J. Am. Chem. Soc. 1991, 113, 5596-5605

create carbon vacancies and initiate pit formation.

The rate of removal of carbon atoms in air at 650 °C was about 0.5 atom/site atom/s. By observing the change in pit dimensions with time, it is thus possible to study the kinetics of the reaction on an almost atom-by-atom basis. This would be easier if the reaction could be carried out in situ, while the sample was held in the STM. However, it is difficult to imagine operating the STM under these high-temperature conditions while still maintaining the needed freedom from thermal drift. It might be possible to study the reaction of HOPG with more reactive species at lower temperatures, assuming that the STM components can be protected under these conditions. Similar surface reactions and pit formation could also be studied with other substrates (e.g., metals) by this approach.

Pits have been formed in HOPG with the STM by applying a voltage pulse to the tip in a moist atmosphere (but not in vacuum).[13] These were quite similar in appearance to those reported here and, as pointed out by Quate,[14] could result from the generation of chemical species by the high field at the tip, which can then react with the graphite. Dioxygen itself will not react with HOPG at ambient temperatures, so unless it is activated during its formation, other intermediates, such as oxygen atoms, dioxygen ions, or hydroxyl radicals, are more likely as the reactants. As discussed earlier,[1] these pits are useful in STM studies as surface markers, calibrators of the *Z*-axis of the STM, and perhaps as molecular containers. They may also prove useful, both in STM and electrochemical studies, as specific sites for nucleation and reaction. Studies of this type are currently under way in our laboratory.

Acknowledgment. The support of this research by the Texas Advanced Research Program and the National Science Foundation (Grant CHE8805685) is gratefully acknowledged. We thank Dr. Jeff Cook for obtaining the AES and XPS results.

---

(13) Albrecht, T. R.; Dovek, M. M.; Kirk, M. D.; Lang, C. A.; Quate, C. F. *Appl. Phys. Lett.* **1989**, *55*, 1727.

(14) Quate, C. F. NATO Science Forum '90, Bairritz, France, Sept. 16-21, 1990. (To be published in the NATO Series; Plenum Press: New York).

Molecular Dynamics Simulation and NMR Study of Water-Acetonitrile Mixtures

Helena Kovacs and Aatto Laaksonen*

Contribution from the Division of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden. *Received October 9, 1990*

Abstract: Pure water, pure acetonitrile, and binary mixtures of these two liquids at 0.12, 0.50, and 0.88 molar fractions were simulated by using the molecular dynamics technique with two different sets of effective pair potentials. The reorientational correlation times were deduced from the NMR relaxation of ^{14}N in acetonitrile and ^{17}O in water for comparison.. A manifold increase was observed in the amplitudes of the water-water radial distribution functions upon dilution with acetonitrile, while the acetonitrile arrangement remained relatively intact. The intercomponent interactions were also intensified as moving from the high to low water concentrations. The simulations reproduced the experimental trends in the self-diffusion and reorientation of acetonitrile but rendered too high a mobility for pure water, a feature known previously. At low water content, however, the agreement between the simulated and observed dynamics of water was better. The simulations indicate a slight initial enhancement of the hydrogen-bonded structure of water upon dilution, followed by a breakdown leading to heterogeneity at the molecular level. In the diluted aqueous solution, the presence of water dimers, trimers, tetramers, etc. leads to faster but correlated molecular motions.

1. Introduction

The study of aqueous solutions is in general of considerable interest not only because of the unique properties of water but also due to the crucial importance of water and its solutions in the biosphere. Owing to its remarkable ability to preferential solvation, the mixed solvent of water and acetonitrile makes a recurrent reaction media in physical organic chemistry[1] and also plays a role in atmospheric chemistry.[2]

In 1945, Frank and Evans[3] introduced the "iceberg hypothesis". Their idea was that nonelectrolytes with inert parts—when dissolved in water at low concentrations—will enhance the water structure instead of occupying interstitial sites in the icelike lattice. Since that time, the concept, as well as insight into this so called hydrophobic effect,[4] has become much refined. The hydrophobic interactions are of two kinds, hydrophobic hydration of the solute (i.e., the iceberg formation, or hydration of the second kind as it is also called) and hydrophobic association of the solute molecules. One of the subjects of both interest and some controversy in this context has been acetonitrile, which is an aprotic but highly polar liquid.

Experimental Studies of Water-Acetonitrile Mixtures. The target of the present study is the characterization of the properties and their concentration dependence in the binary solvent mixture of water and acetonitrile. The study focuses on three compositions of water-acetonitrile from three distinct regions in which different solution structures are proposed to exist. Considering the available literature, several thermodynamic studies on aqueous solutions of acetonitrile[5-11] have been published, as well as investigations

---

(1) Engberts, J. B. F. N. *Faraday Discuss. Chem. Soc.* **1988**, *85*, 289.

(2) Deakyne, C. A.; Meot-Ner, M.; Campbell, C. L.; Hughes, M. G.; Murphy, S. P. *J. Chem. Phys.* **1986**, *84*, 4958.

(3) Frank, H. S.; Evans, M. W. *J. Chem. Phys.* **1945**, *13*, 507.

(4) Franks, F. *Water. A Comprehensive Treatise*; Plenum Press: New York-London, 1973.

(5) Robertson, R. E.; Sugamori, S. E. *Can. J. Chem.* **1972**, *50*, 1353.

(6) Moreau, C.; Douhéret, G. *J. Chim. Phys.* **1974**, *71*, 1313. Moreau, C.; Douhéret, G. *Thermochim. Acta* **1975**, *13*, 385. Moreau, C.; Douhéret, G. *J. Chem. Thermodyn.* **1976**, *8*, 403. Douhéret, G.; Moreau, C.; Viallard, A. *Fluid Phase Equilib.* **1985**, *22*, 289. Douhéret, G.; Moreau, C.; Viallard, A. *Fluid Phase Equilib.* **1986**, *26*, 221.

(7) Davis, M. I. *Thermochim. Acta* **1983**, *63*, 67. Davis, M. I. *Thermochim. Acta* **1984**, *73*, 149. Davis, M. I.; Douhéret, G. *Thermochim. Acta* **1986**, *104*, 203.

(8) Davis, M. I.; Douhéret, G. *Thermochim. Acta* **1987**, *116*, 183.

(9) Luhrs, C.; Schwitzgebel, G. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 623.

(10) de Visser, C.; Heuvelsland, W. J. M.; Dunn, L. A.; Somsen, G. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1159.

0002-7863/91/1513-5596$02.50/0

by a number of experimental techniques such as Raman,[12] IR,[13,14] NMR,[15-20] and other spectroscopic methods.[21-23] Ab initio calculations[24] as well as MC simulations[25] have been employed to investigate the hydration of acetonitrile. In a recent publication, MD simulations were combined with IR and NMR spectroscopy.[26]

Robertson and Sugamori found in their thermodynamic study of the temperature dependence of ΔH and ΔC_p in different aquoorganic mixtures[5] that the effect of acetonitrile on water is quite different from the structure-making effect of alcohols, i.e., the original idea of Franks and Evans, which had received support from several other studies. Robertson and Sugamori observed that the competition between water–water and water–acetonitrile interactions is rather even. According to them, the acetonitrile molecules act rather like small ions that partially melt the water structure. In other words, acetonitrile functions as a structure breaker.

On the basis of studies of excess volumes, viscosity, dielectric constant, and acid–base properties, Moreau and Douhéret[6] concluded that there are three structural regions in the whole composition range of water–acetonitrile. In mole fractions of acetonitrile, these are (i) $0 < x < 0.2$, (ii) $0.2 < x < 0.75$, and (iii) $0.75 < x < 1.0$. In the first, water-rich region, the acetonitrile molecules gradually occupy the cavities between water molecules without enhancing the water structure. In the second region, a disruption of water structure takes place. This is also the region where water–acetonitrile mixtures exhibit a phase separation. That occurs at approximately 272 K and 38 mol % of acetonitrile. Finally, in the third region, it is the acetonitrile arrangement that is disrupted by water molecules. The Raman study of von Kabisch[12] showed that acetonitrile does not stabilize the water structure in the range $0 < x_{\mathrm{CH_3CN}} < 0.2$. A strong tendency for self-association of water exists over a wide concentration range, but at very low water content the H_2O molecules build two weak hydrogen bonds to acetonitrile in a 1:2 complex.

In dissolving acetonitrile in water, the water structure is retained and possibly slightly enhanced up to 15–16 mol % acetonitrile, according to several groups, for instance, Sidorowa et al.[13] and Easteal.[15] Hertz, Leiter, and co-workers[16-18] have published three papers on mixtures of water and aprotic solutes, one NMR study on the velocity correlation and two on association phenomena. They found enhanced water–water correlations (signifying molecular association) but only minor solute–solute correlations in the water–acetonitrile system.

