QUARTERLY REVIEWS

THE STRUCTURAL PROPERTIES OF ALCOHOL–WATER MIXTURES

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Introduction

THE properties of aqueous solutions of hydroxy-compounds are of interest in many fields of enquiry; although much effort has been directed to their study, more is needed fully to solve the problems they present. Among organic compounds, hydroxy-derivatives stand out in virtue of their high solubility in water, but their solutions often show abnormalities in properties, such as viscosity–composition maxima, or negative relative partial molar volumes, which are yet inadequately understood. For monohydric alcohols in dilute aqueous solution, such peculiarities can be attributed in a general way to the bifunctional nature of the solute molecules. The hydrophobic hydrocarbon group may be imagined as resisting the pull into solution exerted by the hydrophilic hydroxyl group, which, either as proton donor or acceptor, can hydrogen-bond with the solvent molecules. A second hydroxyl group in the solute molecule (glycols) shifts the balance of competing influences in favour of "aqueous behaviour" and the anomalies become less marked. Further hydroxylation eventually removes them altogether; thus the sugars are, ostensibly, among the most normal of solutes in water.

In this Review, which can by no means be exhaustive, attention is largely confined to monohydric alcohol–water mixtures, for these are of the greatest interest from the structural viewpoint. Studied over the whole composition range, even a single binary system of this kind may present several problems, according to whether one component or the other (or neither) is present in excess and may (or may not) take major control of such structures as are capable of existing in the liquid state. That hydrogen bonding plays a principal role in the interaction of the components cannot alone account for the oddities in properties that are observed; it is the belief of the Reviewers that they are structural in origin, and will eventually be understood in the light of full knowledge of the "structural behaviour" of the components. To this end, the properties of these systems are surveyed, with special reference to their structural implications, and with the conviction that the problems concerned must be very significant in many connections. This conviction is held because the relatively simple alcohol–water mixtures may serve as models helpful to the better understanding of more complex systems, and because these mixtures are so frequently used as solvents in studies of chemical equilibria and reaction rates which can hardly be devoid of "solvent participation".

The Structure of Liquid Water

There is a pressing need for a structural model of liquid water adequate for quantitative interpretation of all the anomalous properties, such as the maximum of density at 4°, the high dielectric constant, heat capacity, viscosity, thermal conductivity, and critical temperature, and the differences from deuterium oxide. Increased efforts of recent years have provided an embarrassment of partially successful alternative models; these are the subject of current review[1] and are very likely, despite unresolved difficulties, to incorporate between them many ultimately acceptable features. An element of subjective choice can hardly be avoided in the brief summary required for present purposes.

Reliance is placed on Frank and Wen's view of hydrogen bonding in liquid water.[2] Each oxygen atom ($\sim sp^3$ hybridised) can form four approximately tetrahedrally-disposed hydrogen bonds, but the formation of the bonds is an essentially co-operative process because the mutual polarisation of the participating water molecules is of a kind strongly to facilitate further bonding. Thus, when a favourable (low) energy fluctuation promotes the formation of a bond, many are formed simultaneously; a self-stabilising, three-dimensional, hydrogen-bonded cluster jumps into existence, and persists until it suffers collective destruction by an unfavourable (high) energy fluctuation. That the clusters are short-lived is shown by the single dielectric relaxation time ($\sim 10^{-11}$ sec) for liquid water. The uniform activation energy (4600 cal. mole^{-1}) for this relaxation, those of the structural component of excess sound absorption, and for viscous flow and self-diffusion, is consistent with cluster dissolution as the common limiting factor—further steps in accommodation apparently require little or no activation.

The reality of these "flickering clusters" can hardly be challenged. Their life-time, although so short, is still two or three magnitudes greater than the period of molecular vibration. Without them it would be hard to explain the dominant fact that in liquid water the average co-ordination (4·4 at 15°, 4·9 at 83°) but slightly exceeds that in ice (4) and, quite atypically, increases with rising temperature; water is open-structured, and is full of cavities not dissimilar to those which are present in ice. Yet in a liquid

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[1] J. L. Kavanau "Water and Solute-Water Interactions", Holden-Day, Inc., San Francisco, London, Amsterdam, 1964; F. Franks, "The Structural Properties of Water and Aqueous Solutions", Heinemanns Ltd., London, in preparation.

[2] H. S. Frank and Wen Yang Wen, *Discuss. Faraday Soc.*, 1957, **24,** 133.

in which molecular disorder must be prevalent, structural order cannot be other than short in range, and it is not easy to see how these cavities could remain impregnable to occupation. Comparison of the radial distribution from *X*-ray scattering with that to be expected from a statistically smeared-out structure suggested to Samoilov that the cavities are indeed partially populated by non-hydrogen-bonded, monomeric water molecules. This gave rise to the first "interstitial model"[3] which has been extensively developed[4] with considerable success but in a manner which places some emphasis on the concepts of "quasi-crystallinity". However suitable this concept may be for cold water, it can hardly be appropriate over the whole temperature range within which water can exist as a liquid. It is not consistent with the "flexibility" of hydrogen bonds[5], is not implicit in the Frank and Wen view of cluster formation, and finds no part in Némethy and Scheraga's treatment[6] which also rejects the occupation of cavities by monomeric molecules. Instead, liquid water is considered to be a mixture of open, empty clusters with a dense fluid composed of non-hydrogen bonded molecules. New evidence for such a model has recently been adduced.[7]

The two leading types of model have in common a "symbiotic" relation between two forms of water; one maximally hydrogen-bonded and voluminous, the other, non-hydrogen-bonded and dense. Spectroscopic evidence might be expected clearly to confirm this relation, but this is not quite the case. Thus, rise in temperature, by shifting the equilibrium between the two forms in the sense of promoting cluster disintegration, would be thought to increase the intensity of infrared absorption due to free O–H stretching vibration, but no such effect has been observed for the >3400 cm.$^{-1}$ bands,[8] the assignment of which, however, appears not to be simple.[9] On the other hand, the intensities of several well-defined absorption bands (<800 cm.$^{-1}$), associated with hydrogen-bond stretching and libration, decrease rapidly with rising temperature. These observations suggest that some quite strong, but as yet unidentified, water–water interaction other than hydrogen bonding may exist, and, becoming predominant at elevated temperatures, may be mainly responsible for the high critical temperature of water.[7] Pronounced temperature dependence has also been observed for the low-frequency Raman scattering of liquid water.[10]

[3] O. Ya. Samoilov, *Zhur. fiz. Khim.*, 1946, **20**, 12; "Structure of Aqueous Electrolyte Solutions." B. G. Tenbner; trans. D. I. G. Ives, Consultants Bureau, New York, 1965.

[4] L. Pauling, "The Nature of the Chemical Bond", 3rd. edn., Cornell University Press, New York, 1960; H. S. Frank and A. S. Quist, *J. Chem. Phys.*, 1961, **34**, 604; M. D. Danford and H. A. Levy, *J. Amer. Chem. Soc.*, 1962, **84**, 3965.

[5] J. A. Pople, *Proc. Roy. Soc.*, 1951, *A*, **205**, 163.

[6] G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, 1962, **36**, 3382, 3401.

[7] H. S. Frank and F. Franks, in preparation.

[8] J. W. Schultz and D. F. Hornig, *J. Phys. Chem.*, 1961, **65**, 2131.

[9] W. A. Senior and W. K. Thompson, *Nature*, 1965, **205**, 170.

[10] G. E. Walrafen, *J. Chem. Phys.*, 1964, **40**, 3249.

The validity of some kind of "mixture model" is, however, supported by the absorption of ultrasound in liquid water[11,12,13], which can be accounted for only in terms of an equilibrium between modifications with, and without, structure. This is also the case for the scattering of cold neutrons.[14]

To sum up, it is clear that no decisive choice can be made between existing models, which can be regarded, at best, only as gross approximations. There is little doubt, nevertheless, that a senstitive order–disorder balance within liquid water is highly significant to all its properties. This is particularly the case in relation to the reaction of water to the presence of inert solutes with which it has no direct or specific interaction. The excessive heat evolution and entropy loss accompanying the dissolution of inert substances in water are hard to explain except in terms of water-structure promotion. Views on this effect have varied since the graphic "iceberg" concept of Frank and Evans[15]—unduly close association with the existence of crystalline gas-hydrates has been discounted—and are still being actively discussed and developed. Whether or not the name "hydrophobic hydration" is appropriate, there is no doubt about the reality and widespread incidence of an enthalpy- and entropy-depressing effect which originates in the reaction of water to inert molecules, the hydrophobic parts of bifunctional molecules, or even to foreign bulk phases. It is, as will be shown, very relevant in the context of the present review.

The Structure of Liquid Alcohols

Since the oxygen atom of an alcohol molecule carries one proton and two lone pairs of electrons, it might be expected to form three hydrogen bonds with its neighbours. This could not, of course, be the case for every molecule of an assembly, but it is not obvious why there should not be a distribution of molecules forming one, two, or three bonds. All the evidence shows, however, that no more than *two* bonds are formed, each oxygen acting once as proton donor and once as proton acceptor. This apparent limitation to equality of "give-and-take" may be attributed to the essentially co-operative nature of hydrogen bonding; together with the unfavourable steric effect of the organic group, it restricts the degree of order which can be established in the liquid state, and precludes the kind of three-dimensional association which is dominant in water. *X*-Ray radial distribution curves[16] indicate that, instead, linear polymers of the kind shown in

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[11] L. Hall, *Phys. Rev.*, 1948, **73**, 775.

[12] M. C. Smith and R. T. Beyer, *J. Acoust. Soc. Amer.*, 1948, **20**, 608.

[13] K. F. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves", Academic Press, New York, 1959.

[14] D. J. Hughes, H. Palevsky, W. Kley, and E. Tunkelo, *Phys. Rev.*, 1960, **119**, 872; P. A. Egelstaff, *Adv. Phys.*, 1962, **11**, 203.

[15] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 1945, **13**, 507.

[16] W. H. Zachariasen, *J. Chem. Phys.*, 1935, **3**, 158; G. G. Harvey, *J. Chem. Phys.*, 1938, **6**, 111; 1939, **7**, 878.

Figure 1 are formed; in the case of the higher normal alcohols, these may tend to associate non-randomly together, preferred positions for the oxygen atoms lying in planes perpendicular to the parallel hydrocarbons chains.[17] Normally, however, the association in liquid alcohols seems to be of a kind to which the *formal* thermodynamic treatment of the "ideal associated solution" applies,[18] and is well described in terms of equilibria between polymeric species. These are usually considered to be fragments of the polymeric chains which, unlimited in length in the crystalline state, do not, in the liquid, exceed a complexity, *n*, of 5—7 molecules, or less for sterically hindered alcohols.

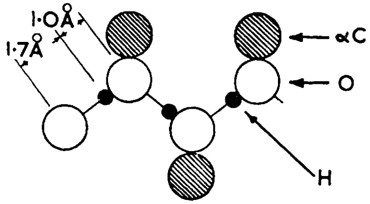

FIG. 1. *Hydrogen bonded chain association of alcohols.*

In contrast to water, liquid alcohols show a range of dielectric relaxation times,[19] typically 10^{-9}, 10^{-10}, and 10^{-11} sec. with a residual high-frequency margin between dielectric constant and the square of the optical refractive index, attributed to librational and atomic polarisations. Variation of these relaxations within homologous series, and the effects on them of freezing, variation of temperature, and dilution with the corresponding hydrocarbons, have led to their assignment to polymer chain destruction, orientation of doubly hydrogen-bonded molecules (within a chain), or the orientation of singly-bonded end, or free, molecules. A picture emerges of rapid equilibrium between very short-lived polymeric chains of assorted but finite lengths, having a degree of rigidity due to appreciable hindrance of internal rotation. Calculations of degrees of polymerisation and of hydrogen bond energy (*e.g.* ~5·8 kcal. mole^{-1}) provide results in substantial agreement with those from other sources.

It is clear that hydrogen bonding has a profound effect on the properties of liquid alcohols, but not, as for water, in the sense of conferring openness of structure (enhanced pressure increases *n*).[20] Over the range of alcohols, however, the effect is subject to strong steric limitations; thus the dielectric constants of the octan-1-, 2-, 3-, and 4-ols and of 4-methylheptan-4-ol are, respectively, 9·8, 7·7, 6·8, 5·0, and 2·9.[21] Clearly this variation within a set

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[17] W. C. Pierce and D. P. MacMillan, *J. Amer. Chem. Soc.*, 1938, **60**, 779.

[18] L. Prigogine and R. Defay, "Chemical Thermodynamics", trans. D. H. Everett, Longmans Green & Co., London, 1954, ch. XXVI.

[19] M. Magat in "Hydrogen Bonding", ed. D. Hadzi and H. W. Thompson, Pergamon Press, London, 1959.

[20] F. E. Harris, E. W. Haycock, and B. J. Alder, *J. Chem. Phys.*, 1953, **21**, 1943.

[21] C. P. Smyth, "Dielectric Behaviour and Structure", McGraw-Hill Book Co., Inc., New York, 1955.

of isomers can only be a function of the stereochemistry of association. For the lower alcohols, the dielectric constants (ϵ at 25°; MeOH, 32·63; EtOH, 24·30; Pr^nOH, 20·1) are roughly proportional to the number of OH groups per unit volume,[22] but are higher than would be anticipated from the moderate value of the OH group moment (1·53 D). This is consistent with the existence of a common mode of co-association which leads to co-operative reinforcement of dipole fields. Such enhancement of dielectric constant is expressed by a Kirkwood correlation parameter, g,[23] which exceeds unity ($g = 1$ only for normal liquids devoid of directional, short-range association forces). It has been pointed out[24] that this situation can arise in two ways. A relatively stable association complex may be formed, long-lived enough to be oriented by the low-frequency field used to measure static dielectric constants; it will reveal itself in a characteristic relaxation. On the other hand, as already indicated, water shows only one very short relaxation time, and contains no orientating complex. In this case, the high correlation parameter must be due to the enhancement of the polarity of the molecules by the dynamic association in which they are taking part, or, possibly to the high proton-mobility in hydrogen-bonded systems. Probably, for the alcohols, co-operative hydrogen bonding is responsible for both kinds of contribution to dielectric constant.

The evidence of infrared spectroscopy is that the association of alcohols tends to decrease with increasing molecular weight, and in the sequence primary, secondary, tertiary. With increasing concentratian of an alcohol in a non-polar solvent, the sharp O–H stretching peak characteristic of monomers is replaced by a diffuse and broad association spectrum,[25] indicating the presence of hydroxyl groups covering a "quasi-continuous" range of interaction energies. This feature has been attributed to the skeletal vibrations and random orientations of neighbouring species of varying complexity. More detailed studies[26] have correlated degrees of association determined spectroscopically with the fugacities of the components, on the basis that the equilibrium constant for the first association step (dimerisation, $K_{1,2}$) is different from that relating to subsequent steps ($K_{n,n+1}$), but the latter may be taken as single-valued for all values of n ($\not> 5$—7; 3 for Bu^tOH). The association is sensitive to temperature because of the entropy loss involved. Although some of the spectroscopic work may have been adversely influenced by unrealised effects of water as impurity, there is substantial evidence that dimers, perhaps because they are of enhanced polarity and reactivity, are disfavoured compared with higher polymers. Thus, $K_{1,2}$ and $K_{2,3}$ for Bu^tOH in an inert solvent have been determined from proton magnetic resonance as 6·75 and 111 mole^{-1}l.

