311. *The t-Butyl Alcohol–Water System.*

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Dielectric constants and partial and total vapour pressures have been measured over the whole composition range for mixtures of t-butyl alcohol and water at 25°. The dielectric constant of this alcohol is initially decreased by addition of water, and this is reflected in a failure of a relation between dielectric constant and activity of water which holds for other alcohol–water systems. Evidence is assembled in support of the suggestion that this is due to a particular kind of water-centred association which is specially favoured in the present system, but, to a smaller extent, is general to analogous systems. Dielectric-constant measurements for some pure liquids are reported, carried out by a modified resonance method which is applicable to liquids of appreciable conductance. A method is described for calculating partial pressures from vapour compositions and the vapour pressure of one pure component.

The three-dimensional, co-operative order characteristic of the structure of water [1,2] is not compatible with the kind of cluster association [3] present in alcohols. Alcohol–water mixtures are therefore subject to the mixed control of competing ordering influences—those peculiar to the pure components and others arising from specific co-operations between them—and consequently present a wealth of structural problems. This paper is concerned with but one feature of structure in such mixtures which, perhaps common to all, seems to be particularly well developed in the t-butyl alcohol–water system. This system has been studied (cf. Martin and Brown [4]) in terms of the Martin–Bell–Kirkwood (MBK) relation,[5] the validity of which, however, requires re-assessment. This relation,

$$-kT \ln \gamma = \frac{\mu^2}{d^3}\left\{\frac{\varepsilon - 1}{2\varepsilon + 2} - \frac{\varepsilon^\circ - 1}{2\varepsilon^\circ + 2}\right\}$$

where γ is the activity coefficient of the more polar component (of dipole moment μ, molecular radius d, and dielectric constant ε° in the pure liquid state) in a medium of dielectric constant ε, is based on a " dimensionless dipole in a spherical cavity " model.[6] Since variations in the model (*e.g.*, a polarisable dipole of finite length, non-centrally situated in a non-spherical cavity) greatly modify the electrostatic energy which ostensibly determines the extent of thermodynamic non-ideality, it is clear that the MBK expression is but a crude approximation, and certainly the term d can be no more than a disposable parameter. Nevertheless, this relation has been used in various connexions,[7] particularly in a modified form which deals with the infrared frequency shifts that accompany the transfer of a vibrating dipole from the vapour phase to liquid media; [8] in this application it generates the " KBM line " (Kirkwood–Bauer–Magat), which has served as a criterion of non-specificity in solute–solvent interaction.[9] Its use in this way has, however, been criticised on various grounds,[10] and there is now a tendency to discount the usefulness of " dipole-in-a-cavity " models in general.[11] Even if such models are competent to deal

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[1] Pauling in " Hydrogen Bonding," ed. Hadži, Pergamon Press, London, 1959, p. 1.

[2] Frank and Quist, *J. Chem. Phys.*, 1961, **34**, 604.

[3] Jacobson, *Acta Chem. Scand.*, 1955, **9**, 997.

[4] Martin and Brown, *Trans. Faraday Soc.*, 1938, **34**, 742.

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

[6] Böttcher, " Theory of Electric Polarisation," Elsevier, Amsterdam, 1952.

[7] Eley, *Trans. Faraday Soc.*, 1944, **40**, 184.

[8] West and Edwards, *J. Chem. Phys.*, 1937, **5**, 14; Bauer and Magat, *J. Phys. Radium*, 1938, **9**, 319.

[9] Jones and Badger, *J. Amer. Chem. Soc.*, 1951, **73**, 3132; Josien and Fuson, *J. Chem. Phys.*, 1954, **22**, 1169, 1264; Greinacher, Lüttke, and Mecke, *Z. Elektrochem.*, 1955, **59**, 23.

[10] Bayliss, *J. Chem. Phys.*, 1950, **18**, 292; Pullin, *Proc. Roy. Soc.*, 1960, *A*, **255**, 39; Bellamy and Williams, *ibid.*, p. 22.

[11] Coulson, *Proc. Roy. Soc.*, 1960, *A*, **255**, 69.

with the large changes in molecular environment involved in transfers from vapour to liquid phases, this may not justify their use in relation to transfers from one liquid phase to another. Application of the MBK relation in this way to alcohol–water mixtures further calls for the assumption that hydrogen bonding is purely electrostatic in nature,[12] which is hardly acceptable.[13] Nevertheless, the relation applies quite well to the cases that have been studied [4] (rather better if a polarisability term is included [14]) and it remains possible [15] that the MBK equation deals with dipole-interaction energy rather like the Born equation deals with ion-solvation energy. Both equations may usefully define limiting cases, but must fail when short-range interactions assume predominant importance. Our attitude is in line with Scatchard's advice about liquid mixtures: [16] "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."

Equilibrium vapour compositions and pressures, and dielectric constants, have now been measured for the t-butyl alcohol–water system at 25°. Total and partial vapour pressures, together with the compositions of phases in equilibrium, are shown in Table 1 and Fig. 1.

TABLE 1.

Compositions of phases in equilibrium; total and partial vapour pressures for t-butyl alcohol–water mixtures at 25°.

Mole fraction of Bu^{t}OH				Pressure (mm.)			Pressure (mm.)		
Liquid phase	Vapour phase	Liquid phase	Vapour phase	Total	Bu^{t}OH	Water	Total	Bu^{t}OH	Water
0	0	0·649	0·630	23·8	0	23·8	47·5	29·9	17·6
0·020	0·215	0·708	0·668	29·0	6·2	22·8	47·2	31·5	15·7
0·048	0·435	0·780	0·722	40·8	17·8	23·0	46·6	33·6	13·0
0·106	0·497	0·840	0·778	44·2	22·0	22·2	45·5	35·4	10·1
0·239	0·520	0·898	0·840	45·9	23·9	22·0	44·6	37·5	7·1
0·358	0·535	1·000	1·000	46·7	25·0	21·7	42·0	42·0	0
0·432	0·557			47·0	26·2	20·8			
0·465	0·564			47·2	26·6	20·6			

In Fig. 1, the points are experimental and the curves are obtained by an application of the Duhem-Margules relation, somewhat similar to that of Boissonnas,[17] which serves the purposes of interpolating and of checking thermodynamic consistency. This method, described in the Experimental section, requires, as a minimum of data, only vapour compositions and the vapour pressure of *one* pure component; the measured vapour pressure of the other component, and those of the mixtures, then provide the necessary checks.