Dynamic properties of water–acetonitrile mixtures have been investigated by von Goldammer and Hertz.[19] They attempted to correlate the molecular motions (rotational correlation times and diffusion constants) to a possible liquid structure. No evidence was found of long-lived hydration cages surrounding solute molecules at low concentrations, but an increase in solution structure was observed. Moreover, evidence of solute–solute association was found leading to a certain degree of "microheterogeneity" (deviation from random distribution of molecules on the local level). Also according to the Naberukhim–Rogov model,[27] a microheterogeneous structure should appear in the binary mixture for mole fractions larger than 0.20 of the nonelectrolyte, in which water exists more structured than in pure water. Balakrishnan and Easteal[22] found the microphase concept appropriate for acetonitrile–water mixtures. One of the proofs for it is the occurrence of the phase separation in this region.

Damewood and Kumpf[24] performed ab initio calculations on 1:1 acetonitrile–water complexes in five different configurations. They obtained the highest binding energies for hydrogen bonding to the nitrile and for a side-by-side arrangement with the dipoles aligned antiparallel. A somewhat lower energy was obtained for the binding of the water–oxygen to the cavity formed by the three CH bonds of the methyl group. Eaton and co-workers[14,26] combined spectroscopic data (IR, C–N stretch; NMR, ^{13}C, ^{14}N relaxation) with molecular dynamics simulation to study the solvation of acetonitrile in water. In the MD simulation of Eaton et al.[26] performed on one single CH_3CN molecule among 215 water molecules, the predicted solvation numbers were found to be in agreement with the spectroscopically determined ones. In brief, the dissolvation of the acetonitrile molecule by water was confirmed, while Dunn and Nagy[25] reported a solvation number of 1.3–1.4 from a Monte Carlo simulation of a single acetonitrile molecule dispersed in 264 water molecules.

Computer Simulations of Binary Mixtures. The current investigation is a part of a series of works performed at our laboratory, in which we study solvation phenomena of small molecules by combining molecular dynamics computer simulations with NMR measurements.[28-32] In these investigations, we are primarily interested in the liquid structure, transport properties, and various models for molecular reorientation. Provided that the computer simulations successfully reproduce the observed experimental trends, conclusions are drawn about the details of the molecular structure and motions based on an analysis of the radial distribution functions and time correlation functions.

A molecular dynamics study to explore the concentration dependence has been reported earlier on the binary mixture system of acetonitrile and chloroform.[31] Basic difficulties encountered in the dilution studies are the construction of the cross potentials between the unlike mixture components and the anticipated reduction of many-body effects upon dilution (particularly if the diluted component happens to be water). In the acetonitrile–chloroform system, the cross potential was devised from the effective pair potentials of the pure compounds by means of the Lorentz–Berthelot combination rules, without adjusting it to experimental data at any concentration. Although unelaborate, the potential model was shown to describe the system fairly well. The reason for this is that the mixture components interact only weakly, as indicated by the dominance of the Lennard–Jones contribution to the intermolecular interaction energy in the system.

In the aqueous mixtures of acetonitrile, on the contrary, the electrostatic effects are of major size, evidently because the mixture components interact strongly through hydrogen bonding and dipolar interaction. Hydrogen bonding in water is also known to be of highly cooperative character.[33,34] The present simulations were performed initially with the six-site acetonitrile potential of Böhm et al.[35] and the simple point charge model (SPC) for water

---

(11) Handa, Y. P.; Benson, G. C. *J. Solution Chem.* **1981**, *10*, 291. Benson, G. C.; D'Arcy, P. J.; Handa, Y. P. *Thermochem. Acta.* **1981**, *46*, 295.

(12) v. Kabisch, G. *Z. Phys. Chem.* (*Leipzig*) **1982**, *263*, 48.

(13) Sidorova, A. I.; Narziev, B. N. *Ukr. Fiz. Zh.* (*Russ. Ed.*) **1967**, *12*, 317. Sidorova, A. I.; Kochnev, I. N.; Moiseeva, L. V.; Narziev, B. N. *Zh. Strukt. Khim.* **1968**, *9*, 607. Sidorowa, A. I.; Moiseeva, L. V. *Strukt. Rol Vody Zhivom Org.* **1968**, *2*, 25. Sidorova, A. I.; Narziev, B. N. *Tepl. Dvizhenie Mol. Mezhmol. Vzaimodeistvie Zhidk. Rastvorakh, Mater. Mezhvuz. Nauchn. Konf., 2nd* **1969**, 120. Sidorova, A. I.; Gurikov, Yu. V.; Moiseeva, L. V.; Braginskaya, T. G. *Zh. Strukt. Khim.* **1969**, *10*, 786.

(14) Eaton, G.; Pena-Nunez, A. S.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2181.

(15) Easteal, A. J. *Aust. J. Chem.* **1979**, *32*, 1379.

(16) Hertz, H. G.; Leiter, H. *Z. Phys. Chem. Neue Folge* **1982**, *133*, 45.

(17) Leiter, H.; Patil, K. J.; Hertz, H. G. *J. Solution Chem.* **1983**, *12*, 503.

(18) Leiter, H.; Albayrak, C.; Hertz, H. G. *J. Mol. Liq.* **1984**, *27*, 211.

(19) v. Goldammer, E.; Hertz, H. G. *J. Phys. Chem.* **1970**, *74*, 3734.

(20) Braun, B. M.; Holz, M. *J. Solution Chem.* **1983**, *12*, 685.

(21) Easteal, A. J. *Aust. J. Chem.* **1980**, *33*, 1667.

(22) Balakrishnan, S.; Easteal, A. J. *Aust. J. Chem.* **1981**, *34*, 943.

(23) Easteal, A. J. *Aust. J. Chem.* **1979**, *32*, 271.

(24) Damewood, J. R.; Kumpf, R. A. *J. Phys. Chem.* **1987**, *91*, 3449.

(25) Dunn, W. J., III; Nagy, P. I. *J. Phys. Chem.* **1990**, *94*, 2099.

(26) Eaton, G.; Pena-Nunez, A. S.; Symons, M. C. R.; Ferrario, M.; McDonald, I. R. *Faraday Discuss. Chem. Soc.* **1988**, *85*, 237.

(27) Naberukhin, Yu. I.; Rogov, V. A. *Russ. Chem. Rev.* **1971**, *40*, 207.

(28) Maliniak, A.; Laaksonen, A. *Mol. Phys.* **1987**, *62*, 489.

(29) Maliniak, A.; Laaksonen, A.; Kowalewski, J.; Stilbs, P. *J. Chem. Phys.* **1988**, *89*, 6434.

(30) Maliniak, A.; Laaksonen, A.; Korppi-Tommola, J. *J. Am. Chem. Soc.* **1990**, *112*, 86.

(31) Kovacs, H.; Kowalewski, J.; Laaksonen, A. *J. Phys. Chem.* **1990**, *94*, 7378.

(32) Laaksonen, A.; Stilbs, P. *Mol. Phys.* **1991**, in press.

(33) Barnes, P.; Finney, J. L.; Nicholas, J. D.; Quinn, J. E. *Nature* **1979**, *282*, 459.

(34) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1985.

(35) Böhm, H. J.; Madden, P. A.; McDonald, I. R. *Mol. Phys.* **1983**, *49*, 347.

Table I. Physical Specification of the Simulated Systems

	mol % CH_3CN				
	0	12	50	88	100
no. of H_2O	256	228	128	28	0
no. of CH_3CN	0	28	128	228	256
time step (fs)	1.0	1.0	1.0	1.0	1.0
density (g/cm^3)	1.0	0.965	0.85	0.79	0.78
temp (K)					
SPC and Böhm	299 ± 6	320 ± 7	331 ± 14	313 ± 23	298 ± 7
TIP4P and Jorgensen	302 ± 7	310 ± 9	324 ± 12	304 ± 17	307 ± 2

Table II. Intermolecular Interaction Energies (kJ/mol)

mol % CH_3CN		H_2O–H_2O	H_2O–CH_3CN	CH_3CN–CH_3CN
		SPC and Böhm		
0	Coulomb	−12711		
0	Lennard–Jones	1873		
12	Coulomb	−10695	−1196	−57
12	Lennard–Jones	1932	−291	−76
50	Coulomb	−4620	−2390	−1116
50	Lennard–Jones	928	−268	−936
88	Coulomb	−330	−1101	−3042
88	Lennard-Jones	74	−42	−2394
100	Coulomb			−4183
100	Lennard–Jones			−2820
		TIP4P and Jorgensen		
0	Coulomb	−11541		
0	Lennard–Jones	1838		
12	Coulomb	−10304	−803	−38
12	Lennard–Jones	1878	−435	−169
50	Coulomb	−3887	−2163	−621
50	Lennard–Jones	820	−590	−1885
88	Coulomb	−429	−869	−1875
88	Lennard–Jones	100	−130	−4288
100	Coulomb			−2307
100	Lennard–Jones			−4939

constructed by Berendsen et al.[36] There was, however, an intense increase in the radial correlation of water upon dilution, suspected to be an exaggerated effect. For this reason, the simulations were repeated with use of another, seemingly quite different set of potentials, namely, the three-site acetonitrile model[37] and the four-site TIP4P water model,[38] both constructed at Jorgensen's laboratory.

