

Diffusion and Structure in Aqueous Amphiphile Mixtures: Water–Acetonitrile

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Data are reported for the intradiffusion of water in aqueous acetonitrile solutions at 0, 10, and 25 °C, at pressures up to 350 MPa. At low acetonitrile concentrations, the enhancement of D_{rel} ($=D(p)/D(0.1 \text{ MPa})$) is never as high as that in pure water under the same conditions. We find no evidence for structural enhancement in this system, though this has been proposed by some past workers in interpreting certain experimental results and molecular dynamics simulations.

Introduction

A range of dynamic interactions between solute and solvent molecules accompanies the solution of amphiphilic solutes in water. In dilute solution, the most important of these is the hydrophobic interaction. The solvent water molecules are believed to encapsulate the apolar solute or moiety and so become more “structured” in causing entropically driven association of the solute molecules. However, there is still a poor understanding of the hydrophobic effect at a molecular level^{1,2} and little direct experimental evidence for structural enhancement of water around apolar solutes.³

What then happens to water structure when an amphiphile dissolves? The increase in the rates of self-diffusion and fluidity with increasing pressure at low temperatures is primary evidence for an H-bonded structure in pure water.^{4,5} We,^{6,7} and others,^{8–11} have used measurements of intradiffusion (self-diffusion) in solutions as a function of temperature and pressure to examine the effect of amphiphilic solutes on water structure. In this paper, we extend that work with a study of acetonitrile solutions.

Acetonitrile (AN) is a very polar amphiphile, and its aqueous solutions are believed to exhibit microheterogeneity. They have been extensively studied by a variety of physical and chemical techniques due to the practical importance of this solvent system in chromatography, solvent extraction, and electrochemistry and because of its fundamental interest. Acetonitrile is an aprotic solvent, and its molecular interaction with water is through van der Waals interactions, principally those due to its large dipole moment.

Here we summarize what has been found for this system. Easteal¹² and Easteal and co-workers¹³ in their studies of water and acetonitrile intra- and interdiffusion discussed their results in terms of a structural model due to Naberukhin and Rogov¹⁴ which proposed “a microheterogeneous structure which contains globules of water in which water exists in a more ordered state than in pure water”.¹² It was suggested that the solution contains microphases of structured water and a disordered phase of water and acetonitrile. Similar ideas were used by other workers in examinations of thermodynamic and other data, and a summary has been given by Kovacs and Laaksonen.¹⁵ Marcus and Mignon¹⁶ have also argued strongly for microheterogeneity on

the basis of a broad examination of thermodynamic data. The sense of microheterogeneity that they employ is one of an association of like molecules over several concentric shells around a central molecule, rather than the formation of clusters in the sense of Naberukhin and Rogov.

In the water-rich region ($x_{\text{AN}} < \sim 0.15\text{--}0.3$), it has been suggested that acetonitrile occupies water cavities, dissolving interstitially.^{13,16} Armitage et al.,¹⁷ noting the exothermic mixing at low AN mole fractions (e.g., below $x_{\text{AN}} \approx 0.07$ at 5 °C¹⁸) have made the obvious suggestion that this is due to H-bonding between water and acetonitrile molecules. This effect is slightly larger at low temperatures and disappears above 35 °C, where the excess enthalpy of mixing, H^E , becomes positive at all concentrations.¹⁸ In water–ethanol, this happens at 110 °C.¹⁹ The endothermic mixing at higher concentrations has led to the conjecture that AN is a classical water “structure-breaker”. This is supported by the observation that its excess partial molar volume V_2^E is negative over the range 5–45 °C^{20,21} (and shows a small minimum at 5 °C,^{21,22} reminiscent of those of alcohols in water). V_2^E becomes less negative at high pressures.²³

In the acetonitrile-rich region ($x_{\text{AN}} > 0.75$), it has been suggested that water disrupts the acetonitrile structure.¹⁶ Between is the region of microheterogeneity, where molecules of each species are believed to be preferentially solvated by molecules of the same species. The consolute point ($T = -1.05$ °C, $x_{\text{AN}} = 0.38$) occurs in this region.¹⁷ The exact nature of the structure of the solution in the region of microheterogeneity has been difficult to establish. Some have argued that in the water microclusters the H-bonded structure is enhanced relative to that in pure water.^{14–16}