Since these measurements were made, an extensive survey of the t-butyl alcohol–water system has been reported [18] and vapour pressures from this source are shown separately in Fig. 1. Agreement is disappointing, but our own results are the more numerous, are better distributed, and respond very well to alternative tests of self-consistency such as Herington's.[19]

The dielectric-constant measurements are recorded in Table 2 and Fig. 2. Towards the alcohol end of the composition scale, they show a flat minimum which does not appear in Åkerlof's earlier data for this system,[20] although, for mixtures containing more than 50 wt. % of water, agreement is quite good. It is believed that the discrepancy is due to Åkerlof's unsatisfactory method of coping with the difficulties of measuring dielectric constants of media with appreciable conductance; he used a small cell with tantalum

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[12] Coulson, "Valence," Oxford, 1952, chap. XII.
[13] Coulson in "Hydrogen Bonding," ed. Hadži, Pergamon Press, London, 1959, p. 339.
[14] Bonner, *Trans. Faraday Soc.*, 1951, **47**, 1143.
[15] Martin, Symposium on the Hydrogen Bond, Roy. Inst. Chem., London, 1950, p. 21.
[16] Scatchard, *Chem. Rev.*, 1949, **44**, 7.
[17] Boissonnas, *Helv. Chim. Acta*, 1939, **22**, 541.
[18] Kentämaa, Tommila, and Martti, *Ann. Acad. Sci. Fenn.*, 1959, *A*, **93**, 1.
[19] Herington, *J. Appl. Chem.*, 1952, **2**, 19.
[20] Åkerlof, *J. Amer. Chem. Soc.*, 1937, **59**, 4125.

electrodes in series with a variable air condenser, an arrangement which is open to serious objections. Our own method, described in the Experimental section, allows satisfactory measurements to be made with media of conductance as high as 10^{-5} ohm^{-1} cm.$^{-1}$, which was not, of course, approached by any of the alcohol–water mixtures.

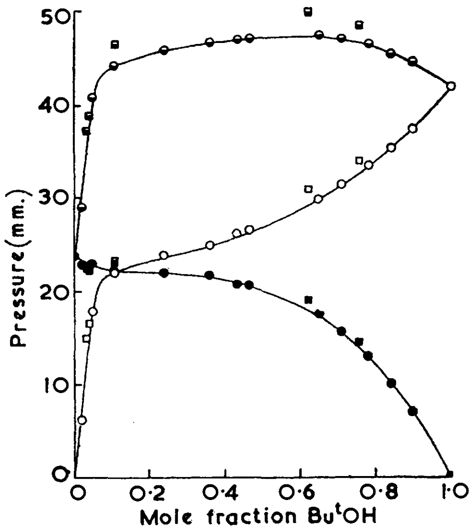

FIG. 1. Partial and total vapour pressures of t-butyl alcohol–water system. Circles, present work; squares, Kentämaa *et al.*[18] Hollow symbols, Bu^{t}OH; full symbols, H_2O; half full, total. Curves calculated from vapour compositions.

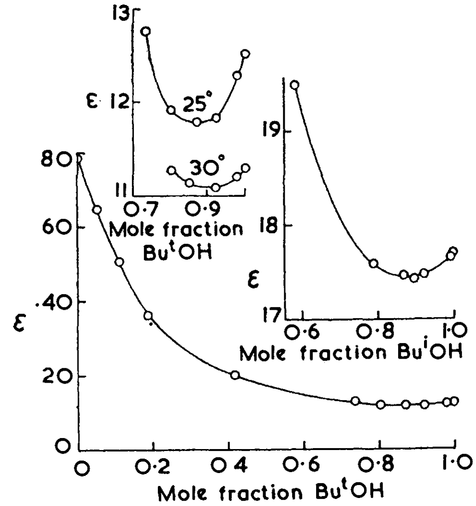

FIG. 2. Dielectric constants of t-butyl alcohol–water mixtures at 25°; insets, at 25° and 30° on enlarged scale, and dielectric constants of isobutyl alcohol–water mixtures at 25°.

TABLE 2.

Dielectric constants of some t-butyl alcohol–water mixtures.

$CMe_3\cdot OH$–water					$CHMe_2\cdot CH_2\cdot OH$–water	
Mole fraction of $CMe_3\cdot OH$	ε at 25°	ε at 30°	Mole fraction of $CMe_3\cdot OH$	ε at 25°	Mole fraction of $CHMe_2\cdot CH_2\cdot OH$	ε at 25°
1·0000	12·52 *	11·30 *	0·7352	12·76	1·0000	17·70 *
0·9797	12·30	11·21	0·4170	20·01	0·9922	17·67
0·9229	11·84	11·09	0·1871	36·14	0·9207	17·48
0·8705	11·79	—	0·1131	50·65	0·8948	17·43
0·8543	—	11·14	0·0546	64·80	0·8688	17·47
0·8038	11·92	11·27	0	78·48	0·7882	17·59
					0·5803	19·51

* Extrapolated values.

