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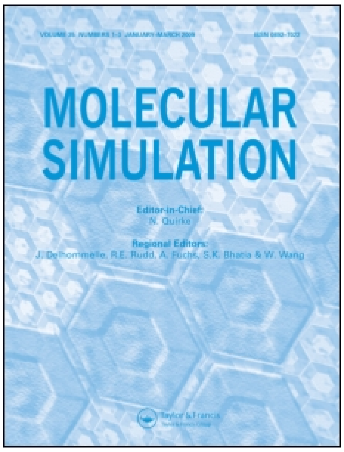

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Structure of Mixed Solvent Electrolyte Solutions via Gibbs Ensemble Monte Carlo Simulation

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STRUCTURE OF MIXED SOLVENT ELECTROLYTE SOLUTIONS VIA GIBBS ENSEMBLE MONTE CARLO SIMULATION

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Previously reported Gibbs ensemble Monte Carlo simulations of vapor-liquid equilibrium in methanol-water and methanol-water-NaCl mixtures are extended to permit study of the microscopic structure of the liquid phases of these systems. The *salt effect* in a prototypical mixed solvent electrolyte solution (water-methanol-NaCl) is microscopically interpreted in terms of the structural changes undergone by the solvation shells of the ions in the liquid phase of water-methanol-NaCl systems in vapor-liquid equilibrium at constant pressure.

KEY WORDS: Salt effect, mixed solvents, electrolyte solutions, solvation shells

1 INTRODUCTION

The relative volatility of solvents in a system composed of two or more miscible species can be substantially modified by the addition of a nonvolatile electrolyte (i.e., a salt). One application of this phenomenon, known as the *salt effect* [1], is to salt-effect extractive distillation in which a dissolved salt, rather than a liquid, is used as the mass separating agent to perform separation of azeotropic or close-boiling systems.

For mixtures of water, alcohol and inorganic salt, the salt effect typically results in the relative volatility of the alcohol being increased due to the presence of the salt - i.e., the alcohol is salted out. The salting out of alcohol in alcohol-water-inorganic salt mixed solvent electolyte solutions has been traditionally explained by assuming that the ions are preferentially solvated by water molecules [2]. These ion-water solvates, due to their high molecular weight, are expected to show lower fugacity in the liquid than water in the corresponding salt-free mixture, and consequently the relative volatility of the non-aqueous solvent is increased. Even though very small salt concentrations might be enough to break azeotropes [3], making the salt effect an attractive alternative to the traditional liquid separating agent in azeotropic distillations [4], a successful separation will depend on the judicious selection of the salt. In order to guide that selection and to be able to predict the thermodynamic properties of the resulting mixed solvent electrolyte solution we must have a better understanding of the complex mechanism underlying the salt

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effect at a microscopic level. This requires the molecular based study of vapor-liquid phase equilibrium and microstructure of model mixtures which explicitly includes solvent(cosolvent)-ions interactions.

We have recently studied the vapor-liquid phase equilibrium of water-methanol and water-methanol-NaCl mixtures at ambient pressure via Gibbs ensemble Monte Carlo simulation (GEMC) [5–7]. Using intermolecular pair potentials taken directly from literature, or inferred without adjustable parameters, we found quantitatively accurate predictions for the vapor-liquid equilibrium (VLE) of water-methanol mixtures and qualitatively accurate predictions for the VLE of water-methanol-NaCl mixtures. In particular, our simulations predicted the salting out of the methanol in water-methanol-NaCl systems, though the salt effect was overestimated [8].

One important piece of information missing from our previously reported GEMC simulations studies [5–7] is the fluid phase microstructure. The analysis of the microstructure of mixed solvent electrolyte systems is essential to shed additional light onto the microscopic mechanism of the salt effect. In this paper we focus on the microstructure of the liquid phase of water-methanol and water-methanol-NaCl mixtures in vapor-liquid phase equilibrium to test the traditional microscopic interpretation of the salt effect.

