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Thermodynamic properties and dielectric constants in water/methanol mixtures by integral equation theory and molecular dynamics simulations

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A dielectrically adjusted version of the RISM equation for the situation of ions in mixed solvents is applied to model mixtures of water with methanol in concentrations covering the complete concentration range. Calculated structures from the integral equation theory are compared to corresponding results from NVT molecular dynamics simulations. The structure calculated from the integral equation is generally in good agreement with the molecular dynamics results. The agreement in calculated energies between integral equation theory and molecular dynamics simulations are also generally good over the entire concentration range for the specific model applied. For the first time this type of integral equation theory is also applied to the direct calculation of free energy. For the specific water model the free energy is lower than the experimental value for pure water. Under-predictions of the structure and corresponding higher entropy for the specific water model might be one of the reasons for these results. The dielectric constant in a uniform liquid mixture can be described in terms of the dipole moments of the molecules involved and the molecular correlation functions for the different molecular pair combinations in the mixture. In this work I reformulate the theory into a corresponding interaction site formulation. The reformulated theory is illustrated for the water/methanol model mixtures.

I. Introduction

Small alcohols like for instance methanol contain hydrophilic as well as hydrophobic parts. The mixing process is dominated by the entropy contributions to the mixing process. Due to the strong hydrophilic part these smaller alcohols are completely soluble in water. However it is well known from experimental results that the hydrophobic part contributes substantially to the thermodynamic properties of water/alcohol mixtures. The hydrophobic parts of these molecules are also responsible for the minimum in partial volume for methanol in water/methanol mixtures (Franks¹). The experimentally measured excess enthalpies for water/methanol are uniformly negative over the whole concentration range (Westmeier,² Lama and Lu³).

Tanaka *et al.*⁴ applied two different potentials for water, MCY (Matsuoka, Clementi, Yoshimine) (Matsuoka *et al.*⁵) and TIPS (transferable intermolecular potentials) (Jorgensen⁶), and the OPLS (optimized potentials for liquid simulations) (Jorgensen⁷) potential for methanol in estimates of mixture structures using the re-normalised reference interaction site model (RISM) integral equation (Hirata and Rossky⁸). This study follows some of the lines from their study. In this work I use molecular dynamics (MD) simulations as a tool for verification of a dielectrically modified version of the RISM integral equation (Kvamme⁹). Since my previous studies¹⁰ indicate that TIPS pure water structures estimated from the RISM equation with HNC (hypernetted chain) closure is not in accordance with recent experimental data (Postorini *et al.*¹¹) I suggest a different potential for water. The water potential applied in this work differs slightly from the one that I used in my previous work. The reason is that the integral equation results are sensitive to the short-range potential of the hydrogen in water. The first motivation for this work is to demon-

strate, relative to my previous paper, how a small change in the short range potential for hydrogen is able to shift the maxima and minima of the correlation function for water to very close agreement with neutron scattering data (Postorini *et al.*¹¹). Van Leeuwen¹² and van Leeuwen and Smit¹³ have applied grand canonical Monte Carlo to the calculation of the phase envelope for methanol. These simulations indicate that the OPLS potential will not give the correct phase envelope. I have therefore applied a slightly modified version of the methanol potential due to van Leeuwen¹¹ in this study. The short-range hydrogen parameters in this work are also modified from the corresponding parameters applied by me in the previous paper.¹⁰ The energy calculated from the integral equation for this methanol model is in better agreement with the experimental energy for real methanol that can be derived from the latent heat of vaporisation.¹⁴

Integral equation theories represent a feasible and simple scheme for estimation of structure and thermodynamic properties of mixtures. In this context it is important to note that the molecular dynamics simulations presented here are only intended as a reference for comparison with results from the integral equation. As such I have not made an extensive review of simulation studies for similar systems. Energy is directly obtainable from the correlation function by a sum of one-dimensional integrals. Free energy and pressure are obtainable from a sum of one-dimensional integrals in real space and Fourier-transformed space. With efficient solution strategies for solving the integral equations the calculation of structure is several orders of magnitudes faster than molecular dynamics simulations in terms of CPU time. In addition it will not suffer from statistical sampling inaccuracies for dilute solutions. Electrolyte solutions of mixed solvents are the primary goal of our project and this issue is therefore an important consideration. In this work I present, for the first time, calculated free

energies for model mixtures of water and methanol over the complete concentration range. This is the second new result of this work. Calculation of chemical potentials and phase equilibrium using this type of integral equation theory is the next step and work is in progress in this direction (Kvamme¹⁵).