The difficulty of fitting models of this kind to bulk property data is well acknowledged, and insight into the nature of microheterogeneity has been sought from molecular dynamics simulations. These require good effective intermolecular potentials, sufficient numbers of molecules in the simulation, and runs of sufficient length to reduce spurious effects. Kovacs and Laaksonen¹⁵ combined molecular dynamics simulations at three compositions ($x_{\text{AN}} = 0.12, 0.50, 0.88$) with ¹⁴N (acetonitrile) and ¹⁷O (water) NMR relaxation time measurements. They found an enhanced radial correlation of water molecules in “dilute” solution ($x_{\text{AN}} = 0.12$), which was rationalized in terms of the presence of water oligomers or clusters, rather than the H-bonded network of pure water. They also concluded that close

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arrangement of antiparallel acetonitrile molecules persists at $x_{\text{AN}} = 0.12$, a conclusion reinforced by the subsequent simulations and RISM calculations of Matsumoto, Tanaka, and Nakanishi²⁴ at a rather lower composition, $x_{\text{AN}} = 0.0078$. The simulations of Satoh and Nakanishi²⁵ support the concept of microheterogeneity, with cluster formation, in the equimolar region (see Figure 6 of their paper).

More recent molecular dynamics simulations by Bergman and Laaksonen²⁶ examined solutions of acetonitrile mole fractions 0.11, 0.5, and 0.89 and concentrated on H-bonded structures. They found that at $x_{\text{AN}} = 0.11$, a water molecule bound to an acetonitrile molecule could still form part of the water network. At higher concentrations, there was no extended network of water molecules, rather clusters with acetonitrile molecules toward the periphery.

These studies have been supplemented by two spectroscopic papers, one employing measurements of IR intensities by multiple attenuated total reflection spectroscopy²⁷ and the other X-ray diffraction and IR band shifts.²⁸ The IR intensity study drew the conclusions (a) that at low AN mole fraction ($x_{\text{AN}} < 0.05$), where H^E is just slightly exothermic, the formation of $\text{OH}\cdots\text{NC}$ bonds exceeds the destruction of $\text{OH}\cdots\text{O}$ bonds, but there is no enhancement of water structure as the concentration of acetonitrile molecules is increased, (b) there is microheterogeneity in solution in the region $0.3 < x_{\text{AN}} < 0.5$, but there is no strengthening of water structure, and (c) that in the region $0.5 < x_{\text{AN}} < 0.85$ the fraction of $\text{OH}\cdots\text{O}$ bonds is such that there are only short chains or rings of water molecules and at higher concentrations water molecules are almost wholly bonded to acetonitrile molecules.

There is thus a development with time of the models used to describe this system. The earlier ones favor both microheterogeneity at intermediate concentrations and an enhancement of water structure in the water-rich microclusters, the later ones discounting enhancement of water structure.

There has been an interesting study of small molecular clusters generated from liquid droplets.²⁹ While these clusters are small, containing some tens of molecules, their structures, as revealed by mass spectrometry, nevertheless offer some insight into water–acetonitrile interactions. A wide range of structures was detected, but patterns were observed, with the most predominate clusters formed having the general formula $\text{H}^+(\text{CH}_3\text{CN})_{q+2}(\text{H}_2\text{O})_q$. The compositions observed correspond to structures where acetonitrile molecules individually H-bond (via the H-bond accepting, electron pair donating nitrile group) with water molecules forming the core of the cluster; that is, the acetonitrile molecules lie on the periphery. This contrasts with the results of experiments employing mixtures of water with small alcohols (methanol, ethanol, propan-1-ol, butan-1-ol, cyclohexanol, and benzyl alcohol). Here, the alcohols form “substitutional” clusters with water molecules; that is, water molecules and alcohol molecules can exchange positions in the outer layer of the cluster, each alcohol molecule being able to form up to two H-bonds in this way.

Further evidence for a difference in the behavior of acetonitrile and alcohols in water comes from the tracer diffusion results of Easteal and Woolf.⁸ They found the tracer diffusion of methanol and ethanol in water to be enhanced by pressure at 25 and 5 °C to a much greater degree than that of water itself. On the other hand, the tracer diffusion coefficient of acetonitrile in water decreased with increasing pressure at the same temperatures.

