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COMPARISONS OF DIELECTRIC AND THERMODYNAMIC IDEALITY. II. MIXTURES OF ASSOCIATED LIQUIDS

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ABSTRACT

Earlier efforts to define ideal composition dependence of the dielectric properties of binary mixtures of Onsager liquids have been extended to the case of mixtures of associated liquids. Two approaches have been adopted. One approach deals solely with bulk properties and closely resembles the treatment of non-structured binary mixtures. The other attempts to incorporate some of the simpler statistical concepts that are embodied in Kirkwood's theory.

INTRODUCTION

In our efforts to establish a meaningful procedure for analyzing and interpreting the composition dependence of the dielectric constants of binary hydroorganic systems, we have become interested in examining a number of plausible ways of defining "ideal" composition dependence [1,2].

While we are primarily interested in binary mixtures of associated (structured) liquids, we found it to be appropriate to start our study of the concept of ideal dielectric behavior by examining the implications of the extensions of Onsager's theory, which deals specifically with non-structured liquids, to describe binary mixtures [2].

Onsager's model, as applied to a binary mixture, assumes that there is random spatial distribution of the molecules of the two components and that in the mixtures, as in the pure component liquids, there is random molecular orientation [3,4]. It would seem that this model is reasonably consistent with regular, but not necessarily thermodynamically ideal, mixing. For that reason, one might chose to adopt the term "dielectric ideality" to describe the condition represented by Onsager's equation for a binary mixture.

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A means of translating the dielectric constant of a polar liquid, in the general context of Onsager's theory, into a quasi-thermodynamic molar dipolar free energy has been furnished by Frohlich [4,5]. In so far as Frohlich's approach is acceptable, we found that it leads to the conclusion that a binary mixture of Onsager liquids has a non-zero excess dipolar internal energy [2].

Onsager's theory provides a poor prediction of the dielectric constants of water and many of the polar organic liquids with which it is miscible. While numerous flaws have been identified in Onsager's model, as applied to structured liquids, it would appear that the major shortcoming is the assumption that the relative orientations of neighboring molecules are completely random.

In attempting to describe the dielectric or quasi-thermodynamic ideal composition dependence of the dielectric properties of mixtures of associated liquids, we find ourselves with two options. One approach is to deal only with the bulk dielectric properties of the mixtures and to employ the same definitions of ideal composition dependence as were found to be appropriate in the case of mixtures of Onsager liquids. The alternative is to attempt to examine the concepts of ideality in the framework of some appropriate body of statistical theory.

PURE ASSOCIATED LIQUIDS

If Onsager's theory may be regarded as being of zero order, the simpler theories of associated polar liquids might be described as being first-order elaborations.

The earliest attempts to develop a dielectric theory, that makes allowances for the tendency of polar molecules to adopt energetically favored mutual orientations, retained Onsager's cavity-in-a-continuum approach. The theory that was pioneered by Kirkwood [6] and subsequently embellished by Frohlich [5] led to the equation

$$(D-1)\bar{V}=\frac{3D(D_\infty-1)\bar{V}}{(2D+D_\infty)}+\frac{Lg\mu^2D(2D+1)(D_\infty+2)^2}{9kT\epsilon_0(2D+D_\infty)^2} \tag{1}$$

where D is the dielectric constant, $\bar{V}$ is the molar volume, D_∞ is the high-frequency dielectric constant of the sample liquid, μ is the gas phase molecular dipole moment, g is the Kirkwood correlation factor for that liquid and ϵ_0 is vacuum permittivity.

Equation (1) can be rearranged to give

$$\frac{Lg\mu^2}{9kT\epsilon_0}=\frac{(D-D_\infty)(2D+D_\infty)\bar{V}}{D(D_\infty+2)^2}=\bar{P} \tag{2}$$

where $\bar{P}$ is referred to as the molar orientational polarizability.

One notes that, in the case where $g = 1$, eqns. (1) and (2) are identical to the expressions derived from Onsager's theory. Since Onsager's model assumes random molecular orientations, it is argued that deviations of the value of g from unity are, in some fashion, measures of the effects of local structural order.

