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COMPARISONS OF DIELECTRIC AND THERMODYNAMIC IDEALITY. I. MIXTURES OF ONSAGER LIQUIDS

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ABSTRACT

An effort has been made to relate several alternative means of defining the ideal composition dependence of the dielectric properties of binary mixtures of polar liquids with the various facets of thermodynamic ideality which constitute the generalization of Raoult's law. Arguments are presented for considering Onsager's equation for binary mixtures to represent a condition in which the mixing is regular but not ideal.

INTRODUCTION

We are interested in the derivation and application of procedures that may be used to extract, from the composition dependence of macroscopic properties of binary hydroorganic systems, clues as to the nature of the dynamic and structural characteristics of the patterns of molecular aggregation which exist within their mixtures.

The magnitude of the relative permittivity (static dielectric constant) of a liquid system is determined by the permanent electric moments and the polarizabilities of its individual molecules and by the nature of their mutual orientations. Given sufficient information about the properties of the individual molecules and an appropriate body of theory, it ought to be possible to translate the composition dependence of the dielectric constants of binary mixtures into some kind of information about the nature of the pattern or patterns of structural organization.

When dealing with totally miscible binary systems, it is considered to be useful to examine the composition dependence of their excess properties. This requires the adoption of suitable choices of ideal composition dependence. For thermodynamic properties, ideal composition dependence may be defined within the context of the widely accepted generalization of

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Raoult's law [1]. For non-thermodynamic properties, such as dielectric constants and viscosities, it is necessary to look further afield for definitions of ideality. In such cases, one must rely upon theories which either offer an intuitive basis for defining ideality or provide a means of translating non-thermodynamic into quasi-thermodynamic quantities.

In an earlier paper, we examined several different ways of defining ideal, and hence excess, dielectric properties for the acetonitrile–water and tertiary butanol–water systems [2]. While there appeared to be a broad level of consistency between the various definitions, there were sufficient disparities to introduce non-trivial ambiguities into the interpretations of detailed analyses of the different excess property curves. Since our choices of conditions for representing ideal dielectric behavior were to a large extent intuitive, we considered that it would be desirable to try to establish the theoretical implications of the differences between them.

The components of the binary systems that were studied in ref. 2 are associated (structured) liquids. It was felt that, before attempting to address the question of the nature of dielectric ideality in mixtures of associated liquids, it would be appropriate to examine the much simpler case of binary mixtures of non-structured (Onsager) liquids.

PURE ONSAGER LIQUIDS

The derivation of Onsager's theory of the dielectric constants of polar liquids has been presented and discussed in numerous books and articles [3,4]. It is expedient to review some of the assumptions upon which that theory is based and to reproduce some of the more important equations.

A representative polar molecule is assigned to a spherical cavity with a volume of $\bar{V}/L$, where $\bar{V}$ is the molar volume and L is Avogadro's number. The cavity is assumed to be embedded in a homogeneous continuum of dielectric constant D. The assumption that the cavity is spherical, regardless of the shape of the molecule, is considered to be a relatively minor defect of the model, as is the decision to equate the cavity volume with the average molecular volume. Treating the environment of the representative molecule as a homogeneous continuum carries with it the implication that there is a random distribution of molecular orientations. This assumption must be regarded as a major flaw insofar as it would appear to be the major source of discrepancies between measured values of dielectric constants and the estimates that stem from Onsager's theory [4–6].

The representative molecule is assigned an isotropic polarizability α, which is related to the high-frequency dielectric constant D_∞ by means of the Lorentz–Lorenz equation:

$$\frac{4\pi L\alpha}{3\bar{V}} = \frac{(D_\infty - 1)}{(D_\infty + 2)} \tag{1}$$

Numerous suggestions have been made as to appropriate choices for the quantity D_∞ (see ref. 2). The common practice of equating D_∞ with the square of the optical refractive index neglects atomic (vibrational) polarization and could well introduce non-trivial problems when dealing with liquids that have very low dielectric constants.

The representative molecule is assigned a permanent dipole moment μ, which is generally assumed to have the same value as in the gas phase. Onsager's theory neglects quadrupole and higher electric moments.

Of particular relevance to Onsager's theory is the average dipole moment component $\langle \bar{\mu} \rangle$ in the direction of an applied external field. Onsager assumed that for a sample of randomly oriented molecular dipoles that quantity is given by the Langevin–Debye equation:

$$\langle \bar{\mu} \rangle = \frac{\mu^2 \vec{E}_\mathrm{d}}{3kT} \tag{2}$$

where $\vec{E}_\mathrm{d}$ (the directing field) is the effective potential gradient acting upon the orientation of the permanent dipole of the representative molecule. k is Boltzmann's constant and T the absolute temperature.