Jorgensen's acetonitrile potential differs from the one devised by Böhm in two principal ways: According to the former model, the methyl group is approximated to a united atom and the charges are adjusted to yield a dipole moment of 3.44 D in contrast to the dipole moment of 4.14 D of the latter model. Despite these differences, the Monte Carlo simulations performed by Jorgensen yielded radial distribution functions, and therewith a liquid structure, virtually identical with that of Böhm.

The SPC and TIP4P potential models for water are both effective pair potentials, where the rigid water monomer is represented by three or four interaction sites, respectively. In the TIP4P model, the negative charge is moved off the oxygen atom toward the hydrogens as it is located at a point on the bisector of the HOH angle. The TIP4P model has been shown to yield a somewhat better description of the long-range structure of water than the three-site model[38] while retaining the correct density.

In the next section, the computational and experimental parts of the work are explained in more detail. Static properties, such as interaction energies and liquid structure deduced from the radial distribution functions, are investigated in section 3. Various dynamic properties of the mixture components are discussed in section 4. Conclusions are presented in section 5.

2. Computational and Experimental Details

Physical Models and Computational Methods. Constant-volume molecular dynamics (MD) simulations have been performed on pure water, pure acetonitrile, and three different water–acetonitrile mixtures consisting of 12, 50, and 88 mol % acetonitrile, respectively. All the simulations contained totally 256 molecules in a cubic box.

Temperatures during the simulations were close to room temperature, and experimental densities were used for the different binary mixtures and the pure substances. Both molecular species, i.e., water and acetonitrile, were kept rigid throughout the simulation, and the equations of motion were solved by using the fifth-order Nordsieck–Gear predictor–corrector integration scheme.[39–40] The rotational motion was treated by using the second-order quaternion method.[41–43]

Pair potentials were of the so-called site–site type, given in the standard Lennard–Jones 6–12 plus electrostatics form. All the Lennard–Jones cross potentials, also those between water and acetonitrile, were constructed by employing the Berthelot–Lorentz combination rules. The first acetonitrile potential, taken from the work of Böhm et al.,[35] has been used earlier with success in several studies by Lynden-Bell and co-workers.[44] As the first water potential, we used the rigid SPC model of Berendsen et al.[36] Jorgensen's three-site model for acetonitrile[37] and four-site model for water[38] were employed in the second set of simulations. Details on the potentials can be found in the above-mentioned papers. A summary of the physical states and characteristic simulation parameters are given in Table I.

The long-range electrostatic interactions were treated with use of Ewald summation techniques. Furthermore, the minimum image convention was used together with the periodic boundary conditions. The number of steps in all the simulations is 70000, while the production was done during the last 20000 steps (equal to 20 ps). All the simulations were performed by using a modified version of McMOLDYN package[45] on a CONVEX C220 supercomputer.

NMR Measurements. The samples for NMR measurements were prepared of doubly distilled water and P. A. grade acetonitrile purchased from Merck, while adding a small amount of CD_3CN as a lock substance; in water, 10 mol % D_2O was used. The samples were prepared by weighing, without degassing, in 10-mm NMR tubes. All experiments were performed at 9.4 T on a JEOL GX 400 spectrometer. Transverse relaxation rates for ^{14}N in acetonitrile and ^{17}O in water were determined manually from the line width. Proton decoupling was used in order to remove line broadening due to scalar relaxation of the first kind. The reported values are averages of at least two measurements, and the experimental uncertainty is approximated at 10%.

The reorientational correlation times were deduced through the usual relation, where the term $(1 + \eta^2/3)^{1/2}(e^2qQ/h)$ was set at the value of 9.3 MHz[46] for oxygen-17 in H_2O. The acetonitrile molecule is a symmetric top, and its nitrogen-14 relaxation rate is related to the reorientational correlation time of the symmetry axis, $\tau_{2,0}$. That is because the nitrogen nucleus lies on the top axis and its principal axis of the electric field gradient coincides with the top axis. The asymmetry parameter is zero due to the cylindric symmetry of the field gradient. The gas-phase value for QCC of 4.224 MHz[44] was used for ^{14}N.

3. Static Properties

Pairwise Interaction Energies. The pairwise intermolecular interaction energies between the like and unlike mixture components, resolved to their Lennard–Jones and electrostatic contributions, are tabulated separately for each set of simulations in Table II. Clearly the Coulombic contribution dominates over the Lennard–Jones part in this system, indicating that the solutions are stabilized by the long-ranging electrostatic effects. That is characteristic of a hydrogen-bonded system. It may be pointed out that the acetonitrile–acetonitrile interaction energies calculated with Jorgensen's potential model make an exception to this statement. The dominance of the Lennard–Jones part over the electrostatic part there can be rationalized by the lower value of the dipole moment, and we might anticipate that Jorgensen's model

---

(36) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; Hermans, J. *Intermolecular Forces*; Pullman, B., Ed.; Reidel: Dordrecht, The Netherlands, 1981.

(37) Jorgensen, W. L.; Briggs, J. M. *Mol. Phys.* **1988**, *63*, 547.

(38) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.

(39) Nordsieck, A. *Math. Comput.* **1962**, *16*, 22.

(40) Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equations*; Prentice-Hall: Princeton, NJ, 1971.

(41) Evans, D. J.; Murad, S. *Mol. Phys.* **1977**, *34*, 327.

(42) Rapaport, D. C. *J. Comput. Phys.* **1985**, *60*, 306.

(43) Sonnenschein, R. *J. Comput. Phys.* **1985**, *59*, 347.

(44) Böhm, H. J.; Lynden-Bell, R. M.; Madden, P. A.; McDonald, I. R. *Mol. Phys.* **1984**, *51*, 761.

(45) Laaksonen, A. *Comput. Phys. Commun.* **1986**, *42*, 271.

(46) Lankhorst, D.; Schriever, J.; Leyte, J. C. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 215.

describes acetonitrile as a more "inert" solvent than does Böhm's potential model. The interaction energies of water as rendered by the SPC and TIP4P models, respectively, are very similar.

The experimental, macroscopic dielectric constant, which is related to the solvent polarity and therefore to its capacity to screen electrostatic interactions, changes from a value of 38 in pure acetonitrile to 80 in water. It is readily observed that the percent Coulombic contribution to the total interaction energy for CH_3CN-CH_3CN and CH_3CN-H_2O pairs diminishes in the direction of increasing dielectric constant in the real solutions. The contributions to H_2O-H_2O interaction energies, having different signs, elude such an observation.

Radial Distribution Functions. The following notation is used in labeling the radial distribution functions (rdf); the nitrile carbon in acetonitrile is denoted by C2, the methyl carbon by C1. The methyl protons are denoted by a sole H, while WH signifies the hydrogens of water and WO denotes the oxygen of water.

Acetonitrile–Acetonitrile. On the basis of a comparative analysis of the radial distribution functions of neat acetonitrile, Jorgensen[37] concluded that, apart from some minor deviations, the three-site model essentially reproduces the rdf results of the six-site model, such as locations of maxima and minima and the peak intensities. The following analysis will focus on the concentration-dependent variations as produced by Böhm's six-site model, as it better illustrates the interactions at the methyl end of the molecule and also renders the parallel and antiparallel orientations of the molecules more discernible.

Three of the ten possible atomic radial distribution functions of acetonitrile are presented in Figure 1. In the concentration range of 100–50 mol % acetonitrile, the peaks of the rdf's decrease only slightly, signifying that the acetonitrile arrangement is hardly affected by the addition of water. Thus, it seems that the water molecules are distributed between the larger acetonitrile molecules without disrupting their arrangement.

A somewhat larger reduction in the intensity of the radial correlation is observed for the first peak of the $g_{N\text{-}H}(R)$ function (shown in Figure 1, top), which stands for the acetonitrile molecules having their methyl protons directed toward the nitrogen of the central molecule. These molecules in the first place are replaced by water. The running coordination number of the $g_{N\text{-}H}(R)$ function gives a measure of the substitution of acetonitrile molecules by water. At its first minimum of 3.7 Å, it goes down from 2.1 molecules in the pure liquid to 0.4 in the diluted acetonitrile solution, and at the second minimum of 5.2 Å it goes down from 5.7 to 1.4. The coordination numbers for the minimum at 5.0 Å in the $g_{N\text{-}C1}(R)$ function are practically the same as those at the second minimum of $g_{N\text{-}H}(*R)$.

More noticeable changes occur in the acetonitrile arrangement in the diluted solution of acetonitrile. All the rdf intensities are strongly reduced, indicating that the more loosely packed acetonitrile molecules around the central molecule have been replaced by water. Quite contrarily, the peak corresponding to the three nearest neighbors, arranged in a slightly shifted antiparallel fashion, has increased very much. Not only that, but in the $g_{N\text{-}N}(R)$ (Figure 1, middle) and $g_{N\text{-}C2}(R)$ functions it has moved slightly to the left, toward shorter interatomic distances. In the $g_{C2\text{-}C2}(R)$ (Figure 1, bottom) and $g_{C1\text{-}C1}(R)$ functions where the peaks corresponding to antiparallel and parallel arrangements overlap, almost only the antiparallel peak remains. Thus, the molecular approach has become closer, and the radial correlatioin between the antiparallel neighbors is enhanced. The closer approach should be possible because of the smaller size of the intruding water molecules. However, this enhancement of the acetonitrile structure cannot be considered a hydrophobic effect, since it involves mainly the polar parts of the molecule. The nonpolar part of acetonitrile is obviously too small to give rise to hydrophobic association in this system.

