Detailed Molecular Model for Dielectric Constant of Multicomponent, Associating Liquids

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We propose a new theory for relating the dielectric constant to the internal structure of association fluids containing any number of associating components, the molecules of which may possess any number of electron-rich and electron-deficient sites. The theory combines concepts proposed earlier by Kirkwood (1939) for describing dielectric behavior with more recent theoretical advances made in the area of associating fluids. The derived expressions account for correlations between all pairs of dipoles located within transient associated clusters of all possible sizes, molecular sequences, and shapes, the only exception being closed-ring structures. They reduce to known forms derived earlier using other methods for relatively simple systems, such as water, alcohols, and aqueous mixtures of alcohols and ketones. An application of the theory to the DMSO−water mixture suggests two modes of association between DMSO and water molecules (in addition to that between water molecules): (i) the oxygen atom of DMSO molecules associating with the protons of water molecules, as proposed by several workers in the recent past, and (ii) the oxygen atom of water molecules associating with the sulfur atom of DMSO molecules, as proposed originally by Tomilla and Murto (1963).

1. Introduction

Dielectric constant is a measure of polarization of fluids in electric fields. Examples of specific application of dielectric constant data, in combination with appropriate dielectric theories, have been in areas related to the understanding of molecular processes contributing to polarization and conduction of biomolecular solutions, analysis of structure of cellular organisms, understanding of the electrical properties of cell membranes and cytoplasm, hydration of proteins, amino acids, and other polar biomolecules, and estimation of the amounts of bound water in moist materials, such as rocks, paints, plant/animal tissues, brick, inks, wood, and food products.

A few decades ago, Kirkwood[1] presented an elegant theory for the dielectric constant of liquids. The central parameter in Kirkwood's theory is the dipolar correlation factor (*g*). In practice, *g* is unknown; either it has to be deduced by fitting Kirkwood's theory to experimentally measured dielectric constant data or one needs to develop a theory relating *g* to intermolecular interactions. The approach that has been more commonly followed in the literature has been the former one,[2] the extracted *g*-values being used to interpret the internal structure of the fluid. This exercise has, however, found only limited utility for two reasons. First, the *g*-factor cannot provide as detailed information on the internal structure of the fluid as, say, spectroscopic experiments can. Second, the dissection of the average *g*-factor of the fluid into explicit terms for interactions between different pairs of molecules, especially in the case of systems containing several associating components the molecules of which may possess many electron-rich and electron-deficient sites, has not been possible in the past.

In the present article, we solve the long-pending above-mentioned problem for a general class of liquids that involve any number of associating components, the molecules of which may possess any number of electron-rich and electron-deficient

sites. The complexity of these systems, arising from the ability of associating molecules to form transient molecular clusters of various shapes, sizes, and compositions, is now well recognized in the literature. Except in the case of a few simple systems,[1,3−5] the treatment of association stoichiometry or dipolar correlations or both has, in general, been found to be extremely difficult both from conceptual and computational points of view.[6−8] The present article is intended to account for correlations between all pairs of dipoles that are located within associated clusters of all possible sizes, molecular sequences, and shapes, the only exception being closed-ring structures, and provide mathematically exact expressions for the same within the mean-field framework.

To demonstrate the utility of the expressions derived in the present article, we study the DMSO−water system. The interest in this mixture arises not only from its unique biological properties but also from its wide use as a solvent and reaction media. The mixture possesses interesting thermodynamic properties, the origins of which have been a subject of intense debate and research for the past five decades. Havemeyer[9] measured a very low freezing point at a mole fraction $x_{DMSO} \approx 0.33$, based on which the author suggested the formation of stable 1DMSO−2H$_2$O clusters. Such clusters have been observed many times in molecular dynamics simulation studies.[10−14] It has been suggested that hydrogen bonding of water molecules at the oxygen sites of DMSO molecules is the primary mode of association, the lifetimes of hydrogen bonds in the mixtures appearing to be longer than those in pure water.[15,16] Another publication,[17] however, revealed a more complex phase diagram at mole fractions $x_{DMSO} = 0.25−0.33$, based on which the authors proposed the formation of stable 1DMSO−3H$_2$O clusters. Experiments and computer simulations have thus far not been able to decisively establish the stability of such structures. On the basis of a study of the influence of solvent on reaction velocities, Tomilla and Murto[18] suggested the formation of 1DMSO−2H$_2$O clusters with one bond being

