

## PHYSICAL CHEMISTRY OF SOLUTIONS

# Mechanism of Solvation in Methanol: Computational Simulation Results

Yu. G. Bushuev and T. A. Dubinkina

Ivanovo State Academy of Chemistry and Technology, Ivanovo, Russia

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**Abstract**—Monte Carlo simulation of infinitely diluted solutions of xenon and  $\text{Cs}^+$  and  $\text{I}^-$  ions in methanol was carried out. Thermodynamical and structural parameters of solvation were determined. It was shown that the relative position and orientation of methanol molecules in the primary solvate shells of the species are strongly influenced by species accommodation within the solvent structure and by the packing of methyl groups of methanol molecules.

### INTRODUCTION

One of the problems of thermodynamics of electrolyte solutions is a dividing of the thermodynamic parameters of solvation of stoichiometric mixtures of ions into ionic constituents. At present, several methods of such a division are used, each differing in their degree of physical adequacy [1, 2]. Lange and Mishchenko suggested that changes in the enthalpy of hydration of  $\text{Cs}^+$  and  $\text{I}^-$  ions are similar [3]. In the case of nonaqueous solvents, an additional assumption was made: the relation between a change in the enthalpy of solvation of a cation and that of an anion is constant for all solvents [4]. Krestov and Zverev suggested a method based on calculating an electrostatic interaction of ions with centers of dipole charges of solvent molecules and charge distribution under the assumption of constancy of coordination numbers [5]. However, there is no sufficient information on intermolecular interactions in various solvents, salt solutions, and small clusters of ions and solvent molecules. The structure of solvate shells may be complex, so that thermodynamic data alone fail to provide for a correct method of dividing an overall value into separate ionic contributions.

Numerical simulation allows a simultaneous determination of the relative position and energy of interaction of molecules in a liquid. But, in this case as well, one has to assume considerable simplifications in describing molecule structures and interparticle interactions. Estimates are made only for systems composed of several hundreds of species. A model inadequacy and assessment of parameters over a small volume of a configuration space of the system may lead to substantial errors in the values to be determined. Nevertheless, the model permits an estimation not only of individual thermodynamic parameters of ions, but also of the contribution of particular types of interactions.

In our work [6], it was shown that mutual compactness of methyl groups is the main factor in the relative

position of molecules in liquid methanol. In methanol and methane at the same density and temperature, the structural parameters of the bond network constructed of the lines connecting the neighboring carbon atoms were similar. Evidently, the spatial order in the molecule arrangement of most organic solvents is also accounted for by molecule packing. In [7, 8], a similar conclusion was drawn for dimethylformamide, neopentane, and isopentane on the basis of an estimation of radical distribution functions (RDF). If the structure of liquids is influenced by universal interactions (molecule shapes), not specific ones, one should expect the solvation parameters in solutions to be dependent on the way of species accommodation within the solvent structure.

In this work, three infinitely diluted solutions of species in methanol are considered. A xenon atom was chosen as a solvated particle because the parameters of its interaction are similar to those of methyl groups of methanol and, consequently, the packing factors manifest themselves most clearly. To compare the effects, the solvation of one-charge ions with the parameters of interaction  $\sigma$  and  $\epsilon$  similar to those of a xenon atom was studied.

### NUMERICAL EXPERIMENT

Monte Carlo simulations were carried out with an NVT-ensemble at 298 K. The species to be solvated and 124 methanol molecules were placed in an elementary cell. Periodic boundary conditions and a spherical cut-off of the potential domain were employed. Intermolecular interactions in methanol were described by a three-center two-body potential with the following parameters:  $\epsilon_{\text{LJ}}(\text{OO}) = 0.7307$ ,  $\epsilon_{\text{LJ}}(\text{CC}) = 0.9151$ ,  $\epsilon_{\text{LJ}}(\text{OC}) = 0.8177$  kJ/mol,  $\sigma(\text{OO}) = 308.3$ ,  $\sigma(\text{CC}) = 386.1$ , and  $\sigma(\text{OC}) = 347.2$  pm. Charges were located on the carbon (0.297 e), the oxygen (−0.728 e), and the hydroxyl hydrogen (0.431 e). The HOC intramolecular angle

was 108.53°, and the OH and OC bond lengths were 94.51 and 143 pm, respectively [9].

Solvation effects were studied for three species. The parameters of interaction of a xenon atom with a methanol molecule were calculated according to combination rules and were as follows:  $\epsilon_{LJ}(\text{XeO}) = 1.179$ ,  $\epsilon_{LJ}(\text{XeC}) = 1.274$  kJ/mol,  $\sigma(\text{XeO}) = 366.85$ , and  $\sigma(\text{XeC}) = 405.75$  pm. The model of ionic solvation included an additional electrostatic contribution to the energy of interaction. At the initial stage, the "hot start" method was employed. The total length of the Markov chain reached 10 to 15 million configurations; the share of the accepted ones was about 50%.

