Extraction Chemistry of Low Molecular Weight Aliphatic Alcohols

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I. Introduction

For the past decade or so there has been a renewed interest in the technology of alcohol recovery from a variety of sources. For example, the possibility of ethanol addition to petroleum fuels was one of the reasons prompting the collection of chemical and engineering data, as the conversion of biomass to ethanol and its recovery from fermentation broth was another. Some of that new interest centers around the extractive recovery of the alcohols, especially of ethanol, and the controversy concerning the net energy balance and the overall economies of the distillative vs. the extractive recovery process.

Distribution data on low molecular weight alcohols between water and organic solvents have been reported with a variety of purposes. Much of the recent information deals with the partition of ethanol. A number of projects have been formulated with the aim of developing processing concepts for ethanol recovery from fermentation broth that involve fermentation, solvent extraction, distillation or stripping, and solvent recovery. It should be mentioned that conventional ethanol fermentation is limited to a final concentration of some 12 wt % due to the inhibitory effect of the product itself, which suppresses further fermentation.[1-3] Some projects[3-10] call for a possible continuous technology, termed extractive fermentation, which involves the removal of the fermented alcohol before it reaches inhibitory levels in the broth. There are several problems associated with such a continuous process. One of them, relevant to the topic under review, is the toxicity of the organic solvent or, more generally, the components of an extractant phase, toward the microorganisms. This is no trivial problem.

Other similar projects involving extraction have been directed toward a somewhat different aim, that of developing a cost-effective and energy-efficient process for recovering fuel-grade ethanol from conventional fermented broth. Fuel-grade ethanol is standardly defined as containing no more than 2 wt % water and is thereby completely miscible throughout a wide temperature range with hydrocarbon gasoline in a 1:9 ratio (gasohol).[11-14] Of course, the most energy-intensive step in such a process is the separation of alcohol from water and its dehydration to the required 98 wt % level. Extraction has been considered as a means of initial recovery as well as a method of final concentration.

A sizeable fraction of the distribution data in the literature and many of the most recent reports on the alcohols under review refer to extraction in the 1-octanol/water system at room temperature. This two-phase system is the accepted standard model for partition and transfer properties of chemicals, where the partition coefficient *P* is adopted as a measure of the hydrophobicity of the organic compound for bioactivity, biotransport, and bioaccumulation.[15-23] In environmental chemistry, log *P* of a compound is thought to correlate with its biological activity by modeling its interaction or degradation via biological membrane systems. In pharmaceutical chemistry, a similar relationship, based on biological response data, has been formulated between log *P* and some significant physical parameters of compounds of known drug activity.[19,24]

Most of the pioneering work in this area, which started decades ago,[25-28] has contributed much to the collection and critical assessment[24] of partition data in the literature. Equally important is the influence of

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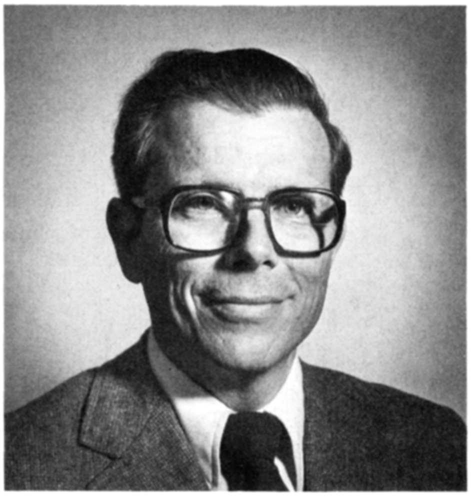
that work on the renewed interest in extractive separation and purification of a large variety of organic compounds, the alcohols among them. The comprehensive monograph of Hansch and Leo[24] provides an extended and detailed listing of log P values of a large number of systems relevant to the present review. We have conducted our own literature search and can attest to the completeness of their coverage of the archival literature data. Though the claims for the general applicability of their method[24,28] to calculate the octanol/water partition coefficient are probably not fully justified (see section VII.H), especially for the high molecular weight organics,[16,29] the concept should be useful for practical correlations in many applied fields.

The primary goal of the present review has been to collect, digest, and critically evaluate published partition and distribution data on the eight lowest monofunctional aliphatic alcohols. The extraction of the alcohols, the partitioning process between an aqueous and an organic phase of this type of nonelectrolyte, is believed to be governed to comparable extents (1) by water–water interactions dominating over alcohol–water interactions—usually termed "hydrophobic interaction", and (2) by the affinity of the extractant toward the alcohol due to some specific interaction. We have thus included in the review a discussion of the thermodynamics and phase equilibria of both aqueous and organic solutions of the alcohols over their complete miscibility range, as well as a summary of the nature and properties of these solutions. That information is believed to be important for an understanding of the fundamental chemistry involved. The detailed analysis of the relevant systems should reveal general patterns of behavior that, in turn, may provide new insight into the problem of extractive recovery of lower alcohols. In that respect the review also serves as a preliminary step toward the design and formulation of a long-term experimental project for developing improved extraction technology for alcohols and related substances.



C. Judson King is Professor of Chemical Engineering and Dean of the College of Chemistry at the University of California, Berkeley. He has been at Berkeley since 1963, following education at Yale University (B.E.) and Massachusetts Institute of Technology (S.M., Sc.D.). Professor King's interests include separation processes, in general, and solvent extraction, adsorption, drying, and mass transfer, in particular. He is the author of *Separation Processes* (McGraw-Hill, 2nd ed., 1980), 170 papers, and 9 patents. He consults for Procter & Gamble, CPC International, and Combustion Engineering. He is Chairman of the Committee on Separation Science and Technology, Board of Chemical Science and Technology, National Research Council, which is issuing a report (1987) titled "Separation and Purification: Critical Needs and Opportunities". He chairs the Science Advisory Board and is a member of the Governing Board of the Council for Chemical Research, is a Director of the American Institute of Chemical Engineers, and was 1986 Chairman of the ACS Subdivision of Separations Science and Technology. A member of the National Academy of Engineering, Dr. King has also received the William H. Walker and Food, Pharmaceutical and Bioengineering Division Awards, been Institute Lecturer for the American Institute of Chemical Engineers, and has received the George Westinghouse Award of the American Society for Engineering Education. He has been a Scoutmaster for the past 11 years.

We have also carried out a similar review of the extraction chemistry of carboxylic acids.[30]

II. *Alcohols, Their Chemical and Physical Properties*

The alcohols under review are listed in Table I along with the chemical shorthand abbreviations used in the text, their Chemical Abstracts Service Registry Num-

TABLE I. Selected Physical and Thermodynamic Properties of Aliphatic Alcohols,[32] Abbreviations, and Chemical Abstracts Service Registry Numbers

alcohol	abbrev	CAS Reg No.	alcohol	abbrev	CAS Reg No.
methanol	MeOH	67-56-1	1-butanol	*n*-BuOH	71-36-3
ethanol	EtOH	64-17-5	2-butanol	*sec*-BuOH	78-92-2
1-propanol	*n*-PrOH	71-23-8	2-methyl-1-propanol	*i*-BuOH	78-83-1
2-propanol	*i*-PrOH	67-63-0	2-methyl-2-propanol	*t*-BuOH	75-65-0

property	MeOH	EtOH	*n*-PrOH	*i*-PrOH	*n*-BuOH	*sec*-BuOH	*i*-BuOH	*t*-BuOH
freezing point, °C	−97.7	−114.1	−126.2	−88.5	−89.3	−114.7		25.8
boiling point, °C	64.70	78.29	97.20	82.26	117.66	99.55	107.87	82.42
vapor pressure, mmHg, 25 °C	125.4	59.8	20.9	45.2	6.18	18.3	10.4	42.0[a]
density, g cm^{-3}, 25 °C	0.7866	0.7851	0.7998	0.7813	0.8060	0.8026	0.7978	0.7812
refractive index, 25 °C	1.3265	1.3594	1.3837	1.3752	1.3971	1.3949	1.3938	1.3852
dipole moment,[b] debye	1.66	1.69	1.68	1.66	1.66	1.66	1.64	
dielectric constant,[c] 20 °C	32.8	24.6	19.5	18.6	18.0		11.3	17.5
$\Delta_{form}H^\circ$(liq), kJ mol^{-1}, 25 °C	−239.0	−277.0	−304.0	−317.9	−327.1	−342.6	−334.1	−359.2
$\Delta_{form}G^\circ$(liq), kJ mol^{-1}, 25 °C	−166.8	−174.2	−170.6	−180.3	−162.5	−177.0		−184.7
$\Delta_{vap}H^\circ$(liq), kJ mol^{-1}, 25 °C	37.4	42.3	47.5	45.4	52.4	49.7	50.8	46.6
C_p°(liq), J deg^{-1} mol^{-1}, 25 °C	81.2	112.0	141.0	150.9	177.0	198.7	180.3	220.1
S°(liq), J deg^{-1} mol^{-1}, 25 °C	127.2	161.0	194.6	180.6	226.4	225.1		192.9

[a] Solid at 25 °C. [b] Reference 33. [c] References 39, 101.

bers, and selected physical and thermodynamic properties. With the few exceptions footnoted, the values are those from the comprehensive compilation and critical evaluation of the Thermodynamic Research Center at Texas A&M University.[31,32] This source appears to be the most complete, accurate, and self-consistent. Some parameters, such as the critical pressure, critical temperature, and enthalpies of combustion, are not included in our table, but can be found in the original compilation. Values for the mean radius of gyration and critical compressibility factors are tabulated by Fredenslund et al.,[33] and those for surface tension, thermal conductivity, and viscosity can be found in the *Industrial Solvents Handbook*.[34]

III. Alcohols in Aqueous Solutions

For the series of alcohols listed in Table I, the properties of their aqueous solutions vary from full miscibility with water in all proportions at all practical temperatures and pressures to only a limited mutual miscibility. The extent of that miscibility depends on the relative importance of the polar and nonpolar constituents of the alcohol molecule. The hydration of the alcohols in the aqueous feed solution is important for the distribution process. Hydration may refer to both the alkyl chain and the hydroxyl group. Obviously these two types of segments provide opposing effects: The functional group can form hydrogen bonds with water, which, in turn, tends to hold the alcohol in the aqueous phase, while the apolar methyl and methylene groups by virtue of their large negative entropies of hydration[35,36] tend to force the alcohols into the organic phase.

The principal aim of this section is to obtain a general picture of the physical, chemical, and thermodynamic properties of aqueous alcohol solutions and their structure. Mutual solubilities, critical solution temperatures, and partial molar and excess functions of solution and mixing are reviewed in tabular and graphical form in order to allow comparison among the alcohols under consideration. Heat capacity information is analyzed because it is a function sensitive to changes in the molecular structure of, and hydrophobic phenomena in, the solutions. This, in turn, is usually related to the relative simultaneous extractability of alcohol and water. Some of the several relationships for correlation and prediction of alcohol solubilities that are considered relevant are reviewed and their suitability is discussed along with those for alcohol partition in section VII.H specifically devoted to the topic.

The existing information on the behavior of aqueous alcohol solutions in the presence of a third component, a salting-in or salting-out agent, is reviewed along with the fundamental concepts of the prevailing theory. The information is analyzed in the form of salting coefficients. In a number of cases phase diagrams are given as examples and analyzed for the effect of salt mutual solubilities in ternary systems. Relevant activity coefficient data are referenced in order to give a complete thermodynamic account of the multicomponent system.

In spite of several simplifications of this particular topic[35] in the present review, we trust that the general model of alcoholic solutes in water as presented here can serve as a guide for applied research aimed toward the extractive recovery and/or separation of alcohols.

A. Binary Systems

1. Solubilities

There is no indication of a miscibility gap for methanol or ethanol with water at any temperature and pressure. The region of liquid–liquid immiscibility in the *n*-PrOH + water system extends between compositions of 26.5 and 73.2 g of alcohol/100 g of solution (0.108 and 0.450 mol fraction) from −10.5 °C to an upper critical miscibility temperature of −1.7 °C at 50 g of alcohol/100 g of solution (0.231 mol fraction).[37] The corresponding region in the *i*-PrOH + water system extends between compositions of 40.80 and 60.00 g of alcohol/100 g of solution (0.171 and 0.310 mol fraction) at −20 °C to an upper critical miscibility temperature of −12 °C at 51 g of alcohol/100 g of solution (0.238 mol fraction).[37] *t*-BuOH, which has a melting point of 25.8 °C, shows no region of liquid–liquid immiscibility with water at atmospheric pressure over the temperature

TABLE II. Mutual Solubilities in Butyl Alcohol + Water Systems[37]

	solubility, 25 °C			
	alcohol in water		water in alcohol	
alcohol	g/100 g soln	mol fraction	g/100 g soln	mol fraction
n-BuOH	7.4 ± 0.1	0.019	20.3 ± 0.3	0.486
i-BuOH	8.5 ± 0.1	0.022	16.7 ± 0.1	0.454
sec-BuOH	18.1 ± 0.8	0.051	33.9 ± 0.7	0.679

TABLE III. Upper Critical Solution Temperature and Composition in Alcohol + Water Systems[37]

alcohol	t_c, °C	g alc/100 g soln[a]	mol fraction alc
n-PrOH	−1.7	50.0	0.231
i-PrOH	−12.0	51.0	0.238
n-BuOH	125.2	32.5	0.105
i-BuOH	134.1	36.2	0.123
sec-BuOH	116 ± 2	~39	~0.13

[a] alc = alcohol, soln = solution.

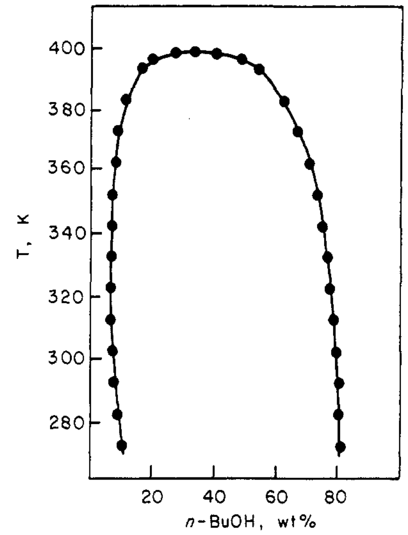


Figure 1. Mutual solubilities in water + *n*-BuOH system.[37]

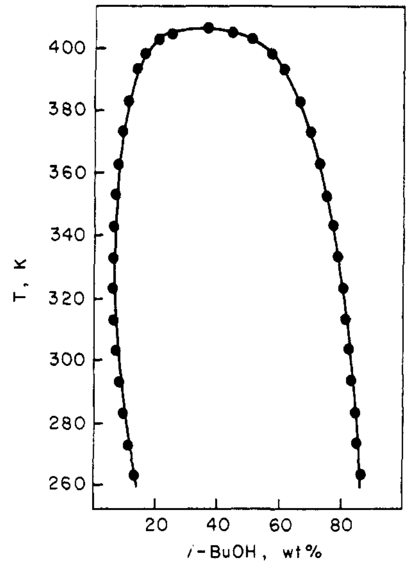


Figure 2. Mutual solubilities in water + *i*-BuOH system.[37]

range −100 to 25 °C. Mutual solubilities in the remaining three butyl alcohol + water systems at 25 °C are compiled in Table II and for *n*-BuOH and for *i*-BuOH plotted in Figures 1 and 2 for the whole temperature range up to the critical miscibility temperature. Table III shows the upper critical solution temperatures for five alcohol + water systems at atmospheric pressure, along with the corresponding compositions of the mixtures.[37,38] The *sec*-BuOH + water system is the only one exhibiting a clearly detectable lower critical solution temperature (LCST), at −8.45 °C. As a consequence, the mutual miscibility curve is complex.[37] It should be noted perhaps that a LCST is exhibited only in systems whose mixing properties are under entropy control.[36]

2. Physical and Thermodynamic Properties

Many physical properties of alcohol + water mixtures over the complete composition range have been compiled in a recently revised and updated edition of *Industrial Solvents Handbook*.[34] Data on freezing, boiling, and flash points, densities and viscosities at several temperatures, volume changes on mixing, surface tension, thermal conductivity, and index of refraction are tabulated and/or presented in graphical form. Though this is not a critical compilation, it is fair to assume that the most comprehensive sets of data have been selected for inclusion in this compilation.

The complex properties of aqueous alcohol solutions as a result of a number of conflicting and competing interactions are reflected in the variation of the molal and excess functions with the composition of the mixtures.[35,39,40] For example, the hydration of both the functional group and the methylene group in water results in large negative entropies of hydration, which in turn affect the distribution of the alkyl-chain portion of the alcohol between water and an organic solvent.

As demonstrated in Figure 3, excess enthalpies of mixing, $\Delta_{mix}H$, of the alcohols with water exhibit a complex dependence on composition.[36,41] ΔH^E values are exothermic in the water-rich region, with an exothermic minimum at an alcohol mole fraction that decreases with increasing molecular weight of the alcohol. As the alcohol mole fraction, x_{alc}, increases in the mixture, ΔH^E becomes endothermic, exhibiting a clear maximum in the case of propyl and butyl alcohols. The exact positions of the extremes depend on the alcohol and temperature.

