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STUDIES OF DIELECTRIC PROPERTIES OF SOME BINARY HYDROORGANIC SYSTEMS

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ABSTRACT

Four alternative hypotheses, for describing the nature of ideal dielectric behavior in binary liquid mixtures, have been explored for the systems acetonitrile–water and *tert*-butanol–water. The various excess properties have been analysed using the four segment composition model. The estimation and interpretation of correlation factors and dipolar free energies in binary mixtures of associated liquids is discussed.

INTRODUCTION

We are interested in the formulation and exploration of procedures for translating the composition dependence of the bulk properties of binary liquid systems into information about the structural and dynamic characteristics of the patterns of molecular aggregation which exist within their mixtures. In this instance, we are concerned with trying to establish reasonable interpretations of static dielectric constant data for the acetonitrile (ACN)–water and *tert*-butanol (TBA)–water systems.

There are several different quantities which one can derive from a combination of dielectric constant and refractive index data; each of which may be regarded as having its own particular significance. We have calculated and analysed the composition dependences of four such quantities.

In order to appraise the significance of the composition dependence of the bulk properties of binary mixtures, it is helpful to make comparisons with estimates of the corresponding properties of ideal mixtures of the same composition.

There exists a thermodynamic definition of an ideal binary mixture, in the form of a generalization of Raoult's Law [1]. In that context, the ideal values of any thermodynamic property of a binary liquid system are unambiguously defined. Dielectric constants, in common with viscosities and ultrasonic

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absorptivities, fall outside the scope of the thermodynamic formalism. Thus, their ideal values can only be estimated by making additional assumptions about what constitutes ideal behavior.

In attempting to define ideal dielectric behavior, one has a choice between some relatively simple options which are, to a large extent intuitive, and more complex alternatives which owe their origins to specific models of molecular scale phenomena. Of particular interest, in this context, are statistical theories which introduce possible links between the thermodynamic and dielectric properties of polar liquids.

Each of the alternative definitions of dielectric ideality, that were explored in this work, led to estimates of excess dielectric quantities, which were analysed using the four-segment composition model [2,3].

DIELECTRIC PROPERTIES

Molar susceptibilities

The electric susceptibility is defined by

$$\chi_e = D - 1 \tag{1}$$

where D is the static dielectric constant (relative permittivity).

The units of the quantity $4\pi\ \epsilon_0 \chi_e \bar{V}$ (where ϵ_0 is the vacuum dielectric permittivity and $\bar{V}$ is the molar volume) are such as to identify it as the effective molar dipole moment that is induced in a bulk sample by a unit field.

Since $\chi_e \bar{V}$ is a molar quantity, it seems to be reasonable to explore the hypothesis that it should be mole fraction additive in an ideal binary mixture.

$$(\chi_e \bar{V})_{id} = X_A (\chi_e \bar{V})_A^+ + X_W (\chi_e \bar{V})_W^+ \tag{2}$$

where X_A and X_W are the respective mole fractions of the components A(organic) and W(water) in their mixtures. $(\chi_e \bar{V})_A^+$ and $(\chi_e \bar{V})_W^+$ are the respective molar properties of the two pure liquids.

In the event that the excess molar volumes are zero, a condition of thermodynamic ideality, eqn. (2) is equivalent to

$$D_{id} = \phi_A D_A^+ + \phi_W D_W^+ \tag{3}$$

where ϕ_A and ϕ_W are the respective ideal volume fractions of components A and W in their mixtures.

$$\phi_A = \frac{X_A \bar{V}_A^+}{X_A \bar{V}_A^+ + X_W \bar{V}_W^+} \tag{4}$$

It is appropriate to note that Decroocq [4] has concluded that eqn. (3) is a close approximation to a definition of ideal behavior that he proposed on the basis of the theoretical work of Onsager [5] and Kirkwood [6]. In that sense, the rudimentary definition of dielectric ideality, represented by eqn. (2) has a theoretical as well as an intuitive basis.

We have chosen to examine the composition dependence of $\chi_e \bar{V}$, rather than of χ_e or D, in the belief that extensive properties are better suited, than are intensive properties, to analytical procedures which attempt to interpret excess quantities in terms of additive effects of different patterns of molecular aggregation.

Molar polarisibilities

Various theories have been proposed to interpret or predict bulk dielectric behavior in terms of individual molecular properties. These theories have provided a number of definitions of molar polarisibility.

The earliest and simplest of these definitions is that associated with the names of Clausius and Mosotti.

$$\bar{P}_{\text{CM}} = \frac{(D-1)}{(D+2)}\bar{V} \tag{5}$$

This definition served as a basis for the Lorentz–Lorenz theory of electronic polarization [7]. It was subsequently used by Debye in the derivation of his theory of the dielectric behavior of polar gases [8].

$$\bar{P}_{\text{CM}} = \frac{4\pi L}{3}\left\{\alpha_0 + \frac{\mu^2}{3kT}\right\} \tag{6}$$

where α_0 is the molecular polarisibility and μ is the permanent molecular dipole moment. L is Avogadro's number, k is Boltzmann's constant and T is the absolute temperature.

The molecular polarisibility may be represented as the sum of two components.

$$\alpha_0 = \alpha_{\text{el}} + \alpha_{\text{vib}} \tag{7}$$

α_{el} is the electronic polarisibility, which is related to the optical refractive index, n, by the Lorentz–Lorenz equation

$$\frac{4\pi L}{3}\alpha_{\text{el}} = \frac{(n^2-1)}{(n^2+2)}\bar{V} \tag{8}$$

The refractive index is a moderately sensitive function of the frequency of the radiation that is used in its measurement. It is generally accepted that the optimum value of n, to be used in eqn. (8) is that which is obtained by extrapolation, to infinite wavelength, of refractive indices that have been measured over a range of radiation frequencies which are all substantially higher than the frequencies of molecular vibrations. This extrapolated refractive index, n_∞ is related to the high frequency dielectric constant D_∞, which appears in many theoretical treatments, by

$$D_\infty = n_\infty^2 \tag{9}$$

In practice, there is relatively little difference between n_∞ and n_D, where n_D is the commonly reported refractive index, obtained using the Sodium D-line. We note that some authors report refractive indices that correspond to other optical frequencies.