## RESULTS AND DISCUSSION

Let us follow the changes in the modeled system, which occur when a methanol molecule is replaced by a noncharged species or an ion; the latter correspond to a xenon atom by their van der Waals parameters. Figure 1 shows the RDFs for the solution  $g_{\text{XeC}}$  and pure methanol  $g_{\text{CC}}$ . The functions differ but little, they reach the extreme at similar values of interatomic distances. However, the relative position of carbon atoms in the primary solvate shells (PSSs) of the species in all the solutions described by the functions  $g_{\text{CC}}$  varies insignificantly. Therefore, one may suggest that the solvation does not cause any significant changes in the methanol structure; the effect of a xenon atom is virtually equivalent to that of a methyl group of a methanol molecule.

The atom-atom RDFs  $g_{\text{AC}}$ ,  $g_{\text{AO}}$ , and  $g_{\text{AH}}$  describe the orientation of methanol molecules that are closest

to a solvated species (Fig. 2). For a xenon-methanol solution, they have the first maxima of about the same height at 420 pm and minima at 595 pm. If the latter is a PSS boundary, the number of methanol molecules in the xenon atom surroundings will be close to 12. The equidistance of atoms from a species suggests a tangent arrangement of the molecules; i.e., the plane of each molecule is almost perpendicular to a radius-vector drawn from a species.

In contrast to the previous case, the specificity of the solvation of a positive ion is a shift of the first peak of the  $g_{\text{AO}}$  function to the region of shorter interatomic distances and a slight change in the  $g_{\text{AC}}$  and  $g_{\text{AH}}$  functions. Hence, a reorientation of the molecules closest to a cation occurs. The second maximum of the  $g_{\text{AC}}$  function shifts to the region of shorter distances because the probability of mutual contact of methyl groups of molecules of the primary and secondary solvate shells of a cation increases.

More drastic changes occur during the anion solvation. In this case, transformations of  $g_{\text{AO}}$  are accompanied by those of  $g_{\text{AH}}$ . A pronounced maximum of  $g_{\text{AH}}$  at 245 pm points to the formation of H-bonds. An important feature of all three types of solvation is the practically same position of the  $g_{\text{AC}}$  peaks, which is evidence of the decisive role played by packing in the PSSs of a species. This conclusion may be drawn on the basis of the integral properties of  $N_{\text{AC}}(R)$  that show how many carbon atoms are contained in the sphere of radius  $R$ . For anion solvation, a narrowing of the first peak of  $g_{\text{AC}}$  with a simultaneous increase in its height does not lead to any significant changes in the function  $N_{\text{AC}}(R)$ .

