Solvent Extraction of Ethanol from Aqueous Solutions. I. Screening Methodology for Solvents

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The evaluation of the potential for separation of aqueous ethanol mixtures by liquid−liquid solvent extraction has been complicated by inconsistent results and differing experimental methodologies among researchers developing distribution coefficient data. A screening method for measuring equilibrium distribution coefficients for solvent extraction of ethanol from dilute aqueous solutions is presented to minimize potential sources of variation. These include entrainment, incomplete equilibration, impurities, and temperature changes during the preparation of samples for analysis. Multiple literature sources of data exist for each of 10 solvents. Results for these 10 solvents are compared among sources and to results generated from this method. The method also has general utility for the screening of solvents for extraction of other useful fermentation products.

Introduction

There is rapid growth in the use of ethanol derived from grains and biomass as a fuel, platform or feedstock chemical, and process fluid in biorefining. For instance, in July 2004, U.S. bioethanol production capacity was 3.3 billion gallons/year from 84 plants, with another 8 plants (310 million gallons of capacity) under construction.[1] Distillation to near the azeotrope, followed by pressure-swing adsorption for final dehydration, is the predominant method in the United States for recovering and purifying ethanol from dilute aqueous fermentation broths. This method consumes 14,000−17,000 BTU/gallon ethanol.[2] This is 18−22% of the fuel value of the ethanol being produced. Solvent extraction may provide a more energy-efficient means to recover ethanol.[3−6]

The requirements for a successful liquid-extraction solvent for aqueous ethanol are (1) a high separation factor for ethanol (ethanol, rather than water, is preferentially extracted into the solvent), (2) a high capacity for ethanol to minimize solvent use, (3) a low solvent solubility in the aqueous phase to minimize solvent losses, (4) a density difference between the organic phase and the aqueous phase to permit rapid phase separation, (5) chemical stability, and (6) an efficient means to recover ethanol from the solvent and recycle the solvent.[6,7] Other important criteria are safety (flammability and toxicity to plant personnel) and environmental risk considerations (release of the solvent in wastewater, solid wastes, or air emissions). If the solvent directly contacts the fermentation broth, it must not inhibit the fermenting microorganism[7] and not be toxic or unpalatable to animals consuming byproducts such as DDGS (distillers dried grains with solubles), a high protein byproduct.

There are two main approaches in the literature for generating and reporting solvent extraction data. In one approach, distribution coefficients and separation factors are calculated from the chemical compositions of the equilibrated phases in the aqueous ethanol concentration range of interest. The solvent−ethanol−water mixture is mixed to ensure equilibrium of the phases, phase-separated via settling or centrifugation, and analyzed to determine the compositions of the phases. In the other approach, a ternary liquid−liquid equilibrium diagram is created, with tie-lines linking the compositions of the equilibrium aqueous and organic phases. This is often done by defining the two-phase boundary by cloud-point measurements and determining tie-line compositions either by direct measurement of each phase or by measuring one phase and calculating the composition of the second phase by mass balance.

The liquid−liquid equilibrium diagram gives a complete picture of the behavior of the system and is desirable when designing a solvent extraction process using a selected solvent.[8] The separation factor/distribution coefficients approach is a view of a portion of the system, focusing on the concentration range near expected process operating conditions. It is useful for screening a large number of solvents, because it is relatively rapid and sparing of the solvent volume.

The objectives of this work were to develop experimental techniques that minimize or eliminate sources of variation and to apply these methods to screening a variety of solvents for comparison with the literature. In a companion paper,[9] the ethanol extractive performance of a wide range of alcohols will be reported, focusing on the effects of progressive changes in chemical structure.

Experimental Method

The solvents used are listed in Table 1. CAS number, source, purity, density, solubility in water, and boiling point are included. These solvents were chosen because there were multiple literature sources of extraction data for each. They comprise a progression of straight-chain 1-alcohols (1-heptanol through 1-dodecanol), other common extraction alcohols (2-ethyl-1-butanol, 2-ethyl-1-hexanol, 2-octanol, and 3-ethyl-3-pentanol), and the esters di-*n*-butyl phthalate (DBP) and tri-*n*-butyl phos-

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Table 1. Solvents Investigated

solvent	CAS #	source	purity, %	density,[10] g/cm^3	sol. in water,[11] wt %	BP,[10] °C
1-heptanol	111-70-6	Aldrich	98	0.8219^{25C}	0.17	176.4
1-octanol	111-87-5	Aldrich	99.93	$0.8262^{25°C}$	0.054	195.1
1-nonanol	143-08-8	Aldrich	99	$0.8273^{20°C}$	0.014	213.3
1-decanol	112-30-1	Aldrich	99.3	$0.8297^{20°C}$	0.0037	231.1
1-undecanol	112-42-5	Aldrich	99	$0.8298^{20°C}$	0.0019	243
1-dodecanol	112-53-8	Aldrich	98.52	$0.8309^{24°C}$	0.0004	259
2-ethyl-1-butanol	97-95-0	Aldrich	98	$0.8326^{20°C}$	0.4	147
2-ethyl-1-hexanol	104-76-7	Eastman	99.84	$0.8319^{25°C}$	0.088	184.6
2-octanol	123-96-6	Aldrich	97	$0.8193^{20°C}$	0.112	180
3-ethyl-3-pentanol	597-49-9	Aldrich	98	$0.8407^{22°C}$	1.7	142
dibutyl phthalate	84-74-2	Eastman	99	$1.0465^{20°C}$	0.0011	340
tributyl phosphate	126-73-8	Aldrich	99.5	$0.9727^{25°C}$	0.028	289

phate (TBP). All chemicals were used as received. Ethanol was 200 proof (anhydrous) grade, from Aaper Alcohol and Chemical Co. The organic-phase diluent, 1-butanol, was anhydrous 99.95% from Aldrich. The organic-phase internal standard, 1-hexanol, was anhydrous 99.49% from Aldrich. Distilled water was used in all solutions.

