

The study of hydrophobic hydration in supercritical water–methanol mixtures

M. Kiselev,* S. Noskov,^{1*} Y. Puhovski,* T. Kerdcharoen,[†] and S. Hannongbua[‡]

*Institute of Solution Chemistry RAS, Ivanovo 153045, Russia

[†]Department of Physics, Faculty of Science, Mahidol University, Bangkok, Thailand

[‡]Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, Thailand

We investigated hydrophobic hydration and heat capacity (C_V) of diluted aqueous solutions of methanol at supercritical region using molecular dynamics method. We performed simulations for several concentrations of methanol and densities of mixtures. Similar to that observed for ambient conditions, the 600 K solution containing 0.12 mole fraction of methanol at the density of 0.98 gm.cm^{-3} yields the highest C_V . The intermolecular structure between water and methanol molecules at this concentration was also found to be enhanced. Hydrophobic hydration, relative to ambient conditions, is diminished slightly at the concentration of C_V maximum and diminishes drastically for the other concentrations. © 2001 by Elsevier Science Inc.

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INTRODUCTION

Water–methanol solutions are good examples of the simultaneous occurrence of hydrophobic and hydrophilic hydrations.^{1–3} A characteristic of hydrophobic hydration is that water reorganizes around nonpolar groups of methanol to form polyhedral cages or clathrates.^{3–5} On the other hand, methanol forms H-bonds with surrounded water molecules.⁴ The physical properties of aqueous mixtures of such multifunctional molecules are only partly understood. In the literature there is a long-standing controversy regarding the effect of methanol on the three-dimensional hydrogen bonded network of water, because there is a delicate balance between “structure-making” and “structure-breaking” effects, i.e., both hydrophilic and hydrophobic effects play equally important roles in the mix-

ture.^{1,3–5} The origin of exothermic mixing of methanol and water is attributed not only to the strong water–methanol hydrophilic interactions but also to water–water structuring around methanol, i.e., hydrophobic effects are the crucial factors in water–methanol mixtures too.

In our recent work^{6–8} this system has been extensively studied using molecular dynamics simulations with methanol concentrations ranging from 0 to 0.20 mole fraction. We observed that significant fluctuation in methanol cluster structure is the main reason for experimentally observed heat capacity maximum at 0.12 methanol mole fraction.

Investigation of hydrophobic hydration in methanol water mixture under supercritical conditions is of a great practical importance for chemical engineering.^{9,10} Computer simulation was successfully employed to study hydrophobic phenomena in supercritical water by J. Gao¹¹ some years ago. His results indicate that there is no hydrophobic enhancement of binding between benzene molecules in supercritical water compared with that in ambient aqueous solutions. However, the Gao observed that solvent–solvent clustering appears to be widespread in supercritical water–benzene mixtures despite diminishing hydrophobic effects.

Although water–methanol mixtures have been extensively investigated at ambient conditions using different experimental and theoretical methods, no theoretical and only a few experimental studies of this system have been made at supercritical conditions.^{12,13} In this study, we examine MD simulations of a series of water–methanol mixtures covering the water-rich region and investigate the mutual manifestation of both kinds of hydration in water–methanol mixture.

SIMULATION DETAILS

For this study, the three-site H1¹⁴ and SPC/E models,¹⁵ which were successfully used in previous studies,^{6,7} were used again without modification to represent methanol–methanol and water–water interactions, respectively. The methanol–water interaction parameters are obtained using Lorenz–Berthelot combining rules.¹⁴ The periodic cube contains 216 rigid molecules of varying mole fractions of methanol (X_m) in aqueous solu-

¹Present address: Division of Structural Biology, Institute of BioMedical Sciences, Academia Sinica, Taipei 11529, Taiwan R.O.C.

Corresponding author: S. Noskov, Institute of Solution Chemistry RAS, Akademicheskaya st.1, Ivanovo 153045, Russia.