Onsager's equation can be written in the form [3]

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

where ϵ_0 is vacuum permittivity.

The equation may be rearranged to give the following important relationship:

$$\frac{L\mu^2}{9kT\epsilon_0} = \frac{(D - D_\infty)(2D + D_\infty)\bar{V}}{D(D_\infty + 2)^2} = \bar{P} \tag{4}$$

where the quantity $\bar{P}$ is termed the molar orientational polarizability.

Equation (4) offers a means of predicting the dielectric constant of a pure liquid of known dipole moment, density and refractive index.

Onsager's theory has been used to define and evaluate a quantity $\bar{F}_\mu$ (the molar dipolar free energy), which represents the contribution to the molar Helmholtz free energy which is due to the electrostatic interactions between the molecular dipoles and their homogeneous dielectric environments [4,6,7].

$$F_\mu = \frac{-RTL\mu^2(D-1)(D_\infty + 2)}{\bar{V}9kT\epsilon_0(2D + D_\infty)} \tag{5}$$

BINARY MIXTURES OF ONSAGER LIQUIDS

We which to explore expressions for the dielectric properties of binary mixtures of Onsager liquids. We shall assume that the mixing is isochoric:

$$\bar{V} = X_\mathrm{A}\bar{V}_\mathrm{A} + X_\mathrm{B}\bar{V}_\mathrm{B} \tag{6}$$

where X_A and X_B are the respective mole fractions of components A and B and $\bar{V}_A$ and $\bar{V}_B$ are the corresponding molar volumes.

The molecules of the two components are assumed to be randomly distributed, giving rise to a homogeneous dielectric continuum. Both the pure liquids and their mixtures are assumed to have randomly oriented molecules. This seems to be consistent with the assumption that the entropy change, due to the mixing, is ideal:

$$\Delta \bar{S}_V = -R\left[X_A \ln(X_A) + X_B \ln(X_B)\right] \tag{7}$$

Since the entropy change of eqn. (7) is entirely due to the nature of the spatial distribution of the molecules, the contribution that is associated with the orientations and interactions of the molecular dipoles is assumed to be zero:

$$\Delta \bar{S}_\mu = 0 \tag{8}$$

Bottcher [4] has suggested that the net polarization of a binary mixture of this type may be represented by the following analog of eqn. (3):

$$(D-1)\bar{V} = \sum_{A+B} \frac{3D(D_{\infty A}-1)X_A\bar{V}_A}{(2D+D_{\infty A})} + \frac{X_A\bar{P}_A D(2D+1)(D_{\infty A}+2)^2}{(2D+D_{\infty A})^2} \tag{9}$$

where $\bar{P}_A$ may be evaluated from either μ_A or D_A, using eqn. (4).

We note that eqn. (9) may be rearranged in the form

$$(D-1)\bar{V} = \sum_{A+B} X_A\bar{V}_A(D_A-1) + \frac{X_A\bar{V}_A(D-D_A)\left[(D_A-1)(2D+1)D_{\infty A}^2 - 2DD_A(D_{\infty A}-1)^2\right]}{D_A(2D+D_{\infty A})^2} \tag{10}$$

Equation (9) provides a means of estimating an "ideal" value for the dielectric constant of a binary mixture of Onsager liquids, from the properties of the pure components. It seems to be appropriate to refer to the behavior that is represented by eqn. (9) as "dielectric ideality".

One of the approaches to defining dielectric ideality that has received serious consideration is volume fraction additivity of the dielectric constants of the pure components [2,8,9]. This is equivalent to mole fraction additivity of the molar susceptibilities:

$$(D-1)\bar{V} = X_A\bar{V}_A(D_A-1) + X_B\bar{V}_B(D_B-1) \tag{11}$$

We have ascertained that the values of the "ideal" dielectric constants of binary mixtures that are derived from eqn. (11) differ to only a modest extent from those obtained from eqn. (9).

One may define the molar orientational polarizability of a binary mixture by means of the following generalization of eqn. (4):

$$\bar{P}=\frac{(D-D_{\infty})(2D+D_{\infty})\bar{V}}{D(D_{\infty}+2)} \tag{12}$$

where for an ideal binary mixture it is deemed to be reasonable to write [10]

$$D_{\infty}=(X_{\mathrm{A}}\bar{V}_{\mathrm{A}}D_{\infty\mathrm{A}}+X_{\mathrm{B}}\bar{V}_{\mathrm{B}}D_{\infty\mathrm{B}})/\bar{V} \tag{13}$$

Values of "ideal" molar orientational polarizabilities may be calculated by inserting the dielectric constant values of eqn. (9) into eqn. (12).