Distribution coefficients and separation factors[12] were calculated from data at a given extraction temperature and aqueous-phase ethanol concentration. The equilibrium distribution coefficient for ethanol is defined as $K_{DE} = [EtOH]_{org}/[EtOH]_{aq}$, the ratio of the weight percent of ethanol in the organic phase to the weight percent of ethanol in the aqueous phase. K_{DW}, the equilibrium distribution coefficient for water, is defined similarly: $K_{DW} = [H_2O]_{org}/[H_2O]_{aq}$. The separation factor is $\alpha = K_{DE}/K_{DW}$, or the ratio of the ethanol distribution coefficient to that of water.

The extraction and sample preparation temperature chosen for screening solvents was 33 °C. While 40% of the authors in the comparison papers used 25 °C, this temperature is difficult to control because of fluctuations in laboratory temperature. A warmer temperature that is fully controllable is desirable, but too high a temperature could cause evaporative and cooling effects in sample handling. The temperature of 33 °C was convenient because it was the lowest heated temperature reliably attainable in the centrifuge used for phase separation.

The extractions, for screening solvents, were performed in 1.3 cm diameter × 10 cm long glass tubes with an aqueous-to-organic phase volume ratio of 2:1 and total liquid volumes of 7.5 mL. The capped tubes were placed in a lab oven set to 33 ± 1 °C to maintain a constant extraction temperature. The filled tubes, when fully equilibrated with the temperature of the oven, were shaken vigorously to completely emulsify the organic and aqueous layers. The layers were then allowed to settle for 30−45 min with the tubes in a vertical position. This process of emulsification and settling was repeated 6−7 times at a constant temperature, to ensure that the extraction system had reached equilibrium.

Sample preparation of the extractions started with the centrifugation of the tubes in a temperature-controlled Labconco Centrivap concentrator (model 78100). The actual centrifugation temperature was 33 ± 1 °C, measured independently using a thermocouple gauge in the headspace. To fully phase-separate most extraction mixtures, 20 min at 276*G* was used. However, in the case of viscous solvents, the centrifugation lasted up to 2 h before both layers were completely clear and there was no residual aqueous phase clinging to the tube walls surrounding the organic layer.

After centrifugation, an aliquot of the organic phase (usually the top phase) was removed with a polyethylene pipet that had been warmed to 33 °C and weighed into a separate glass tube to which a solution of an organic-phase diluent and internal standard (ISO) was then added. The boundary layer, containing the bottom ~0.5 mL of the organic phase and the top ~0.5 mL of the aqueous phase, was then removed and discarded before an aliquot of the aqueous phase was weighed into a new tube and mixed with a solution of an aqueous-phase diluent and internal standard (ISA). The ISO was an ~3.1 wt % 1-hexanol in 1-butanol solution, in which the former acted as the internal standard and the latter as a diluent to ensure a single, homogeneous phase at room temperature. The ISA was an ~3.7 wt % 1-butanol in water solution, the former being the internal standard. These internal standard solutions were combined at a ratio of 1:1, by weight, to the organic or aqueous aliquot being analyzed. The exact ratios were recorded for each sample.

The organic and aqueous-phase compositions were determined using an HP 6890 gas chromatograph with a split/splitless inlet running in a split ratio of 31:1, with helium as the carrier gas, and a thermal conductivity detector. The column was an Agilent Technologies 30 m DB−WAXetr capillary column with a 0.45 mm diameter and 0.85 μm film thickness. The column temperature was programmed for an initial temperature of 60 °C for 5 min, followed by a ramp increase of 10°/min to the final hold temperature of 220 °C. This system provided good separation of the small alcohols and water while still allowing higher molecular weight species to elute within 60 min. Quantitative weight percent data were obtained from the integrated area percents using an internal standard calibration.

Three calibration curves were generated: one for ethanol in the organic layer, $[EtOH]_{org}$; one for water in the organic layer, $[H_2O]_{org}$; and one for ethanol in the aqueous layer, $[EtOH]_{aq}$. To calculate the concentration of water in the aqueous layer, $[H_2O]_{aq}$, it was assumed that the only components in the aqueous layer were water and ethanol, i.e., that the solubility of the solvent in water was negligible, as suggested by the solubility data in Table 1. Therefore, $[H_2O]_{aq}$ was calculated as $100 - [EtOH]_{aq}$, where all concentrations are in weight %. In the set of validation samples used to verify the accuracy of the calibration curve and internal standard solutions, the weight % values, calculated from the calibration curves, were within ±0.13 wt % of the known concentration for $[EtOH]_{org}$, within ±0.09 wt % for $[H_2O]_{org}$, and within ±0.06 wt % for $[EtOH]_{aq}$. Each time a new ISO or ISA solution was made, the exact concentrations of internal standard were recorded and a new validation set was analyzed to ensure that the