E-mail address: <syn@ihnr.polytech.ivanovo.su> or <syn@ibms.ibms.sinica.edu.tw> (S. Noskov)

tions. We performed ten simulations at 660 K using NVT ensemble and experimental density (ρ). Structural properties were displayed for six simulations at $\rho = 0.98 \text{ g.cm}^{-3}$ and $\rho = 0.50 \text{ g.cm}^{-3}$ with $X_m = 0.05, 0.12$, and 0.20 . In addition, two more simulations at $X_m = 0.12$ for both densities have been examined using an assumption of Lennard–Jones fluids, i.e., Coulombic terms were excluded from the H1 and SPC/E models. The time step used was $2.0 \times 10^{-15} \text{ s}$. Each simulation was extended for 400 ps after equilibration. Shifted force modification of potential was employed to avoid truncation error.¹⁶ The internal geometry of the methanol molecules was kept rigid and thus the Newton equations of motion were solved using the SHAKE algorithm.¹⁶ The temperature was controlled by coupling to an external bath thermostat.¹⁶ A leap-frog algorithm¹⁶ was used for the explicit integration of the cartesian motion equations.

RESULTS AND DISCUSSION

The Models

Some comments should be made concerning the use of rigid models to represent the simulated systems in supercritical regions. Recently, Cordeiro¹⁷ performed classical Monte Carlo calculations using the rigid TIP4P, SPC, and SPC/E water models to reproduce the structural features of supercritical water. Cordeiro concluded that although these models were parameterized to reproduce the water properties at ambient conditions, there was good agreement between simulated and the experimental pair correlation functions at supercritical conditions. Similar conclusions have been also reported¹⁸ for the rigid H1 methanol model. These results indicate reliability of the rigid H1 and SPC/E models used in this study.

Heat Capacity

Dependence of heat capacity (C_V) on the CH_3OH concentration is depicted in Figure 1. The calculations have been performed as described elsewhere.¹⁶

$$< \Delta E_{TOT}^2 >_{NVT} = k_B C_V T^2 \quad (1)$$

where ΔE_{TOT} denotes fluctuation of total energy, k_B is the Boltzmann constant and T is temperature in Kelvin. The experimental results¹² are given in Figure 1 for comparison. This is the first time that C_V for a methanol–water mixture at supercritical region has been measured experimentally. Although direct comparison with the MD results could not be made because the values are for different temperatures and concentrations, based on an assumption of ideal solution behavior, extrapolated values of the experimental C_V at 660 K for pure methanol of 2.7 and pure water of 5.2 (Figure 1A) lead to the C_V at $X_m = 0.12$ of approximately 3.2. This is very close to the MD results at the same temperature and indicates reliability of the results reported in this study. As a function of concentration, the C_V at supercritical conditions obtained from the MD simulations shows maximum at $X_m = 0.12$ (Figure 1B). The maximum, which indicates hydrophobic hydration of the solution, is detected at the same methanol concentration for ambient condition, 298 K and 1 atm,^{6–8} This observation suggests that hydrophobic hydration in supercritical regions would be also take place.^{6–8,19} More detailed investigation and discussion are given in the next section.