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formed between the sulfur atom of DMSO molecule and oxygen atom of water molecule and the other being formed between the oxygen atom of DMSO molecule and proton of water molecule. A quantum chemical study performed more recently[19] suggested that although this structure appeared to be favorable to begin with because of the partial charge on the S and O atoms ($Me_2S^{\delta+}=O^{\delta-}$), it was found to be unfavorable after relaxation. The same study also suggested that the assumption of pairwise additivity could be one of the reasons for the earlier reported MD simulations not being able to predict the formation of $1DMSO-3H_2O$ clusters. Neutron diffraction data[20,21] and related MD simulations[11] could not unambiguously answer the question of how many hydrogen bonds DMSO forms with water but revealed the following broad features: (a) there was no evidence of hydrophobic association of DMSO molecules suggested earlier;[22-24] (b) DMSO and water molecules associate through two predominant modes, hydrogen bonding between the proton of water molecules and the lone pairs on DMSO molecules and hydration around the methyl groups in the form of disordered hydrogen-bonded cages. Borin and Skaf[25] proposed, on the basis of far-infrared spectroscopy and related MD simulations, that yet another type of complex, namely, two DMSO molecules bound to a water molecule, also forms in the mixture.

In the present paper, we apply the proposed theory to evaluate two plausible association models for the DMSO−water system for their ability to describe the dielectric constant behavior of mixtures at various compositions and temperatures. Both models account for association between water molecules and between water and DMSO molecules at the donor−acceptor sites. The number of association sites present in a water molecule, as well as their location, is assumed to be the same as that specified in an earlier paper.[5] The two models differ in their assignment of the number of association sites in a DMSO molecule and their specific location within the molecule; one allows for the possibility of the two electron-rich sites near the oxygen atom of DMSO molecules associating with the protons of water molecules thus forming $1DMSO\cdots2H_2O$ clusters. The other model additionally allows for the possibility of association between the sulfur atom of DMSO molecule and the oxygen atom of water molecule, thus forming $1DMSO\cdots3H_2O$ clusters.

The rest of the article is organized as follows. In section 2, we propose the theory based on the principles of statistical mechanics. In section 3, we outline the method of calculating the dielectric constant of associating mixtures using the derived expressions. In Section 4, we demonstrate that the derived expressions for dipolar correlation factors and association stoichiometry reduce to known forms derived earlier[5,8] for relatively simple systems, such as pure water, pure alcohol, and aqueous mixtures of alcohol. In section 5, we study the DMSO−water mixture and propose an association model that reasonably describes the dielectric constant behavior at different concentrations and temperatures. Finally, we conclude in section 6.

2. Theory

Consider a liquid mixture containing C components with i, j, k, ... representing the types of different components. Let the molar density of this liquid be ρ and the mole fraction of the component of type i be x_i. A molecule of a given type, say i, may possess N_{d_i} (electron) donor sites, the different donor sites being denoted by the symbols α_{d_i}, β_{d_i}, γ_{d_i}, etc., and may possess N_{a_i} (electron) acceptor sites, the different acceptor sites being denoted by the symbols α_{a_i}, β_{a_i}, γ_{a_i}, etc. Let μ_i be the instantaneous dipole moment of a molecule of type i in the liquid phase, $\Phi_{(\alpha_{d_i})}$ be the angle between the bond formed at a site of
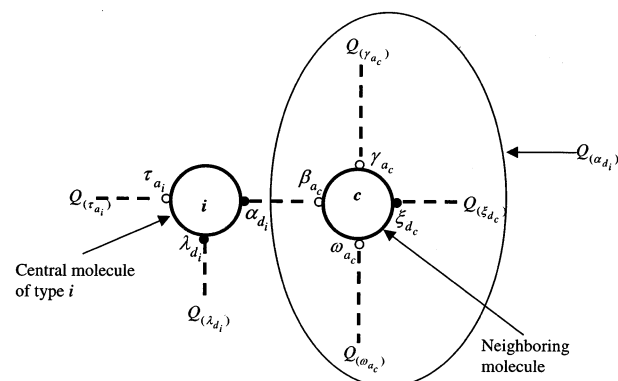

Figure 1. Snapshot of a multicomponent system at a certain instant of time. The neighboring molecule can be of any type (c = i, j, k, etc.). The dashed lines denote bonds formed between electron donor sites (small filled circles) and electron acceptor sites (small open circles). The symbol Q represents a cluster of molecules originating from the site denoted by the corresponding subscript. The physical and chemical characteristics of the clusters are assumed to change with time.

type α_{d_i} and the dipole moment vector of the same molecule, and $\theta_{(\alpha_{d_i}, \beta_{d_i})}$ be the angle between bonds formed at sites of types α_{d_i} and β_{d_i} of a given molecule of type i.