That the addition of water to t-butyl alcohol should initially cause a decrease in dielectric constant is surprising. It has nothing to do with the closeness of the temperature of measurement (25°) to the freezing point of the alcohol (24·7°), for it occurs (significantly less) at 30°, and a similar effect is found with isobutanol (insets to Fig. 2). It is accompanied by a decrease in viscosity,[18] and there can be little doubt that it reflects a structural change in the liquid phase.

The MBK plot is shown in Fig. 3. Linear between mole fractions of water from 0·3 to 0·6, it resembles the corresponding plots for other alcohol–water systems[4] in showing a deviation at the water end of the composition scale, and this has been attributed [4,15] to persistence of the water structure. It differs from the other systems in showing a deviation at the other end of the scale, which suggests the existence of some kind of specific interaction which is dominant in this alcohol–water system but recessive in the others. As it stands, this evidence is not substantial and leaves open the question whether such an effect, variable in incidence, is general to alcohol–water mixtures. Progress can be made in two ways: by more detailed consideration of the significance of the MBK relation, and by correlation of other recorded properties of these mixtures. This is the objective of the remainder of the discussion.

Since neither water nor alcohols have large molecular moments,[21] the high dielectric constants of these substances and of their mixtures arise because co-association favours molecular orientations which lead to co-operative reinforcement of dipole fields. This is expressed in terms of a correlation parameter, g,[22] which has, in such cases, a value greater than unity. For normal liquids, devoid of specific, short-range association forces, $g = 1$, and the interaction between a dipolar molecule and its surroundings is then " just that which would exist if the surroundings were replaced by material of the same macroscopic dielectric constant." [23] Since the MBK relation is derived on this basis, it seems to be invalid to apply it to any system for which g exceeds unity, as for water,[23] alcohols,[24] and their mixtures. Indeed, the minimum in the dielectric constant curve which we have observed can only be due to a minimum in g, arising from the way in which the stereochemistry of association changes with the composition of the liquid mixture. These considerations, however, do not necessarily vitiate the MBK treatment. If an associated complex is very short-lived, it cannot contribute directly to static dielectric constant by orientation as a molecular entity. Thus, in water, the unique relaxation time (10^{-11} sec.) is characteristic of H_2O molecules as the only orientating units,[25] and g exceeds unity, not as a function of the stereochemistry of any frozen-out complex, but because the molecules engaged in dynamic association are of enhanced polarity, or, in this special case, because of high proton mobility in hydrogen-bonded systems.[26] This is in line with Frank and Wen's views on the structure of water [27] and with the idea that the measured dielectric constant depends on the polarity of the orientating units averaged over about 10^{-6} sec. If the life-time of the complexes is from 10^{-8} to 10^{-10} sec. (as for water and alcohols [28]), the interactions involved are effectively smeared out into spherical symmetry, and then the dipole-in-a-cavity model becomes not inappropriate. It is important that association always increases the polarity of the participating molecules whether, for the complex formed, g is greater or less than unity. If a kind of association occurs which reduces static dielectric constant, it must be contra-association ($g < 1$) involving complexes long-lived enough to be orientated as polymeric units in response to the low-frequency field. Contra-association, however, need not always reduce the dielectric constant; this will depend upon the life-time of the complexes which are formed.

It is suggested, on this basis, that the MBK relation may hold either when association is of randomised, promiscuous type, or, if organised structures are produced, when these are very short-lived so that the uni-directional applied field " sees " only a continuum. It may fail when a longer-lived complex is formed, and this is regarded as the significance of the characteristic non-linearity of the plot in Fig. 3. This plot indicates that reduction in dielectric constant is accompanied by increase in the escaping tendency of water, and this is consistent with the formation of discrete complexes, each with a reduced " association field." That no such behaviour is apparent from the MBK plots for other alcohol–water systems does not exclude its existence; it may be that this method of examination is insensitive to events on a time-scale removed by orders of magnitude from its own. Such insensitivity of static dielectric constant to liquid-state phenomena is perhaps illustrated by its failure to respond to characteristic changes in water structure at about 35°

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[21] Smith, " Electric Dipole Moments," Butterworths Scientific Publns., London, 1955.
[22] Kirkwood, *J. Chem. Phys.*, 1939, **7**, 911.
[23] Harris and Alder, *J. Chem. Phys.*, 1953, **21**, 1031.
[24] Oster and Kirkwood, *J. Chem. Phys.*, 1943, **11**, 175.
[25] Collie, Hasted, and Ritson, *Proc. Phys. Soc.*, 1948, **60**, 145.
[26] Eigen in " Hydrogen Bonding," ed. Hadži, Pergamon Press, London, 1959, p. 429.
[27] Frank and Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.
[28] Magat in " Hydrogen Bonding," ed. Hadži, Pergamon Press, London, 1959, p. 309.

for which evidence is accumulating,[2,29] or to the hydration of non-polar solutes,[30] although the latter does affect relaxation times.[27] It is also clear that g may remain unaffected by changes between geometrically equivalent states, or because, for water, g is not maximal (cf. the influence of pressure [31]) so that multiple effects upon it may be self-cancelling.

It is desirable to supplement this evidence for discrete complex formation by collating available information on the self-association of alcohols and the way in which it is modified by additions of water.