[22] R. W. Gurney, "Ionic Processes in Solution", McGraw-Hill Book Co., Inc., New York, 1953, p. 197.

[23] J. G. Kirkwood, *J. Chem. Phys.*, 1939, **7**, 911.

[24] A. C. Brown and D. J. G. Ives, *J. Chem. Soc.*, 1962, 1608.

[25] E. Bauer and M. Magat, *J. Phys. Radium*, 1938, **9**, 319.

[26] R. Mecke, *Discuss. Faraday Soc.*, 1959, **9**, 161.

respectively.[27] The enhanced stability of a tetramer over that of a dimer is illustrated by the standard enthalpy changes for the processes $2ROH \rightarrow (ROH)_2$ (ΔH_2^0) and $4ROH \rightarrow (ROH)_4$ (ΔH_4^0). For Bu^sOH, $\Delta H_2^0 = -5250$ cal., $\Delta H_4^0 = -23{,}118$ cal.;[28] for MeOH, $\Delta H_2^0 = -4470$ cal. and $\Delta H_4^0 = -30{,}060$ cal.[29] The enthalpy difference ($\Delta H_4^0 - 4\Delta H_2^0$) can perhaps be considered as indicating the superior stability of the tetramer.

Although there is general agreement on the main features of alcohol association that have been outlined, precise knowledge about the polymeric entities is lacking. There is disagreement on the extent to which dimers are "by-passed" in the association and on their nature. Bridged, non-polar dimers, with a pair of bent hydrogen bonds between oxygen atoms (*cf.* B_2H_6) have been proposed,[30] perhaps co-existing with open dimers.[31] However this may be, there is strong evidence that the dimers are structurally different from the higher polymers.[32] There is, however, a considerable body of opinion that the higher polymers are cyclic.[33] It has been pointed out[34] that the presence of cyclic polymers in the liquid phase would be consistent with the normal latent heats of fusion and melting points of the alcohols (showing little effect of hydrogen-bond breaking), compared with their abnormal latent heats of evaporation and boiling points (showing very strongly the effect of bond breaking).

It is evident that, as in the case of water, certainty of detail is lacking from existing knowledge of the liquid alcohols. The general statement can be made, however, that although water and alcohols resemble each other in hydrogen bonding facility, the structures to which these bonds can give rise are very dissimilar in the two cases, and appear to be mutually exclusive. Any discussion of alcohol–water mixtures must take these competing effects into account.

Thermodynamic Properties of Alcohol–Water Mixtures

The ethanol–water system may be taken as a first basis for discussion of the thermodynamic excess functions of mixing of the lower monohydric alcohols with water. For this system at 25°, the terms in the relation $\Delta G^E = \Delta H^M - T\Delta S^E$ are shown as functions of alcohol mole fraction

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[27] B. Lemanceau, C. Lussan, and N. Souty, *J. Chim. phys.*, 1962, **59**, 148.

[28] J. J. McKetta, *J. Phys. Chem.*, 1962, **66**, 1444.

[29] G. A. Miller, *J. Chem. Eng. Data*, 1964, **9**, 418.

[30] F. A. Smith and E. C. Creitz, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 145; G. C. Pimentel and A. L. McClellan in "The Hydrogen Bond", W. H. Freeman & Co., San Francisco & London, 1960.

[31] I. Prigogine, *J. Chim. phys.*, 1948, **45**, 17.

[32] E. D. Becker, U. Liddel, and J. N. Shoolery, *J. Mol. Spectroscopy*, 1958, **2**, 1, J. Malecki, *J. Chem. Phys.*, 1962, **36**, 2144; A. Piekara, *J. Chem. Phys.*, 1962, **36**, 2145.

[33] C. Reid and T. M. Connor in "Hydrogen Bonding", ed. D. Hadzi and H. W. Thompson, Pergamon Press, London, 1959; W. Weltner, and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1957, **73**, 2606; R. J. W. Le Fèvre and A. J. Williams, *J. Chem. Soc.*, 1960, 108; L. H. Thomas, *J. Chem. Soc.*, 1963, 1995.

[34] L. Pauling, "The Nature of the Chemical Bond", 3rd. edn., Oxford, 1960, p. 473.

x_2, in Figure 2. The excess Gibbs free energy of mixing, positive and nearly symmetrical about $x_2 = 0{\cdot}5$, is a function of negative and unsymmetrical enthalpy and excess entropy of mixing. The unusual relative magnitudes of $T\Delta S^E$ and ΔH^M show clearly that it is $T\Delta S^E$ which is decisive in determining the nature of the deviations from Raoult's law so that even mixtures formed with evolution of heat show positive deviations from ideal behaviour. This general disposition of the excess functions is always encountered in systems which separate, with rising temperature, into two liquid phases at a lower consolute temperature; such a separation occurs as a result of a large, negative ΔS^E—as opposed to separation, with falling temperature, at an upper consolute temperature, which arises from energy effects.[35] Although glycol ether–water systems provide examples of closed immiscibility loops, no simple alcohol–water system shows a lower critical solution temperature: Bu^{s}OH and water, however, come close to doing so, with very marked retrograde solubility[36] between 0° and 60°. Each of the butyl alcohols other than Bu^{t}OH forms a two phase system with water which becomes homogeneous at an upper consolute temperature. Without detailed thermodynamic treatment[37] it is clear that such incomplete miscibility, and its sometimes complex dependence on temperature, arises from accentuation of "excess function behaviour" of a kind to be looked for in

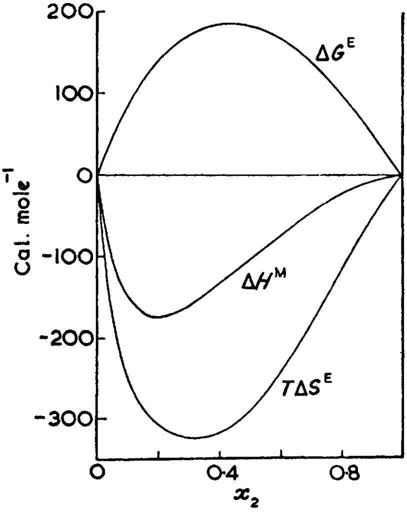

FIG. 2. *Thermodynamic excess functions for the ethanol–water system at 25°. x_2 = mole fraction of* EtOH.

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[35] I. Prigogine and R. Defay, "Chemical Thermodynamics", trans. Everett, D. H., Longmans Green & Co., London, 1954, p. 392.

[36] Landolt-Bornstein, "Zahlenwerte und Funktionen", Springer, Berlin, 1960, vol. II, pp. 406 ff.

[37] J. S. Rowlinson, "Liquids and Liquid Mixtures", Butterworths Scientific Publications, London, 1959.

the simpler, but closely related, homogeneous alcohol–water systems. In these, it appears that, at room temperature, entropy dominates the energy–entropy balance which controls the excess free energy, and therefore the overall deviations from ideal behaviour, but there is strong indication that this balance is itself sensitively dependent on temperature.

Interpretation of the thermodynamic excess functions is not eased by the virtual certainty that they are, at the simplest, the resultants of opposed contributions. Thus, if when a mixture is made, some hydrogen bonds are broken endothermically and new ones are made exothermically, ΔH^M will be a difference between two much larger thermal effects. Over the whole composition range, the relative magnitudes, and even the origins, of such contributions may vary widely, and uncertainty must attend all "interpretations by inspection" of the excess functions. Nevertheless, some tentative conclusions, to be tested by independent evidence, can be drawn in the following way.

To consider first a mixture rich in ethanol, and arbitrarily choosing $x_2 = 0{\cdot}8$, it may be noted that the number of "moles" of hydroxyl group per mole of liquid phase for pure water, the mixture, and pure ethanol are 2, 1·2, and 1, respectively. It is more significant that the *concentrations* of protons available for hydrogen bonding in these liquids are, in the same order, 111, 24, and 17 mole l^{-1}. It is not conceivable that in such a mixture any remnant of the three-dimensionally hydrogen bonded water structure can remain, and it is therefore evident that the formation of the mixture must be attended by a wholesale endothermic destruction of water–water hydrogen bonds yet the mixing occurs with evolution of heat and appreciable relative entropy loss. Normally, this would denote the establishment of order by the satisfaction of attractive forces, and, in the present case, this indication is reinforced because of the concomitant bond breaking and loss of order involved in the "depolymerisation" of the water. It may be inferred that rather strong and well organised ethanol–water hydrogen bonds are formed. Since ethanol is, statistically, twice as likely to act as a proton acceptor than as a donor, and since the inductive effect of the alkyl group may promote the same tendency, it is probable that in this mixture ethanol is "more basic than water": this, however, is a vexed question discussed in a later section.

Figure 3 shows how the excess functions for the same system change with rising temperature. For the same mixture of $x_2 = 0{\cdot}8$, ΔH^M and ΔS^E become more positive and ΔH^M changes in sign, so that the mixing becomes endothermic at the higher temperatures. ΔG^E is hardly changed because of compensation between ΔH^M and $T\Delta S^E$. $\Delta C_p{}^M$ is positive but not large. This, in general, is consistent with an expected change in balance, with rising temperature, between inter-component bond- and structure-making effects (thermally vulnerable) and bond-breaking, disordering effects, in favour of the latter. If attention is given to mixtures of progressively decreasing x_2, it appears that the same description of events

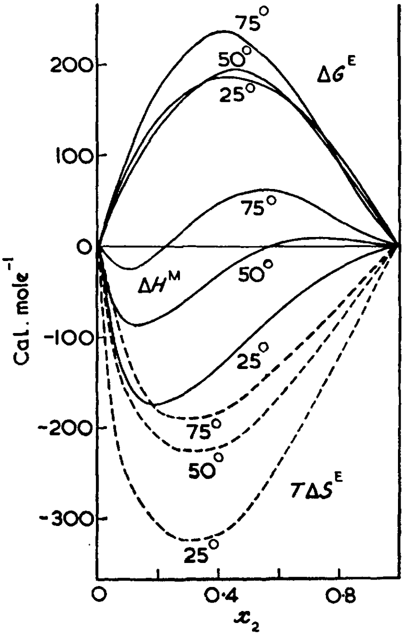

FIG. 3. *Variation with temperature of the excess functions of the ethanol–water system.*

associated with mixing would equally apply to the larger, but similarly disposed excess functions which are at first encountered. This may be so, but caution is necessary in case some new factor enters in passing from one composition range to another, and it is best, in the immediate context of discussion, not to depart from unambiguously alcohol-rich mixtures. This point is well illustrated by the excess functions for the Bu^tOH water system at 25°, shown in Figure 4. In general comparison with the ethanol–water functions (Figure 2), it is seen that ΔG^E is a little more positive, but remains a nearly symmetrical function of x_2. ΔS^E is not more negative, but its minimum lies at lower x_2. In contrast to these minor differences, the ΔH^M—x_2 curve is markedly changed; although not dissimilar to that for the ethanol–water system at 75° (Figure 3), the striking features of the maximum in the alcohol-rich region (mixing endothermic) and the sharp minimum in the essentially aqueous region (mixing exothermic) emphasises the necessity for separate consideration of at least these two composition ranges, for they may involve quite separate problems. Continuing, therefore, to confine attention to an alcohol-rich mixture of $x_2 = 0{\cdot}8$, the change of ΔH^M on passing from ethanol to t-butyl alcohol can be well understood in terms of the effects already distinguished. There is evidence that $MeOH < EtOH < Pr^nOH < Bu^tOH$ is the order of increasing proton-accepting facility[38] so that hydrogen bonding between Bu^tOH and water

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[38] W. Gerrard and E. D. Macklen, *Chem. Rev.*, 1959, **59**, 1105; L. P. Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.

should be energetically favoured; it may, however, be subject to the same steric limitation which restricts the degree of association in the pure alcohol. Fewer, if stronger, inter-component bonds are therefore to be expected in this mixture, with, perhaps, a reduced exothermic contribution to the overall ΔH^{M}. The major shift in balance between the main thermal processes of mixing is, however, evident from the "proton concentrations" in water, the mixture, and the pure alcohol, to be compared with those previously quoted for the ethanol–water system; they are 111, 15 and 13 mole l.$^{-1}$ respectively. Even more extensive hydrogen-bond breaking must be involved in the formation of this mixture, making a larger positive contribution to ΔH^{M}. The dielectric constants of the ethanol- and t-butyl alcohol–water mixtures, each of $x_2 = 0{\cdot}8$, are 27·5 and 11·3; the considerable difference between these values lends general support to the above view.

Comparison of dioxan–water (Figure 5) and Bu^{t}OH–water (Figure 4)

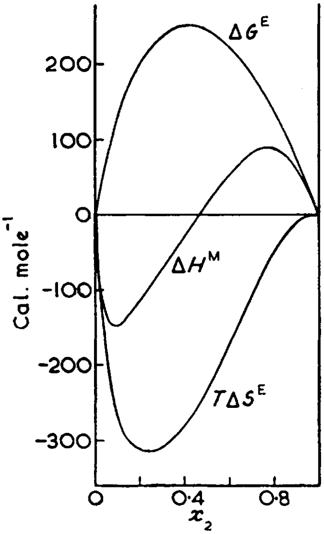

FIG. 4. *Thermodynamic excess functions for the* Bu^{t}OH–H$_2$O *system at* 25°. x_2 = *mole fraction of* Bu^{t}OH.

systems at 25° reveals almost indistinguishable thermodynamic characteristics. Since dioxan is not an associated liquid, it may be inferred that in neither case can depolymerisation of the nonaqueous component play any significant part in determining the excess functions of mixing. If excess of water is added to Bu^{t}OH, then, of course, depolymerisation of the alcohol must ensue, but bond-breaking is matched by bond-making, and there is no such far-reaching effect as that which accompanies the addition of excess of Bu^{t}OH to water. It is probable that this asymmetry in the effects of "adding the other component" extends in greater or less degree to all the other alcohol–water systems of interest.

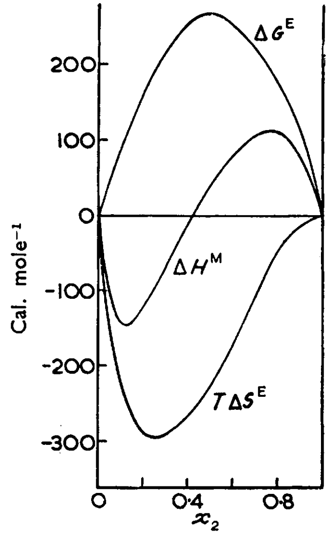

FIG. 5. *Thermodynamic excess functions for the dioxan–water system at 25°.* x_2 = *mole fraction of dioxan.*

The line of thought about alcohol-rich mixtures which has been followed has led to the view that depolymerisation of one highly associated component, and strong inter-component attraction are dominant factors in the formation of alcohol–water mixtures. If this is so, relationships should be apparent on comparison with systems which are separately dominated by these same factors, one at a time. The acetone–chloroform and methanol–carbon tetrachloride binary systems provide the basis for such a comparison; they are illustrated side-by-side in Figure 6. In the first case, one-to-one hydrogen bonding occurs between the components, giving rise to symmetrical relative entropy loss and heat evolution. In the second case methanol is depolymerised by carbon tetrachloride, with heat absorption—not, however, very easily, for the maximum in ΔH^M is not reached until excess of carbon tetrachloride has been added, and there is relative entropy loss due to occlusion of molecules of the "diluent" in a network of polymer chains. Inspection of the pair of diagrams in Figure 6 shows that, with suitable adjustment of scales of ordinates, combination of the two could provide excess function curves resembling those for alcohol–water systems (*cf.* Figures 2—4). Whilst this general resemblance may be regarded as more or less satisfactory, attempts to improve it by reasonable adjustment of the stoicheiometry of maximal inter-component action (possibly 2:1, instead of 1:1) are not very successful, and, in the present case, they infringe the cautionary rule that inferences drawn from behaviour within a restricted composition range (alcohol-rich) cannot safely be extended outside of that range.

