63	102.18
3-Methyl-3-pentanol	122.4	4.25	102.18
	7-Carbon Alcohols		
1-Heptanol	176	0.175	116.21
2,4-Dimethyl-3-pentanol	138.7	0.781	116.21
2,2-Dimethyl-3-pentanol	135	0.876	116.21
2-Methyl-2-hexanol	143	1.08	116.21
3-Methyl-3-hexanol	143	1.35	116.21
2,4-Dimethyl-2-pentanol	133.1	1.50	116.21
2,3-Dimethyl-2-pentanol	—	1.69	116.21
2,3-Dimethyl-3-pentanol	139.7	1.87	116.21
3-Ethyl-3-pentanol	143.1	1.91	116.21

TABLE 3
Effect of Branching on Solubility in Water and on Pure Component Boiling Point. Data Are from Refs. *13*, *14*, and *21*.

Compound	Boiling point (°C)	Solubility in water (wt%)	Molecular weight (g/mol)
Ketones			
2-Hexanone	127	1.4	100.16
4-Methyl-2-pentanone	116.8	2.0	100.16
Organic Acids			
Hexanoic acid	205.2	0.968	116.16
2-Ethylbutyric acid	194	0.22	116.16

TABLE 4
Effect of Aromatic Versus Aliphatic Nature of Carbon Backbone on Solvent Solubility in Water and on Pure Solvent Boiling Point. Data Are from Refs. *13* and *21*.

Compound	Boiling point (°C)	Solubility in water (wt%)	Molecular weight (g/mol)
Unsubstituted Hydrocarbons			
Pentane	36		72.15
Benzene	80	0.198	78.11
Hexane	69	0.00139	86.18
Toluene	111	0.050	92.14
Heptane	98	0.0001	100.21
Ethylbenzene	136		106.17
Octane	126	0.000072	114.23
Hydroxyl-Substituted Hydrocarbons			
Phenol	182	7.5	94.11
c-Hexanol	161	3.6	100.16
1-Hexanol	158	0.587	102.18
m-Methylphenol	203	2.18	108.14
(+ −)-2-Heptanol	161	0.35	116.20
p-ethylphenol	219	1.94	122.17

The effect of solvent functional group on the boiling point decreases as the molecular weight or the number of aliphatic CH_2 groups increases, as is shown for the pure component normal boiling point data in Fig. 14. The highest boiling solvents shown here are aliphatic diols, followed by phenols, acids, and alcohols. For all solvent classes considered here, the boiling point increases roughly linearly with molecular weight. This means that the relative volatility increases exponentially with increasing molecular weight.

The location of the functional group affects the boiling point. For the example of alcohols, data shown in Table 2 suggest that primary alcohols have a boiling point 20–30°C greater than secondary or teritary alcohols. Differences between the latter are less marked for 7-carbon alcohols than for 6- or 4-carbon alcohols, suggesting a reduced importance of the functional group in determining boiling point for more highly aliphatic compounds.

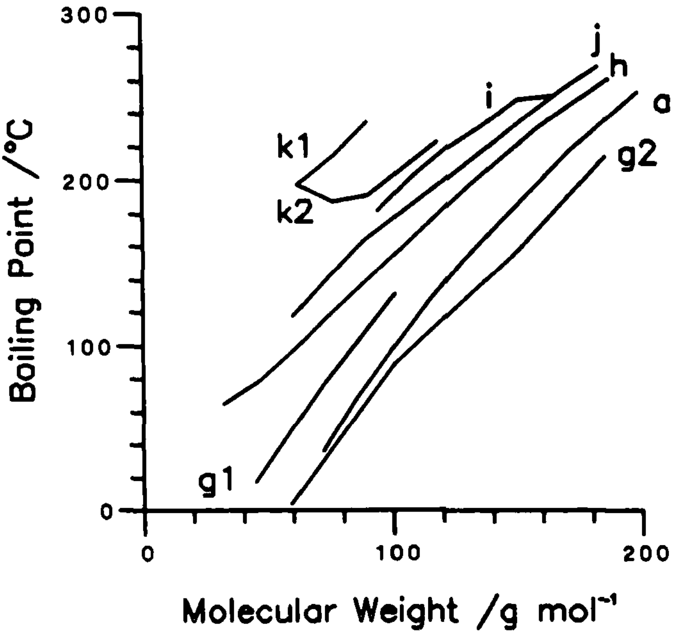

FIG. 14. Data for pure solvents: boiling point as a function of molecular weight for various homologous serires, where the functional group remains identical but the number of CH_2 groups is changed. Data are from Ref. *21*.