The average dipolar correlations, $\langle g \rangle$, in the liquid, which can also be independently estimated from experimental dielectric constant measurements, are defined as follows:[6,8]

$$\langle g \rangle = \sum_{c=i,j,k,...} (x_c g_c \mu_c^2) \tag{1}$$

where

$$g_c = 1 + \frac{M_c}{\mu_c} \tag{2}$$

$g_c\mu_c$ represents the component of instantaneous dipole moment vector of an imaginary sphere, drawn about a central molecule of type c, taken in the direction of μ_c. The sphere must be small compared to the specimen but large enough so that the material outside it may be considered to be homogeneous. All molecules within this sphere, except the central dipole, are allowed to take all permissible configurations. g_c can be physically interpreted as being a measure of alignment of neighboring dipoles about a central dipole of type c.

In systems containing associating fluids, g_c generally differs from unity because of the formation of transient molecular clusters of various shapes, sizes, and molecular sequences. The statistical thermodynamic aspects of this physical picture have been fairly well studied over the past two decades. The final expression for the *mean-field* probability for the $\alpha_{d_i}\cdots\beta_{a_j}$ bond to be formed is given by[26]

$$P_{(\alpha_{d_i}, \beta_{a_j})} = \frac{M_{(\alpha_{d_i}, \beta_{a_j})}}{n_{(\alpha_{d_i})}} = K_{(\alpha_{d_i}, \beta_{a_j})} Y_{(\alpha_{d_i})} Y_{(\beta_{a_j})} \tilde{\rho} x_j \tag{3}$$

$$Y_{(\alpha_{d_i})} = \frac{1}{1 + \sum\limits_{(c=i,j,k,...)} \sum\limits_{(s_{a_c}=\alpha_{a_c}, \beta_{a_c},...)} \tilde{\rho} x_c K_{(\alpha_{d_i}, s_{a_c})} Y_{(s_{a_c})}} \tag{4}$$

where M denotes the number of bonds, K the equilibrium constant for bond formation, and n the total number of associations sites, of which a fraction, Y, would be, on an average, unbonded. $\tilde{\rho}$ is the reduced density of the fluid with

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the reference temperature taken to be 293 K. In deriving the above equations, the probability of bonding at any given site of a molecule has been assumed to be independent of bonding patterns at other sites of the same molecule. Also, contributions to the free energy arising from the presence of closed associated rings have been neglected on the basis of the assumption that formation of such structures involves large entropic costs.

We now turn to evaluating dipolar correlations. For this purpose, consider a central molecule of type, say, i held fixed in a certain orientation. Associated clusters could originate from each of the several association sites that this molecule may possess. For example, in Figure 1, a cluster could originate from the site of type α_{d_i}, which we denote by the symbol $Q_{(\alpha_{d_i})}$. The central molecule would experience correlations with molecules present within each of such clusters. Also, because the clusters are transient in nature, the dipolar correlations would vary with time. Hence, a more relevant quantity to be evaluated would be the time-averaged dipolar correlation factor, g_i, which can be expressed without any loss of generality as follows:

$$g_i = 1 + \sum_{(s_{d_i}=\alpha_{d_i},\beta_{d_i},\cdots)}\left(\frac{m_{(s_{d_i})}}{\mu_i}\cos[\phi_{(s_{d_i})}]\right) + \sum_{(s_{a_i}=\alpha_{a_i},\beta_{a_i},\cdots)}\left(\frac{m_{(s_{a_i})}}{\mu_i}\cos[\phi_{(s_{a_i})}]\right) \quad (5)$$

$m_{(s_{d_i})}$ denotes the time-averaged correlations between the central molecule of type i and all molecules belonging to the cluster $Q_{(s_{d_i})}$, as taken in the direction of the bond involving the site s_{d_i} and pointing toward the donor site. A similar definition holds for $m_{(s_{a_i})}$.