In our earlier paper, we considered the expedient of assuming that the molar orientational polarizabilities of "ideal" binary mixtures are mole fraction adducts of those of the pure components:

$$\bar{P}=X_{\mathrm{A}}\bar{P}_{\mathrm{A}}+X_{\mathrm{B}}\bar{P}_{\mathrm{B}} \tag{14}$$

In the case that $D_{\infty\mathrm{A}}=D_{\infty\mathrm{B}}$, the combination of eqns. (9) and (12) is exactly equivalent to eqn. (14). Such is not the case, however, when the two high-frequency dielectric constants are different. In view of the manner in which the high-frequency dielectric constants appear in Onsager's theory, it seemed to be appropriate to consider, as an alternative to eqn. (12) the following:

$$\bar{P}=\sum_{\mathrm{A+B}}\frac{X_{\mathrm{A}}\bar{V}_{\mathrm{A}}(D-D_{\infty\mathrm{A}})(2D+D_{\infty\mathrm{A}})}{D(D_{\infty\mathrm{A}}+2)^{2}} \tag{15}$$

We note that, if eqn. (14) is adopted as the preferred definition of dielectric ideality, eqns. (12) and (15) offer alternative means of estimating ideal dielectric constants of binary mixtures.

Equation (5) provides us with a means of translating the dielectric constant of a pure polar liquid into a quasi-thermodynamic property. Since the concept of ideality has been explicitly defined for thermodynamic properties, one would like to be in a position to evaluate the molar dipolar free energies of binary mixtures.

There appear to us to be two distinct approaches to defining "ideal" dipolar free energies. A reasonable analog to eqn. (5) is the expression

$$\bar{F}_{\mu}=-RT(D-1)\sum_{\mathrm{A+B}}\frac{X_{\mathrm{A}}\bar{P}_{\mathrm{A}}(D_{\infty\mathrm{A}}+2)}{\bar{V}_{\mathrm{A}}(2D+D_{\infty\mathrm{A}})} \tag{16}$$

where D for the binary mixture might be obtained from eqn. (9) or the combination of eqns. (14) and (15).

We commented earlier that Onsager's model, as extended to the case of binary mixtures, satisfies the volumic (eqn. 6) and entropic (eqn. 7) requirements for thermodynamic ideality. It does not, however, address the enthalpic requirement which, in this context, would be given by

$$\Delta\bar{H}_{\mu}=\Delta\bar{E}_{\mu}=0 \tag{17}$$

Combining eqns. (6), (8) and (17) leads to the condition that

$$\bar{F}_\mu = X_A \bar{F}_{\mu A} + X_B \bar{F}_{\mu B} \tag{18}$$

It is interesting to compare the predictions of eqn. (18) with those of eqns. (9) and (16).

CALCULATIONS AND DISCUSSION

Numerous calculations were performed to estimate the properties of binary mixtures of components with a variety of combinations of values of the three quantities D, D_∞ and $\bar{V}$. In Tables 1–3 we have set out the results for a hypothetical mixture of components which have substantial differences in their dielectric constants and molar volumes and a non-trivial difference between their high-frequency dielectric constants.

It is noted that the columns headed D(I) and D(II) are virtually identical. Here, one is comparing the predictions of eqns. (11) and (9), respectively. Larger differences between the magnitudes of those two columns were encountered for other hypothetical mixtures, but in no case did they exceed 0.1. It may thus be concluded that, within experimental accuracy, eqn. (11) is arithmetically equivalent, if not algebraically so, to eqn. (9).

There are only modest differences between columns D(III) and D(IV) of Table 1. Such differences do not exist in the cases where the two high-

TABLE 1

Ideal dielectric constants

$D_A = 10$, $D_{\infty A} = 2.0$, $\bar{V}_A = 100$ cm^3

$D_B = 80$, $D_{\infty B} = 1.8$, $\bar{V}_B = 20$

X_A	D(I) [a]	D(II) [b]	D(III) [c]	D(IV) [d]
0	80.00	80.00	80.00	80.00
0.1	55.00	55.01	56.57	56.68
0.2	41.11	41.12	42.82	42.90
0.3	32.27	32.28	33.78	33.83
0.4	26.15	26.16	27.38	27.42
0.5	21.67	21.67	22.62	22.64
0.6	18.24	18.24	18.94	18.95
0.7	15.53	15.53	16.01	16.02
0.8	13.33	13.34	13.63	13.63
0.9	11.52	11.52	11.66	11.66
1.	10.00	10.00	10.00	10.00

[a] Based on eqn. (11).