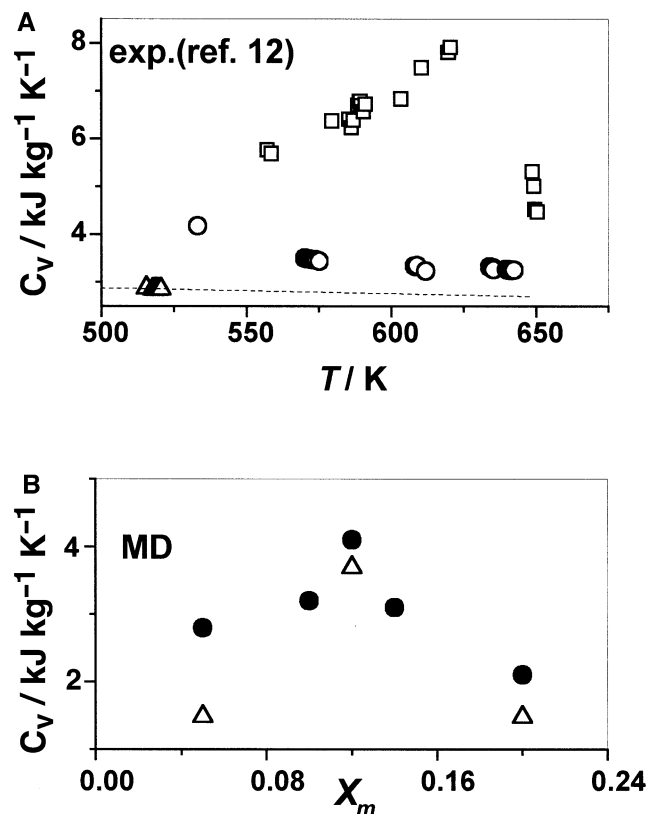


Figure 1. (A) Experimental heat capacity (C_V) of pure water (squares), pure methanol (open triangles) and 0.5 mole fraction of methanol (X_m) in methanol–water mixtures (open circles) as a function of temperature. Dashed line denotes extrapolation to high temperature for pure methanol. (B) Isochoric heat capacity as a function of X_m obtained from the present simulations at 660 K and experimental density of 0.98 g.cm^{-3} (full circles) and 0.5 g.cm^{-3} (triangles).

Structural Properties

One of the main goals of this study is to examine to what extent hydrophobic interactions diminish in water–methanol mixture in the supercritical regions compared with ambient conditions. Such data can be extracted from the site–site radial distribution functions (RDF) shown in Figures 2–4.

The water oxygen–oxygen ($\text{O}_w \text{O}_w$) RDFs for the eight simulations show a prominent first-peak (Figure 2). At $\rho = 0.98 \text{ g.cm}^{-3}$, the $\text{O}_w \text{O}_w$ RDF first-peak for $X_m = 0.12$ is much sharper and higher than those of the other two concentrations, $X_m = 0.20$ and $X_m = 0.05$. In addition, all plots from this density exhibit clear first as well as second-maxima. The position of the second peak for $X_m = 0.12$ takes place at the same distance as the minima for the other two concentrations. It is well known that the $\text{O}_w \text{O}_w$ RDF second peak at position of 0.45 nm for pure water at ambient condition reflects tetrahedral arrangement of the molecules.¹ Hence, the results for $X_m = 0.20$ and $X_m = 0.05$ indicate the low probability of tetrahedral arrangement. Similar findings have been reported for pure water at 600 K.²⁰ Therefore, at $X_m = 0.12$ the water structure is much more pronounced than for the other two

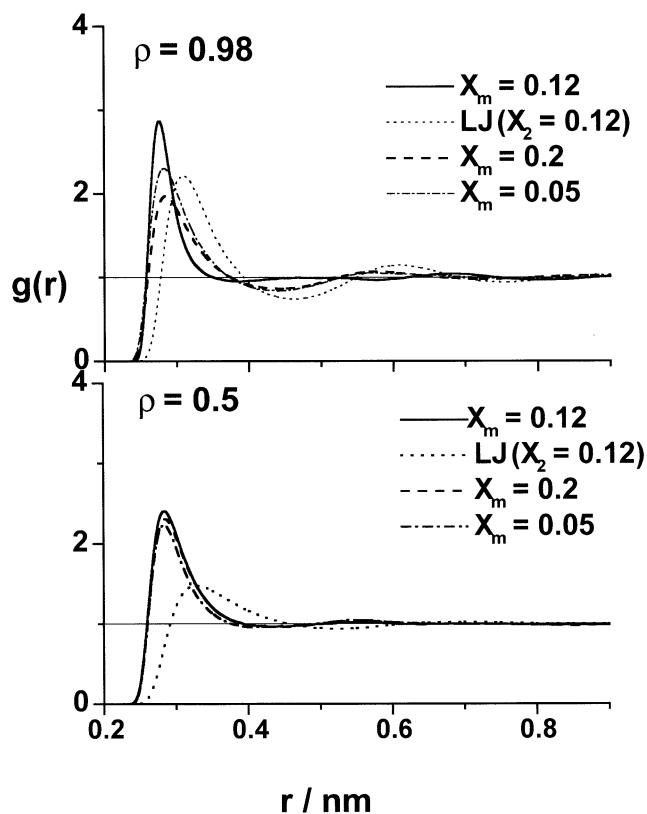


Figure 2. Water oxygen–oxygen radial distribution functions at 660 K for different mole fractions of methanol in water–methanol mixtures (X_m) and experimental densities (ρ in $\text{g}\cdot\text{cm}^{-3}$) labeled in the insert. LJ denotes molecular dynamics simulations using Lennard–Jones potentials (see text for more details).

concentrations. These phenomena, which are observed at supercritical region, are surprisingly consistent with those found for the ambient conditions.^{6–8} It is clear from the previous discussion that hydrophobic hydration is not drastically diminished at $X_m = 0.12$.