While it is obvious that serious objections may be raised to the adoption of cavity-in-a-continuum models, it has been observed that the Kirkwood correlation factor cannot be dismissed as a mere artefact of that approach since expressions, which are algebraically equivalent to eqns. (1) and (2), have been derived from purely statistical first-order treatments [7]. It is appropriate to note, in that context, that Wertheim has suggested an alternative first-order statistical result [8].

A general interpretation that may be offered for the introduction of the correlation factor into eqn. (1) is that the polarization of an individual molecule in a polar liquid sample is due in part to its long-range interactions with the bulk of the sample and in part to short-range interactions with neighboring molecules with which it is to some extent structurally correlated.

From statistical considerations, Winkelmann and Quitzsch have concluded that the molar dipolar free energy of a pure associated liquid is given by the expression [9]

$$\bar{F}\mu = \frac{-RTLg\mu^2(D-1)(D_\infty+2)}{\bar{V}9kT\epsilon_0(2D+D_\infty)} \tag{3}$$

If $g = 1$, eqn. (3) reduces to the form obtained from Frohlich's interpretation of the interactions between molecular dipoles and their reaction fields for the case of a pure Onsager liquid [4,5].

IDEAL BINARY MIXTURES OF ASSOCIATED LIQUIDS

Our first concern was with the selection of a suitable analog to eqn. (1), to represent the ideal molar susceptibility, $(D-1)\bar{V}$, of a binary mixture of associated liquids. From our considerations of mixtures of Onsager liquids [2], we feel that it is appropriate to write

$$(D-1)\bar{V} = \sum_{\mathrm{A+B}} \frac{3X_\mathrm{A}\bar{V}_\mathrm{A}D(D_{\infty\mathrm{A}}-1)}{(2D+D_{\infty\mathrm{A}})} + \frac{X_\mathrm{A}\bar{P}_\mathrm{A}D(2D+1)(D_{\infty\mathrm{A}}+2)^2}{(2D+D_{\infty\mathrm{A}})^2} \tag{4a}$$

where $\bar{P}_\mathrm{A}$ may be evaluated from D_A, $D_{\infty\mathrm{A}}$ and $\bar{V}_\mathrm{A}$, using eqn. (2).

Alternatively, we may write the equation in a form which involves the molecular dipole moments and the correlation factors:

$$(D-1)\bar{V} = \sum_{\mathrm{A+B}} \frac{3X_\mathrm{A}\bar{V}_\mathrm{A}D(D_{\infty\mathrm{A}}-1)}{(2D+D_{\infty\mathrm{A}})} + \frac{X_\mathrm{A}Lg_\mathrm{A}\mu_\mathrm{A}^2D(2D+1)(D_{\infty\mathrm{A}}+2)^2}{9kT\epsilon_0(2D+D_{\infty\mathrm{A}})^2} \tag{4b}$$

We noted, in ref. 2, that eqn. (4a) closely approximates the condition of mole fraction additivity of the molar susceptibilities of the pure components:

$$(D-1)\bar{V} = X_A\bar{V}_A(D_A-1) + X_B\bar{V}_B(D_B-1) \tag{5}$$

Equation (4b) contains reference to both g_A and g_B, which are related to the orientational correlation of like molecular pairs and might therefore be termed "self-correlation" factors. There is, however, no mention of any mutual correlation factor, g_{AB}. As we pointed out in ref. 1, g_{AB} would need to be some kind of weighted average of g_A and g_B, for a binary mixture to be ideal.

Winkelman and Quitzsch have described the role of a quantity g_{AB} in the contexts of both the polarization [10] and the dipolar free energy [9] of a binary mixture. It is our contention that there is a conflict of logic between those two papers and that the approach adopted in ref. 9 is the more correct. From that standpoint, one obtains

$$\begin{aligned}(D-1)\bar{V} = {} & \sum_{A+B} \frac{3X_A\bar{V}_A D(D_{\infty A}-1)}{(2D+D_{\infty A})} \\ & + \frac{(X_A\mu_A^2 + X_A^2(g_A-1)\mu_A^2)LD(2D+1)(D_{\infty A}+2)^2}{9kT\epsilon_0(2D+D_{\infty A})^2} \\ & + \frac{2X_AX_B(g_{AB}-1)\mu_A\mu_B LD(2D+1)(D_{\infty A}+2)(D_{\infty B}+2)}{9kT\epsilon_0(2D+D_{\infty A})(2D+D_{\infty B})}\end{aligned} \tag{6}$$