We shall have occasion to explore the general proposition that a molar polarisability should be mole fraction additive, in the case of an ideal binary mixture.

$$\bar{P}_{id} = X_A \bar{P}_A^+ + X_W \bar{P}_W^+ \qquad (10)$$

In that context, it is appropriate to note that Dusart, Grolier and Viallard [9] have provided some experimental justification for the relationship

$$\alpha_{el.id} = X_A \alpha_{el.A}^+ + X_W \alpha_{el.W}^+ \qquad (11)$$

α_{vib} is the vibrational (atomic) polarisibility. It is argued that an external electric field causes distortions to the molecular vibrations which alter the molecule's mean dipolar character. In theory, one should be able to obtain estimated of α_{vib} from refractive indices that have been measured using far infrared radiation in the gas phase. In practice such measurements are difficult to carry out and, as a consequence, there is very little information to be found in the literature.

Several different strategies may be employed to get around the lack of information about vibrational polarisibility. Some authors, recognizing that α_{vib} is quite small compared to α_{el}, have estimated α_0 using eqn. (8) with n set equal to 1.05 n_D [10] or 1.10 n_D [11]. Others have chosen to ignore α_{vib} and to consider that the effects of vibrational polarisibility are absorbed, as a minor component, in the dipole moment term. That is the strategy that we have adopted. A third approach involves setting the n of eqn. (8) equal to the far-infrared refractive index of the liquid state [12]. Since the radiation frequency is somewhat less than the frequencies of the pseudo-lattice vibrations, it appears to us that this approach casts aside important information about short range structure, which is the major object of our investigations.

The Clausius–Mosotti–Debye model, for the interactions of individual molecules with their polarizible environments, was found to be inappropriate for describing polar liquids. Of the various approaches, which were proposed to interpret the bulk dielectric behavior of polar liquids, that which gained the widest level of acceptance was devised by Onsager [5]. Most of the more recent theoretical innovations which lend themselves to interpretation, rather than prediction, of bulk dielectric properties, may be regarded as being extensions of Onsager's work.

In the general context of Onsager's "cavity in a continuum" approach, Kirkwood proposed the following alternative to eqns. (5) and (6).

$$\bar{P}_K = \frac{(D-1)(2D+1)\bar{V}}{9D} = \frac{L}{3\epsilon_0}\left\{\alpha_0 + \frac{\mu_{eff}^2}{3kT}\right\} \qquad (12)$$

where μ_{eff} is the effective molecular dipole moment, which may be anticipated to differ from the gas phase value if there is significant correlation between the orientation of the dipolar axes of neighboring pairs of molecules.

While the concept of an effective molecular dipole moment represented an important theoretical innovation, it has been shown that Kirkwood's model is faulty. Frohlich [13] and Buckingham [14] have given somewhat different derivations for a quantity which may be termed the molar orientational polarisibility.

$$\bar{P}_{\mathrm{F}} = \frac{(D - D_{\infty})(2D + D_{\infty})}{D(D_{\infty} + 2)^2}\bar{V} = \frac{L}{9kT\epsilon_0}\mu_{\mathrm{eff}}^2 \tag{13}$$

We note that, in the event that the effective dipole moment is identical to the gas phase dipole moment, eqn. (13) is identical to an equation originally derived by Onsager. We have chosen to concentrate our attention upon the Frohlich–Buckingham orientational polarisibility, which we have assumed, in accordance with Oster [15], to be mole fraction additive for ideal mixtures.

Correlation factors

Assuming eqn. (13) to be applicable to binary mixtures, it is possible to estimate values of average effective dipole moments from measured dielectric constants and refractive indices.

The finding that, for many pure liquids, μ_{eff} differs quite significantly from the gas phase dipole moment μ_{g} is regarded as evidence of extensive molecular association. Oster and Kirkwood [16] saw fit to introduce a quantity called the correlation factor, which is defined by

$$g = \frac{\mu_{\mathrm{eff}}^2}{\mu_{\mathrm{g}}^2} \tag{14}$$

A unit value of g corresponds to random mutual orientation of neighboring molecular dipolar axes. For pure hydrogen bonding liquids, such as water and the alkanols, the g values are found to be significantly greater than one, as might be expected to result from end-on parallel dipolar alignment [14]. That $g < 1$ for acetonitrile might be attributed to a preference for sideways-on antiparallel dipolar alignment, but some reservations have been expressed about that interpretation [17].

To evaluate g for a binary mixture, it is necessary to adopt a suitable definition for the quantity μ_{g}. We have chosen to accept the definition of Moreau and Douheret [18].

$$\mu_{\mathrm{g}} = X_{\mathrm{A}}\mu_{\mathrm{gA}} + X_{\mathrm{W}}\mu_{\mathrm{gW}} \tag{15}$$

We note that Hasted [19] assumed that it is μ_{g}^2 that is mole fraction additive.

Combining eqns. (10) and (13) leads to

$$\mu^2_{\mathrm{eff.id}} = X_A \mu^2_{\mathrm{eff.A}} + X_W \mu^2_{\mathrm{eff.W}} \tag{16}$$

However, by analogy with eqn. (15), we might write an equation of the type

$$\mu^2_{\mathrm{eff.id}} = X_A^2 g_{AA} \mu^2_{gA} + 2 X_A X_W g^0_{AW} \mu_{gA} \mu_{gW} + X_W^2 g_{WW} \mu^2_{gW} \tag{17}$$

where g_{AA} and g_{WW} are the respective correlation factors for the two pure liquids and g^0_{AW} is an ideal correlation factor for the unlike molecular pairs.