An examination of the coordination numbers from the $g_{C2\text{-}C2}(R)$ function (note that the position of the nitrile carbon, C2, almost coincides with the molecule's center of mass) reveals that the number of molecules of the like kind in the coordination sphere up to 6.3 Å is reduced from 11.3 in the pure liquid to 3.0 in the 12 mol % acetonitrile solution. The coordination numbers for the $g_{N\text{-}N}(R)$ and $g_{C1\text{-}C1}(R)$ functions corroborate this result. The maximum in the $g_{C2\text{-}C2}(R)$ function consists of two overlapping peaks. The first one of them arises from the three acetonitrile molecules arranged in a slightly shifted antiparallel fashion around the central molecule. This peak is discerned only as a "shoulder", except in the diluted acetonitrile solution where is it has become a strong, shifted peak. The integral of the $g_{C2\text{-}C2}(R)$ function over this first peak up to 4.5 Å decreases from 3.0 to 1.0 acetonitrile

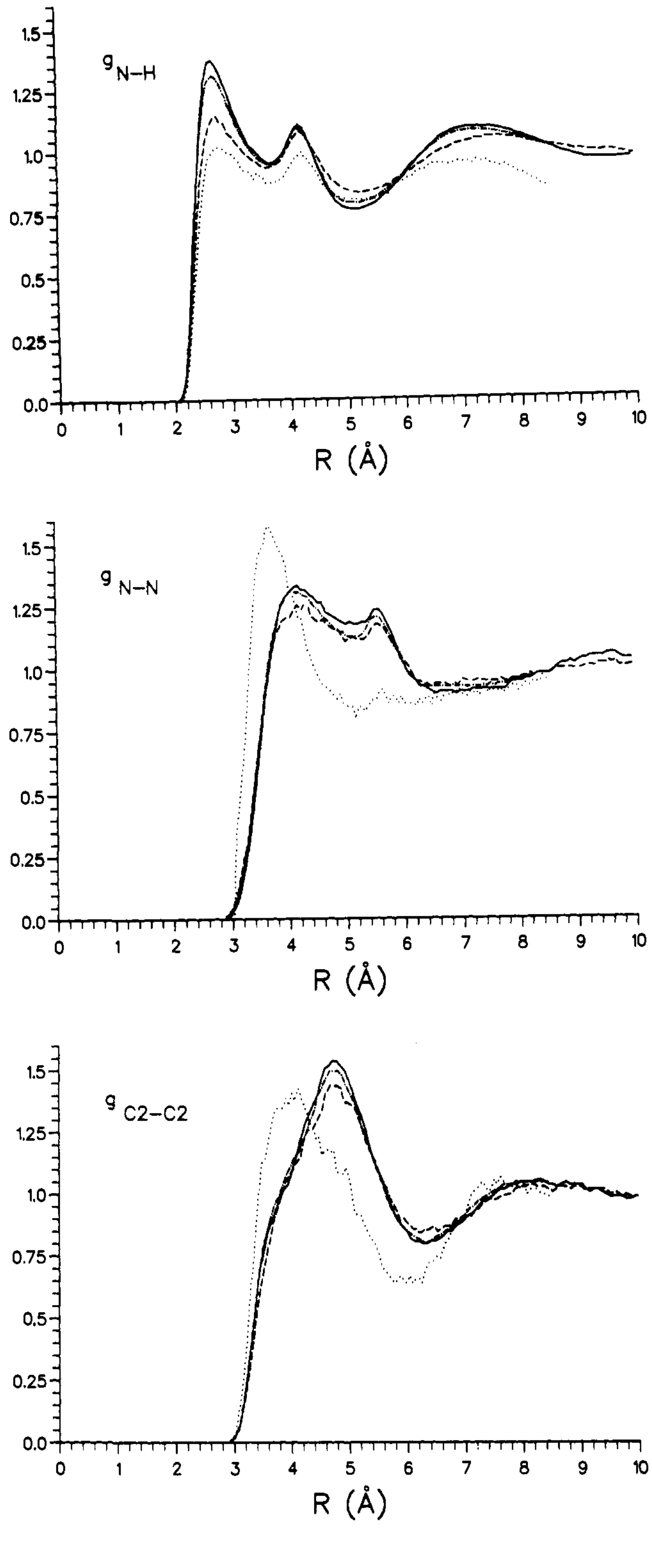

Figure 1. Three radial distribution functions between acetonitrile molecules, $g_{N\text{-}H}(R)$ (top), $g_{N\text{-}N}(R)$ (middle), $g_{C2\text{-}C2}(R)$ (bottom), as calculated with use of Böhm's six-site potential model in combination with the SPC model: (—) 100 mol % CH_3CN, (-·-·-) 88 mol % CH_3CN, (- - -) 50 mol % CH_3CN, and (···) 12 mol % CH_3CN.

Table III. A Comparison of Atomic Radial Distribution Functions in Pure Water[a]

	no. 1 max		no. 1 min		no. 2 max	
	R (Å)	*g*(*R*)	*R* (Å)	*g*(*R*)	*R* (Å)	*g*(*R*)
			$g_{\mathrm{O\text{-}O}}$			
exptl	2.87	3.09	3.32	0.73	4.48	1.14
SPC	2.78	2.82	3.37	0.88	4.56	1.08
TIP4P	2.78	2.90	3.42	0.84	4.42	1.08
			$g_{\mathrm{O\text{-}H}}$			
exptl	1.85	1.39	2.35	0.26	3.35	1.60
SPC	1.79	1.43	2.43	0.23	3.27	1.53
TIP4P	1.84	1.40	2.43	0.23	3.22	1.50
			$g_{\mathrm{H\text{-}H}}$			
exptl	2.45	1.26	3.05	0.76	3.85	1.17
SPC	2.43	1.29	3.03	0.75	3.92	1.15
TIP4P	2.38	1.24	2.98	0.77	3.82	1.15

[a] The experimental values are taken from the neutron diffraction study by Soper and Phillips (ref 47).

molecules upon dilution with water over the present concentration range. Likewise according to Jorgensen's model, the location of the rdf peaks signifying the antiparallel neighbors moves to closer distances at 12 mol % acetonitrile. But unlike Böhm's model, the peak intensities are enhanced up to around 2 units, indicating an enforcement in the structural correlation of the near neighbors.

Water–Water. Firstly, we note that the peak positions and intensities from the simulated rdf's for pure water are in good agreement with the newly published neutron diffraction results of Soper and Phillips,[47] as illustrated in Table III, apart from the third solvation sphere, which is more pronounced in the experimental distribution functions. A virtue of the four-site model, TIP4P, is claimed to be that, while retaining the correct density, it yields a more distinct long-range structure.

The atomic radial distribution functions of water calculated by the TIP4P model are presented in Figure 2. The rdf's of water in the 12 mol % acetonitrile solution have slightly sharper maxima than those in pure water, indicating that the water structure is slightly enhanced as acetonitrile is added. This observation is supported by the fact that experimental values for the rotational and translational motions of water are slightly retarded as 12 mol % acetonitrile is added to pure water. The local number density of water molecules is virtually unchanged, implying that the acetonitrile molecules in the simulated liquid are distributed within the water structure.

The radial correlation between water molecules increases in the 50:50 mixture considerably, just to be further intensified in the diluted solution. A strong increase in the rdf intensity of water has been observed earlier in simulations where the temperature has been lowered, bringing about a "frozen" structure.[48] Considering the fact that the acetonitrile structure seems to remain quite intact at the concentration of 12 mol % water compared with the pure liquid, it is feasible to explain the water structure as clusters or chains of water molecules interlocked by hydrogen bonds, inserted in the cavities between acetonitrile molecules. Since acetonitrile is a weaker hydrogen-bond acceptor than water, it has been proposed earlier that a water molecule hydrogen bonded to an acetonitrile molecule will form up to three bonds to other water molecules.[49] The simulation results implicitly support the hypothesis of microheterogeneity, i.e., the persistance of the water structure leading to a nonrandom distribution at the local level. The simulation results are also in accordance with the conclusions of von Kabisch[12] and Leiter and co-workers[17] who claim that the self-association of water is enhanced as it is diluted by acetonitrile.

To enable a closer inspection of the water structure at the concentration of 12 mol % water, an arbitrary configuration from the TIP4P simulation is presented in Figure 3. The presence of dimers, trimers, tetramers, and even a ring structure involving five hydrogen-bonded water molecules can be observed. Of the 28 water molecules, 6 are dissolved among the acetonitrile molecules as monomers. However, the extreme increase in the rdf intensity and molecular association of water could be explained in the present case partly by the fact that the water potential, having been parametrized to give an optimal description of the strong many-body effects within the hydrogen-bonded network of pure water, overestimates the molecular interactions and structural correlation in the diluted solutions.