The standard[36] interpretation of such S-shaped excess enthalpy curves, not quite unique for the systems under consideration, takes into account the opposing contributions from a number of complex interactions. The most significant is the endothermic breaking of the H-bonds in both liquids and the formation of new ones of the solute–solvent type exothermically. The resulting excess function is thus the difference between the two effects. The positive deviation from Raoult's law, ΔG^E positive, exhibited by these solutions is the consequence of $T\Delta S^E > H^E$ rather than $\Delta H^E > 0$, since excess enthalpies are mostly negative. The solution properties of alcohol + water mixtures are thus entropy controlled. It should be noted that the entropic component of ΔG plays a large role also in the position of the equilibrium determining the numerical value of the distribution ratio.[24] In simple physical terms, Franks and Reid[36] consider the water-miscible lower alcohols as having a "structure breaking" effect on water, whereas the higher ones with a limited water miscibility behave as hydro-

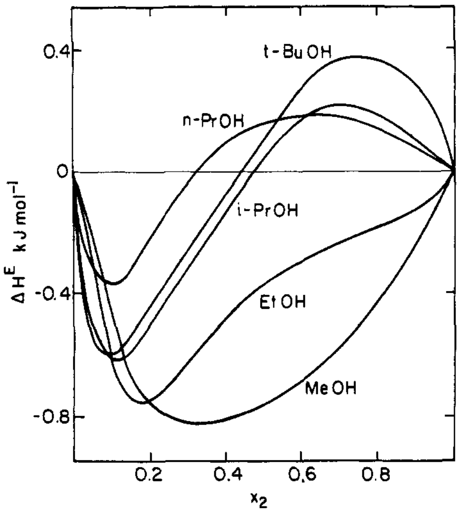


Figure 3. Excess enthalpies of mixing in alcohol + water mixtures as a function of alcohol mole fraction,[36] 25 °C.

phobic "structure makers". The two effects are almost balanced with *i*-PrOH. The relative magnitudes of $T\Delta S^E$ and ΔH^E are themselves an indication of this precarious balance that exists in alcohol + water mixtures.

There is a fairly large body of excess enthalpy of mixing data for binary alcohol + water mixtures, which has been reviewed and compiled[42] as recently as 1982. For specific numerical information this compilation and the references therein should be consulted. Included are aqueous mixtures of all eight alcohols under review here, for most of them at several temperatures in the 25–75 °C range. There are as many as 16 separate sets of data each for methanol and ethanol, though only two sets each for *i*-BuOH and *t*-BuOH.

For the past 15 years there were many systematic studies[43–53] on the enthalpies of solution of alcohols in water. These data are, of course, directly related to the enthalpy of mixing data shown in Figure 3. Alexander and Hill,[46] Kover and Carter,[43] and Krishnan and Friedman[52] have reported comprehensive sets of data, some at several temperatures,[46] and have reviewed those prior to 1968/1969. The calorimetrically measured enthalpies of solution of the alcohols, invariably exothermic in dilute solution of the alcohol, regardless of the degree of hydrophobicity, appear to be concentration independent,[46,47] at least in the dilute range, ≤0.01 mol fraction, although exceptions are known.[48] From such calorimetric data[46] in the 5–35 °C range, the temperature dependence of the $\Delta_{soln}H^\circ$, the standard enthalpy of solution at finite dilution, and the corresponding ΔG_p°, the heat capacity of solution, have been derived by least-squares calculations. The values at 25 °C, compiled[36,43,46,52] in Table IV, are believed to be precise and the enthalpy values accurate within ±1%, though those for the heat capacity are probably no better than ±10% despite the fact that they were derived by first-derivative treatment of enthalpy data believed to be of a sufficiently high precision. It is apparent[46,52] that there is no constant-increment change in ΔH° with chain length, which is contrary to earlier claims.[44,46,54,55] Enthalpies are less negative for the normal alcohols than for the corresponding isomers. Heat capacities of solution increase, essentially linearly, with the number of carbon atoms or molar volume of the alcohols. Surprisingly, however, branching of the alkyl chain affects ΔC_p° only slightly, perhaps ±5% for the four butyl alcohols. It should be noted for further reference that heat capacities of solution of the alcohols in water reflect the hydrophobic interaction between the components via the effect of alcohol on the structure of water.

TABLE IV. Standard Enthalpies of Solution of Alcohols in Water at Infinite Dilution and Molar Heat Capacities of Solution, 25 °C

alcohol	$-\Delta_{soln}H^\circ$, kJ mol^{-1}	ΔC_p°,[a] J K^{-1} mol^{-1}
MeOH	7.24	75.2
EtOH	10.09	141.7
n-PrOH	10.12	208.6
i-PrOH	12.97	205.7
n-BuOH	9.27	260.0
i-BuOH	9.28	284.4
sec-BuOH	13.17	284.2
t-BuOH	17.33	265.0

[a] $-\Delta C_p^\circ = \partial(\Delta H^\circ)/\partial T$.

The general shape of the excess molar volume vs. mole fraction curves, as exemplified[36] in Figure 4, is not substantially different from that of ΔH^E vs. x_{alc}. Even at high dilutions the plots have a finite, non-zero slope, indicating probably a solute–solute interaction. As a rule, the excess volumes are negative and the ΔV^E vs. x_{alc} curves exhibit a minimum that, by the way, corresponds to a minimum in the similar curves representing the coefficient of adiabatic compressibility with the alcohol mole fraction.[36] It is rather speculative to interpret the shape of such curves because the excess volumes must include contributions from solvent–solvent and solvent–solute interactions, in addition to that between the solute molecules. The qualitative reasonings of Franks and Reid[36] give general guidance. The negative slope increases with the molecular weight of the alcohol, indicating that more polar molecules, ones with higher proportions of the polar group, have a decreased capability to influence water structure. The positive slopes of the curves at high alcohol mole fractions were taken[36] to indicate the structure-breaking role of the alcohol: $\partial V^E/\partial x$ becomes more negative as the alkyl group increases in size,[56] and the minimum in the curve moves to lower x_{alc} values. This effect appears to be most pronounced in the case of *t*-BuOH, although the differences in the solution properties among the four butyl alcohols may be too subtle for a meaningful differentiation among the isomers.

B. Ternary Systems

As mentioned earlier, the aqueous feed from which alcohols are recovered by an extractive fractionation technology may contain other solutes in concentrations which easily exceed that of the alcohol. It is thus desirable to summarize briefly the phase behavior and some thermodynamic data on ternary systems of alcohol with water and an electrolyte or nonelectrolyte. It should be kept in mind that the extractability of alcohols and other nonelectrolytes from aqueous salt solutions is usually higher than from water.

Although electrolytes and nonelectrolytes can either increase[57–63] or decrease[45,58] the solubility of alcohols in water—processes being termed salting-in or salting-out, respectively—addition of an electrolyte to a homoge-

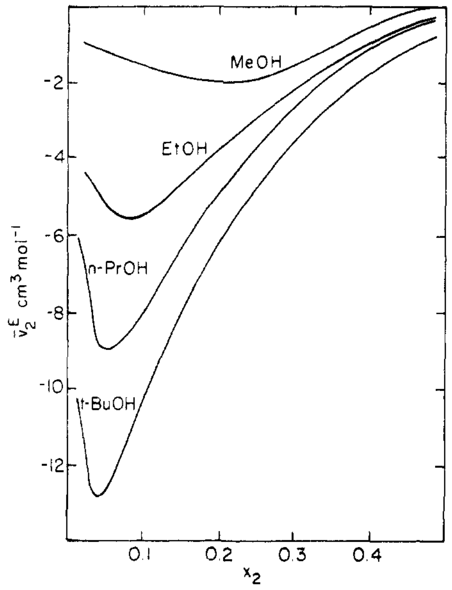


Figure 4. Excess volumes of mixing in alcohol + water mixtures as a function of alcohol mole fraction,[36] 25 °C.

neous alcohol + water mixture will usually promote segregation into two liquid phases. The phenomenon will occur even before the solubility limit of the salt in either of the phases is reached,[41] as demonstrated for several propyl[45,62,63] and butyl alcohol[45,57-61] systems with various electrolytes, but mostly sodium chloride. The salt-induced miscibility gap increases in width with the salt concentration as shown in Figure 5 for the system[59] n-BuOH + H_2O + NaCl. The lines depict the lower legs, those in the 20–40 °C range, of the miscibility curve shown previously in Figure 1 in the absence of the salt. As can be seen in Figure 5, the tendency to unmix is equally pronounced in both the alcohol-rich and the water-rich regions of the mixture. This is rather unusual as in most cases the trend is more pronounced in the alcohol-rich region,[61] due to a higher solubility of water in alcohol. The presence of an electrolyte increases the partial pressure of the alcohol in its more dilute solutions, but decreases it in more concentrated ones. Figure 6 shows the effect of NaCl on the solubility of alcohols in the aqueous salt solutions.[63] Branched alcohols exhibit a higher aqueous solubility than normal alcohols.

In the simplest of cases, in the absence of strong solute–solute interactions, the solubility of the alcohol in aqueous salt solution can be expressed by the semiempirical Setchenov salting equation[45]

$$\log S_0/S = k_{s,alc}C_s \qquad (1)$$

where S_0 and S are the solubilities of the alcohol in pure water and aqueous solution at C_S salt concentration. The salting coefficient k_s depends on the nature of the salt and temperature, and its numerical value depends on the concentration scale, molar, molal or mole fraction, used.[45] For the majority of the cases involving alcohols and at moderate electrolyte concentrations, the $k_{s,alc}C_s$ product in eq 1 also equals $\log \gamma/\gamma_0$, the log of the ratio of the activity coefficients of the alcohol in the salt solution and pure water. The salting coefficient k_s, which is not highly temperature sensitive,[59] can be evaluated by using the scaled particle theory.[59,63,64]

In the context of alcohol enrichment by extraction or in that of its separation from water, it is useful to define in a similar way the salting coefficient of water, $k_{s,w}$. The two salting coefficients, as derived from solubilities on the mole per cubic decimeter scale, for ternary systems of n-BuOH, water, and an alkali metal halide are compiled in Table V. From Korenman's data[60,61] on these and similar systems with higher normal alcohols, it appears that $k_{s,alc}$ increases with the molecular weight of the alcohol, while $k_{s,w}$ decreases. Though the phenomenon may be associated with a lesser solubility of the alcohol in water with increasing chain length, the data in Table VI do not show that trend. Branching of the alkyl chain appears to be a far more important factor affecting the $k_{s,alc}$ values. Although branched isomers are more water soluble, their solubility is reduced by salt much more than that of the normal isomers. $k_{s,w}$ appears to be rather insensitive to the nature of the salt.

The standard enthalpies of solution, $\Delta_{soln}H°$, of the alcohols in aqueous electrolyte solutions[45,47,49,57] decrease (become less negative) linearly with increasing molar concentration of the electrolyte. Attempts[57] to correlate $\Delta_{soln}H°$ values via the scaled-particle theory were reasonably successful for the homologous series of normal alcohols but failed[47] in the case of the branched chain isomers.

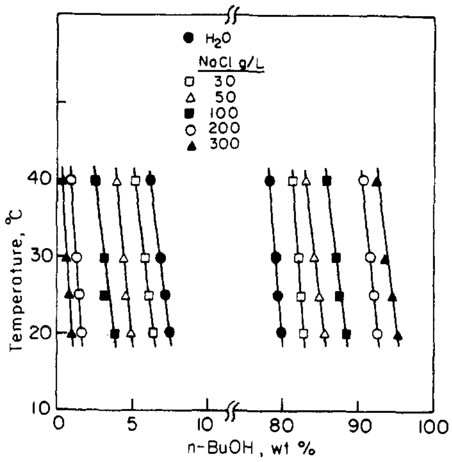


Figure 5. Effect of sodium chloride concentration on the miscibility gap in water + n-BuOH system.[59]

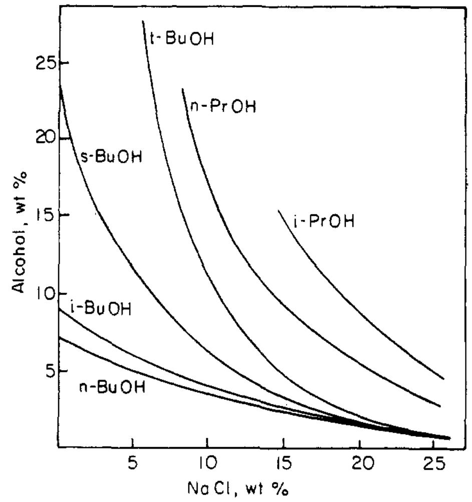


Figure 6. Salting-out of alcohols as a function of sodium chloride concentration in the aqueous phase,[63] 25 °C.

TABLE V. Salting Coefficients for 1-Butanol and Water in Ternary Systems Containing Alkali Metal Halides,[60,61,63] 25 °C

salt	$k_{s,alc}$	$k_{s,w}$	salt	$k_{s,alc}$	$k_{s,w}$
LiCl	0.129	0.085	KF	0.225	0.090
NaCl	0.180	0.095	KBr	0.144	0.099
KCl	0.172	0.106	KI	0.106	0.040

TABLE VI. Salting Coefficients for Propyl and Butyl Alcohols in Ternary Systems of Aqueous Sodium Chloride,[63] 25 °C

alcohol	$k_{s,alc}$	alcohol	$k_{s,alc}$
n-PrOH	0.200	*i*-BuOH	0.201
i-PrOH	0.215	*sec*-BuOH	0.480
n-BuOH	0.179	*t*-BuOH	0.490

C. Structure of Solutions

Many aspects of the structural models of aqueous solutions of solutes in general, but especially those of the lower, fully or partially water-miscible alcohols, are helpful and frequently even essential for a better understanding of the extraction equilibria. This is particularly relevant in view of the generally low extractability of alcohols into hydrocarbons, substituted hydrocarbons, or their solutions of extractants.

The structure of alcohol + water mixtures, no less than the physicochemical behavior, is complex. Even after more than three decades of intensive studies it is still to a large extent speculative and entirely qualitative. The structure of the mixture is sensitive to alcohol concentration, especially in the water-rich region. It is generally believed that the self-associated hydrogen-bonded water structure is enhanced by adding small volumes of alcohols, less than about 0.04 mol fraction. This phenomenon is possibly due to increased formation of water dimers with H-bonds stronger than those in the three-dimensional cross-linked water structure with the tetrahedral orientation, in which most water molecules form four such bonds with four neighbors.[47,56,65] The model is uncertain, mainly because the data on the strength of the H-bonds involved are in dispute.[66] The alcohol concentration range in which such water structuring is prompted depends, obviously, on the properties of the alcohol. The higher ones considered here, *i*-PrOH and the butanols, are taken[47] to be structure makers at sufficiently low concentrations.

Though the possibility for hydrophobic-type clustering of alcohol molecules at high dilution cannot be ruled out,[66] little if any alcohol self-association can be expected.[56,67] For example, it has been suggested[68,69] that, at 0.03 mol fraction of *t*-BuOH in water, each solute molecule has a water shell containing some 28 water molecules. At higher alcohol concentrations, 0.03–0.06 mol fraction, water molecules constituting the shell may be shared by two adjacent alcohol molecules. Such a structure obviously works against alcohol self-association at that dilution. The structure breaks down rapidly at higher alcohol concentrations.

Perhaps the most prevailing and the least subtle element affecting the structure of alcohol + water mixtures, at practically any composition, is the hydrogen bonding between the two different molecules. Such bonding can take place either to the oxygen atom of the alcohol or to that of water.[70] Water is thus respectively either the proton donor or the acceptor. Because of the electron-donating character of the alkyl group, the first reaction is considered to result in stronger bonds.

The properties and behavior of alcohol-rich binary mixtures are believed to be caused by destruction of the three-dimensional water structure.

IV. Alcohols in Organic Solvents

Binary mixtures of alcohols (solute) with aliphatic or aromatic hydrocarbons or their derivatives (solvent) have received considerable attention with many reports dealing with specific and nonspecific interactions between the components, as well as specific solute–solute interactions leading to the formation of molecular associates. Mixtures of saturated alkanes and the alcohols under consideration appear to be the simplest conceivable model suited for testing theories of ideally associated liquids. Namely, in such mixtures that have only three fragmental entities, $-CH_3$, $-CH_2-$, and $-OH$, the relative proportion of those entities is the only variable. Additionally, as the alkane is the ideal nonreacting component, any deviation from an ideal behavior of such binary liquid mixtures is governed by the alcoholic component exclusively.

Many comprehensive critical reviews have dealt with the behavior, property, and structure of such systems, and they usually contain extensive bibliographies.[71,72] Thus, no attempt is made here to discuss such systems in any detail, except for making reference to some thermodynamic data believed to be relevant to the state of the alcohol solute in organic solutions. This, in turn, bears heavily on the partition behavior of alcohols between water and hydrocarbons.

The conclusions in these reviews are clear in saying that the problem of alcohol association in organic solvents is far from being finally resolved. Hydrogen bonding produces varying extents of alcohol aggregates, some linear, some cyclic, as discussed briefly under the subheading IV.A.1. The information on association of alcohols in organic solvents and that on the thermodynamics of mixing and phase behavior and also structural considerations are relevant to our review. However, probably not all of that quantitative information is strictly valid for an organic phase in equilibrium with an aqueous solution. The alcohols under review are, as a rule, transferred into the organic phase along with a relatively high concentration of water. And no hydrogen bonding or dipole–dipole interaction in the organic solution can be independent of the water content. This is true in spite of the fact that the transfer of the alcohol from an aqueous solution to a water-immiscible organic solvent involves some degree of dehydration of the polar group. The dehydration, however, is never complete, as the alcohol molecule contains a water cage supported by hydrophobic exclusion.[68] Such hydrated alcohol molecules have little driving force toward aggregation, and only in "water deficient" organic media will an aggregation set in.

A. Binary Systems

A large volume of data on the properties of binary systems of alcohols and hydrocarbons is known. Part of these data pertain to the self-association of the alcohols and part to the thrmodynamic properties of such mixtures. These aspects are reviewed briefly under the subsequent subheadings.