The classical infrared evidence is that the association of alcohols tends to decrease with increasing molecular weight and in the sequence primary, secondary, tertiary. With gradually increasing concentration of an alcohol in a non-polar solvent, the association band which replaces the sharp monomer peak appears as a whole, indicating the direct production of polymers as complex as those present in the pure alcohol, with no intervening steps. The broadness of this band, and its freedom from fine structure, indicate the presence of hydroxyl groups covering a statistically continuous range of interaction energies. More detailed studies have correlated spectroscopic degrees of association in such " ideal associated solutions " 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 values for all values of n. The degree of association, sensitive to temperature because of the considerable entropy loss involved in association, is limited and varies from case to

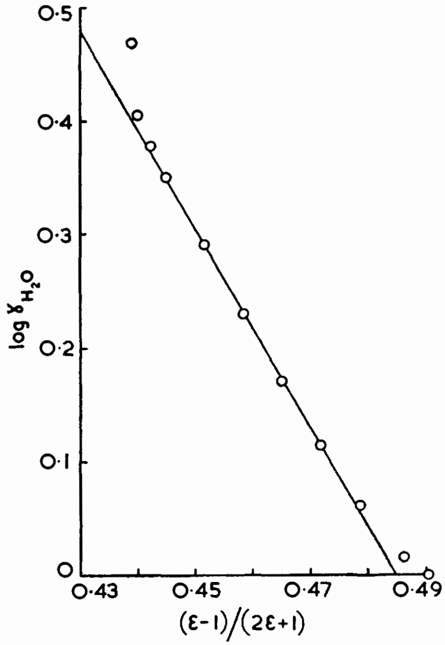

Fig. 3. MBK plot for t-butyl alcohol–water system.

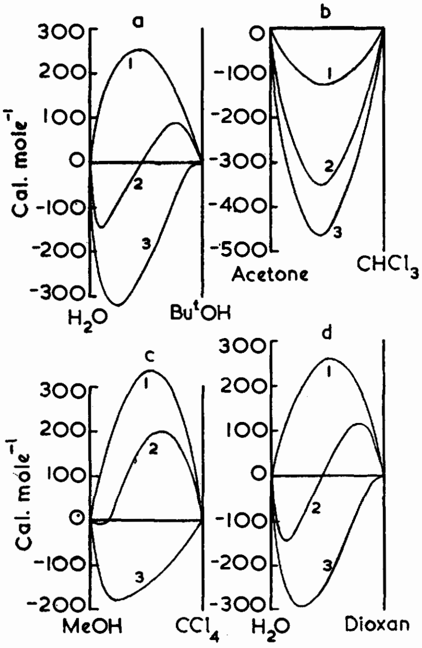

Fig. 4. Excess thermodynamic functions of mixing for (a) water + Bu^{t}OH; (b) acetone + CHCl$_3$; (c) methanol + CCl$_4$; (d)water + dioxan. 1, ΔG^E; 2, ΔH^M; 3, $T\Delta S^E$.

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[29] (*a*) Feates and Ives, *J.*, 1956, 2798; (*b*) Franks and Ives, *J.*, 1960, 741.

[30] Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507.

[31] Hamann, " Physico-chemical Effects of Pressure," Butterworths Scientific Publns., London, 1957, p. 104.

case; an average of 5—7 has been quoted for room temperature, with a maximum of 3 for the special case of t-butyl alcohol.

These conclusions have been supplemented by later work in other fields. Dielectric-constant data [32] indicate the importance of steric factors in alcohol association, which may involve the formation of cyclic or helical polymers.[33] There is a body of opinion in favour of cyclic structures,[34,35] even to the extent of doubly-bridged dimers with bent hydrogen bonds.[35,36] This perhaps shows that questions about structures in liquid alcohols remain open, but a general picture emerges of long, associated chains which become increasingly predominant with fall in temperature and thus produce a marked increase in viscosity. Dielectric dispersion [28] and nuclear magnetic resonance studies [37] indicate that, although these chains have a degree of rigidity due to appreciable hindrance of free rotation, the average life of an associated complex is very short, and that rapid exchange is in operation. It is important that the existence of dimers (and, to a smaller extent, of other low polymers) is disfavoured, partly because the entropy loss is the greatest in the first step of association,[38] but mainly because of the enhanced polarity arising from hydrogen bonding. That dimers can be regarded as highly reactive, amphiprotic intermediates is in line with Frank's discussion of hydrogen bonding [39] and with detailed evaluations of the energies of successive association steps.[40] It is clear that the association of alcohols is a function of the interplay of energy and entropy effects, the generally unfavourable influence of the latter being partially compensated by the disorderly entanglement of polymeric chains in the liquid state.

X-Ray examination [41] has provided the familiar picture of chain-like association in which each alcohol molecule tends to attach itself to two others. Formally, each oxygen atom could participate in three hydrogen bonds by accepting two protons and donating one; but this does not occur, no doubt partly because it would upset the give-and-take balance upon which a degree of co-operation in extended bond formation depends. Water can preserve this balance by giving two and taking two protons, thus making possible the three-dimensional, co-operative order not available to alcohols. There is, however, some *X*-ray evidence [42] of a tendency towards an orderly arrangement of oxygen atoms in liquid alcohols.

The influence of water on the association complex of a liquid alcohol must largely depend on competitive hydrogen bonding, akin to an acid–base equilibrium.[43] The order $\mathrm{MeOH} < \mathrm{EtOH} < \mathrm{Pr^nOH} < \mathrm{Bu^tOH}$ has been established as that of increasing basic strength [44] and also, from infrared studies, as that of increasing tendency to act as proton acceptor in hydrogen-bond formation.[45]

It is thus certain that hydrogen bonding between t-butyl alcohol and water molecules is energetically favoured, yet mixtures of the two show large positive deviations from Raoult's law. The reasons for this appear from an examination of the thermodynamic functions of mixing, which are illustrated in Fig. 4a.[18]

The nearly symmetrical, positive, excess free energies of mixing arise from compensation

[32] Smyth, " Dielectric Behaviour and Structure," McGraw-Hill, New York, 1955.

[33] Le Fèvre and Williams, *J.*, 1960, 108.

[34] Mecke, *Discuss. Faraday Soc.*, 1950, **9**, 161; Weltner and Pitzer, *J. Amer. Chem. Soc.*, 1951, **73**, 2606.

[35] Pimentel in " Hydrogen Bonding," ed. Hadži, Pergamon Press, London, 1959, p. 107.

[36] Smith and Creitz, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 145; Becker in " Hydrogen Bonding," ed. Hadži, Pergamon Press, London, 1959, p. 155.