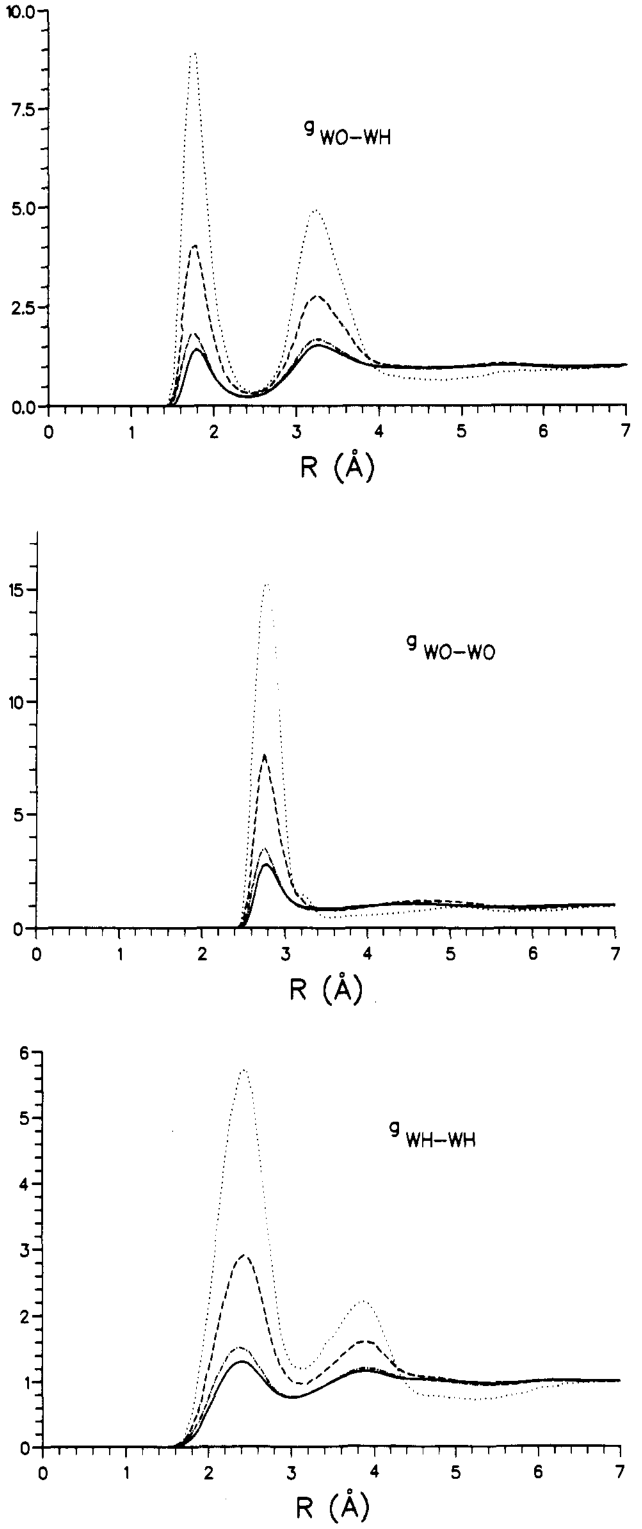

Figure 2. Three radial distribution functions between water molecules, $g_{\mathrm{WO\text{-}WH}}(R)$ (top), $g_{\mathrm{WO\text{-}WO}}(R)$ (middle), $g_{\mathrm{WH\text{-}WH}}(R)$ (bottom), as calculated with use of the SPC model in combination with Böhm's six-site acetonitrile model: (—) 100 mol % water, (-·-·-) 88 mol % water, (- - -) 50 mol % water, and (···) 12 mol % water.

---

(47) Soper, A. K.; Phillips, M. G. *Chem. Phys.* **1986**, *107*, 47.

(48) Jorgensen, W. L.; Madura, J. D. *Mol. Phys.* **1985**, *56*, 1381.

(49) Kleeberg, H.; Symons, M. C. R. *Faraday Discuss. Chem. Soc.* **1988**, *85*, 288.

Figure 3. Configuration from the simulation of 12 mol % water with the TIP4P model. The acetonitrile molecules have been removed for clarity.

Although both the SPC and TIP4P models produce this startling effect of extremely high rdf peak intensities and clustering at low water concentration, it is more pronounced in the simulation using Jorgensen's models. The explanation is probably not found in the description of the diluted water molecules themselves but in their environment, i.e., the differences between the two acetonitrile models. Böhm's model with a higher dipole moment, yielding strong electrostatic interactions, damps the water–water interactions more efficiently.

Acetonitrile–Water. Three of the eight intercomponent radial distribution functions are presented in Figure 4. The main site for the acetonitrile–water interactions is the nitrogen in acetonitrile. A sharp peak at a hydrogen-bonding distance of 1.85 Å is found in the rdf between the nitrogen in acetonitrile and the hydrogen in water, $g_{N\text{-}WH}(R)$ (Figure 4, top). Another, less intense peak appears at 3.3 Å, corresponding to the second solvation sphere. The intermolecular distances are exactly the same as those between the oxygen and hydrogen in water, although the maxima are less pronounced here if compared to the water rdf. In the mixture of 88 mol % water, the intercomponent interactions extend only to the firist hydration sphere (that is, the second and the third peaks are missing). The more extensive solvation structure appears in the 50:50 mixture and is further intensified at the 12 mol % water concentration.

The running coordination number down to the first minimum is 1.0 for the $g_{N\text{-}WH}(R)$ function of 88 mol % water when acetonitrile is the central molecule. In the 50:50 mixture, the corresponding coordination number is reduced to 0.4, while it is 0.1 in the 12 mol % water solution. Although acetonitrile is hydrated in aqueous solutions, the coordination numbers show that the intercomponent interaction does not lead to clusters.

The interatomic distances and coordination numbers from the $g_{C2\text{-}WH}(R)$ function (Figure 4, middle) essentially corroborate the above results for the hydrogen-bonding type of interaction at the nitrogen site. Also here the growth of the structure upon dilution of water is clearly seen. Similarly the first maxima in the rdf's between the water–oxygen and the nitrogen or nitrile–carbon also lie at distances appropriate for interaction at the nitrogen site. A comparison with the distances from the quantum mechanical calculations of Damewood and Kumpf[24] for this energywise favorable interaction site (which they denote with configuration 1a) shows that although the simulated distances are shorter, they differ by a constant factor.

Except for the hydrogen bonding at the nitrogen site, the methyl protons of acetonitrile also seem to interact with the water–oxygen in the mixture with low water concentration, as indicated by the $g_{O\text{-}H}(R)$ function (Figure 4, bottom). This rdf shows three peaks that originate from hydration at a distance of 2.3 Å and from the second and the third solvation scale. It is interesting to note that the ab initio calculations by Damewood and Kumpf[24] gave a fairly high binding energy for the arrangement where the water molecule resides in the cavity formed by C–H bonds of the methyl group in acetonitrile (refered to as configuration 1d in ref 24). According to their calculations, however, another configuration was found to be energywise more stable. It is the side-by-side arrangement where the dipoles of water and acetonitrile are oriented in a complementary fashion. The rdf's from the present simulation do not exhibit peaks that would agree with the distances calculated for that kind of arrangement.