If there is structural enhancement of water in acetonitrile solutions, as suggested by some studies,^{12,14,15,28} one would

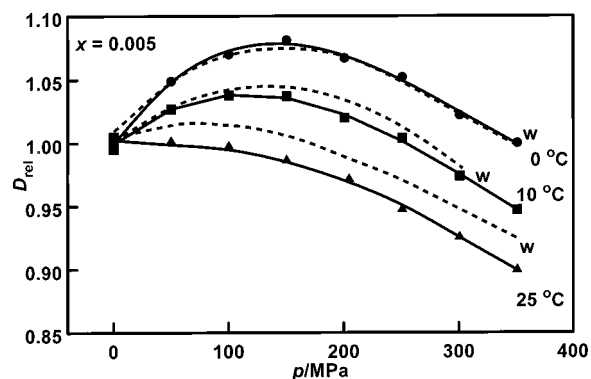


Figure 1. Relative intradiffusion coefficients for water in water– CD_3CN ($x_{\text{AN}} = 0.005$). Symbols: (●) 0 °C; (■) 10 °C; (▲) 25 °C. The dashed curves labeled “w” refer to the self-diffusion coefficient of pure water at the same temperatures.

expect to see an increase in the intradiffusion coefficient of water, relative to that at atmospheric pressure, with increasing pressure over and above that seen for the self-diffusion of pure water. This is what has been experimentally observed for propan-2-ol (2-PrOH)⁶ and 2-methylpropan-2-ol (TBA).^{6,7} Accordingly, we have made measurements both in dilute solution, where such structural enhancement has been postulated, and at the consolute point composition, where cluster formation has been suggested.²⁵

Experimental Section

Self-diffusion coefficient measurements were carried out by the NMR spin–echo technique at 20 MHz using a Be–Cu pressure vessel in a glass Dewar thermostat. The techniques used have been described previously.^{6,30,31} Results obtained at 0.1 MPa were checked against results from a second probe employing a different gradient coil used only at atmospheric pressure. The accuracy is estimated at $\pm 1\%$.

Deuterated acetonitrile (CD_3CN , Aldrich 99+%) was used without further purification. (Fully deuterated solutes are necessary, as the NMR apparatus employed does not resolve protons at its frequency of 20 MHz. This is governed by the magnetic field employed, which is defined by the dimensions of the pressure vessel and its thermostat.) High-purity water (resistivity, 18 $\text{M}\Omega\text{ cm}$) was obtained by passing the product of a Millipore reverse osmosis purification system through a Milli-Q ion-exchange system (Waters–Millipore Ltd). Solutions were prepared gravimetrically from these materials. The molar masses of water and CD_3CN were taken to be 18.0153 and 44.070 g/mol, respectively.

Results and Discussion

The data are presented in Table 1S of the Supporting Information and Figures 1–4 as relative diffusion coefficients, $D_{\text{rel}} (= D(p)/D(0.1\text{ MPa}))$. The data were obtained at three dilute compositions, $x_{\text{AN}} = 0.005$, 0.025, and 0.076 and one, 0.386, very near the consolute composition, 0.380.^{17,32} A summary is given in Table 1 in the form of polynomials in the pressure p at each temperature, 0, 10, and 25 °C.

Data at atmospheric pressure obtained at 0, 5, 10, and 25 °C (Table 2) are shown in Figure 5 for comparison with those for HTO in water– CH_3CN obtained by Easteal¹² at 5 and 25 °C. The results show a similar composition dependence with a change in sign in the isotope effect at about $x_{\text{AN}} = 0.105$ at 25 °C and 0.025 at 5 °C, presumably due to the use of CD_3CN in place of CH_3CN . The effect of using HTO as a measure of self-

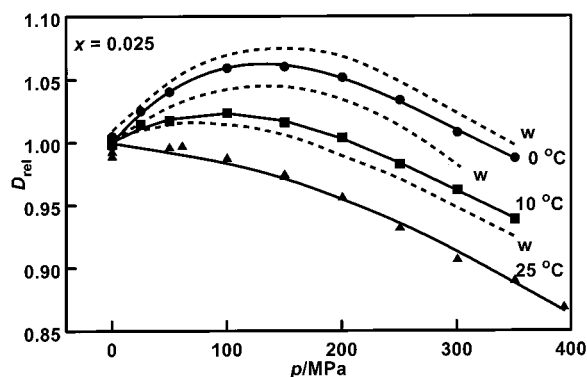


Figure 2. Relative intradiffusion coefficients for water in water–CD₃–CN ($x_{\text{AN}} = 0.025$). Symbols are same as in Figure 1.