Since eqn. (4) is a viable candidate as a definition of dielectric ideality (or regularity), equating the right-hand sides of eqns. (4b) and (6) provides an estimate of an ideal value for g_{AB}:

$$\frac{2(g_{AB}-1)\mu_A\mu_B(D_{\infty A}+2)(D_{\infty B}+2)}{(2D+D_{\infty A})(2D+D_{\infty B})} = \sum_{A+B} \frac{(g_A-1)\mu_A^2(D_{\infty A}+2)^2}{(2D+D_{\infty A})^2} \tag{7}$$

which, in the event that $D_{\infty A} = D_{\infty B}$, reduces to

$$(g_{AB}-1) = \frac{(g_A-1)\mu_A^2 + (g_B-1)\mu_B^2}{2\mu_A\mu_B} \tag{8}$$

For modest differences in the high-frequency dielectric constants, g_{AB} as estimated from eqn. (7) is virtually independent of composition and differs to only a modest extent from the value given by eqn. (8).

For the case of a mixture of Onsager liquids, where all of the correlation factors equal unity, we argued that eqn. (4) represents a regular mixture, on the grounds that it is based upon the assumption that there is a random spatial distribution of the component molecules and random molecular orientations in both the pure components and their mixtures [2]. Equation (6) is also based upon the assumption of random spatial distribution. Deviations of the correlation factors of the pure components from unity, whether positive or negative, imply a decrease in the orientational entropy. One might then regard the introduction of the quantity g_{AB} as an expedient to represent the condition of a zero excess orientational entropy and thus of regular mixing.

An alternative means of defining dielectric ideality (or regularity), that we considered in our earlier papers [1,2], is the mole fraction additivity of the molar orientational polarizabilities of the pure components:

$$\bar{P} = X_A \bar{P}_A^0 + X_B \bar{P}_B^0 \tag{9}$$

Combining eqns. (8) and (9) leads to

$$\bar{P} = L\big[X_A \mu_A^2 + (g_A - 1) X_A^2 \mu_A^2 + X_B \mu_B^2 + (g_B - 1) X_B^2 \mu_B^2 + 2 X_A X_B \mu_A \mu_B (g_{AB} - 1)\big]/9kT\epsilon_0 \tag{10}$$

In ref. 2, we considered two different ways of defining the molar orientational polarizability of a binary mixture. Equation (11) is a generalization of eqn. (2), involving the properties of the mixture:

$$\bar{P} = \frac{(D - D_\infty)(2D + D_\infty)\bar{V}}{D(D_\infty + 2)^2} \tag{11}$$

In the case of a hypothetical ideal mixture, D might be derived from eqn. (4), $\bar{V}$ would be assumed to be the mole fraction adduct of $\bar{V}_A^0$ and $\bar{V}_B^0$ and the high-frequency dielectric constant would be estimated using

$$D_\infty = \left(X_A \bar{V}_A^0 D_{\infty A} + X_B \bar{V}_B^0 D_{\infty B}\right)/\bar{V} \tag{12}$$

The alternative is to assign to each molecular species its own high-frequency dielectric constant (and hence polarizability) and its own molecular volume:

$$\bar{P} = \sum_{A+B} \frac{X_A \bar{V}_A^0 (D - D_{\infty A})(2D + D_{\infty A})}{D(D_{\infty A} + 2)^2} \tag{13}$$

There are only small differences between the "ideal" molar orientational polarizabilities, estimated from eqns. (11) and (13). The two sets of values are identical in the case that $D_{\infty A} = D_{\infty B}$; they also equal the values obtained from eqn. (9). When $D_{\infty A} \neq D_{\infty B}$, there are fairly large differences between the values obtained from the combination of eqns. (4a) and (11) and those obtained using eqn. (9).

Equation (14) represents a quasi-thermodynamic definition of ideal mixing:

$$\bar{F}_\mu = X_A \bar{F}_{\mu A} + X_B \bar{F}_{\mu B} \tag{14}$$

where the molar dipolar free energy of pure component A, $\bar{F}_{\mu A}$, is defined by eqn. (3).