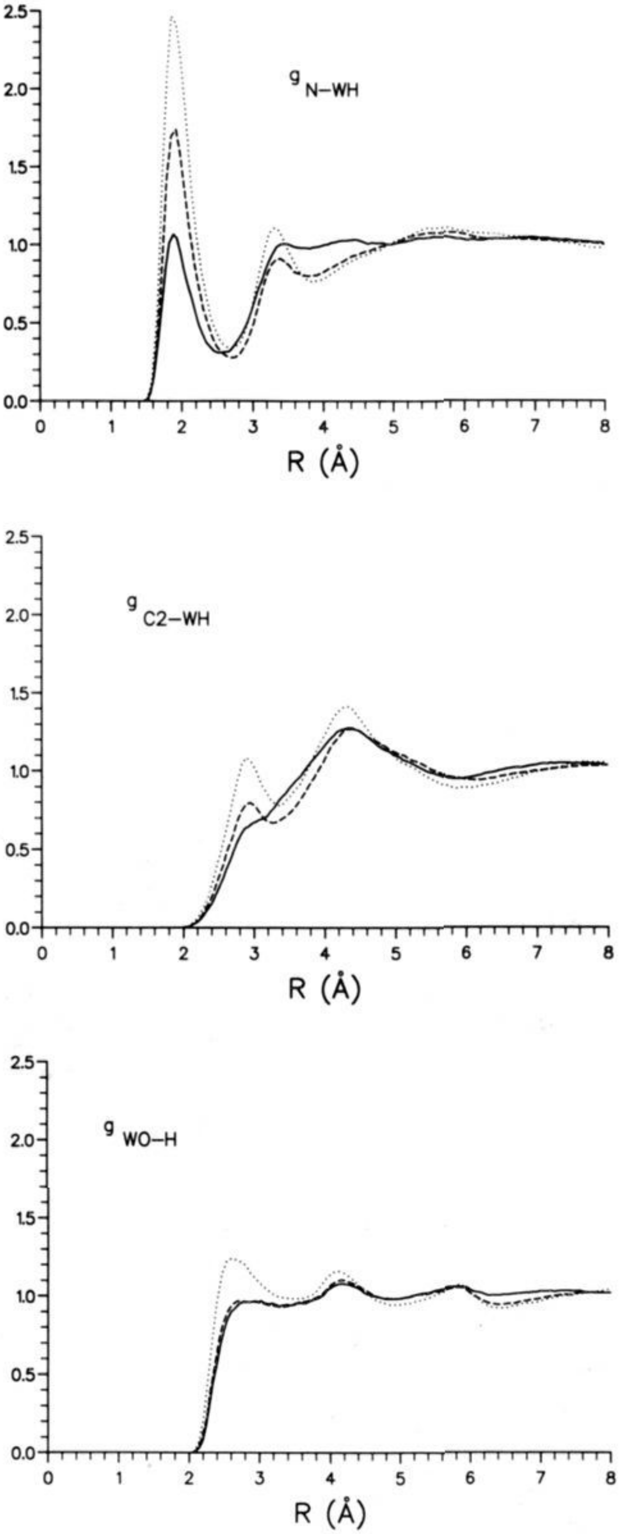

Figure 4. Three radial distribution functions between acetonitrile and water, $g_{N\text{-}WH}(R)$ (top), $g_{C2\text{-}WH}(R)$ (middle), $g_{WO\text{-}H}(R)$ (bottom), as calculated with use of Böhm's six-site potential model in combination with the SPC water model: (—) 88 mol % water, (- - -) 50 mol % water, and (···) 12 mol % water.

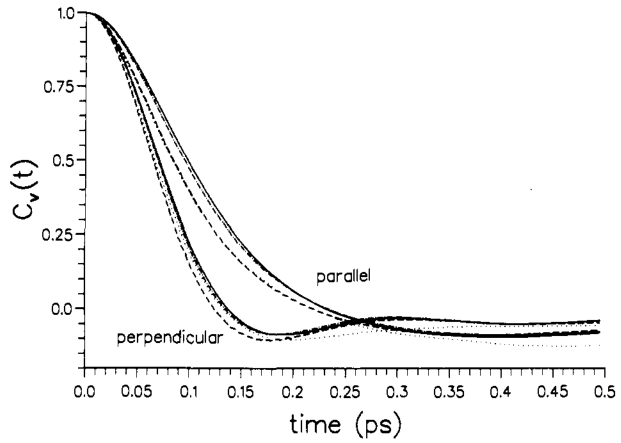

Figure 5. Time correlation functions of the linear velocity of acetonitrile, $C_v(t)$, at different mixture compositions as calculated by using Jorgensen's three-site potential model: (—) 100 mol % CH_3CN, (-----) 88 mol % CH_3CN, (---) 50 mol % CH_3CN, and (···) 12 mol % CH_3CN.

Table IV. Diffusion Coefficients (10^{-9} m^2 s^{-1})

	mol % CH_3CN				
	0	12	50	88	100
		CH_3CN			
Böhm model		3.83	6.001	5.15	4.90
Jorgensen model		3.14	3.53	3.89	3.99
NMR[a]		1.77	3.25	4.10	4.28
		H_2O			
SPC	4.35	4.11	4.50	5.81	
TIP4P	4.27	3.46	4.06	4.47	
NMR[a]	2.30	2.10	3.00	4.89	

[a] Reference 16 (298 K, corrected for viscosity).

The simulations performed by using Jorgensen's potential models gave virtually identical results for acetonitrile–water rdf's, except that the rdf maxima were not enhanced quite as much as in the simulations using the SPC and Böhm's models when moving toward lower water content. The weaker electrostatics of the acetonitrile model of Jorgensen are again evoked as the cause.

4. Dynamic Properties

Translation. The translational motion is characterized by the normalized time autocorrelation function (tcf) for the center of mass velocity of the molecule

$$C_v(t) = \langle \mathbf{v}(t)\mathbf{v}(0)\rangle / \langle \mathbf{v}(0)\mathbf{v}(0)\rangle$$

where v denotes the linear velocity and ⟨ ⟩ denotes the ensemble average. The self-diffusion coefficient is calculated from the time integral, τ_v, of the linear velocity tcf by the relation

$$D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}(t)\mathbf{v}(0)\rangle \,\mathrm{d}t = (k_B T/m)\tau_v$$

where m is the mass of the molecule.

The time autocorrelation function for the center of mass linear velocity of acetonitrile, which is a symmetric top molecule, has been separated to its components parallel and perpendicular to the main symmetry axis. These functions calculated by using Jorgensen's potential model are plotted in Figure 5. The smooth decay of the parallel component shows that acetonitrile diffuses preferably in the direction along with its top axis. The perpendicular component displays a negative portion significant of a rebounce in the translational motion; this "cage effect" is less pronounced in the simulations with Böhm's model.

The self-diffusion coefficients of acetonitrile simulated with the two different models are presented in Table IV together with some experimental data from Hertz and Leiter.[16] Jorgensen's potential model produces results that follow the experimental trend while, due to temperature fluctuations, the diffusion coefficients simulated with Böhm's model are too high, especially in the 50:50 mixture.

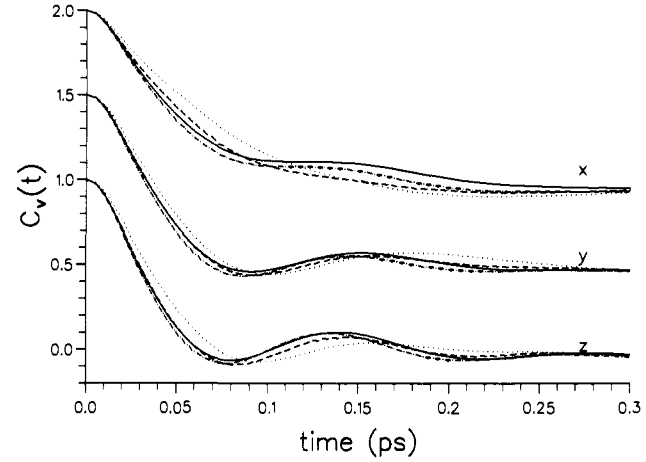

Figure 6. Time correlation functions of the linear velocity of water, $C_v(t)$, at different mixture compositions, the x-component (top), the y-component (middle), and the z-component (bottom) as calculated by using the TIP4P model: (—) 100 mol % water, (-----) 88 mol % water, (---) 50 mol % water, and (···) 12 mol % water.

In both cases, the agreement is better at high acetonitrile concentration. At low acetonitrile concentration, the slowing down of the observed self-diffusion coefficients is interpreted as hydration of acetonitrile. The simulations do not fully reproduce the effect, presumably because the diffusion of the hydrated acetonitrile is affected by the high mobility of water. This is particularly the case in the simulation with the SPC and Böhm models where the electrostatic intercomponent interactions are strong.

Concerning water, the autocorrelation functions were calculated for the three components of the center of mass velocity in x-, y-, and z-directions, defined in the molecular coordinate system so that the water molecule lies in the yz-plane while the z-axis coincides with the dipole axis. Each of the three components of the linear velocity, calculated with the TIP4P model, are plotted in Figure 6 separately at each mixture composition. The x-component is, as observed by Impey et al.,[50] distinctly different from the other two. Its only slightly uneven decay with a large integral correlation time shows that the translation in the direction perpendicular to the molecular plane is preferential and relatively unhindered. The oscillatory decay of the y- and z-components indicates that the motion in these directions is jerky. However, the oscillations become clearly damped as the water concentration is lowered to 12 mol %, indicating that the water molecules have broken free from their tetrahedrally hydrogen-bonded structure. The components of the linear velocity as simulated with the SPC water model are similar to the TIP4P curves except that there the x-component decays smoothly at all concentrations.

The self-diffusion coefficient for water were calculated as the average of the time integrals of the three velocity autocorrelation functions. The values are reported in Table IV together with the results from an NMR self-diffusion measurement performed by Hertz and Leiter.[16] The experimental data have been corrected for the difference in viscosity of the deuteriated substances. As 12 mol % acetonitrile is added to pure water, the experimental diffusion coefficient of water decreases slightly. The reduction—considered to be real since it occurs both in the simulated and experimental data—is rationalized by a minor enhancement of the hydrogen-bonded structure of water, i.e., a minor "hydrophobic hydration" effect. The diffusion coefficient increases with further dilution, suggesting a higher mobility of water molecules due to a distortion or breakdown of the hydrogen bond network.

In pure water, the ratio of the simulated and experimental diffusion coefficient of water is about 2. That the SPC model yields significant overestimates of the diffusion coefficient in pure water has been demonstrated before by, for instance, Jorgensen

---

(50) Impey, R. W.; Madden, P. A.; McDonald, I. R. *Mol. Phys.* **1982**, *46*, 513.