Equating the right hand sides of eqns. (16) and (17) leads to

$$g^0_{AW} = \frac{g_{AA} \mu^2_{gA} + g_{WW} \mu^2_{gW}}{2 \mu_{gA} \mu_{gW}} \tag{18}$$

The implication of eqn. (18) is that, for a binary mixture of two associated liquids to behave ideally, the orientational correlation between the dipolar axes of unlike molecular pairs should be a suitably weighted average of the correlations between like pairs of the two components. While we feel that the general implication is reasonable, we are not certain that the simple relationship of eqn. (18) is necessarily the most appropriate sort of averaging.

An excess correlation factor may be defined in the context of eqns. (15) and (16)

$$\Delta g = \frac{\mu^2_{\mathrm{eff}} - \mu^2_{\mathrm{eff.id}}}{\mu^2_g} \tag{19}$$

The theory of Winkelmann and Quitzsch

Before discussing dipolar free energies, it is appropriate to give some consideration to the statistical theory of Winkelmann and Quitzsch [20,21].

Several statistical theories have been proposed to interpret the measured dielectric properties of binary liquid mixtures. Bottcher [22] is one of several authors to have derived equations for mixtures of a polar with a non-polar component. Winkelmann and Quitzsch derived the following equation for mixtures of two dipolar liquids [20].

$$\begin{aligned} \frac{D-1}{D} = {} & \sum_{A+W} 3\phi_A \frac{(D_{\infty A} - 1)}{(2D + D_{\infty A})} \\ & + \sum_{A+W} X_A \frac{L}{9kT\epsilon_0} \cdot \frac{g_{AA} \mu^2_{gA}}{\bar{V}} \frac{(D_{\infty A} + 2)^2 (2D+1)}{(2D + D_{\infty A})^2} \\ & + \frac{(D_{\infty A} + 2)(D_{\infty W} + 2)}{(2D + D_{\infty A})(2D + D_{\infty W})} (2D+1) \frac{L}{9kT\epsilon_0} \frac{(g_{AW} - 1)}{\bar{V}} \mu_{gA} \mu_{gW} \end{aligned} \tag{20}$$

The authors have assumed that the self-correlation factors g_{AA} and g_{WW} remain constant across the entire composition range. Their quantity g_{AW} is composition dependent with unit values at $X=0$ and $X=1$, and is, consequently, a very different entity from the g_{AW}^0 of eqn. (17).

It is noted that, in the limiting case of a pure liquid, eqn. (20) is exactly equivalent to eqn. (13).

Winkelmann and Quitzsch have not addressed the question of ideal dielectric behavior, in the context of eqn. (20). We have noted, however, that the first two terms of eqn. (20) constitute a close approximation to the estimates of ideal dielectric quantities as represented by both eqn. (2) and by eqn. (10), as applied to the molar orientational polarisibility of Frohlich and Buckingham.

Adopting the approximation that $\phi_A\bar{V} = X_A\bar{V}_A^+$ leads to the following expression for the molar susceptibility

$$\chi_e\bar{V} = \sum_{A+W} X_A(\chi_e\bar{V})_A^+ \times \left\{1 + \frac{(D-D_A)\left[(D_A+1)(2D_A+1)D_{\infty A}^2 - 2DD_A(D_{\infty A}-1)^2\right]}{D_A(D_A-1)(2D+D_{\infty A})}\right\} + \frac{(D_{\infty A}+2)(D_{\infty W}+2)}{(2D+D_{\infty A})(2D+D_{\infty W})}(2D^2+D)\frac{L}{9kT\epsilon_0}(g_{AW}-1)\mu_{gA}\mu_{gW} \qquad (21)$$

The second term within the parentheses is quite small compared to 1. Hence the sum is very nearly equal to the right hand side of eqn. (2).

The adoption of the additional approximation that $(D_{\infty A}+2)(2D+D_\infty) = (D_\infty+2)(2D+D_{\infty A})$ leads to

$$\bar{P}_F = \sum_{A+W} X_A\bar{P}_{FA}^+\left\{1 - \frac{3D - D(2D_\infty + D_{\infty A}) + (D_{\infty A} - D_\infty)}{(2D+D_{\infty A})(D-1)} + \frac{3(D_{\infty A}-1)(D-D_\infty)D_A}{(D-1)(D_A-D_{\infty A})(2D_A+D_{\infty A})}\right\} + \frac{L}{9kT\epsilon_0}(g_{AW}-1)\mu_{gA}\mu_{gW}\left\{1 - \frac{3D(D_\infty-1)}{(2D+D_\infty)(D-1)}\right\} \qquad (22)$$

The second and third terms, within the parentheses of the summation, combine to give a quantity which is quite small compared to 1. Thus, the summation is very nearly identical to the right hand side of eqn. (10) in the context of the molar orientational polarisibilities.

Thus, it would seem that, within the context of what might be termed conventional concepts of dielectric ideality, the quantity $(g_{AW}-1)$ of eqn. (20) is associated with deviation from ideality. That idea is substantiated by the strong similarities (shown below) between the quantity Δg of eqn. (19)

and $(g_{AW}-1)$, as estimated from eqn. (20), for both the ACN–water and TBA–water systems. We note that our estimates of $(g_{AW}-1)$ for the TBA–water system differ quite substantially from those shown graphically in ref. 23.

Excess dipolar free energies

Frohlich [13] suggested a way in which one might estimate that contribution to the Helmholtz free energy of a pure polar liquid which arises from the interactions of molecular dipoles with their polarizible environments. That suggestion has been pursued by Haskell [24], by Bottcher [22] and subsequently by Winkelmann and Quitzsch [21].

For a pure liquid A, ref. 21 provides the following equation

$$\bar{F}_{\mu A}^{+} = -RT\frac{L}{9kT\epsilon_0}\frac{g_{AA}\mu_{gA}^2}{\bar{V}_A^{+}}\frac{(D_A-1)(D_{\infty A}+2)}{(2D_A+D_{\infty A})} \tag{23}$$

Excluding the quantity g_{AA}, this equation is identical to that given by Haskell [24].

