CLATHRATE-LIKE STRUCTURE OF WATER AROUND SOME NONELECTROLYTES IN DILUTE SOLUTION AS REVEALED BY COMPUTER SIMULATION AND X-RAY DIFFRACTION STUDIES

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ABSTRACT. An X-ray diffraction measurement has been carried out for a 3.9 mol% aqueous solution of TBA (tertiary butylalcohol) with an energy-dispersive diffractometer. Constant temperature molecular dynamics calculation has also been made for an aqueous solution model simulating the above-mentioned mixture. Both results suggest the formation of a fairly stable clathrate-like structure of water around TBA molecules.

1. INTRODUCTION

Tertiary butylalcohol (TBA) can mix with water in all proportions at room temperature and form a uniform solution, even though it has a fairly large hydrophobic group. However, the aqueous solution of TBA is one of the most interesting aqueous systems since it exhibits very unusual behavior in its physico-chemical properties especially in the dilute region. A deep and sharp minimum in the partial molar volume vs. composition curve for TBA (Nakanishi, 1960) [1] and a large peak in the excess heat capacity vs. composition curve (Desnoyers et al., 1980) [2] are well known examples of such anomalies. For other experimental results reported earlier, we refer to a review by Glew et al. (1968) [3]. Recently Iwasaki and Fujiyama (1979) [4] have observed an anomalous concentration fluctuation in their light scattering experiment.

On the basis of such experimental evidence, it has been suggested that there should be the formation of clathrate-like structure of water around TBA and some other hydrophobic solutes in dilute solution. The purpose of the present study is to examine whether or not the structure of water in the solution is different from that of pure water and whether the difference, if any, can be accounted for by the clathrate-like structure. The internal structure of a liquid can be investigated both by diffraction measurements using X-ray or neutron radiation and

computer simulations using Monte Carlo or molecular dynamics (MD) methods. These two techniques have recently been developed to the extent that they can give consistent results for essentially any types of liquid mixtures. Therefore we have combined in this study X-ray analysis with MD simulation for the elucidation of the hydration structure in a dilute aqueous solution of TBA.

2. X-RAY DIFFRACTION STUDY

An X-ray diffraction experiment has been carried out for a 3.9 mol% aqueous solution of TBA by means of energy-dispersive diffractometry (Nishikawa and Iijima, 1984) [5] at room temperature. For comparison, a similar diffraction measurement has also been performed for pure water.
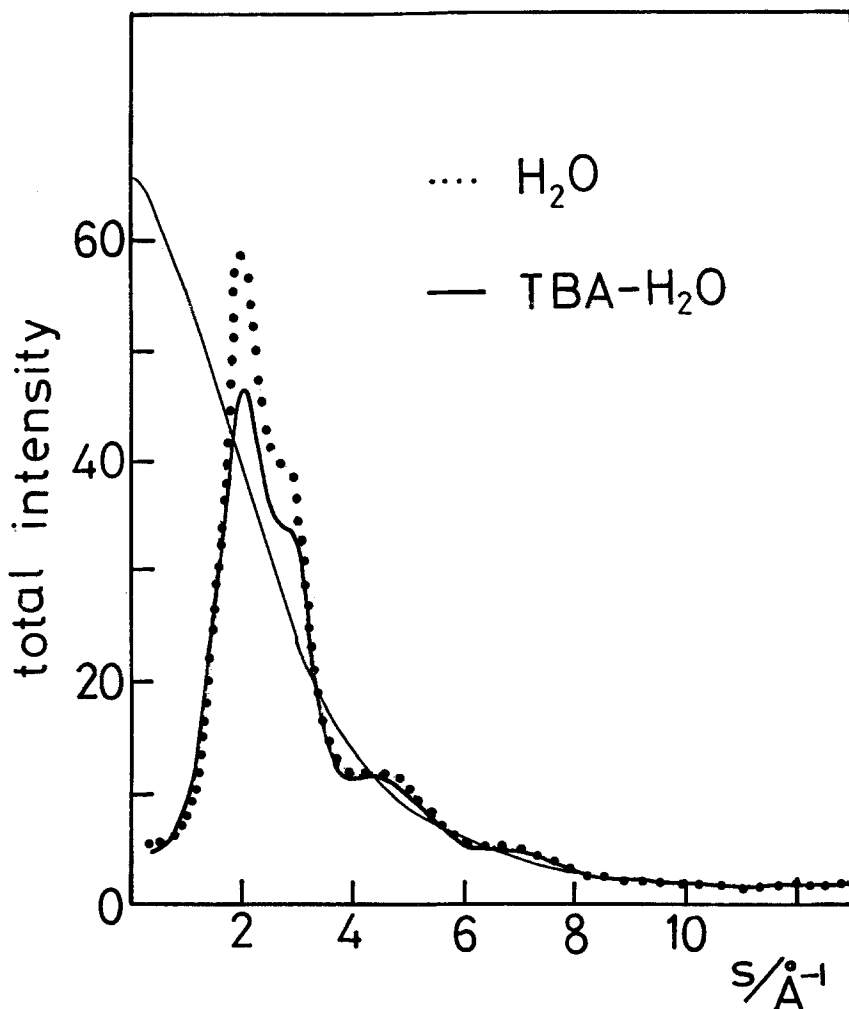