2 MICROSTRUCTURE

The GEMC simulations which form the basis of this work have been previously reported [5–7], with the most detailed description given in Reference 5. The simulation methodology and the intermolecular potentials used are briefly summarized in the Appendix. The microstructure of the mixed solvent and mixed solvent-salt mixtures is described in this paper by the site-site radial distribution functions (RDFs) $g_{ij}(r)$ where i, j are species indices and $g_{ij}(r)$ is proportional to the probability density that the center of a species j molecule is located at distance r away from the center of a species i molecule. For the water-methanol mixtures, we study the water-water (W-W), the water-methanol (W-Me), and the methanol-methanol (Me-Me) RDFs. In addition to these, for the mixed-solvent-salt systems we have the sodium ion-water (Na-W), the chloride ion-water (Cl-W), the sodium ion-methanol (Na-Me), the chloride ion-methanol (Cl-Me), RDFs. A related quantity $N_{ij}(r)$ is the number of molecules of species j surrounding a species i molecules at distance r in excess of what would be present if the local density of species j molecules were uniform. Thus, $N_{ij}(r)$ is defined by

$$N_{ij}(r) = 4\pi x_j \rho \int_0^r [g_{ij}(r') - 1] r'^2 dr' \tag{1}$$

where x_j is the mole fraction of species j and ρ is the total number density of the mixture.

In the following sections, we analyze the microstructures for the liquid phase of water-methanol and water-methanol-NaCl systems obtained by GEMC at the state conditions and compositions of vapor-liquid equilibrium given in Tables 1 and 2 [5], and finally we give a microscopic interpretation of the salting out of methanol in the water-methanol-NaCl systems.

Table 1 Vapor-liquid equilibrium results for water-methanol VLE at P = 1 atm obtained by GEMC [5].

T (K)	X_{water}	Y_{water}	ρ_l(g/cc)	ρ_v(g/cc)
344	0.442	0.196	0.701	0.00111
360	0.856	0.522	0.835	0.00084

Table 2 Vapor-liquid equilibrium results for water-methanol-NaCl VLE at P = 1 atm obtained by GEMC [5].

T (K)	X_{water}	X_{salt}	Y_{water}	ρ_l(g/cc)	ρ_v(g/cc)
344	0.433	0.0156	0.148	0.694	0.00111
360	0.839	0.0148	0.434	0.820	0.00093

Water-methanol system

In Figure 1, we display the water-water, water-methanol and methanol-methanol RDFs at T = 360 K and 344 K. These equilibrium conditions correspond to liquid densities $\rho\sigma^3 = 0.886$ and 0.743 (where $\sigma = 3.166$ Å is the diameter of the water molecule in the model used), as well as to water mole fractions $x_{\rm water} = 0.856$ and 0.442 respectively. Since we are considering mixtures at different densities and at very different compositions, we have replotted Figure 1 as the excess number of particles of a species with respect to that of its uniform distribution at the prevailing bulk density in Figure 2.

Despite the higher liquid phase density and water mole fraction at T = 360 K, the first peak of the water-water RDF is almost half that corresponding to T = 344 K (Figure 1). This translates into an excess number of water molecules around a water molecule showing opposite trends with temperature (top graph of Figure 2). The excess number of water molecules around a methanol molecule (middle graph of Figure 2) suggests that the depletion of waters around water at higher temperature is a consequence of a stronger methanol solvation by water. Consequently, the methanol solvation by methanol in presence of water decreases at higher temperature as indicated by the bottom graph of Figure 2.

Water-methanol-NaCl system.

In Figures 3-5, we present the RDFs of these mixtures in vapor-liquid phase equilibrium at two temperatures, T = 360 K and 344 K, corresponding to the liquid phase densities $\rho\sigma^3 = 0.870$ and 0.736, and to the liquid phase water mole fractions $x_{\rm water} = 0.839$ and 0.433, respectively.