Branching of the aliphatic CH_2 chain seems to reduce the boiling point by a few degrees, as examination of the data in Tables 2 and 3 shows.

Aromatic compounds have a boiling point 20–40°C higher than aliphatic compounds with similar functional groups and molecular weight.

4.4. Summary

For the recovery of polar compounds from dilute aqueous solution, we find:

1. The functional group(s) on the solvent must be chosen carefully as this can affect K_D and losses by one order-of-magnitude and solvent boiling point by up to 200°C. We have shown an effective search strategy using properties predicted with the UNIFAC group contribution method.
2. There is an optimum number of CH_2 groups on the solvent (measured here by molecular weight for a homologous series). We have clearly demonstrated that as the number of CH_2 groups increases, the distribution coefficient decreases linearly, while solvent losses decrease exponentially, and (if the solvent has the higher boiling point) the relative volatility of the solvent–solute pair increases exponentially.
3. The solvent "shape" has a significant effect, but less than that of the functional group or the number of CH_2 groups.* The effect of "shape" is more difficult to determine as current prediction techniques are inadequate. Experiment and data must be used for these instances. We have found the following three effects of "shape":
   (a) Choice of functional group location (primary, secondary, or tertiary) alters K_D and can affect losses by one order-of-magnitude and solvent boiling point by about 40°C.
   (b) Choice of aromatic versus aliphatic molecules has an effect similar to that of choice of functional group location.
   (c) Aliphatic CH_2 chain branching has less effect than functional group location.

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*We use the unconventional term "shape" here to refer to functional group location, choice of aromatic versus aliphatic, and chain branching. The conventional term "structure" is more general and includes choice of functional groups and chain length.

Furthermore, for the specific case of 1-butanol recovery from dilute aqueous solution, Results 1 and 2 are demonstrated in Figs. 15 and 16. These are the results from Figs. 12, 13, and 14, together with Eq. (10), drawn together. They show that solvent losses and relative volatility can be varied considerably with little loss in the distribution coefficient.

5. CONCLUSIONS

1. We have shown that the complexity of the task of solvent selection for recovery from dilute aqueous solution can be reduced significantly by identifying important costs and interrelationships between system properties.

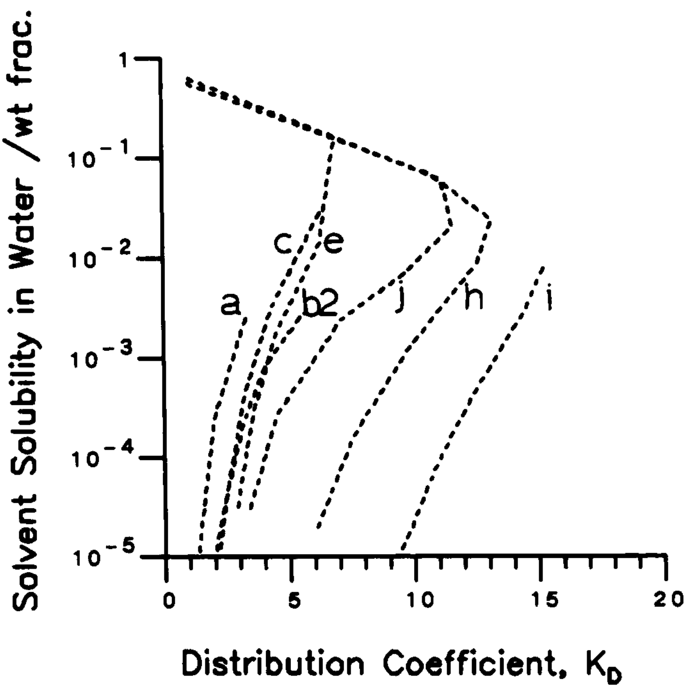

FIG. 15. UNIFAC LLE predictions for solvent-1-butanol-water: solvent losses into water versus distribution coefficient of 1-butanol into solvent for some solvents in a homologous series. These results are for ternary liquid-liquid equilibrium predicted using UNIFAC with LLE parameters.