The ideal values of the total Helmholtz free energy for a binary mixture are rigorously defined [1].

$$\bar{F}_{id} = X_A\bar{F}_A^{+} + X_W\bar{F}_W^{+} + RT(X_A \ln X_A + X_W \ln X_W) \tag{24}$$

If one treats F_μ as an independent component of F, it follows that

$$\bar{F}_{\mu id} = X_A\bar{F}_{\mu A}^{+} + X_W\bar{F}_{\mu W}^{+} \tag{25}$$

Combining eqns. (13) and (23), for the case of a pure liquid, leads to the following expression

$$\bar{F}_\mu = -RT\frac{(D-1)(D-D_\infty)}{D(D_\infty+2)} \tag{26}$$

We explored the consequences of adopting the assumption that a combination of eqns. (25) and (26) is applicable to binary mixtures. The resulting values of the excess free energy were positive for all compositions of the ACN–water and TBA–water systems and of such great magnitude (maxima at 7.2 kJ mol^{-1} for ACN–water and 21.3 kJ mol^{-1} for TBA–water) as to be obviously inconsistent with miscibility, even making allowances for dispersion and random mixing contributions.

It is appropriate to consider the manner in which Winkelmann and Quitzsch chose to evaluate the quantities $\bar{F}_\mu$ and $\bar{F}_{\mu.id}$ for binary mixtures. They start out by setting up the following general expression

$$\bar{F}_\mu = X_A\bar{F}_{\mu A} + X_W\bar{F}_{\mu W} \tag{27}$$

where $\bar{F}_{\mu A}$ and $\bar{F}_{\mu W}$ are partial molar quantities, which are evaluated by adopting the following sequence of assumptions.

(1) The terms $L/\bar{V}_A^+$ and $L/\bar{V}_W^+$, of eqn. (23) are preserved in the appropriate partial molar quantities across the entire composition range. This amounts to assuming that each molecule is located in a cavity of its own characteristic volume.

(2) Equation (23) is replaced by two separate terms, as per

$$g_{AA}\mu_{gA}^2 = \mu_{gA}^2 + (g_{AA} - 1)\mu_{gA}^2 \tag{28}$$

The first term is intended to represent the free energy associated with the interaction of an individual dipole with the reaction field that it creates by polarising a continuous homogeneous environment. The second term takes into account the additional effects of interactions with other neighboring dipoles with which it is structurally correlated.

(3) In a mixture, the term $(g_{AA} - 1)$ of eqn. (28) is replaced by $X_A(g_{AA} - 1) + X_W(g_{AW} - 1)$. Thus, the molecules of species A are depicted as being orientationally correlated with both their own kind and those of species W.

These assumptions lead to the following expression for the ideal dipolar molar free energy of a mixture.

$$\bar{F}_{\mu.\mathrm{id}} = -RT\cdot\frac{L}{9kT\epsilon_0}\sum_{A+W}\frac{(D_A - 1)(D_{\infty A} + 2)}{(2D_A + D_{\infty A})}\cdot\frac{1}{\bar{V}_A^+}$$
$$\times\left\{X_A\mu_{gA}^2 + X_A^2(g_{AA} - 1)\mu_{gA}^2 + X_A X_W(g_{AW} - 1)\mu_{gA}\mu_{gW}\right\} \tag{29}$$

This expression gives values which are significantly different from those obtained using eqn. (25).

The equation for the total dipolar free energies is obtained by replacing both D_A and D_W in eqn. (29) by the measured dielectric constant D of the mixture.

The values obtained for the excess dipolar free energy, using this approach are significantly smaller than those obtained using eqns. (25) and (26). We believe that we have identified flaws in both approaches.

It is our contention that the values for the effective dipole moment of a mixture μ_{eff} that are derived from the use of eqn. (13), correspond to an average molecular dipole that occupies a cavity of the average molecular volume $\bar{V}/L$. We concur with both Haskell and Winkelmann that, in order to calculate the dipolar free energies of a mixture, each of the two molecular species needs to be treated as though it resides in a cavity of its own characteristic volume $\bar{V}_A/L$ or $\bar{V}_W/L$. We have devised a relatively simple means of making allowances for the free energy change that is associated with transferring the molecules from their own to the average volume cavities.

$$\bar{F}_\mu = -RT\frac{(D-1)(D-D_\infty)}{D(D_\infty + 2)} - \sum_{A+W} X_A RT\frac{(D_A - 1)(D_A - D_{\infty A})}{D_A(D_{\infty A} + 2)}\left(1 - \frac{\bar{V}_A^+}{\bar{V}}\right) \tag{30}$$

The ideal dipolar free energy is assumed to be represented by eqn. (25).

The excess molar dipolar free energies, that are obtained from eqns. (25) and (30) are substantially smaller than those obtained using eqns. (25) and (26).

Our principal objection to the Winkelmann–Quitzsch approach is concerned with their inclusion of the term ($g_{AW} - 1$) in their expression for the ideal dipolar free energies, since the manner in which they evaluate it appears to us to identify it as a measure of departure from ideality.

While we are conscious of the fact that eqn. (30) represents a very simplistic approach to relating static dielectric constants to quasi-thermodynamic properties, we believe it to be more realistic than either of the other two approaches that are discussed above.

SOURCES OF EXPERIMENTAL DATA

We have combined three sets of values for the static dielectric constants of acetonitrile–water mixtures at 25°C [25–27]. Refractive indices for the mixtures were taken from ref. 18. Values of the molar volumes were derived from the data of Handa and Benson [28]. For each type of data, a cubic splines procedure was used to obtain estimates at rounded mole fractions, with a modest degree of smoothing.

We combined three sets of values for the dielectric constants of tertiary butanol–water mixtures [23,29,30]. Refractive index values for the mixtures were estimated from the values given for the pure liquids, assuming volume fraction additivity of n^2. The molar volumes were calculated from the density data of de Visser and coworkers [31].