This observation can be tentatively attributed to the decrease of spatial density correlation at supercritical conditions due to the lack of long-range interactions. To verify this simple assumption, we performed simulations of Lennard–Jones (LJ) mixtures (the Coulombic parts of the H1 and SPC/E potentials have been excluded from consideration) at $X_m = 0.12$ for both densities (Figure 2). The first peak of the O_wO_w RDFs for the LJ fluids are much broader and shift to much longer distances, especially for $\rho = 0.50 \text{ g}\cdot\text{cm}^{-3}$. At $X_m = 0.12$, the first minimum of the LJ RDF was shifted to a longer distance so that it would place at the same position as the second maximum of normal simulations (the potential functions have been used without modification) and of ambient condition.^{6–8} This means that without Coulombic interactions, icelike structure in the solution was rarely detected. Therefore, it can be concluded from these facts that the increase of water structure for $X_m = 0.12$ is a consequence of specific interactions, most probably hydrogen bonding.

No significant difference was found between the O_wO_w RDFs obtained from different concentrations at $\rho =$

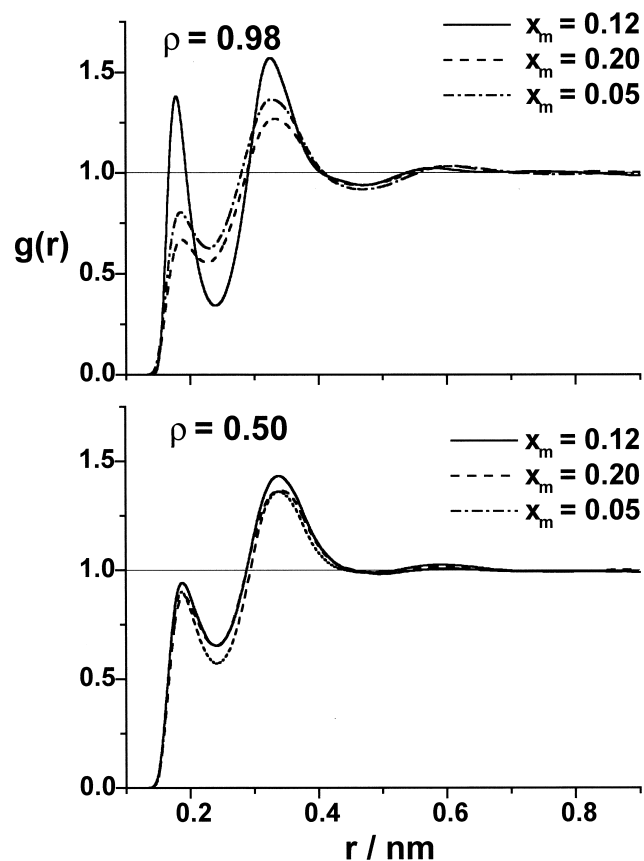


Figure 3. Water oxygen–hydrogen radial distribution functions at 660 K for different mole fractions of methanol in water–methanol mixtures (X_m) and experimental densities (ρ in $\text{g}\cdot\text{cm}^{-3}$) labeled in the insert.

$0.50 \text{ g}\cdot\text{cm}^{-3}$. In comparison with the higher density, $\rho = 0.98 \text{ g}\cdot\text{cm}^{-3}$, the O_wO_w RDFs display less pronounced features, i.e., the first minima and the second maxima are almost completely absent. This is consistent with the findings of Yoshii et al.²⁰ for supercritical water at $\rho = 0.54 \text{ g}\cdot\text{cm}^{-3}$ and $T = 600 \text{ K}$.