[37] Luz, Gill, and Meiboom, *J. Chem. Phys.*, 1959, **30**, 1540.

[38] Saroléa-Mathot, *Trans. Faraday Soc.*, 1953, **49**, 8.

[39] Frank, *Proc. Roy. Soc.*, 1958, *A*, **247**, 481.

[40] Coggeshall, *J. Chem. Phys.*, 1950, **18**, 798.

[41] Zachariasen, *J. Chem. Phys.*, 1935, **3**, 158; Harvey, *ibid.*, 1938, **6**, 111; Prietzschk, *Z. Phys.*, 1941, **117**, 482.

[42] Pierce and MacMillan, *J. Amer. Chem. Soc.*, 1938, **60**, 779.

[43] Gordy and Stanford, *J. Chem. Phys.*, 1940, **8**, 170; 1941, **9**, 204.

[44] Gerrard and Macklen, *Chem. Rev.*, 1959, **59**, 1105.

[45] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.

between highly unsymmetrical heats and excess entropies of mixing. Interpretation of the heat-of-mixing curve is not eased by the certainty of overlap of the composition ranges in which endo- and exo-thermic processes occur, so that one may tend to mask the other and both may be underestimated. In these circumstances, it is desirable to make comparisons with other systems in which effects which are thought to be operating are likely to act in isolation. Thus, if exothermic mixing is due to strong interaction between the components, there might be a resemblance to the acetone–chloroform system[46] (Fig. 4b) in which this is the only kind of interaction of significance. Maximal interaction at a mole ratio other than 1 : 1 will, of course, displace the curves from symmetry; probably in the t-butyl alcohol–water system, towards the alcohol side. If the breaking up of the associated water structure were the predominant effect, comparison with the carbon tetrachloride–methanol system might be relevant;[47] here, carbon tetrachloride is the depolymerising diluent for methanol, as t-butyl alcohol might be for water. The comparison may be made by reference to Fig. 4c,[48] which shows some resemblance to Fig. 4a; a combination of Figs. 4b and 4c would show a still closer resemblance. That the two effects of strong interaction and depolymerisation of water are prominent in the t-butyl alcohol–water system is confirmed by the close similarity in thermodynamic behaviour to that of the dioxan–water system[49] (Fig. 4d). In this case, dioxan is non-associated and can act only as proton acceptor in hydrogen-bond formation.

It is not suggested that these are the only effects of significance, but attention is confined to alcohol-rich mixtures. For these, mixing is endothermic, which reflects a net "melting" or bond-dissociation, yet the excess entropy of mixing remains negative. Comparison with related systems shows that, at 25°, the mixing of methanol with water is exothermic over the whole composition range. This is also the case for ethanol–water, but here the curve is displaced to less negative values of ΔH, predominantly on the alcohol side of the composition scale—a tendency which increases rapidly with rise of temperature. This effect is so much more developed in the propan-1-ol–water system that mixing is endothermic for all mixtures containing more than about 0·3 mole fraction of the alcohol. In the t-butyl alcohol–water system, the effect is again increased, to give the result shown in Fig. 4a. There is clearly a systematic gradation in behaviour from one alcohol to the next of higher molecular weight. Since the water structure must be completely destroyed in a mixture of, say, 0·7 mole of methanol with 0·3 mole of water, it is clear that the heat liberated when such a mixture is made reflects the superior stability of the hydrogen bonds which are formed between unlike molecules. In spite of the extensive bond breaking that must have occurred, the heat so absorbed is more than compensated by the heat liberated in the formation of perhaps a smaller number of new, stronger bonds. For a t-butyl alcohol–water mixture of the same composition, on the other hand, the absorption of heat shows that there is a net bond breaking and, since it is certain that the energy liberated for each bond made is greater, the bonds formed must be fewer. This is due to steric hindrance and to the over-all dilution effect produced by the hydrocarbon residue of the alcohol molecule.

The evidence that discrete complexes are formed in solutions of water in t-butyl alcohol is therefore considerable and can be understood in terms of the high tendency of the alcohol molecules to become protonated, to which a limitation is applied by steric hindrance. The complex must be centred on a water molecule which, as donor, forms two strong hydrogen bonds with two butyl alcohol molecules. This exercise of its acidic function by the water molecule favours the simultaneous operation of its basic function so that, as acceptor, it forms hydrogen bonds with two more butyl alcohol molecules. This

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[46] Prigogine and Defay, "Chemical Thermodynamics," Longmans, London, 1954, p. 390.

[47] Rowlinson, "Liquids and Liquid Mixtures," Butterworths Scientific Publns., London, 1959, p. 183.

[48] Scatchard, Wood, and Mochel, *J. Amer. Chem. Soc.*, 1946, **68**, 1962.

[49] Malcolm and Rowlinson, *Trans. Faraday Soc.*, 1957, **53**, 921.

satisfies the equality of give-and-take in hydrogen bonding and the requirement of symmetry upon which optimum stability probably depends. Further bonding of the four peripheral alcohol molecules is disfavoured, and the five-molecule complex, involving in its structure a degree of contra-association, is postulated to be the sufficiently stable entity needed to explain the facts that have been recorded.