1. Association

There has been a long and continuing controversy regarding the self-association process in neat liquid alcohols and their solutions in organic solvents. The consensus appears to be in favor of a broad, rather noncommittal, definition that most experimental evidence supports a monomer–tetramer equilibrium, although the presence of some dimers and possibly trimers cannot be ruled out. Similarly, the consensus allows for linear and cyclic oligomers, including the dimer. Inherent properties of a solvent such as its dipole moment, polarizability, and dielectric constant affect the interaction of the solvent with an alcohol solute. Thus, for example, the self-association of the alcohols in zero-dipole-moment benzene or carbon tetrachloride is markedly weaker than in paraffinic hydrocarbons, reflecting, possibly, the competing interaction between the solute and the solvent that occurs because of the self-association process.[73,74] In the case of benzene the solute–solvent interaction is due to the π-electrons, whereas in carbon tetrachloride it is the lone pairs of electrons that provide the stability of the adduct.

A large volume of data on the physical properties of binary systems is known.[32,72,74–81] Two important measures of the degree of association are the fraction of monomers and the fraction of the unbound free OH groups, as determined from spectroscopic and/or thermodynamic data. Partition measurements, being of a much less discriminatory type, are not highly reliable for checking association models for alcohols or even for deriving qualitative information about the process, in spite of statements to the contrary.[82] For the purpose of deriving association constants in solutions via physical property, spectral, or thermodynamic data, solute concentrations above 0.1 mol dm^{-3} will usually not yield reliable data.[77] On the other hand, association at solute concentrations below 0.01 mol dm^{-3} is small even in the most inert of solvents.[19,75,83,84]

The mass-action law equilibria accounting for the oligomerization of alcohols can be defined in several forms, and the choice is essentially one of convenience.[34,75,79,83,85–87] It should be kept in mind, however, that the association is weak and the constants are small; thus, their determination with any reliability is not trivial, especially as the simultaneous formation of several oligomers cannot be neglected. Indeed, several association equilibria must be superimposed upon each other. The experimental evidence for self-association is attributed to the presence of O–H···O–H bonds, with an enthalpy of some 16–24 kJ/mol of bond at room temperature.[74,79,88–92] The strength of the bond, as derived from vapor pressure[78] and calorimetric[79] data for the alcohol + alkane mixtures, is almost the same for different alcohols in a given solvent, with perhaps a slight trend to increase with increasing molecular weight of the alcohol.[74,79,89,91]

An accepted[75,79,83,85–87,92] approach is to assume the stepwise formation of alcohol oligomers via a series of sequential association reactions such as those shown in eq 2. The model assumes that the deviation from an

$$\begin{aligned} \mathrm{ROH} + \mathrm{ROH} &\rightleftarrows (\mathrm{ROH})_2 \qquad K_2 \\ (\mathrm{ROH})_2 + \mathrm{ROH} &\rightleftarrows (\mathrm{ROH})_3 \qquad K_3 \\ (\mathrm{ROH})_n + \mathrm{ROH} &\rightleftarrows (\mathrm{ROH})_{n+1} \qquad K_{n+1} \end{aligned} \tag{2}$$

ideal behavior is due solely to the formation of these oligomers, and the solution is thus treated as an ideal multicomponent mixture of alcohol monomers, dimers, trimers, etc., all coexisting in a dynamic equilibrium at concentrations which depend on the stepwise formation constants K and the total alcohol concentration. The solvent is ideally inert in relation to the solute; thus no solute–solvent interaction interferes with the oligomerization process. This then implies that the K values depend on the alcohol alone. This, of course, is not strictly true, except perhaps at very low solute concentrations and in similar alkane solvents,[85,86] and even then only when the rather unusual volume fraction concentration scale is used.[86]

A significantly simplified, thus rather questionable,[70,75] method of calculating the association constants is that of Mecke and Kempter[93] and Kretschmer and Wiebe,[94] who assume that all association constants have the same value. In some simple systems and at high enough dilutions this method of calculation gives data in reasonable agreement with the experimentally determined ones only because at low alcohol concentrations only one aggregate, probably the dimer, predominates.

Many attempts have been made during the past three decades to identify the sizes of the oligomers and to evaluate the equilibrium constants.[71,75–77,79,86,90,92,95,96] The results continue to be ambiguous, and there is little consensus regarding the physical picture of the state of alcohols in hydrocarbon solvents, much less numerical data on the oligomerization constants. Linear and cyclic tetramers of the lower alcohols in inert solvents appear to be the predominant aggregates. In the room-temperature range, the formation constants of the tetramers of the lower alcohols were found to be of the order of K_4 = 500–700 dm^9 mol^{-3}, with somewhat higher stability of the cyclic form.[80] The real problem is, of course, the comparable stabilities of the various complexes superimposed upon each other. Firmer conclusions are possible only if data obtained by different methods of experimentation are consistent. This, however, is not easy to achieve since the type and stability of the reported aggregate depend frequently on the physical, spectral, or thermodynamic property measured. Thus, for example, an experiment designed to detect monomeric alcohol molecules (unbound OH groups) will reveal and measure free groups only if the time scale of measurement is shorter than the time for which the OH group is free in the process of dynamic equilibrium among various aggregates. In most cases the association models are idealized since they are often based on mathematical parameters which are sensitive to the precision of the input data and the total number of experimental points.

From a practical point of view for the extractive behavior of the alcohols the exact association model in hydrocarbon solvents is probably irrelevant. Namely, most of the solvents for which the stepwise aggregation model of eq 2 might apply are not practical for the extractive removal of the alcohols from their aqueous solutions. As shown by the partition data in section VII, these inert solvents are very poor extractants for the lower alcohols.

In binary systems of alcohols with solvents less inert than the paraffins, the above fundamental assumption on the ideal behavior is not correct. Such solvents are ethers, ketones, esters, and aromatic and higher aliphatic alcohols, which are significantly better extractants for the lower alcohols. In these solvents, in addition to some alcohol self-association, there is a solute–solvent interaction. These systems are very complex as both types of reactions, solute–solute and solute–solvent, affect the fraction of the unbound OH group. We know of only one instance,[97] to be discussed in section VII.B, in which the solute–solvent adduct formation was explicitly investigated. In many cases the hydrogen bonds appear to be stronger in the adduct than in the alcohol aggregate.

2. *Physical and Thermodynamic Properties*

There are numerous reliable literature data for phase diagrams and mutual solubilities of alcohol + organic solvent systems. A bibliography,[98] which compiles primary sources up to 1980, tabulates solubilities on a mole percent scale along with UNIQUAC constants for mixtures. Most of the information refers to methanol, the higher alcohols being completely miscible with organic solvents used as extractants. Thus, for example,[99] the solubility of methanol in *n*-hexane, expressed on the mole fraction scale, increases from 0.270 at 25 °C to 0.330 at 30 °C to become fully miscible at 45 °C. With increasing molecular weight of the solvent, solubility decreases. The solubility in *n*-heptane is 0.210 mol fraction at 30 °C, and at 45 °C is 0.317, rather than being fully miscible as with *n*-hexane.[88,99] Methanol is not fully miscible with heptane below 60 °C.

Enthalpies of solution of the alcohols reviewed here in many different organic solvents have been determined, and there is a wealth of good numerical data.[19,41,71,72,76,77,80,84,85,89,99,100] The general conclusion has been that the standard enthalpy of solution of alcohols in aliphatic hydrocarbons is little affected by the molecular weight of either component. In the process of dissolution the alkyl chain of the alcohol solute does not enter a very different environment from that of the neat alcohol solute. Consequently, the enthalpy change of the process of dissolution is determined essentially by the transfer of the OH group from pure solute to the dilute solution in the hydrocarbon. The enthalpy of solution (and transfer) is thus made up of the endothermic enthalpy required to break the hydrogen bonds in the neat alcohol and the exothermic interaction of the OH group with the solvent. The second effect is usually small, and thus the overall enthalpies of solution are always endothermic. The reason for the small, if any, variation of $\Delta_{\mathrm{soln}}H^\circ$ of the alcohols in alkanes, which is around 24 kJ mol^{-1} at 25 °C, is the fact that the standard enthalpy refers to the dissolution of the monomeric alcohol which, of course, is the only important species at high dilution.[41] This value is related to the energy of the hydrogen bond in the dimeric alcohol.[85,89]

In view of the markedly higher extractability of the low molecular weight alcohols into the water-immiscible higher alcohols (see sections VII.A and B), there is a need for a better understanding of the thermodynamics of such mixtures. Reviews[71,76] give references to the excess functions of mixing in binary systems consisting of a lower and a higher alcohol. Enthalpies of mixing in ternary systems consisting of ethanol or *n*-propanol with a higher alcohol, octanol or decanol, and an alkane have been compiled[42] and some critically compared.[71] From the limited amount of data, it is difficult to draw conclusions relevant to the extractive capability of the higher alcohols. A closer look at the properties of such systems and similar ones is called for.

B. Ternary Systems

In the typical ternary system of alcohol extraction from water into an organic solvent, the equilibrium organic phase contains both alcohol and water. Quantitative interpretation of the physical property data is hampered by the simultaneous participation of the three components in several equilibria that are closely related. In addition to the solute–solute and solute–solvent reactions discussed under the previous heading on binary systems, in real extraction systems interactions occur between water and alcohol, leading to the formation of usually unspecified hydrogen-bonded associates, and also between water and the solvent, except when the latter is an inert hydrocarbon. It is thus rather obvious, as emphasized in the Introduction, that the phase behavior and the thermodynamic properties of the organic solution are affected by the presence of water. In some instances this effect is small, although measurable, but in most cases there is a substantial difference in the stabilities of the solvates and hydrates, which in turn should affect the process of alcohol transfer.

The water uptake by mixtures of alcohols with hydrocarbons depends very strongly on the alcohol content of the mixture. In other words, the presence of the alcohol in the hydrocarbon solvent phase increases the solubility of water in that phase. Figure 7 demonstrates the solubility of water in mixtures of cyclohexane with propanols and butanols.[67,70] At low alcohol levels in the organic phase, less than about 0.5 mol dm^{-3}, the water content in the organic phase is similar for the six alcohols. Above an alcohol level of about 1 mol dm^{-3}, a measurable difference starts. Mixtures with the two propanols and *t*-BuOH, the more water-soluble ones, have a higher water affinity at comparable alcohol molarities than do the other butanol isomers, which have a lower water solubility.

Huyskens et al.[70] and Hala[101] have also measured water solubilities in other binary systems consisting of these alcohols (and some pentanols and hexanols) and benzene or carbon tetrachloride in the wide alcohol concentration range of 0.1–4 mol dm^{-3}. The general shape of these solubility curves is comparable to those in Figure 7. The authors assume that water molecules are part of the alcohol oligomers, water being incorporated in the association chain of the alcohol in the organic solution. The solubility of water in the hydrocarbon + alcohol mixture is not related to the association of the alcohol in the hydrocarbon. In other words, the presence of water does not affect the state of the alcohol solute. Furthermore, the proposed model may include more than one water molecule per alcohol oligomer in spite of the possible competition of the hy-

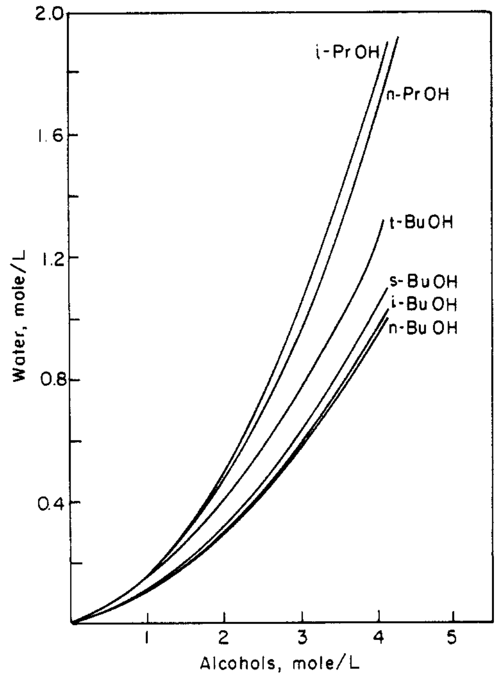


Figure 7. Solubility of water in cyclohexane as a function of alcohol concentration in the cyclohexane phase,[70] 25 °C.

drogen-bonding reaction sites. The equilibrium constants for the incorporation of the first water molecule are 11.7, 4.6, and 1.7 dm^3 mol^{-1} respectively in cyclohexane, carbon tetrachloride, and benzene. The constants derived for the incorporation of a second water molecule have roughly the same value of around 2.3 dm^3 mol^{-1} for all three solvents. A similar analysis of partition data of ethanol into aliphatic hydrocarbons[82] gave an average equilibrium constant of 44 dm^3 mol^{-1} for the formation of the monohydrated ethanol. This information is directly related to water coextraction along with the alcohols and the alcohol/water separation factor that can be achieved (section VII.C).

For mixtures of ethanol with hydrocarbons, the trend of water solubility is similar,[94] as shown by the family of curves in Figure 8. Comparing the effect of the alkanes, one should note that water tolerance increases with decreasing boiling point of the hydrocarbon at a given alcohol level.[94] In the wide temperature range between −45 and 45 °C, a logarithmic plot of water solubility, expressed on a volume percent scale, against $1/T$ yields a straight line for mixtures containing 25–90% ethanol in several aliphatic hydrocarbons. The overall tolerance of such mixtures toward water decreases with increasing molecular weight of the hydrocarbon, both aliphatic and aromatic.

There is a considerable body of systematic information on phase equilibria in ternary systems of water + alcohol + solvent. The data are compiled in the form of mutual solubility curves and/or phase diagrams.[34,98,101–105] For most ternary systems detailed tabulated and graphical information on the composition of the conjugate solutions throughout a wide range of concentrations has been measured. Frequently, UNIQUAC or UNIFAC equations predicting mutual solubilities supplement the experimental data.[14,98,104,105] The largest volume of data[12,37,98,101,106–111] refers to ethanol and includes as solvents aliphatic hydrocarbons, benzene, toluene, alkyl esters of acetic acid, and higher alcohols[1,12] that are water immiscible. Figures 9 and 10 show typical ternary phase diagrams at 25 °C for water, ethanol, and benzene[112] or cyclohexane,[126] respectively. For benzene as the organic solvent, similar diagrams are given[98] for all eight alcohols under review. The reason for the availability of that detailed information is interest in the use of ethanol as an entraining agent in the separation of aromatic hydrocarbons from paraffins and naphthenes by azeotropic distillation.

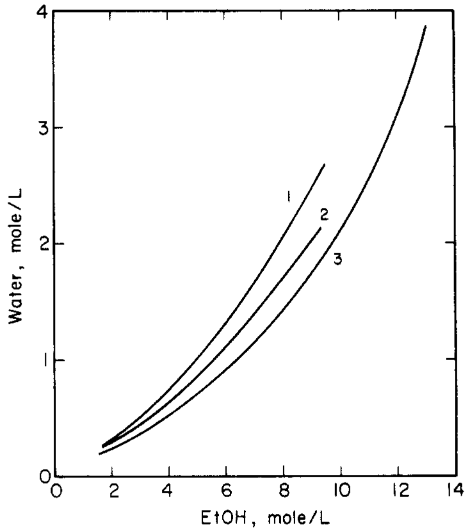


Figure 8. Solubility of water in (1) 2,2-dimethylbutane, (2) cyclohexane, and (3) 2,2,4-trimethylpentane as a function of ethanol concentration in the organic solvent,[94] 25 °C.

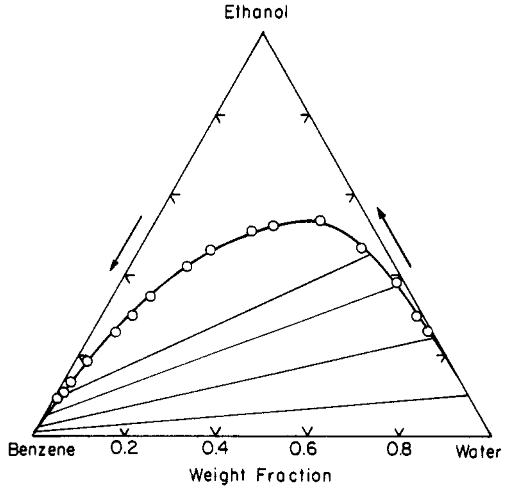


Figure 9. Ternary phase diagram for the ethanol + water + benzene system,[112] 25 °C.

The typical ternary phase diagrams as shown in Figures 9 and 10 give the concentrations of the saturated single-phase system. This solubility curve is made of two curves, one giving the solubility of alcohol in the hydrocarbon saturated with water and the other the solubility of alcohol in water saturated with the hydrocarbon. The two curves approach and finally meet at the plait point. All mixtures above the curved line are unsaturated single-phase systems. Mixtures with compositions beneath the curve separate into two conjugate layers, each saturated and each represented by the tie lines and the points on the curve. From these phase relations it is possible to predict the partition behavior of the alcohol solute and the amount of water coextracted along with the alcohol. Obviously, aims of the extractive separation are to have a minimum

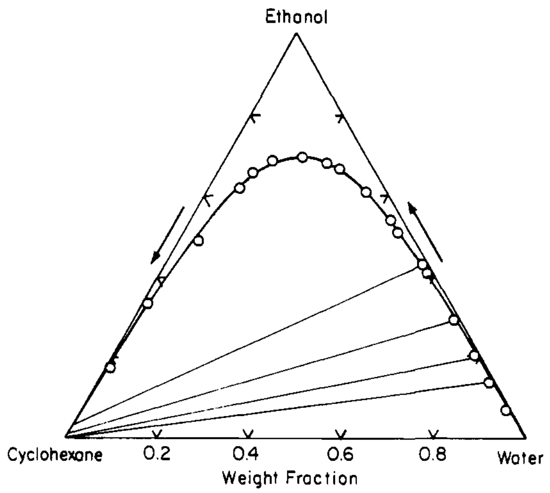


Figure 10. Ternary phase diagram for the ethanol + water + cyclohexane system,[126] 25 °C.