Developing expressions for $\{m\}$ is our next task. If we were to observe the bonding pattern on a given site, say of type α_{d_i}, belonging to the central molecule (considered above) over time, the fraction of time during which it would be bonded to an acceptor site of type, say, s_{a_c}, belonging to a molecule of type c would be $P_{(\alpha_{d_i},s_{a_c})}$. During these times, the central molecule would be expected to experience dipolar correlations with (i) nearest neighboring molecule (of type c here) and (ii) molecules that lie beyond the first-nearest shell in clusters originating from the various donor and acceptor sites of type c, except the one of type s_{a_c} (since it is already bonded to the central molecule). We shall now evaluate each of these terms separately.

(i) Dipolar Correlations between the Central Molecule of Type i and Nearest Neighbors. At times during which the $s_{a_c}\cdots\alpha_{d_i}$ bond is formed, the orientation of the neighboring molecule could be continuously changing. As Kirkwood[1] suggested, an approximate method to arrive at the various permissible orientations would be to freely rotate the neighboring molecule about the $s_{a_c}\cdots\alpha_{d_i}$ bond axis while holding fixed the orientation of the central molecule. Following this procedure and accounting for the probability $P_{(\alpha_{d_i},s_{a_c})}$ for the $s_{a_c}\cdots\alpha_{d_i}$ bond to be formed, the time-averaged component of dipole moment of the neighboring molecule along the direction of $s_{a_c}\cdots\alpha_{d_i}$ bond becomes $P_{(\alpha_{d_i},s_{a_c})}\mu_c\cos(\Phi_{s_{a_c}})$.

(ii) Dipolar Correlations between the Central Molecule of type i and Molecules Lying beyond the First-Nearest Shell. Consider any acceptor site of arbitrary type s''_a, except the one of type s_{a_c}, belonging to the neighboring molecule of type c (for example, in Figure 1, s''_{a_c} could represent sites of type γ_{a_c} or ω_{a_c} but not β_{a_c}). By definition, the time-averaged dipolar correlations between the molecule of type c, held fixed in a

certain orientation and all members of the cluster $Q_{(s''_{a_c})}$ would be $m_{(s''_{a_c})}$. Hence, the expression for the component of dipolar correlations between the central molecule and all molecules present in the cluster $Q_{(s''_{a_c})}$ as taken in the direction of $s_{a_c}\cdots\alpha_{d_i}$ bond (after accounting for free rotation of the cluster $Q_{(s''_{a_c})}$ about the $s_{a_c}\cdots\alpha_{d_i}$ bond axis), becomes $-P_{(\alpha_{d_i},s_{a_c})}m_{(s''_{a_c})}\cos(\pi - \theta_{(s''_{a_c},s_{a_c})})$. The corresponding expression for correlations between the central molecule and all members of the cluster $Q_{(s''_{d_c})}$ would be $+P_{(\alpha_{d_i},s_{a_c})}m_{(s''_{d_c})}\cos(\pi - \theta_{(s''_{d_c},s_{a_c})})$. For the general case, the molecule of type c could possess several acceptor sites and donor sites with a cluster originating from each one of them. The central molecule would experience dipolar correlations with members belonging to each of these clusters. Summing up all of these contributions, we obtain

$$P_{(\alpha_{d_i},s_{a_c})}\{[\sum_{s''_{d_c}}m_{(s''_{d_c})}\cos(\pi - \theta_{(s''_{d_c},s_{a_c})})] -$$
$$[\sum_{(s''_{a_c}\neq s_{a_c})}m_{(s''_{a_c})}\cos(\pi - \theta_{(s''_{a_c},s_{a_c})})]\}$$

Summation of terms derived above in subsections i and ii leads to contributions to $m_{(\alpha_{d_i})}$ arising from the possibility for the $\alpha_{d_i}\cdots s_{a_c}$ bond being formed. Of course, s_{a_c} could represent any of the several acceptor sites that the neighboring molecule may possess. Adding contributions arising from all such possibilities, we obtain the following expression for dipolar correlations between the central of molecule of type i and cluster $Q_{(\alpha_{d_i})}$:

$$m_{(\alpha_{d_i})} = \sum_c\sum_{s_{a_c}}P_{(\alpha_{d_i},s_{a_c})}\{[\mu_c\cos(\Phi_{(s_{a_c})})] +$$
$$[\sum_{s''_{d_c}}m_{(s''_{d_c})}\cos(\pi - \theta_{(s''_{d_c},s_{a_c})})] - [\sum_{(s''_{a_c}\neq s_{a_c})}m_{(s''_{a_c})}\cos(\pi - \theta_{(s''_{a_c},s_{a_c})})]\}$$

$$(6)$$

Similar expressions can be derived for correlations between (a) a central molecule of type i and molecules present within various other clusters (e.g., $Q_{(\beta_{d_i})}$, $Q_{(\beta_{a_i})}$, ...), and (b) central molecules of various types and their neighbors. The total number of such equations is equal to the number of association sites belonging to all types of molecules present in the system. Solving them, along with the chosen model parameters, would yield values for $\{m\}$.