The outstanding feature in these results is the difference in the ion-solvation structure for each solvent species. From Figure 6 it is clear that methanol does not solvate either the Na^+ or the Cl^- since the local density of methanol around these ions is depleted, this effect being more pronounced at the higher temperature. However, note that at the lower temperature the local density of methanol around methanol is also depleted to a larger extent than around an ion. This suggests that the methanol shows more affinity toward the ions than toward other methanol

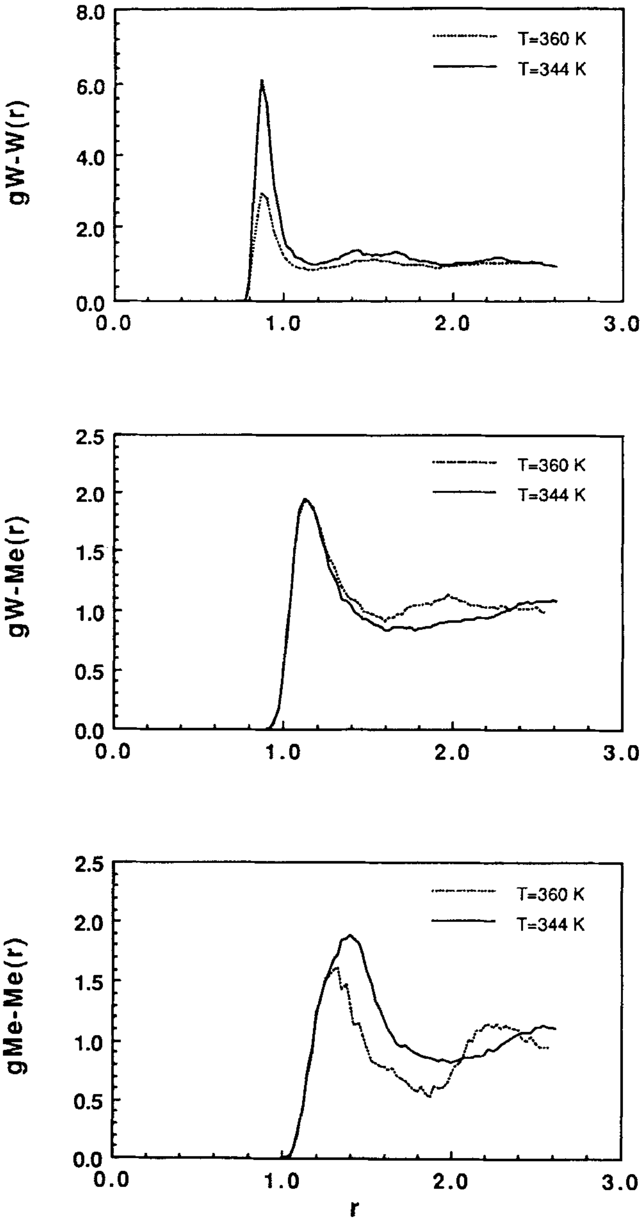


Figure 1 Water-water (top), water-methanol (middle) and methanol-methanol (bottom) radial distribution functions for the liquid phase of water-methanol mixtures in vapor-liquid equilibrium at P = 1 atm.