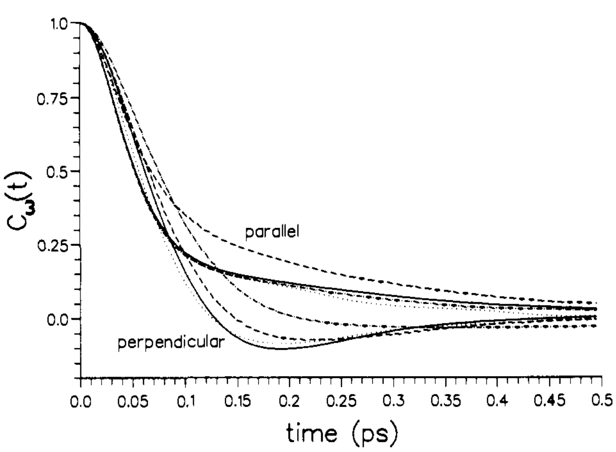

Figure 7. Time correlation functions of the angular velocity of acetonitrile, $C_\omega(t)$, at different mixture compositions, the parallel component (top) and the perpendicular component (bottom) as calculated by using Böhm's six-site model: (—) 100 mol % CH_3CN, (-----) 88 mol % CH_3CN, (- - -) 50 mol % CH_3CN, and (···) 12 mol % CH_3CN.

Table V. Angular Velocity Autocorrelation Functions of Pure Water

	no. 1 min		no. 1 max		no. 2 min	
	t (ps)	$C_v(t)$	t (ps)	$C_v(t)$	t (ps)	$C_v(t)$
			x-Component			
SPC	0.03	−0.59	0.065	0.18	0.105	−0.05
TIP4P	0.03	−0.57	0.065	0.18	0.105	−0.07
			y-Component			
SPC	0.025	−0.60	0.045	0.20	0.065	−0.11
TIP4P	0.025	−0.59	0.045	0.18	0.065	−0.09
			z-Component			
SPC	0.035	−0.47	0.065	0.09	0.095	−0.010
TIP4P	0.030	−0.51	0.060	0.10	0.115	−0.009

and co-workers[38] and Berendsen.[36] Here, too, Jorgensen's model gives a slightly better agreement with the experiment in the mixtures. The SPC values for the mixtures would be somewhat lower if the temperature fluctuation could be taken properly into account. The simulated values resemble the diffusion coefficients of the real liquids more in the diluted aqueous solutions than in pure water.

Angular Velocity and Reorientation. The angular velocity time correlation function is expressed by

$$C_\omega(t) = \langle\omega(0)\omega(t)\rangle/\langle\omega(0)\omega(0)\rangle$$

where ω is the angular velocity of the molecule.

The angular velocity of the symmetric top molecule of acetonitrile as described by Böhm's potential model can be resolved to its two components parallel and perpendicular to the main symmetry axis. These curves are presented in Figure 7. The perpendicular component exhibits a large negative region, indicating that the angular velocity is reversed due to strong intermolecular torques that make the molecule liberate in a cage formed by surrounding molecules. However, the negative region almost disappears at the concentration of 88 mol % acetonitrile. This agrees with the acetonitrile self-association being disrupted by adding a small amount of water. At 50 mol %, the cage effect reappears, and it is further promoted in the diluted solution of acetonitrile. This time the solvent cage should consist of water molecules. The ratio between the parallel and perpendicular correlation times of the angular velocity is invariantly about 2, indicating that both motions are affected equally by the presence of water molecules. Jorgensen's potential model describes acetonitrile as a linear molecule, and only the perpendicular rotational component is defined. According to this model, the cage effect is more intense though the electrostatic interactions are weaker.

The angular velocity of water was resolved to its *x*-, *y*-, and *z*-components in the principal coordinate axis system. The first maxima and minima of these curves as calculated with the two water molecules, SPC and TIP4P, in pure water are listed in Table V. The results are practically identical. Furthermore, according to both potential models, the curves at 100, 88, and 50 mol % water nearly coincide, while the 12 mol % curve differs strongly from the others. The oscillations of the curves, which originate from librations within the tetrahedrally hydrogen-bonded water structure, exhibit at 12 mol % of water a noticeably higher amplitude while they are shifted to lower frequencies.

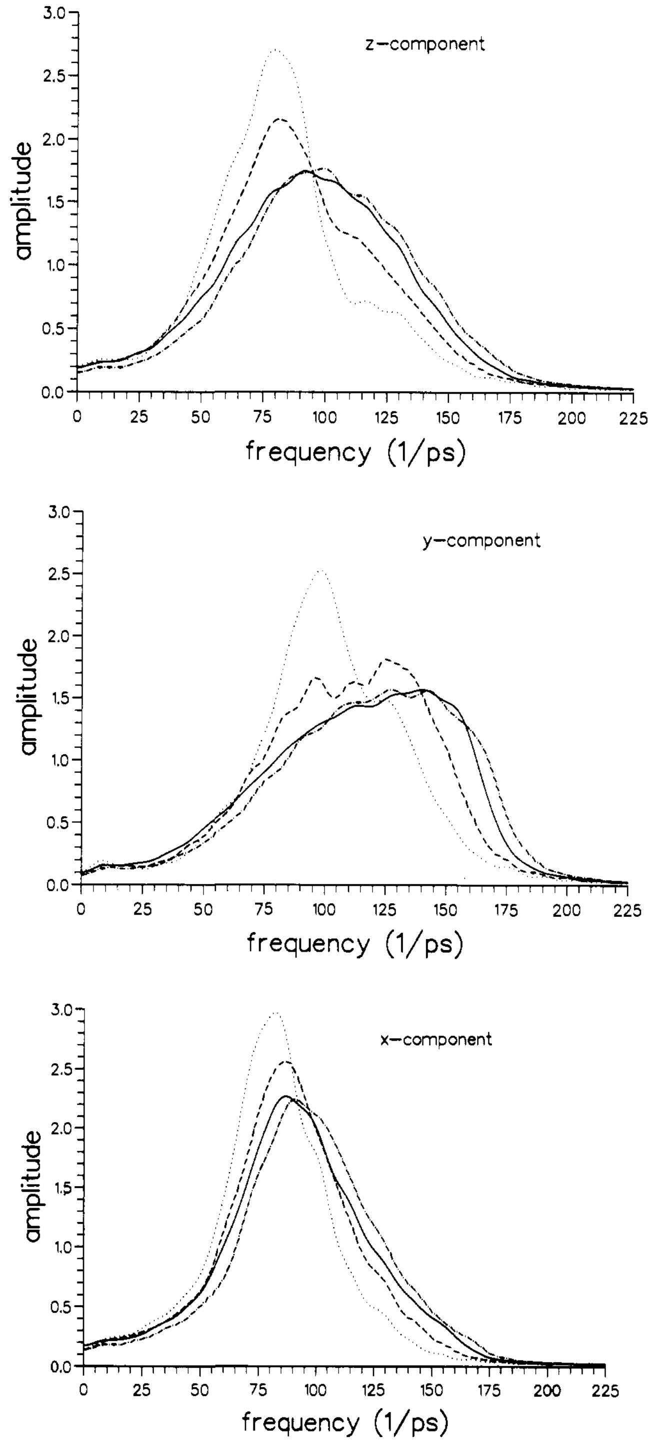

Figure 8. Power spectra from the principal components of angular velocity of water at different mixture compositions, the *x*-component (top), the *y*-component (middle), and the *z*-component (bottom) as calculated by using the TIP4P model: (—) 100 mol % water, (-----) 88 mol % water, (- - -) 50 mol % water, and (···) 12 mol % water.

In order to make the effect more perspicuous, the angular velocity tcf's were Fourier transformed. The power spectra extracted from the principal components of the angular velocity at different mixture compositions are displayed in Figure 8. The

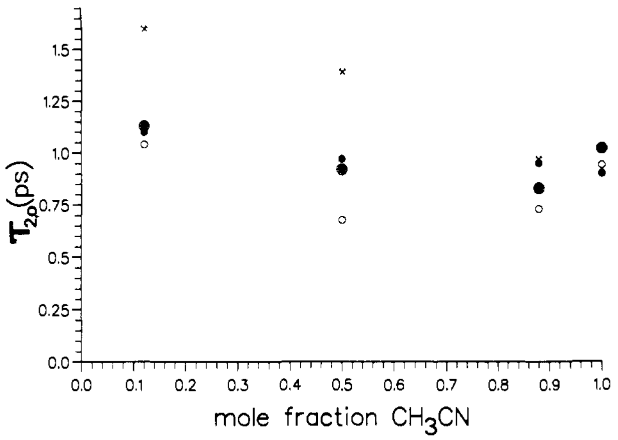

Figure 9. Reorientational correlation times of acetonitrile as a function of mixture composition: (○) Böhm's model, (●) Jorgensen's model, (●) ^{14}N NMR at 25 °C, and (×) ^{14}N NMR at the temperature of the Böhm SPC simulations.

frequency distribution in the power spectrum reflects the density of rotational states of the individual water molecules, which in turn depends on the intermolecular interactions and here particularly on the local hydrogen-bonding environment. It has been demonstrated that a shift of the maxima to higher frequencies reflects an enhanced H-bond structure and augmented local binding energy that are brought about by, for instance, hydrophobic hydration or lower temperature.[32,51] Actually, adding 12 mol % acetonitrile to pure water does cause such a shift toward higher frequency, although only a minor one. This is taken as further evidence of some hydrophobic hydration effect in the model systems.