The water hydrogen–oxygen (H_wO_w) RDFs shown in Figure 3 confirm the above conclusion. The plots show first and second sharp-peaks. The difference in positions of the peaks for both densities and all concentrations are almost negligible, while the height of both peaks for $X_m = 0.12$ is higher than the others, especially for $\rho = 0.98 \text{ g}\cdot\text{cm}^{-3}$. This indicates hydrogen bond peculiarity of the solution at $X_m = 0.12$ and is fully consistent with the heat capacity data shown in Figure 1, the O_wO_w RDFs in Figure 2, and the previous results for ambient conditions.^{6–8}

The other interesting aspect of hydrophobic effects in water–methanol system is the methanol–methanol correlation. Figure 4 shows the methanol oxygen–oxygen (O_mO_m) RDFs. The other methanol–methanol RDFs are not displayed because they are strictly connected with the O_mO_m RDFs. The previous findings for both ambient and supercritical conditions are fully supported by these plots where the O_mO_m RDFs for $\rho = 0.98 \text{ g}\cdot\text{cm}^{-3}$ and $X_m = 0.12$ exhibits sharp first-peak and a pronounced minimum. This indicates the hydrophobic enhancement of binding between methanol molecules. At lower

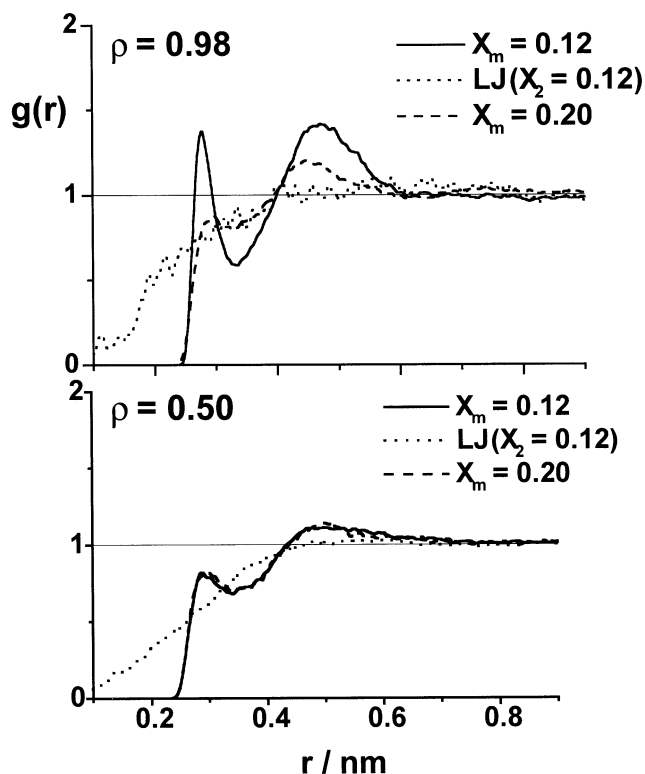


Figure 4. Methanol oxygen–oxygen radial distribution functions at 660 K for different mole fractions of methanol in water–methanol mixtures (X_m) and experimental densities (ρ in $\text{g}\cdot\text{cm}^{-3}$) labeled in the insert. LJ denotes molecular dynamics simulations using Lennard–Jones potentials (see text for more details).

density, $\rho = 0.50 \text{ g}\cdot\text{cm}^{-3}$, the plots show pronounced first-maxima but their features are close to isotropic-like structure. The LJ RDFs (see calculation details) display pure isotropic characters, starting from the hard core radius of methanol molecule of $\sim 0.4 \text{ nm}$. These facts confirm the above conclusion on the crucial role of the specific interactions in “structure-making” process of supercritical methanol–water mixture, especially for high density.

Hydrogen Bond Networks

The discussion on hydrogen bond networks depends on the definitions of hydrogen bonds applied in a simulation. As follows from the previous works, one of the most adequate and simple criterion of hydrogen bond is a geometrical one.^{6,–8,21,22} Hence, the geometrical criterion based on the angle and length of H-bonds described by Kiselev et al.²² was used in this simulation. In accordance with this criterion, two water molecules are bonded by a hydrogen bond if the distance between oxygen and hydrogen is less than 0.25 nm . The average number of hydrogen bonds per water molecule (n_{HB}) found for water–methanol mixture for $\rho = 0.98 \text{ g}\cdot\text{cm}^{-3}$ is 0.4, 0.8, and 0.3 for $X_m = 0.05$, 0.12, and 0.20, respectively. These results are in good agreement with MC simulations of supercritical water reported by Kalinichev.²³ Recently, Yoshii et al.²⁰ reported simulation results for supercritical water using a polarizable model and found that, even as temperature increases, the num-

ber of hydrogen bonds per molecule decreases monotonically from 3.2 at 280 K to 1.9 at 600 K. However, such numbers are still higher than the percolation threshold. Therefore, we consider these results to be overestimated since several authors have found hydrogen bond clusters rather than hydrogen bonds networks at similar conditions.^{22,23,24}