The static dielectric constant in a mixture is uniquely defined in terms of the molecular correlation functions, as derived by Høye and Stell^{16,17} more than twenty years ago. I have reformulated their results into the corresponding appropriate expressions for interaction site systems and this result is the third new result presented in this paper.

The paper is organised as follows. Section II gives a brief overview of the most essential details of the theory and the molecular dynamics simulation procedures. Section III gives details of the calculated correlation functions. Derived thermodynamic properties are discussed in section IV. Interaction site formulation of the mixture equation for the dielectric constant, and corresponding results for the water/methanol model system, is discussed in section V. My conclusions are given in section VI.

II. Theory and simulation details

The integral equation theory applied in this study is a renormalized and dielectrically adjusted version of the RISM equation,^{9,10,18} hereafter denoted as DMRISM, using the hypernetted chain (HNC) closure.

For the molecular dynamics (MD) simulations I have modified and extended the McMDyn package, originally written by Laaksonen.¹⁹ All simulations are performed using periodic boundary conditions and an ensemble of 256 molecules. The simulation box is cubic and the volume is kept constant during the simulation. Periodic boundary conditions in three dimensions are applied. Long-range Coulomb forces are treated by the Ewald summation method (see for instance the compilation by Allen and Tildesley.²⁰ The temperature is controlled according to the thermostat procedure of Hoover²¹ and Toxvaerd²² using separate thermostats for the rotational and translational degrees of freedom. We (Kuznetsova and Kvamme²³) fix the control parameters for the two thermostats according to an analysis of the frequencies for pure liquid model water at 273 K according to the procedure discussed. Representative indications of values for the water parameters are also given in that paper. Within the notation of Toxvaerd²² the optimum thermostat masses for TIP4P water are 66 fs for translation and 33 fs for rotation when a time step of 0.25 fs is applied. The corresponding parameters for optimal ergodicity of methanol differ only slightly from the optimal water control parameters (less than 2 per cent). The water parameters have therefore been used consistently for all pure components and mixtures. See also the paper by Kuznetsova and Kvamme²⁴ describing the application of temperature control in grand canonical molecular dynamics simulations for water model systems.

Simulations are started from an fcc lattice. Translational as well as rotational momenta are zero at the start. The time step is 0.25 fs and the simulation time is 250000 time steps. The last 200000 are sampled for analysis.

III. Calculated structures

In all simulations presented in this section as well as in the subsequent section interactions between atoms are modelled as a short range Lennard-Jones 12-6 plus a charge or partial charge on atoms that are ionic or parts of a dipole. The models for water and methanol are given in Table 1. It is the same model that was applied by me in a previous study.¹⁰ The model for methanol is a modified version of the model due to van Leeu-

Table 1 Parameters for water and methanol. The water model is from Kvamme,¹⁰ the methanol model is a slightly modified version of the model due to van Leeuwen¹²

	Water		Methanol		
	H	O	C	O	H
$\sigma/\text{\AA}$	1.2963	2.8653	3.740	3.03	1.9191
$(\epsilon/k_B)/\text{K}$	1.0781	51.560	105.20	86.5	0.2733
Z/e	+0.392	-0.784	+0.265	-0.700	+0.435
$l_{\text{O-H}}/\text{\AA}$	0.9189869		0.945		
$l_{\text{O-CH}_3}/\text{\AA}$			1.410		
$\angle/^\circ$	105.17		108.5		

wen.¹² The only difference is the addition of a small short-range interaction on the hydrogen. The short-range hydrogen Lennard-Jones parameters are slightly adjusted so that the integral equation theory gives reasonable energy at the normal boiling point compared to experimentally measured values¹⁴ when the experimental liquid density is used in the solution of the integral equation.

Comparison of the results for pure water is included in order to illustrate the effect of the short-range core on the hydrogen in this type of interaction site integral equation sampling. It should however be noted that the experimental neutron scattering data used for comparison (Postorini *et al.*¹¹) may not be the best data available, as discussed by Zetterstrom and Soper²⁵ in a more recent paper. The location of the maxima and minima are basically the same as in the revised analysis but the heights of the peaks differ slightly. The energy for this model at 298.15 K and the experimentally measured¹⁴ density is $-41.08 \text{ kJ mol}^{-1}$ from integral equation theory and from molecular dynamics simulations. Pure water is of course well studied in a large number of publications but the correlation functions for pure water is in this context included in Figs. 1–3 for two reasons. The first is of course the direct comparison to results derived from neutron scattering experiments. The other reason is related to the calculated thermodynamic properties and will be discussed in more detail in the next section. From the pair correlation functions in Figs. 1–3 we particularly note that the peaks in the site–site correlation functions from molecular dynamics simulations are generally sharper and higher than the corresponding values calculated from the iterative solution of the integral equation.