It seems likely that this water-centred association is common to alcoholic solutions of water in general; even if long-lived complexes are not usually formed, the rate of proton exchange is known to decrease markedly with falling water content.[50] The suggested structure is the same as that used by Prietzschk [41] to explain why traces of water increase the viscosity of alcohol at low temperatures and why wet, but not anhydrous, alcohol will form a glass. The water forms a centre for three-dimensional polymerisation which, if the peripheral alcohol molecules are not (as in the case of t-butyl alcohol) debarred from hydrogen bonding, can form the basis for the formation of disordered, silicate-like structures. Water-centred association is also consistent with the observation [51] that, while the Stokes–Einstein radius of the ethanol molecule is the same whether it is diffusing in pure ethanol or in water, the radius of the water molecule is greater when it is diffusing in ethanol than when it is diffusing in water. Even for the first member of the homologous series, signs of this effect are to be found; it can be advanced to explain the minimum in the excess mobility of hydrogen ions in predominantly methanolic methanol–water mixtures.[52]

EXPERIMENTAL

Dielectric-constant Measurements.—The difficulties of damping which appreciable conductance of the medium introduces in the resonance method of measuring dielectric constant have been minimised by use of the circuit indicated in Fig. 5.

The oscillator, controlled by a quartz crystal X (Quartz Crystal Co. Ltd.; 180·55 kc. sec.$^{-1}$ at 20°), was based on a relatively high-gain output beam tetrode (V_1, 6V6) and developed considerable power in its tuned anode circuit (L_1, 352·7 μH Sullivan–Griffiths secondary inductance standard). This circuit was loosely coupled (L_2, 20 turns 18 S.W.G. wire on 6 cm. diam. ceramic former, parallel to, and spaced 6 cm. from, L_1) to a " buffer " amplifier incorporating an output pentode (V_2, 6K7G) the anode circuit of which contained a high inductance (L_3, radio-frequency choke) which could be tuned to resonance with the crystal with a shunt capacitance not exceeding about 35 μμF. This inductance was coupled (L_4, 16 turns 18 S.W.G. wire on 4 cm. diam. ceramic former enclosing L_3 and at right angles to L_1 and L_2) to a feeding circuit (co-axial cable) which terminated in a single-turn coupling (L_5, 10 cm. diam. loop of co-axial cable with earthed screen, fixed rigidly 2 cm. from L_6) to the resonance circuit. The use of co-axial cable in this way ensured a very loose, purely inductive coupling, the metal screening of the wire forming a Faraday cage.

The resonance circuit consisted of a secondary inductance standard (L_6, 391 μH, Sullivan–Griffiths), shunted by fixed (C_{S1}, 499·5 μμF; C_{S2}, 999·5 μμF) and variable (C_V, 700 μμF) Sullivan air condensers (calibrated by the makers) and the dielectric constant cell, C_O. Resonance was detected by means of a diode rectifier (V_3, 6D1) feeding a balanced valve voltmeter [53] based on matched triodes (V_4, 6C5), operating a Cambridge " Unipivot " meter, with universal shunt.

The apparatus was screened by means of earthed copper boxes, as indicated in Fig. 5, and was energised by a stabilised power pack ($\pm 0{\cdot}25$ v output for ± 50 v input; $\pm 0{\cdot}06$ v output for ± 100 ohms load). Pyrex cells of the Sayce and Briscoe type,[54] with pinch-seal electrical contacts,[55] were made with rather greater than normal spacings between the silvered surfaces and, to minimise end-effects,[56] were mounted centrally in an oil-filled bath 36 cm. in diameter.

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[50] Weinberg and Zimmerman, *J. Chem. Phys.*, 1955, **23**, 748.

[51] Hammond and Stokes, *Trans. Faraday Soc.*, 1953, **49**, 890.

[52] Shedlovsky in " The Structure of Electrolytic Solutions," ed. Hamer, Wiley, New York, 1959, p. 268.

[53] Hartshorn, " Radio-frequency Measurements," Chapman and Hall, London, 1940.

[54] Sayce and Briscoe, *J.*, 1925, **127**, 315.

[55] Campbell, *J. Amer. Chem. Soc.*, 1929, **51**, 2419.

[56] Sugden, *J.*, 1933, 768.

Contact was made or broken by lowering or raising a wire link (40 S.W.G.) which dipped into small mercury wells 1 cm. below the top level of the silvering of the cells. The bath was kept anhydrous by means of silica gel, and was thermoregulated to ±0·01°. Temperatures were adjusted by reference to N.P.L. standards. The resonance adjustment of the standard condenser was found by taking means of the two settings which gave identical meter readings. For the most highly conducting solutions used (aqueous pyridine, $\kappa \sim 10^{-5}$ ohm^{-1} cm.$^{-1}$) the scatter of replicate means was about ±0·4 μμF, but was normally less than half of this. Conductance of the liquid medium reduces the power developed at resonance, but has no effect upon the capacity.

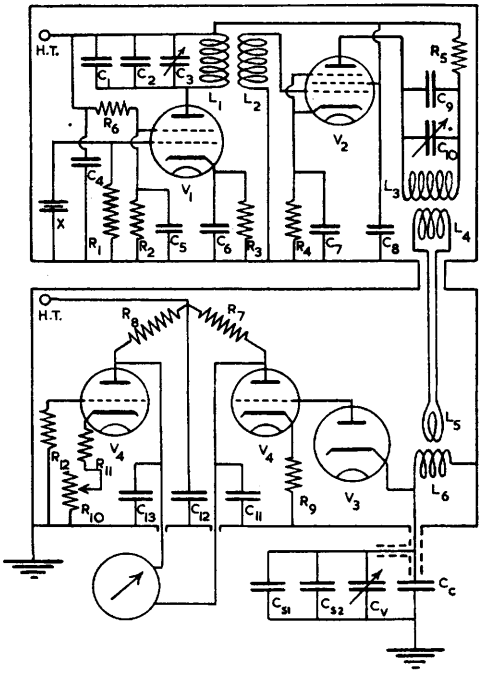

FIG. 5. Dielectric constant apparatus. Components not defined in the text are as follows: C_1 0·002 μF, mica; C_2 75 μμF, mica; C_3 25 μμF, air; C_4, C_5, C_6 0·1 μF; C_7 500 μμF; C_8 0·02 μF; C_9 20 μμF; C_{10} 25 μμF, air; C_{11}, C_{13} 2 μF; C_{12} 10μF. R_1 2MΩ; R_2 75 kΩ; R_3, R_4 500Ω; R_5 1·5 kΩ; R_6 30 kΩ; R_7, R_8 10 kΩ; R_9 1 kΩ; R_{10} 2 kΩ; R_{11} 500 Ω; R_{12} 1 MΩ.