The molar dipolar free energy of an ideal mixture may thus be expressed as

$$\bar{F}_\mu = -RT \sum_{\mathrm{A+B}} \frac{X_\mathrm{A} L g_\mathrm{A} \mu_\mathrm{A}^2 (D_\mathrm{A} - 1)(D_{\infty \mathrm{A}} + 2)}{\bar{V}_\mathrm{A}^0 9kT\epsilon_0 (2D_\mathrm{A} + D_{\infty \mathrm{A}})} \tag{15}$$

Employing the logic of ref. 9, we may rewrite eqn. (15) in a form which involves the mutual correlation factor g_AB:

$$\bar{F}_\mu = -RT \sum_{\mathrm{A+B}} \{ L(D_\mathrm{A} - 1)(D_{\infty \mathrm{A}} + 2)[X_\mathrm{A} \mu_\mathrm{A}^2 + X_\mathrm{A}^2 (g_\mathrm{A} - 1)\mu_\mathrm{A}^2 + X_\mathrm{A} X_\mathrm{B} \mu_\mathrm{A} \mu_\mathrm{B} (g_\mathrm{AB} - 1)] \} \{ \bar{V}_\mathrm{A}^0 9kT\epsilon_0 (2D_\mathrm{A} + D_{\infty \mathrm{A}}) \}^{-1} \tag{16}$$

Equating the right-hand sides of eqns. (15) and (16) leads to the following expression for g_AB:

$$(g_\mathrm{AB} - 1) = \frac{(g_\mathrm{A} - 1)\mu_\mathrm{A}^2 Y_\mathrm{A} + (g_\mathrm{B} - 1)\mu_\mathrm{B}^2 Y_\mathrm{B}}{(Y_\mathrm{A} + Y_\mathrm{B})} \tag{17}$$

where

$$Y_\mathrm{A} = \frac{(D_\mathrm{A} - 1)(D_{\infty \mathrm{A}} + 2)}{\bar{V}_\mathrm{A}^0 (2D_\mathrm{A} + D_{\infty \mathrm{A}})}$$

The values of g_AB obtained from eqn. (17) differ quite significantly from those of eqn. (8).

An alternative expression for the molar dipolar free energy, which is based upon the theoretical arguments of Winkelmann and Quitzsch [9] is

$$\bar{F}_\mu = -RT(D - 1) \sum_{\mathrm{A+B}} \frac{L(D_{\infty \mathrm{A}} + 2)[X_\mathrm{A} \mu_\mathrm{A}^2 + X_\mathrm{A}^2 (g_\mathrm{A} - 1)\mu_\mathrm{A}^2 + X_\mathrm{A} X_\mathrm{B} (g_\mathrm{AB} - 1)\mu_\mathrm{A} \mu_\mathrm{B}]}{\bar{V}_\mathrm{A}^0 (2D + D_{\infty \mathrm{A}}) 9kT\epsilon_0} \tag{18}$$

Equation (18) may be used in two different ways. One may obtain estimates of the dipolar free energies making use of the dielectric constants from eqn. (4) and the g_AB values of either eqn. (8) or (17). Alternatively, one may chose to use the equation to determine the values of g_AB, which, together with the dielectric constants of eqn. (4), lead to the dipolar free energy estimates of eqn. (14).

There are two additional ways in which we have attempted to estimate the molar dipolar free energies of binary mixtures without involving molecular-scale properties. Equation (19) was introduced in ref. 1 as a means of estimating the energies of real mixtures of known dielectric constant. In this context, it can be used with the "ideal" dielectric constants of eqn. (4):

$$\bar{F}_\mu = \frac{-RT(D - 1)(D - D_\infty)}{D(D_\infty + 2)} + \sum_{\mathrm{A+B}} X_\mathrm{A} \bar{F}_{\mu \mathrm{A}} (1 - \bar{V}_\mathrm{A}^0 / \bar{V}) \tag{19}$$