3. Method for Evaluating Dielectric Constant of Associating Mixtures

The method to evaluate dielectric constant, which is given in detail in refs 5 and 8, briefly involves the following steps: (i) The molecular models for each type of molecule present in the system are selected. They must completely specify the number of electron-donor and electron-acceptor sites present on each type of molecule, the location of these sites on the molecule, the dipole moment vector, and the various covalent bond angles. (ii) The pure component model parameters of the association theory, namely, the enthalpy and entropy changes accompanying bond formation, are then determined by fitting the set of eqs 3 and 4 (written for all pairs of bonding sites) to data extracted from spectroscopic measurements. (iii) The unknown parameter of the Kirkwood−Forhlich theory (refer to eq 2 of ref 8), namely, r_k, is determined for each pure component by fitting the theoretical results for dielectric constant to experimental data. r_k denotes the refractive index of a pure liquid, containing molecules of type "k", at a frequency that is

sufficiently low for atomic and electronic polarization but sufficiently high for intermolecular relaxation processes involving the movement of permanent dipole moments to be inoperative. (iv) Steps i−iii completely determine all pure component model parameters. The mixture-specific model parameters are the enthalpy and entropy changes accompanying the formation of bonds between unlike types of molecules. These are determined by fitting the theoretical results for bonding probabilities at various types of sites present in the mixture to data extracted from spectroscopic measurements. (v) The dipolar correlations experienced by the different types of molecules present in the mixture are evaluated using eqs 5 and 6, along with the model parameters determined in steps i−iv. (vi) The dielectric constant of the mixture is predicted using eq 2 of ref 8.

Clearly, the predicted dielectric constant will reflect assumptions involved in the association theory, as well as the Kirkwood−Frohlich theory, and it is difficult to decouple the impact of each of them. It is, however, possible to study the limitations of the association model alone in the context of it describing the internal structure of associating fluids. This exercise, which does not involve any of the approximations of the Kirkwood−Frohlich theory, was performed in the earlier papers (ref 5 and 8) for water, ethanol, methanol, water−methanol, and water−acetone systems. For these systems, the theoretical results for bonding probabilities, given by eqs 3 and 4, were shown to be in good agreement with data extracted from related spectroscopic measurements and molecular dynamic studies.

4. Comparison with Earlier Treatments

We now compare the above expressions for water, alcohol, and water−alcohol mixtures with those derived earlier in refs 5 and 8.

4.1. Pure Water. The molecular model for water is the same as that adopted in ref 5. The set of eqs 6 reduce to

$$m_{(d_w)} = 2P_{(d_w,a_w)}\{\mu_w \cos(\Phi_{(a_w)}) + 2m_{(d_w)} \cos(\pi - \theta_{(a_w,d_w)}) - m_{(a_w)} \cos(\pi - \theta_{(a_w,a_w)})\} \quad (7a)$$

$$m_{(a_w)} = 2P_{(a_w,d_w)}\{\mu_w \cos(\Phi_{(d_w)}) + 2m_{(a_w)} \cos(\pi - \theta_{(d_w,a_w)}) - m_{(d_w)} \cos(\pi - \theta_{(d_w,d_w)})\} \quad (7b)$$

where subscript "w" denotes water molecules. Solving the above set of equations and combining with eq 5 of the present article yields eq 2 of ref 5. (Note that the parameter $P_{(a_w,d_w)}$ appearing in the above equation is equal to the parameter $P/2$ appearing in eq 2 of ref 5. This is because P in ref 5 refers to the probability of bonding at a given site, while $P_{(a_w,d_w)}$ in the present paper refers to the probability of bonding between two specific types of sites.)

