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Interaction-Site Representation of Polar Mixtures and Electrolyte Solutions[1]

B. Kvamme[2]

In this work we present an interaction-site theory for mixture electrolyte solutions. The theory is semitheoretically adjusted for dielectrical properties. The theory preserves the correct asymptotic limits of the dielectric constant when the solution approaches the limit of any of its pure component. In the intermediate concentration range it interpolates the dielectric constants according to a quadratic mixing rule in relative dipole densities. For the simplified interaction-site models applied here, the excess energies of water/methanol at 293.15 K and experimentally measured densities are in fair agreement with experimental values. The estimated average number of hydrogen bonds for a mole fraction of water equal to 0.75 also compares well with published simulations. Estimated energies with and without the dielectric correction indicate that the dielectric constant may have a significant impact on the energy for this molecule. Excess energies for mixtures of water and ethanol are estimated to be too low.

KEY WORDS: interaction site; RISM equation; mixtures; thermodynamics.

1. INTRODUCTION

Recently Perkyns and Pettitt [1] presented an extended reference interaction-site (RISM) formalism for electrolyte solutions, denoted DRISM in the subsequent discussion, by introducing a dielectrical correction to the original RISM equation. The correction is based on the formal results of Høye and Stell [2] that relates the dielectric constant of a fluid to the site–site correlation functions. A convenient property of this correction scheme is that the dielectric correction is only related to the solvent. This feature is particularly convenient when the solvent is a mixture of polar components and the solute may be a mixture of different ionic species. These types of systems occur in a number of important industrial and biochemical

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[2] Telemark Institute of Technology, Kjølnes, N-3914 Porsgrunn, Norway.

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processes. Estimation of thermodynamic properties for these types of systems may be complicated. It is therefore of interest to develop a general and feasible formalism for treating such systems. In this first work we extend the formalism of Perkyns and Pettitt [1] to include solvents that are mixtures of dipolar components. We demonstrate the extended theory by calculations on model systems of water/methanol and water/ethanol.

2. THEORY

The dielectrically corrected RISM equation due to Perkyns and Pettitt [1] is conveniently expressed in Fourier-transformed 3 space in matrix notation as

$$\rho\tau(k)\,\rho=[I-(V(k)+\Theta(k))\,c_s(k)]^{-1}\,(V(k)+\Theta(k))\,c_s(k)(V(k)+\Theta(k)) + \chi(k)-\rho c_s\rho \tag{1}$$

$$\Theta(k)=V(k)\,\phi(k)\,V(k)[I-\phi(k)\,V(k)]^{-1} \tag{2}$$

$$V(k)=\rho\omega(k)+\chi(k) \tag{3}$$

$$Q(k)=\rho^{-1}\Theta(k)\,\rho^{-1} \tag{4}$$

The elements of $\phi(k)$ and $\tau(k)$ in inverse-transformed space are given by

$$\phi_{\alpha_M\gamma_{M'}}(r)=\frac{-\beta Z_{\alpha_M}Z_{\gamma_{M'}}e^2}{r} \tag{5}$$

$$\tau_{s_{\alpha_M\gamma_{M'}}}(r)=h_{\alpha_M\gamma_{M'}}(r)-c_{s_{\alpha_M\gamma_{M'}}}(r)-Q_{\alpha_M\gamma_{M'}}(r) \tag{6}$$

$h(r)$ are the site–site total correlation functions, with subscripts indicating atom and molecule indexes of the two sites in consideration. Subscript s merely indicates that equations are expressed in renormalized formalism. $\omega(k)$ is the intramolecular correlation matrix with elements

$$\hat{\omega}_{\alpha_M\gamma_M}(k)=\frac{\sin(kL_{\alpha_M\gamma_M})}{(kL_{\alpha_M\gamma_M})} \tag{7}$$

for rigid intramolecular distances L between the sites indicated by subscripts α and γ, both in molecule M. All elements in $\omega(k)$ involving different molecules are zero and diagonal elements are unity. The matrix ρ is a diagonal matrix containing the site densities of all molecules in the mixture. The dielectric correction is implemented though the matrix $\chi(k)$ by the following equations:

$$\chi(k)=\rho D_{0x}D_{0y}D_{1z}h_c(k)\,D_{1z}D_{0y}D_{0x}\rho \tag{8}$$

The elements of $h_c(k)$ are zero for elements that are not defined to be part of the solvent. For solvent molecules of type M and M', the elements of $h_c(k)$ are given by

$$h_{c_{MM'}}(k) = \frac{z_M z_{M'}}{\rho_T \sqrt{x_M x_{M'}}} \left(\frac{\varepsilon_{MM'} - 1}{y_{MM'}} - 3 \right) \exp(-ak^2) \tag{9}$$

$$y_{MM'} = \frac{4\pi\beta\rho \sqrt{x_M x_{M'}}\, \mu_M \mu_{M'}}{9} \tag{10}$$

$$\varepsilon_{MM'} = \sqrt{\varepsilon_M \varepsilon_{M'}} \tag{11}$$

$$z_M = \frac{y_M}{\sum_{l=1}^{l=n_s} y_l} \tag{12}$$

μ and ε are the dipole moment and dielectric constant, respectively, for the components indicated by the index. Subscript T denotes total particle density and x is the mole fraction. The sum in Eq. (12) is over all solvent molecules n_s.

The matrixes D are diagonal with elements

$$D_{i,\mathrm{mv}} = j_{\mathrm{m}}(kd_{i\mathrm{v}}) \tag{13}$$

for all solvent molecules i, other elements are zero, and j indicates the Bessel-function with order given by the subscript m. The distances $d_{i\mathrm{v}}$ in the argument is the distance of site i in the orthonormal direction v from the site charge. These distances are constrained by the specific dipole moment of the solvent. In the formulation used here the dipole vector is arranged along the z axis, and correspondingly the nonzero elements in the x and y directions are unity. Equations (9)–(12) represents the extended form of the specific long-range correction suggested by Perkyns and Pettitt. A mole fraction of unity will lead to the original correction of Perkyns and Pettitt [1] in Eq. (9). A value of 0.1 for a (as suggested by Perkyns and Pettitt [1]) is adopted throughout this study. The extension is not theoretically rigorous since the dielectric constant in a polar mixture [14] is an implicit function of all the correlation functions in the fluid.

The HNC closure corresponding to the renormalized equation is given by

$$\begin{aligned} c_{s_{\alpha_M \gamma_{M'}}}(r) &= \exp(-u_{s_{\alpha_M \gamma_{M'}}}(r) + \tau_{\alpha_M \gamma_{M'}}(r) + Q_{\alpha_M \gamma_{M'}}(r)) \\ &\quad - 1 - \tau_{\alpha_M \gamma_{M'}}(r) - Q_{\alpha_M \gamma_{M'}}(r) \end{aligned} \tag{14}$$

where

$$u_{s_{\alpha_M \gamma_{M'}}}(r) = u_{\alpha_M \gamma_{M'}}(r) + \phi_{\alpha_M \gamma_{M'}}(r) \tag{15}$$

Equations (1) and (14) are solved using Gillan's [4] procedure in an extension similar to that suggested by Zichi and Rossky [5]. Fourier transforms are performed by means of a logarithmic grid [6, 7]. The residual energy of the fluid is directly related to the structure of the fluid through the energy equation. An approximate hydrogen bond analysis is accomplished using the superposition approximation to construct estimates for the molecular correlation functions. An average number of hydrogen bonds is estimated from a geometric concept. This concept is discussed in more detail by Palinkas et al. [10, 11].

3. RESULTS

Parameters of water and methanol are given in Table I. The model for methanol is based on a recalculation of TIPS parameters [15] for methyl and oxygen to corresponding Lennard–Jones parameters. Short-range parameters for the hydrogen site are adjusted by regression against experimental energies along the liquid branch of the coexistence curve. Lorentz–Bertehlot rules are applied for cross-interactions. A more extensive evaluation of the models for water and methanol is given by Kvamme [3] and Holta and Kvamme [17]. A rigid model for ethanol is constructed from that of methanol by connecting a methyl group in trans to the hydrogen atom and with a dihedral angle of 100° relative to the CH_2–O axis. Short-range parameters for the methyl-group are given in Table I. Short-range parameters for the CH_2 group ($\sigma = 3.9833$ Å and $\varepsilon/k_B = 57.51$ K) are again recalculated from the TIPS parameters of Jorgensen [15].