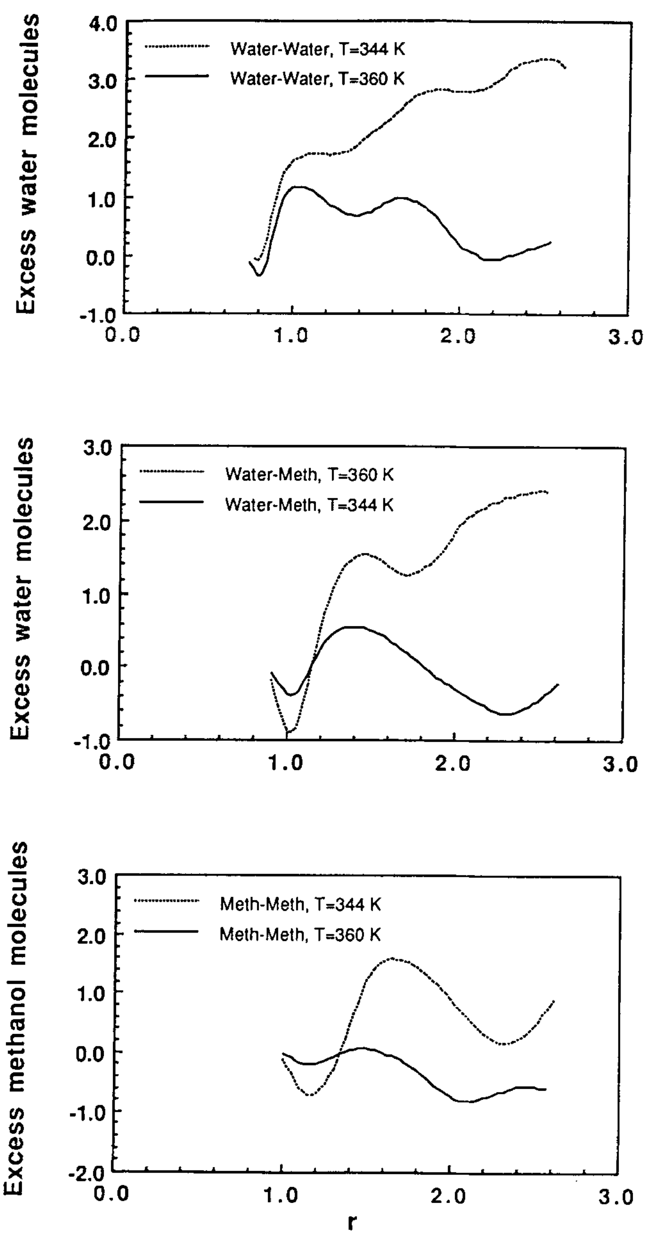


Figure 2 Excess numbers of water molecules surrounding a water molecule (top), water molecules surrounding a methanol molecule (middle) and methanol molecules surrounding a methanol molecule (bottom) in their respective solvation shells in the liquid phase of water-methanol mixtures in vapor-liquid equilibrium at P = 1 atm.