Equation (20) was adopted in ref. 2 for the case of binary mixtures of Onsager liquids:

$$\bar{F}_{\mu} = -RT(D-1) \sum_{\mathrm{A+B}} \frac{\bar{P}_{\mathrm{A}}(D_{\infty\mathrm{A}}+2)}{\bar{V}_{\mathrm{A}}(2D+D_{\infty\mathrm{A}})} \tag{20}$$

CALCULATIONS AND DISCUSSION

We have calculated, from the properties of the pure liquids, ideal (or regular) values of dielectric properties for three binary hydroorganic systems. Table 1 contains, for each system, three alternative estimates of ideal dielectric constants. It is seen that eqns. (4) and (5) provide virtually identical estimates in all three cases, but there are substantial differences between them and the values obtained from a combination of eqns. (9) and (11). These differences are less marked in the case of the acetonitrile–water system where the high-frequency dielectric constants of the pure components are nearer to being equal.

Our reason for considering eqn. (4) as a means of defining dielectric ideality, is that it appears to be appropriate for mixtures of liquids in which there is random spatial distribution and random molecular orientation [4]. While the associated liquids with which we are presently concerned have non-random orientations, we would argue that the condition of regular mixing does not require any specific pure component characteristics and that eqn. (4) appears to represent a viable means of describing a binary system in which the molar entropy of mixing is represented by the expression:

$$\Delta\bar{S} = -R[X_{\mathrm{A}} \ln(X_{\mathrm{A}}) + X_{\mathrm{B}} \ln(X_{\mathrm{B}})] \tag{21}$$

The fact that eqn. (4) is very closely approximated by eqn. (5) makes the latter an attractive choice for defining ideal dielectric behavior. It is simple to estimate excess molar susceptibilities, when experimental values of D and V are available. The mole fraction additivity of the orientational polarizibilities (eqn. 9) is more of an intuitive than a theoretically based definition of ideality.

Table 2 contains a variety of values for the mutual correlation factors g_{AB}. The values obtained using eqn. (7) are composition dependent but differ from the tabulated values by no more than 0.01. These values are seen to be very similar to those obtained using eqn. (8), implying that normal differences in the high-frequency dielectric constants have very little impact upon them. The differences between the values obtained using eqns. (8) and (17), respectively, are substantial. This is to be expected from consideration of the differences between the two weighting schemes. It appears to us that these differences underline the significant disparity between the definitions of ideality that are represented by eqns. (4) and (14).

TABLE 1

Ideal dielectric constants

X (1)	D(I)	D(II)	D(III)
Tertiary butanol (1) – water (2)			
t-BuOH: $D = 12.47$, $D_\infty = 1.9191$, $\bar{V}$ (cm) = 94.97, μ (D) = 1.65			
Water: $D = 78.54$, $D_\infty = 1.7761$, $\bar{V}$ (cm^{-1}) = 18.06, μ (D) = 1.85			
0.1	54.18	54.17	55.32
0.2	41.02	41.01	42.22
0.3	32.78	32.78	33.81
0.4	27.14	27.13	27.97
0.5	23.03	23.02	23.67
0.6	19.91	19.90	20.37
0.7	17.45	17.45	17.77
0.8	15.47	15.47	15.67
0.9	13.84	13.84	13.93
Acetonitrile (1) – water (2)			
ACN: $D = 35.95$, $D_\infty = 1.8012$, $\bar{V}$ (cm) = 52.87, μ (D) = 3.92			
Water: $D = 78.54$, $D_\infty = 1.7761$, $\bar{V}$(cm^{-1}) = 18.07, μ (D) = 1.85			
0.1	68.09	68.09	68.19
0.2	60.55	60.55	60.68
0.3	54.85	54.85	54.98
0.4	50.38	50.38	50.51
0.5	46.80	46.80	46.90
0.6	43.85	43.85	43.94
0.7	41.39	41.39	41.45
0.8	39.30	39.30	39.34
0.9	37.51	37.51	37.53
Ethylene glycol (1) – water (2)			
HOEtOH: $D = 40.72$, $D_\infty = 2.046$, $\bar{V}$ (cm) = 62.068, μ (D) = 2.28			
Water: $D = 78.35$, $D_\infty = 1.7766$, $\bar{V}$ (cm^{-1}) = 18.068, μ (D) = 1.85			
0.1	67.98	67.95	69.15
0.2	61.00	60.96	62.46
0.3	55.98	55.94	57.40
0.4	52.19	52.16	53.44
0.5	49.24	49.20	50.27
0.6	46.86	46.84	47.67
0.7	44.91	44.89	45.50
0.8	43.29	43.27	43.66
0.9	41.91	41.90	42.08

D(I), based on eqn. (4). D(II), based on eqn. (5). D(III), based on eqns. (9) and (11).