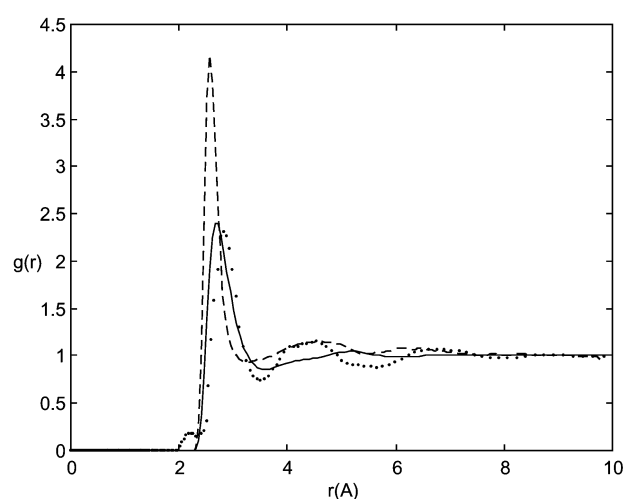


Fig. 1 Correlation functions for oxygen–oxygen at 293.15 and a density of 991.0 kg m^{-3} . Solid line is the results from integral equation theory and dashed line is the corresponding result from NVT molecular dynamics simulations, both for the water model described in the text. Dotted line is experimental results from neutron scattering experiments of real water (Postorini *et al.*¹¹).

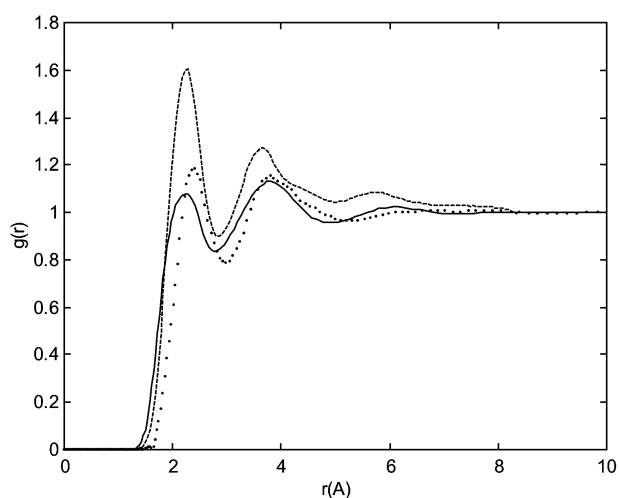


Fig. 2 Correlation functions for hydrogen–hydrogen at 293.15 and a density of 991.0 kg m^{−3}. Notations as in Fig. 1.

I have solved the integral equation theory for the model system of water and methanol at 298.15 K and nine different concentrations as given in Table 2. The applied densities correspond to densities measured for real mixtures of water and methanol.¹⁴ A limited number of the calculated correlation functions are given in Figs. 4–9. The complete sets of correlation functions for the 15 site–site correlation functions for the 9 conditions, from MD as well as DMRISM, are available from the author. The selected ones are not necessarily those in best agreement. In particular Fig. 7 is included to illustrate some of the sampling differences between the integral equation and the molecular dynamics simulation. While the MD results give a more pronounced cusp for typical effects of intramolecular correlations in pure methanol the DMRISM results give a smoother function reflecting a more complex mixture of different inter- and intra-molecular couplings.

$$n_{s_{\alpha_i \gamma_j}} = 4\pi \rho_{\gamma_j} \int_0^{r_{\min}} g_{\alpha_i \gamma_j} r^2 dr \quad (1)$$

r_{\min} is the radial distance of first minimum for the actual correlation function in consideration. The total molecular correlation functions are not directly obtainable from the DMRISM

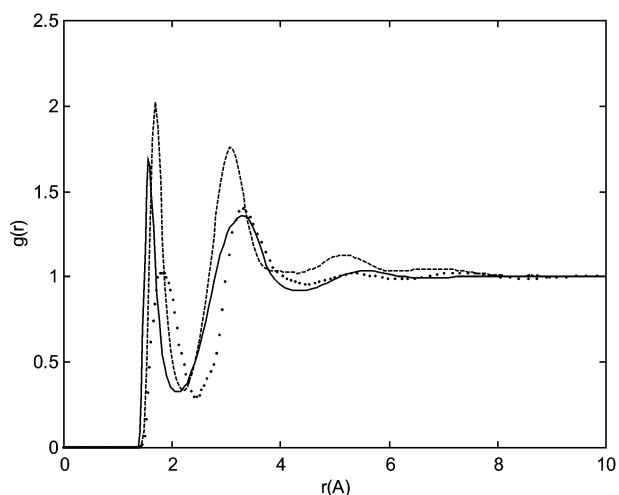


Fig. 3 Correlation functions for hydrogen–oxygen at 293.15 and a density of 991.0 kg m^{−3}. Notations as in Fig. 1.