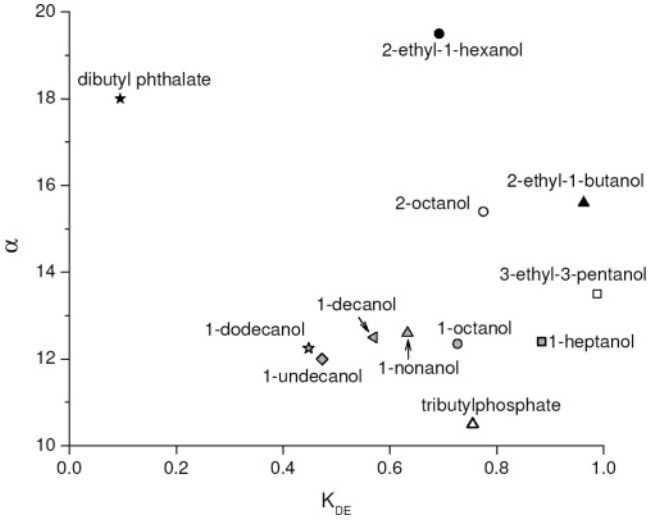

Figure 1. Experimental results for ethanol capacity and separation factors of various solvents at 33 °C and 5 wt % $[EtOH]^{\circ}_{aq}$ as determined using the method described in this paper. Coefficient of variation is 1.3% for K_{DE} and 1.1% for α.

result fell within these ranges. Internal standard solutions were also periodically checked with a validation set to ensure that selective evaporation or water pickup had not occurred.

Results and Discussion

Extraction Results and Comparison to Literature. The separation factor, α, and the ethanol distribution coefficient, K_{DE}, obtained for all solvents at 5 wt % initial aqueous ethanol concentration $[EtOH]^{\circ}_{aq}$ and 33 °C are displayed in Figure 1. To determine the experimental variation, duplicate extraction runs were carried out for 1-octanol, 1-undecanol, and 1-dodecanol, and five runs were done for 2-ethyl-1-hexanol. The coefficient of variation (standard deviation divided by the mean, expressed as a percent) was determined to be 1.3% for K_{DE}, 1.1% for K_{DW}, and 1.1% for α. In Figure 1, the average value for each of these solvents is displayed.

The initial aqueous-phase concentration affects the distribution coefficients and the separation factor as shown in Figure 2a, for 2-ethyl-1-hexanol at 33 °C and a concentration range of 1−20 wt % ethanol. K_{DE} and K_{DW} both increase with initial aqueous-phase ethanol concentration, $[EtOH]^{\circ}_{aq}$, with K_{DW} increasing by a factor of 2 and K_{DE} increasing by a factor of 1.3; hence, α is seen to decline.

The extraction temperature affects distribution coefficients but not the separation factor as shown in Figure 2b, for 2-ethyl-1-hexanol, with an $[EtOH]^{\circ}_{aq}$ of 5 wt % and temperatures ranging from 33 to 55 °C. It can be seen that, for this solvent, as the extraction temperature increases, K_{DE} increases by a factor of 1.2, K_{DW} increases by a factor of 1.2, and the separation factor is, therefore, unchanged. Murphy et al.[6] studied the effects of extraction temperature on 1-octanol and 1-dodecanol and observed similar results.

As Murphy et al.[6] point out, the distribution coefficients for ethanol and water would be expected to decrease as the concentration of solvent hydroxyl groups decreases because of increasing alkyl chain length. Since the weight fraction of the solvent hydroxyl groups is the ratio of the molecular weight of hydroxyl to that of the organic solvent, K_{DE}, K_{DW}, and α are plotted against the inverse of the molecular weight for the progression 1-heptanol through 1-dodecanol in Figure 3. The results can indeed be accurately fit by simple linear relationships. The separation factor is nearly constant. Error bars were estimated from the internal standard validation set.

Results from this study are compared with those in the literature in Table 2. The literature values are ranked within each solvent first by the final (equilibrium) aqueous ethanol concentration, $[EtOH]^{f}_{aq}$, and then by extraction temperature. The values from this study are listed beside the nearest equivalent extraction condition. Though some sources report $[EtOH]^{0}_{aq}$, the ratio of organic-to-aqueous phases will affect the degree of depletion of the aqueous-phase ethanol and, hence, the resulting value of $[EtOH]^{f}_{aq}$. Since this ratio varies among (and within) literature sources, the final aqueous ethanol concentration is used so that the data from various sources may be compared on an equivalent basis. In several cases, $[EtOH]^{f}_{aq}$ has been calculated here from reported values of $[EtOH]^{0}_{aq}$, phase ratio, and distribution coefficients.

It can be seen that for most solvents there is substantial variability among literature sources in both K_{DE} and α, though multiple results from a single source can be reasonably consistent. This variability was also observed by Kertes and King.[23] For example, the separation factor for 2-ethyl-1-hexanol is plotted in Figure 4 against final ethanol concentration in the aqueous phase for this study and all referenced data sources. Extraction temperature did not affect α, as shown previously; hence, this factor is ignored in the figure. A linear relationship accurately fits the data in this study over the 1−15 wt % $[EtOH]^{f}_{aq}$ range.