That some third important factor needs identification is suggested by the inter-comparison of alcohol–water systems made in Figure 7, in terms of $\Delta H^{M} - x_2$ curves at 25°. ΔH^{M} is the most characteristic of the excess functions to use for this purpose—for the others, the $\Delta G^{E} - x_2$ curves show nearly symmetrical maxima in all four cases, notably lower for the

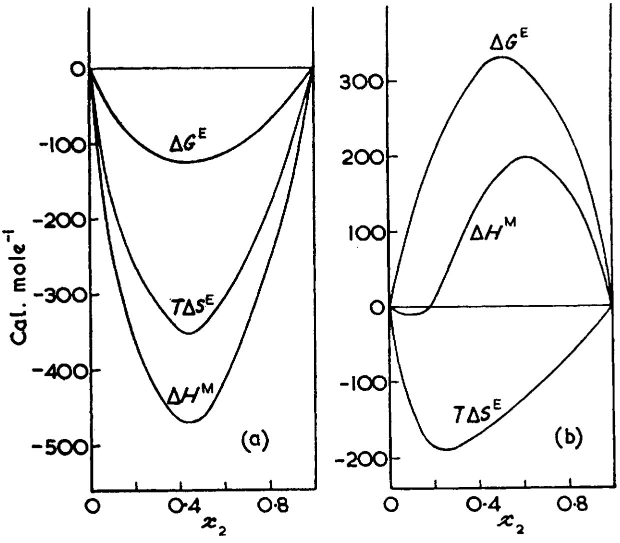

FIG. 6. (a) *Thermodynamic excess functions of the acetone–chloroform system at* 25°. x_2 = *mole fraction of* $CHCl_3$.
(b) *Thermodynamic excess functions of the methanol–carbon tetrachloride system at* 25°. x_2 = *mole fraction of* CCl_4.

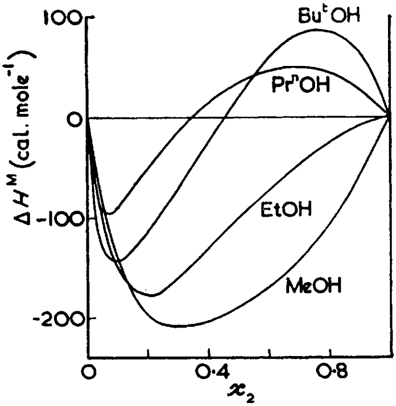

FIG. 7. *Heats of mixing* (ΔH^{M}) *with water at* 25° *of* MeOH, EtOH, Pr^{n}OH, *and* Bu^{t}OH.

methanol–water system (which forms no azeotrope) than for the others; the $\Delta S^E - x_2$ curves show minima shifting to lower x_2 in homologous sequence, in the compensatory way ($\Delta G^E = \Delta H^M - T\Delta S^E$) required by the uniform near-symmetry of ΔG^E. It is seen that, for high x_2, ΔH^M varies from one alcohol to the next in the regular way to be expected from the even trends of hydrogen-bonding facility and of the major "proton dilution effect" that has been discussed. On the other hand, at low x_2, there is a remarkable inversion of order between Pr^{n}OH and Bu^{t}OH which suggests the entry of some stereochemically-sensitive effect. Why maximum heat evolution on mixing should occur when water is in quite large excess calls for explanation: that Bu^{t}OH best hydrogen-bonds with many water molecules at a time can be dismissed as an absurdity. The conclusion can hardly be avoided that occurrences in the low-x_2 region must be examined on the assumption that it is an essentially *aqueous* region: one in which a resistance to depolymerisation and a preservation of structure is based upon the three-dimensional co-operation so fundamental to the nature of liquid water. The corollary to this is the concept that water is able to act as host to molecules which, although alien, have a certain affinity for water. With increasingly extensive invasion by the foreign species, however, rather sudden "co-operative failure" of structure retention is to be expected—the sooner the more "foreign" the invader. This seems to fit in quite well with the main features of Figure 7. It is at least certain that the predominantly aqueous composition range of alcohol–water mixtures requires separate and careful study—with little doubt in terms of what is known about the structure of water and its reaction to the presence of uncharged solutes.

Transfers of the monohydric aliphatic alcohols (C_1—C_6) between suitably standardised ideal gas and infinitely dilute aqueous solution states are accompanied by entropy and enthalpy changes, per mole of alcohol transferred, which are linearly related to each other. Recent revision of the older data[39] has modified, but not worsened, the linearity of the ΔS^0–ΔH^0 plot. Such relationships between these thermodynamic functions of solution (or evaporation) processes are not uncommon, but appear to be of two kinds. The first to be recorded[40] relates to the entropies and enthalpies of solution of a given solute in a set of different solvents. The second (oddly) to be observed is concerned with a set of different solutes in a given solvent; it is more widespread in incidence and has become known as the Barclay and Butler rule.[41] A possible view[42] is that the two effects have different origins. The first arises when solvent cannot be properly distinguished from solute in a set of binary systems with a common component, and behaviour is graded mainly by the enthalpy of intercomponent action. The second, on the other hand, is found when there is

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[39] R. Aveyard and A. S. C. Lawrence, *Trans. Faraday Soc.*, 1964, **60**, 2265.
[40] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1333.
[41] I. M. Barclay and J. A. V. Butler, *Trans. Faraday Soc.*, 1938, **34**, 1445.
[42] D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 1965, 649.

no ambiguity in defining the solvent, which remains in predominant control of all the systems it forms with the members of a set of solutes; solvent–solvent, rather than solute–solvent, interactions remain decisive (*cf.* Bell[43]). The distinction between the two cases may coincide with that between ascendency of enthalpy control or of entropy control, respectively. The latter, *inter alia*, may well be relevant to the infinitely dilute aqueous alcohol systems to an extent depending on the identity of the alcohol.

The Barclay and Butler rule, which applies to the evaporation of pure liquids as well as that of solutes from solutions, was given a theoretical basis in Frank's free-volume theory of liquids:[44] the treatment made it possible to establish a "B–B line", relating ΔS^0 with ΔH^0, representing normal behaviour. It was the highly abnormal behaviour of nonpolar solutes (rare gases, hydrocarbons, *etc.*), evaporating from water as solvent (ΔS^0–ΔH^0 line half as steep again, displaced positively on the ΔS^0 scale by 10 cal. deg.$^{-1}$ mole^{-1} or more), that led to the original "iceberg" concept which, if subsequently modified, has lost nothing in thermodynamic reality. It is of particular interest in the present context that the ΔS^0–ΔH^0 line for the evaporation of the alcohols from aqueous solution runs, even steeper, from close to the B–B line to that for the non-polar solutes. Water (evaporating from itself) is near to the B–B line and is also (in its guise as the zeroth alcohol) close to the alcohol line. On the latter, methanol and ethanol follow in sequence, then the other alcohols in an order determined nearly as much by stereochemistry as by homology, until n-pentyl alcohol is reached (behaving more like a hydrocarbon than an alcohol) on the "non-polar line". Clearly, each succeeding alcohol more and more resembles a non-polar solute, with solubility increasingly under entropy control,[45] in a manner dependent on molecular size and shape.[46] It seems that these geometrical factors (describing the demand for "Lebensraum" made by the solute molecule on the water) primarily determine ΔS^0, almost independently of the chemical nature of the solute. Thus, ethane, methyl chloride, and methanol have the same ΔS^0 within experimental error, but the ΔH^0 values vary widely, falling in the expected sequence of increasing solute–solvent direct interaction.[47] It is therefore a reasonable interpretation of the steep alcohol line that it is a function of both Evans and Polanyi and Barclay and Butler "entropy–enthalpy linking": hydrogen bonding displaces ΔH^0 in graduated ratio to the enhancement of ΔS^0 mainly attributable to the "solvent reaction" peculiar to water. That the latter is the previously invoked "third factor" is otherwise confirmed in the sequel.

That other structural subtleties may remain to be solved in relation to

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[43] R. P. Bell, *Trans. Faraday Soc.*, 1937, **33**, 496.

[44] H. S. Frank, *J. Chem. Phys.*, 1945, **13**, 493.

[45] J. A. V. Butler, *Trans. Faraday Soc.*, 1937, **33**, 229.

[46] J. A. V. Butler, C. N. Ramchandani, and D. W. Thomson, *J. Chem. Soc.*, 1935, 280.

[47] J. A. V. Butler and W. S. Reid, *J. Chem. Soc.*, 1936, 1171.

these systems is, however, strongly indicated by the observation of Franks and Ives[48] that *traces* of MeOH, EtOH, Pr^nOH, but not Bu^nOH, raise the interfacial tension between hexane and water at temperatures below, but not above, 35°. Pointing to other indications that this temperature may be structurally critical for water itself, the authors, whilst unable to choose between alternative explanations for these remarkable effects, noted that surface tension and vapour pressure deviations from ideality should be of opposite sign.[49] They were led to suggest that very dilute aqueous solutions of the lower alcohols might show negative deviations from Raoult's law. The existence of such negative deviations (although not quite of the kind anticipated) has recently been proven by the extensive studies of Knight.[50]

Knight has measured freezing-point depressions, heats of mixing and heat capacities of dilute aqueous solutions of all eight C_1—C_4 alcohols, and from his results (which agree well with the best existing data where comparison can be made) has calculated Raoult's law activity coefficients, γ_1, of the solvent. This method is of greatly superior accuracy (errors of 0·2% in ΔT, 0·02% in x_2, 1% in ΔH^M and C_p lead to no more than 0·02% uncertainty in γ_1) compared with the use of partial vapour-pressure measurements. The latter are at a disadvantage in the high-dilution region of greatest interest, and require correction for vapour non-ideality if quite large errors in γ_1 are to be avoided (*e.g.* $\sim$2% in the analogous dioxan–water system[51]). The new data show that, for most of the systems studied $\left(\frac{\partial \ln \gamma_1}{\partial x_2}\right)_T$ is negative at low temperatures and low alcohol concentrations, but changes sign with increasing x_2, eventually leading to positive values of $\ln\gamma_1$. This is illustrated for the case of the $Pr^iOH–H_2O$ system in Figure 8a, which shows $\ln\gamma_1$ as a function of x_2 at several temperatures. The results indicate that, at 0°, the partial pressure curve for water must cross the Raoult's law line near $x_2 \sim 0·08$. Such behaviour, although not disallowed by the Duhem–Margules equation, is only rarely observed for liquid mixtures, and McGlashan[52] has recently reviewed such apparently abnormal behaviour. It appears, however, that the activity coefficients of the components in alcohol–water mixtures cannot be represented by the three-parameter equations which are normally used to relate $\ln\gamma_i$ with x_i and which, as McGlashan shows, can also account for the crossing of the Raoult's law line. Figure 8b shows typical data (derived by one of the standard modifications of the Gibbs–Duhem relation[53]) for the activity, a_2, of Pr^iOH in the same system, in comparison with the Henry's law line. At low temperature the volatility of the alcohol becomes

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[48] F. Franks and D. J. G. Ives, *J. Chem. Soc.*, 1960, 741.

[49] I. Prigogine and R. Defay, *Bull. Soc. chim. belges*, 1944, **53**, 115.

[50] W. S. Knight, Ph.D. Thesis, Princeton University, July 1962; (*Diss. Abs.*, 1963, **24**, 993).

[51] A. L. Bacarella, A. Finch, and E. Grunwald, *J. Phys. Chem.*, 1956, **60**, 573.

[52] M. L. McGlashan, *J. Chem. Educ.*, 1963, **40**, 516.

[53] M. L. Lakhanpal and B. E. Conway, *Canad. J. Chem.*, 1960, **38**, 199.

higher with increasing x_2 than expected by Henry's law, but the opposite effect is observed at the higher temperature: this leads to $a_2(x_2)$ curves which cross the reference line, giving rise to pseudo-ideal solutions.

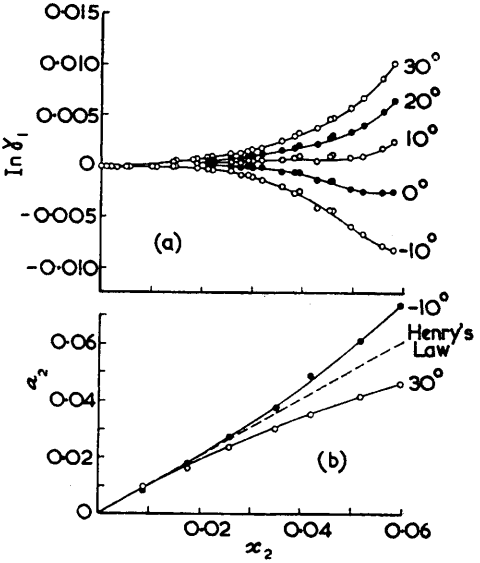

FIG. 8. *The* Pr^iOH-H_2O *system:* (a) $\ln\gamma_1(x_2)$ *at several temperatures,* (b) a_2 (x_2) *at* −10° *and* 30°, x_2 = *mole fraction of* Pr^iOH, γ_1 = *Raoult's law activity coefft. of* H_2O, a_2 = *activity of* Pr^iOH.

For the n-alcohols, the extent of this anomalous behaviour decreases with successive homologues, Bu^nOH behaving normally at all the temperatures. The most marked abnormalities were found for secondary and tertiary alcohols, increasing in the sequence Bu^sOH Pr^iOH Bu^tOH, again illustrating the considerable influence of the shape, as well as the size, of the solute molecules. A similar influence appears in the differential heats of solution at infinite dilution; selected values, at a mean temperature of 2°, are: MeOH, −2·2; EtOH, −3·2; Pr^nOH, −3·6; Pr^iOH, −4·4; Bu^nOH, −3·7; Bu^tOH, −5·7 kcal. mole^{-1}. These quantities reflect the initial steepness of the $\Delta H^M(x_2)$ curves, and (allowing for alcohol depolymerisation) the very exothermic consequences of introducing alcohol molecules to pure water, particularly at a low temperature.

It would, at present, be unwise to try to explain these remarkable results beyond drawing the inferences that two or more competing influences are at work, and that, for these systems, the ranges −10° to 30° in temperature and 0 to 0·2 in x_2 may be *structurally* very wide indeed.