Table I. Models for Methanol and Water[a]

	Methanol			Water	
	CH_3	O	H	O	H
σ (Å)	3.8610	3.0800	1.0051	2.8385	1.1674
ε/k_B (K)	91.060	88.340	8.118	78.40	8.708
Z	0.2850	−0.6850	0.4000	−0.8042	0.4021

[a] For water the H–O bond length is 0.9003 Å and the H–O–H angle is 105.96°. For methanol the bond length between oxygen and hydrogen is 0.945 and the bond length between methyl and oxygen is 1.410 Å. The CH_3–O–H angle is 108.5°.

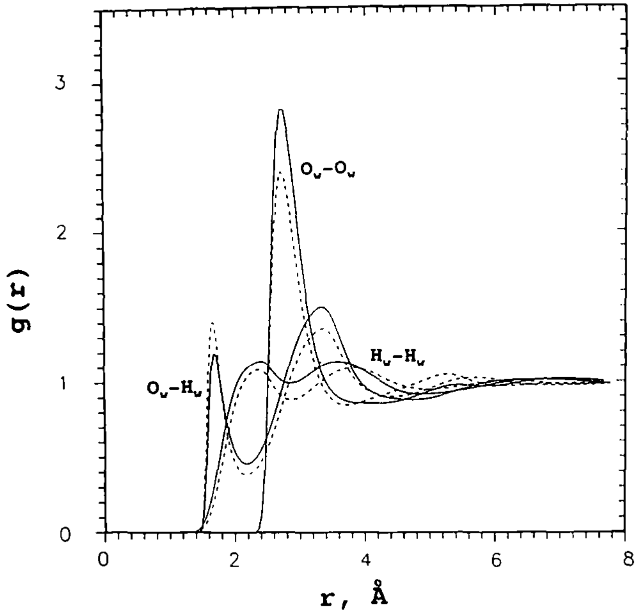

Fig. 1. Partial correlation functions for water in a water/ethanol mixture at a temperature of 293.15 K and an experimentally measured [19] density of 886.5 $kg \cdot m^{-3}$ for a mole fraction of water equal to 0.6886. Solid lines are mixture results and dashed lines are pure component results at experimentally measured densities [18].

We have applied this theory to mixtures of water and methanol at 293.15 K and at experimentally measured densities [19] for mole fractions for water in the range from 0 to 1 with an interval of 0.05. As indicated in Ref. 3 we expect the numerical uncertainty in estimated energies to be less than 70 $J \cdot mol^{-1}$. These uncertainties will be significant for excess energies. We therefore discuss only the qualitative features. The minimum energy is obtained for a mole fraction of water equal to 0.75 with a value -0.6 $kJ \cdot mol^{-1}$. This value is to be compared to the experimental value of -0.9 $kJ \cdot mol^{-1}$ [19] and a simulated (molecular dynamics) value of -1.0 $kJ \cdot mol^{-1}$ [20]. A plot of excess energies versus mole fraction water exhibits the same qualitative features as that observed by MD but the curve is shifted toward higher values as also indicated by the minimum value. The estimated number of water–water hydrogen bonds at this minimum excess energy condition is 2.7.

The estimated energies for the model of pure ethanol are -39.34 and -36.45 $kJ \cdot mol^{-1}$ in XRISM [21] and DRISM [1] theories, respectively, at 351.4 K and 789.0 $kg \cdot m^{-3}$. These values are to be compared to the