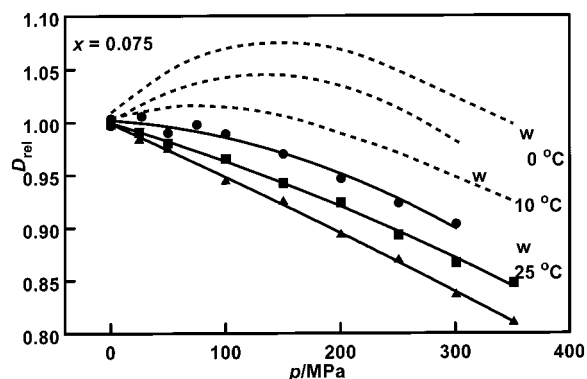


Figure 3. Relative intradiffusion coefficients for water in water–CD₃–CN ($x_{\text{AN}} = 0.076$). Symbols are same as in Figure 1.

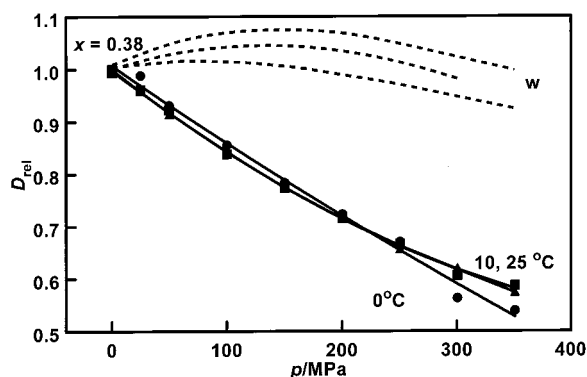


Figure 4. Relative intradiffusion coefficients for water in water–CD₃–CN ($x_{\text{AN}} = 0.386$). Symbols are same as in Figure 1.

diffusion in water is about 3%.³³ It can be noted that the consolute point and the solubility curves for water–CH₃CN (used by Eastal) and water–CD₃CN (used by us) differ very little, the UCST for the latter system being only 1.1 K above that of the former.³²

There is no enhancement of the intradiffusion coefficient relative to the atmospheric pressure value over and above that of pure water (Figures 1–3). This contrasts to what we have found in cold, dilute mixtures of 2-propanol⁶ and TBA^{6,7} with water. The enhancement is essentially that of water itself at the lowest temperatures and composition observed and becomes smaller with increasing temperature and acetonitrile concentration. By mole fraction 0.076 (Figure 3), the enhancement has disappeared almost entirely, though the decline of D with increasing pressure is still greater the higher the temperature.

There is therefore no evidence in the diffusion data to support any enhancement of water structure in the dilute acetonitrile solutions. This is in accord with the conclusions of Marcus and

TABLE 1: Coefficients for $D(\text{H}_2\text{O}; \text{H}_2\text{O} + \text{CD}_3\text{CN}) = D_0(1 + a_1p + a_2p^2 + a_3p^3)$ for Each Composition at Various Temperatures

x_{AN}	T (°C)	$10^9 D_0$ (m ² s ⁻¹)	$10^3 a_1$ (MPa ⁻¹)	$10^5 a_2$ (MPa ⁻²)	$10^8 a_3$ (MPa ⁻³)	δ (%) ^a
0.005 05	0	1.066	0.053 28	−0.098 94	0.0	0.4
	10	1.475	0.736 81	−0.385 37	0.378 32	0.3
	25	2.232	1.243 14	−0.571 07	0.617 24	0.3
0.025 00	0	1.015	−0.070 90	−0.068 54	0.0	0.5
	10	1.421	0.516 63	−0.323 72	0.360 97	0.2
	25	2.163	1.047 22	−0.510 66	0.574 49	0.2
0.076 01	0	0.908	−0.075 22	−0.088 96	0.0	0.5
	10	1.313	−0.333 07	−0.031 44	0.0	0.3
	25	1.988	−0.494 73	−0.012 33	0.0	0.3
0.386 20	0	1.233	−1.521 33	0.043 80	0.0	1.5
	10	1.651	−1.731 95	0.152 78	0.0	0.6
	25	2.323	−1.728 14	0.148 75	0.0	0.4

^a δ is the standard deviation of the fit expressed as a percentage of D_0 , the value of D at atmospheric pressure. ^b D_{rel} values were fitted rather than absolute D values.