The gas phase molecular dipole moments were assumed to be 1.85 D (water) [32], 3.91 D (ACN) [33] and 1.66 D (TBA) [34]. We note that the TBA value was obtained from solution rather than gas phase measurements and must thus be regarded with a degree of caution. It is, however, sufficiently similar to gas phase values for other alkanols to be a reasonable estimate.

THE FOUR-SEGMENT MODEL

The various excess property data sets were analysed using the four-segment composition model. The model equations are based upon the assumption that it is reasonable to treat binary hydroorganic systems as though their total composition ranges consist of four discrete segments, in each of which there is a simple characteristic functional dependence of the bulk physical properties upon mole fractional composition.

The evolution and derivation of the model equations are given in refs. 2 and 3. The equations themselves are set out in the appendix. The model has been demonstrated to be an effective curve fitting tool for excess thermodynamic property data of binary hydroorganic systems. Earlier applications of the model have led to each of its seven parameters being associated with a specific aspect of the patterns of molecular aggregation which exist within the mixtures [35,36].

RESULTS

The molar susceptibilities, $\chi_e\bar{V}$, of the three pure liquids are respectively 1401 cm^3 (water), 1848 cm^3 (ACN) and 1089 cm^3 (TBA).

The excess molar susceptibility curves for the two systems are shown in Fig. 1. The optimized four-segment model parameters are listed in Table 1. We note that the departures from dielectric ideality, as it is defined by eqn. 2, are much larger for the TBA–water system than the ACN–water system.

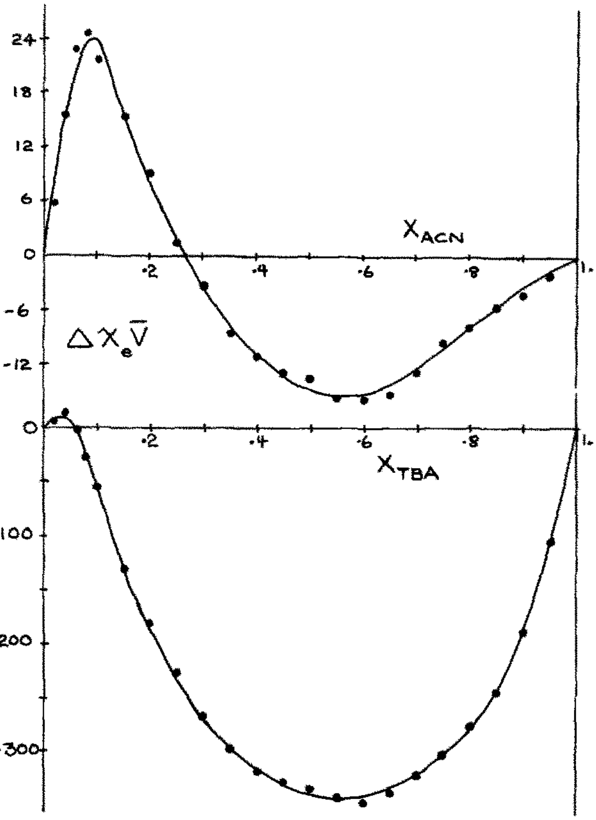

Fig. 1. Excess molar susceptibilities $\Delta(\chi_e\bar{V})$ cm^3 of the acetonitrile–water and *tert*-butanol–water systems. Solid lines are four-segment model curves. Circles represent data points.

TABLE 1

Four-segment model parameter values for excess dielectric properties

	$\Delta(\chi_e\bar{V})$ (cm^3)	$\Delta\bar{P}_F$ (cm^3)	Δg_D	Δg_W	$\Delta\bar{F}_\mu$ (kJ)
Acetonitrile–water					
B	−171	−29.5	−0.138	−0.200	3.44
$\Delta\bar{Q}^0_W$	39	2.7	−0.008	0.018	−0.37
$\Delta\bar{Q}^0_A$	17	3.1	0.025	0.021	−0.50
$\Delta\bar{Q}^0_S$	47	6.1	0.078	0.041	−1.56
D_S	5	−0.3	0.014	−0.002	−0.38
D_W	−64	−8.6	−0.097	−0.058	1.95
D_A	−9	−2.3	−0.028	−0.015	0.50
σ	1.11	0.154	0.0018	0.0010	0.033
tert-Butanol–water					
B	−1012	−141.1	−2.20	−2.29	6.17
$\Delta\bar{Q}^0_W$	−19	−7.8	−0.06	−0.13	4.36
$\Delta\bar{Q}^0_A$	−146	−18.4	−0.38	−0.29	0.31
$\Delta\bar{Q}^0_S$	137	18.2	0.26	0.29	−3.70
D_S	0	0	−0.04	0	1.20
D_W	−168	−22.3	−0.33	−0.36	3.81
D_A	−122	−17.1	−0.28	−0.27	1.41
σ	3.37	0.46	0.007	0.007	0.072

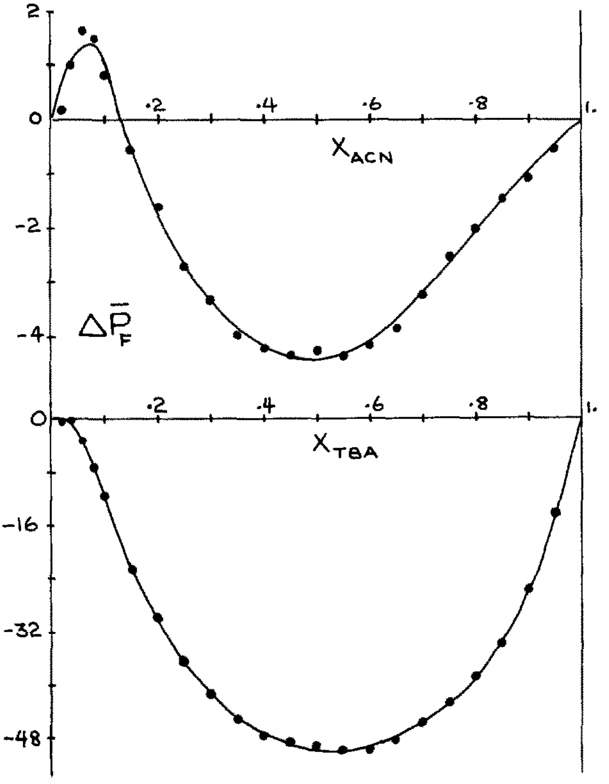

Fig. 2. Excess molar orientational polarisabilities $\Delta\bar{P}_F$ cm^3 of the acetontrile–water and *tert*-butanol–water systems. Solid lines are four-segment model curves.