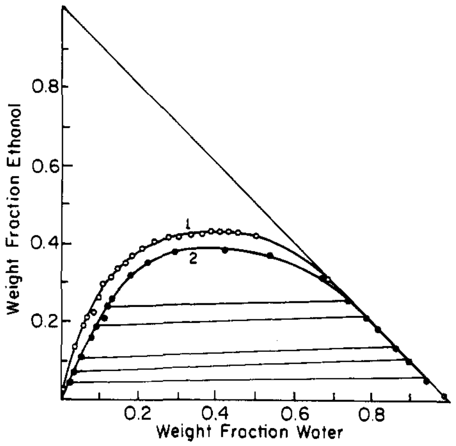


Figure 11. Mutual solubilities of water and ethanol in (1) decyl alcohol and (2) 2-octanol, 23 ± 1 °C. Tie lines are those for the octanol system.[12]

amount of water dissolved in the solvent phase and a minimum amount of solvent dissolved in the aqueous phase. Such a condition is indicated by the degree to which the branches of the mutual solubility curve rise with increasing alcohol concentration close to the 0% water and the 0% solvent sides of the ternary diagram.[107] In the phase diagram with cyclohexane (Figure 10) the region of homogeneity is smaller than in that with benzene (Figure 9). With aliphatic hydrocarbons at room temperature, the region of homogeneity is even slighter. Mutual miscibility decreases with increasing chain length of the paraffin, but increases with the molecular weight of the alcohol component.[101]

Recently, Tedder et al.[12,104,105,113] have reported mutual solubility diagrams for a large number of ternary and quaternary systems of water and ethanol with extractants such as 2-ethylhexyl alcohol, 2-octanol, decanol, tridecanol, tributyl and tricresyl phosphates, 2-ethylhexyl phosphate, dodecyl phenol, and their mixtures with gasoline, kerosene, tetrachloroethane, and some commercial hydrocarbon mixtures. The data are presented graphically on a weight fraction triangular diagram, as shown in Figure 11 for 2-octanol and decanol and in Figure 12 for kerosene and unleaded gasoline. The general trend in these diagrams is no different from that in the literature on the large volume of similar systems.[98,106,108,109]

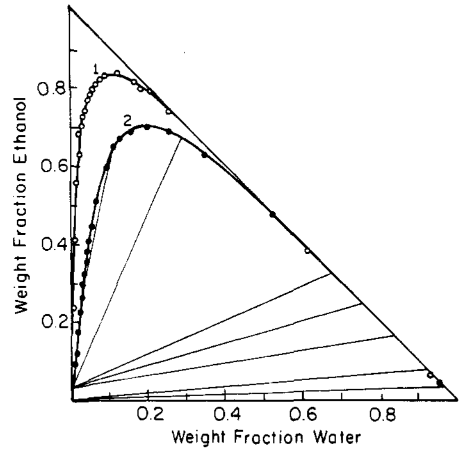


Figure 12. Mutual solubilities of water and ethanol in (1) kerosene and (2) unleaded gasoline, 23 ± 1 °C. Tie lines are those for the gasoline system.[12]

Figure 13. Ternary phase diagram for the ethanol + water + liquid propylene system,[114] 23.9 °C and 14.6 atm. Filled circle: two liquid layers.

Finally, Figure 13 shows a ternary phase diagram with liquid propylene as the extractant.[114] It is reproduced here in view of the recent interest in using supercritical liquids in liquid extraction.[115-118] It should be noted, however, that the mutual solubility relationship, and thus the extractive capacity, in the ternary system with benzene (Figure 9) are very similar. There appears to be little advantage for the use of supercooled liquids, except possibly for the toxicity aspect of raffinate contamination.

As a rule, the construction of such phase diagrams requires a large body of experimental data. Most of the data are obtained by the so-called synthetic method, which consists of titration of a two-component system by the third component to a cloud point or else to a point where turbidity is removed. The method does not provide data of high precision, and the sources vary widely in reliability. For most systems the precision appears to be satisfactory,[12,107] but the question of their accuracy is more important for the design of a detailed flow sheet for a liquid–liquid extraction technology.

V. Partition Conventions and Mass-Action Law

Equilibrium partitioning of alcohols (or nonelectrolytes in general) between two immiscible phases is achieved when the chemical potential of the solute is equal in the two phases

$$\mu = \bar{\mu} \qquad (3)$$

where the potential in the aqueous phase is given as

$$\mu = \mu^\circ + RT \ln x\gamma \qquad (4)$$

and that in the organic phase (barred symbols and quantities refer to the organic phase) as

$$\bar{\mu} = \bar{\mu}^\circ + RT \ln \bar{x}\bar{\gamma} \qquad (5)$$

and μ° and $\bar{\mu}^\circ$ are the standard potentials, x and $\bar{x}$ are the mole fractions of the alcohol, and γ and $\bar{\gamma}$ are activity coefficients. By one[124] commonly used reference-state convention, $\bar{\gamma}$ and γ tend to unity as $\bar{x}$ and x tend to unity. A similar definition can be based on fugacity rather than chemical potential when the ratio f/f_R, that of the solute fugacity (in atm) in solution to that of the neat liquid alcohol is equal to the $x\gamma$ product.[16] Consequently, the standard free energy of transfer of the monomeric alcohol for which the mole fraction partition coefficient

$$P^* = \bar{x}/x \qquad (6)$$

applies is then given by

$$\bar{\mu} - \mu^* = \Delta G^{\circ*} = -RT \ln P^* \qquad (7)$$

For the distribution of nonelectrolytes it is often justified to assume that their activity coefficients are close to infinite-dilution values in common organic solvents at concentrations usually not exceeding 0.1 mol dm^{-3}. At this level of solute concentration the self-association of the alcohols is weak, as discussed under a previous heading (section IV.A.1.).

Except for some specific thermodynamic correlations for which mole fraction partition coefficients P^* are preferred,[17,87,119] partition coefficients are commonly expressed as dimensionless ratios of concentrations of the distribuend in the equilibrium phases on either mole per cubic decimeter or mole kilogram concentration scales. Obviously, the resulting partition coefficients are numerically different. They are interrelated to a good approximation either via the densities of water and the solvent d and $\bar{d}$ or via their molar volumes V and $\bar{V}$, according to the relationships

$$P^* = P(\bar{V}/V) \qquad (8)$$

and

$$P^\circ = P(d/\bar{d}) \qquad (9)$$

where P° is the partition coefficient on the mole per kilogram of solvent scale and P is that on the mole per cubic decimeter of solution scale. Since $\bar{V} > V$, P^* is usually larger than P by factors ranging from 6 to 10, which is the ratio $\bar{V}/V$ for most common organic solvents. Regardless of the scale on which P is expressed, a correct calculation should take into account that the two liquid phases are mutually saturated. If mutual solubilities are not negligible, which is often the case due to the unique hydrophobic-hydrophilic character of the alcohols, partition coefficients expressed on the mole (or volume) fraction scale may be misleading.[15] For example, molar volumes of water-saturated organic solvents are usually lower than those of pure, dry solvents by perhaps as much as 30%, as in the case of 1-octanol.[16]

The standard free energy of transfer on the mole per cubic decimeter scale is defined accordingly and relates to eq 7 via

$$\Delta G^\circ = -RT \ln P = \Delta G^{\circ*} + RT \ln V/\bar{V} \qquad (10)$$

when the hypothetical ideal unit molarity is used in each phase as the reference state.

Similar to the symbols and nomenclature used in our earlier review of the extraction chemistry of carboxylic acids,[30] we term the distribution ratio D as the unaltered, uncorrected ratio between the total, analytical concentration of the alcohol solute in the organic phase, $\bar{c}$, and that in the aqueous phase, c, expressed on the mole per cubic decimeter concentration scale. There is no correction for the volume change upon equilibration, a factor especially important for the distribution of an alcohol as its transport from an aqueous into an organic phase is frequently accompanied by an important coextraction of water (section VII.C). Similarly to the partition process of carboxylic acids,[30] the correction procedure and the derivation of the relevant Nernst partition coefficient P for the monomeric alcohol must account for possible interactions in either or both phases. While these requirements have been shown to be reasonably simple in the case of partition of carboxylic acids,[30] they cannot be met for the partition process involving alcohols. The aqueous dissociation constants of acids are dependably known, and the assumption that dimerization of the acid in relatively nonpolar organic phase is the predominating aggregation reaction has been proved correct for most, if not all, mono- and polybasic carboxylic acids. In more polar solvents, solute–solvent interactions may become important. On the other hand, the association of the alcohols in the organic phase and their possible interaction with water in the aqueous phase remain the most vexing problems for the quantitative interpretation of the experimentally accessible distribution ratio.

In the case of the alcohols under review, a precise definition of aqueous interaction and organic solvent aggregation in a strict quantitative sense is not yet possible. As discussed under an earlier heading (section III.A), the behavior of these alcohols in water is complex on a molecular level, and no accepted numerical values exist to reflect the varying degree of water–alcohol interaction. Our understanding of the solute–solute and solute–solvent interaction in the organic phase is no more quantitative, as we have discussed earlier (section IV.A). Alcohols are prone to form H-bonded adducts with oxygen-containing organic extractants, probably to an extent comparable to their self-association in low-polarity media. Consequently, at the present time, no reliable mass-action law equilibrium constants are available for a quantitative derivation of the Nernst partition coefficient from the experimentally determined distribution ratios.

In view of the above limitations, the partition coefficient is usually derived on the assumption that an extraction system at high alcohol dilutions exhibits the limiting behavior of monomeric species.[67,73,87,119–123] At high enough dilutions a plot of log $\bar{c}$ vs. log c for different initial aqueous alcohol concentrations, c_i, will yield a straight line of unit slope, indicating that P is concentration independent. This is taken to indicate that the monomeric form of the alcohol exists in the organic phase as well. A positive deviation from linearity, which usually occurs at higher alcohol levels, can be attributed to the self-association of the alcohol in the organic phase, with the alcohol thereby existing in different forms in the two phases at equilibrium. How dilute the system must be in order to exhibit the limiting behavior of monomeric species varies from system to system. It depends on a number of factors that are not all independently variable. Thus, for example, the amount of coextracted water will certainly have a significant effect on the alcohol self-association (section IV.B).

Before we discuss the thermodynamic functions of transfer, mention should be made of the partition conventions for systems in which alcohol is extracted by virtue of some specific interaction between the components. Some of the more recently published partition data on alcohols in general, and on ethanol in particular, refers to mixed-solvent systems (section VII.B). In these systems the organic phase consists of two, or even three, organic components that may or may not act synergistically on alcohol extraction. The distribution ratio deviates from additivity if derived on the assumption of physical distribution only.[124] This, in general, indicates that the extraction is due to the formation of specific solvates between the alcohol and either or both components of the organic phase or between the other components of the organic phase,[124] because in the absence of such solvates the partition coefficients for two inert, nonpolar solvents should be additive.[125]

The interaction between the alcohol, A, and the extractant, B, leading to the formation of a stoichiometrically defined adduct

$$\mathrm{A} + n\bar{\mathrm{B}} \rightleftarrows \bar{\mathrm{A}}\bar{\mathrm{B}}_n \qquad K = [\bar{\mathrm{A}}\bar{\mathrm{B}}_n]/[\mathrm{A}][\bar{\mathrm{B}}]^n \tag{11}$$

has the distribution ratio of

$$D = \frac{[\bar{\mathrm{A}}\bar{\mathrm{B}}_n] + [\bar{\mathrm{A}}]}{[\mathrm{A}]} = \frac{[\bar{\mathrm{A}}] + \mathrm{K}[\bar{\mathrm{A}}][\bar{\mathrm{B}}]^n}{[\mathrm{A}]} = \frac{[\bar{\mathrm{A}}](1 + \mathrm{K}[\bar{\mathrm{B}}]^n)}{[\mathrm{A}]} = P(1 + K[\bar{\mathrm{B}}]^n) \tag{12}$$

where

$$P = [\bar{\mathrm{A}}]/[\mathrm{A}] \tag{13}$$

is the partition coefficient of the monomeric alcohol on the mole per cubic decimeter scale. A plot of log $[(D/P) - 1]$ vs. log $[\bar{\mathrm{B}}]$ will yield a straight line with a slope of n and an intercept of log K, thus identifying the stoichiometry of the adduct and its stability. This analysis assumes that no other specific interactions among species are present. It also requires that P be known, or assumed, independently.

Finally, in the particular context of using solvent extraction for alcohol recovery from a large volume of an aqueous feed, it is useful to define the degree of extraction, R, in terms of the amount of the alcohol extracted into the organic phase, $\bar{Q}$, and its amount in the feed, Q_i, as

$$R = \bar{Q}/Q_i = [\bar{\mathrm{A}}]\bar{v}/([\bar{\mathrm{A}}]\bar{v} + [\mathrm{A}]v) = D/(D + r) \tag{14}$$

where $[\bar{\mathrm{A}}]$ and $[\mathrm{A}]$ are the concentrations of the alcohol, $\bar{v}$ and v are the volumes of the phases, $r = v/\bar{v}$, and it is assumed that no specific associations exist. The distribution ratio D is related to the degree of extraction by

$$D = [\bar{\mathrm{A}}]/[\mathrm{A}] = Rr/(1 - R) \tag{15}$$

The degree of extraction is higher when r is smaller and D larger. For a 99% extraction, D must be 100, and for a 99.9% extraction, D must have the value of 1000, provided $r = 1$.

VI. Thermodynamics of Partition

The distribution coefficient obtained experimentally at any one temperature allows the calculation of the standard free energy of transfer via the conventional van't Hoff expression

$$\Delta_{\mathrm{trans}}G^\circ = -RT \ln P \tag{16}$$

in which the numerical value of the free energy term depends on the concentration scale used for the partition coefficient. In eq 16, P is given on the mole per cubic decimeter scale. On the mole fraction scale, for sufficiently dilute solutions, the free energy change is to a good approximation given by

$$\Delta_{\mathrm{trans}}G^{\circ *} = -RT \ln P^* = \Delta_{\mathrm{trans}}G^\circ + RT \ln V/\bar{V} \tag{17}$$

where V and $\bar{V}$ are the molar volumes of the aqueous and the organic phases, respectively. The free energy in mole per kilogram of solvent units, $\Delta G^{\circ **}$, is related to that in mole fraction units by

$$\Delta_{\mathrm{trans}}G^{\circ **} = -RT \ln P^{**} = \Delta_{\mathrm{trans}}G^{\circ *} - RT \ln \mathrm{MW}/\bar{\mathrm{MW}} \tag{17a}$$

where MW and $\bar{\mathrm{MW}}$ are the molecular weight of water and solvent. Note that the conversion from $\Delta_{\mathrm{trans}}G^{\circ *}$ is independent of the solute, unless it affects V and/or $\bar{V}$.

A number of possibilities exist to calculate the corresponding enthalpy and entropy changes. The enthalpy of transfer can be obtained by any one of four methods: (1) direct measurement by two-phase calorimetry; (2) derivation from calorimetrically determined standard enthalpies of solution in one-phase systems; (3) derivation via enthalpies of solution in one-phase systems as obtained from solubility measurements over a range of temperature; and (4) derivation from P data obtained over a range of temperature.

The last method is the one most frequently used to derive enthalpies of transfer and is the one that usually yields the least reliable enthalpy data.[7,43,87,126] This is the case in spite of the fact that the method is thermodynamically correct as it represents the first derivative of P with respect to reciprocal temperature

$$\Delta_{\mathrm{trans}}H^\circ = RT[\partial \ln P/\partial(1/T)] \tag{18}$$

It is based on the assumption that the standard molar enthalpy is temperature-independent; thus, a plot of log P vs. $1/T$ should give a straight line for the temperature range in which the assumption is valid. The line has a slope of $-\Delta H^\circ/R$ and an intercept of $\Delta S^\circ/R$. However, only isolated cases have shown the validity of this expression and the assumption underlying it. There are several reasons for the lack of reliability. The routinely determined P values are seldom precise enough to stand the stress of taking the first derivative. They are also directly affected by the mutual solubilities of the phases and their changing molar volumes. Both factors are only exceptionally temperature independent. The simplifying assumption concerning the heat capacity should be confirmed experimentally, since it is known to be quite sensitive to changes in the molecular structure, solute concentration, and medium,[43] which are especially pronounced in aqueous systems. An expanded form of the van't Hoff expression as suggested by Arnett et al.[43] is

$$\ln P = \Delta H^\circ/RT + (\Delta S^\circ - \Delta G_p^\circ)/R + (\Delta C_p^\circ/R)\ln T \quad (19)$$

which takes into account the heat capacity, thus yielding more reliable enthalpy and entropy data than the log P vs. $1/T$ treatment.

The standard enthalpies of transfer of the alcohol solutes from an organic solvent into water as derived from the difference between enthalpies of solution at infinite dilution in the two phases

$$\Delta_{\text{trans}}H^\circ = \Delta_{\text{soln}}H^\circ - \Delta_{\text{soln}}\bar{H}^\circ \quad (20)$$

are considered more reliable even if the corresponding enthalpy of solution values were derived via the van't Hoff isochore of the temperature derivative of solubility (method 3), rather than determined calorimetrically (method 2). The enthalpies of solution derived by method 3 are much less prone to the limitations discussed above in connection with the temperature variation of P. An exception may occur when the resulting $\Delta_{\text{trans}}H^\circ$ represents the difference between large numbers. It should be noted in addition that the integral enthalpies of solution are frequently functions of concentration, and the standard enthalpy values, $\Delta_{\text{soln}}H^\circ$, must be obtained by extrapolation to infinite dilution.