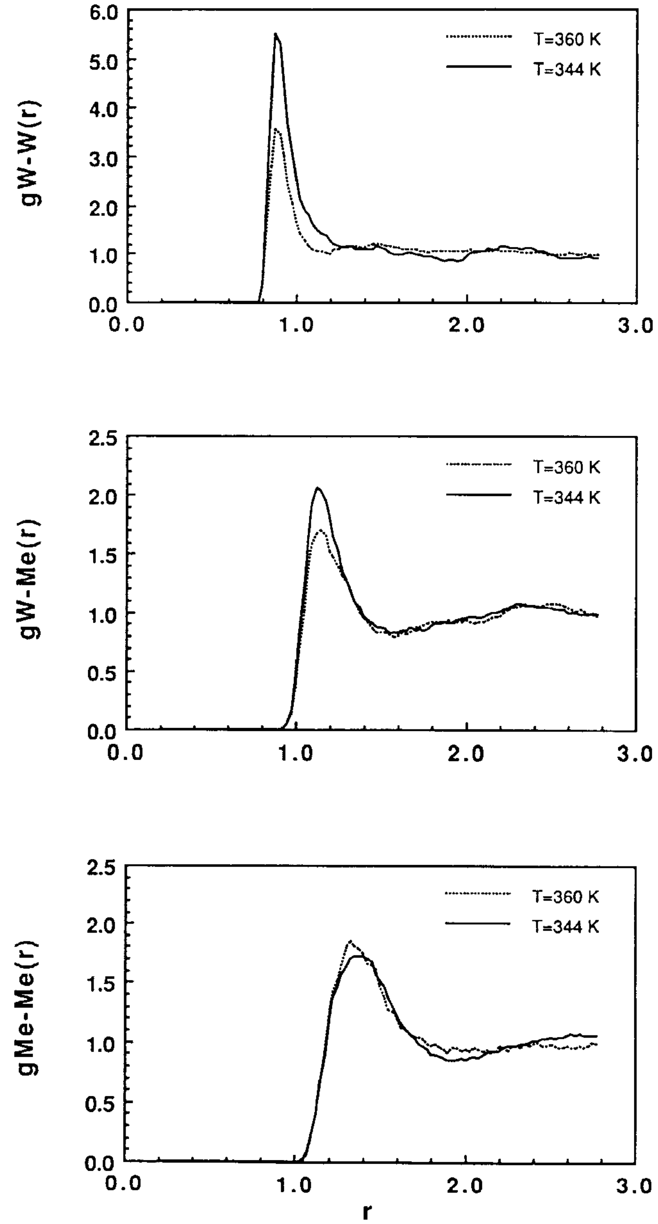


Figure 3 Water-water (top), water-methanol (middle) and methanol-methanol (bottom) radial distribution functions for the liquid phase of water-methanol-NaCl mixtures in vapor-liquid equilibrium at P = 1 atm.

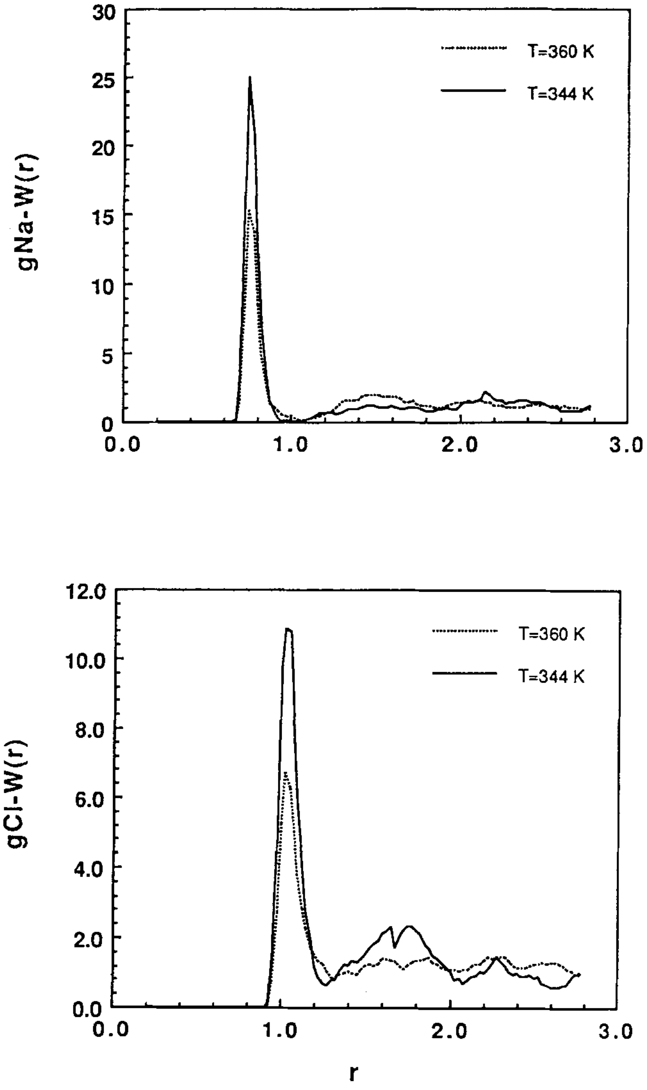


Figure 4 Sodium ion-water (top) and chloride ion-water (bottom) radial distribution functions for the liquid phase of water-methanol-NaCl mixtures in vapor-liquid equilibrium at P = 1 atm.

molecules which is clearly a result of the strong electrostatic interactions between the ions and the methanol molecules. Note also that the affinity of methanol toward water is stronger than toward methanol at the lower temperature (top graph in Figure 7) and weaker at the higher temperature (bottom graph in Figure 7).