It might be expected that heat capacity, more than any other property, would be sensitive to the complexity of alcohol–water interactions, but there is a scarcity of reliable data. It is, however, established that, except for methanol, C_P for alcohol–water mixtures increases monotonically with x_2. In dilute aqueous alcohol solutions, the effect of temperature on C_P is small, but C_P passes through a shallow minimum near 40°: this can be seen from Figure 9, relating to data for the $Pr^iOH–H_2O$ system.[54] It is also noteworthy that the dependence of C_P on x_2 changes greatly with temperature at $x_2 > 0{\cdot}2$ but not $<0{\cdot}2$; systems of $x_2 < 0{\cdot}2$ remain essentially water-like in behaviour, perhaps because of the resistance to a point, of the water structure to disruption. The $MeOH–H_2O$ system, however, shows the peculiarity of $C_P(x_2)$ isotherms with maxima shifting to higher x_2 with rise of temperature.[50,54,55]

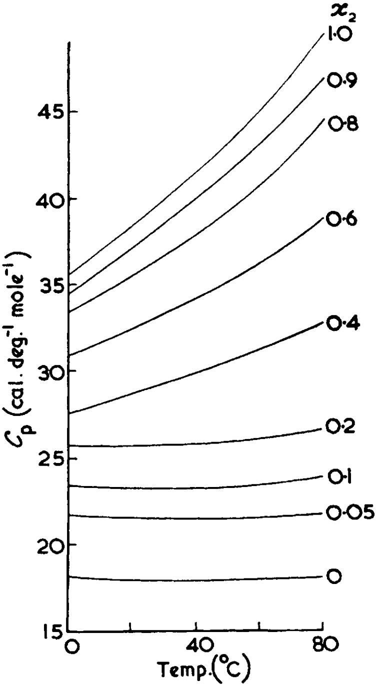

FIG. 9. *The* $Pr^iOH–H_2O$ *system. Heat capacities at constant pressure as function of temperature for various* x_2.

Heat capacity at constant pressure contains an internal work contribution $\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial E}{\partial V}\right)_T$ which may greatly confuse the issue; for dilute aqueous alcohol solutions at low temperatures, it is small, but changes sign and becomes increasingly significant with rising temperature. For this reason, C_V may be easier to interpret, and has been studied in relation to liquid

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[54] T. Katayama, *Chem. Eng.* (*Japan*), 1962, **26**, 361.
[55] E. Bose, *Z. phys. Chem.*, 1907, *A*, **58**, 585.

mixtures by Staveley, Hart, and Tupman.[56] Removal of intramolecular contributions from C_V leaves a term containing major contributions from molecular rotation (C_r) and, if it occurs, association (C_a). For associated liquids, C_a will shift according to the dependence of the association equilibria on temperature. Increase of temperature covering the entire range from complete association to complete dissociation will see C_a rise from zero, pass through a maximum, and return to zero again as all the stages of endothermic depolymerisation are traversed. The maximum will occur at a lower temperature, and its height will be less, the weaker the association. If this is very feeble, only the falling part of the $C_a(T)$ curve may be observable: if strong, only the rising part. The latter is the case with pure ethanol. In the light of this reasoning, ΔC_V^M data for the EtOH–H_2O system, shown in Figure 10 are of great interest. Since all three $\Delta C_V^M(x_2)$ curves return to zero at $x_2 = 0$ and 1, it is evident that the isotherm for 20° must show a high and narrow peak at $x_2 < 0{\cdot}2$, and another, perhaps less marked, at $x_2 > 0{\cdot}8$. Both of these peaks have vanished at 70°, and somewhere within the unexplored "end" composition ranges, the temperature coefficients of ΔC_V^M must be large and negative. Because of the considerable height of the "aqueous peak" at $x_2 < 0{\cdot}2$, this speaks less for the intrinsic weakness of the association that is presumably concerned than for its peculiar vulnerability to rise of temperature. Such a "falling to pieces" tendency is, of course, typical of the *co-operative* order–disorder transformation involved in the "melting" of "icebergs" and, indeed, excessive apparent heat capacity commonly accompanies "hydrophobic hydration". The smaller peak at $x_2 > 0{\cdot}8$ requires a different explanation since there is little evidence for co-operative *structures* in essentially alcoholic media. Molecular rotation, by no means unhindered in liquids, may, however, be specially significant as a

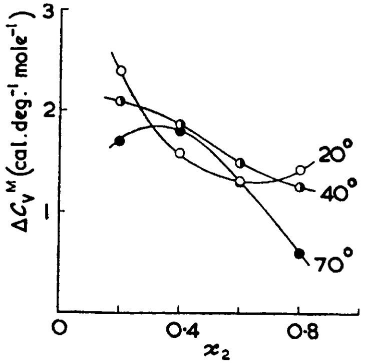

FIG. 10. *Excess heat capacity at constant volume for the* EtOH–H_2O *system at three temperatures.*

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[56] L. A. K. Staveley, K. R. Hart, and W. I. Tupman, *Discuss. Faraday Soc.*, 1953, **15**, 130.

co-operative *process* in these alcoholic solutions of water: in this case C_r, rather than C_a, may be involved in the second peak. Support for this will be found in evidence, adduced later, on the nature of these mixtures of high x_2.

It is noteworthy that rise of temperature from 20° to 40° makes a profound change in the $\Delta C_V{}^M(x_2)$ isotherm, but less so than the rise to 70°, where a complete inversion of curvature has occurred, leaving only one broad maximum at $x_2 \sim 0{\cdot}33$. Here the value of $\Delta C_V{}^M$, initially positive, clearly passes through a maximum with rising temperature—this may be the reflexion of intercomponent association in a region of "structural compromise".

P–V–T Relations

When ethanol and water are mixed, there is a contraction in volume which might seem to reflect the strength of intercomponent attraction, but detailed study shows that there are far more complex effects than this to explain. At 0°, the change in molar volume of ethanol on transfer from the pure liquid state to that of infinitely dilute solution in water ($\bar{V}_2{}^0 - V_2{}^0$) is —4·0 cm.³: the corresponding change for the transfer of water to infinitely dilute solution in ethanol ($\bar{V}_1{}^0 - V_1{}^0$) is —4·3 cm.³ The symmetry these volume losses might suggest is illusory. Not only is the volume loss of the water proportionally the greater, but the partial molar volume-mole fraction isotherms are quite dissimilar for the two components. These isotherms are shown in Figure 11, in comparison with those for the

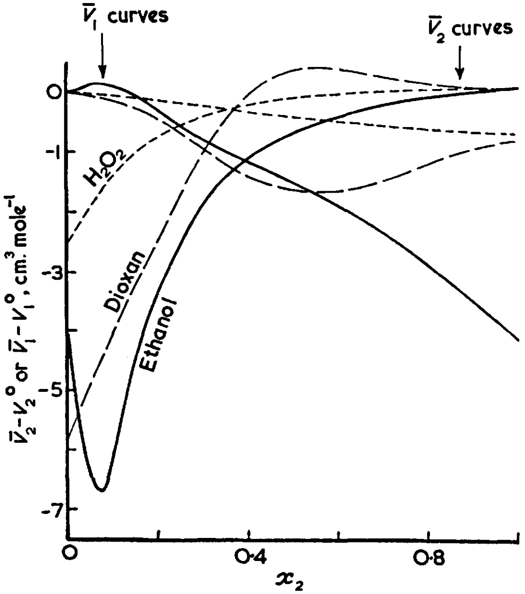

FIG. 11. *Partial molar volumes for ethanol–, dioxan– and hydrogen peroxide–water systems at* 0°, 25°, *and* 0°, *respectively.*

dioxan–water[57] and hydrogen peroxide–water[58] systems. Both of the latter, with strongly interacting components, show negative $\bar{V}_1^0 - V_1^0$, which therefore appears to be less remarkable than the minimum in the $\bar{V}_2(x_2)$ isotherm for the ethanol–water system at $x_2 \sim 0{\cdot}08$. In conformity with the Gibbs–Duhem relation, the $\bar{V}_1(x_2)$ isotherm simultaneously passes through a maximum. At this composition, ethanol added to the system contracts; water added to it expands. At high dilution $\partial \bar{V}_2/\partial x_2$ is negative, whereas for the other two systems it is positive.

A new method for precise evaluation of partial molar quantities[59] has led to the results shown in Figure 12. For the EtOH–H_2O system, it is

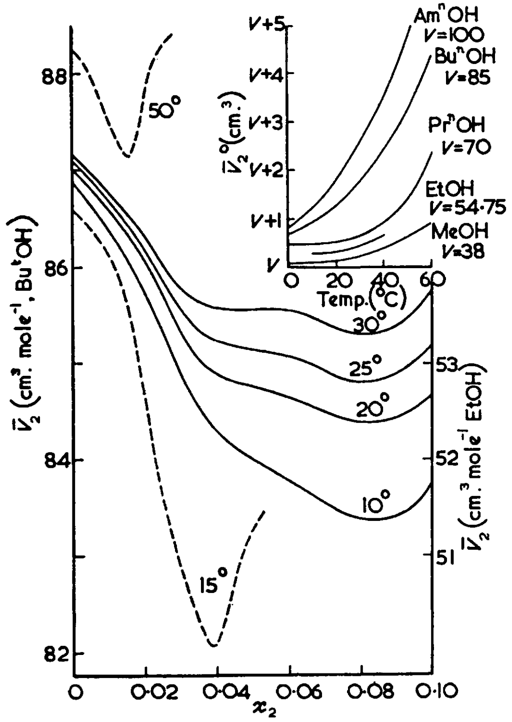

FIG. 12. *Partial molar volumes of* EtOH (———) *and* Bu^{t}OH (- - - -) *in admixture with water. Inset: partial molar volumes at infinite dilution of the n-alcohols as functions of temperature.*

seen that the shapes of the $\bar{V}_2(x_2)$ isotherms are more complex than previously recorded. There are good grounds for believing that the inflexions near $x_2 = 0{\cdot}03$ are real (despite minor inconsistencies in the density data); they are accentuated by temperature rise to the extent that the 30° isotherm

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[57] G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, 1957, **53**, 921; J. S. Rowlinson, "Liquids and Liquid Mixtures", Butterworths, London, 1959, p. 133.

[58] A. G. Mitchell and W. F. K. Wynne-Jones, *Discuss. Faraday Soc.*, 1953, **15**, 161.

[59] F. Franks and H. H. Johnson, *Trans. Faraday Soc.*, 1962, **58**, 656.

shows a shallow maximum. The minimum, which is at $x_2 = 0{\cdot}085$ at 10°, shifts slightly to lower x_2 and becomes less deep as temperature rises. The latter trends are shown more strongly by Bu^{t}OH which also, compared with EtOH, has the greater $\bar{V}_2{}^0 - V_2{}^0$ ($-6{\cdot}0$ cm.^{3} mole^{-1}, *cf.* $-3{\cdot}8$ cm.^{3} mole^{-1}, at 30°) and the $\bar{V}_2$ minima at much lower x_2. The temperature-dependence of the partial molar volumes is of particular interest. The inset to Figure 12 shows Alexander's data[60] for $\bar{V}_2{}^0$ of the n-alcohols as a function of temperature. For the alcohols with not more than three carbon atoms, $\bar{V}_2{}^0$ is nearly independent of temperature below, but not above, 30°. $\partial \bar{V}_2{}^0 / \partial x_2$ is positive and large from 40° to 60° for the C_3—C_5 normal alcohols. A very different situation is found at finite, rather than infinite, dilution. Thus, for ethanol in solution in water at the mole fraction corresponding with the minimum in $\bar{V}_2$, the partial molar expansibility is very large—about twice that of the pure alcohol. It may be preferable to view this from the angle that alcohol contraction (and water expansion) may, in this x_2 region, stem from some structural feature which is very adversely affected by rise of temperature. This sensitivity seems not to be confined, in contrast to the case of the lower alcohols at $x_2 \rightarrow 0$, to temperatures above 30°. In attempting to divide the x_2 scale as a whole into ranges in which distinct structural effects predominate, it may be advisable to subdivide the "essentially aqueous" region, discriminating between the dilute and the extremely dilute aqueous solutions of the alcohols.

Care is needed in choosing between alternative interpretations of "contraction of the solute" on solution in water, if only because the problem of the structure of water itself is unsettled. There are, however, analogies which can hardly be fortuitous between alcohols in infinitely dilute aqueous solution and the very low concentrations of hydrocarbons (or other non-interacting solutes) that water will accept into solution. Thus, the unexpectedly low partial molar volumes of the hydrocarbons in aqueous solution[61] can be set beside the negative values of $\bar{V}_2{}^0 - V_2{}^0$ for the alcohols, supplementing the similarity in the enthalpy–entropy relations of solution (or evaporation), which becomes increasingly faithful as the change from water-like to hydrocarbon-like behaviour is spanned on passing from the lower to the higher alcohols. It may be inferred that the "solute contractions" in the two cases have nothing to do with inter-component attraction, but have a common origin in "hydrophobic hydration". Unfortunately, there is no general agreement on the precise nature of this effect, nor even on the suitability of this name for it. There can be no doubt, however, that the "openness" of water and its facility of structure-making lie at the root of the matter. Eley[62] expressed the view that a mole of water contains 9 cm.^{3} of empty space provided by ice-like cavities, ready for small, non-polar solute molecules to enter, with loss of

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[60] D. M. Alexander, *J. Chem. Eng. Data*, 1959, **4**, 252.

[61] J. C. Gjaldbaek and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1950, **72**, 1077; W. L. Masterton, *J. Chem. Phys.*, 1954, **22**, 1830.

[62] D. D. Eley, *Trans. Faraday Soc.*, 1939, **35**, 1281, 1421.

effective volume and without the normal prerequisite of cavity formation with its energy requirement. Energy needed to enlarge a cavity could be partly supplied by the formation of hydrogen bonded structures round it. It was thought that water begins to lose this abnormal solvent reaction to non-polar solutes at about 50°—in the case of alcoholic solutes, this may be reflected in the enhanced $\partial \bar{V}_2^0/\partial T$ above this temperature (inset to Figure 12).

Since the advent of the Frank and Evans "icebergs"[15] some emphasis has been laid on local structure-promotion in water by inert solute molecules. The view that this may be due to stabilisation by "packing out" of open structures, otherwise vulnerable to being thermally crushed into closer-packed disorder, has been modified in various ways. Frank and Wen[2] have proposed what might be called an "oil on troubled waters" action of inert solute particles. Because of their feeble polarisability and consequent inability to transmit cluster-disrupting influences, they have a local "calming effect" and, by disfavouring high-energy fluctuations, afford "boundary protection" to ice-like clusters adjacent to them. Némethy and Scheraga[6] consider that less than fully hydrogen-bonded water molecules seek to increase their co-ordination and lower their energy levels by alternative, rather strong, water-water van der Waals association, which opposes the establishment of nearest neighbour juxtaposition with solute molecules. Only a fully hydrogen-bonded water molecule can assume a lowered energy state by accepting a solute particle as a "fifth neighbour": when it does so, the latter finds itself "embraced" in an incomplete cavity at the boundary of a cluster, in a situation stabilised somewhat by weaker water–solute van der Waals attraction. This is in line with Namiot's suggestion[63] that inert solutes interact, not with all water molecules, but only with clusters. Glew[64] on the other hand, argues strongly that, just as bulk water can be regarded as retaining remnants of the ice structure, water under the influence of an inert solute particle can be regarded as retaining remnants of the appropriate gas-hydrate structure.