The $\Delta_{\text{trans}}H^\circ$ values derived by methods 2 and 3 may not correspond strictly to those obtained by methods 1 and 4. The former may not yield absolutely correct values. The reason is that the enthalpies of solution obtained by either method 2 or 3 refer usually to binary systems of an alcohol in a solvent, water, or organic. On the other hand, the partition coefficient refers to the transfer process from and to mutually saturated phases. The extent of mutual solubility between the phases and the effect of the alcohol on it will determine the difference in $\Delta_{\text{trans}}H^\circ$ as derived by the different methods. In at least one case, that of n-BuOH partition between water and hexadecane,[87] no detectable difference was found in the enthalpy value when the phases were preequilibrated. The differences can be expected to be larger when there is a higher degree of mutual miscibility induced by the presence of alcohol. The standard assumption should be that different methods yield different $\Delta_{\text{trans}}H^\circ$ values, unless proved otherwise.

VII. Distribution

A. Partition Coefficients in Nonpolar Solvents

Partition coefficients P of the alcohols on the mole per cubic decimeter concentration scale, as defined in section V, are compiled in Tables VII and VIII for the normal-chain and branched-chain alcohols, respectively. Most of the data appear in previous compilations by Hansch et al.[24,28] Their more recent compilation[24] of partition coefficients covers the literature on alcohols up to 1975. As we have noted earlier, the coverage is comprehensive, and their tables include the published data for the period covered, though two primary sources appear to have escaped the compilers' attention. One is that of Huyskens et al.,[67] which gives carefully determined partition coefficients of propanols and butanols in cyclohexane at 25 °C. The other is a brief report[127] tabulating P data for the four normal alcohols in hexane at 25 and 40 °C.

TABLE VII. Partition Coefficients of Monomeric Normal Alcohols between Water and Organic Solvents, 25 °C (See Text Section VII.A)

	MeOH	EtOH	*n*-PrOH	*n*-BuOH
n-hexane	0.0024	0.0083	0.03	0.25
n-heptane		0.0074		
n-octane	0.0024	0.0068	0.03	0.25
n-nonane		0.0064		
n-decane	0.0024	0.0060	0.03	0.25
n-undecane		0.0057		
n-dodecane		0.0055		
n-tridecane		0.0053		
n-tetradecane		0.0052		
n-hexadecane		0.0051		
cyclohexane	0.0016	0.0079	0.028	0.13
benzene	0.013	0.031	0.23	0.66
toluene	0.007	0.03	0.15	0.50
chlorobenzene	0.011	0.021	0.18	0.50
chloroform	0.055	0.14	0.40	2.2
carbon tetrachloride	0.008	0.018	0.12	0.51
diethyl ether	0.14	0.32	0.95	4.1
1-octanol	0.18	0.50	1.8	7.6
tri-*n*-butyl phosphate	0.20	0.54	2.7	14.6

TABLE VIII. Partition Coefficients of Monomeric Branched-Chain Alcohols between Water and Organic Solvents, 25 °C

	i-PrOH	*i*-BuOH	*sec*-BuOH	*t*-BuOH
cyclohexane[67]	0.017	0.14	0.11	0.068
carbon tetrachloride[73]	0.044	0.39	0.29	0.14
benzene[73]	0.11	0.69	0.54	0.24
diethyl ether[25,138]	0.64	6.9	4.5	2.2
1-octanol[24]	1.1	4.5	4.1	2.3
oleyl alcohol[29]	0.56	2.9	1.9	1.2

A considerable volume of additional distribution and partition data has become available since 1975. Most of it refers to ethanol extraction.[2,11,12,82,97,113,128–130] Single partition points were reported for n-PrOH and n-BuOH in octane[131] and for the latter in octanol.[15] Coefficients for all eight alcohols from water into 1-octanol and oleyl alcohol, at 37 °C, were derived via experimentally determined P values in the nitrogen gas–water and nitrogen gas–octanol (or oleyl alcohol) systems.[29]

The partition coefficients of the monomeric alcohols given in Table VII are recommended values at 25 °C. We have arrived at these values as the result of a critical evaluation of literature data that we consider reliable.[27,67,73,82,87,97,119,121–123,127,132–141] No graphically presented partition data, or those given as percent extraction, or those measured at high, >0.1 mol dm^{-3}, alcohol concentrations were taken into consideration in the evaluation process. Our recommended P values are more conservative, frequently significantly so, than some of those reported in the cited primary sources and/or included in Hansch's compilations.[24,28] As a rule, our P values are given to two significant figures. The reason for this additional precaution is the usually low experimentally accessible distribution ratio typical of most of the systems under consideration. It is difficult to determine distribution ratios of alcohols of the order of 10^{-3} because of limitations in analytical methods available. No present method can determine alcohol concentrations in organic solvents to a precision that justifies reporting *P* values to three significant figures.

As an example of the problem of significant figures, consider the partition coefficients for ethanol as reported by Coleman and Roddy[82] and Korenman and Chernovkova.[121] The latter authors, using a spectrophotometric method in the ultraviolet region for the determination of ethanol concentration in the organic phase, could not distinguish between partition coefficients in the five *n*-alkanes from hexane to decane. For all five solvents, $P = 0.008$ at 20 °C. On the other hand, for the same solvents, Coleman and Roddy, using the apparently more sensitive analytical tool of radiotracers checked occasionally by gas chromatography, report *P* values for ethanol of 0.00831 ± 0.00015 and 0.00601 ± 0.00013 for hexane and decane at 25 °C, respectively. The results of Coleman and Roddy, stated somewhat more conservatively, are included in Table VII. It may be overly optimistic to claim a ±2% reproducibility in view of the obviously very low ethanol content in the alkane phase. For *n*-BuOH, which is much more extractable, the differentiation of *P* values among the alkane solvents is straightforward.[87]

The recent strong interest in synthetic fuels from renewable, biological resources has prompted a number of studies wherein many different solvents are rapidly screened for extraction capacity, usually for ethanol (ref 2, 11, 12, 104, 105, 113, 129, 130). These studies vary widely in the amount of attention that has been given to determination of precision and reproducibility, development and documentation of experimental techniques and conditions, and rigorous comparison with pertinent results of previous measurements. Great care must be taken in assessing the accuracy and reliability of screening measurements of this sort. It is also important that such studies strive to follow the standards that are sought for publication in refereed journals.

Before we turn to an analysis of the tabulated partition data, mention should be made of the *P* values included as the last entries in Tables VII and VIII, referring to polar, reactive, usually oxygen-bearing, solvents. These values are larger, sometimes by orders of magnitude, than those for inert solvents. Although no firm evidence, with the possible exception of the tributyl phosphate + ethanol system,[97] is readily available, it can be assumed that alcohols are extracted into these solvents by virtue of specific interactions between the components, possibly via relatively strong hydrogen bonds. Consequently, in addition to the partition coefficient referring to the alcohol monomer, the extraction process involving such reactive solvents is governed by one, or perhaps more, simultaneous alcohol-extractant interactions.

One of the obvious trends in the partition data compiled in Table VII concerns their correlation with the chain length of the normal alcohols. Claims for the additive character of the partition coefficients of organic compounds in general, and that of the methylene group in homologous series in particular, are not new.[24] Some of these correlations and their semiquantitative character are discussed in section VIII. Linearity of the plot of log *P* against the number of carbon atoms in the series of normal primary alcohols has been repeatedly claimed[121,122,137,142] for a large number of extractants, including the aliphatic and aromatic hydrocarbons, chloroform, carbon tetrachloride, and ether given in Table VII. The constant partition value for the CH_2 increment does not usually apply to methanol and ethanol, although it appears to apply to higher alcohols.[121,122] Huyskens et al.[122] emphasize this limitation, whereas Korenman et al.[121,142] do not. We have replotted their log *P* values for MeOH to *n*-BuOH series but have been unable to confirm their claim for the validity of the linear function throughout the series, including the first two members. The log *P* values that deviate the least from linearity are those of Levina and Zheleznyak[137] in butyl acetate and of Sandell[136,143] in chloroform and diethyl ether. The reported *P* values, however, are not considered to have high accuracy.

B. Extraction into Polar Solvents

Tables VII and VIII contain a few entries on the partition coefficients of the alcohols into some oxygen-containing, reactive, polar extractants. *P* values into these and similar solvents are higher, frequently by 2 orders of magnitude, than into the alkanes, aromatic hydrocarbons, and even halocarbons. This makes the polar solvents much stronger candidates for use in industrial extraction processes. Such a dramatic effect on alcohol extractability can be explained only as being due to a specific interaction between the alcohol and the polar extractant. The partition coefficients cited for more polar solvents in Tables VII and VIII are those that are felt to be most reliably documented and for which the infinite-dilution condition is best established. Distribution ratios have been reported for many other polar solvents and solvent mixtures, but the data are often fragmentary and obtained under incompletely specified conditions which do not allow confidence that the true, infinite-dilution partition coefficients have been obtained.

Among the polar extractive solvents, high molecular weight alcohols have received the most attention. They are among the polar solvents exhibiting the highest distribution ratios for the extraction of ethanol. Included in exploratory experiments on ethanol distribution are a variety of normal and branched hexyl,[128-130] heptyl,[128,130] octyl,[11,12,113,128-130] nonyl,[128,130] decyl,[12,128-130] dodecyl,[11,128] tridecyl,[12,104,113,128] and oleyl[133] alcohols. Distribution ratios for ethanol in these alcohol solvents range usually from 0.2 to 0.7 at room temperature. Comparable distribution ratios for ethanol are obtained into tributyl phosphate[11,104,121,128-130] and some other alkylphosphorus compounds,[11,12,128] and into high molecular weight liquid carboxylic acids.[11,130] Somewhat lower *D* values have been reported for ketones,[113,129,130] aldehydes,[11] and ethers.[24,25] Data reported in these screening studies reveal a considerable variation of *D* values for seemingly comparable systems, indicating the sensitivity of the distribution values to all parameters of the extraction systems. Differences in *D* values of a factor of 2, or even 3, are not uncommon. These differences probably stem from a variety of reasons which cannot be discerned well from descriptions of the experiments. No doubt, some are due to artifacts in the experiments, such as inadequate control of entrainment. Others are probably the result of uncontrolled, or differing, conditions of initial ethanol concentration, phase ratio, temperature, time of equilibration, etc. It should be recognized that distribution ratios can be quite sensitive to such parameters, since they represent a complex combination of phenomena. Finally, it should be noted that the data shown in Table VIII for extraction into diethyl ether are from a different source than those in Table VII. Hence, comparison of the diethyl ether data between these two tables is not appropriate.

As we have mentioned earlier, there is little evidence of a stoichiometric interaction between ethanol, or for that matter any of the alcohols presently under review, and a reactive extractant. The only study of which we are aware that specifically aimed to determine the composition and stability of an adduct is that on tributyl phosphate–ethanol, reported by Roddy and Coleman.[97] The slope analysis method[124] applied to the distribution ratio in the system tributyl phosphate + *n*-octane + ethanol + water at 25 °C and at five different initial aqueous ethanol levels ranging from 0.1 to 10 mol dm^{-3} suggests the formation of a monoalcoholate adduct with TBP, regardless of the initial ethanol concentration. All log D vs. log [TBP] plots[97,140] yield a straight line of unit slope. One of the plots is reproduced in Figure 14 from tabulated data.[140] Infrared spectral data, however, were inconclusive, and no evidence for a strong TBP–EtOH bond was found. The conventional curve-fitting method[82,124] of the experimental distribution ratios[140] compiled now for the first time in Table IX could not identify any unique TBP–EtOH stoichiometry, much less determine the stability of the adduct formed.

There is also a unit slope over a shorter range in the logarithmic plot of D_{EtOH} against the mole per cubic decimeter concentration of tridecyl alcohol in an alkane blend,[113] as shown in Figure 14. A similar statement[11] was made for the ethanol distribution ratio in the dodecyl alcohol + tetradecane system but no experimental data were provided in support.

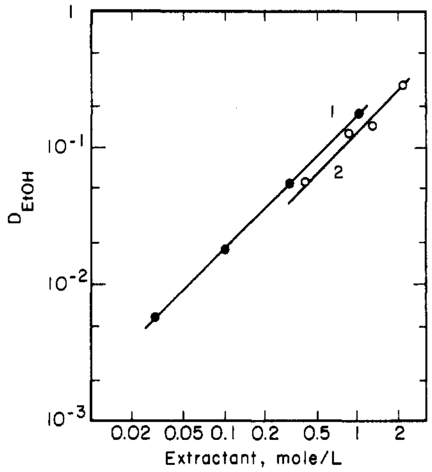


Figure 14. Distribution ratio of ethanol into (1) tributyl phosphate/octane[97,140] and (2) tridecyl alcohol/alkane[113] mixtures as a function of the concentration of the reactive extractant in the hydrocarbon. The ethanol concentration in the initial aqueous phase is 3 mol/L, at 25 °C, and 2.2 mol/L, at 27 °C, respectively.

TABLE IX. Distribution Ratios of Ethanol between Aqueous Solutions and Tributyl Phosphate in *n*-octane,[a] 25 °C

$[\mathrm{EtOH}]_{\mathrm{init}}$	$[\mathrm{TBP}]_{\mathrm{org}}$	$[\mathrm{EtOH}]_{\mathrm{org}}$	$[\mathrm{EtOH}]_{\mathrm{aq}}$	D_{EtOH}
10.00	3.65	3.26	3.57	0.091
	1.00	1.56	6.97	0.22
	0.30	0.57	8.95	0.064
	0.10	0.18	9.73	0.019
	0.03	0.051	9.99	0.0051
3.00	1.00	0.43	2.36	0.18
	0.30	0.14	2.60	0.056
	0.10	0.048	2.67	0.018
	0.03	0.016	2.72	0.0059
1.00	1.00	0.14	0.78	0.17
	0.30	0.044	0.88	0.050
	0.10	0.015	0.90	0.016
	0.03	0.0048	0.91	0.0053
0.30	3.65	0.027	0.047	0.57
	1.00	0.012	0.076	0.15
	0.30	0.0044	0.091	0.048
	0.10	0.0014	0.097	0.014
	0.03	0.0004	0.099	0.004
0.10	3.65	0.0028	0.0043	0.64
	1.00	0.0012	0.0077	0.15
	0.30	0.00043	0.0091	0.047
	0.10	0.00015	0.0097	0.016
	0.03	0.0005	0.0099	0.005

[a] Data originally reported graphically[97] are now provided tabulated.[140] This is gratefully acknowledged. Concentrations are given in mol/L.

C. Coextraction of Water

Most of the information on water coextraction along with the alcohols refers to ethanol[9,11,12,82,97,104,113,128–130] and is essentially concerned with the ethanol–water separation factor. The information again is fragmentary, most of it of the screening type. Distribution ratios of water, along with those of ethanol, are reported for aliphatic[11,12,82,128,130] and aromatic[11,128] hydrocarbons, ketones,[11,113,129,130] esters,[9,129] alkylphosphorus extractants,[11,97,129] carboxylic acids,[11,130] and high molecular weight alcohols[9,11,12,113,128–130] at widely varying experimental conditions. The general pattern of water transfer into inert hydrocarbons appears to differ from that into polar reactive extractants. This is in addition to the substantial quantitative difference in the amount of coextracted water.

The distribution ratio of water, $D_{\mathrm{H_2O}}$, into aliphatic hydrocarbons, cyclohexane, kerosene, gasoline, and other commercial blends, is very low, typically around 10^{-5}–10^{-4}. It is perhaps an order of magnitude higher into aromatic hydrocarbons. Partly because of the scarcity of data, but also because of poor quality, no trend in the extractive pattern can be identified with any degree of confidence. One can generalize with reasonable certainty[82] that the organic-phase water content increases with the ethanol concentration in the initial solution. This occurs in spite of the fact that the activity of water in that solution decreases from unity in neat water to about 0.8 in a 10 mol of water to 10 mol dm^{-3} aqueous ethanol solution at room temperature. The trend appears to be true for most of the solvent types screened, including hydrocarbons and alcohols.[11,12,82,113] With normal hydrocarbons as the extractants, the organic-phase water content is a linear function of the ethanol content.[82] At 25 °C, for *n*-hexane or *n*-undecane the water-to-alcohol mole ratio is 0.1, at least up to about 0.2 mol dm^{-3} organic-phase ethanol content, corresponding to very high alcohol content of the initial feed. Since the distribution ratio of ethanol into a hydrocarbon is fairly constant up to about 3 mol dm^{-3} initial concentration level and since that of water increases with increasing ethanol level in the system, the separation factor, as a rule, decreases. In some systems the drop in the separation factor may be dramatic: The separation factor into alkanes of 4500 at 0.1 mol dm^{-3} (~0.46 wt %) initial ethanol level drops to 20 or less at 10 mol dm^{-3} ethanol level.