TABLE 2

Mutual correlation factors, g_{AB}

A	Eqn. (7)	Eqn. (8)	Eqn. (17)	Eqns. (14), (18)	g_{A}
t-BuOH	2.70	2.71	2.95	3.18–3.23	2.54
ACN	1.24	1.24	1.55	1.56–1.57	0.82
HOEtOH	2.90	2.87	2.66	2.69–2.71	2.84

$g(\mathrm{H_2O}) = 2.82$

TABLE 3

"Ideal" molar dipolar free energies

X (1)	$\bar{F}_\mu$(I)	$\bar{F}_\mu$(II)	$\bar{F}_\mu$(III)	$\bar{F}_\mu$(IV)
t-Butanol (1) – water (2)				
$\bar{F}_\mu$ (t-BuOH) = −6.15 kJ mol^{-1}, $\bar{F}_\mu$ (water) = −49.75 kJ mol^{-1}				
0.1	−45.39	−44.61	−44.99	−44.99
0.2	−41.03	−39.64	−40.30	−40.60
0.3	−36.67	−34.84	−35.70	−36.29
0.4	−32.31	−30.22	−31.19	−32.00
0.5	−27.95	−25.77	−26.77	−27.70
0.6	−23.58	−21.49	−22.44	−23.40
0.7	−19.22	−17.39	−18.21	−19.09
0.8	−14.86	−13.46	−14.08	−14.78
0.9	−10.50	−9.71	−10.05	−10.46
Acetonitrile (1) – water (2)				
$\bar{F}_\mu$ (ACN) = −21.65 kJ mol^{-1}, $\bar{F}_\mu$ (H_2O) = −49.75 kJ mol^{-1}				
0.1	−46.94	−45.47	−46.83	−46.90
0.2	−44.13	−41.52	−43.94	−44.08
0.3	−41.32	−37.92	−41.08	−41.27
0.4	−38.51	−34.64	−38.24	−38.47
0.5	−35.70	−31.69	−35.43	−35.66
0.6	−32.89	−29.06	−32.64	−32.86
0.7	−30.08	−26.74	−29.87	−30.06
0.8	−27.27	−24.73	−27.11	−27.26
0.9	−24.46	−23.04	−24.37	−24.45
Ethylene glycol (1) – water (2)				
$\bar{F}_\mu$ (HOEtOH) = −23.11 kJ mol^{-1}, $\bar{F}_\mu$ (H_2O) = −49.62 kJ mol^{-1}				
0.1	−46.97	−47.39	−46.85	−46.61
0.2	−44.32	−45.07	−44.12	−43.88
0.3	−41.67	−42.67	−41.43	−41.25
0.4	−39.02	−40.17	−38.76	−38.66
0.5	−36.37	−37.58	−36.11	−36.07
0.6	−33.72	−34.89	−33.49	−33.49
0.7	−31.07	−32.10	−30.87	−30.90
0.8	−28.41	−29.21	−28.28	−28.31
0.9	−25.76	−26.21	−25.69	−25.71

$\bar{F}_\mu$(I), estimated using eqn. (14).
$\bar{F}_\mu$(II), estimated using eqn. (18) (g_{AB} from eqn. 8).
$\bar{F}_\mu$(III), estimated using eqn. (20).
$\bar{F}_\mu$(IV), estimated using eqn. (19).

Table 3 contains a number of different estimates of the molar dipolar free energies of the three systems. Of the four estimates, those corresponding to mole fraction additivity (eqn. 14) appear to us to be the most acceptable. The values in the columns headed $\bar{F}_\mu$(II) were obtained from eqn. (18), using the dielectric constants of eqn. (4) and the g values of eqn. (8). They differ quite significantly from the values of eqn. (14). We suggest that these values correspond to the free energies of regular mixtures which are not necessarily ideal.