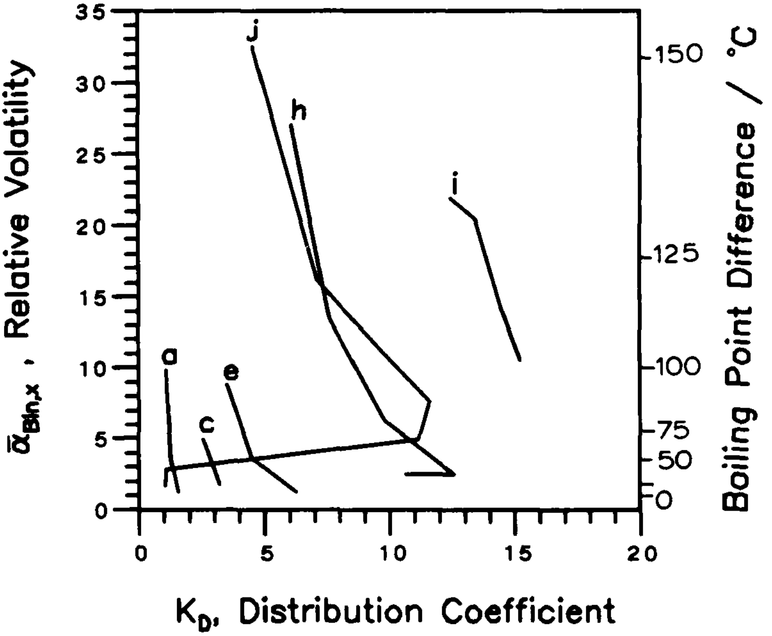

FIG. 16. UNIFAC LLE predictions for solvent-1-butanol-water and results derived from pure solvent boiling point data plus rules-of-thumb: relative volatility versus solute distribution coefficient.

2. Low solvent losses, a high solute distribution coefficient, and a high relative volatility are primary goals for solvent selection for recovery of polar organics from dilute aqueous solution. Selectivity is less important.
3. Selectivity, solvent losses, and immiscibility are interrelated, and screening for low solvent losses will ensure adequate selectivity and the formation of two phases.
4. Relative volatility, azeotropes, and boiling point are interrelated, and selecting solvents with a high boiling point difference from the solute will reduce the chance of azeotrope formation and increase the relative volatility.
5. Recommended properties for solvents for 1-butanol recovery include a boiling point difference from 1-butanol of greater than 50°C, and phenol or organic acid functional groups.
6. Polar nitrogen-containing compounds were not considered in this work, but deserve further study.

APPENDIX

A. Derivation of Simple Rules to Predict Binary Average Relative Volatility from Boiling Point Data

In this appendix we derive two simple rules-of-thumb that can be used to predict the relative volatility of any solvent relative to a selected solute. As well as the two rules-of-thumb derived here, many other similar relationships are easily derived. The results of these rules are shown in Fig. 9 for the example of 1-butanol and a range of solvents. We suggest why these two simple rules work.

A.1. Rule Based on the Pictet-Trouton Rule

The relative volatility, α, is defined for systems at low pressure where one may assume the vapor phase to be an ideal gas, as

$$\alpha = \gamma_1 P_1^{sat}/\gamma_2 P_1^{sat} \tag{1}$$

and if $\gamma_1 \approx \gamma_2$ (we test this assumption below), then

$$\alpha \approx P_1^{sat}/P_2^{sat} \tag{2}$$

We shall be concerned here with predictions of a typical relative volatility for a binary system, $\bar{\alpha}_{Bin}$. We will not consider yet the composition and temperature dependence of α, nor how to average it over composition or column position.