Quite other views are also held. Aranow and Witten[65] draw attention to the restriction imposed by an aqueous environment on the motions of a hydrocarbon group, and to the constraint upon it to assume a conformation minimising the hydrocarbon–water "interfacial area". Loss in entropy and volume might well originate in the solute—not, however, in the case of the inert gases. Perhaps, more recently, not enough consideration has been given to the formation of a cavity to accommodate the solute molecule. It has been suggested[42] that, in addition, to the promotion of co-operative, temperature-sensitive ice-likeness, a more general "tensile cavity" effect should be taken into account, involving neither more nor less structure promotion than occurs in the generation of a free (rather than an internal) liquid surface. It would vary between zero for the ideal solution case and a

[63] A. Yu. Namiot, *J. Struct. Chem.*, 1961, **2,** 381, 444.
[64] D. N. Glew, *J. Phys. Chem.*, 1962, **66,** 605.
[65] R. H. Aranow and L. Witten, *J. Phys. Chem.*, 1960, **64,** 1643.

maximum for the "hard sphere", non-interacting solute, as discussed by Rice.[66] It may be noted, however, that there is much evidence for enhanced structure at the surface of a liquid,[67] particularly in the case of water.[68]

In the most recently developed theory of the structure of water[7] an equilibrium is envisaged between open, hydrogen-bonded clusters (half-life $\not> 10^{-10}$ sec.) and a dense, non-hydrogen-bonded fluid. A hydrocarbon solute is distributed between two situations—occupation of interstitial sites in the clusters, and formation of a regular solution with the dense fluid. As the size of the hydrocarbon molecule is increased, fewer sites are able to accommodate it, and the fraction of solute enclosed in clusters decreases, notwithstanding that interstitial solution is energetically favoured.

At this stage in the development of ideas in this field, a rather generalised explanation of the space-saving effect is required, consistent with the wide incidence of the characteristic thermodynamic features of the solution of substances of low polarity in water. It is therefore proposed, for purposes of present discussion, that the effect need not depend exclusively on use by solute molecules of the pre-existing cavities natural to pure water (although this may be preferred), nor to the formation of cavities peculiar to the structures of a limited number of stable gas-hydrates. Instead, it is envisaged that, in virtue of its versatility in three-dimensional hydrogen bonding, water may have an intrinsic cavity-stabilising function that meets, in greater or lesser degree, the steric requirements of any solute molecule, perhaps better for a spherical molecule than for one of another shape. In effect, a solute molecule will control and protect the hydrogen-bonded packing of water molecules in its vicinity, replacing by its own volume one or more of the natural cavities that would otherwise have been present, with appropriate overall economy of space.

An additional problem arises in the case of amphipathic solute molecules, such as those of the alcohols, which possess both hydrophobic and hydrophilic functions—how hydrophobic hydration and solute–solvent hydrogen-bonding are to be reconciled, and whether there is opposition or co-operation between these two effects. This problem may be cautiously explored in terms of studies of clathrate hydrates.

Until recently, it was believed that these crystalline hydrates were formed only by compounds which do not interact strongly with water, but new evidence shows that this is not the case. Thus, elucidation of the crystal structures of the hydrates of quaternary ammonium halides[69] has shown that they exist in the same well-known pentagonal dodecahedral form as the hydrates of the inert gases. In the cases of $Bu_4NF,30H_2O$ and the

[66] S. A. Rice, *J. Chem. Phys.*, 1947, **15**, 875.

[67] J. C. Henniker, *Rev. Mod. Phys.*, 1949, **21**, 322.

[68] B. Stuke, *Z. Elektrochem.*, 1959, **63**, 140; W. Göring, *Z. Elektrochem.*, 1959, **63**, 1069, 1077; N. H. Fletcher, *Phil. Mag.*, 1962, **7**, 255.

[69] R. K. McMullan and G. A. Jeffrey, *J. Chem. Phys.*, 1959, **31**, 1231.

corresponding bromide, it appears that the anion is incorporated as a unit in the clathrate framework which is interstitially stabilised by the alkylated cation. With the proviso that crystal and solution states may differ, this suggests that ionic (and, still less, dipolar) fields are not necessarily inimical to hydrophobic hydration. It has been reported by Glew[70] that ethylene oxide and tetrahydrofuran form crystalline hydrates of the clathrate type: freezing-point studies led him to propose that for each solute the unbonded electron pairs of the oxygen atom participate in hydrogen-bond formation, while the nonpolar part of the molecule stabilises a polyhedral cavity. On the other hand, recent *X*-ray studies[71] indicate that the ethylene oxide molecule is *not* bonded to its clathrate cage, but resides within it just like an inert, interstitial guest, despite its proton-accepting property. Since ethylene oxide probably owes its complete miscibility with water to this same property, either there is an important difference between crystalline hydrate and solution states, or alternative solution states exist. In general, these somewhat surprising results must widen our views on the possible interactions between water and solutes of various kinds, and it may be necessary to envisage alternative cases: on the one hand non-co-operation, on the other, specific participation by a solute in forming the structure of its own clathrate cage.

The examination of alcohol–water systems in this context is unrewarding. Alcohol hydrates have been abundantly reported in the older literature, but the only one subjected to crystal structure analysis, $MeOH,\frac{1}{2}H_2O$[72] is not of clathrate type. Hydrates of Bu^tOH and of $CMe_3{\cdot}CMe_2{\cdot}OH$ are known (it may be relevant that both these alcohols are of compact molecular shape), but the only definite evidence of clathrate hydrate formation by an alcohol, or by any other proton-donor guest molecule, seems to be the recently reported hydrate of ethanol, ($EtOH$, $17H_2O$, m.p. $-72°$) and amine hydrates.[73] Nevertheless, there are strong indications that the solute–solvent situation equivalent to the clathrate hydrate can occur in aqueous solutions of the alcohols. Thus, Glew[74] considers that this is the significance of the nature of the freezing point and $\bar{V}_2(x_2)$ curves of the ethanol–water system. This contention is most strongly supported by the recent observation[75] that the tetra-alkylammonium bromides in aqueous solution show $\bar{V}_2(x_2)$ curves with minima, which occur *at* the compositions of the known, crystalline hydrates. It might be inferred that, for these solutions (and perhaps for those of the alcohols), maximum "volume loss of the solute" corresponds with optimum stabilisation of an open solvent structure. The question remains as to *what* structure is stabilised,

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[70] D. N. Glew, *Nature*, 1964, **201**, 922.

[71] G. A. Jeffrey, private communication.

[72] K. G. R. Pachler and M. Stackelberg, *Z. Krist.*, 1963, **119**, 15.

[73] A. D. Potts and D. W. Davidson, *J. Phys. Chem.*, 1965, **69**, 996; D. N. Glew, *Trans. Faraday Soc.*, 1965, **61**, 30.

[74] D. N. Glew, *Nature*, 1962, **195**, 698.

[75] W. Y. Wen and S. S. Saito, *J. Phys. Chem.*, 1964, **68**, 2639.

whether that of pure water, or another better adapted to the requirements of the solute.

Water is unique in showing a maximum in density as a function of temperature: this is due to the promotion by rising temperature of both structural expansion and progressive structural breakdown. It is to be expected that the temperature of maximum density (TMD) should be sensitive to the addition of any solute which influences the order–disorder balance in water. Somewhat surprisingly, the effect of solutes is so general and regular as to be summarised in the classical "Despretz law"[76] to the effect that the TMD is lowered by each solute in proportion to its concentration. Electrolytes conform, each ion exerting its own, independent, TMD-lowering effect.[77] It is therefore of particular interest that alcohols do not conform to the law, and, as yet, are the only solutes which have been observed to raise the TMD.[78,58] This is to be regarded as but one unusual feature in the topography of V, T, x_2 surfaces which have yet to be described in accurate detail, and Frank[79] has shown that its existence leads to the following interesting inference.

The change in the TMD, $\Delta\theta$, produced by a solute at molality m, is related to the apparent molar expansibility of the solute, $\phi_E = (\partial\phi_V/\partial T)_P$, where ϕ_V is the apparent molar volume of the solute, by the expression

$$\frac{\Delta\theta}{m} = \frac{-\phi E}{\delta}$$

where δ is a converging series which, for water, is

$$\delta = \left(\frac{\partial^2 V}{\partial T^2}\right)_{\substack{m=0\\ t=3\cdot98^\circ}} + \frac{\Delta\theta}{2!}\left(\frac{\partial^3 V}{\partial T^3}\right)_{\substack{m=0\\ t=3\cdot98^\circ}} + \frac{(\Delta\theta)^2}{3!}\left(\frac{\partial^4 V}{\partial T^4}\right)_{\substack{m=0\\ t=3\cdot98^\circ}}$$

Thus, for $\Delta\theta$ to be positive (TMD raised), ϕ_E must be negative, and since at $m = 0$, $\theta_V = \bar{V}_2{}^0$, $\bar{V}_2(x_2)$ isotherms (*cf.* Figure 12) should cross in the appropriately low-temperature range. At present there are no sufficiently numerous and precise density determinations to establish this effect.

Wada and Umeda[80] have made an extensive study of the effects of alcohols on the TMD of water. They point out that the raising of the TMD is all the more remarkable because the presence of a solute which forms an ideal solution with water must depress the TMD. An ideal shift in the TMD, $\Delta\theta_{\text{id}}$, can be calculated by expressing $V_2{}^0$ as a linear function, and $V_1{}^0$ as a parabolic function of temperature (in close approximation to experimental observation), and by assuming zero volume of mixing. This allows a structural contribution, $\Delta\theta_{\text{str}} = \Delta\theta_{\text{obs}} - \Delta\theta_{\text{id}}$, to the raising

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[76] M. C. Despretz, *Ann. Chim. Phys.*, 1839, **70**, 49; 1840, **73**, 296.

[77] R. Wright, *J. Chem. Soc.*, 1919, **115**, 119.

[78] J. P. McHutchison, *J. Chem. Soc.*, 1926, 1898; G. Tammann, *Z. anorg. Chem.*, 1928, **174**, 222.

[79] H. S. Frank, unpublished work, cited by Wen Yang Wen, Ph.D. thesis, University of Pittsburgh, 1957.

[80] G. Wada and S. Umeda, *Bull. Chem. Soc. Japan*, 1962, **35**, 646.

of the TMD to be distinguished. Values of $\Delta\theta_{\text{str}}$ are shown as functions of x_2 for eight alcohols in Figure 13, together with two curves for $\Delta\theta_{\text{obs}}$: they present several features of great interest. It may be noted first that the maximum in the $\Delta\theta_{\text{str}}$ (x_2) curve for ethanol does not occur at the same x_2 as the minima in the $\bar{V}_2(x_2)$ curves for the same solute in Figure 12: it matches better with the inflections of these curves. It follows that neither the maximum in the one case nor the minimum in the other can be given the simple significance of "optimum structure stabilisation". It is also obvious from Figure 13 that there are two effects at work. The normal alcohols, MeOH, EtOH, $\text{Pr}^{\text{n}}\text{OH}$ and $\text{Bu}^{\text{n}}\text{OH}$, have decreasing $\Delta\theta_{\text{str}}$ with maxima shifting to lower x_2. On the other hand, $\text{Pr}^{\text{n}}\text{OH}$, $\text{Pr}^{\text{i}}\text{OH}$, and the butanols in sequence, show a very marked effect of chain branching in the opposite direction. Since it can hardly be doubted that elevation of the TMD is basically due to some kind of structure stabilisation or promotion, it is difficult to avoid the conclusion that, for example, MeOH and $\text{Bu}^{\text{t}}\text{OH}$ exert their effects in this sense in different ways. This conclusion is supported by the $\bar{V}_2$–$V_2{}^0$ data[81] shown in the inset of Figure 13. Methanol dissolves in water with relatively little volume loss, but

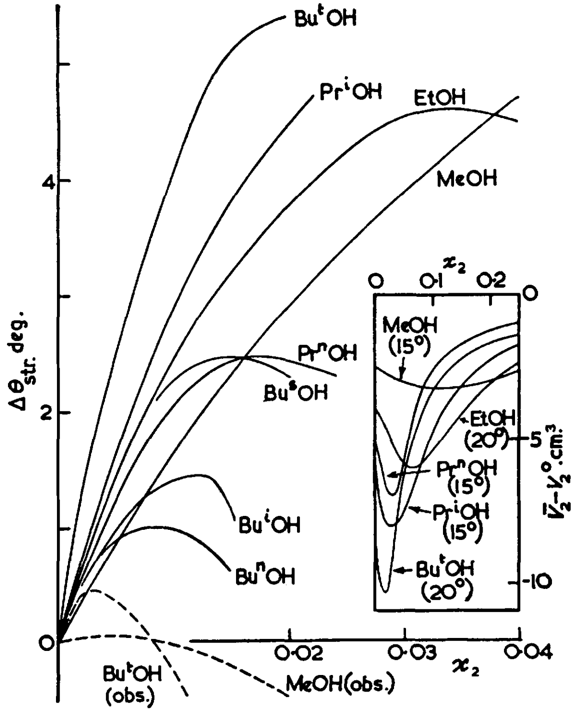

FIG. 13. *Elevations of the temperature of maximum density of water by the alcohols. Inset: partial molar volumes of the alcohols in water.*

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[81] K. Nakanishi, *Bull. Chem. Soc. Japan*, 1960, 33, 793.

produces a large $\Delta\theta_{str}$ which extends to the highest x_2 of any. Bu^{t}OH, on the other hand, suffers a large volume loss on solution in water (accompanied by water expansion), and also produces a large $\Delta\theta_{str}$ which, however, reaches a maximum at a much lower x_2. Although exception might be taken to evidential use of a hypothetical $\Delta\theta_{str}$ it has in this instance drawn attention to the fact that the concept of "structure stabilisation" is, of itself, inadequate, and must be widened. This need may be met by the hypothesis that the structural participation (stabilisation, promotion) of solutes may vary between extremes of substitutional and interstitial association, either with the structure of (pure) water, or with a greater variety of other structures which water can locally form on demand. Insofar as their hydroxyl groups are almost certain to act as hydrogen-bonding "substituents", alcohols as solutes will fall between these extremes, but it is very likely that MeOH is predominantly substitutionally dissolved in water (little volume loss—occupation of cluster "framework sites") whereas Bu^{t}OH is mainly interstitially dissolved (much volume loss —occupation of cavities)—perhaps with local change of structure (water clusters to gas-hydrate cages). The suggestion has previously been made[48] that although the lower alcohols are excluded from ice, the other structures of limited dimensions which water can form will tolerate them up to a limit, beyond which something akin to a submerged phase-transformation may occur. It is tempting to consider this possibility in relation to the inflections of the isotherms of Figure 12, which, as previously noted, seem to come between x_2 regions with some rather widely differing properties.

Under the present heading of P–V–T relations, it is legitimate to consider measurements of the velocity and absorption of ultrasound, since compressibility is intimately concerned in both; absorption particularly has proved to be important in studies of structural aspects of liquids. The classical "shear viscosity treatment" gives the velocity of sound in a liquid as $C = (\rho\beta)^{-\frac{1}{2}}$, where ρ is undisturbed density, and $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_s$ is adiabatic compressibility. It also provides a frequency-independent absorption parameter which, to a close approximation, is $\frac{2\alpha}{\nu^2} = \frac{8\pi^2\eta}{3\rho C^3}$ where α is the amplitude absorption coefficient (2α is that for intensity), ν is frequency, and η is shear viscosity.