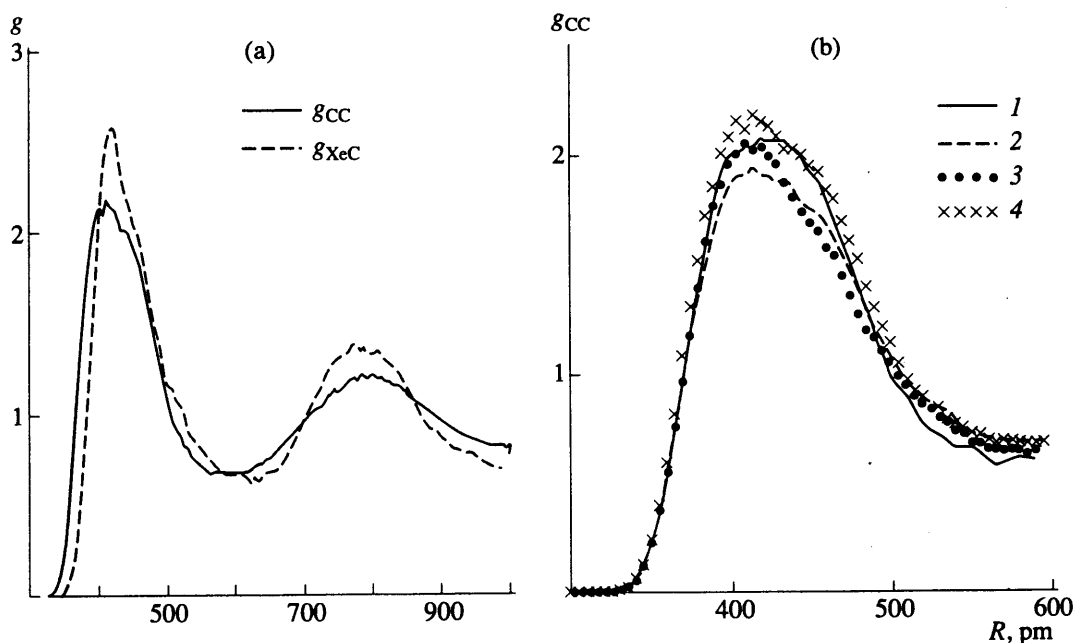


Fig. 1. (a) Radial distribution functions,  $g_{\text{CC}}(R)$  and  $g_{\text{XeC}}(R)$ , for pure methanol and a xenon solution in methanol. (b) The first maximum of the function  $g_{\text{CC}}(R)$ : (1-3) for the PSS of Xe,  $\Gamma$ ,  $\text{Cs}^+$  particles, (4) for pure methanol.

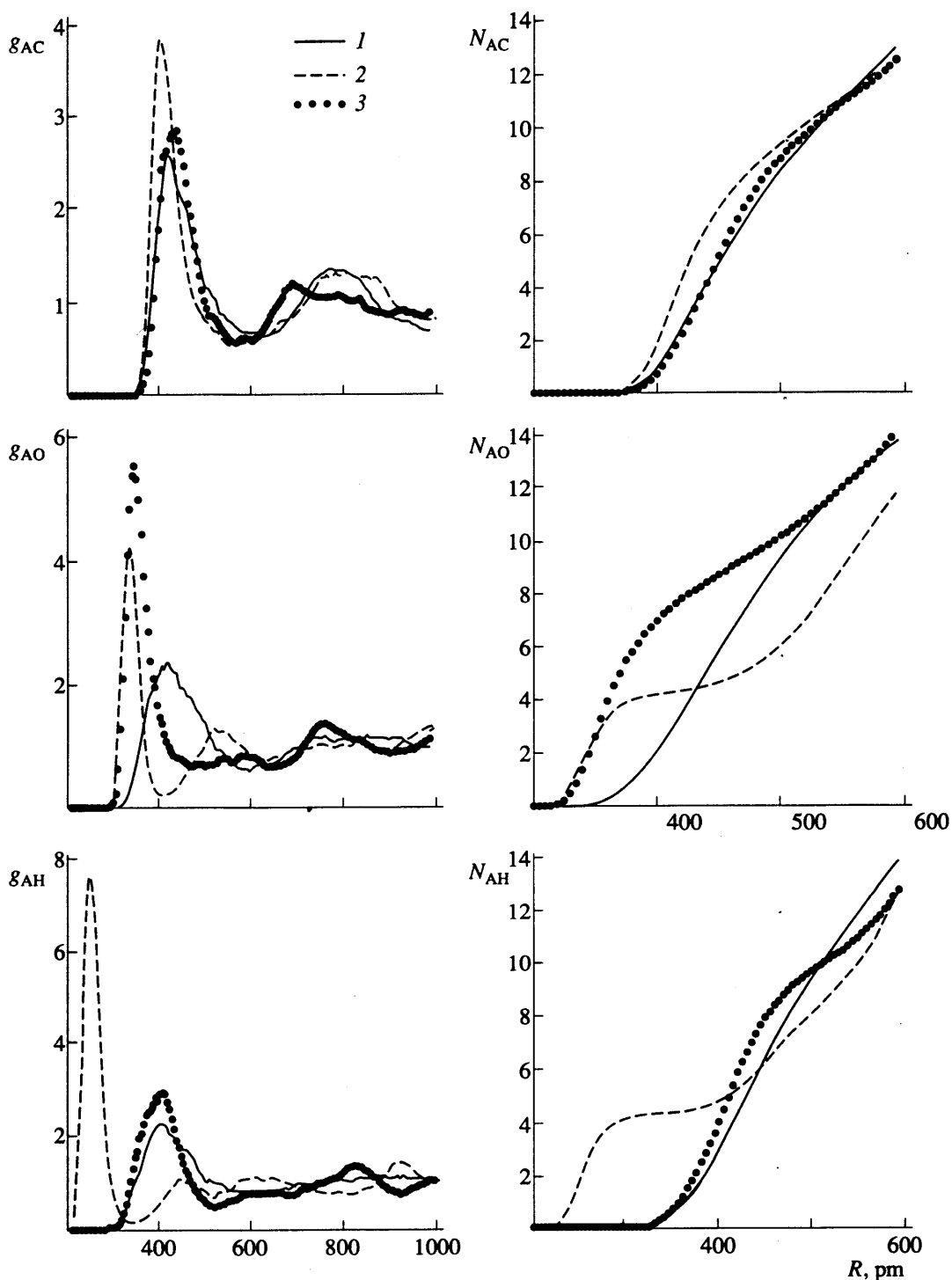


Fig. 2. Radial distribution functions describing the relative spatial position of atoms of methanol molecules with respect to a solvated species and the corresponding dependences of coordination numbers  $N(R)$  for the solutions: (1) Xe, (2)  $\Gamma^-$ , and (3)  $\text{Cs}^+$ .