4.2. Pure Alcohol. The molecular model for alcohol is the same as that adopted in ref 8. The set of eqs 6 reduce to

$$m_{(a_e)} = P_{(a_e,d_e)}\{\mu_e \cos(\Phi_{(d_e)}) + m_{(a_e)} \cos(\pi - \theta_{(d_e,a_e)}) - m_{(d_e)} \cos(\pi - \theta_{(d_e,d_e)})\} \quad (8a)$$

$$m_{(d_e)} = 2P_{(d_e,a_e)}\{\mu_e \cos(\Phi_{(a_e)}) + 2m_{(d_e)} \cos(\pi - \theta_{(a_e,d_e)})\} \quad (8b)$$

where subscript "e" denotes alcohol molecules. Solving the set of eqs 5 and 8 yields eq 9 of ref 8.

4.3. Aqueous Mixture of Alcohol. The set of eqs 5 for dipolar correlations reduces to the following forms:

$$g_w = 1 + 2\frac{m_{(a_w)}}{\mu_w} \cos[\phi_{(a_w)}] + 2\frac{m_{(d_w)}}{\mu_w} \cos[\phi_{(d_w)}] \quad (9a)$$

$$g_e = 1 + 2\frac{m_{(d_e)}}{\mu_e} \cos[\phi_{(d_e)}] + \frac{m_{(a_e)}}{\mu_e} \cos[\phi_{(a_e)}] \quad (9b)$$

where, from the set of eqs 6,

$$m_{(a_w)} = 2P_{(a_w,d_w)}\{\mu_w \cos(\Phi_{(d_w)}) + 2m_{(a_w)} \cos(\pi - \theta_{(d_w,a_w)}) - m_{(d_w)} \cos(\pi - \theta_{(d_w,d_w)})\} + 2P_{(a_w,d_e)}\{\mu_e \cos(\Phi_{(d_e)}) + m_{(a_e)} \cos(\pi - \theta_{(d_e,a_e)}) - m_{(d_e)} \cos(\pi - \theta_{(d_e,d_e)})\} \quad (10a)$$

$$m_{(d_w)} = 2P_{(d_w,a_w)}\begin{Bmatrix} \mu_w \cos(\Phi_{(a_w)}) \\ + 2m_{(d_w)} \cos(\pi - \theta_{(a_w,d_w)}) \\ - m_{(a_w)} \cos(\pi - \theta_{(a_w,a_w)}) \end{Bmatrix} + P_{(d_w,a_e)}\begin{Bmatrix} \mu_e \cos(\Phi_{(a_e)}) \\ + 2m_{(d_e)} \cos(\pi - \theta_{(a_e,d_e)}) \end{Bmatrix} \quad (10b)$$

$$m_{(a_e)} = 2P_{(a_e,d_w)}\begin{Bmatrix} \mu_w \cos(\Phi_{(d_w)}) \\ + 2m_{(a_w)} \cos(\pi - \theta_{(d_w,a_w)}) \\ - m_{(d_w)} \cos(\pi - \theta_{(d_w,d_w)}) \end{Bmatrix} + 2P_{(a_e,d_e)}\begin{Bmatrix} \mu_e \cos(\Phi_{(d_e)}) \\ + m_{(a_e)} \cos(\pi - \theta_{(d_e,a_e)}) \\ - m_{(d_e)} \cos(\pi - \theta_{(d_e,d_e)}) \end{Bmatrix} \quad (10c)$$

$$m_{(d_e)} = 2P_{(d_e,a_w)}\begin{Bmatrix} \mu_w \cos(\Phi_{(a_w)}) \\ + 2m_{(d_w)} \cos(\pi - \theta_{(a_w,d_w)}) \\ - m_{(a_w)} \cos(\pi - \theta_{(a_w,a_w)}) \end{Bmatrix} + P_{(d_e,a_e)}\begin{Bmatrix} \mu_e \cos(\Phi_{(a_e)}) \\ + 2m_{(d_e)} \cos(\pi - \theta_{(a_e,d_e)}) \end{Bmatrix} \quad (10d)$$

Clearly, the above equations are relatively much simpler in form as compared to the set of eqs 7 of ref 8. This is despite the fact that the above equations account for correlations between molecules present within all neighboring shells, while those of ref 8 account for correlations between molecules present within, at most, four neighboring shells only. Figure 2 shows that the theoretical results for dielectric constant of methanol−water mixture are in good agreement with experimental data. They are quite similar to those obtained by considering correlations between molecules present within only four nearest neighboring shells (Figure 7 of ref 8), suggesting that, for this mixture, the higher order terms do not significantly contribute to the dielectric constant.