Liquids may be classified into three groups according to their sound-absorbing properties.[13] The first group, of "normal" liquids, is small; sound absorption no more than slightly exceeds the classical value. The second group contains the majority of organic, and a few inorganic, non-associated liquids and shows large excess absorption: α/α_{class} is 3—400 (1150 for CS_2). This is attributed to a thermal relaxation due to slow exchange of internal and external energy;[82] these "Kneser liquids" have positive temperature coefficients of absorption. Associated liquids, form-

[82] H. O. Kneser, *Ann. Physik*, 1938 [5], **32**, 277.

ing the third group, show no thermal relaxation because of the efficiency of collisional de-excitation: instead, the pressure-dependence of structure gives rise to a structural relaxation. The excess sound absorption due to this effect is of the order $\alpha/\alpha_{\text{class}} \sim 3$, and has a negative temperature coefficient. The relevance of this kind of excess sound absorption to the special case of water has been previously mentioned.

Alcohol–water mixtures show excess sound absorption over and above that to be expected from the already excessive absorption coefficients of the pure components. This extra absorption varies greatly from one alcohol to another, depends strongly on the composition of the mixture with water, and decreases rapidly with rising temperature; it must be due to some additional intermolecular relaxation effect. Figure 14 shows $\alpha/\nu^2(x_2)$ for five alcohol–water systems at 25°:[83] the classical absorption is imperceptible on the scale of plotting. Attempts to account for the excess absorption in terms of the *thermal* effect of accoustical compression on inter-component complex formation[84] are not consistent with known heats of mixing. An alternative interpretation[85] is based on the volume change which accompanies transfer of hydrogen bonding between like and unlike molecules (AA + BB $\rightleftharpoons$ 2AB), the transfer equilibrium being displaced by the compression of the acoustical wave. Such displacement is opposed by potential barriers, and the molecular translations and re-orientations called upon to occur within each half-cycle introduce a relaxation which is the source of the excess absorption. Quantitative success of this treatment in two cases (EtOH and Bu^{t}OH) does not, however, unequivocally identify

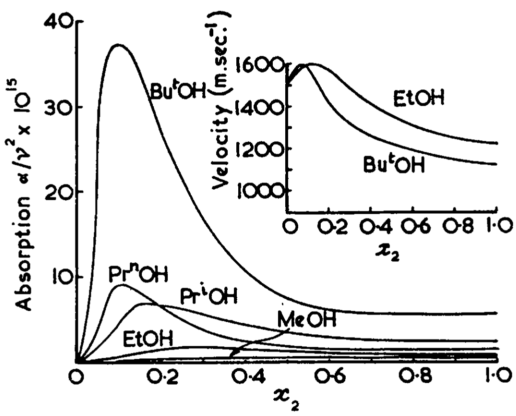

FIG. 14. *Sound absorption in alcohol-water mixtures. Inset: velocity of sound in* EtOH–H_2O *and* Bu^{t}OH–H_2O *systems.*

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[83] C. J. Burton, *J. Acoust. Soc. Amer.*, 1948, **20**, 186.

[84] L. R. O. Storey, *Proc. Phys. Soc.*, 1952, **65**, 943.

[85] W. G. Schneider, *Colloque internat. Centre. nat. Recherche sci. (Paris)*, 1959, **77**, 529.

the origin of the significant volume change with hydrogen-bond transfer; whatever structural change may be responsible for volume loss on mixing could be reversibly sensitive to compression and thus have similar consequences. The very rapid decrease of the excess absorption with rising temperature (as for pure water *below* 35°,[12] to which the theory is not applicable) suggests that a more co-operative structural effect is concerned. It is of interest (*cf.* Figure 14) that the effect is very small for MeOH and large for Bu^{t}OH, and that, for the latter the elevation of α/ν^2 *per mole* of alcohol is not maximal at $x_2 \rightarrow 0$. The excess absorption is also frequency-dependent: relaxation times (10^{-9}—10^{-10} sec.) are longer than for pure water (10^{-11} sec.), as for dielectric relaxation[86] but decrease as x_2 is either decreased or increased from the value at which maximum absorption occurs.

The velocity of sound in alcohol–water mixtures is also anomalous. The $c(x_2)$ curves (inset to Figure 14), indicate that although the alcohols are more compressible than water, small additions of an alcohol to water cause a decrease in compressibility, just as if some compression-resistant structure were being formed or fortified. An ostensibly successful attempt to interpret this effect in terms of the making and breaking of hydrogen bonds[87] is difficult to reconcile, in its simplicity, with other complex properties of these systems. The temperature coefficients of compressibility present features of interest. For water itself, there is a structural contribution to compressibility that decreases with rise of temperature, so that $\partial\beta/\partial T<0$. For alcohols, as for all normal liquids, $\partial\beta/\partial T>0$. For alcohol–water mixtures, $\partial\beta/\partial T$ changes sign appropriately with increasing x_2. The $c(x_2)$ isotherms for the ethanol–water system intersect at $x_2 \sim 0{\cdot}08$, corresponding with $\partial\bar{V}_2/\partial x_2 = 0$ in Figure 12; thus a mixture of this composition has a constant, temperature-invariant compressibility.[88] This, in a manner not yet clearly seen, supplements the considerable evidence that this composition has some special significance for the ethanol–water system: no doubt there is a similar composition characteristic of each alcohol.

Spectroscopic Properties

Infra-red spectroscopy is of limited use in the study of alcohol–water systems because the very complex interactions, covering a wide and continuous range of energies, gives rise to broad, unresolvable absorption bands. The information more recently available from n.m.r. measurements is not extensive and, because some of it is contradictory, requires critical assessment. This unfortunate situation may be due to the very great sensitivity of proton exchange to catalysis by trace impurities, particularly of acids or bases;[89] this calls for rigorous purification of experimental

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[86] G. H. Haggis, J. B. Hasted, and T. J. Buchanan, *J. Chem. Phys.*, 1952, **20,** 1452.
[87] B. Jacobson, *Arkiv Kemi*, 1950, 2, 177.
[88] A. Giacomini, *Acta Pontif. Acad. Sci.*, 1942, **6,** 87.
[89] J. T. Arnold, *Phys. Rev.*, 1956, **102,** 136.

systems, and full credence cannot be given to results which are unaccompanied by the necessary criteria of purity of the materials used.

Transfer of a hydrogen-bonding substance from the nearly ideal, non-bonded gaseous state to the liquid state gives rise to a negative "association shift" (to lower frequency or field), similar in magnitude to chemical shifts.[90] If a proton can exist in two situations, such as

$$0^1\text{–H} \;\ldots\ldots\ldots\; 0^2 \text{ and } 0^1 \;\ldots\ldots\ldots\; \text{H–}0^2$$

between which the rate of exchange is slow, two signals are recorded. If the rate of exchange is progressively increased, perhaps by rise of temperature, the signal peaks broaden and eventually merge together when the lifetime of the proton in either position, τ, is of the order of $(\Delta\nu)^{-1}$, where $\Delta\nu$ is the maximum frequency difference between the signals in absence of exchange. Exchange can, however, occur only during the period of existence of a hydrogen bond, which is much shorter than τ. In relation to association between like molecules in pure ethanol, it is found there is only one OH signal. If the ethanol is highly purified, but not otherwise, the single resonance peak has the expected triplet structure due to spin–spin coupling with adjacent $>CH_2$ protons. Thus, only an average proton environment is recorded, despite the differences in situation of OH groups in various polymeric entities, occupying end or median positions in polymeric chains, or in the monomers that may be present in very small proportion. The magnitude of the association shift indicates that the lifetime of the hydrogen bond is less than 10^{-3} sec. but its temperature-dependence[91] shows that the average period between proton exchanges is much longer than this. With rising temperature, the triplet structure of the OH peak is averaged out, and the signal moves to higher frequency or field, which indicates a net breaking of hydrogen bonds. At 88°, $\tau \sim 3 \times 10^{-2}$ sec. At the boiling point of ethanol, as for the other lower alcohols, the association shift is such as to confirm the retention of extensive hydrogen-bonding. Dilution of ethanol with an inert solvent (*e.g.* CCl_4) leads eventually to complete dissociation into monomers. This is clearly indicated (in agreement with the infrared evidence) by the attainment of a limiting shift (at $\sim 5 \times 10^{-2}$ mole $l.^{-1}$ of alcohol), which is a function of the environment provided by the particular "inert" solvent used.[92]

Alcohol–water mixtures of low water–content at low temperatures give two, discrete, OH proton signals, indicating that the exchange of protons between oxygen atoms belonging to different molecular species is slow: τ has been quoted as 5×10^{-2} sec.[93] Increase of temperature or water content leads to merging of the signals, ultimately to a single, sharp peak—a change which is effected immediately by addition of a trace of acid or

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[90] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York, 1959, ch. 15.

[91] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, 1951, **19**, 1608.

[92] A. D. Cohen and C. Reid, *J. Chem. Phys.*, 1956, **25**, 790.

[93] I. Weinberg and J. R. Zimmerman, *J. Chem. Phys.*, 1955, **23**, 748.

base. Contrary to earlier results, it has recently been found[94] that the rate of proton exchange increases linearly with water concentration, and, that under otherwise standardised conditions, τ for the attachment of the proton in the alcoholic OH group increases in the sequence MeOH $\leqslant$ EtOH $<$ Pr^nOH $<$ Bu^nOH $<$ Bu^iOH $<$ Pr^iOH $<$ Bu^sOH $<$ Bu^tOH. This is essentially the same order as that of increasing proton-accepting facility established by other evidence, previously mentioned.

A recent study of the effects of solutes on the water proton shift[95] has shown that EtOH and Bu^nOH increase the negative shift in a manner to be expected from a net strengthening of hydrogen bonding. A series of sodium alkylsulphates (C_2—C_{12}), however, gave relative positive shifts increasing with chain length, indicating that, far enough removed from the ionic head group, each methylene group provided its own constant, positive "molal shift". In line with the usual interpretation of p.m.r. data, this would indicate a net hydrogen-bond breaking, unless a covalent, co-operative contribution to hydrogen bonding is invoked. A later study[96] has indicated that the same solutes (including the alcohols) increase the rate of spin–lattice relaxation of the water protons, but in this case the effect of increase in chain length is uniform; each $> CH_2$ group exerts the same contribution, whether near the head group or not. This is consistent with a strengthening of hydrogen bonding, or with close range dipole–dipole interactions between alkyl and water protons, or both. Although the detailed interpretation of these p.m.r. results is not yet clear, they may prove to be significant to views on hydrophobic hydration, particularly in relation to the structural shift proposed by Némethy and Scheraga.[6] It is not unreasonable to suppose that the proximity of an unbonded alkyl group may cause additional polarisation of a hydrogen bond—there may be some relation with a recent suggestion about the hydration of alkylated carboxylate ions.[42]

Dielectric and Solvent Properties

Static dielectric constants of alcohol–water mixtures show no very direct effects of structural complexity: the $\epsilon(x_2)$ curves for several systems at 25°, shown in Figure 15a, are smooth. The "droop" in these curves, increasing from one alcohol to the next of higher molecular weight, is mainly due to the "dipole dilution" effect previously mentioned. Comparison of the alcohols with one another (and with dioxan as a non-associated analogue) is better made in terms of ϵ as a function of the ideal volume fration (ΔV^E assumed zero), as in Figure 15b. Two factors can be distinguished which may affect the shape of these curves. Insofar as ΔV^E is really negative, the dilution effect is lessened, and a positive displace-

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[94] W. G. Paterson, *Canad. J. Chem.*, 1963, **41**, 714, 2472; W. G. Paterson and H. Spedding, *Canad. J. Chem.*, 1963, **41**, 2477.

[95] J. Clifford and B. A. Pethica, *Trans. Faraday Soc.*, 1964, **60**, 1483.

[96] J. Clifford and B. A. Pethica, *Trans. Faraday Soc.*, 1965, **61**, 182.

ment from a rectilinear mixture law is to be expected: features of the curves can be seen possibly explicable in this way. Superimposed on this, and hardly independent of it, there may be displacements due to variation of the Kirkwood correlation parameter, *g*, as a function of composition for either of the reasons previously indicated. Inspection of the alcohol curves (in comparison with that for dioxan) suggests that such an effect enters markedly in alcohol-rich mixtures; not discernable for MeOH, it increasingly depresses the curves from EtOH to Bu^{t}OH, leading in the latter case to a remarkable "hook" at the alcohol end of the curve.

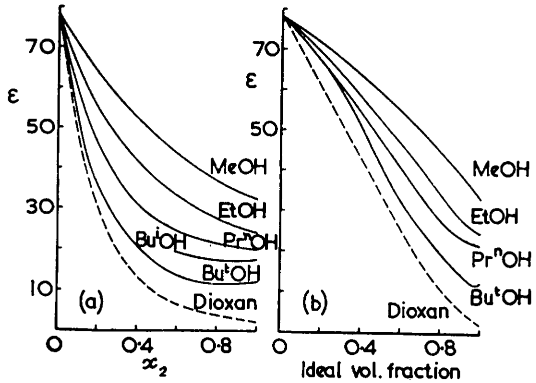

FIG. 15. *Dielectric constants of alcohol–water mixtures* (a) *as functions of mole fraction,* (b) *as functions of ideal volume fraction of alcohol.*

Although an "electrostatic-dielectric continuum" model may seem to be inappropriate to these systems, the Martin–Bell–Kirkwood (MBK) relation[97] applies quite well to them over considerable ranges of composition and temperature. The requirement of this "dipole-in-a-cavity" theorem is that log γ_1 (γ_1 is the Raoult's law activity coefficient of the more polar component) should be linear with $(\epsilon - 1)/(2\epsilon + 1)$; some examples of how surprisingly well this is satisfied are shown in Figure 16.[98,24] A possible implication is that, as far as can be "seen" by the low frequency field used in static dielectric constant measurements, there are no specific short-range interactions which are not effectively "averaged out", and no particular structural effects to disturb the near-constancy of *g* ($\sim$ 2·5 for both water and ethanol), or its regular variation with composition. Even if it is not entirely safe to assume that the MBK relation is valid within a composition range where rapidly exchanging, randomised association presents no structural problems, failure of the relation may be accepted as diagnostic of a structurally significant change in *g*. The relation fails, in general, at

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[97] A. R. Martin, *Phil. Mag.*, 1929, **8**, 547; *Trans. Faraday Soc.*, 1934, **30**, 759; 1937, **33**, 191; R. P. Bell, *Trans. Faraday Soc.*, 1931, **27**, 797; 1935, **31**, 1557; J. G. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351.

[98] A. R. Martin and A. C. Brown, *Trans. Faraday Soc.*, 1938, **34**, 742.