The curves illustrating these various cases converge at 550 pm. On the average, the sphere of this radius contains 11 carbon atoms. For a crystalline structure, a coordination number 12 denotes a tight packing; for a liquid, a close value indicates a random high-density structure. The closest contact of methyl groups of

methanol molecules in the PSSs is observed for the anion solvation.

There are far more differences in the behavior of the functions  $N_{\text{AO}}(R)$  and  $N_{\text{AH}}(R)$ . During the cation solvation, about ten methanol molecules change their orientation to some degree. They turn to a solvated species

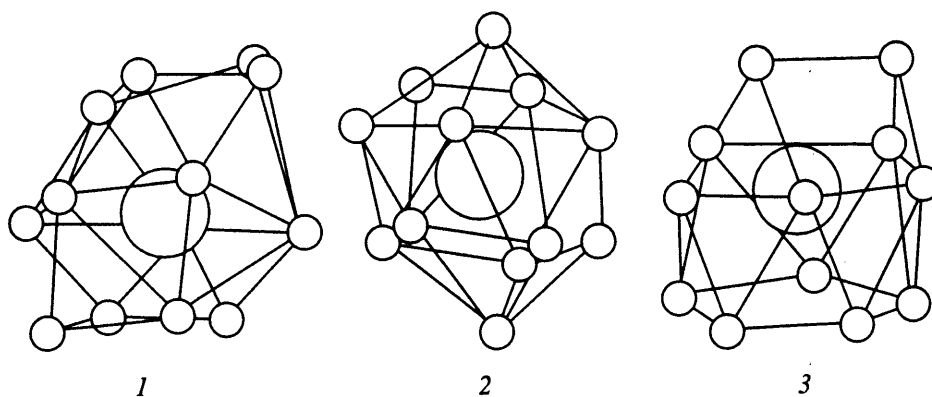


Fig. 3. The position of methyl groups of methanol molecules in the PSSs of species for the solutions: (1) Xe, (2)  $I^-$ , and (3)  $Cs^+$ .

with their negative oxygen atom. As is seen from the graph of dependences, an average of four methanol molecules form a H-bond with an ion in the presence of an anion. A visual analysis of instantaneous configurations showed that three H-bonds are approximately in one plane, the fourth bond is perpendicular to it. The asymmetry in the position of the H-bonds seems to be dependent on the packing of methyl groups. Figure 3 shows instantaneous configurations for the PSSs of solvated particles. As in the case of closely packed systems of balls, triangular cycles in the network constructed of lines connecting the closest carbon atoms were observed. The figures represented consist of pre-

cisely the same fragments as the Archimedean anti-prism and a tetragonal dodecahedron, i.e., characteristic elements of a spatial structure of random closely packed systems.

Important information on particle solvation may be obtained from studying various energy distributions. Figure 4 shows the graphs of dependences of a full energy of interaction of methanol molecules on a particle-oxygen distance. This value is defined as an average for an ensemble of total interactions of methanol molecules with the environment and consists of contributions of the species-methanol interaction  $E_{AM}$  and methanol-methanol one  $E_{MM}$ . Each case of solvation is