Values of the separation factor tend to be more variable than those of the ethanol distribution coefficient. This higher variability is probably due to both a propagation-of-errors effect (since α is calculated from one calculated concentration and three measured concentrations) and the fact that variations in the measurement of the water concentration in the organic phase will have a large effect on the separation factor (division by small numbers). In the comparison references, a variety of analytical methods are used for analysis of water in the organic phase, with concomitant variations in accuracy. The water concentration in the organic phase may be near the detection limit for some analytical methods and, therefore, subject to a relatively large error. This suggests why, as seen in Figure 4, others have obtained higher α values than found in this study at low $[EtOH]^{f}_{aq}$, where $[H_2O]^{f}_{org}$ would be lowest.

Karl Fischer titration of the organic phase for water is one of the most accurate methods, but it is not used in any referenced paper. GC methods are commonly used, though one paper[13] used radiotracers and another[20] used refractometry. The Karl Fischer method requires a relatively large sample size (2−5 g) for titration in the 0.01−0.1% water range. This large sample size, and a desire to combine all analyses into one method, influenced the selection of the internal standard GC method used in this study.

The assumption that the solvent concentration in the aqueous phase could be neglected in calculating the distribution coefficients and the separation factor was tested, because it could be expected that ethanol in the aqueous phase would enhance the solubility of the solvent above the pure water solubilities listed in Table

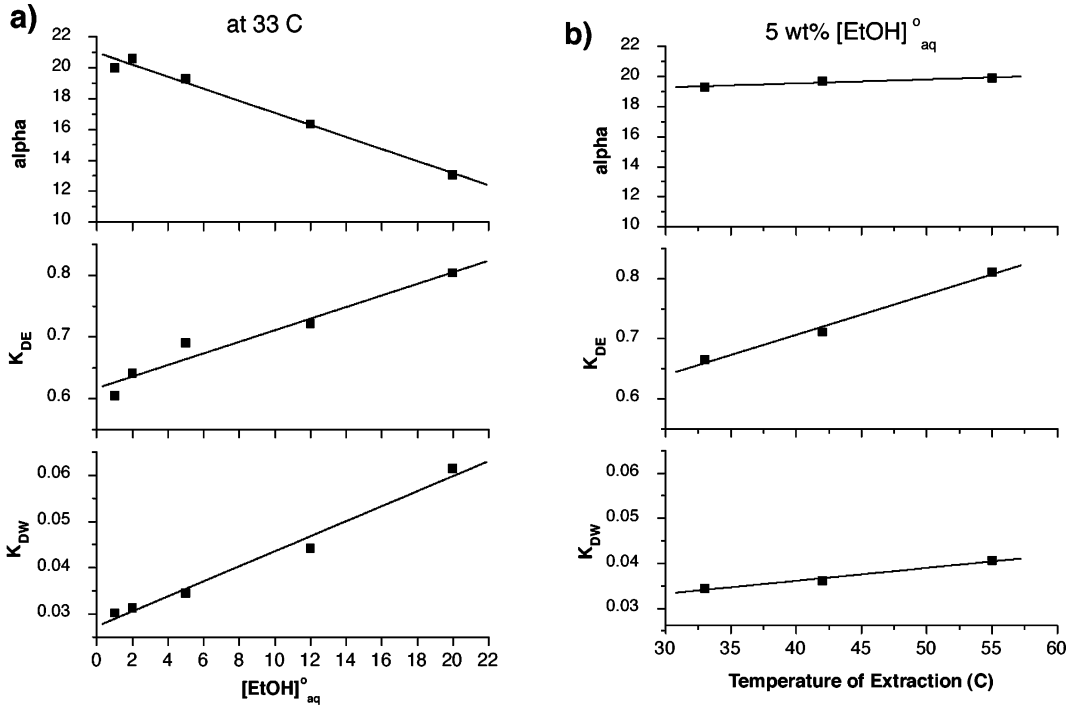

Figure 2. K_{DW}, K_{DE}, and α results for 2-ethyl-1-hexanol: (a) at 33 °C with varying initial aqueous-phase ethanol concentrations ranging from 1 to 20 wt %; (b) using a 5 wt % initial ethanol concentration and performing extractions at 33, 42, and 55 °C.

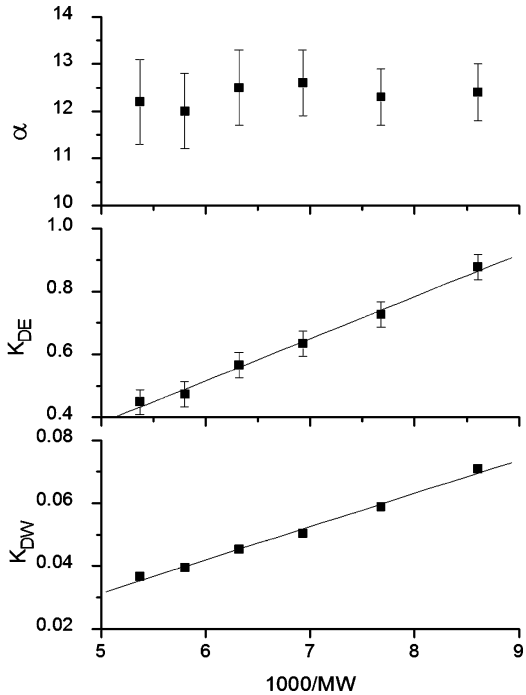

Figure 3. Extraction results for the progression of 1-heptanol through 1-dodecanol at 33°C and 5 wt % [EtOH]°$_{aq}$. Error bars, estimated from internal standard validation sets, are shown for all three cases. The separation factor (α) is essentially constant over the range of chain lengths. K_{DE} and K_{DW} decrease with increasing numbers of carbons and fit linearly to 1000/MW.