Figures 8 indicates strong ion solvation by water, with a greater effect at higher temperature. However, the ions behave differently according to their charge and the system's temperature. Water solvates Na^+ stronger than Cl^- at the high temperature (bottom graph in Figure 8), while the opposite is true at the lower

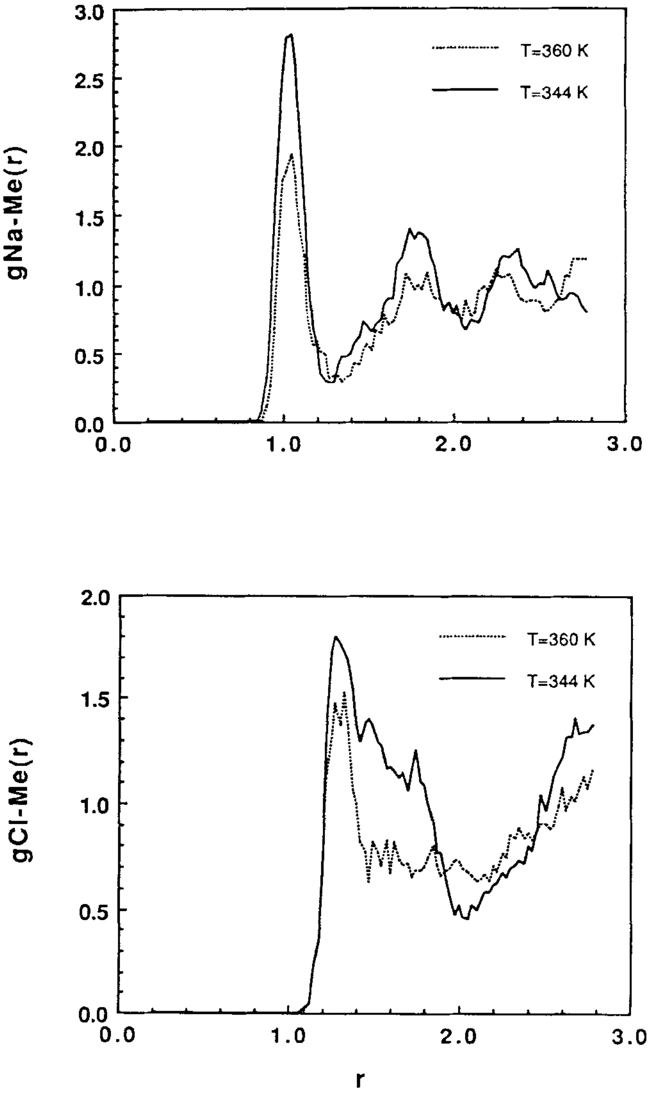


Figure 5 Sodium ion-methanol (top) and chloride ion-methanol (bottom) radial distribution functions for the liquid phase of water-methanol-NaCl mixtures in vapor-liquid equilibrium at P = 1 atm.

temperature (top graph in Figure 8). Even though Na^+ and Cl^- are solvated by as many as four water molecules within the first shell at T = 344 K, Na^+ shows a depletion at the second solvation shell, and this effect is more pronounced at lower temperature. These results are in qualitative agreement with recent NVT-MC simulations of Cl^- in an equimolar methanol-water system at room temperature [13].