Figure 1. The total coherent X-ray intensities for pure water and a 3.9 mol% aqueous solution of TBA at room temperature.

In Figure 1, the total coherent scattering intensities from a 3.9 mol% aqueous solution of TBA (solid curve) and pure water (dotted curve) are shown. A monotonically decreasing curve (thin solid curve) is the theoretical self-scattering intensity. The difference in the intensity between water and solution is clearly seen in the large first peak and the second shoulder peak, but there is no difference in the phase (peak position) in the two curves. Note that, in spite of the very low concentration of TBA, the decrease in the intensity mentioned above is drastic.

By the Fourier transformation of the scattering intensities, radial distribution functions (RDF) are obtained as shown in Figure 2. A shoulder-like small peak is detected at $r = 1.6$ Å in the RDF for the solution, which is ascribed to the intramolecular C-C and C-O interferences of TBA. However, due to the low concentration of TBA, the contribution of the structural correlation between water and TBA molecules to the RDF is very small and smeared. The radial distribution curve shows only water-water(more exactly, oxygen-oxygen) correlation even for the TBA aqueous sulution.

The first large peak at $r = 2.9$ Å in Figure 2 is due to the hydrogen bonding oxygen-oxygen interference. The position of the first peaks for the two systems is the same, but that of the second peaks is different from each other, namely, it is at 4.65 Å for the solution and 4.5 Å for pure water, respectively. This fact indicates that the oxygen-
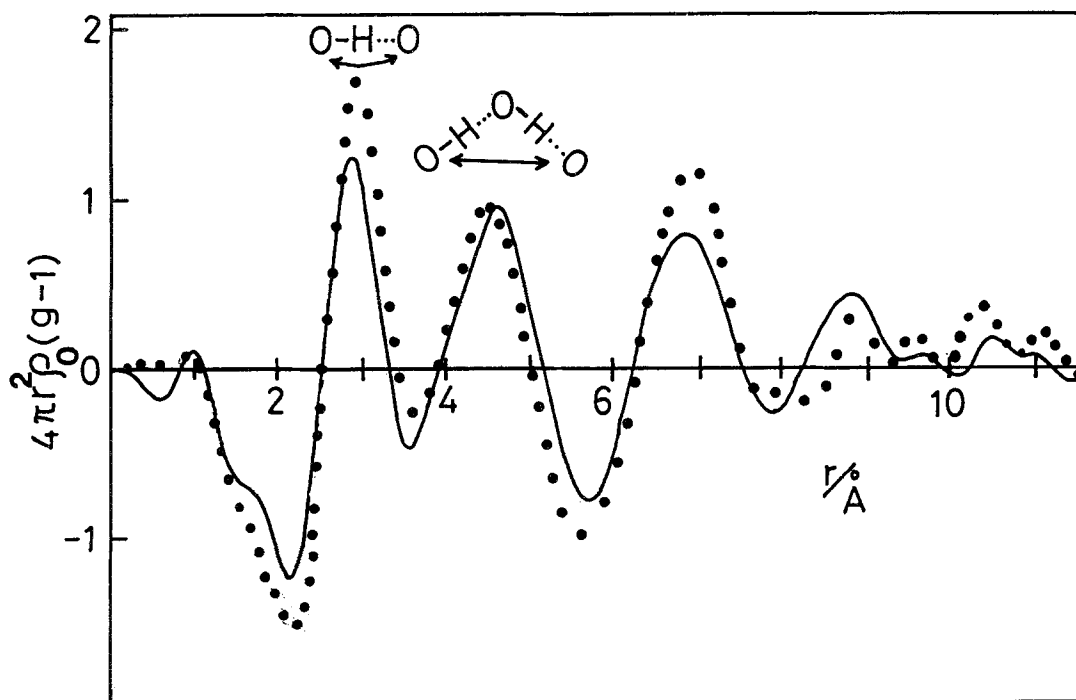