1. The most water-soluble solvent investigated here, 3-ethyl-3-pentanol, was chosen for examination. The quantitative determination of the concentration of organic solvent in the aqueous phase from the GC traces requires a calibration set for each solvent. This was not done. Instead, the GC area % was ratioed to the internal standard area % to estimate concentration. For 3-ethyl-3-pentanol, this gave [3-ethyl-3-pentanol]$^{f}_{aq}$ = 1.1% (compared to the reported[11] pure water solubility of 1.7%). Using [3-ethyl-3-pentanol]$^{f}_{aq}$ = 1.1%, K_{DW} increases 1% (relative), K_{DE} is unchanged since both the organic and aqueous-phase ethanol concentrations are measured directly, and α, as a consequence, decreases 1% (relative), from 13.5 to 13.3. As this is within our experimental error, the effect of solvent concentration in the aqueous phase could be safely ignored. Although a rigorous measurement and calculation would be justified in the case of investigations of solvents with higher aqueous-phase solubilities, these solvents would generally not be chosen as extraction candidates, since it is highly desirable to minimize solvent loss to the aqueous phase in the operation of a solvent extraction process.

Sources of Variation. Given the often large difference in extraction results reported in the literature (Table 2), it is useful to investigate the potential sources of variation, as well as the magnitudes of their effects. What follows is a discussion of seven potential sources of variation that could affect results, as well as the steps taken here to minimize these sources. The seven factors to be discussed are incomplete equilibration, entrainment, temperature, analytical method, solvent or water impurities, sample volatility, and hydrophilic/hydrophobic surface area effects.

If equilibration is incomplete, then the concentrations of ethanol and water in the two phases do not provide equilibrium information on the ternary system. The amount of time it takes for an extraction system to reach equilibrium is governed by mass transfer, which is a function of the solvent and aqueous-phase viscosities, the interfacial surface area-to-volume ratio (S/V) between the two phases, and fluid motion and interface perturbations. Vigorous, repeated agitation to emulsify the phases is an effective method to generate small droplets with high surface-to-volume ratios, and it provides fluid motion to increase convective mass transfer.

Table 2. Comparison of Results from Present Study with Literature Data

	this study				literature[a]				
solvent	[EtOH]$^f_{aq}$	T, °C	K_{DE}	α	[EtOH]$^f_{aq}$	T, °C	K_{DE}	α	ref
1-octanol					0.25	25	0.64	11	3
					0.8	23	0.61	12	6
					1.4−2.1	25	0.6	12	13
					2.04	35	0.79	12.9	14
					2.53	25	0.68	11.9	14
	3.85	33	0.73	12.3	4.0	23	0.6	11	6
					4.09	35	0.72	9.7	14
					4.72	25	0.75	9.8	14
					5.8	21−24	0.46	11	15
					7.48	25	0.78	7.1	14
					9.1	23	0.64	9.4	6
					9.60	25	0.84	5.2	14
					12.25	35	0.39	4.2	14
1-nonanol					0.23	30	0.72	13	3
	3.89	33	0.63	12.6	8.82	30	0.64	11.2	16
1-decanol					0.27	30	0.57	13	3
	3.99	33	0.57	12.5	5		0.52	19	17
1-dodecanol					2.3−3.1	25	0.25	21	13
	4.2	33	0.45	12.2	7.4	23	0.35	10	6
					9.02	25	0.43	7.6	18
2-ethyl-1-butanol					0.18	30	0.97	19.6	3
					1.3	23	0.7	12	6
					1.1−1.7	25	0.82	30	13
					1.9	30	0.94	14.6	19
	3.4	33	0.96	15.6	4.0	23	0.64	14	6
					4.9	21−24	0.73	29	15
2-ethyl-1-hexanol	0.73	33	0.61	20.0	0.24	30	0.66	24	3
	3.9	33	0.69	19.5	5		0.64	27	17
	3.9	42	0.71	19.7	5.75	35	0.78	24.5	20
					5.9	21−24	0.43	23	15
					6.00	45	0.78	21	20
					6.03	25	0.66	20.8	8
	9.3	42	0.77	16.3	9.75	35	0.77	18.2	20
	9.5	33	0.73	16.2	10		0.67	19	17
					10.85	45	0.88	18.1	20
					11.1	25	0.77	18.3	8
	14.9	42	0.86	13.0	14.35	35	0.77	13.9	20
	15.4	33	0.80	13.1	16.00	45	0.89	13.7	20
					18.15	35	0.83	11.8	20
					19.05	45	0.96	11	20
					22.10	35	0.86	9.7	20
2-octanol	3.8	33	0.77	15.4	3.6	23	0.56	13	6
					5		0.7	15	17
3-ethyl-3-pentanol					0.16	30	1.1	18	3
	3.6	33	0.99	13.5	3.3	23	0.93	11	6
dibutyl phthalate						35	0.17	33	21
	4.66	33	0.095	18.0	7.0	21−24	0.13	34	15
tributyl phosphate					0.17−0.28	30	0.79	12	3
					1.3−2.1	25	0.55	8.3	13
	3.5	33	0.76	10.5	2.54	25	0.59	10.5	22
					0.5−6.0	23	0.46	7.3	6
					5.02	25	0.62	8	22
					7.08	25	0.70	7	22