Table 2 Calculated energies and free energies as functions of the methanol mole fraction. MD denotes the results from molecular dynamics simulations and DMRISM are the corresponding results from the integral equation. The temperature is 298.15 K and the densities used are the experimentally measured values for real mixtures¹⁴

	Density/kg m ^{−3}	Energy/kJ mol ^{−1}		Free energy/kJ mol ^{−1}
		MD	DMRISM	
1	998.2	−41.083	−41.112	−29.541
0.95	996.7	−40.919	−39.873	−27.655
0.9	971.75	−40.300	−39.404	−26.922
0.85	960.75	−39.955	−39.085	−26.010
0.7506	937.10	−39.139	−38.437	−24.372
0.4556	876.30	−34.796	−36.383	−20.217
0.35	854.88	−34.422	−34.805	−16.876
0.2531	836.50	−34.408	−34.618	−18.562
0.1016	808.90	−33.103	−33.380	−16.620
0.05	800.50	−32.454	−33.067	−13.784
0	791.70	−32.012	−32.042	−13.648

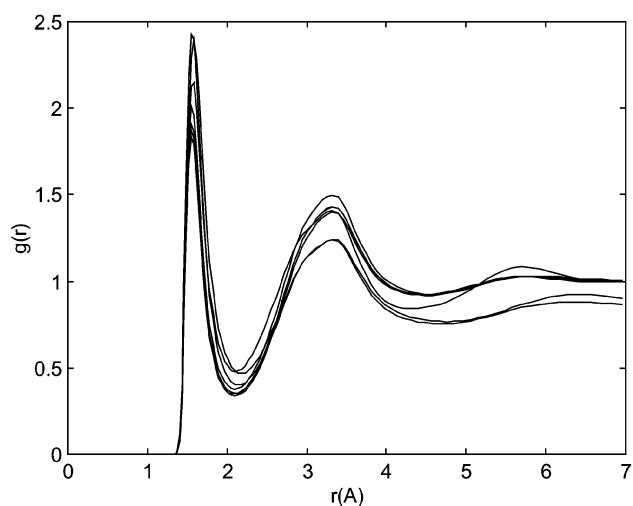


Fig. 4 Water hydrogen–oxygen correlation functions as functions of methanol mole fraction in water/methanol mixtures. Highest first peak is for water mole fraction 0.05 and lowest first peak is for water mole fraction equal to 0.95.

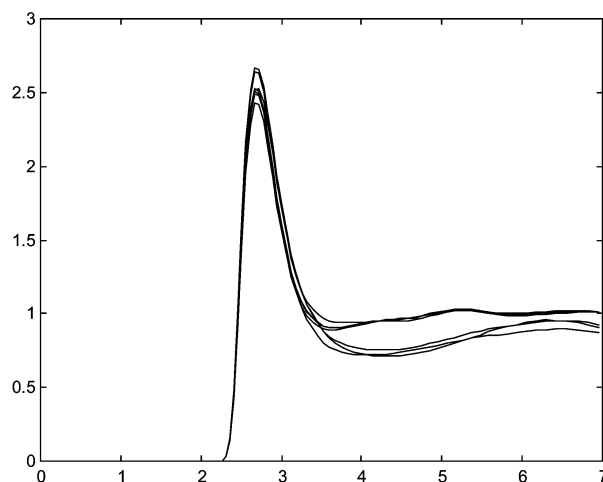


Fig. 5 Water oxygen–oxygen correlation functions as functions of methanol mole fraction in water/methanol mixtures. Highest first peak is for water mole fraction 0.05 and lowest first peak is for water mole fraction equal to 0.95.

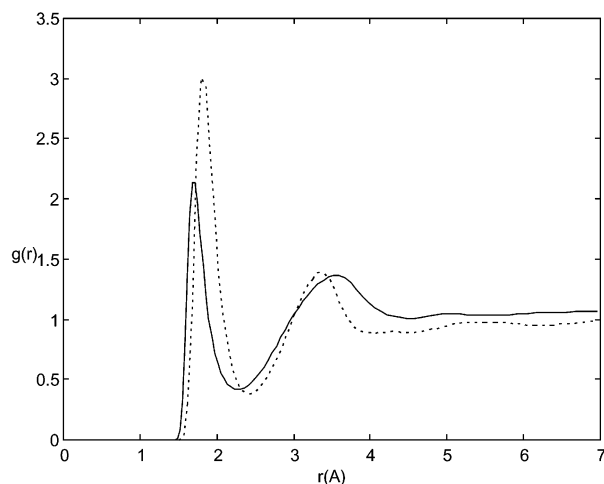


Fig. 6 Oxygen water-hydrogen methanol correlation function for a methanol mole fraction equal to 0.5. Temperature is 298.15 K and experimental densities¹⁴ are used. Solid line is calculated from DMRISM and dashed lines are MD results.