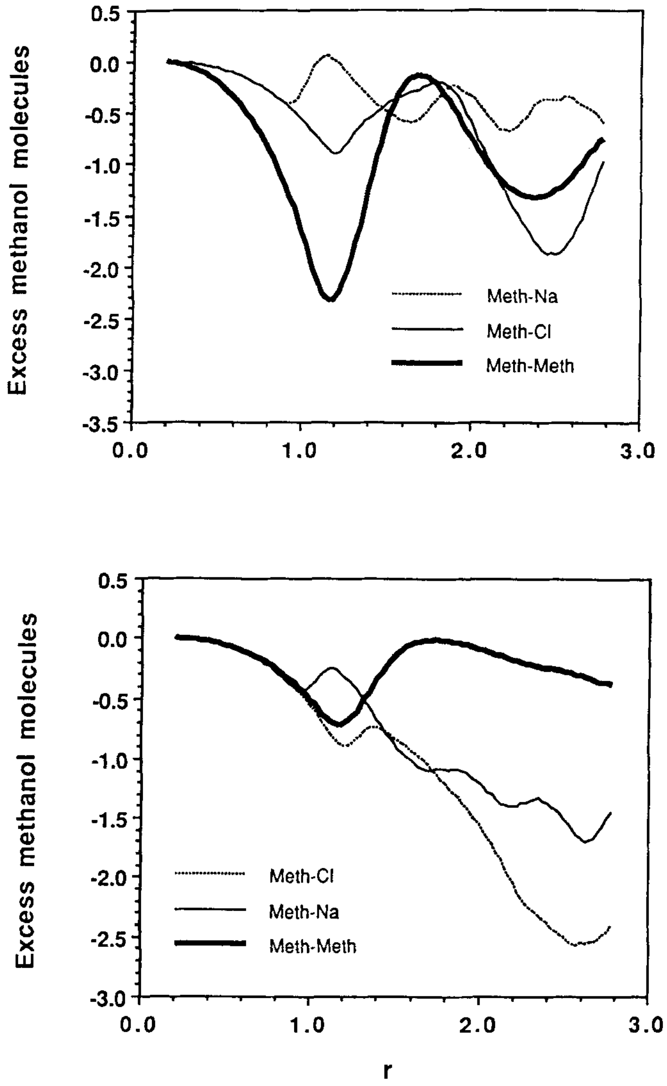


Figure 6 Excess number of methanol molecules in the solvation shells of methanol, Na^+ and Cl^- molecules in water-methanol-NaCl mixtures in vapor-liquid equilibrium at P = 1 atm and T = 344 K (top) and T = 360 K (bottom).

3 SUMMARY

This is the first molecular simulation study of the microstructure of mixed solvent electrolyte solutions in vapor-liquid phase equilibrium at constant pressure. The microstructure of these water-methanol-NaCl mixtures indicates that the observed salting out of methanol in the liquid phase (the enrichment of methanol composition

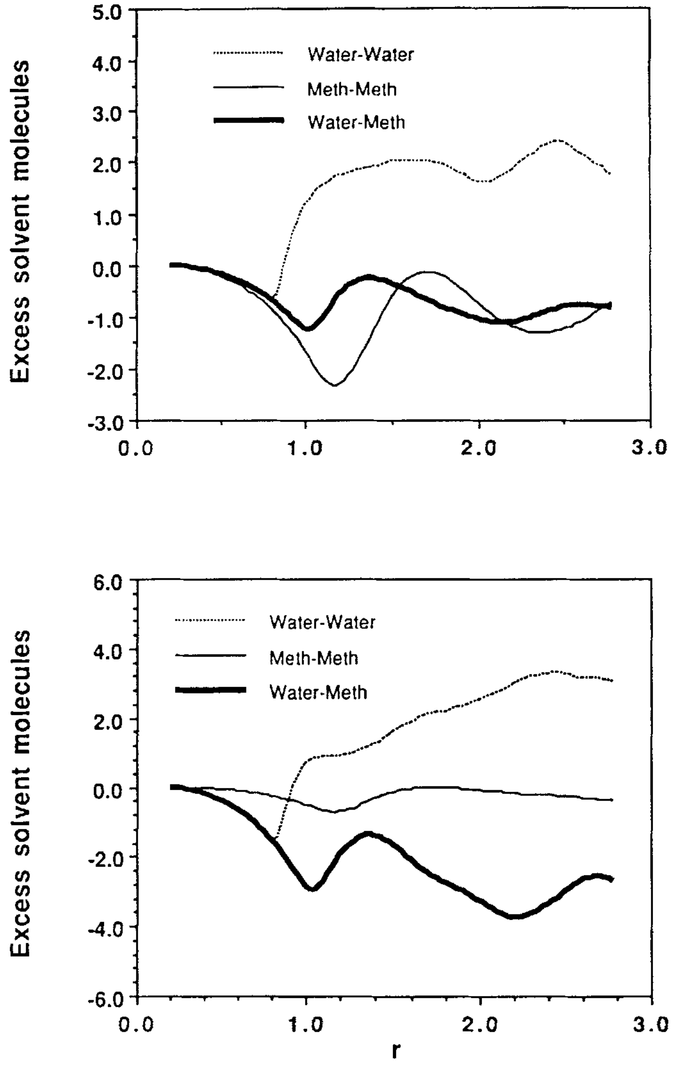
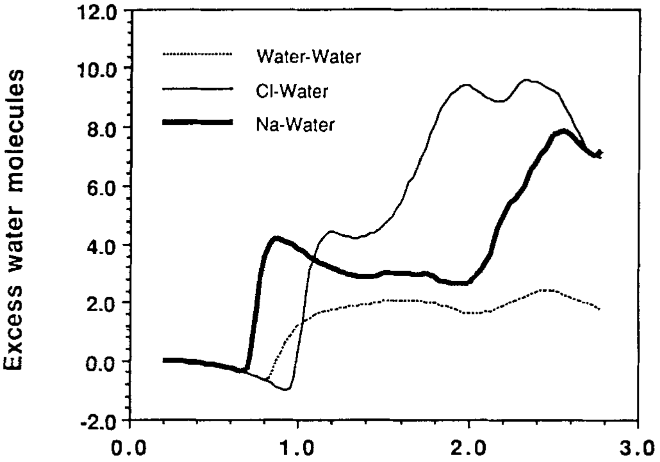