[a] [EtOH]$^f_{aq}$ was calculated from [EtOH]°$_{aq}$ for refs 3, 13, 15, and 19. Molar concentrations were converted to weight percents for refs 14 and 22. K_{DE} and α were calculated from tie-line concentrations for refs 8, 18, and 20.

To illustrate the effect of emulsification, a series of extractions using 2-ethyl-1-butanol were performed without mixing (stagnant conditions) at 33°C with [EtOH]$^0_{aq}$ = 5 wt %. Figure 5 shows the time approach to equilibrium, as well as the equilibrium values obtained using the emulsification method described in the Experimental Method Section of this paper. After 14 days of equilibration, the K_{DE} value had reached 98.5% of the emulsified value and extrapolation via a logarithmic fit showed that it would take almost 19 days to reach complete equilibration under stagnant conditions. Clearly, it is much more time efficient to emulsify the phases involved in an extraction than to employ stagnant extraction conditions.

To determine the approach to equilibrium, a set of four room-temperature extractions were performed using 5 wt % [EtOH]°$_{aq}$ and 1-decanol as the solvent. Each extraction in this series was emulsified 1, 2, 5, and 10 times before being centrifuged for 15 min and analyzed. The results showed that, after one emulsification, the K_{DE} and α values were 0.45 and 10.4, respectively. After 10 emulsifications, the results for K_{DE} and α were 0.46

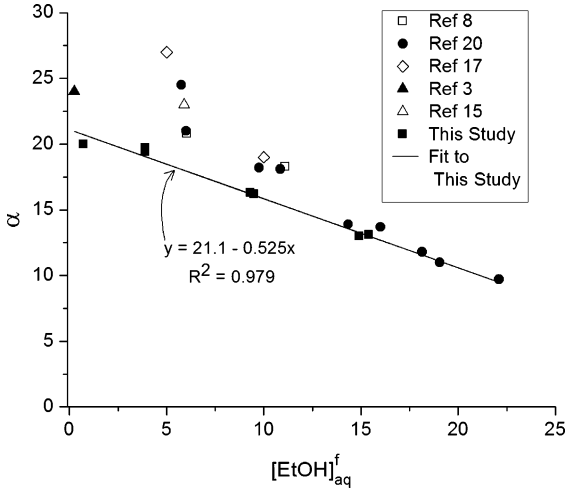

Figure 4. Comparison of results for 2-ethyl-1-hexanol between the literature and this study for the separation factor as a function of the final aqueous-phase ethanol concentration. The separation factor decreases with $[EtOH]^f_{aq}$ in this range and can be fit with a simple linear equation with $R^2 = 0.979$.

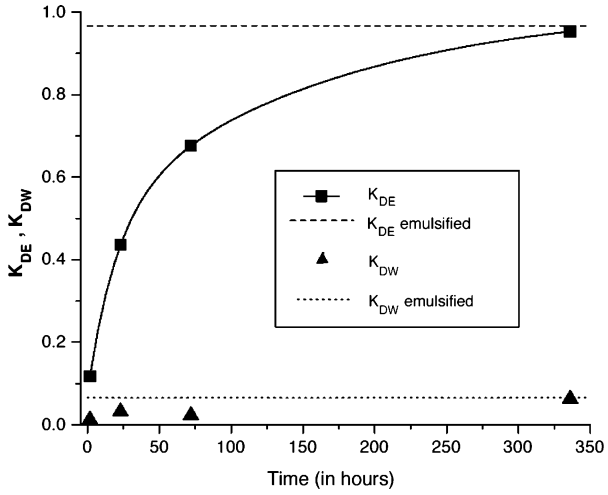

Figure 5. Time course of extraction between stagnant phases using 2-ethyl-1-butanol at 33°C. Results from the emulsified method are shown by the dashed and dotted lines for K_{DE} and K_{DW}, respectively.

and 10.4, respectively. Although one emulsification was sufficient to bring the 1-decanol system to complete equilibration, the screening included more solvents of higher viscosity, so the general method used 7−8 emulsification steps.

One method used to decrease the equilibration time without emulsifying the sample is to stir or shake it gently without breaking the aqueous/organic interface.[13] Several solvents were tested using both the emulsification method and a nonemulsification method of gently agitating the extraction sample in a temperature-controlled reciprocating water bath. The nonemulsification runs were allowed to equilibrate for 24−36 h. A comparison of these trials (Table 3) shows small differences between the extraction values in the two methods. On average, the emulsification method resulted in ~5% higher K_{DE} values and 4% higher α values.

A possible disadvantage to emulsification is the potential of entrainment of one phase into the other if the emulsion is not completely broken before sample preparation and analysis. Table 4 shows the calculated effect of aqueous-phase entrainment into the organic layer for six combinations of K_{DE} and α solvent values.