Figure 2. Radial distribution functions for pure water and a 3.9 mol% aqueous solution of TBA.

oxygen distance between hydrogen-bonding water molecules are the same, but the angles in the network structure formed by the hydrogen-bonding are different between the two systems.

3. MOLECULAR DYNAMICS STUDY

A constant temperature MD calculation has been carried out for a 3.2 mol% aqueous solution of TBA containing 7 TBA and 209 water molecules at 298 K and 0.9792 g/cc. The computer program used for keeping the temperature of the solution constant is based on the one developed by one of us (Tanaka et al., 1983) [6] as a realization of the proposal of Andersen (1980) [7]. The time step in integrating the Newton-Euler equation of motion for all the molecules is 0.0004 picoseconds and the calculation is extended up to 84,000 time steps (approximately 26 picoseconds).

Three pair potential functions are required to represent water-water, water-TBA, and TBA-TBA interactions. The MCY potential (Matsuoka et al., 1976) [8] is adopted for water-water interactions, while the other two have been prepared by quantum mechanical LCAO SCF MO calculations for many relative configurations in each dimer with STO-3G basis set and multi-parameter fitting of the MO values to a semi-empirical 12-6-3-1 type potential energy function. Other details will be given elsewhere (Tanaka et al., 1984) [9].

Computer simulations such as that described above can afford abundant information on structural and dynamic properties of fluid systems. Here we focus attention on the trajectory diagram of the solution. Figure 3 shows 10 picosecond trajectories for the molecules in a layer of 20 Å x 20 Å x 3.3 Å. This is one of six layers which are produced by dividing the cubic cell. Incidentally this layer contains two TBA molecules indicated by shading for illustration.

Three important conclusions can be drawn from the figure. In the first place, the orientaion of water molecules is quite regular in the solution. Of the other five layers not given here, four layers exhibit a similar pattern of the structurization of water. This may be due to a cage formation induced by a cooperation of hydrophobic hydration in the hydrophobic group of TBA with hydrogen bonding in the hydroxyl group of the same molecule. This means that even such a low concentration of 3.2 mol% is sufficient for large hydration spheres of TBA to cover almost the whole solution. Secondly, in spite of a fairly large time duration of 10 picoseconds, most of the trajectories of the water molecules seem to be unexpectedly tight, indicating the presence of so-called "iceberg formations." This observation can be supplemented by the fact that the mean square displacement vs. time plot shows much difference between pure water and water in the TBA solution. The values of the self-diffusion coefficient estimated from this plot indicate that the decrease in the diffusion coefficient in the TBA solution from that for pure water is as large as 15%. The final important observation is that TBA molecules can self-associate even in such a dilute solution. However, because of the entropy effect, this association is of the solvent-separated type (Franks, 1982) [10], which means the presence of

one water layer between two TBA molecules. Moreover, the pair
interaction distribution function calculated from the MD data clearly
indicates that there is no strong interaction such as that by hydrogen
bonding between two TBA molecules, in other words, TBA molecules tend to
approach each other with their hydrophobic groups in contact. This is
crucial evidence for the so-called hydrophobic interaction.