[b] Based on eqn. (9).

[c] Based on a combination of eqns. (14) and (15).

[d] Based on a combination of eqns. (12) and (14).

TABLE 2

Ideal molar orientational polarizabilities

X_A	$\bar{P}$(I) [a] (cm^3)	$\bar{P}$(II) [b] (cm^3)	X_A	$\bar{P}$(I) [a] (cm^3)	$\bar{P}$(II) [b] (cm^3)
0	219.1	219.1	0.6	147.6	153.6
0.1	202.3	208.2	0.7	138.1	142.7
0.2	189.2	197.2	0.8	128.7	131.8
0.3	177.8	186.3	0.9	119.3	120.9
0.4	167.3	175.4	1.	110.0	110.0
0.5	157.3	164.5			

[a] Based on a combination of eqns. (9) and (15).

[b] Based on eqn. (14).

frequency dielectric constants are identical. That the differences are relatively small indicates that eqn. (12) is a fairly good approximation to eqn. (15).

A fairly substantial difference is observed between the columns headed *D*(II) and *D*(III). This difference also disappears if the two high-frequency dielectric constants are identical. In this instance we are dealing with the distinction between two different ways of defining dielectric ideality. That distinction is also to be found between the two estimates of the "ideal" molar orientational polarizabilities given in the columns *P*(I) and *P*(II) of Table 2. It is appropriate to note that Decroocq [8] has addressed the question of alternate definitions of dielectric ideality in this general context.

When translated into molar dipolar free energies, using eqn. (16), the differences between the dielectric constant values of columns *D*(II) and

TABLE 3

Ideal molar dipolar free energies (kJ)

X_A	$\bar{F}_\mu$(I) [a]	$\bar{F}_\mu$(II) [b]	$\bar{F}_\mu$(III) [c]
0	−50.38	−50.38	−50.38
0.1	−45.38	−45.42	−45.78
0.2	−40.44	−40.52	−41.19
0.3	−35.58	−35.67	−36.60
0.4	−30.80	−30.90	−32.01
0.5	−26.11	−26.21	−27.42
0.6	−21.52	−21.60	−22.83
0.7	−17.04	−17.11	−18.24
0.8	−12.69	−12.73	−13.64
0.9	−8.49	−8.51	−9.05
1.	−4.46	−4.46	−4.46

[a] Based on a combination of eqns. (9) and (16).

[b] Based on a combination of eqns. (14), (15) and (16).

[c] Based on eqn. (18).

D(III) result in energy differences no greater than 0.1 kJ mol^{-1}. The appropriate values are given in columns F(I) and F(II) of Table 3. The free energy values in both of those columns differ substantially from those in column F(III), which were calculated using eqn. (18).

The differences between the molar dipolar free energy values of columns F(I) and F(III) are particularly interesting.

We noted that Onsager's model, as extended to the case of binary mixtures, would appear to be consistent with the condition of entropic ideality (eqn. 7). Consequently it would seem to be reasonable to suggest that eqn. (9) represents the condition of regular mixing [11] but not necessarily ideal mixing. That there should be such substantial differences between the sets of energy values of columns F(I) and F(III) indicates that, in the context of Onsager's theory, there is a fairly substantial excess internal energy. In the event that the excess volume is zero, as assumed here, or relatively small, these calculations also indicate a substantial excess enthalpy of mixing.

SUMMARY

We have explored some of the implications of Onsager's theory of polar liquids as extended to binary systems. It is apparent that the theory is approximately consistent with volume fraction additivity of the dielectric constants of the two components. In the case where the high-frequency dielectric constants of the two components are identical, Onsager's theory is equivalent to mole fraction additivity of the molar orientational polarizabilities, but only in that case.

It is argued that the Onsager–Bottcher equation for a binary mixture represents a condition of regular, but not necessarily ideal mixing. Indeed, consideration of the molar dipolar free energies of the mixture, as defined by Frohlich's interpretation of the Onsager theory, leads to the conclusion that these mixtures have fairly substantial excess internal energies and enthalpies.

We intend to extend this line of enquiry to the case of mixtures of associated liquids.

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