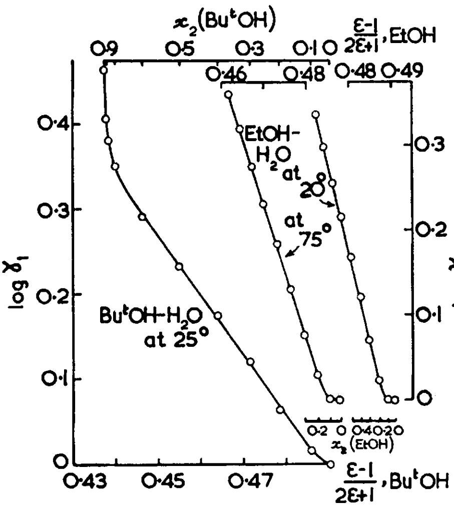

FIG. 16. *BMK plots for* EtOH–H_2O *at* 20° *and* 75°, *and for* BuᵗOH–H_2O *at* 25°.

$x_2 < 0{\cdot}1$ and, in the case of BuᵗOH, at $x_2 > 0{\cdot}6$ as well. Other evidence is not wanting that the low- and high-x_2 regions are structurally critical.

Although, in general, dielectric constant seems to be a "smoothed out" function, it provides decisive evidence in one respect. Thus, in the high-x_2 region, the fact that addition of a little water ($\epsilon = 78{\cdot}3$) to BuᵗOH ($\epsilon = 12{\cdot}3$), or to BuⁱOH ($\epsilon = 17{\cdot}7$) causes a *decrease* in ϵ is unmistakable evidence for contra-association involving the formation of comparatively long-lived complexes: the value of g is then depressed because dipoles are held in opposition. This would be the case for water-centred association which, if less marked for the lower alcohols, is not inconsistent with the curves in Figure 15b. Such "centrosymmetrical" association, favouring peripheral presentation of alkyl groups, is of a kind to hinder extended polymerisation, or co-operation in hydrogen bonding beyond the limits of a discrete polymer. This is consistent with the action of water in depolymerising the cyclic or linear aggregates present in the pure alcohols, and with considerable positive deviations from Raoult's law.

Since this structural feature is not unimportant, it may be examined, parenthetically, in the light of points of evidence already recorded. In a solution of water in alcohol ($x_2 \sim 0{\cdot}8$), each water molecule has a predominance of alcoholic neighbours with which it is all the more free and "anxious" to hydrogen bond because of the greatly reduced proton concentration (compared with that in water), the somewhat less depleted concentration of lone pairs, and the reduced dielectric constant. Apart from questions of relative "basic strengths", an alcohol molecule is twice as likely to act as proton acceptor than donor, and the chances will favour the formation by the water molecule, acting as (acidic) proton-donor, of two hydrogen bonds with (basic) alcohol neighbours. As a result, the basic function of the water molecule will be accentuated, and it may form additional bonds, acting as acceptor, with two more (acidic) alcohol neighbours, thus increasing, in absence of steric inhibition, its co-ordination to four, and meeting the requirement of equality of co-operative "give and take" for maximum hydrogen-bonding stability. It is certain from the exothermic contribution to ΔH^M that strong alcohol–water bonds are formed. That the thermodynamic similarity between alcohol–water and dioxan–water systems in this region of composition is somewhat illusory (there is a certain bond breaking-bond making balance in the one case which is not present in the other) is shown by the $\bar{V}_1-V_1^0$ data recorded in Figure 11. The much smaller volume loss of water on dissolution in dioxan (0·9 cm.^{3} mole^{-1}) than in ethanol (4·3 cm.^{3} mole^{-1}) suggests that the water is much more effectively "tucked away" in the latter. The stability of the suggested discrete, water-centred complexes is perhaps reflected in the p.m.r. evidence of slow proton-exchange, and they are of a kind to give rise to a co-operative rotational contribution to C_V, in line with previous discussion, particularly if the peripheral molecules were not inhibited from bonding to others in the normal chain-forming fashion.

Three other items of evidence for water-centred association may be mentioned. The Stokes–Einstein radius of the water molecule is greater when it is diffusing in ethanol than when it is diffusing in water.[99] Addition of a little water to alcohol increases its viscosity at low temperatures by an order of magnitude; wet, but not dry, alcohol will supercool to form a glass—water molecules form junctions for cross-links between alcohol chains, so that an amorphous silicate-like structure can be formed.[100] Such additions also increase dielectric relaxation times,[101] and it is interesting that this effect is very small for MeOH, but increases in sequence EtOH, Pr^{i}OH, Bu^{n}OH.[102]

Evidence from the physical properties of alcohol–water mixtures may be less informative and less chemically interesting than their behaviour in association with solutes or reacting systems in solution. Some consideration of solvent properties is therefore indispensable.

Alcohol–water mixtures have been extensively used in studies of the influence of the dielectric constant of the solvent on the equilibria and rates of reactions in which charge centres are produced or neutralised, often with the object of studying the usefulness of "electrostatic–dielectric continuum" models. The general result that emerges from much work of this kind is that the models are reasonably satisfactory when long-range coulombic forces alone are significant (as for ion–ion interactions in dilute solutions), or in circumstances in which the effects of all other forces

[99] B. R. Hammond and R. H. Stokes, *Trans. Faraday Soc.*, 1953, **49**, 890.
[100] A. Prietzschk, *Z. Physik*, 1941, **117**, 482.
[101] F. X. Hassion and R. H. Cole, *J. Chem. Phys.*, 1955, **23**, 1756.
[102] V. Sarojini, *Trans. Faraday Soc.*, 1961, **57**, 1534.

cancel out, or are separately considered. The models fail to cope with systems and phenomena predominantly controlled by close-range forces (as for ion–solvent interactions).[103,104]

Attempts to adapt simple physical models to the study of partially aqueous solvents are less profitable than the use of ions as "internal indicators" of the *electrochemical* properties of these solvents. Thus, experimental standard free energies of transfer, ΔG_t^0,[104,105] of electrolytes from water to alcohol–water mixtures have shown that the Born equation by which this quantity should be calculable in terms of ionic radii, r^+, r^- and the change in dielectric constant $\epsilon_W \rightarrow \epsilon_S$, namely

$$\Delta G_t^0 = \frac{Ne^2}{2}\left\{\frac{1}{\epsilon_S} - \frac{1}{\epsilon_W}\right\}\left\{\frac{1}{r^+} + \frac{1}{r^-}\right\}$$

can do no more than correctly predict the sign of ΔG_t^0—the calculated numerical value may be in error by an order of magnitude. Non-thermodynamic assumptions have to be made in order to divide ΔG_t^0 into single-ion contributions, but this division has been made by credible alternative methods[106,107] which agree in showing the free energies of transfer of cations and anions to be *opposite in sign*: Figure 17a shows data for the methanol-water system.[105] Since there are excellent grounds for accepting the general trend of these results (recently supplemented[108]), it is evident that failure of the Born treatment is complete, and that ΔG_t^0 for ions must be largely determined by short-range interactions. It is seen that whereas the anions are in a "higher free-energy state" in methanol–water mixtures than in water, the reverse is the case for the cations. The preferential stabilisation of cations, including the "hydrogen ion", apparently caused by replacing H_2O by MeOH, implies that methanol is "more basic" (as an electron-pair donor) than water. This is contrary to general opinion, which is that water is a stronger base than methanol or the other alcohols. It is essential to interpolate an attempt to resolve this discrepancy, as follows.

Classical studies of the conductance of HCl and other electrolytes in alcohol–water mixtures have been confirmed by more recent work.[109] It is established that the excess mobility of "hydrogen ion" in an anhydrous alcohol is progressively destroyed by addition of water: when x_2 has

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[103] D. H. Everett and C. A. Coulson, *Trans. Faraday Soc.*, 1940, **36**, 633; R. F. Hudson and B. Saville, *J. Chem. Soc.*, 1955, 4114.

[104] D. Feakins and C. M. French, *J. Chem. Soc.*, 1957, 2581.

[105] D. Feakins and P. Watson, *J. Chem. Soc.*, 1963, 4734.

[106] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London, 1959, pp. 69, 355.

[107] E. Grunwald, G. Baughman, and G. Kohnstam, *J. Amer. Chem. Soc.*, 1960, **82**, 5801.

[108] D. Feakins and D. J. Turner, *Chem. and Ind.*, 1964, 2056.

[109] I. I. Bezman and F. H. Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1330; G. Kortum and H. Wilski, *Z. phys. Chem.* (*Frankfurt*), 1954, **2**, 256; T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, 1956, **60**, 151; T. Erdey-Gruz, *et al.*, *Acad. Sci. Hung.*, 1958, **13**, 429; H. Strehlow, *Z. phys. Chem.* (*Frankfurt*), 1960, **24**, 240.

decreased to $\sim$0·9, conversion of ROH_2^+ to H_3O^+ (solvation of these ions is but seldom considered[110]) is sensibly complete, and proton jump transfer is lost—only slowly to be recovered with further decrease in x_2, when the appropriate mechanism (proton tunnelling "across" hydrogen bonds, rate-limited by rotation of H_2O in the field of H_3O^+)[111] can be restored by increased probability of encounters between H_2O and H_3O^+. The water-centred association proposed for the high-x_2 region of alcohol–water mixtures (promoting hydrogen bonding between *unlike* molecules in discrete polymers) would be inimical to field-induced, uni-directional proton-transfer except by normal ionic migration. Capture of a proton by the central water molecule would, moreover, rearrange but reinforce its hydrogen bonding to its enclosing alcohol neighbours. It is then logical to regard the effectiveness of proton localisation as a function of the structure of a complex $[H_3O(ROH)_n]^+$. Nevertheless, naive use of conductances of HCl in alcohol-rich solvents to calculate equilibrium constants for the simple proton transfer reaction $ROH_2^+ + H_2O \rightleftharpoons ROH + H_3O^+$ has given results (*e.g.* $K \sim 100$ for MeOH, ~ 250 for EtOH), supported by indicator,[112] e.m.f.,[113] and catalytic[114] studies, taken to mean that "water is a much stronger base than the alcohols".

As an expression of experimental results obtained under defined conditions, this conclusion can hardly be disputed, but there are at least three ways in which it can deceive: (i) the hypothetical proton-transfer reaction to which the law of mass action was bent to get an "equilibrium constant", K, is a gross over-simplification of something far more complex happening in a polymerised, condensed system having a considerable degree of structure: (ii) the thermodynamic significance of K is doubtful: (iii) if the conclusion is generalised, and taken to indicate an intrinsic difference between water and alcohol molecules which will exert its influence in the same sense in all circumstances. The opposite conclusion can indeed be reached under other circumstances: thus the pK values of cation acids NH_4^+ and RNH_3^+ (determined by homoionic equilibria) are decreased by the addition of ethanol to water,[115] suggesting that ethanol is more basic than water. These apparently conflicting views have prompted the following restatement and examination of the problem.

In a hydrogen-bonded liquid system, it is not always possible, or even meaningful, to assign relative, intrinsic basic or acidic strengths to molecular species which exist so strongly under each other's influence. "Proton potential" is a function of the whole system, and is as much determined by molecular interactions, and the structures to which they may give rise, as by the "properties of the molecules" which the system contains: as yet,

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[110] C. F. Wells, *Discuss. Faraday Soc.*, 1960, **29**, 219.

[111] B. E. Conway, J. O'M. Bockris, and H. Linton, *J. Chem. Phys.*, 1956, **24**, 834.

[112] L. S. Guss and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1940, **62**, 1494.

[113] J. Koskikallio, *Suomen Kem.*, 1957, **30**, *B*, 38.

[114] C. E. Newall and A. M. Eastham, *Canad. J. Chem.*, 1961, **39**, 1752.

[115] R. G. Bates, "Determination of pH", Wiley & Sons, New York, 1964, p. 195.

disentanglement of the intra- and intermolecular effects is impracticable. This is, of course, the basic idea of the Hammett acidity function,[116] which has been so successful in *essentially aqueous* media. Difference in proton potential between dissimilar media must, however, be as indeterminate as a difference of electrical potential between dissimilar phases, for a precisely similar reason: there is no test system which is devoid of all other properties than that of proton affinity. Medium effects can never be eliminated. This is, of course, the basic reason why there is difficulty in the interpretation of pH scales in alcohol–water solvents.[117] It seems a particularly harsh dispensation that colour-change indicator systems are just those for which medium effects are expected to be the greatest,[118] and this is very adverse to the extension of the acidity function to other than purely aqueous solvent systems. If, however, the view is taken that the difficulty is largely academic and that the acidity function remains serviceable, at least in predominantly aqueous systems, attention may be given to the finding[119] that addition of ethanol to aqueous HCl largely reduces acidity. Disregarding where the protons may have been captured, this might well be taken to indicate that ethanol—in terms of a partial molar property—is more basic than water. The more general finding, however, is that great difficulties are encountered in extending the acidity function concept to aqueous-alcoholic solvents[120] to the extent of provoking the assertion that the acidity functions H_0 and H_- "do not exist" in alcohol–water mixtures of high x_2.[121]

It is suitable to consider medium effects in terms of a proton transfer such as $ROH_2^+ + H_2O = ROH + H_3O^+$. For a particular ROH–$H_2O$ mixture (the solvent, s), an equilibrium constant, K, can be *defined* by $\ln K = -{}^{s}\Delta G^0/\boldsymbol{RT}$, where ${}^{s}\Delta G^0$ is a standard free-energy change determined by a choice of standard states appropriate to that one solvent. This K is of no interest if the composition of the solvent is to be varied. To study the latter case, compatible, invariant standard states for all the participating species must be chosen. These might be such as to define ${}^{W}\Delta G^0$, a standard free-energy change determined by standard states all in a solvent of pure water. It is easily shown that

$${}^{s}\Delta G^0 = {}^{W}\Delta G^0 + \boldsymbol{R}T\ln {}^{W}\gamma_{H_3O^+} + \boldsymbol{R}T\ln {}^{W}\gamma_{ROH} - \boldsymbol{R}T\ln {}^{W}\gamma_{ROH_2^+} - \boldsymbol{R}T\ln {}^{W}\gamma_{H_2O}$$

where ${}^{W}\gamma_i$ is the activity coefficient of the species i as it exists in a particular solvent s, referred to a standard state in pure water. Then, for example,

$$\boldsymbol{R}T\ln {}^{W}\gamma_{H_3O^+} = {}^{s}\mu^0_{H_3O^+} - {}^{W}\mu^0_{H_3O^+}$$

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[116] L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., New York, 1940, p. 267.

[117] R. G. Bates, M. Paabo, and R. A. Robinson, *J. Phys. Chem.*, 1963, **67**, 1833.

[118] E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, 1964, **86**, 4517.

[119] E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1948, 1976.

[120] R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, 1955, **38**, 699; C. L. de Ligny, H. Loriaux, and A. Ruiter, *Rec. Trav. chim.*, 1961, **80**, 725.

[121] B. Gutbezahl and E. Grunwald, *J. Amer. Chem. Soc.*, 1953, **75**, 559.

can be regarded as the standard free-energy of transfer of hydronium ion from water to the solvent in question. Then to obtain ${}^{s}\Delta G^0$ from ${}^{W}\Delta G^0$, one must add the standard free energies of transfer of H_3O^+ and of ROH from water to the solvent, and subtract the corresponding standard free energies of transfer of ROH_2^+ and of H_2O. To get ${}^{s}\Delta G^0$ for one solvent mixture from that of another, a similar algebraic summation of standard free-energies of transfer must be added. It is thus obvious that K cannot, except fortuitously, be a constant over any composition range and has little to do with relative "basicities" of H_2O and ROH. It may be noted that the assumption that it *has*, places the alcohols in the reverse order of proton-accepting facility to that indicated by other evidence, previously quoted.