Attempts have been made to identify the stoichiometry of the alcohol hydrates in hydrocarbons. Because of the self-association of alcohols, discussed previously (section IV.C), the chemistry of the system is complex. The spectral evidence, coupled with mass-action law equilibria computation evidence for the stability of the ethanol–monohydrate, appears to be the most reliable information presently available.[70,82]

The distribution ratio for water into polar and oxygen-containing extractants is usually higher, by perhaps as much as 2 or 3 orders of magnitude. The highest distribution ratios are recorded for tributyl phosphate and high molecular weight alcohols. D_{H_2O} values into alcohols in the 0.05–0.6 range are common, the exact values depending on practically all experimental parameters. Distribution ratios of water into ketones, aldehydes, and alkyl esters have values intermediate between those in alcohols and hydrocarbons. Among the molar polar solvents, the highest separation factors for a given distribution ratio of ethanol appear to be given by the solvents that are more acidic in the Lewis sense (alcohols, carboxylic acids, chlorinated hydrocarbons) and, for the higher alcohols and carboxylic acids, by solvents that are more highly branched.[130]

For ethanol extraction into high molecular weight alcohols, Tedder's data,[12,113] though admittedly of low precision, are still the only systematic set to cover initial alcohol concentrations of several moles per cubic decimeter. For illustration only, Figure 15 reproduces the linear dependence of D_{H_2O} as plotted by the authors.[12,113] The concentration dependence of the distribution ratio may or may not be as sharp as shown in the figure, but it should be taken as real at least into alcohols and possibly other polar extractants.

Coextraction of water along with ethanol into solvent mixtures of tributyl phosphate[97] or high molecular weight alcohols[12,113] with alkanes depends very markedly on the concentration of the polar extractant. In the TBP + *n*-octane system,[97] a log D_{H_2O} vs. log [TBP] mol dm^{-3} plot is linear with a slope of 1.5, suggesting[124] a $(TBP)_3(H_2O)_2$ stoichiometry. The line corresponding to a 3 mol dm^{-3} initial EtOH concentration is reproduced in Figure 16, along with a similar plot of log D_{H_2O} against the mole per cubic decimeter concentration of tridecyl alcohol in Norpar 12 (a normal paraffinic solvent blend of C_{11} and C_{12} alkanes) diluent.[113] The lines, drawn with a slope of 1.5, fit the points for the phosphate ester reasonably well, but probably not those for the alcohol. It should be noted, however, that the scatter of the experimental points as initially recorded[12] is too large for a firmer conclusion to be justified. With the higher alcohols as the extractants, the drop in the separation factor with increasing initial ethanol concentration level is not as dramatic as for extraction systems into alkanes. Namely, D_{EtOH} increases with initial ethanol level as does D_{H_2O}. This illustrates qualitatively the tradeoff that exists between the distribution ratio of ethanol and the ethanol/water selectivity.[130] No detailed information on that tradeoff is at hand. The separation factor in the mixed-solvent systems composed of a reactive component and an alkane diluent is very sensitive to the concentration of the former, as is D_{EtOH} in these systems. For example,[97] at low TBP concentration and low, say, 0.03 mol dm^{-3}, initial aqueous ethanol concentration, a separation factor of 160 decreases to about 9 for undiluted TBP and an aqueous ethanol concentration of more than 3 mol dm^{-3}. With tridecyl alcohol as the reactive component, the effect appears to be less dramatic.[12,113]

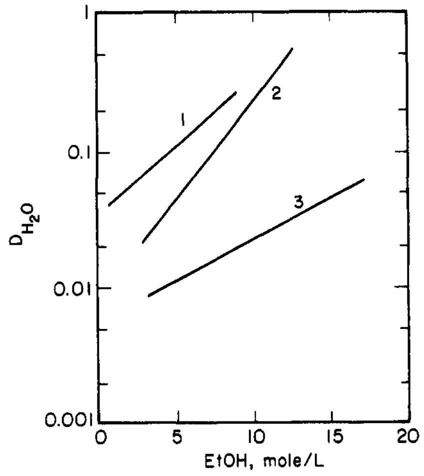


Figure 15. Distribution ratio of water into (1) 2-octanol, (2) 2-ethyl-1-hexyl alcohol, and (3) dimethylheptanone as a function of ethanol concentration in the equilibrium aqueous phase (raffinate),[12,113] 27 °C.

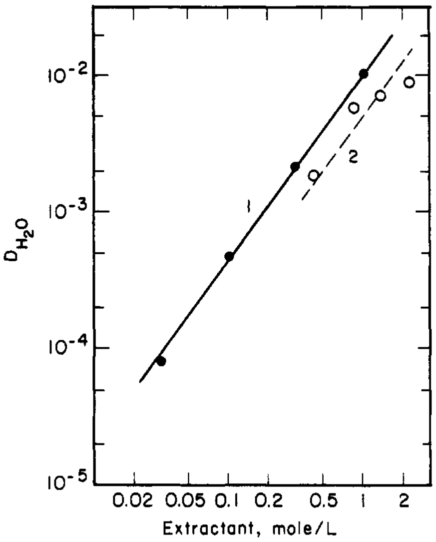


Figure 16. Distribution ratio of water into (1) tributyl phosphate/octane[97,140] and (2) tridecyl alcohol/alkane[113] mixtures as a function of the concentration of the reactive extractant in the hydrocarbon. The ethanol concentration in the initial aqueous phase is 3 mol/L, at 25 °C, and 2.2 mol/L, at 27 °C, respectively.

Screening studies provide some orientation on the effects of temperature upon coextraction of water along with ethanol.[11,104,113,128,129] At high initial ethanol concentration levels, say, 6–8 mol dm^{-3}, the water distribution ratio increases with temperature in the 23–85 °C range. This trend appears to be true for alkanes and also reactive extractants.

Little information on coextraction of water is at hand for the rest of the alcohols presently under review. Relevant are the tabulated[67] data on the alcohol and water contents in saturated cyclohexane at 25 °C for the six alcohols, shown graphically in Figure 7. Similar to the ethanol system, the amount of water in the organic phase depends on the alcohol content. In the dilute range, below about 1 mol dm^{-3} of alcohol, the water/alcohol molar ratio is around 0.1, as is the case in the ethanol + alkane systems mentioned above.[82] As the overall alcohol content increases in the cyclohexane phase, proportionally more water is transferred, and the ratio increases. In the *t*-BuOH + cyclohexane + water system at 20 °C, the water/alcohol mole fraction ratio reaches unity at high butanol concentrations.[144]

D. Effect of Salting Agents

The information on the effect of electrolyte and/or nonelectrolyte in the aqueous feed upon extractability of alcohols is very limited and mostly no better than qualitative. Extraction of ethanol from aqueous solutions containing fermentation broth constituents, such as glucose and molasses[145] or dextrose,[104] and from synthetic fermentation broth[129] was compared with that from pure water. Even that limited information is contradictory. The distribution ratio of ethanol appears to be higher when extracted from the synthetic fermentation broth rather than water into hexanol or methylisobutyl ketone[129] at 35 °C. The synthetic broth contained 5 g/L glucose, 7.5 g/L citric acid, and 5–6 g/L inorganic salts, mainly disodium phosphate and ammonium chloride. On the other hand, at an ethanol level of 0.5–2 mol dm^{-3} in the initial feed, unspecified quantities of added glucose and molasses do not affect the extractability of ethanol into 1-butanol.[145] If dextrose is added to the feed[104] up to 60 wt %, it will increase D_{EtOH} into tributyl phosphate/hydrocarbon mixtures. The extent of the effect depends on the ethanol and dextrose concentrations in the aqueous feed, the phosphate concentration in the solvent phase, and temperature.

The distribution ratios of *n*-PrOH and *n*-BuOH into *n*-octane from aqueous $ZnCl_2$ solutions up to 10 mol dm^{-3} increase in the 0–50 °C temperature range.[131,146] The effect is most pronounced at around 4 mol dm^{-3} salt content, with D_{EtOH} values roughly twice those from pure water.

E. Effect of Initial Alcohol Concentration

The effect of alcohol concentration is relevant both from fundamental and applied points of view. From a basic point of view, the parameter should be regarded in the context of the distinction between the Nernst partition coefficient and the experimentally accessible distribution ratio. It should be recalled that, in the case of alcohols, partition coefficients cannot be calculated because of limited knowledge on their solution properties in organic solvents (section IV). For any practical purpose partition coefficients are estimated from a limiting-law form of the distribution ratio (section V).

In spite of the considerable volume of information on the effect of the initial aqueous feed content on the measurable distribution ratio, the information needed for understanding of the more fundamental aspects of the extraction process is largely missing. Most of the experimental information refers to ethanol[11,82,97,112,113,119,121,122,126,128,129,132,134,145,147,148] and some to propanols[119,121,122,132,135,147,148] and butanols.[87,119,121-123,132,135,144,147,148] No numerical information[121] on methanol appears to have been published. In most cases the information is no more than semiquantitative and refers to a limited range of alcohol concentration.

The distribution ratios of ethanol into aliphatic hydrocarbons and cyclohexane are independent of the initial concentration in the aqueous solution up to about 3 mol dm^{-3}, or around 13 wt %. However, the experimental points scatter considerably, since the D_{EtOH} values are very low at room temperature. The distribution ratio in these solvents increases by a factor of 2–3 as the initial ethanol content increases to about[82,113,122,126,147] 10 mol dm^{-3}. Similarly, no marked increase in the distribution ratio has been observed for the less inert solvents such as benzene,[11,112,128,134] carbon tetrachloride,[134] or carbon disulfide[134] as long as the initial alcohol concentration is kept below 2 mol dm^{-3}. Again, at higher initial ethanol levels, the distribution ratio increases.[112,113,122] With the polar and reactive extractants, D_{EtOH} appears to be more affected by the initial ethanol concentration. An increase in the distribution ratio with increasing alcohol concentration has been observed for high molecular weight alcohols,[11,12,113] ketones,[129] and tributyl phosphate[97] and their mixtures with hydrocarbon diluents. Because of the limited number of data points in any given set of experiments and their extensive scatter, firm conclusions cannot be drawn.

There is a marked quantitative difference of the concentration effect on the distribution ratio with propyl and butyl alcohols as the solutes. Except for very low alcohol concentrations,[87,119,132,148] less than about 0.1 mol dm^{-3}, distribution ratios into alkanes, benzene, and carbon tetrachloride increase with the alcohol content of the initial solution.[64,87,122,123,135,144] An exmaple is shown in Figure 17 for 1-butanol extraction into benzene, carbon tetrachloride, and cyclohexane, presenting plots based on some 25–30 experimental points for each system.[123] The dependence is linear, or close to it, when D is plotted against the equilibrium concentrations in either phase. Similar linearity has been observed for extraction of *t*-BuOH into cyclohexane.[144]

F. Effect of Temperature

The numerical information on the effect of temperature on alcohol distribution ratio, fragmentary and limited as it is, indicates an increase of D with temperature in systems where aliphatic[11,127,128,147] or aromatic[11,128] hydrocarbons are the solvent phase. The effect is considerable. A temperature difference of 20 °C will double the distribution ratio, at least in the 20–50 °C range. This has been shown for most of the alcohols under review.[127,147] The plots of log D against $1/T$, reproduced[147] in Figure 18, are close to linearity in the above temperature range. The distribution data refer to an initial alcohol concentration of 0.001 mol dm^{-3}.

The temperature effect is much less noticeable when the alcohols are extracted into polar liquids, high molecular weight alcohols,[11,129] methylisobutyl ketone,[129] tributyl phosphate,[11] and some other extractants.[6,127] The information is fragmentary.

Tedder[113] has measured ethanol distribution into

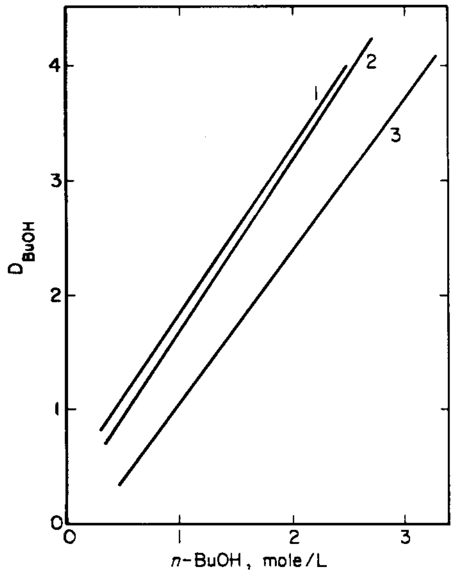


Figure 17. Distribution ratio of 1-butanol between water and (1) benzene, (2) carbon tetrachloride, or (3) cyclohexane as a function of the total alcohol concentration in the system,[123] 25 °C.

dimethylheptanone and 2-ethylhexyl alcohol and a solution of tridecyl alcohol in alkanes at three temperatures in the 23–80 °C range at varying initial alcohol concentrations in the 5–15 mol dm^{-3} range. Using a brute-force least-squares calculation procedure based on a limited number of experimental points, Tedder has correlated the distribution ratios via empirical polynomials with three constants. The same simplistic approach was subsequently applied to more complex systems,[104] with two additional parameters. One was the concentration of the reactive extractant (tridecyl alcohol or tributyl phosphate) dissolved in an alkane diluent, and the other was the concentration of dextrose as the salting agent in the aqueous solution. The constants of the nonlinear least-squares correlation equations were calculated from a total of 18 and 27 experimental input data, respectively, to cover the four independent variables for each system. The fit is rather poor, and a more fundamental approach to interpretation would be desirable.

G. Free Energy and Enthalpy of Partition

Literature data on the thermodynamic functions of transfer of several nonelectrolytes, among them the normal alcohols presently under consideration, from an alkane solvent into water have recently been reviewed[19,148] with the intention to present a complete thermodynamic description of the enthalpic and entropic contributions to the free energy of transfer. In addition, the authors have determined by direct-flow calorimetry—considered to be a reliable experimental tool—the enthalpies of transfer of these alcohols from *n*-octane or isooctane into aqueous buffer of pH 7 at 25 °C. The free energy change associated with the process was determined from distribution ratios between the phases at an overall alcohol level below 0.01 mol dm^{-3}, a range where the distribution ratio should be numerically close to the partition coefficient of the monomeric alcohol solute. The ranges of the reported[19,41,66,87,119,120,147,148] enthalpies of transfer of six alcohols from *n*-octane solution into water, at 25 °C, are compiled in Table X along with the corresponding free energy and entropy changes. The enthalpy values listed are within a ±4% confidence limit, in spite of the difference in the experimental procedures used and in the methods of derivation applied. It should be noted that the molecular weight of the normal alkane has little effect upon $\Delta_{\text{trans}}H°$.[41,66,87] Branching of the chain in the alkane solvent affects the calorimetrically determined enthalpy value for EtOH, *n*-PrOH, and *n*-BuOH, making it more negative by as much as 7% in going from *n*-octane to isooctane.[19] Excluded from the range in the $\Delta H°$ values in Table X are data obtained[147] via eq 18 representing the van't Hoff isochore, which, with the exception of *n*-BuOH, gives values lower by some 10%. Excluded also are the calorimetrically generated data of Goffredi and Liveri,[120] which are significantly lower. In the latter report, the authors[120] have not referenced relevant earlier information[66,87,119] nor attempted to explain the dramatic differences in their enthalpy data.

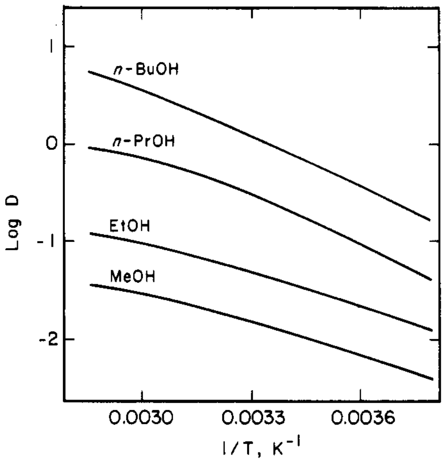


Figure 18. Effect of temperature on the distribution ratio of alcohols between water and heptane.[147]

All enthalpy values for the transfer of alcohols from alkanes into an aqueous phase are exothermic: hydration of the alcohol in water at 25 °C is more favored than their solvation in alkanes. A constant CH_2 increment for $\Delta H_{\text{trans}}°$ in this series has been claimed,[19] although it is not certain whether it generally applies.[120,147] The incremental value of 1.58 kJ/mol of CH_2 was found[19] for *n*-octane as the solvent, but 1.91 kJ was found in isooctane. This difference is much higher than the variations of the $\Delta_{\text{trans}}H°$ values given in Table X would justify.

The free energy changes associated with the process of transfer of the alcohols given in Table X are derived via eq 16 from the *P* values given in Tables VII and VIII for *n*-octane and cyclohexane, respectively. Although these are believed to be the best available partition data for the monomeric alcohols, it should be noted that they are much less sensitive to experimental parameters than the calorimetrically determined enthalpy values. The $\Delta_{\text{trans}}G°$ values are sensitive to the alcohol chain length, much more than $\Delta_{\text{trans}}H°$, becoming less negative with increasing chain length. At least in one case,[148] a linear relationship between $\Delta G°$ and $\Delta H°$ was shown for the transfer process of EtOH, *n*-PrOH, and *n*-BuOH from isooctane to aqueous buffer. The relationship of $\Delta_{\text{trans}}G°$ with the alkyl chain carbon number of the normal alcohols appears to be linear in different sol-

TABLE X. Thermodynamic Functions of Transfer of Alcohols from *n*-Octane into Water, 25 °C (See Text Section VII.G)

	$-\Delta_{trans}H°$, kJ/mol	$-\Delta_{trans}G°$, kJ/mol	$-\Delta_{trans}S°$, J deg^{-1} mol^{-1}
MeOH	30.7–31.7	14.8	55 ± 2
EtOH	32.8–34.9	12.3	73 ± 3
n-PrOH	31.7–34.2	8.6	82 ± 4
i-PrOH	37	10.0	91
n-BuOH	31.2–33.2	3.4	96 ± 4
t-BuOH	41	6.6	115

vents.[87,120,147] A CH_2 increment for $\Delta_{trans}G°$ of −3.6 kJ/mol of CH_2 at 25 °C (excluding MeOH) is in reasonable agreement with those in the series of normal carboxylic acids and alkanes, as well as in the free energies for alcohol solubilities in water.[119,147]

In keeping with the routine approach to the correlation of $\Delta G°$ values with molecular structure, the free energy term for the alcohol transfer is additive and composed of separate $\Delta G°$ terms for the transfer of CH_2, CH_3, and OH groups.[66,87,119,147] The $\Delta_{trans}G°$ for the OH group is about 18.5 kJ/mol of OH. A refinement[66] of the approach is to allow for the latter values to be affected by the energy of interaction of OH with water, or, for that matter, with a functional group of the solvent in the case of interacting extractants.