TABLE 2: $D_0(\text{H}_2\text{O}; \text{H}_2\text{O} + \text{CD}_3\text{CN})$ at Atmospheric Pressure at 0, 5, 10, and 25 °C

x_{AN}	$10^9 D_0/\text{m}^2 \text{s}^{-1}$			
	0 °C	5 °C	10 °C	25 °C
0.00505	1.07		1.48	2.23
0.02449	1.01	1.20	1.42	2.15
0.02500	1.02		1.42	2.18
0.02500	1.01		1.43	2.16
0.02500	1.01		1.42	2.17
0.0753	0.93	1.14	1.31	2.01
0.0760	0.90		1.27	1.97
0.0760	0.90		1.27	
0.1257	0.96	1.14	1.34	2.03
0.2009	1.02	1.20	1.39	2.08
0.2510	1.06	1.25	1.44	
0.3819	1.22	1.43	1.62	2.32
0.3862	1.25		1.69	
0.5017		1.60	1.86	2.56

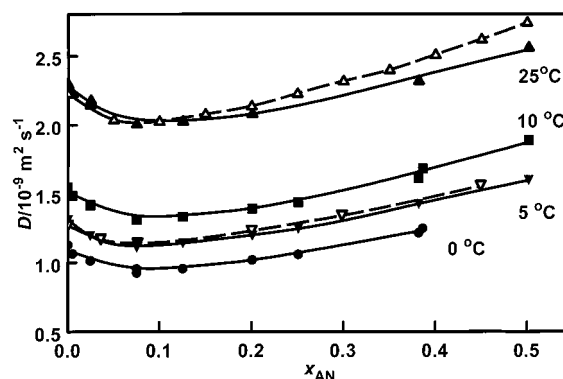


Figure 5. Diffusion coefficients for water in water–CD₃CN (this work, filled symbols) and of HTO in water–CH₃CN. Symbols: filled, this work; open, Eastal.¹²

Mignon,¹⁶ based on thermodynamic evidence, and of Bertie and Lan,²⁷ based on IR band intensities, but not those of Takamuku et al.,²⁸ which are largely based on IR band shifts.

We note that the inverse temperature dependence of the relative diffusion coefficients, that is, that D_{rel} is larger the lower the temperature, extends at least as far as $x_{\text{AN}} = 0.076$. Consequently, the water structure is largely retained (though not enhanced) to this composition. This is consistent with the picture of acetonitrile molecules bonded to water molecules, but not substituting for them in the water structure in the way alcohol molecules might, as proposed by Wakisaka et al.²⁹ In this context it is interesting, as mentioned in the Introduction,

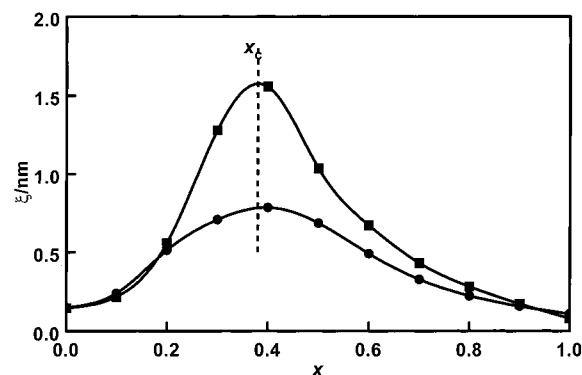


Figure 6. Correlation lengths for water–CH₃CN calculated from mutual diffusion coefficients and viscosities. Symbols: (■) 5 °C; (●) 25 °C. x_c denotes the composition at the UCST.

that the tracer diffusion of alcohols in infinitely dilute solution is enhanced considerably by pressure, whereas that of acetonitrile is reduced.⁸ This might be expected if acetonitrile molecules fit interstitially between water molecules; their motion would then be impeded by compression, even though that of water molecules is enhanced by the effects of pressure on the H-bonded structure.

At $x_{AN} = 0.386$, again there is no evidence in the diffusion data shown in Figure 4 to support any enhancement of water structure in solutions. Mutual diffusion (D_{12}) and viscosity (η) data¹³ do reveal the expected increase in the Ornstein–Zernicke correlation length, $\xi (=k_B T / (6\pi\eta D_{12}))$ where k_B is Boltzmann's constant,^{34,35} as the temperature (T) falls toward the UCST (Figure 6). This is associated with increasing concentration fluctuations, and the tendency for D_{12} to approach zero while the viscosity remains finite. If microheterogeneity, with water clustering, exists, it is not apparent from the diffusion results. The more usual temperature dependence of D_{rel} is observed: almost coincident isotherms, with perhaps a slightly weaker pressure dependence at the higher temperatures.

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Supporting Information Available: Table 1S contains all the high-pressure diffusion data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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