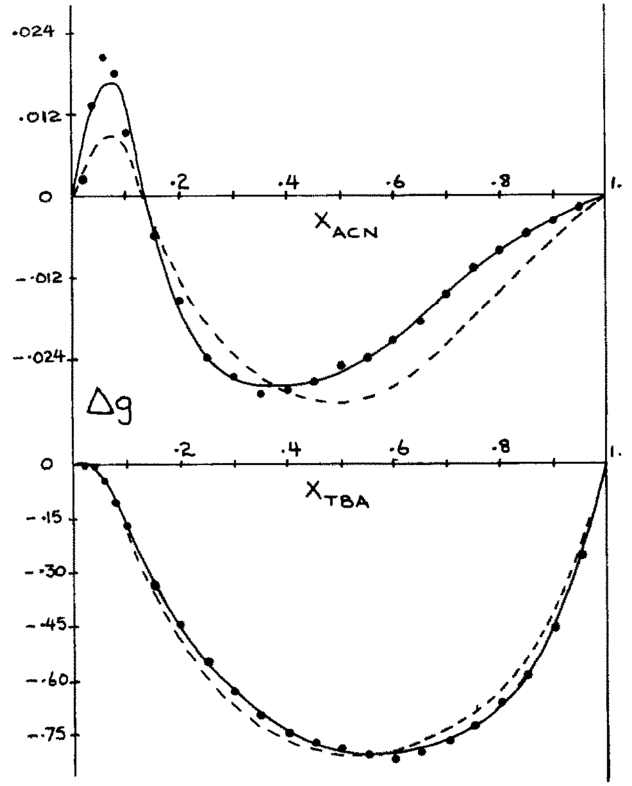

Fig. 3. Excess correlation factors Δg for the acetonitrile–water and *tert*-butanol–water systems. Solid lines are the four-segment model curves for Δg. Broken lines represent the four segment model curves for the quantity $g_{AW} - 1$ of eqn. (20).

The molar orientational polarisibilities for the three pure liquids are, respectively, 197 cm^3 (water), 256 cm^3 (ACN) and 141 cm^3 (TBA). The excess molar polarisibility curves, for the two systems are shown in Fig. 2. The optimized four-segment model parameters are listed in Table 1. Again, the departures from ideality for the TBA–water system are by far the larger of the two. We note the strong similarities between the shapes of the curves of Figs. 1 and 2.

The correlation factors, g, for the pure liquids are 2.80 (water), 0.82 (ACN) and 2.53 (TBA). In Fig. 3, we have shown plots of both Δg, as defined by eqn. 19, and the quantity ($g_{AW} - 1$) as defined by eqn. (20). The resemblance between the two quantities for both systems is obvious. The optimized four segment model parameters for both quantities are listed in Table 1.

The molar dipolar free energies $\bar{F}_{\mu}$, for the pure liquids, as calculated using equation 23 are −49.7 kJ (water), −21.7 kJ (ACN) and −6.1 kJ (TBA). In Fig. 4, we show the excess molar free energy curves, as defined by Winkelmann and Quitzsch, together with the version that we prefer which is

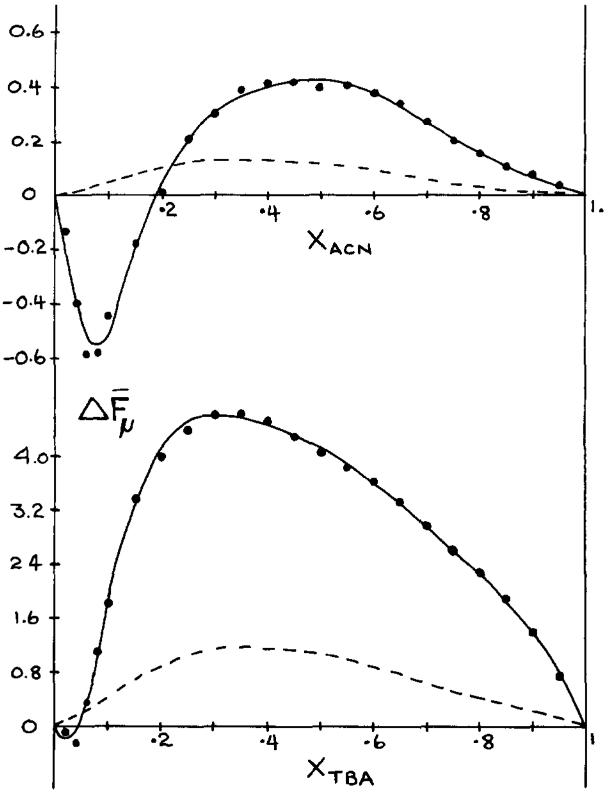

Fig. 4. Excess molar dipolar free energies $\Delta\bar{F}_\mu$ kJ of the acetonitrile–water and *tert*-butanol–water systems. Solid lines are four-segment model curves for $\Delta\bar{F}_\mu$ as calculated using eqns. (25) and (30). Broken lines are four-segment model curves for $\Delta\bar{F}_\mu$ as calculated from the formulas of ref. 21.

obtained using eqns. (25) and (30). The optimized four segment model parameters for the latter version are given in Table 1.

DISCUSSION

We note the general similarities in the profiles of the three curves $\Delta(\chi_e\bar{V})$, $\Delta\bar{P}_F$, and Δg for both systems. There is therefore no apparent major incongruity between the respective concepts of dielectric ideality. We note, in addition, that the prominent peaks in the excess molar susceptibility curves at $X_A \simeq 0.1$ are reminiscent of peaks in the excess viscosity molar volume products $\Delta(\eta\bar{V})$ [22,26]. We suggest that both the dielectric constant and viscosity data for these systems may be interpreted in terms of enhanced aqueous structural rigidity in mixtures with modest organic mole fractions.