At 50 and 12 mol % water, however, the maxima of the power spectra are shifted strongly to the opposite direction, i.e., toward a lower frequency. This means that the oscillations of the angular velocity originating from librations within the rigid, long-ranging structure subside and the water molecules gain in motional freedom upon dilution due to fewer and weaker H bonds. At the same time, the maxima of the power spectra become higher, while the distribution of frequencies becomes narrower. This indicates that the molecular motions have become more correlated—a phenomenon that was indicated by the enhanced intensities of the water rdf's as well and rationalized by the presence of water oligomers.

The reorientational correlation function can be written as

$$C_{l,m}(t) = \langle \hat{Y}_{l,m}(\Theta(t)\varphi(t))\hat{Y}^*_{l,m}(\Theta(0)\varphi(0))\rangle = \langle \sum_r D^{*l}{}_{m,r}(\Omega(t))D^l{}_{m,r}(\Omega(0))\rangle$$

where the reorientation of the molecules in dense fluids is expressed in terms of the spherical harmonics $\hat{Y}_{l,m}$ or the Wigner functions $D^l{}_{m,r}(\Omega(t))$. The argument $\Omega(t)$ is equal to the time-dependent changes in the Euler angles due to molecular reorientation with respect to the laboratory coordinate system. The time integral of the reorientational tcf is called the rotational correlation time and denoted by $\tau_{l,m}$. Presently the tcf's of the second order are inspected in particular as their time integrals can be compared to the reorientational correlation times derived from NMR.

The reorientational correlation times of acetonitrile from the simulations, $\tau_{2,0}$, are depicted in Figure 9. Since the experimental values give the reorientational correlation time for the main symmetry axis of the molecule, they are to be compared with $\tau_{2,0}$. Two experimental values are given, one at the same temperature as the simulations using the SPC and Böhm's models and the other at 25 °C. Although the values calculated with Böhm's potential model are a little higher than the observed ones, they follow the observed reorientational correlation times. Jorgensen's acetonitrile potential also produces data in reasonable accord with the experiments. The variations with concentration are minor experimentally and as simulated with Jorgensen's potential. Besides, temperature variations in the simulated systems obscure the detection of possible trends. Conclusions here are analogous to the discussion on the translational motion of acetonitrile. The slight initial decrease of the rotational correlation time as water is added to pure acetonitrile signifies disruption of the acetonitrile structure. At the high water concentration, the acetonitrile reorientation is slowed down by hydration.

Table VI. Reorientational Correlation Times for Water (ps)

	mol % CH_3CN			
	0	12	50	88
		SPC		
$\tau_{2,0}$	0.80	1.12	1.35	0.73
$\tau_{2,1}$	0.75	1.01	1.08	0.69
$\tau_{2,2}$	0.71	0.91	0.86	0.67
		TIP4P		
$\tau_{2,0}$	0.75	1.03	0.88	0.82
$\tau_{2,1}$	0.75	1.00	0.85	0.78
$\tau_{2,2}$	0.80	0.99	0.86	0.85
NMR(^{17}O)*	2.03	2.11	1.77	1.13
NMR(^{17}O)#	2.03	1.53	1.12	1.00

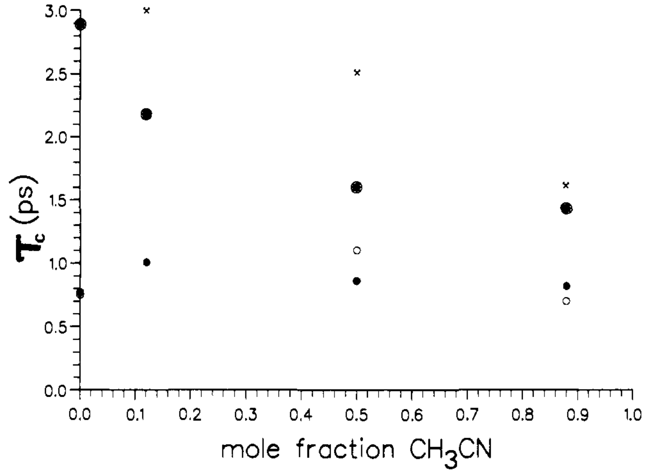

Figure 10. Reorientational correlation times of water as a function of mixture composition: (○) the SPC model, (●) the TIP4P model, (●) ^{17}O NMR at 25 °C, and (×) ^{17}O NMR at the temperature of the Böhm SPC simulations.

The reorientational correlation times of water with $l = 2$, $m = 0$, 1, or 2, are reported in Table VI. It can be observed that the TIP4P model gives a slightly less anisotropic description of the reorientation of water. Since water is an asymmetric top molecule, no simple relation exists between the effective correlation time from the ^{17}O relaxation and the calculated values. Instead, an arithmetic mean was deduced for comparison with the experiment. The reorientational correlation times of water are plotted in Figure 10. The experimental rotational correlation times at 25 °C, deduced from oxygen-17 relaxation, increase upon dilution with 12 mol % acetonitrile, evidently because of enhanced water structure. But in the mixtures with lower water content, the water molecules seem to gain motional freedom. The values calculated with SPC and TIP4P models are very similar, particularly if the differences in temperature are born in mind, and quite insensitive to the mixture concentration. The simulations render too rapid a reorientation in the pure water. The observed values, however, approach the simulated values as the water concentration diminishes, just as the self-diffusion coefficients did. This leads to a better agreement between the simulated and observed dynamics in the diluted solution of water.

5. Concluding Remarks

The questions concerning the structure in the liquid mixtures that we have wanted to clarify are the following: (i) Does acetonitrile function as a structure promoter or breaker in the

---

(51) Zichi, D. A.; Rossky, P. J. *J. Chem. Phys.* **1986**, *84*, 2814.

water-rich region? (ii) Can microheterogeneity be detected in the intermediate concentration range? (iii) Does addition of water disrupt the arrangement of pure acetonitrile? Do the water molecules associate to any extent in diluted aqueous solutions?

Adding acetonitrile to water causes an enhancement of the radial correlation of water, which persists even at the low water concentration. Water and acetonitrile interact strongly, preferably through hydrogen bonding at the nitrogen site. The interactions are intensified upon dilution of water. The acetonitrile structure remains relatively intact in the aqueous solutions. At low acetonitrile content, the close arrangement of the acetonitrile molecules with their dipoles antiparallel, remains.

The enhancement of the water rdf intensity in diluted solutions is rationalized by the presence of water dimers, trimers, etc., rather than the extensive hydrogen-bonded network prevalent in pure water. Although these oligomers move more freely than the structured water, the translations and rotations of the participating water molecules take place in a more concerted manner, thus resulting in enhanced radial correlation. The oscillations of the angular velocity correlation functions of water shift noticeably toward lower frequencies at low water content, also indicating a breakdown of the H-bond structure. Besides, the heightened amplitudes of oscillation observed in the power spectra of the angular velocity correlation functions signify more highly correlated molecular motions fully in accord with the interpretation of the water rdf results. It is of interest to note that recent results from IR spectroscopic measurements on water–acetonitrile mixtures[52] do not contradict the simulation results.

Due to the obvious difference between a six-site and three-site model, the two sets of acetonitrile rdf's differ somewhat in outlook. The simplified model does not illuminate the methyl group interactions in detail. The two water models produce similar static results despite the difference of SPC being a three-site and TIP4P a four-site model. Both acetonitrile potentials reproduce the observed dynamics in a satisfactory manner. It seems that the potential models for water, known to yield a good structural description but somewhat excessive mobility in the pure liquid, here, in the diluted solutions (where the hydrogen-bonding network is about or has collapsed) overestimate the structural correlation to some extent but are in better accord with the observed dynamics.[53]

A general feature of the calculated dynamic properties is that they are fairly insensitive to the varying concentration. At the outset, this was thought to be typical only of weakly interacting systems such as acetonitrile–chloroform, but the present investigation of the strongly interacting system of water and acetonitrile demonstrated that the same statement applies here as well. In order to reproduce the concentration dependence of dynamic properties, it appears necessary to reparametrize the potentials at each concentration.

In the case of rigid molecules, the potentials are best optimized by scaling the fractional charges by a constant factor. The charges in the acetonitrile model of Jorgensen had been initially chosen so as to mimic the ab initio results of Damewood and Kumpf[24] in combination with the TIP4P model for water. We tested Böhm's acetonitrile model in the same manner in conjunction with the SPC water potential in the four energywise most likely orientations. The latter potentials rendered essentially the same energy minima at identical distances as the ab initio calculations, and thereby also as the Jorgensen's potentials. This testifies to the close resemblance of two sets of potentials in describing the acetonitrile–water interaction, and a natural consequence is the similarity of the results.

Acknowledgment. This work has been supported by the Swedish Natural Science Research Council. We express our appreciation to Dr. Arnold Maliniak for interesting discussions.

Registry No. H_2O, 7732-18-5; CH_3CN, 75-05-8.

---

(52) Prof. J. Lindgren, Uppsala University, private communication.

(53) As pointed out by the reviewer, the above results—particularly as the water is diluted—should be compared with a study by using a water model that explicitly includes the polarizability of the molecules.