The cells were prepared for use and filled by normal procedures. They were calibrated by means of nitrogen, benzene, and nitrobenzene as standards, for which the following dielectric constants at 25° were adopted; 1·0005, 2·2725, 34·75. These values were chosen as a result of a critical survey of recorded data and agree, within the assigned probable limits of accuracy, with the more recent recommendations of the National Bureau of Standards.[57] The determined cell constants (μμF *in vacuo*), with stray capacitance corrections in parentheses, were as follows: cell A, 70·81 (0·63); cell B, 25·55 (0·57); cell C, 3·382 (0·35). The dielectric constants of a number of pure liquids determined on the basis of these calibrations are recorded, and compared with critically selected data,[57] in Table 3.

It is seen that agreement is excellent in a number of cases but not in others; it is suggested that, for these, the provision of new data is timely. The most recent re-determination of the dielectric constant of water, however, includes the figure of 78·30 at 25°,[58] about 0·3% lower than the previously accepted value; it is probable that we are not alone in being disconcerted at this change, which carries the weight of authority. If the first three entries in Table 3 can be adopted for reference standards, it can be said that our calibrations of three cells by means of six pure substances show a mean deviation of only 0·08%. Examination of sources of error (temperature variation of crystal frequency,[59] non-linearity of condenser scale, random error in condenser setting) indicates a maximum deviation of ±0·3 μμF. In the least favourable case (ethanol in cell C), this corresponds to ±0·09 in the dielectric constant; on all counts,

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[57] Maryott and Smith, Nat. Bur. Stand. Circular 514, 1951.

[58] Malmberg and Maryott, *J. Res. Nat. Bur. Stand.*, 1956, **56**, 1.

[59] Booth and Dixon, *J. Inst. Elec. Eng.*, 1935, **77**, 197.

TABLE 3.
Dielectric constants of pure substances at 25°.

		Dielectric constant				Dielectric constant	
Substance	Cell	Present work	N.B.S.[57]	Substance	Cell	Present work	N.B.S.[57]
Benzonitrile	B	25·23	25·20	Butan-1-ol	B	17·42	17·1
,,	C	25·23		Isobutanol	B	17·70 *	17·7
Cyclohexane	A	2·013	2·015	t-Butyl	B	12·52 *†	—
,,	B	2·013		alcohol			10·9
Ethanol	B	24·32	24·3	Pyridine	B	13·06	12·3
,,	C	24·30		,,	C	13·04	
Propan-1-ol	B	20·20	20·1	Water	C	78·48	78·54

* Extrapolated values. † At 30°, 11·30*.

the error in our value for the dielectric constant of water should not exceed $\pm 0{\cdot}1$. The anomaly must therefore remain unresolved, but is not unduly serious in relation to the primary objective of this work.

Measurements of Partial and Total Vapour Pressure.—A re-cycling equilibrium still, similar in principle to that of Jones, Schoenborn, and Colburn,[60] was used. The distillate passed from the receiver (6 ml.; magnetically stirred) *via* a capillary tube to an electrically heated flash-chamber (Variac control; *ca.* 10 w), where it was completely vaporised and delivered by a Landsberger tube into the main boiler (100 ml.), which was immersed in a thermostatic bath (~26°). Refluxing from the upper parts of the boiler was obviated by means of local electrical heating (*ca.* 5 w). Vapour passed from the boiler to a glycol-cooled (0° to −20°) reflux condenser, which returned the total distillate to the receiver vertically beneath it. The boiler was equipped with a re-entrant pocket containing a little mercury and a Thermistor (Stantel type F.2311/300; calibrated before each experiment), by which the equilibrium temperature was adjusted (by pressure control) to 25° ± 0·03°. A side-arm attached to the receiver carried a tube ending in a fine capillary. This was used for sampling and, during equilibration, for delivery of a minute leak of filtered, carbon dioxide-free air. The value of this device in promoting steady boiling can hardly be over-emphasised; the trace of permanent gas so introduced was far too small to affect the accuracy of the total vapour-pressure measurements.

The outlet from the condenser led, *via* a cold trap, to a pressure reservoir (45 l.), a manostat,[61] a rising meniscus mercury manometer, and vacuum-pumps. The performance of the still was checked by charging the receiver and the boiler with the separate components of a mixture. After operation for 80 min. the same compositions of liquid and vapour phases were attained for either of the initial distributions. On attainment of equilibrium, distillation was stopped by sudden increase of pressure, and liquid samples were analysed by pyknometric density determinations (probable error $<\pm 0{\cdot}00004$ g. ml.$^{-1}$, $<0{\cdot}0005$ mole fraction). For the preparation of alcohol–water mixtures of known composition (for the density reference curve, and for the dielectric constant measurements), intensively dried t-butyl alcohol was not used. Instead, the water content of the otherwise pure alcohol was determined by Karl Fischer titration, the dead-stop end-point method being used.[62]

Calculation of Partial Vapour Pressures.—A method based on the following argument was used. If ideal behaviour of the vapour phase is assumed, the Duhem-Margules relation may be written in the approximate form

$$\frac{x_2 N_1}{x_1 N_2}\cdot\frac{\Delta p_1}{\Delta p_2}+1=0, \qquad (3)$$

where p_1 is the partial pressure of component 1, x_1 and N_1 are its mole fractions in the vapour and the liquid phase, respectively, and p_2, x_2, and N_2 similarly relate to component 2.