While we are reluctant to place much faith in the absolute magnitudes of the excess molar dipolar free energies, as they are predicted using eqns. (30)

and (25), we do believe that the minima at low organic mole fractions represent a more realistic account of the effects of dipole–dipole interactions than is provided by either of the alternatives that we have considered. We note that these minima correspond nicely with the maxima that are found for the excess Eyring free energies of activation for viscous flow [37]

$$\Delta\overline{G}_{\eta}^{\neq} = RT\Delta\ln(\eta\overline{V}) \tag{31}$$

We note that there are extrema in several of the thermodynamic excess properties of the two systems at modest organic mole fractions. Notable examples are $\Delta\overline{H}$ [38] and $\Delta\overline{C}_V$ [39] for ACN–water and $\Delta\overline{C}_p$ [31] for TBA–water.

The microheterogeneous segment $X_{II} \leqslant X_A \leqslant X_{III}$

The use of the term microheterogeneous, as applied to roughly equimolar mixtures, has been suggested by Naberukhin and Rogov [40]. The limits of the microheterogeneous segments of both systems were defined by setting $X_{\mathrm{II}} = 1/3$ and $X_{\mathrm{III}} = 2/3$, in accordance with the results of earlier studies of excess thermodynamic properties [35,36]. The earlier studies led to the suggestion that, within this segment, there is a tendency towards the formation of metastable laminar molecular aggregates in which there is preferred contact between the polar groups of the organic molecules and structurally enhanced aqueous aggregates.

Parameters of the type $\Delta\overline{Q}_{\mathrm{w}}^{0}$ are treated as being excess molar properties of a hypothetical standard state of water. Thus they are measures of the effects of the changes in the patterns of aqueous self aggregation on going from the pure liquid to, what may be loosely described as, a microphase state. The excess molar thermodynamic quantities $\Delta\overline{Q}_{\mathrm{W}}^{0}$ (see Table 2) indicate that this microphase is more compact and of lower enthalpy than the pure liquid. The excess dielectric quantities $\Delta\overline{Q}_{\mathrm{W}}^{0}$ for the ACN–water

TABLE 2

Four segment model parameter values for some excess molar thermodynamic properties

	Acetonitrile–water			*tert*-Butanol–water		
	$\Delta\overline{V}$ (cm^3)	$\Delta\overline{H}$ (kJ)	$\Delta\overline{C}_{\mathrm{p}}$ (J/K)	$\Delta\overline{V}$ (cm^3)	$\Delta\overline{H}$ (kJ)	$\Delta\overline{C}_{\mathrm{p}}$ (J/K)
B	−1.46	3.1	30.2	−2.41	1.7	−15.3
$\Delta\overline{Q}_{\mathrm{W}}^{0}$	−0.43	−0.2	0.7	−0.73	−1.2	18.6
$\Delta\overline{Q}_{\mathrm{A}}^{0}$	0.14	0.7	1.2	0.28	0.5	−3.0
$\Delta\overline{Q}_{\mathrm{S}}^{0}$	−0.11	−0.3	4.2	−0.42	−0.8	21.2
D_{S}	−0.08	0.4	−0.2	0.31	0.2	−2.7
D_{W}	0.14	0.0	−1.0	0.86	0.4	−40.9
D_{A}	0.06	−0.2	−9.6	−0.22	−0.2	10.8

system are of relatively small magnitude and thus too poorly defined to warrant interpretation. In the case of the TBA–water system, these quantities are more substantial. It is interesting to try to reconcile the large enthalpy decrease ($\Delta \overline{H}_{\mathrm{W}}^{0} = -1.2$ kJ mol^{-1}) with the apparent drop in the correlation factor g_{W}^{0}.

The correlation factor, for the mutual orientations of molecular pairs, might be regarded as being dependent upon two separate factors. One factor is obviously the degree of local structural order that exists; the other is the average angle between neighboring dipoles. That $\Delta \overline{H}_{\mathrm{W}}^{0}$ is significant and negative is regarded as evidence of enhanced structural association of water in the microheterogeneous segment of the TBA–water system. The large negative value of $\Delta \overline{V}_{\mathrm{W}}^{0}$ is interpreted in terms of a substantial transfer of individual water molecules from ice-like to alternative, more compact, types of structural sites. If the negative value of $\Delta g_{\mathrm{W}}^{0}$ is a real phenomenon, as opposed to being an artifact of our theoretical approach, it would indicate larger mean angles between adjacent molecular dipolar axes. We are inclined to believe that the value of 4.7 kJ mol^{-1} for $\Delta \overline{F}_{\mu\mathrm{W}}^{0}$ is excessive and a clear indication that eqn. (30) provides no better than a crude estimate of the dipolar free energy.

Parameters of the type $\Delta \overline{Q}_{\mathrm{A}}^{0}$ are regarded as being measures of the effects of the changes in the patterns of organic self-aggregation, on going from the pure liquid to the laminar clusters of the microheterogeneous segment. It is interesting to note that for acetonitrile, where g for the pure liquid is 0.82, $\Delta g_{\mathrm{A}}^{0} = +0.02$, while for *tert*-butanol, where g for the pure liquid is 2.52, $\Delta g_{\mathrm{A}}^{0} = -0.4$. Thus, in both systems, there would seem to be a decrease in the degree of self-association of the organic component. That conclusion is consistent with the substantial positive $\Delta \overline{H}_{\mathrm{A}}^{0}$ values for both species. It is worth drawing attention to a possible problem with eqn. (23), which associates an increase in the correlation factor with a decrease in the dipolar free energy. That would seem to be a reasonable state of affairs for a liquid with $g > 1$, where increased g represents enhanced molecular association, but not for one with $g < 1$.