Concerning with tetrahedral arrangement from which one can learn about hydrogen bond networks, we have successfully used the coordinated simplices approach in our previous work.^{7,8} The coordinated simplices are constructed as simplices around one central water molecule, and vertices coincide with positions of water molecules in the first solvation shell of central molecule. With this approach, it is possible to introduce criteria of tetrahedrality²⁵:

$$D = \sum_{i>j}^{15} \frac{(l_i - l_j)}{15l^2} \quad (2)$$

where l_i is the length of the i -th edge of the simplex, and l is the average length.

The criteria of tetrahedrality means deviation from the ideal tetrahedron at which D equals to 0. Deviations from ideal tetrahedrality are shown in Figure 5 for different systems, including pure water and water–methanol systems with a composition $X_m = 0.12$ at ambient conditions. The D distribution for $X_m = 0.12$, $\rho = 0.98 \text{ g}\cdot\text{cm}^{-3}$ and $T = 660 \text{ K}$ overlaps with the D distribution for $X_m = 0.12$ at ambient conditions. It starts to be detected even before the position of the D distribution maximum of the ambient condition. Therefore, at this concentration, regular tetrahedral arrangement in supercritical methanol–water mixtures is available. The maximum of D distribution for $X_m = 0.2$ and $\rho = 0.98 \text{ g}\cdot\text{cm}^{-3}$ corresponds to statistical weight of D distribution for pure water around 0. Therefore, icelike structure, such as tetrahedral arrangement observed for liquid water at ambient conditions, does not exist in this composition.

The simulated results reported for $X_m = 0.20$ are in good agreement with the recently published work,²⁶ where electronic structure and structural and thermodynamic properties of liquid water were studied over a wide range of temperatures (0–600°C) and density (0.6 – $1.4 \text{ g}\cdot\text{cm}^{-3}$) based on the ab initio

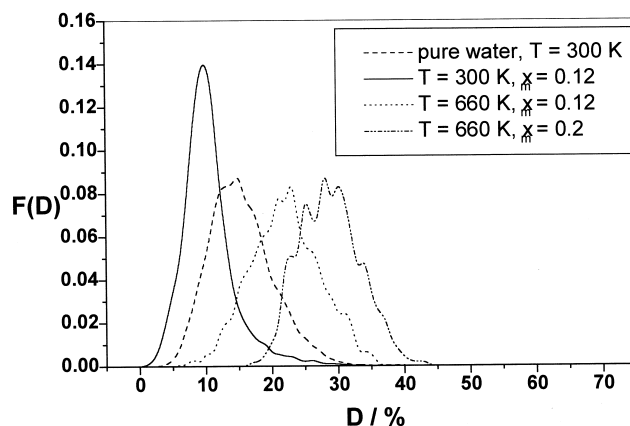


Figure 5. Percentage of deviation from ideal tetrahedrality, (D), of coordinated simplices for water molecules in different mole fractions of methanol in water–methanol mixtures labeled in the insert.

molecular orbital theory combined with the integral equation method.²⁶ The icelike characteristics of water were found to disappear at $\rho = 0.6 \text{ g.cm}^{-3}$ and $T = 870 \text{ K}$. Similar conclusions follow from the results reported by Bursulaya et al.²⁷ and Kalinichev et al.²² at about 600 K.

CONCLUSION

Our major findings are separated into two parts. First, for the compositions of methanol–water mixtures outside the region where heat capacity reaches the maximum, hydrophobic hydration drastically diminished in the supercritical region at high density as well as lower density. This result is similar to that found by Gali¹¹ for diluted aqueous solution of benzene. Second, for the compositions around C_V maximum, hydrophobic hydration can still be noticed. These observations are similar to results observed by the Raman spectroscopy experiment of methanol–water mixture at supercritical conditions. Ebukuro et al.¹³ reported that at a low concentration of methanol the Raman spectra are not evidently characterized for the temperature below 600 K, which indicates that the methanol molecule is isolated in a water cage and the molecular structure remains unaltered up to 600 K. In addition, Coulombic interactions play a very crucial role in the “structure-making” process of supercritical methanol–water mixture.

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