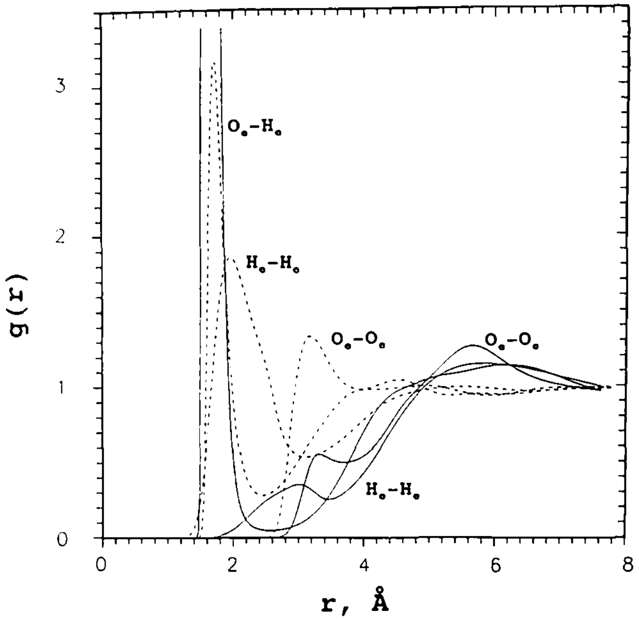

Fig. 2. Partial correlation functions for ethanol in a water/ethanol mixture. Symbols and thermodynamic condition as given in the caption to Fig. 1. The maximum peak in $g(r)$ for O_e–H_e is 19.01 at $r = 1.65$ Å.

experimental value of $-36.33\ \mathrm{kJ \cdot mol^{-1}}$ [18]. In mixtures of water and ethanol there are 21 different site–site correlation functions. In Figs. 1, 2, and 3 we present site–site correlation functions involving oxygen and hydrogen sites, estimated at a temperature of 293.15 K and an experimental density of $886.5\ \mathrm{kg \cdot m^{-3}}$ for a mole fraction water of 0.6886 [19]. Subscripts to the site symbols denote parent molecule (w = water, e = ethanol). The corresponding calculated excess energies for water/ethanol mixtures are too low compared to experimental values [19]. From Fig. 1 it is seen that some of the O–H correlation functions for this system are very large and significantly changed from the pure-component values. Such a narrow, high peak will necessary also induce increased numerical uncertainty since only a limited number of values for $g(r)$ are used to represent this energetically important region in the integrations. For this reason we do not present the numerical values before we know more about the significance. We should also keep in mind that the models applied here are oversimplified and basically intended to illustrate qualitative features of the theory.

The RISM formalism is not an exact theory [22]. Some diagrams in the indirect correlations are missing and some illegal diagrams are

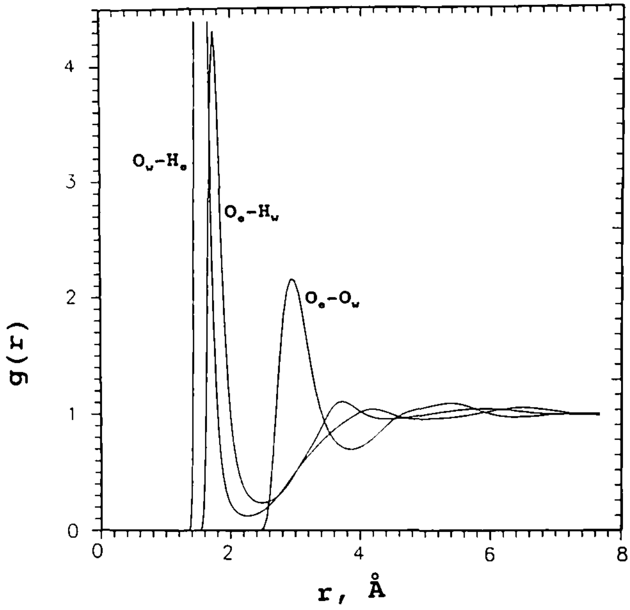

Fig. 3. Partial correlation functions for cross-correlations in a water/ethanol mixture. Symbols and thermodynamic condition as given in the caption to Fig. 1. The maximum peak in $g(r)$ for O_w-H_e is 11.06 at $r = 1.55$ A.

included. In addition, the summations of diagrams are limited to diagrams contained in the HNC closure. The impact of a semitheoretical correction as suggested here is therefore difficult to analyze. For the original RISM equation, the dielectric constant for the water model presented here is approximately 18, as opposed to the experimental value of 78.54. The extension of the DRISM/HNC theory [1] proposed in this work will at least change the estimated dielectric constant to a value that is interpolated between pure-component values according to the quadratic mixing rule in equation (12), and in accordance with the original theory of Perkyns and Pettitt [1], it will always reproduce the correct value for pure components. The consequences of the dielectric deficiency for the thermodynamic properties of small polar fluids such as water and methanol seems to be small [3], but may be more significant for ethanol as shown here. The main purpose of suggesting this type of extension is, however, the possibility of obtaining a theory for electrolyte solutions where the solvent is a mixture of polar fluids and the ions may be of several different types. These types of systems are frequently encountered in industrial and biochemical processes.

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