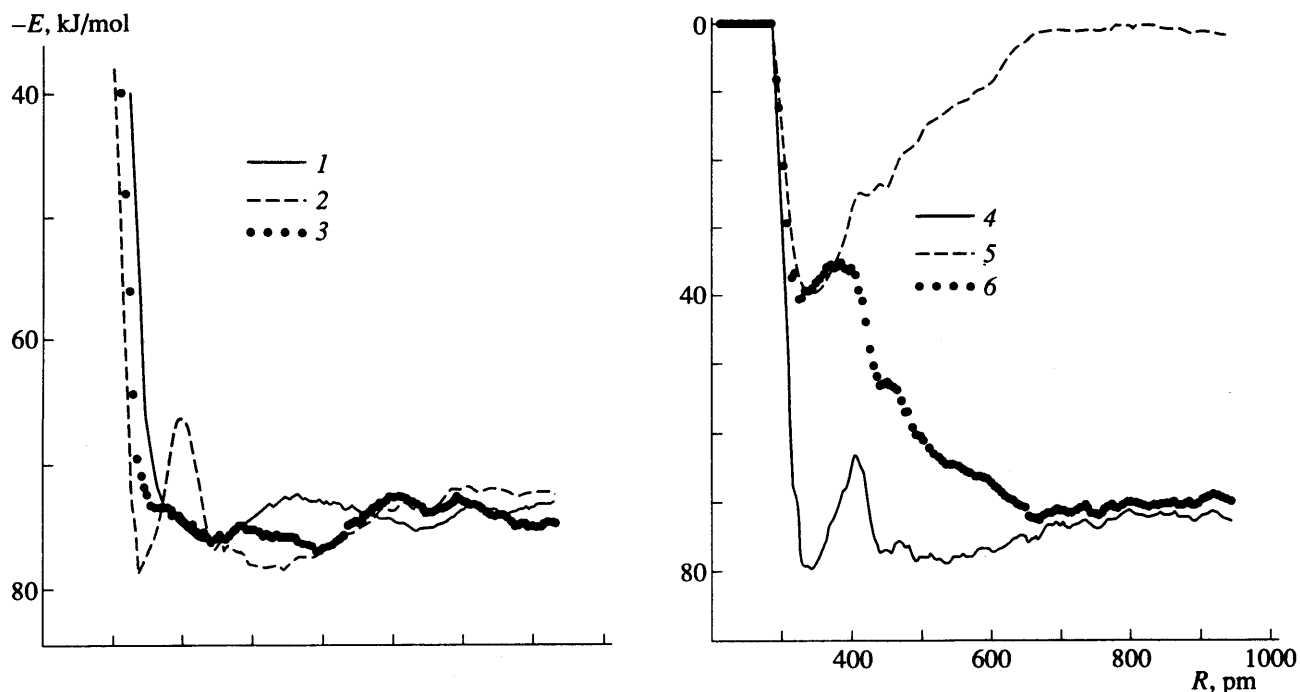


Fig. 4. Dependences of full potential energy of interactions of methanol molecules on the species-oxygen distance for various solutions: (1) Xe, (2, 4)  $I^-$ , and (3)  $Cs^+$ . Dependences of the (5) anion-methanol and (6) methanol-methanol interactions in the  $I^-$  solution.

peculiar. When xenon is solvated, the curve shows two shallow minima at 450 and 730 pm. This means that there are more stable energy states of molecules relative to a xenon atom.

During the cation solvation, a rapid drop in the function, caused by steric factors, changes into a smooth noncharacteristic one. A minimum is located in the vicinity of 600 pm, i.e., outside the PSS. A more complicated behavior is observed for an anion. In this case, the two minima at 340 and 520 pm are divided by a high energy barrier. The contributions of  $E_{AM}$  and  $E_{MM}$  to the first minimum are practically identical. The estimates show that each methanol molecule forms, on average, one H-bond both with an anion and with a neighboring methanol molecule. The 400 pm maximum is accounted for by an increase in the two constituents of the sum. As the distance between a molecule and an ion increases, intermolecular interactions that compensate for a decrease in the interaction with an anion become stronger. Evidently, the exchange of molecules between the two layers divided by the energy barrier is impeded. If the PSS is regarded as a structural unit, its energy state, which is more stable than that of a bulk solvent, should account for a positive anion solvation. Cation seems to solvate negatively.

Compare the estimated enthalpies of solvation of particles with the literature data. For a xenon solution, the value obtained was  $-8.7$  kJ/mol, which is in good agreement with the calorimetric one ( $-9.35$  kJ/mol [10]). For ions, direct comparison with experimental data is impossible because of the ambiguity of dividing a combined value into ionic constituents. However, one may compare the enthalpies of the solvation of a stoichiometric mixture because a cation with its interaction parameters of the cation and anion are close, respectively, to those of the  $Cs^+$  and  $I^-$  ions. The computational estimates yielded the values  $-278$  and  $-219$  kJ/mol for the cation and anion, respectively. According to the literature, the total value is  $-577$  kJ/mol [5]. The discrepancy between the experimental data and theory does not exceed 15%, which is a good result despite the

primitive method of obtaining the parameters of intermolecular interactions. A correlation between thermodynamic properties of the computational models and real systems ensures an adequate reproduction of the molecular structure of solutions.

Thus, to investigate and describe solvation at a molecular level, one should consider the effects of species accommodation within the solvent structure. For methanol solutions, where the species sizes are close to those of a xenon atom, the packing of methyl groups of methanol molecules is a key factor for the structural and energetic properties of solvation.

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