The Clapeyron equation (Eq. 6-36 in Ref. *24*) for liquid and vapor phases in equilibrium can be simplified for the case of an ideal gas at low pressure,* where $v_g \gg v_l$, to the Clausius-Clapeyron equation:

$$\frac{d \ln P^{sat}}{d\, 1/T} = -\frac{\Delta H^{vap}}{R \Delta Z^{vap}} \tag{3}$$

---

*Note that for many systems data for ln P^{sat} vs $1/T$ is approximately linear and thus Eq. (3) suggests that ΔH^{vap} is constant and independent of temperature, which is true at low pressures and over limited temeprature ranges.

Here ΔZ^{vap} is the difference in compressibility factors between saturated vapor and saturated liquid at the system temperature T. If ΔH^{vap} is constant and independent of temperature, then Eq. (3) can be integrated to give Eq. (4) (also called the Clapeyron equation sometimes, but not to be confused with the unintegrated Clapeyron equation referred to above) for predicting pure component vapor pressures:

$$\ln P^{sat} = \frac{\Delta H^{vap}}{RT\Delta Z^{vap}} + A \tag{4}$$

This is commonly simplified further for low pressures by assuming that $\Delta Z^{vap} \approx 1.0$.

Pictet and also Trouton (e.g., Ref. *19*) found that for nonpolar low to moderate molecular weight compounds the enthalpy of vaporization could be predicted from the normal boiling point (the boiling point at atmospheric pressure) of the compound, thus

$$\Delta H^{vap}/T^b = 88 \text{ Joule} \cdot \text{mol}^{-1} \cdot {}^\circ\text{K}^{-1} \tag{5}$$

The heat of vaporization for polar compounds is greater than that for nonpolar compounds of similar molecular weight, and thus the Pictet-Trouton rule (Eq. 5) requires a larger constant, K, than the 88 J/mol used for nonpolar hydrocarbons. Further, Hala (*19*) suggests that for polar compounds any agreement between predicted and actual ΔH^{vap} is coincidental. Nevertheless, this remains a useful guiding rule, if used with caution.

For a pure component at the boiling point, $P^{sat} = P$, where P is the system pressure. Thus, for any component where Eq. (5) holds, we find that

$$A = \ln P - 88/R \tag{6}$$

Combining Eqs. (2), (4), (5), and (6) gives

$$\ln \bar{\alpha}_{Bin} = \frac{88}{RT}(T_1^b - T_2^b) \tag{7}$$

Now we express the system temperature in terms of T_1^b and T_2^b by assuming that the boiling point of the mixture will be the average of the boiling points of the two components. This assumption is valid for nonpolar compounds, and does not cause severe error for many systems involving polar compounds (see later example and Fig. 19). Thus we can write

$$T \approx 0.5(T_1^b + T_2^b) \tag{8}$$

and thus

$$\ln \bar{\alpha}_{Bin} = 2\,\frac{88 + c}{R}\,\frac{T_1^b - T_2^b}{T_1^b + T_2^b} = 2\,\frac{88 + c}{R}\,\frac{\Delta T^b}{\sum T^b} \tag{9}$$

where 1 = solvent and 2 = solute.

This equation can be simplified further by considering solvents with boiling points 0 to 200 K greater than that of the solute, and linearizing about a point, say 100°C, greater than T_2^b. Then assume $\Sigma T^b \approx 100 + 2T_2^b$. For the example of 1-butanol as the solute, $\Sigma T_2^b \approx 100 + 2 \times (117 + 273) = 880$ K, and thus if the Pictet-Trouton constant is left at the value of hydrocarbons and if $c = 0$, then the rule-of-thumb for binary pairs involving 1-butanol is

$$\log \bar{\alpha}_{Bin} \approx 0.010 \Delta T^b \tag{10}$$

This equation is shown in Fig. 9. The qualitative trend is in agreement with the specific points calculated using UNIFAC, but the equation underestimates $\bar{\alpha}_{Bin}$ by about 30%. As expected, a higher value of the Pictet-Trouton constant will give a better fit.

A variety of more complex empirical correlations has been proposed for the prediction of the ideal relative volatility of nonpolar binary mixtures (*18*). These have been successfully used to obtain quantitative predictions of the relative volatility for pairs of hydrocarbons.

For our case, we are concerned with screening a variety of solvents for one given solute, and simple equations such as Eq. (10) provide adequate, rapid, early guidance.