Figure 7 Excess number of water or methanol molecules in the solvation shells of water and methanol molecules in water-methanol-NaCl mixtures in vapor-liquid equilibrium at P = 1 atm and T = 344 K (top) and T = 360 K (bottom).



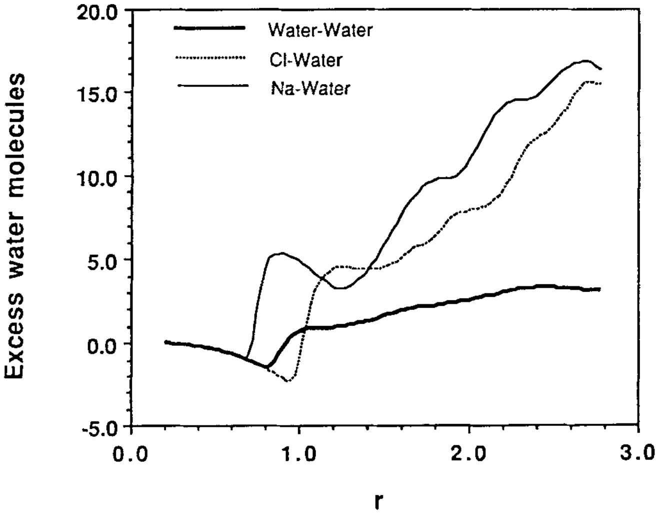


Figure 8 Excess number of water molecules in the solvation shells of water, Na^+ and Cl^- molecules in water-methanol-NaCl mixtures in vapor-liquid equilibrium at P = 1 atm and T = 344 K (top) and T = 360 K (bottom).

in the vapor phase) is the result of the strong solvation of the ions Na^+ and Cl^- by the water molecules and the relatively weak solvation of the ions by the methanol molecules. This confirms quantitatively that the traditional qualitative picture of the microscopic basis for salting out of the alcohol is correct.

APPENDIX

We have performed Gibbs ensemble Monte Carlo (GEMC) simulations of water-methanol and water-methanol-NaCl mixtures. In both cases, the water-water and the methanol-methanol interactions were described by Berendsen's simple point charge (SPC) potential [9] and by Haughney's H1 potential, [10] respectively. The Na-Na, Cl-Cl, and Na-Cl interactions were given by the Fumi-Tosi-Huggins-Mayer potential, [11] while the ion-water interactions by those developed by Chandresakhar *et al.* [12] Water-methanol interactions were obtained from the corresponding site-site pair interactions using Lorentz-Berthelot combining rules. The Ewald summation method was used for both liquid and vapor phases to take into account the long-ranged nature of the electrostatic interactions. Most simulation details were already given in the earlier, detailed report of this work [5] and will not be repeated here. The radial distribution functions were determined at the end of the normal GEMC simulation by running an additional 10^6 steps allowing only translational and angular displacements to sample the RDF each 10^3 steps. Because we are interested in the salt effect while the vapor phase is salt-free and can be considered as an imperfect gas, we analyze only the microstructure of the liquid phase.

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