It must be pointed out here that the formation of a stable
hydration sphere around TBA had also been observed in our previous Monte
Carlo calculation for an infinitely dilute aqueous solution of TBA
(Nakanishi et al., 1984) [11]. We have given density distribution
diagrams for water molecules around TBA in Figure 19 of our paper.
Figure 4 is a bird's eye view of the hydration sphere. The original
3-dimensional model of this photo has been prepared by sandwiching
transparent copies of the diagrams alternately with plastic plates. We
can clearly see that the volume occupied by one hydration sphere is
certainly much larger than that of the TBA molecule itself.

4. DISCUSSION AND CONCLUSION

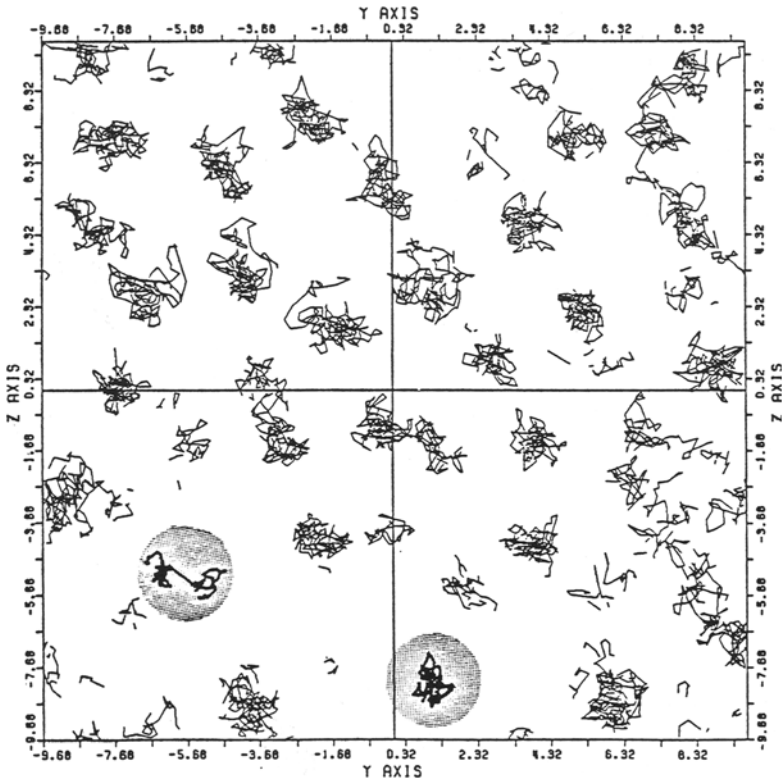Although the structure of pure liquid water is not fully