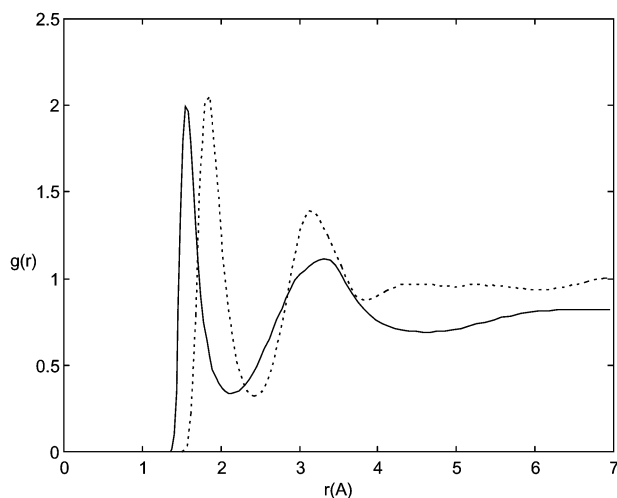


Fig. 7 Oxygen methanol-hydrogen water correlation function for a methanol mole fraction equal to 0.5. Temperature is 298.15 K and experimental densities¹⁴ are used. Solid line is calculated from DMRISM and dashed lines are MD results.

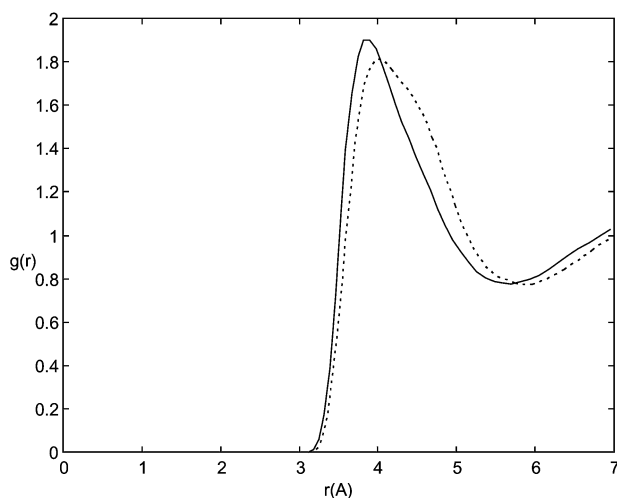


Fig. 8 Methanol methyl-methyl correlation function for an equimolar mixture of water and methanol at 298.15 K and experimentally measured density.¹⁴ Solid line is calculated from DMRISM and dashed lines are MD results.

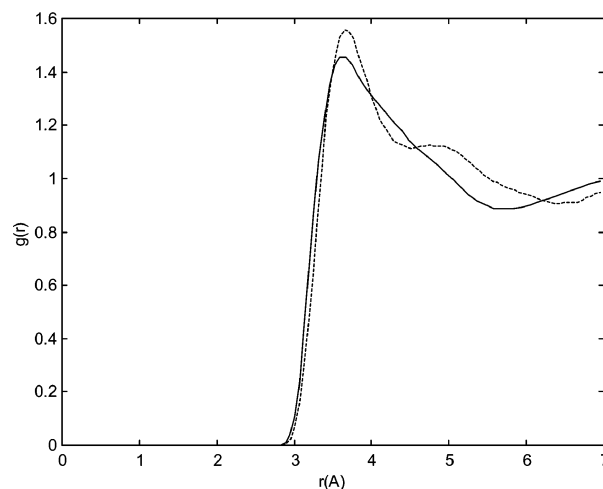


Fig. 9 Methanol methyl-methanol hydrogen correlation function for a water mole fraction equal to 0.5. Solid line is DMRISM result and dashed are results from molecular dynamics simulations.