The composition scale is divided into any number of equal small parts, say 50, and relevant quantities are tabulated in the following way:

$N_1 - 0{\cdot}02$	N_1	$N_1 + 0{\cdot}02$
p_1'	p_1	p_1''
p_2'	p_2	p_2''
x_1'	x_1	x_1''
x_2'	x_2	x_2''

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[60] Jones, Schoenborn, and Colburn, *Ind. Eng. Chem.*, 1943, **35**, 666.

[61] Clan and Shaw, *J. Sci. Instr.*, 1939, **16**, 354.

[62] Wernimans and Hopkinson, *Ind. Eng. Chem.*, *Analyt.*, 1943, **15**, 272.

It can be seen that equation (3) can be re-written as:

$$\frac{x_2}{x_1}\cdot\frac{N_1}{N_2}(p_1''-p_1')+(p_2''-p_2')=0,$$

or

$$\frac{x_2}{x_1}\cdot\frac{N_1}{N_2}\cdot p_1''+p_2''=\frac{x_2}{x_1}\cdot\frac{N_1}{N_2}\cdot p_1'+p_2'. \tag{4}$$

If the vapour is ideal in behaviour, then

$$p_2''=\frac{x_1''}{x_1''}\cdot p_1''. \tag{5}$$

Therefore,

$$\frac{x_2}{x_1}\cdot\frac{N_1}{N_2}\cdot p_1''+\frac{x_1''}{x_1''}\cdot p_1''=\frac{x_2}{x_1}\cdot\frac{N_1}{N_2}\cdot p_1'+p_2'.$$

Therefore,

$$p_1''=\frac{\dfrac{x_2}{x_1}\cdot\dfrac{N_1}{N_2}\cdot p_1'+p_2'}{\dfrac{x_2}{x_1}\cdot\dfrac{N_1}{N_2}+\dfrac{x_2''}{x_1''}}. \tag{6}$$

Similarly, by eliminating p_1'', we obtain

$$p_2''=\frac{\dfrac{x_2}{x_1}\cdot\dfrac{N_1}{N_2}\cdot p_1'+p_2'}{\dfrac{x_2}{x_1}\cdot\dfrac{N_1}{N_2}\cdot\dfrac{x_1''}{x_2''}+1}=p_1''\cdot\frac{x_2''}{x_1''}. \tag{7}$$

The calculation is started at $N_1 = 0{\cdot}02$, so that $p_1' = 0$ and $p_2' = p_2^\circ$, the vapour pressure of pure component 2. Then the first computation is:

$$\text{For } N_1 = 0{\cdot}02,\quad p_1''=\frac{p_2^\circ}{\dfrac{x_2}{x_1}\cdot\dfrac{0{\cdot}02}{0{\cdot}98}+\dfrac{x_2''}{x_1''}}\quad\text{and } p_2''=p_1''\cdot\frac{x_2''}{x_1''}.$$

Values of p_1'' and p_2'' are next calculated for $N_1 = 0{\cdot}04$; in this calculation, the previous values of p_1'' and p_2'' now become the values of p_1' and p_2' for use in equation (6). This procedure is followed all along the composition scale until the last value of p_1'' and p_2'' is reached. These are, respectively, p_1° and zero. These fixed points, and the agreement between observed and calculated total vapour pressures, provide a check on the thermodynamic self-consistency of the data and the assumption of vapour ideality. A further check is to carry out the entire calculation starting at the other end of the composition scale; the same curves must be retraced. These criteria are well satisfied by the data of Scatchard and Raymond[63] for the ethanol–chloroform system, chosen as one of the most complete and accurate studies available, and reasonably well by our own data on the t-butyl alcohol–water system (cf. Fig. 1).

Materials.—*Water.* Conductance water, $\kappa \sim 0{\cdot}1 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$, was prepared by methods previously described.[29a]

Benzene. Thiophen-free benzene was dried (Na_2SO_4) and fractionally crystallised three times, dried (Na), and fractionated from fresh sodium wire with use of a 4 ft. vacuum-jacketed column packed with Fenske helices and fitted with proportionating head. The product had b. p. 80·1°, d_4^{25} 0·87365.

Nitrobenzene. Fractional distillation, followed by fractional crystallisation and final redistillation, gave material of b. p. 210·8°, d_4^{25} 1·19817.

Benzonitrile. Three successive fractional distillations (2 ft. column) afforded material of constant b. p. 191·0°, d_4^{25} 1·00061.

Cyclohexane. Three successive crystallisations, followed by two fractional distillations (4 ft. column), gave cyclohexane, b. p. 80·8°, d_4^{25} 0·77379.

Ethanol. A highly purified and intensively dried specimen was kindly provided by Professor D. C. Bradley, whom the authors thank.

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[63] Scatchard and Raymond, *J. Amer. Chem. Soc.*, 1938, **60**, 1278.

Propan-1-*ol.* Some trouble was experienced in obtaining material that did not give a slight haze with water. This was obviated by partial bromination (to remove allyl alcohol), refluxing with sodium hydroxide, and treatment with, and distillation from, Hewitt's reagent. A final fractional distillation (4 ft. column) afforded material of b. p. 97·1—97·3°, d_4^{25} 0·79995.

Butyl alcohols. These were highly purified specimens kindly supplied by Dr. A. R. Martin, whom the authors thank. The water contents and refractive indices were: butan-1-ol, 0·13%, n_D^{25} 1·39756; isobutyl alcohol, 0·12%, n_D^{20} 1·39640; t-butyl alcohol, 0·13%, n_D^{20} 1·38779.

Pyridine. Analytical-grade pyridine was fractionally distilled, refluxed over potassium hydroxide, and re-fractionated. Final distillation was carried out from a few drops of 96% sulphuric acid, a device effective in minimising the conductance of subsequently prepared mixtures with water. The product had b. p. 115·5°, d_4^{25} 0·97811.

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