Table 3. Shaken versus Emulsified Trials

		shaken	emulsified
2-ethyl-1-hexanol	K_{DE}	0.65	0.69
	α	19.3	19.5
1-octanol	K_{DE}	0.73	0.77
	α	13.9	14.7
1-decanol	K_{DE}	0.70	0.73
	α	11.8	12.3

The table presents percent changes in K_{DE}, K_{DW}, and α values as calculated at entrainment levels of 0.01, 0.1, and 1.0 wt %. Table 5 shows the effect of organic-phase entrainment in the aqueous phase at entrainment levels of 0.01, 0.1, 1.0, and 10.0 wt %. In both cases, it was assumed that $[EtOH]_{aq} = 5$ wt % and $[H_2O]_{aq} = 95$ wt %. K_{DE} was set at 0.25, 0.75, or 1.25, and α was either 10 or 30 for the values without entrainment.

As would be expected, this calculation shows that extraction parameters are more greatly affected by the entrainment of the aqueous phase into the organic phase than by the other way around. This is due to the relatively low ethanol and water concentrations in the solvent phase as compared to the aqueous phase. The effect is particularly pronounced when the solvent in question has a low K_{DE} and a high separation factor. In this case, not only is the capacity for ethanol low, the capacity for water is even lower (~3% that of K_{DE}). Therefore, a small amount of entrainment of the 5 wt % ethanol aqueous phase will cause a dramatic increase in K_{DW} and only a small increase in K_{DE}. At the level of 1% entrainment, K_{DW} increases by 120% whereas K_{DE} only increases by 3%, so the separation factor drops by 53%. It is this low K_{DE} and high separation factor scenario in which entrainment effects are likely to have the greatest effect. In general, the entrainment of the aqueous phase in the organic phase is less critical for solvents with low separation factors and high ethanol capacities.

The effect of entrainment of the organic layer into the aqueous phase results in changes of K_{DE}, K_{DW}, and α of <1% at the 1 wt % entrainment level (basically, a simple dilution effect). Water capacities are affected similarly for all solvents, but K_{DE} values increase for solvents with low capacities and decrease for solvents with high capacities.

Entrainment can be caused by incomplete phase separation, aqueous or organic phase droplets clinging to the walls in the opposite phase layer, and direct pick up of the wrong phase at the interface by the sampling pipet. Incomplete phase separation and droplets clinging to the walls are both easily solved by centrifuging the extraction sample before sampling the phases. It was found that, once the two phases were clear and there were no droplets on the walls, centrifuging for longer amounts of time did not change the measured K_{DE} and α values. Since, in almost all cases, the top layer is the organic phase, pickup of the aqueous layer in the organic phase was easily avoided by leaving the lower 2−3 mm of organic layer above the interface in place. To avoid picking up the organic phase when sampling the lower aqueous layer, we removed and discarded the residual organic layer and the top portion of the aqueous layer. Air was gently blown out of the pipet as the tip passed through the surface to sample the aqueous layer to minimize pickup of any remaining organic phase. Fortunately, entrainment of solvent into the aqueous layer has only a small effect on the measured capacities and separation factors.

Table 4. Entrainment Effects of the Aqueous Layer into the Organic Layer

	wt % entrainment	low K_{DE} solvent (K_{DE} = 0.25) % change of			medium K_{DE} solvent (K_{DE} = 0.75) % change of			high K_{DE} solvent (K_{DE} = 1.25) % change of		
		K_{DE}	K_{DW}	α	K_{DE}	K_{DW}	α	K_{DE}	K_{DW}	α
low α	0.01	0.03	0.39	−0.36	0.003	0.12	−0.12	−0.002	0.07	−0.07
solvent	0.1	0.30	3.9	−3.5	0.03	1.2	−1.2	−0.02	0.70	−0.71
α = 10	1.0	3.0	39	−26	0.33	12	−11	−0.20	6.9	−6.7
high α	0.01	0.03	1.2	−1.2	0.003	0.39	−0.39	−0.002	0.03	−0.23
solvent	0.1	0.30	12	−10	0.03	3.9	−3.7	−0.02	2.3	−2.3
α = 30	1.0	3.0	120	−53	0.33	39	−28	−0.20	23	−19

Table 5. Entrainment Effects of the Organic Layer into the Aqueous Layer

	wt % entrainment	low K_{DE} solvent (K_{DE} = 0.25) % change of			medium K_{DE} solvent (K_{DE} = 0.75) % change of			high K_{DE} solvent (K_{DE} = 1.25) % change of		
		K_{DE}	K_{DW}	α	K_{DE}	K_{DW}	α	K_{DE}	K_{DW}	α
low α	0.01	0.01	0.01	−0.002	0.002	0.009	−0.007	−0.002	0.009	−0.011
solvent	0.1	0.07	0.10	−0.02	0.02	0.09	−0.07	−0.02	0.09	−0.11
α = 10	1.0	0.75	0.97	−0.22	0.25	0.92	−0.67	−0.25	0.87	−1.1
	10.0	7.3	9.7	−2.2	2.3	9.2	−6.3	−2.2	8.6	−10.0
high α	0.01	0.01	0.01	−0.002	0.002	0.01	−0.007	−0.002	0.01	−0.01
solvent	0.1	0.07	0.10	−0.02	0.02	0.10	−0.07	−0.02	0.1	−0.12
α = 30	1.0	0.75	0.99	−0.24	0.25	0.97	−0.72	−0.25	0.96	−1.2
	10.0	7.3	9.9	−2.4	2.3	9.7	−6.7	−2.2	9.5	−11