equation and the orientation correlation function can therefore not be studied directly. We can reconstruct approximate angle dependent correlation functions from the site-site correlation function, as I did earlier for the water/ethanol system.⁹ The effect of these orientational correlations should however also be visible by cross-examining coordination numbers of the different atoms. We first consider the average packing of sites around methanol. In Fig. 10 we plot the packing around the methyl group, which is the volume term dominating in methanol. It is seen that the co-ordinations of methyl and oxygen around the methyl group are consistent and give the average number of nearest neighbours of methanol around methanol as function of methanol concentration. In Fig. 11 we plot the co-ordination numbers around the methanol oxygen for the same condition and concentrations of methanol. As a combination of Figs. 10 and 11 it is seen that the methanol molecules will tend to orient mutually so as to reduce the average number of oxygen methanol contacts. If we now look at the average distribution of water around the methanol methyl and oxygen respectively we may calculate the average fraction of water molecules in the first co-ordination shell around these

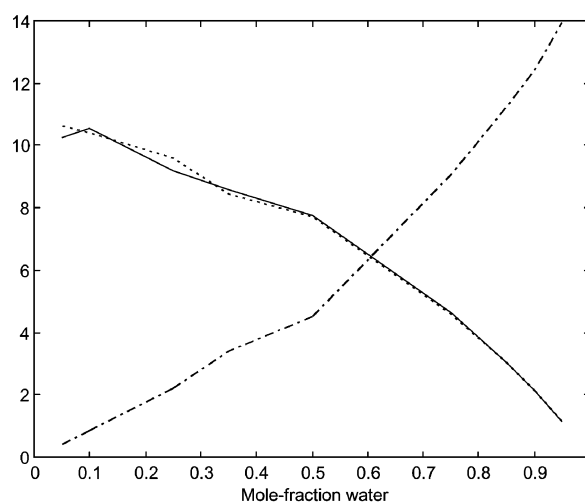


Fig. 10 Calculated co-ordination numbers around the methyl group in methanol as functions of water concentration. Temperature is 298.15 K. Experimentally measured densities for real water/methanol mixtures¹⁴ is applied. Solid line is methyl, dashed is methanol oxygen and dash-dot is water oxygen.

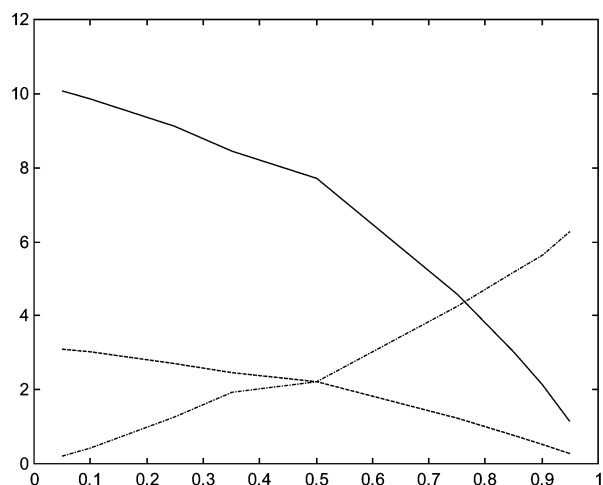


Fig. 11 Co-ordination numbers around methanol oxygen as function of water concentration. Temperature is 298.15 K and experimentally measured densities for real water/methanol mixtures¹⁴ is used. Solid line is methyl, dashed is methanol oxygen and dash-dot is water oxygen.

two types of site. The calculated values show a slight preference for packing around the oxygen group for the entire range of concentrations (Fig 12). We note that these observations coincide with experimentally observed negative excess chemical potentials.²

IV. Thermodynamic properties

The residual energies for the different systems are directly accessible from the energy equation. Free energies and corresponding chemical potentials for the two components are calculated according to the general equations derived by Singer and Chandler.²⁶ In Table 2 calculated energies from the integral equation and from molecular dynamics simulations are listed together with Helmholtz free energies calculated from the integral equation. The experimental free energy for pure water at 25 °C is -24 kJ mol^{-1} (Sarkisov *et al.*²⁷) and thus higher than the DMRISM value for this particular water model. One of the reasons for this might be that the integral

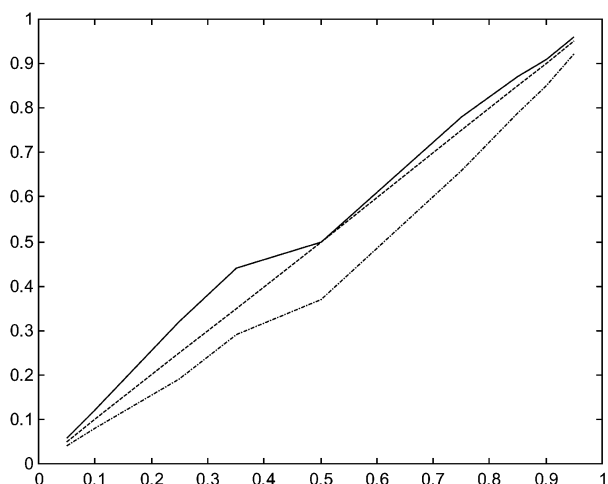


Fig. 12 Fraction of water molecules in the packing around methanol methyl group and methanol oxygen. Solid line is the fraction of water molecules in the first co-ordination shell around methanol oxygen. Dash dot is the corresponding fraction of water around the methyl group.