Parameters of the type B are treated as being measures of the effects of forming interfaces between the organic and aqueous microlaminar aggregates. For both systems, we find a decrease from ideal correlation and an increase in the dipolar free energy. It is seen, from Table 2, that $B(\Delta \overline{H})$ is quite large and positive for both systems.

The secondary segment $X_I \leqslant X_A \leqslant X_{II}$

The X_{I} value adopted for the ACN–water system was 0.111, that for TBA–water was 0.083. It is suggested that in this segment the organic molecules tend to form small metastable aggregates which, in common with micelles, tend to have their polar groups in contact with water. The water molecules are treated as being distributed betwen two kinds of sites; those which are in contact with the organic aggregates and those which, being more remote, might be termed interstitial.

Parameters of the type $\Delta\bar{Q}_S^0$ are treated as being measures of the effects of the interactions between molecules in interstitial sites, relative to those of the pure liquid. Parameters of the type D_S are regarded as measures of the effects of interactions between water molecules in interstitial sites and those in interfacial sites, which might be expected to include modification of the shapes of the organic aggregates. It is clearly the terms associated with these two parameters which are most closely associated with the peaks in $\Delta(\chi_e \bar{V})$ and the minima in $\Delta\bar{F}_\mu$ at low organic mole fractions. That there is marked structural enhancement of water, within this segment, seems to be consistent with the conclusions drawn by Hertz and his coworkers, on the basis of their studies of diffusion processes and nuclear polarization relaxation times [41,42].

The water rich segment $0 \leqslant X_A \leqslant X_I$

Within the water-rich composition segment, it has been suggested that the organic molecules exhibit a tendency to self associate by contact between their apolar hydrocarbon moieties [43]. This tendency, which results in the formation of labile aggregates, is thought to be responsible for diminishing the level of contact between water and the hydrocarbon groups to negligeable proportions at $X \simeq 0.1$ [44].

Parameters of the type D_W are regarded as being measures of the effects of dispersing the metastable aggregates of the secondary segment, by the addition of water and of introducing water–hydrocarbon contact (hydrophobic hydration). For both systems, the D_W values imply a decrease in correlation and an increase in the dipolar free energy.

The organic rich segment $X_{III} \leqslant X_A \leqslant 1$

It is suggested that, within the organic rich segment, the water molecules tend to remain clustered, forming the cores of metastable reverse-micelle-like aggregates. Parameters of the type D_A are regarded as being measures of the effects of interactions between these mixed aggregates and aggregates of the pure organic liquid, together with the effects of dispersion of the aqueous clusters. For the ACN–water system, the D_A values for the various excess quantities of the ACN–water system are too small to be informative. The values for the TBA–water system are more substantial and imply diminished molecular association and increased free energy.

CONCLUSION

In principle, the study of the composition dependence of the dielectric properties of binary liquid mixtures offers a unique perspective of the structural and dynamic characteristics of their patterns of molecular aggregation. The theoretical framework of Kirkwood and Frohlich, in which we have carried out our analyses, is obviously rather crude, particularly when applied to binary mixtures. More elegant theoretical treatments do exist [45–47], but they are of an essentially predictive nature and, in our view, are not readily adaptable to an interpretive role.

While we are aware of the need for improved interpretive theories of the thermodynamic and dielectric properties of binary mixtures of polar liquids, we are reasonably satisfied that the conventional concepts of dielectric ideality that we have employed in this work are at least approximately consistent with thermodynamic ideality. We are further of the belief that our interpretation of the role that the correlation factor plays in the adaptation of Frohlich's eqn. (13) to binary mixtures is an improvement on that suggested in refs. 20 and 21. We also contend that our eqn. (30) represents a more realistic approach to defining the dipolar molar free energy of a binary mixture than that used by Winkelmann and Quitzsch.

The results of the four-segment model analyses seem to provide a reasonably consistent, albeit crude, account of the variations in the degree of molecular orientational correlation with composition, for both the ACN–water and TBA–water systems. The results also appear to be consistent with those obtained for excess thermodynamic properties, as interpreted in earlier articles [35,36].

We intend to explore, in greater detail, the temperature dependence of the dielectric constants of acetonitrile–water mixtures.

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APPENDIX: THE FOUR-SEGMENT MODEL EQUATIONS

The microheterogeneous segment $X_{II} \leqslant X_A \leqslant X_{III}$

$$\Delta\bar{Q}(\text{micro}) = BX_\text{A}(1 - X_\text{A}) + \Delta\bar{Q}^0_\text{W}(1 - X_\text{A}) + \Delta\bar{Q}^0_\text{A}X_\text{A}$$

The secondary segment $X_I \leqslant X_A \leqslant X_{II}$

$$\Delta\bar{Q}(\mathrm{sec}) = \Delta\bar{Q}(\mathrm{micro}) + (\Delta\bar{Q}_S^0 - \Delta\bar{Q}_W^0)[(X_{II} - X_\mathrm{A})/X_{II}]^3 + D_\mathrm{S} X_\mathrm{A}(X_{II} - X_\mathrm{A})^2/X_{II}^3$$

The water-rich segment $0 \leqslant X_A \leqslant X_I$

$$\Delta\bar{Q}(\mathrm{wat}) = \Delta\bar{Q}(\mathrm{sec}) - \Delta\bar{Q}_\mathrm{S}^0[(X_I - X_\mathrm{A})/X_I]^3 + D_\mathrm{W} X_\mathrm{A}(X_I - X_\mathrm{A})^2/X_I^3$$

The organic-rich segment $X_{III} \leqslant X_A \leqslant 1$

$$\Delta\bar{Q}(\mathrm{org}) = \Delta\bar{Q}(\mathrm{micro}) - \Delta\bar{Q}_\mathrm{A}^0[(X_\mathrm{A} - X_{III})/(1 - X_{III})]^3 + D_\mathrm{A}(1 - X_\mathrm{A})(X_\mathrm{A} - X_{III})^2/(1 - X_{III})^3$$

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