In addition to the thermodynamic functions of transfer in Table X and/or those discussed above, information is available on ethanol systems with reactive organic solvents. Tedder[113] has derived the functions from the temperature variation of D_{EtOH} for very concentrated solutions, 5–15 mol dm^{-3}, into 2-ethylhexyl alcohol, dimethylheptanone, tridecyl alcohol, and a hydrocarbon mixture at three temperatures in the 20–85 °C range. Their reported enthalpy values for the water to organic solvent transfer process are in the −8 to −25 kJ mol^{-1} range. Obviously, the values are wrong in sign, an error noted earlier.[11] The error in the absolute value is due to the use of D_{EtOH} values measured at high initial ethanol concentrations, rather than of the relevant thermodynamically sound partition coefficients. The absolute enthalpy values appear to be too low, both as given in the original report[113] and as recalculated.[11] For example, the enthalpy of transfer of ethanol from water into alkane at 25 °C is given[113] as −16 kJ mol^{-1}, while the correct value should be around 33 kJ mol^{-1}.

H. Statistical Analysis, Correlation, and Prediction

Efforts to correlate partition data with physical, chemical, and/or structural properties of the distribuend date back to the turn of the century. Hansch et al.[24,28] have reviewed earlier attempts with a special emphasis on those based on what is today known as the hydrophobic effect on the partition coefficient. There are no generally valid methods for precise estimation of partition of chemical compounds from considerations of structure and physical properties, in spite of claims to the contrary. More successful are the attempts for estimating solubilities in water and organic solvents and via them the partition coefficients, especially for simple systems involving nonpolar nonelectrolytes in the liquid state. A number of group-contribution methods have been developed during the past two decades for predicting solubilities of nonelectrolytes, and some were extended to include predictive tools for partition coefficients. Generally speaking, the methods considered here vary in sophistication, and the results obtained by more elaborate correlating equations appear to deviate less from the experimentally observed values. The success of any group-contribution prediction rests on a large number of reliable group-interaction parameters, which in turn must be derived from a large volume of high-quality experimental data. Thus, the only reliable test for any computational method is how well it predicts the experimentally determined partition coefficient. However, in most instances there are several different experimental *P* values reported in the literature, and no critical comparison and evaluation of the reported numerical information exists. The data in Tables VII and VIII are felt to be the most reliable values of partition coefficients, although for a limited number of alcohols and solvents.

In principle, the group-contribution concept assumes that the sum of contributions made by the distribuend's functional groups reflects the physical property of the molecule. Furthermore, the assumption is that the contribution made by one group is independent of that made by another group within that molecule. Both assumptions have been stated[33] to be reasonably valid for liquid nonelectrolyte mixtures of low or zero polarity. However, the assumptions are generally not applicable to systems in which the partitioning process involves an aqueous phase. For other systems, the overall correlation statistics are quite satisfactory, especially for the normal homologues, meaning a correlation coefficient higher than 0.9 and a standard deviation lower than 0.2.

UNIQUAC and UNIFAC are typical of such group-contribution methods. The methods,[33,149] introduced initially to predict liquid-phase activity coefficients in fluid mixtures of nonpolar and nonassociating liquids via sets of group volumes, surface area, and interaction parameters, are major simplifications of complex equilibria and should be considered only as an approximation.[14] While these methods are useful for less polar systems and for initial orientation, it is unrealistic to expect that the methods can be extended indefinitely to predict partition equilibria in two-phase systems of which one phase is an aqueous phase. Indeed, for systems involving aqueous ethanol solutions, the UNIFAC method does not even predict a phase split.[11] In the best of the cases for dilute ethanol solutions,[104] the distribution predictions were qualitatively correct, but never quantitative.

Several other group-contribution methods have been proposed over the past two decades. They relate the partition coefficient of nonelectrolyte solutes between water and an organic solvent to properties such as solubility, molar volume, surface area, cavity volume, hydrophobicity, dipole moment, and solubility parameter. Mainly because of the biological and environmental importance as mentioned in the Introduction, most of the correlation work has been done by using partition coefficients in the 1-octanol/water system. However, this fact should not be taken to mean that this particular system is best suited for deriving the group-contribution values. Generally speaking, the procedures are moderately successful for a variety of organic compounds, although less so for the aliphatic alcohols under consideration, most carboxylic acids, and high molecular weight compounds.

One group-contribution method, regarded[150] as more successful than others and based on the hydrophobicity of the solute and/or the physical, chemical, and structural properties responsible for it, was reformulated by Hansch and Leo from similar but more primitive concepts introduced earlier in the chemical literature,[24,28,139,151,152] The approach is essentially a structural additivity scheme composed of sets of fragment values derived from experimentally measured partition coefficients. The function π_X, defined as

$$\pi_X = \log P_X - \log P_H \qquad (21)$$

represents the difference between the logarithm of the partition coefficient of a derivative having the fragment X and that of its parent (hydrocarbon) molecule. π_X is then proportional to the free energy of transfer of the fragment X from one phase to another. For transfer from water it is a measure of hydrophobicity; thus, a negative value indicates the hydrophilic character of the fragment relative to the parent compound. π_X can be regarded as an extrathermodynamic term that is strongly dependent on electronic interactions in a manner similar to that of the Hammett acidity function. Empirically, it includes also the inductive effect of one substituent on the other fragments of the molecule. The effect is not easily determined independently, because it is frequently sensitive to the electron-withdrawing or electron-releasing character of neighboring fragments of the molecule. If such field and resonance effects become important, or when strong electron interactions occur, the π_X values derived from experiments may not be constant, and thus simple additivity of log P values fails. Fortunately, a systematic collection of experimental partition data[22,24] has resulted by now in a data bank with generally reliable values for a large number of segments that have different numerical values for a given segment depending on inductive, resonance, and conformational effects, as well as branching, and isomerism of parent molecules. For most simpler compounds, π_X values for the methyl and methylene fragments are relatively constant, regardless of other substituents on the parent hydrocarbon molecule. Halogen fragments are more sensitive, as are substituents carrying a lone pair of electrons.

The hydrophobic forces in the aqueous phase are considered as the main driving force governing the partition coefficient of the nonelectrolyte in the model octanol/water system. Since essentially the same forces dictate the aqueous solubility of the nonelectrolyte, it is not surprising that a plot of log P against the logarithm of aqueous solubility on the mole per kilogram scale is a linear function for the various butyl alcohols.[152] Subsequently, several attempts were made to derive P values from the aqueous solubility, which is a more dependable, and also experimentally more accessible, property.

Rather straightforward relationships between aqueous solubility of nonelectrolytes and their P values in the octanol/water system have served as the basis for another group-contribution approach for predicting partition data via either experimentally determined or estimated solubilities.[15,16,23,153-156] Basically, the relationships, presented in the form of semiempirical equations, have terms for physical constants that are specific to the size and structure of the nonelectrolyte, the thermodynamic functions of mixing, activities and fugacities, and possible solute–solute, solute–solvent, and even solvent–solvent interactions.

Among these correlation parameters, molecular size and/or surface and cavity area related methods for predicting solubilities have received prime attention.[151,153,154,157,158] The parameters are believed to be more consistent with experimental solubility and partition data than those based on the empirical effect of hydrophobic forces.[151,152] For the alcohols under review the solubility predictions appear to be no more than moderately successful. For the three butyl alcohols the predicted values are about 40%[153,155] different from the experimentally determined ones. On the other hand, at least in one case,[151] log P of the alcohols in the octanol/water system is a linear function of the molar volume of the alcohols MeOH to *n*-BuOH, including *i*-BuOH.

The justification of size, area, and cavity correlations with solubility and partition data invokes the physical picture of water molecules packed around the solute molecule, where the number of such water molecules depends on the surface area of the solute. The approach considers the transfer process to consist of removal of the solute from its aqueous environment, creation of a cavity in the organic solvent, and placement of the solute into the cavity. The procedures for calculating the surface area allow for the effect of branching of the aliphatic segment and that of the polar segment.[29,153,154,157] For example,[153,154] the exposed surface area of a terminal methyl group is 85 Å^2, about 3 times that of the methylene unit, 32 Å^2. Table XI compiles the surface areas of the alcohols under review here and those of their fragments.[29] The tabulated values differ by 1–2% from earlier data on butyl alcohols.[153,154] The sensitivity of the derived surface area to branching and the effect of it on the molecular size are not negligible. The distinction between the alcohol isomers and the specific values assigned to the fragments depends on the ability of the OH group to interact with water (determining its hydrophilic character), the cavity size in the organic medium, and the ability of the hydroxyl groups to self-associate in the organic medium. The latter is essentially the effect of structure on the proton-donating and proton-accepting abilities of the hydroxyl group. The net effect is a smaller surface area of the hydroxyl fragment in the branched alcohols.

Routinely, the group-contribution parameters, for both solubility and partition, are determined by regression analysis using experimental partition coefficients and computed surface area. The overall statistics are satisfactory, although the computed average correlation coefficients are usually better for solubilities than for partition of various nonelectrolytes, including the eight alcohols of this review.[22,23,29,153,159]

From the contribution parameters thereby computed, the free energies of transfer of the different segments can be derived.[16,17,24,29,153] Thus, for example, a plot of $\Delta_{\text{trans}}G°$ of the alcohols vs. the total molecular surface area is a straight line for the normal alcohols.[17] Or, the free energy of transfer of these alcohols from water to dodecane is composed[119,153,154] of additive contributions of their methyl, methylene, and hydroxyl fragments, which have $\Delta_{\text{trans}}G°$ values of −8.7, −3.6, and 18.2 kJ/mol of fragment at 25 °C.[119]

TABLE XI. Surface Area, Å^2, of Alcohol Molecules and Their Fragments[29]

alcohol	total	normal chain	branched chain	polar group
MeOH	173	103	0	70
EtOH	209	147	0	62
n-PrOH	241	179	0	62
i-PrOH	237	0	183	54
n-BuOH	270	208	0	62
i-BuOH	264	41	168	55
sec-BuOH	262	192	21	49
t-BuOH	260	0	213	47

Finally, a brief mention should be made of a more recent approach, termed solvatochromic,[160] which is another variation of the earlier reviewed group-contribution methods. It is based on semiempirical and fully empirical relationships between the solubilities of nonelectrolytes in water or their partition coefficients in octanol/water systems and the solubility parameter of the organic phase, the molar volume of the distribuend, and an empirical dipolar term called the solvatochromic measure of dipolarity–polarizability. The correlating polynomials usually have three adjustable parameters, but four for the alcohols of interest to us. The fourth parameter is a correction term to account for an empirical fraction of alcohol monomer in the system. The log P values calculated in this way were compared (in Table 2 of ref 160) with observed data taken from an unidentified source (probably from the several values in Hansch's compilation[24]), which are not necessarily our recommended values in Tables VII and VIII. The differences in their P values between calculated and observed range from less than 8% for *n*-BuOH, *i*-BuOH, and *t*-BuOH to 55% for MeOH. When their calculated values are compared with our recommended P values, the differences range from 8% for *t*-BuOH to 89% for MeOH.

VIII. Conclusions

Extractability of low molecular weight alcohols, methanol to butanols, from their aqueous solutions into any water-immiscible organic solvent increases with increasing molecular weight of the alcohol, concentration in the aqueous feed, and temperature. This supports the thesis that hydrophobicity is the most important single factor governing extractability of aliphatic alcohols. The Nernst partition coefficients of the monomeric alcohols are low into inert, nonpolar, and low dielectric constant hydrocarbons and their derivatives, but are significantly higher into polar solvents having oxygen-containing functional groups. Qualitative data suggest that the higher extractability of the alcohols into such solvents takes place, at least partially, by virtue of specific interactions leading possibly to hydrogen- and/or dipole–dipole-bonded adducts. There is no firm evidence of any specific stoichiometry of the organic-phase complex.

Under all conditions water is coextracted along with the alcohol into the organic phase, more so into oxygen-containing reactive solvents. The overall water content of the organic phase increases with that of the alcohol, and there is some indication of a possible stable hydrate of the alcohol-extractant adduct being formed in the case of polar, oxygen-bearing extractants. Some observations indicate that salting-out of alcohols can be a powerful tool for transferring them into an organic phase.

Most of the numerical distribution data in the literature are not suited for quantitative chemical interpretation. The bulk of the information, especially that on ethanol collected over the past several years, is essentially phenomenological, consisting of fragmentary distribution ratios which can be strongly affected by changes in conditions and which do not relate readily to fundamental thermodynamic enthalpy and entropy parameters.

The chemistry of the transfer process of alcohols, and probably also other organic electrolytes of comparable polarity, between an aqueous solution and an organic phase is a complex process, no less so than the partition of metal salts and complexes. A concentrated research effort is needed to understand the fundamentals of the partition process of nonelectrolytes in general and of alcohols in particular.

IX. Glossary of Terms and Symbols

The following list gives the definitions of symbols and quantities used in this paper. Symbols that occur only once in the text have been explained there and are not included. Barred symbols and quantities refer to the organic phase, unbarred to the aqueous solutions. Some of the symbols may be modified further, with obvious meaning, by adding superscripts or subscripts. IUPAC recommended notations are used throughout the text.

A. Thermodynamic Quantities

C_p°	molar heat capacity at infinite dilution
D	distribution ratio, analytical, mol dm^{-3} concentration scale
ΔG°	change in Gibbs free energy, standard state
ΔH°	change in enthalpy at infinite dilution
ΔS°	change in entropy at infinite dilution
ΔV	change in volume
H^E	excess enthalpy
$K, \bar{K}$	equilibrium constant
P	partition coefficient, mol dm^{-3} scale
P^*	partition coefficient, mol fraction scale
P°	partition coefficient, wt fraction or mol kg^{-1} scale
$V, \bar{V}$	molar volume
$a, \bar{a}$	activity
$d, \bar{d}$	density, g cm^{-3}
$f, \bar{f}$	fugacity
k_s	salting coefficient
$v, \bar{v}$	phase volume
$\gamma, \bar{\gamma}$	activity coefficient
$\mu, \bar{\mu}$	chemical potential

B. Compositions, Concentrations, Units

$c, \bar{c}$	analytical concentration, mol dm^{-3} or mol L^{-1} solution
$m, \bar{m}$	molality, mol kg^{-1} solvent
$x, \bar{x}$	mol fraction

wt	weight
L	liter, 1 dm^3
cal	4.184 J

C. Processes

form	formation
mix	mixing
soln	solution, dissolution
trans	transfer
vap	vaporization