equation result for this particular water model is less structured than the experimentally measured structure. See for instance the second and subsequent peaks in the oxygen–oxygen correlation function in Fig. 2. Even though the applied short range potential for the methanol hydrogen is small the effect in the integral equation results for the structure is significant as it successively shifts the location and heights of the peaks responsible for the average hydrogen bonding. These changes in average structure will change the entropy of the system. It is not clear at this stage if possible changes in entropy due to changes in short range potential is the main reason for the calculated high value of free energy in pure model methanol. The original methanol model due to van Leeuwen is able to reproduce the coexistence curve for methanol reasonably well when grand canonical Monte Carlo (GCMC) is used. Within the allocated resources for this project it was not possible to look into this issue in detail. By changing the short-range hydrogen potential systematically and calculating the corresponding free energies by integral equation theory as well as by molecular dynamics simulations using the procedures described by Kuznetsova and Kvamme²³ we should be able to quantify the effect of this short-range hydrogen potential on the free energy as calculated from the integral equation.

Another issue as discussed above is the shortcomings of the applied water model. Previous applications of the SPC and TIPS models (Kvamme²⁸) show that the integral equation results for the oxygen–hydrogen correlation function are significantly shifted from the experimentally measured value and that significant short-range hydrogen potential is needed in order to shift this to the experimental location. Another alternative that is the ST2 model due to Stillinger and Rahman.²⁹ Recent studies indicate that this specific water model is able to estimate glass transitions in model water (Debenedetti³⁰). It would therefore be of interest to investigate that same type of systems using this water model as well as other models for methanol.

V. The dielectric constant

The dielectric constant in a mixture is formally given by Høye and Stell^{16,17} as the solution to the equation (for $\lim k \rightarrow 0$):

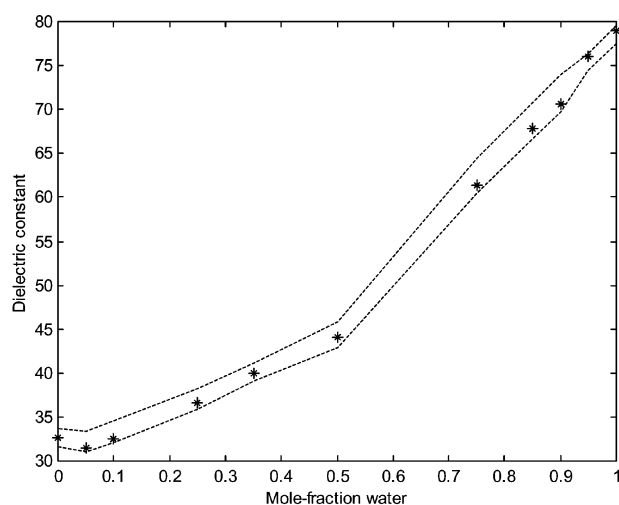


Fig. 13 Calculated dielectric constants as functions of water mole fraction in water/methanol mixtures. Temperature is 298.15 K and experimentally measured mixture densities for real water are used.¹⁴ The stars indicate calculated values for minimum k used in the solution for structure while the dashed lines are for $k_{\min} = 3.64 \times 10^{-5}$ (upper line) and $k_{\min} = 3.72 \times 10^{-5}$ (lower line).

$$\begin{aligned} & \left[3(\hat{s}_1 \hat{k})(\hat{s}_2 \hat{k}) - 3\hat{s}_1 \hat{s}_2 \right] \varepsilon^2 \\ & - \left[3(\hat{s}_1 \hat{k})(\hat{s}_2 \hat{k}) - 3\hat{s}_1 \hat{s}_2 - (9\hat{s}_1 \hat{s}_2 + 3\alpha)y \right] \varepsilon \\ & + 3(\hat{s}_1 \hat{k})(\hat{s}_2 \hat{k}) = 0 \end{aligned} \quad (2)$$

$$\alpha = \rho \sum_i \sum_j \sqrt{x_i x_j} M_{ij} \tilde{h}_{ij} \quad (3)$$

$$M_{ij} = \frac{\mu_i \mu_j \sqrt{x_i x_j}}{\sum_i x_i \mu_i^2} \quad (4)$$

$$y = \frac{4\pi}{9} \beta \rho \sum_j x_i \mu_i^2 = \frac{4\pi}{9} \beta \rho \sum_j x_i \left(\sum_\gamma d_{j\gamma} q_{j\gamma} \right)^2 \quad (5)$$