Inconstant temperatures of extraction and sample preparation can also be a factor that can affect equilibrium and cause results to vary. As shown in Figure 2b, in which extractions were done at 3 different temperatures, the temperature effect is more pronounced on K_{DE} than on K_{DW}. Using the data shown in this figure, it was calculated that a 5 °C drop in temperature, when starting at 33°C, resulted in 3.0% and 1.7% reductions in K_{DE} and K_{DW}, respectively. Likewise, a 5 °C rise in the extraction temperature gave a 3.6% and 2.3% increase in K_{DE} and K_{DW}, respectively. Therefore, steps were taken to ensure that the extraction, centrifugation, and sample removal steps were performed at the same temperature until the phases were separated. When this was not done, it was observed that the organic layer became cloudy either during centrifugation or as a cool pipet was inserted.

The analytical technique chosen was GC with thermal conductivity detection (TCD) with an internal standard calibration. This was used instead of the more sensitive GC with flame ionization detection (FID) because of the need to quantify water concentrations and the desire to be able to do all of the analyses using a single analytical method. The Karl Fischer method could have been applied with GC/FID but it would have added to the analytical complexities and would have required larger sample volumes. Refractometry instead of GC was also considered, but this method would require extensive calibrations in order to ensure accurate results. An external standard GC method is dependent on injection size being rigorously constant. An internal standard calibration of the GC was chosen instead to avoid errors due to injection volume variations.

One potential difficulty with the internal standard GC method was that the internal standard solutions themselves (ISO and ISA) could pick up water from the air and invalidate the calibration. The concern lay mainly with the organic phase internal standard, since it was used to measure small concentrations of water in the organic phase. The internal standard for the aqueous phase was not a concern since the diluent used in that case was water. It was calculated that if the ISO solution contained water at the level of 0.1 wt %, K_{DE} would remain unchanged, K_{DW} would increase, and α would decrease by 4%. The organic layer internal standard solutions were prepared from solvents that were dried over 3A molecular sieves and analyzed regularly using validation samples to ensure that results matched the calibration curve sufficiently.

Impurities in the solvents and water used in the extraction could also influence results. These impurities could be in the form of surfactants that enhance and stabilize emulsions. Since the solvents were used as-received, the presence of surface-active agents could not be ruled out. However, contamination from external sources was minimized by avoiding the use of soaps or detergents in the cleaning of glassware. Electrolytes in the water can cause salting-out (or salting-in) effects,[23−25] but this effect is negligible at the low levels of electrolytes usually encountered in tap water. Organic impurities within the extraction solvent also contribute to variation among the reported K_{DE}, K_{DW}, and α values. These effects are sometimes not additive, based on literature results for mixtures of solvents.[3,19,26] Only one solvent in this study had as much as 3% of impurities (Table 1).

Sample volatility can lead to differential depletion or enrichment of the measured components. For example, ethanol may evaporate more quickly than water or solvent from the organic phase or, if the solvent is highly volatile, the solvent may evaporate more quickly than the other constituents, changing the overall concentrations of ethanol and water. Therefore, all extractions were carried out in well-sealed tubes, and the exposure time to air during sample preparation was kept as short as possible.

The last factor, preferential adsorption or desorption of solvent or water molecules on hydrophilic or hydrophobic surfaces, was anticipated to be small. It could arise as a problem if the surface area-to-volume ratio is high and the concentration of the adsorbed component is very low, as could be the case in the analysis of water in the organic layer if glass pipets, with a hydrophilic inner surface, had been used to transfer the solvent

layer or if multiple transfers had been done. We estimated that K_{DW} could be decreased by at most 5% when the organic phase is transferred in glass pipets (based on data for cyclohexane by Roddy,[13] where $[H_2O]^f_{org}$ was ~0.002 wt %). On the other hand, the use of polyethylene pipets to transfer the aqueous phase will have a negligible effect on the ethanol measurement because $[EtOH]^f_{aq}$ is relatively high (1−5 wt %). Researchers interested in measuring the organic solvent concentration in the aqueous phase, which for highly hydrophobic solvents may be very low, should take this consideration into account. In this study, both the organic and aqueous phases were transferred using polyethylene pipets.

Conclusions

The extraction method presented in this paper is robust and suitable for solvent screening. Tie-line data generation, which provides a comprehensive picture of the phase-composition behavior of a ternary mixture, is not desirable in a screening context and would hinder the screening of large numbers of solvents because of the time required for extended data generation and the higher solvent volumes needed. The results presented here are in reasonable agreement with results in the literature. However, reported data on a given solvent sometimes show large variation. This can partly be explained by differences in the extraction and analytical techniques. The analysis undertaken here of potential sources of variation and the magnitude of their effects should be useful to others working in this area and should help to explain the differences in results seen in data from different sources. The companion report[9] will apply the method described here to determine the molecular structural effects on extraction performance for a wide range of straight-chain and branched alcohols.

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