A case has been made that relative basic (or acidic) strength (in whatever sense the term is used—Brönsted, Lewis, or something in between) cannot be unambiguously assigned to the molecules of a component of a liquid mixture, in disregard of the powerful influence of medium effects, which may be of a co-operative nature if there is appreciable structure formation. If these effects are radically altered, as they may well be in the presence of ionic fields, then the behaviour of the molecules may be greatly modified. The evidence of the free energy of transfer of ions from water to methanol–water mixtures (Figure 17a) suggests that this is the case and this evidence can be used without valid objection as a basis for discussing the solvent properties of alcohol–water mixtures in relation to ionic solutes, along the lines proposed by Feakins and Watson.[105]

It is first assumed that, relative to the case of pure water, the influence of ionic fields on the structure of the solvent (modifying solvent–solvent interaction) will mainly appear in compensating contributions to ΔH_t^0 and $T\Delta S_t^0$, having little or no effect on ΔG_t^0. Thus, $-\Delta G_t^0$ will remain the best available measure of the relative affinity of ion–solvent interaction, mainly arising in a nearest-neighbour, primary solvation zone. Primary solvation is regarded as closely akin to a hydrogen-bonding interaction—no doubt ultimately to be described in terms of detailed information about molecular and ionic structures, local charge distributions, polarisabilities and the like. Failing such information, no other assumption can be made but that methanol is "a stronger base" than water, in the sense that it is a more effective electron-pair donor (if not to the proton, with some certainty to H_3O^+ and other cations). Methanol will, moreover, confer "greater basicity" on water to which it is hydrogen bonded. This idea, which is in line with the views of Frank and Wen,[2] and with the discussion given above, is of importance because the smoothing out of the individualities of the components in this respect means that some progress can be made without assumptions about the composition of the first solvation sheath of the ion. Three other factors, however, can be distinguished relevant to the distribution in ionic solvation systems of the components of alcohol–water mixtures. The first is a self-evident steric effect which will favour the occupation of the inner solvation zone by water, rather than by bulkier molecules. The second, operating in the same sense, may arise from repulsion of the "low dielectric constant residue", R in ROH, to a region of reduced field strength: this is known to occur in response to the charge on an ideally polarised electrode[122] and can give rise to significant de-mixing of methanol and water.[123] The third factor has been brought to light by the recent, important paper by Grunwald and Price[118] which demonstrates the significance of London dispersion interactions between solute and solvent. These are strengthened by the higher density of oscillators in the close vicinity of a solute particle provided by an ambience of, for example, ethanol, rather than water, molecules, and thus promote "close alcoholation" in preference to hydration. This is the source of the large medium-effects, already noted, on indicator systems, and, apparently, by no means insignificant for simpler ionic solutes.[124]

Despite the undoubted complexity of the problems of solvation in these mixed solvents, it is generally acceptable that cation solvation (lone-pair donation from oxygen atoms of solvent molecules) becomes more stable, and anion solvation (proton donation from hydroxyl groups of solvent molecules) becomes less stable, in an alcohol–water mixture of enhanced "basicity". Although it is the primary solvation zone which dominates the control of $\Delta G_t{}^0$, a secondary zone is envisaged in which field-induced molecular orientation may be strongly assisted by hydrogen-bonded correlation with molecules in the primary hydration shell, and in which dielectric saturation may occur. With further increasing distance from the centre of ionic charge, the detailed distribution of local charges within the solvent molecules becomes of less significance, and eventually the field becomes weak enough, and thermal randomisation strong enough, for any further contribution to the free-energy of solvation to be correctly computed by "Born charging". Although detailed analysis of these distinguishable effects is as yet impracticable, it is clear that the latter contribution to $\Delta G_t{}^0$ will be in the same sense (positive) for both cations and anions, opposing and reinforcing, respectively, the effects of primary solvation. The main features of Figure 17a are well explained in this way.

Figure 17b shows enthalpies of transfer, $\Delta H_t{}^0$ of some electrolytes from water to methanol–water mixtures.[125] It is seen that the course of $\Delta H_t{}^0$ with x_2 is quite different from that $\Delta G_t{}^0$, and shows no uniform trend such as would be expected from any simple electrostatic theory. Choosing KCl as an example, it is noted that below $x_2 \sim 0{\cdot}4$, transfer is endothermic; above, exothermic. The thermodynamic situation is dominated, however, by a $T\Delta S_t{}^0$ term which rapidly becomes more negative with increasing x_2. The large entropy loss, greatest for the transfer to pure methanol, is not

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[122] A. N. Frumkin, *Z. phys. Chem.*, 1923, **103**, 43.

[123] R. Parsons and M. A. V. Devanathan, *Trans. Faraday Soc.*, 1953, **49**, 673.

[124] D. Feakins and R. P. T. Tomkins, private communication.

[125] C. M. Slansky, *J. Amer. Chem. Soc.*, 1940, **62**, 2430; R. L. Moss and J. H. Wolfenden, *J. Chem. Soc.*, 1939, 118.

unexpected on electrostatic grounds.[126] It denotes a greater enhancement of order by the ionic fields in methanol than in water. Not only is there less order before the ions are introduced, but, in the medium of lower dielectric constant and lower dipole concentration, the fields to which dipoles can respond are of wider range and greater intensity. This interpretation of the entropy loss (which applies equally to cations and anions) is consistent with the uniform net structure-making influence (positive viscosity B coefficients) of ionic solute on alcohols. It is also consistent with heat evolution on transfer, implying more extensive satisfaction of ion–solvent attraction. It is evident, however, that some other factor must enter in the region of $x_2 = 0$—0·4, where the transfer is endothermic. The maximum in ΔH_t^0 is barely apparent, if at all, in ΔG_t^0 because it is cancelled out in effect by a droop in the negative $T\Delta S_t^0$. This situation is consistent with the existence of positive, compensating contributions to ΔH_t^0 and $T\Delta S_t^0$, such as would arise from the breaking of solvent structure: if this view is correct, the implication is that in this region the solvent is more highly structured than water itself.

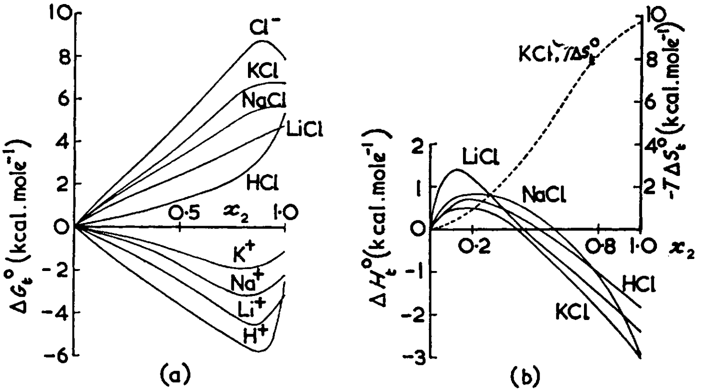

FIG. 17. (a) *Standard free energies of transfer at 25° of electrolytes and ions from water to methanol–water mixtures,* (b) *Standard enthalpies of transfer at 25° of electrolytes from water to* $MeOH–H_2O$ *mixtures.*

Some evidence from ionic transport in $MeOH–H_2O$[127] and EtOH–H^2O[128] mixtures, in a wider context than that previously considered, is presented in Figure 18, in the form of Walden products ($\Lambda_0\eta_0$ or $\lambda_0\eta_0$ at 25°), together with the relevant solvent viscosity data. It is seen that the macroscopic viscosities, themselves showing maxima of intrinsic interest, do not directly control ionic mobilities. Thus, for the $EtOH–H_2O$ system,

[126] R. W. Gurney, "Ionic Processes in Solution", McGraw-Hill Book Co., New York, 1953, pp. 198, 265.

[127] T. Shedlovsky in "The Structure of Electrolytic Solutions", ed. W. J. Hamer, Wiley & Sons, New York, 1959, p. 268.

[128] R. L. Kay and A. Fratiello, private communication.

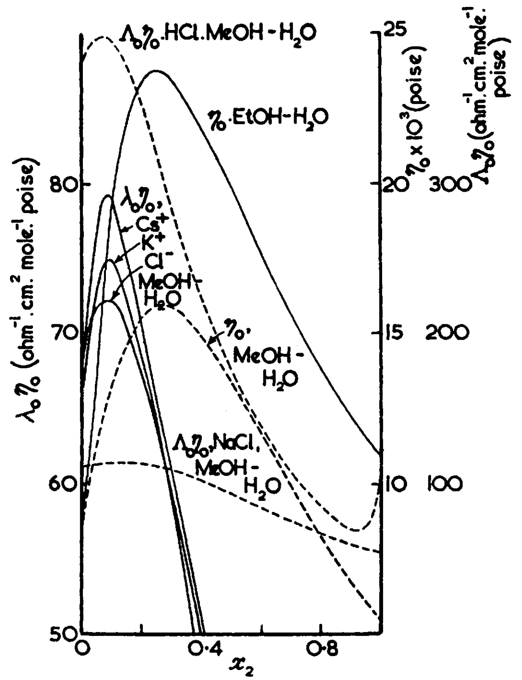

FIG. 18. *Walden products and viscosities at 25° for* MeOH–H_2O *and* EtOH–H_2O *systems.*

η_0 is maximal at $x_2 \sim 0{\cdot}25$, whereas $\lambda_0\eta_0$ for three univalent ions show sharper maxima at $x_2 \sim 0{\cdot}08$. This composition corresponds with the minimum in the $\bar{V}_2(x_2)$ curve for this solvent system, and approximately with a maximum in $\partial\eta_0/\partial x_2$. As in the case of sound absorption, it appears that a maximum in a function may be of less structural significance than a maximum in the derivative of the function with respect to composition, although why this should be so is not at present understood. It would be difficult to explain these results other than in terms of local solvent-structure breaking by ionic fields. It is particularly noteworthy that the difference in mobility between K^+ and Cs^+ ions is almost doubled on transfer from water to aqueous ethanol of $x_2 \sim 0{\cdot}08$. This suggests that a more highly structured solvent can discriminate better than water between the relative structure-breaking powers of ions. It is also of interest that $\Lambda_0\eta_0$ for HCl in the MeOH–H_2O system shows a similar maximum at low x_2, despite the fact that, in water, the hydronium ion has a structure-making effect slightly greater than the small structure-breaking effect of the chloride ion. With increasing x_2 for this system, there is clearly a rapid decline in the excess, proton-jump, conductance ($\Lambda_0\eta_0$ for NaCl serves as a basis for comparison), suggesting an equally rapid falling away in the probability of the occurrence of the co-ordinated, hydrogen-bonded paths required for proton tunnelling. The further course of this $\Lambda_0\eta_0$ (x_2) curve has been covered in previous discussion.

The profound significance of "non-electrolyte interactions" is very strikingly shown by recent determinations of the thermodynamic functions of solution of argon in ethanol–water mixtures:[129] these are illustrated in Figure 19, and do not lend themselves to ready interpretation. It may, however, be suggested that if heat evolution and entropy loss on dissolution are diagnostic of structure making, then this effect of argon decreases with increasing x_2, to reach zero at $x_2 \sim 0{\cdot}25$. Over the first part of this range, this can be attributed to the enhancement of structure which the ethanol has already promoted. The minimum and maximum in the $\Delta G^0(x_2)$ curves, the rapid change in shape of these curves with temperature, and the inflections in the $\Delta H^0(x_2)$ curves can only be left for future elucidation. General support is given to the suggestion previously made, that it may be desirable to discriminate between dilute and extremely dilute aqueous solutions of the alcohols.

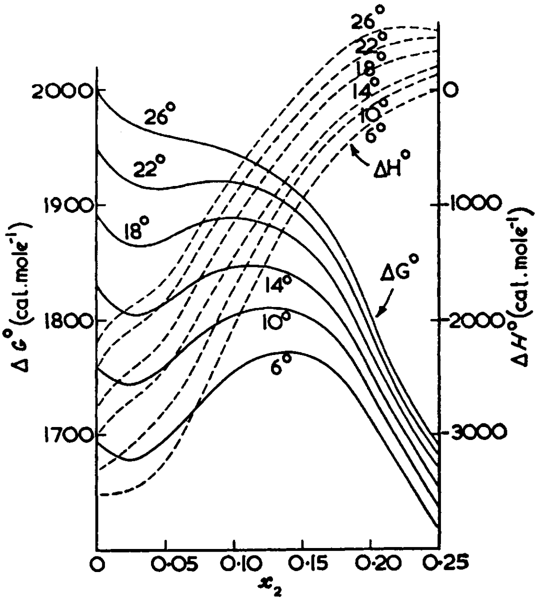

FIG. 19. *Thermodynamic parameters for the dissolution of argon in* EtOH–H$_2$O *mixtures.*

Similar remarkable effects have been previously observed[130] for the solution of a variety of substances (iodine, salicylic acid, dimethylglyoxime) in ethanol–water mixtures, with extrema in the vicinity of $x_2 \sim 0{\cdot}1$, and, in two cases, $x_2 \sim 0{\cdot}3$ as well. That these phenomena are not to be dismissed

[129] A. Ben-Naim and S. Baer, *Trans. Faraday Soc.*, 1964, **60**, 1736.
[130] I. G. Mikhailov, *Zhur. strukt. Khim.*, 1961, **2**, 677.

as unimportant oddities is shown by the fact that quite similar effects are observed in kinetic parameters for reactions carried out in mixed solvents. The results of Winstein and Fainberg[131] on the solvolysis of Bu^tCl in $EtOH–H_2O$ mixtures may be quoted as an example. Whereas the free energy of activation, $\Delta G^\ddagger$, increases monotonically with x_2, $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ show complementary maxima and minima along the x_2 scale in the region $x_2 = 0$—0·3. This is an example of the operation of the Compensation Law[132] on which the existence of linear free-energy relationships[133] largely depends. Although it is notorious that apparent compensation of this kind can too easily be an artefact,[134] this is very unlikely to be so in this instance because it has been shown[135] that the eccentricities in the parameters of activation have their origins in the ground state. They can therefore only be ascribed to peculiarities of solvation which are annulled in the polar transition state. A case has recently been made[42] that the source of compensation is usually to be found in solvational changes in which equilibrium with bulk solvent is continuously maintained. Whilst this confers upon ΔG^0 or $\Delta G^\ddagger$ the properties of a "well-behaved" function, it may rob them of usefulness in getting to grips with the complexities of reactions in solution. Evidence is not lacking of the existence of these complexities when aqueous-alcoholic solvents are used.

Conclusion

Scatchard's celebrated counsel[136] remains appropriate:

"The best advice which comes from years of study of liquid mixtures is to use any model in so far as it helps, but not to believe that any moderately simple model corresponds very closely to any real mixture."

[131] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

[132] J. E. Leffler, *J. Org. Chem.*, 1955, **20**, 1202; R. F. Brown, *J. Org. Chem.*, 1962, **27**, 3015.

[133] P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

[134] O. Exner, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1094; *Nature*, 1964, **201**, 488.

[135] E. M. Arnett, P. M. Duggleby, and J. J. Burke, *J. Amer. Chem. Soc.*, 1963, **85**, 1351.

[136] G. Scatchard, *Chem. Rev.*, 1949, **44**, 7.