Subscripts i and j denote types of molecule. The last sum in eqn. (5) involves the sum of sites in each molecule and the distances for each site is the distance along the dipole-vector. q denotes partial charges of each site. For interaction site systems the appropriate reformulation of eqns. (3) and (4) into interaction site representation yields:

$$\alpha = \rho \sum_i \sum_j \sqrt{x_i x_j} \sum_\alpha \sum_\gamma M_{i\alpha j\gamma} \tilde{h}_{i\alpha j\gamma} \quad (6)$$

$$M_{i\alpha j\gamma} = \frac{d_{i\alpha} q_{i\alpha} d_{j\gamma} q_{j\gamma} \sqrt{x_i x_j}}{\sum_j x_j \left(\sum_\gamma d_{j\gamma} q_{j\gamma} \right)^2} \quad (7)$$

with $\hat{s}_1 = -1$, $\hat{s}_2 = 1$ and $\hat{k} = 1$ within the interaction site formulation in eqns. (6) and (7). Subscripts α and γ denote sites in the actual molecules i and j . The necessary site-site correlation functions involved in eqn. (6) are already available from the solutions discussed in sections III and IV.

Dielectric constants as calculated from the 15 distinct site-site correlation functions are given in Fig. 13. For the calculation of the dielectric constants the limiting value for the correlation functions is approximated by the smallest value of k in the logarithmic grid (1024 points and logarithmic partition of 0.02) applied in the solution of the integral equation ($k_{\min} = 3.57 \times 10^{-5}$). The limiting value in this point is calculated from:

$$\begin{aligned} \tilde{h}_{\alpha_i \gamma_j}(k_{\min}) &= \tilde{c}_{s_{\alpha_i \gamma_j}}(k_{\min}) + \tilde{Q}_{i\gamma_j}(k_{\min}) \\ &+ \tilde{\tau}_{s_{\alpha_i \gamma_j}}(k_{\min}) \end{aligned} \quad (8)$$

where τ and Q are the indirect contributions to the correlation functions in the renormalized version and c_s are the short-range direct correlation function. For details see ref. 9 and 10. The use of this value instead of the true limiting value as k goes to zero will limit the accuracy of the calculations. For the purpose of illustration these are considered 0 as appropriate since they were already available. A rough indication of uncertainties in the dielectric constants based on these correlation functions is obtained from comparisons with corresponding values calculated from $k_{\min} = 3.64 \times 10^{-5}$ and $k_{\min} = 3.72 \times 10^{-5}$ which are the two next values in the logarithmic grid values for k . Results using these values in eqn. (8) are also plotted in Fig. 13.

VI. Conclusions

I have examined an extended dielectrically adjusted RISM equation for model systems of water and methanol using molecular dynamics simulations for comparison of calculated structures and thermodynamic properties. The structure calculated from the integral equation is generally in good agreement with the corresponding molecular dynamics results. The agreement in calculated energies between integral equation theory and

molecular dynamics simulations is also generally good over the entire concentration range for the specific models applied. For the specific models applied here there are, however, some differences in the locations of the first peaks of different hydrogen-oxygen correlation functions. For the first time this type of integral equation theory is also applied to the direct calculation of free energy. For the specific water model the free energy is lower than the experimental value for pure water. Under-predictions of the structure and corresponding higher entropy for the specific water model might be one of the reasons for these results. The exact expression for the dielectric constant in a uniform liquid mixture is reformulated into a corresponding interaction site formulation. Dielectric constants for the water/methanol model mixtures are calculated using the available site-site correlation functions.

Nomenclature

n	= average coordination number
ε	= dielectric constant for a liquid mixture
\hat{s}_i	= unit vector in the direction of the dipole moment
\hat{k}	= unit vector in Fourier-transformed space
α	= average dipole distribution, see eqn. (3)
β	= inverse of Boltzmann's constant \times temperature
ρ	= molecular density
h_{ij}	= molecular correlation function in Fourier-transformed space
d	= distance from charge neutrality centre to a specific site as denoted by subscript
σ	= Lennard-Jones diameter
ε	= Lennard-Jones well depth
q	= partial charge
x	= mole fraction
y	= dipole density

Subscripts

α	= site index
i	= molecule index
γ	= site index
j	= molecule index

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