5. Association Model for the DMSO−Water Mixture

Our goal in the present section is to study the DMSO−water system and propose a plausible model for the various association processes taking place in this system, based on the ability to describe the concentration and temperature dependence of dielectric constant. The molecular model for water molecule and the relevant association constants are taken from ref 5. For the DMSO molecule, we evaluate two models, both based on
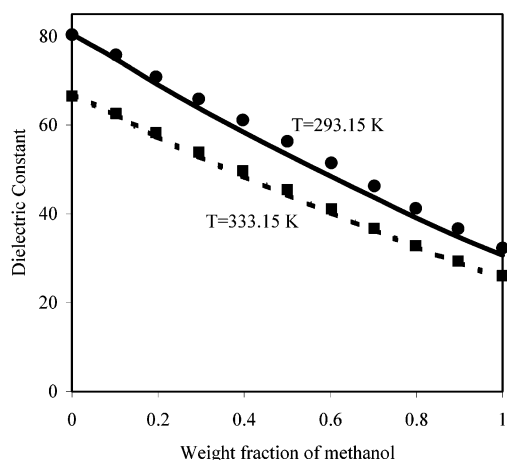
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Figure 2. Dielectric constant of methanol−water mixture at various compositions. The temperatures are indicated in the figure. Symbols represent experimental data,[31] and lines represent theoretical results.

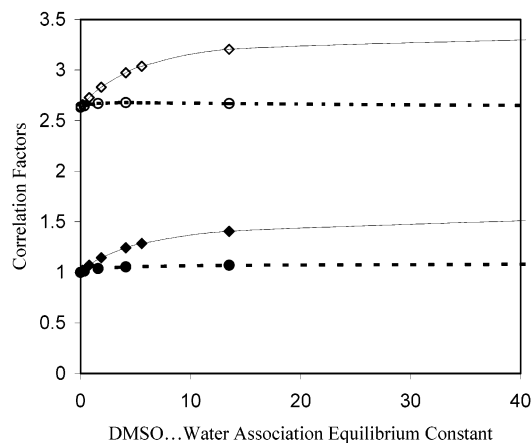**Figure 3.** Theoretical calculations of dipolar correlation factors for 28:72 molar ratio of DMSO−water mixture at different assumed values of DMSO···water association equilibrium constant. Circles and diamonds represent results of models I and II, respectively. Unfilled and filled symbols represent g_w and g_e, respectively. Lines are drawn to guide the eye.

the assumption that the doubly bonded covalent structure is the major contributor to the resonance hybrid.[27] In model I, the two lone pairs of electrons on the oxygen atom are assumed to represent the two (electron) donor sites. The angle between these donor sites, as well as between any of them and the S═O bond, is 120°. Association is assumed to take place between them and protons of water molecules, in addition to the association between donor and acceptor sites both belonging to water molecules. The angle between the direction of dipole moment and the S═O bond of the DMSO molecule is taken from ref 28 to be 26° 25′. By geometric consideration, the angle between the dipole moment and the two bonds then becomes 86°25′ and 33°35′, respectively. Model II is similar to model I except that it additionally includes the possibility, proposed earlier,[18] for the sulfur atom of DMSO molecules to associate with the oxygen atom of water molecules. This bond is assumed to be collinear with the S═O bond of the DMSO molecule. Although no spectroscopic evidence has yet been detected for the same, we explore the possibility of its presence for two reasons. First, it allows for model II to offer a possible explanation for the relative stability of 1DMSO/3H$_2$O clusters observed in the freezing point experiments. No molecular dynamic study[10−14] carried out thus far has been able to establish the stability of such structures. Second, the interpretation of spectroscopic data is not entirely free of ambiguity. Apart from the usual complications faced during deconvolution of spectroscopic peaks, one has to most often employ a secondary model for interpreting the spectroscopic data; hence, the various assumptions involved in the secondary model are reflected in the interpretation of spectroscopic data. We treat the $S^{+\delta}···O^{-\delta}$ electrostatic interactions using the same association theory, detailed in section 2. Considering that some success has been achieved in describing some of the properties of hydrogen-bonded systems using electrostatic models,[29,30] our view is that this approximation will not qualitatively alter our conclusions.