Figure3. Trajectories of molecules for 10 picoseconds in one of six
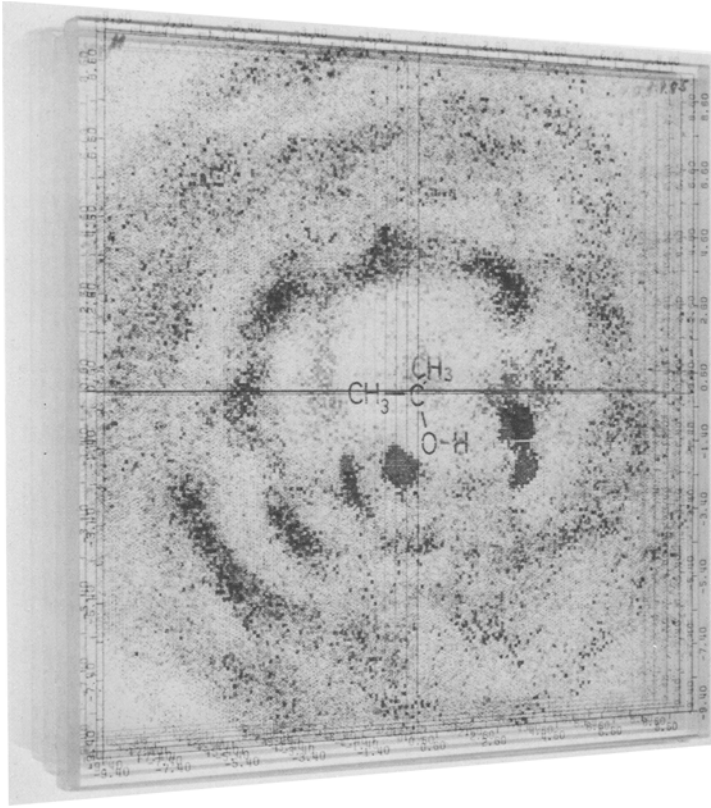layers which constitute the cubic basic cell as obtained from MD data.

Figure 4. Stereographic view of the hydration structure around TBA at infinite dilution as obtained by Monte Carlo calculation.
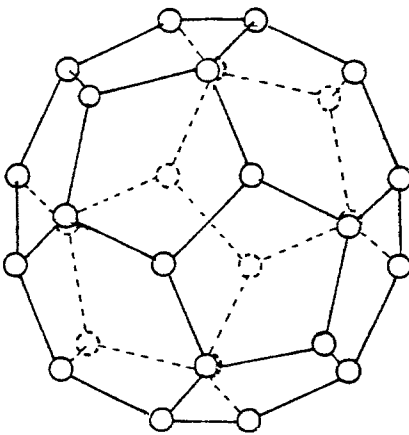

Figure 5. Hexakaidecahedron model for clathrate-like structure.

understood (Iijima and Nishikawa, 1984) [12], it is certain that each water molecule in the network retains tetrahedrally-distributed nearest neighbors (Narten, 1972 [13]; Ohtomo et al., 1981 [14]). The difference in the position of the second peak (see dotted line for pure water and solid line for TBA aqueous solution in Figure 2) may be interpreted reasonably if one assumes a cage structure of water around TBA molecules which is distorted from the normal tetrahedral angle. One of the possible structures is a hexakaidecahedron structure (see Figure 5) around a TBA molecule by taking into account the bulkiness of TBA and the experimental fact (Glew et al., 1968) [3] that TBA forms a type II clathrate hydrate (Davidson, 1973) [15] with a "help gas." The hexakaidecahedron is formed by pentagons and hexagons. The distance between the second nearest neighbors in a pentagon is almost the same as that in the tetrahedral configuration, but is larger than that in a hexagon. This contribution will shift the second peak to a larger distance in the TBA solution.

The assumed cage structure containing 28 water molecules can give X-ray diffraction intensities that are consistent with the present experimental data at least for $s > 3\text{Å}^{-1}$. However, it is difficult to simulate the scattering intensity for $s < 3\text{Å}^{-1}$ because of the truncation effect. This number of water molecules, 28, which can be regarded as a hydration number, is close to the values using other techniques as summarized below.

Authors	Technique	Hydration Number
Goldhammer and Hertz (1970) [16]	NMR	25
Antosiewicz and Shugar (1983) [17]	Ultrasonic velocity	22.4
Nakanishi et al. (1984) [11]	Monte Carlo	20 – 25
This work	X-ray diffraction	28

Due to the lack of a full understanding of the structure of pure water, it is difficult to determine the unique configuration of water molecules in the solution of TBA or other nonelectrolytes and to understand the structure as a whole. However, a consistent result has been obtained by the combination of two completely different approaches. Therefore, one can conclude from the present study that the structure of water around a TBA molecule is different from that of pure water and that the difference can be interpreted as the formation of a polyhedral structure.

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