A.2. Rule Based on Ramsay-Young and a Vapor Pressure Correlation

The Ramsay-Young rule (e.g., Ref. *19*) assumes that the molar enthalpy of vaporization will be similar for two chemically similar substances. Hence, by using the Clausius-Clapeyron relationship, the vapor pressure change with temperature will be similar, or

$$\frac{T_1^b}{T_2^b} = \frac{T_1'}{T_2'} \tag{11}$$

where T_1^b and T_2^b are the normal boiling points of Components 1 and 2 (i.e., their boiling points at atmospheric pressure) and T_1' and T_2' are the boiling points at some other pressure.

Thus

$$P_1^{sat}(at\ T_1') = P_2^{sat}\left(at\ \frac{T_1' T_2^b}{T_1^b}\right) \tag{12}$$

and this together with Eq. (2), at the average of the boiling points of the two components, gives

$$\bar{\alpha}_{Bin} \approx \frac{P_2^{sat}(at\ 0.5(T_1^b + T_2^b)}{P_2^{sat}(at\ 0.5(T_1^b + T_2^b)(T_2^b/T_1^b)} \tag{13}$$

Thus all we need is a method to predict the vapor pressure of the solute of interest as a function of temperature. Correlations available, such as the Antoine equation or those found in Yaws (*25*), are suitable, the latter being more accurate and covering a wider temperature range. This is shown for the case of 1-butanol as the solute in Fig. 9.

A.3. Why These Simplifications Are Adequate

Why do these simplifications work? We refer here to the process design examples of the preceeding section. In Fig. 17 we see that the binary relative volatility varies dramatically as the liquid mole fraction changes. In Fig. 18 we see that the ratio of the activity coefficients of the two components in a binary liquid mixture at the boiling point is close to 1.0 for equimolar mixtures of the two components. This is the justification for the assumption made in Eq. (2). In Fig. 19 we see that the ratio of the actual column temperature to the average boiling point of the two components does not vary by more than 20%. This is the justification for the assumption made for Eq. (10) that the temperature, *T*, can be replaced by the average of the boiling points of the two components.

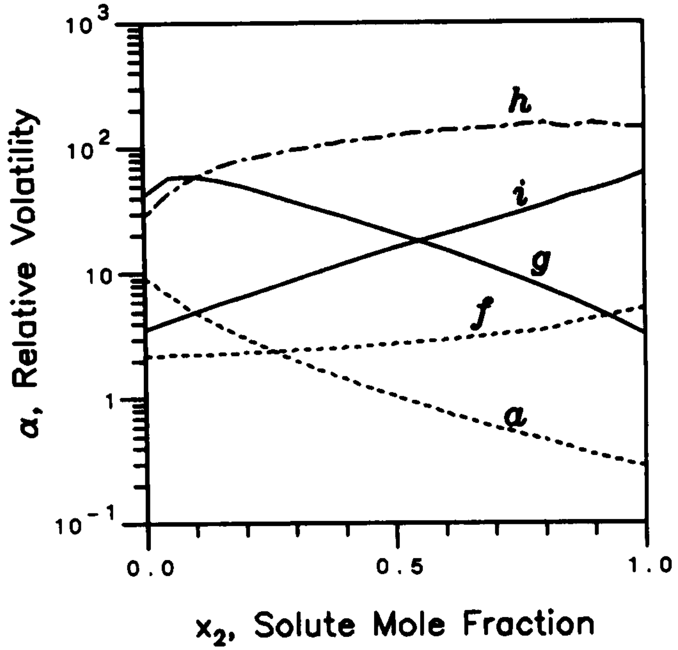

FIG. 17. UNIFAC VLE predictions for solvent–1-butanol: variation of the relative volatility with liquid-phase 1-butanol mole fraction for 1-butanol–solvent binary pairs, generated with UNIFAC VLE predictions.