Figure 3 shows the theoretical results for dipolar correlation factors, g_w and g_e, for a 28:72 molar ratio of DMSO−water mixture. The calculations were performed for different assumed values of DMSO···water association equilibrium constant. r_k for DMSO was set at 1.6, and entropy change (S) upon association between DMSO and water molecules was set at −2.8 cal/deg/mol of bonds (refer later in the text for selection of these parameters). In the case of model I, both g_w and g_e are relatively insensitive to the water···DMSO association equilibrium constant. If one attaches primary importance to only the first-

neighbor interactions (as in ref 7), this result is nonintuitive; one would expect g_e to increase with the cross-association equilibrium constant because of increased bonding by the central DMSO molecule to the nearest water neighbors. However, if we probe the structure of the fluid beyond the nearest neighbors, the result is not surprising. For example, an increase in the DMSO···water association equilibrium constant results in a decrease in the positive contribution to g_e arising from the formation of d (first neighboring water molecule)···a (second neighboring water molecule) bond and an increase in the negative contribution arising from the formation of a (first neighboring water molecule)···d (second neighboring water or DMSO molecule) bond. The symbols d and a are used here to represent the donor and acceptor sites, respectively. The contribution to g_e arising from the presence of second nearest neighbors thus decreases. These complex competing effects are elegantly captured in the following simple expression (derived from the set of eqs 6): $m_{(d_e)} = (P_{(d_e,a_w)}/P_{(d_w,a_w)})m_{(d_w)}$. An increase in the DMSO···water association equilibrium constant simultaneously results in an increase in the factor $(P_{(d_e,a_w)}/P_{(d_w,a_w)})$ and a decrease in $m_{(d_w)}$. The net result for the system under consideration is that g_e remains largely insensitive to the DMSO···water association equilibrium constant. In the case of water being the central molecule, an increase in the water···DMSO association constant results in an increase in the probability of a (water)···d (DMSO) bond to be formed and, simultaneously, a decrease in the probability of a (water)···d (water) bond to be formed. These two opposing effects result in the g_w being largely unchanged.

Inclusion of the additional possibility of the S···O bond to be formed (model II) results in the correlation factors being much more sensitive to changes in the water···DMSO association constant. This result can be understood on the basis of additional contributions to g_w and g_e over that obtained within the framework of model I, resulting from the formation of d (water)···a (DMSO) bonds. Figure 4 shows a comparison of experimental data and theoretical results for the dielectric constant of DMSO−water mixtures over the entire composition range and at two different temperatures. Using the method outlined in section 3, we deduced the refractive index parameter, r^*, for DMSO to be 1.6. The DMSO−water association constant was tuned to best fit the theoretical results to experimental data. With a choice of $H = -2.0$ kcal/mol of bonds and $S = -2.8$
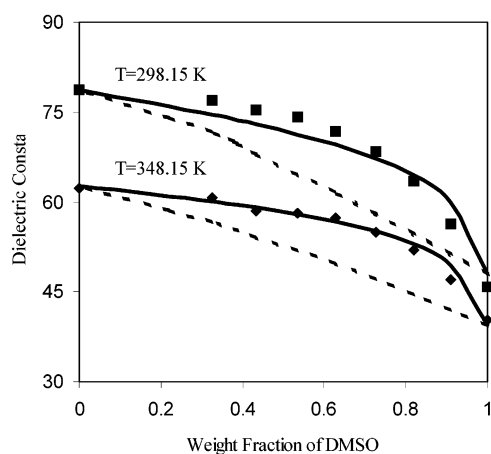
Figure 4. Dielectric constant of DMSO−water mixture at various compositions. The temperatures are indicated in the figure. Symbols represent experimental data,[32] and lines represent theoretical results. Dotted and thick lines represent results of models I and II, respectively.

cal/K/mol of bonds, model II clearly provides a good correlation. The corresponding correlations with model I, on the other hand, were found to be poor irrespective of the choice of the DMSO−water association constants, in line with the above discussions.

6. Summary

The expressions derived in the present articles are expected to be valuable for the following reasons: (1) They can be used to predict both the association stoichiometry and the dielectric constant in associating mixtures at conditions (temperature, composition, etc.) for which experimental data is not available. (2) They are valid for systems containing multiple components, the molecules of which may contain any number of electron-rich and electron-deficient sites each, for which no solutions exist to date. (3) Their closed form would aid in the clear interpretation of the role of molecular association on the dielectric constant of associating fluids. (4) They can be used, in combination with other techniques, to probe into the internal structure of associating fluids, as was demonstrated in the case of DMSO···water mixtures in the present paper. (5) They can help clarify some of the existing uncertainties related to the

magnitude of enthalpy and entropy changes accompanying bond formations. These extracted properties may be applied in the context of other theories that employ similar association models as used in the present paper for predicting a wide variety of bulk and interfacial properties of associating fluids.

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