It is appropriate to draw attention to an important distinction between the tertiary butanol–water and ethylene glycol–water systems, on the one hand, and the acetonitrile–water system on the other. It seems reasonable to assume that such self-correlation as exists in pure tertiary butanol and pure ethylene glycol involves hydrogen bonding (i.e. strong, parallel, dipolar correlation), which is consistent with g values substantially greater than one. In such cases, the assumption that the free energy decrease from the Onsager (random orientation) case is proportional to $g-1$ would seem to be plausible. In the case of pure acetonitrile, however, the g value of 0.82, which might superficially appear to arise from a modest degree of antiparallel correlation, is more likely to be due to a combination of both parallel and antiparallel dipole orientational correlation with the latter dominant. In either event, the existence of correlation ought to result in a free energy decrease instead of the increase predicted by eqn. (3).

Equations (19) and (20) lead to free energy values which are closer to those of eqn. (14) than are the estimates of eqn. (18), but the differences are still fairly substantial. Each of the three equations (18–20) constitutes an attempt to represent a regular binary mixture. Equation (19) was introduced in ref. 1 as a rather simple means of modifying the expression for the dipolar free energy of a pure liquid in a manner that recognized the necessity of assigning each molecular species to a cavity of its own specific volume. In that sense, it should probably be regarded as a pragmatic rather than a theoretically based definition.

Equation (18) reduces to eqn. (20) in the event that the various correlation factors are of unit value. We are inclined to believe that eqn. (18) is the more realistic means of representing the molar dipolar free energy of a regular binary mixture of associated liquids.

SUMMARY

We have considered a number of different ways of predicting ideal dielectric behavior in binary mixtures of associated polar liquids. Such predictions are helpful, if not necessary, for the interpretation of the measured dielectric properties of real hydroorganic systems. Of the various options, eqn. (5) is probably the most useful. The molar susceptibility of a real binary mixture can be calculated directly from the measured dielectric constant and density. Unlike the molar orientational polarizability and the molar dipolar free energy, its significance is not tied to any particular theoretical model. At the same time, its use is encouraged on the grounds that its predictions are virtually identical to those derived from eqn. (4) which is a generalization of Onsager's theory. We have presented arguments

for considering eqn. (4a) as being representative of regular, as opposed to completely ideal, binary mixtures. Consequently, deviations of real molar suceptibilities of mixtures from the predictions of eqn. (5) represent the effects of departures from ideal entropies of mixing and might be interpreted in terms of structural reorganization,.

Equation (9) is an intuitively reasonable means of defining dielectric ideality. There are, however, some problems in deciding how one ought to define the molar orientational polarizabilities of binary mixtures, particularly real mixtures.

Equations (3) ought not to be regarded as more than a tentative suggestion as to how one might translate dielectric constants into quasi-thermodynamic quantities. There are problems in deciding how one should generalize that equation to describe the properties of binary mixtures. Nevertheless, we are inclined to the view that this is a useful property, and would be more so if one could extract, from the prevailing theories of polar liquids, a more explicit understanding of its significance.

We are of the opinion that eqns. (4) and (14) represent different aspects of ideality, neither of which is complete. Equation (4) may be taken to represent the condition

$$\Delta \bar{S}_\mu = 0 \tag{22}$$

From Frohlich's interpretation of Onsager's theory, it would appear that this type of regular mixing must lead to a non-zero excess dipolar internal energy.

Equation (14) represents the condition

$$\Delta \bar{F}_\mu = 0 \tag{23}$$

which requires that

$$\Delta \bar{U}_\mu = T\Delta \bar{S}_\mu \tag{24}$$

but does not require that either $\Delta \bar{U}_\mu$ or $\Delta \bar{S}_\mu$ need to be zero.

That these two types of partial ideality are different from each other is supported by the differences in the respective "ideal" values of the mutual correlation factor g that they require.

It is appropriate to comment that changes in relative molecular dipole orientations must affect not only those intermolecular energy contributions which directly involve the permanent dipole moments, and which are represented by quantities of the type $\bar{U}_\mu$ and $\bar{F}_\mu$, but also dispersion energies which are not addressed in that context.

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