SYMBOLS

A_i	constant in Appendix A.1, Eqs. (4) and (6)
c	constant in Appendix A.1, Eq. (9)
ΔH^{vap}	enthalpy of vaporization (Joule · mol^{-1})
K_D	distribution coefficient of solute into the solvent phase
K_W	distribution coefficient of water into the solvent phase
P_i^{sat}	vapor pressure of Component i (kPa)
R	gas constant (Joule · mol^{-1} · °C^{-1})
T	temperature of the system (°C or °K)
T_i^b	boiling point of Component i (°C or °K)
ΣT^b	sum of boiling points, Components 1 and 2 (°K)
ΔT^b	boiling point difference, Component 1 minus Component 2 (°C or °K)

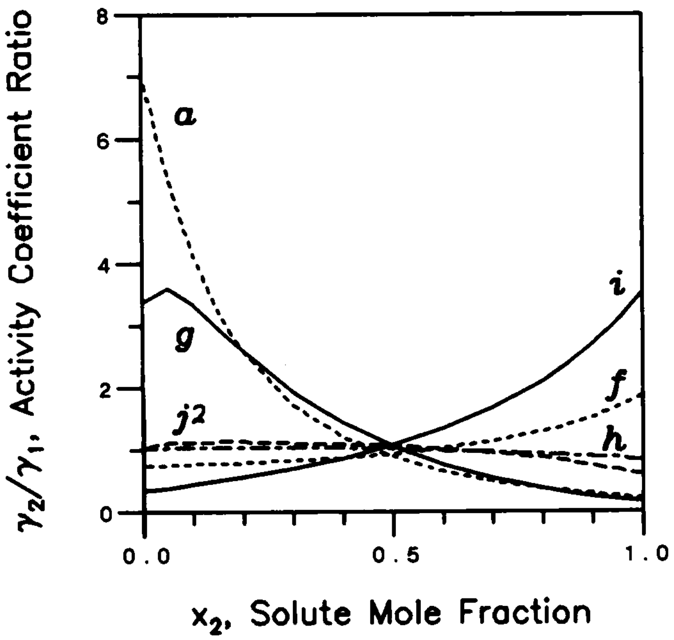

FIG. 18. UNIFAC VLE predictions for solvent-1-butanol: variation of the ratio of the activity coefficient of 1-butanol to that of the solute with liquid-phase 1-butanol mole fraction.

w_i	weight fraction of Component i
ΔZ^{vap}	difference in compressibility factors between saturated vapor and saturated liquid phases

Greek

α	volatility of solute relative to solvent
$\bar{\alpha}_{Bin,x}$	volatility of solute relative to solvent for a binary system, averaged for evenly spaced liquid phase mole fractions
$\bar{\alpha}_{Ter,tray}$	volatility of solute relative to solvent for a ternary system, averaged over all the trays of a distillation column with a feed from an extractor
β	selectivity of solvent for solute relative to water
γ_i	activity coefficient of Component i

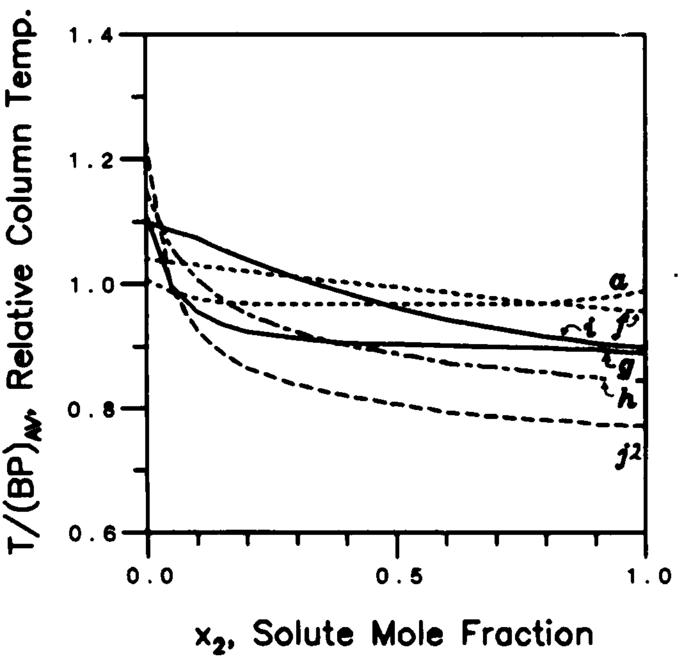

FIG. 19. UNIFAC VLE predictions for solvent-1-butanol: the ratio of system temperature to average boiling point of the two compounds in a binary pair versus the mole fraction of one of the components in the liquid phase.