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X. References

(1) M. Minier and G. Goma, *Biotechnol. Bioeng.*, **24**, 1565 (1982).
(2) G. Zacchi, G. Aly, and R. Wennersten, *Proceedings of the International Solvent Extraction Conference* (*ISEC 1983*), American Institute of Chemical Engineers, New York, 1983, p 507.
(3) M. Minier and G. Goma, *Biotechnol. Lett.*, **3**, 405 (1981).
(4) E. S. Lipinski, S. Kresovich, T. A. McClure, D. R. Jackson, W. T. Lawhon, A. A. Kabyonen, and E. L. Daniels, "Sugar Crops as a Source of Fuels", TID 29400/1, Battelle, Columbus, OH, 1978.
(5) D. Zudkevitch, S. E. Belsky, and P. D. Krautheim, U.S. Patent 4 428 798 (1984).
(6) J. Feldman, U.S. Patent 4 346 241 (1982).
(7) S. E. Kagan and Yu. N. Kovalev, *Tr. Inst.-Mosk. Khim.-Teknol. Inst. im. D. I. Mendeleeva*, **40**, 122 (1963).
(8) R. M. Busche, *Biotechnol. Prog.*, **1**(3), 165 (1985).
(9) M. Matsumura and H. Maerkl, *Appl. Microbiol. Biotechnol.*, **20**, 371 (1984).
(10) H. Brueckner, German Patent DE 3 236 496, April 1984; *Chem. Abstr.*, **100**, 93254c (1984).
(11) T. K. Murphy, H. W. Blanch, and C. R. Wilke, Lawrence Berkeley Laboratory Report, LBL-17979, April 1984.
(12) D. W. Tedder, C. L. Liotta, K. B. Garg, W. Y. Tawfik, and L. H. Krosnowski, "Fuel Grade Ethanol Recovery by Solvent Extraction", Progress Report, Georgia Institute of Technology, September 1981.
(13) S. A. Leeper and P. C. Wankat, *Ind. Eng. Chem. Process Des. Dev.*, **21**, 331 (1982).
(14) I. A. Furzer, *Ind. Eng. Chem. Process Des. Dev.*, **23**, 387 (1984).
(15) Y. B. Tewari, M. M. Miller, S. P. Wasik, and D. E. Martire, *J. Chem. Eng. Data*, **27**, 451 (1982).
(16) D. Mackay, A. Bobra, W. Y. Shiu, and S. H. Yalkowsky, *Chemosphere*, **9**, 701 (1980).
(17) F. A. Vilallonga, R. J. Koftan, and J. P. O'Connell, *J. Colloid Interface Sci.*, **90**, 539 (1982).
(18) W. J. Dunn and S. Wold, *Acta Chem. Scand.*, **B32**, 536 (1978).
(19) W. Riebesehl and E. Tomlinson, *J. Phys. Chem.*, **88**, 4770 (1984).
(20) E. O. Dillingham, R. W. Mast, G. E. Bass, and J. Autian, *J. Pharm. Sci.*, **62**, 22 (1973).
(21) Y. Yonezawa and Y. Urushigawa, *Chemosphere*, **3**, 139 (1979).
(22) G. C. Nys and R. F. Rekker, *Eur. J. Med. Chem.*, **9**, 361 (1974).
(23) G. Klopman, K. Namboodiri, and M. Schochet, *J. Comput. Chem.*, **6**, 28 (1985).
(24) C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley, New York, 1979.
(25) R. Collander, *Acta Chem. Scand.*, **3**, 717 (1949).
(26) R. Collander, *Acta Chem. Scand.*, **4**, 1085 (1950).
(27) R. Collander, *Acta Chem. Scand.*, **5**, 774 (1951).
(28) A. Leo, C. Hansch, and D. Elkins, *Chem. Rev.*, **71**, 525 (1971).
(29) R. Kühne, K. Bocek, P. Scharfenberg, and R. Frank, *Eur. J. Med. Chem.-Chim. Ther.*, **16**, 7 (1981).
(30) A. S. Kertes and C. J. King, *Biotechnol. Bioeng.*, **28**, 269 (1986).
(31) A. P. Kudchadker, G. H. Alani, and B. J. Zwolinski, *Chem. Rev.*, **68**, 659 (1968).
(32) R. C. Wilhoit and B. J. Zwolinski, *J. Phys. Chem. Ref. Data Suppl.* **1**, 1973.
(33) A. Fredenslund, J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria Using UNIFAC*, Elsevier, Amsterdam, 1977.
(34) E. W. Flick, Ed., *Industrial Solvents Handbook*, 3rd ed., Noyes Data, Park Ridge, NJ, 1985.
(35) F. Franks, Ed., *Water. A Comprehensive Treatise*, Plenum, New York, 1973.
(36) F. Franks and D. S. Reid, in ref 35, Vol. 2, Chapter 5, p 323.
(37) A. S. Kertes, Editor-in-Chief, *Alcohols with Water*, A. F. M. Barton, Ed., Solubility Data Series 15, Pergamon, Oxford, 1984.
(38) A. W. Francis, *Critical Solution Temperatures*, Advances in Chemistry Series 31, American Chemical Society, Washington, DC, 1961.
(39) J. B. Hasted, in ref 35, Vol. 2, Chapter 7, p 405.
(40) F. Franks and D. J. G. Ives, *Q. Rev., Chem. Soc.*, **20**, 1 (1966).
(41) A. S. Kertes and W. C. Lai, *Colloids Surf.* **1**, 197 (1980).
(42) J. J. Christensen, R. W. Hanks, and R. M. Izatt, *Handbook of Heats of Mixing*, Wiley-Interscience, New York, 1982.
(43) E. M. Arnett, W. B. Kover, and J. V. Carter, *J. Am. Chem. Soc.*, **91**, 4028 (1969).
(44) R. Aveyard and R. W. Mitchell, *Trans. Faraday Soc.*, **64**, 1757 (1968).
(45) R. Aveyard and R. Heselden, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1953 (1974).
(46) D. . Alexander and D. J. T. Hill, *Aust. J. Chem.*, **22**, 347 (1969).
(47) A. S. Kertes and W. C. Lai, *J. Colloid Interface Sci.*, **76**, 48 (1980).
(48) R. Sköld, J. Snurkuusk, and I. Wadsö, *J. Chem. Thermodyn.*, **8**, 1075 (1976).
(49) E. M. Arnett, J. J. Burke, J. V. Carter, and C. F. Douty, *J. Am. Chem. Soc.*, **94**, 7837 (1972).
(50) E. L. Taylor and G. L. Bertrand, *J. Solution Chem.*, **3**, 479 (1974).
(51) K. Bocek, *J. Chromatogr.*, **162**, 209 (1979).
(52) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 1572 (1969).
(53) J. E. Desnoyers, G. Perron, L. Avedikian, and J. P. Morel, *J. Solution Chem.*, **5**, 631 (1976).
(54) J. A. V. Butler, C. N. Ramchandani, and D. W. Thomson, *J. Chem. Soc.*, 280 (1935).
(55) J. A. V. Butler, D. W. Thomson, and W. H. Maclennan, *J. Chem. Soc.*, 674 (1933).
(56) F. Franks, in ref 35, Vol. 2, Chapter 1, p 1.
(57) R. Aveyard and R. Heselden, *J. Chem. Soc., Faraday Trans. 1*, **71**, 312 (1975).
(58) L. A. Reber, W. M. McNabb, and W. W. Lucasse, *J. Phys. Chem.*, **46**, 500 (1942).
(59) R. De Santis, L. Marrelli, and P. N. Muscetta, *J. Chem. Eng. Data*, **21**, 324 (1976).
(60) I. M. Korenman, A. A. Gorokhov, and G. N. Polozenko, *Russ. J. Phys. Chem.*, **48**, 1065 (1974).
(61) I. M. Korenman, A. A. Gorokhov, and G. N. Polozenko, *Russ. J. Phys. Chem.*, **49**, 877 (1975).
(62) V. Ya. Ryashentsev, E. S. Vainerman, and S. V. Rogozhin, *J. Chromatogr.*, **288**, 43 (1984).
(63) R. De Santis, L. Marrelli, and P. N. Muscetta, *Chem. Eng. J.*, **11**, 207 (1976).
(64) F. L. Wilcox and E. E. Schrier, *J. Phys. Chem.*, **75**, 3757 (1971).
(65) D. N. Glew and H. Watta, *Can. J. Chem.*, **49**, 1830 (1971).
(66) N. Laiken and G. Nemethy, *J. Phys. Chem.*, **74**, 3501 (1970).
(67) J. Mullens, I. Hanssens, and P. Huyskens, *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 1417 (1971).
(68) M. C. R. Symons and M. J. Blandamer in *Hydrogen-Bonded Solvent Systems*, A. K. Covington and P. Jones, Taylor and Francis, London, p 211, 1968.
(69) D. N. Glew, H. D. Mak and N. S. Rath, in *Hydrogen-bonded Solvent Systems*, A. K. Covington and P. Jones, Eds., Taylor and Francis, London, 1968, p 195.
(70) P. L. Huyskens, M. Cl. Haulait-Pirson, I. Hanssens, and J. Mullens, *J. Phys. Chem.*, **84**, 28 (1980).
(71) F. Smith, *Aust. J. Chem.*, **30**, 43 (1977).
(72) Yu. I. Naberukhin and V. A. Rogov, *Russ. Chem. Rev.*, **40**, 207 (1971).
(73) J. Mullens, I. Hanssens, and P. Huyskens, *Bull. Soc. Chim. Belg.*, **79**, 539 (1971).
(74) H. C. van Ness, J. Van Winkle, H. H. Richtol, and H. B. Hollinger, *J. Phys. Chem.*, **71**, 1483 (1967).
(75) E. E. Tucker and S. D. Christian, *J. Phys. Chem.*, **81**, 1295 (1977).
(76) R. H. Stokes and K. N. Marsh, *Annu. Rev. Phys. Chem.*, **23**, 65 (1972).
(77) F. Smith, *Aust. J. Chem.*, **30**, 23 (1977).
(78) A. A. Slavin and A. A. Abramzon, *Russ. J. Phys. Chem.*, **46**, 1044 (1972).

(79) B. D. Anderson, J. H. Rytting, S. Lindenbaum, and T. Higuchi, *J. Phys. Chem.*, **71**, 2340 (1975).
(80) A. S. Kertes, S. Chaston, and W. C. Lai, *J. Colloid Interface Sci.*, **73**, 94 (1980).
(81) I. Hanssens, *Medd. Vlaam. Chem. Ver.*, **30**, 18 (1968).
(82) J. W. Roddy and C. F. Coleman, *Ind. Eng. Chem. Fundam.*, **20**, 250 (1981).
(83) W. A. P. Luck, in ref 35, Vol. 2, Chapter 4, p 235.
(84) R. H. Stokes and C. Burfitt, *J. Chem. Thermodyn.*, **5**, 623 (1973).
(85) M. K. Woycicka and W. M. Recko, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **20**, 783 (1972).
(86) A. Bellemans, *Rozn. Chem.*, **50**, 1749 (1976).
(87) R. Aveyard and R. W. Mitchell, *Trans. Faraday Soc.*, **65**, 2645 (1969).
(88) G. Elbe, *J. Chem. Phys.*, **2**, 73 (1934).
(89) C. G. Savini, D. R. Winterhalter, and H. C. van Ness, *J. Chem. Eng. Data*, **10**, 168 (1965).
(90) A. N. Fletcher, *J. Phys. Chem.*, **76**, 2562 (1972).
(91) F. Smith and I. Brown, *Aust. J. Chem.*, **26**, 691 (1973).
(92) S. Martinez and J. Edwards, *Monatsh. Chem.*, **112**, 563 (1981); **112**, 683 (1981).
(93) H. Kempter and R. Mecke, *Z. Phys. Chem., Abt. B*, **46**, 229 (1940).
(94) C. B. Kretschmer and R. Wiebe, *Ind. Eng. Chem.*, **37**, 1130 (1945).
(95) A. I. Brodskii, V. D. Pokhodenko, and V. S. Kuts, *Russ. Chem. Rev.*, **39**, 347 (1970).
(96) P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972).
(97) J. W. Roddy and C. F. Coleman, *Ind. Eng. Chem. Fundam.*, **22**, 51 (1983).
(98) J. M. Sorensen and W. Arlt, *Liquid–Liquid Equilibrium Data Collection*, Chemistry Data Series, Vol. V., Parts 1–3, Dechema, Frankfurt, 1979, 1980.
(99) C. G. Savini, D. R. Winterhalter, and H. C. van Ness, *J. Chem. Eng. Data*, **10**, 171 (1965).
(100) R. H. Stokes and M. Adamson, *J. Chem. Thermodyn.*, 8, 683 (1976).
(101) J. Hala in *Ion Exchange and Solvent Extraction*, J. A. Marinsky and Y. Marcus, Eds., Dekker, New York, 1981, Vol. 8, p 369.
(102) L. B. Itsikson, M. S. Boruhova, and I. B. Rapoport, *Tr.–Vses. Nauchno-Issled. Inst. Pererab. Nefti*, **13**, 200 (1970).
(103) V. P. Sazonov, *Zh. Prikl. Khim.*, **57**, 2204 (1984).
(104) D. W. Tedder, "Fuel-Grade Ethanol Recovery by Solvent Extraction", Progress Report, Georgia Institute of Technology, Atlanta, August 1984.
(105) D. W. Tedder, Georgia Institute of Technology, Atlanta, private communication, July 1985.
(106) J. C. Upchurch and M. van Winkle, *Ind. Eng. Chem.*, **44**, 618 (1952).
(107) D. F. Othmr, R. E. White, and E. Trueger, *Ind. Eng. Chem.*, **33**, 1240 (1941).
(108) C. M. Onalline and M. van Winkle, *Ind. Eng. Chem.*, **44**, 1668 (1952).
(109) P. Dakshinamurty, C. Chiranjivi, P. V. Rao, and V. Subrahmanyam, *J. Chem. Eng. Data*, **17**, 379 (1972).
(110) V. Brandani, A. Chianese, and M. Rossi, *J. Chem. Eng. Data*, **30**, 27 (1985).
(111) E. R. Washburn, A. E. Beguin, and O. C. Beckerd, *J. Am. Chem. Soc.*, **61**, 1694 (1939).
(112) E. R. Washburn, V. Hmizda, and R. Vold, *J. Am. Chem. Soc.*, **53**, 3237 (1931).
(113) D. W. Tedder, "Fuel-Grade Ethanol Recovery by Solvent Extraction", Georgia Institute of Technology, Atlanta, October 1982.
(114) J. G. Victor, *Proceedings of the International Solvent Extraction Conference* (*ISEC 1983*), American Institute of Chemical Engineers, New York, 1983.
(115) W. Fogel and J. P. Arlie, *Rev. Inst. Fr. Pet.*, **39**, 617 (1984).
(116) M. E. Paulaitis, M. L. Gilbert, and C. A. Nash, *Proc. 2nd World Congr. Chem. Eng.*, **4**, Montreal (1981).
(117) W. G. Schultz and J. N. Randal, *Food Technol.*, **24**, 94 (1970).
(118) J. G. Victor, U.S. Patent 4508928 (April 1985); *Chem. Abstr.*, **102**, 222480v (1985).
(119) M. Manabe, M. Koda, and K. Shirahama, *Bull. Chem. Soc. Jpn.*, **48**, 3553 (1975).
(120) M. Goffredi and V. T. Liveri, *J. Solution Chem.*, **10**, 693 (1981).
(121) I. M. Korenman and Z. G. Chernorukova, *Russ. J. Appl. Chem.*, **47**, 2595 (1974).
(122) I. Hanssens, J. Mullens, C. Denenter, and P. Huyskens, *Bull. Soc. Chim. Fr.*, 3942 (1968).
(123) E. Meeussen and P. Huyskens, *J. Chim. Phys.*, **63**, 845 (1966).
(124) Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, London, 1969.
(125) Ya. I. Korenman, *Russ. J. Appl. Chem.*, **43**, 1107 (1970).
(126) R. D. Vold and E. R. Washburn, *J. Am. Chem. Soc.*, **54**, 4217 (1932).
(127) K. Heinonen and E. Tommila, *Suom. Kemistil.*, **42**, 113 (1969).
(128) J. W. Roddy, *Ind. Eng. Chem. Process Des. Dev.*, **20**, 104 (1981).
(129) A. Souissi and F. C. Thyrion, *Proc. 2nd World Congr. Chem. Eng.*, **4**, 443 (1981).
(130) C. L. Munson and C. J. King, *Ind. Eng. Chem. Process Des. Dev.*, **23**, 109 (1984).
(131) G. L. Starobinets, E. M. Rakhmanko, and T. K. Khaletskaya, *Russ. J. Phys. Chem.*, **54**(8), 1177 (1980).
(132) M. Tanaka and I. Kojima, *J. Inorg. Nucl. Chem.*, **29**, 1769 (1967).
(133) K. H. Meyer and H. Hemmi, *Biochem. Z.*, **277**, 39 (1943).
(134) S. Bugarszky, *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.*, **71**, 753 (1910).
(135) E. M. Kuznetsova and L. L. Gurarii, *Russ. J. Phys. Chem.*, **45**, 1761 (1971).
(136) K. B. Sandell, *Naturwissenshcaften*, **51**, 336 (1964).
(137) K. S. Levina and A. S. Zheleznyak, *Russ. J. Phys. Chem.*, **49**, 499 (1975).
(138) R. Collander, *Phys. Plant.*, **7**, 420 (1954).
(139) C. Hansch and S. M. Anderson, *J. Org. Chem.*, **32**, 2583 (1967).
(140) C. F. Coleman and J. W. Roddy, private communication, October 1985.
(141) E. M. Rakhamanko, A. P. Kruglik, G. L. Starobinets, O. N. Bubel, and S. M. Leschev, *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk*, **1**, 3 (1985).
(142) I. M. Korenman, Z. G. Chernorukova, N. Yu. Gurevich, T. M. Dobromyslova, and N. A. Shemarova, *Russ. J. Phys. Chem.*, **48**, 100 (1974).
(143) K. B. Sandell, *Monatsh. Chem.*, **89**, 36 (1958).
(144) S. Balanicka and J. Malecki, *Fiz. Dielektr. Radiospektrosk.*, 9(2), 153 (1977).
(145) R. Varma, U. D. Sawant, and N. G. Karanth, *Enzyme Microb. Technol.*, **6**, 233 (1984).
(146) G. L. Starobinets, E. M. Rakhmanko, T. K. Khaletskaya, and L. A. Berezina, *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk*, **4**, 34 (1980).
(147) E. A. Lissi, *Acta Sud Am. Quim.*, **1**, 69 (1981).
(148) W. Riebesehl, E. Tomlinson, and H. J. M. Grünbauer, *J. Phys. Chem.*, **88**, 4775 (1984).
(149) J. M. Prausnitz, T. F. Anderson, E. A. Grens, C. A. Eckert, R. Hsieh, and J. P. O'Connell, *Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, NJ, 1980.
(150) A. J. Hopfinger and R. D. Baltershell, *J. Med. Chem.*, **19**, 569 (1976).
(151) A. Leo, C. Hansch, and P. Y. C. Jow, *J. Med. Chem.*, **19**, 611 (1976).
(152) C. Hansch, J. E. Quinlan, and G. L. Lawrence, *J. Org. Chem.*, **33**, 347 (1968).
(153) G. L. Amidon, S. H. Yalkowsky, and S. Leung, *J. Pharm. Sci.*, **63**, 1858 (1974).
(154) G. L. Amidon, S. H. Yalkowsky, S. T. Anik, and S. C. Valvani, *J. Phys. Chem.*, **79**, 2239 (1975).
(155) S. H. Yalkowsky and S. C. Valvani, *J. Pharm. Sci.*, **69**, 912 (1980).
(156) J. Hine and P. K. Mookerjee, *J. Org. Chem.*, **40**, 292 (1975).
(157) R. B. Hermann, *J. Phys. Chem.*, **76**, 2754 (1972).
(158) R. D. Cramer, *J. Am. Chem. Soc.*, **99**, 5408 (1977).
(159) J. T. Chou and P. C. Jurs, *J. Chem. Inf. Comput. Sci.*, **19**, 172 (1979).
(160) R. W. Taft, M. R. Abraham, G. R. Famini, R. M. Doherty, J. L. M. Abboud, and M. J. Kamlet, *J. Pharm. Sci.*, **74**, 807 (1985).