Subscripts

1	solvent
2	solute
Bin,x	binary approximation to system, averaged over liquid mole fraction
Ter,tray	ternary system, averaged over all trays in distillation column

Superscripts

overline	average
b	boiling point
vap	phase change from liquid to vapor state

REFERENCES

1. E. N. Lightfoot and M. C. M. Cockrem, *Sep. Sci. Technol., 22*(2&3), 165 (1987).
2. R. M. Busche, *Biotech. Prog., 1*(3), 165 (1985).
3. M. C. M. Cockrem, R. A. Meyer, and E. N. Lightfoot, *Sep. Sci. Technol., 21*(10), 1059 (1986).
4. M. C. M. Cockrem, "Recovery of Chemicals from Dilute Solution," PhD Thesis, University Wisconsin-Madison, 1987.
5. A. M. Dadgar and G. L. Foutch, *Biotech. Bioeng. Symp., 15,* 61 (1985); (published 1986).
6. H. Honda et al., *Chem. Eng. Sci., 42*(3), 493 (1987).
7. S. Ishii, M. Taya, and T. Kobayashi, *J. Chem. Eng. Jpn., 18,* 125 (1985).
8. M. Matsumura and H. Markl, *Appl. Microbiol. Biotechnol., 20,* 371 (1984).
9. C. L. Munson and C. J. King, *Ind. Eng. Chem., Process Des. Dev., 23,* 109 (1984).
10. T. K. Murphy, "Recovery of Fermentation Products from Dilute Aqueous Solution," PhD Tehsis, University California-Berkeley, 1984.
11. K. Shimizu and M. Matsubara, *Chem. Eng. Sci., 42*(3), 499 (1987).
12. G. Zacchi, G. Aly, and R. Wennersten, *Proc. Int. Solvent Extr. Conf., Colorado,* AIChE, 1983, p. 507.
13. J. M. Sorenson and W. Arlt, "Liquid-Liquid Equilibrium Data Collection, Binary Systems," in *DECHEMA Chemistry Data Series,* Vol V, Part 1, DECHEMA, Frankfurt, 1979.
14. E. W. Flick (ed.), *Industrial Solvents Handbook,* 3rd ed., Noyes Data Corp., New Jersey, 1985.
15. J. Gmehling, P. Rasmussen, and A. Fredenslund, *Ind. Eng. Chem., Process Des. Dev., 21,* 118 (1982).
16. R. J. Edgeworth-Johnstone, *Inst. Pet. Tech., 25,* 558 (1943).
17. Kh. E. Khcheyan, and O. M. Revenko, *Nov. Metody Sint. Org. Soedin Osn. Neftekhim. Syr'ya:* (Kh. E. Khcheyan, ed.), TsNI-ITEneftekhim, Moscow, USSR, 1982, pp. 28–35; *Chem. Abstr., 101*(4), 29199m.
18. F. W. Melpolder and C. E. Headington, *Ind. Eng. Chem., 39*(6), 763 (1947).
19. E. Hala, J. Pick, V. Fried, and O. Vilim, *Vapor-Liquid Equilibrium* (translated by G. Standart), Pergamon, New York, 1958. pp. 214–221.
20. M. Hirato, S. Ohe, and K. Nagahama, *Computer-Aided Databook of Vapor-Liquid Equilibria,* Kodansha, Tokyo, 1975.
21. R. Weast, *CRC Handbook of Chemistry and Physics,* 59th ed., CRC Press, Florida, 1983.
22. L. H. Horsley, "Graphical Method for Predicting Azeotropism and the Effect of Pressure on Azeotropic Constants," in *Azeotropic data,* (Adv. Chem. Ser. 6), American Chemical Society, Washington, D.C., 1952, pp. 321–328.
23. L. H. Horsley, in *Azeotropic Data* (Adv Chem Ser. 6), American Chemical Society, Washington, D.C., 1952, pp. 8, 124–126.
24. J. M. Smith and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics,* 3rd ed., McGraw-Hill, New York, 1975, p. 184.
25. C. L. Yaws, *Physical Properties,* McGraw-Hill, New York, 1977, pp. 214–216.

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