Disproving the Iceberg Effect? A Study of the Deuteron Quadrupole Coupling Constant of Water in a Mixture with Dimethyl Sulfoxide via Computer Simulations

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Abstract: The deuteron quadrupole coupling constant of water in the binary system water/dimethyl sulfoxide was calculated for different compositions at ambient conditions. To that purpose molecular dynamics simulations were combined with quantum chemical ab initio calculations in a cluster approach. The calculated values are in the same quantitative range as that observed in the experimental study of Gordalla and Zeidler,[1] although their dependence on composition differs.

Introduction

The fundamental chemical importance of aqueous solvation has prompted us to undertake computer simulations of mixtures of water and dimethyl sulfoxide (DMSO). One interesting goal in treating such mixtures is to gain insight into how a substance with rather aprotic properties affects the structure of the system. The link between the simulations and experiment is the deuterium quadrupole coupling constant, which has been measured for different water/DMSO mole fractions by Gordalla and Zeidler.[1]

Interesting structural effects, such as the hydrophobic effect, are possible in aqueous mixtures. Frank and Evans[2] defined the hydrophobic effect as the formation of crystalline-like regions in water when an apolar substance is dissolved in it. One explanation attributes the promotion of crystalline-like regions to the fact that solid water has more space for host−guest molecules in a clathrate-like manner within it (the so-called iceberg effect).[2] An alternative model, known as the flickering cluster model, proposes that small regions of given structure in water undergo sudden cooperative transitions.[3] Both of these models imply the formation of more rigid overall structures. Other approaches to the solvation of apolar molecules in water have been discussed in the literature. An overview of the area is given in ref 4.

Several factors complicate theoretical treatments of water/DMSO mixtures. To begin with, DMSO is bifunctional, having polar and nonpolar groups, and exhibits hydrophilic and hydrophobic interactions simultaneously. Furthermore, DMSO has a rather large dipole moment (4.3 D)[5] and a relatively free oxygen atom that can interact with water molecules. The way DMSO affects the water structure is therefore complex, and there are conflicting views on the effect of DMSO on the water structure with reports of both structure breaking[6−8] and structural enhancement.[9,10]

In 1986 Gordalla and Zeidler[1] reported a comprehensive NMR study of water−DMSO mixtures. Among other properties, they determined the deuterium quadrupole coupling constant (QCC) in deuterated water for mixtures of different concentrations by measuring the deuteron relaxation time T_1. In the extreme narrowing regime experimentalists usually use the following inverse proportionality for T_1:

$$\frac{1}{T_1} \propto \mathrm{QCC}^2 \cdot \tau \tag{1}$$

They measure T_1 and use an experimentally obtained τ, which is the rotational correlation time of the O−D vector. The more fundamental equation under these conditions is, however,

$$\frac{1}{T_1} \propto \langle V(0){:}V(0)\rangle \cdot \tau_{\mathrm{efg}} \tag{2}$$

where $V(t)$ is the electric field gradient in the laboratory coordinate system at time t, the colon marks an internal tensor product, and τ_{efg} is

$$\tau_{\mathrm{efg}} = \int_0^\infty \frac{\langle V(0){:}V(t)\rangle}{\langle V(0){:}V(0)\rangle}\,\mathrm{d}t \tag{3}$$

Equation 1 can be derived from eq 2 under the assumption that the origin of the QCC is completely intramolecular,[11] an assumption hardly fulfilled in the present case.

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The experimentally observed variation of the QCC as a function of the water mole fraction is remarkable. As DMSO is added to the water, the QCC drops at a mole fraction of water $x_{water} = 0.95$ from the pure water value to a value approximately equal to that of solid ice. With increasing DMSO concentration the quadrupole coupling constant rises to the gaseous water value. This behavior has been interpreted as implying that at low DMSO concentration rigidification of the water structure occurs, while at higher concentration the water structure breaks down. These results suggest that an iceberg effect is being observed.

Several computer simulation studies of DMSO−water mixtures have been reported, and a useful overview of work up to 1996 has been given by Hawlicka.[12] Vaismann and Berkowitz[13] studied three concentrations of water in DMSO, and found an enhancement of the structure at a water mole fraction of $x_{water} = 0.995$ and a breakdown at other mole fractions. However, in their conclusions they question the reliabilty of pair correlation functions as indicators of structure changes at different concentrations. Luzar and Chandler[14] found that the first molecular coordination shells become more structured with increasing DMSO concentration. A recent study by Borin and Skaf[15] addresses the problem in a similar context to that considered here. They consider the structure and dynamics of mixtures over a wide range of different concentrations, dealing mainly with radial pair distribution functions but also with the reorientational correlation times. They find similar behavior of the correlation time variation with composition to that observed by Gordalla and Zeidler. Recently, two additional studies[16,17] appeared on the solvation response of water/DMSO mixtures to ions.

The aim of this paper is to examine whether the computer simulations, which provide additional insights into the microscopic behavior of the water/DMSO system, show the same variation of QCC with composition as seen in the experimental measurements.

The QCC is very sensitive to changes in the bond length and hydrogen bond formation and, therefore, also is a sensitive indicator to changes in the local structure. It is probably much better suited to probe fine structural changes than, e.g., the pair correlation function (for which experiments of only limited accuracy are available).

Methods and Calculations

To obtain the quadrupole coupling constants we used the cluster approach applied previously by Hermansson et al. to study the solvent shift of the infrared spectrum of HDO[18] and in our group to calculate the D and ^{17}O QCC in pure water.[19−21] In this approach, clusters of molecules are extracted from classical simulation ensembles and treated as supermolecules in quantum chemical ab initio calculations, thereby making accessible properties which are not described under the classical formalism. An average over many clusters gives then a representative value for the corresponding property in the liquid.

Table 1. Simulation Input Data: The Macroscopic Water Mole Fraction x_{water}, the Number of Water Molecules n_{H_2O}, the Number of DMSO Molecules n_{DMSO}, the Experimental Density ρ, and the Cutoff Radius r

x_{water}	n_{H_2O}	n_{DMSO}	ρ [mol m^{-3}]	r [pm]
1.00	500	0	55259	1233
0.95	475	25	48692	1286
0.80	400	100	35605	1428
0.65	325	175	28012	1547
0.50	250	250	22844	1656
0.30	150	350	18139	1788

a. Simulation Details. To describe the intermolecular interactions, we utilized empirical potentials: the TIP3P[22] potential of Jorgensen for water−water interactions, the DMSO−DMSO potential of Rao and Singh,[13] and standard combination rules for the water−DMSO potential.[13] The Rao/Singh potential for DMSO was selected because it gives a better structure than the other available potentials, as shown by Liu et al.[23] All three intermolecular potentials are site−site potentials and have a Lennard-Jones functional form plus a Coulomb term. The methyl groups of the DMSO are treated as united atoms with atomic mass 15.03506 au. Since the structure of the water molecules plays a crucial role in determining the deuterium quadrupole coupling constant, their intramolecular motions were taken into account using the Dang−Pettitt potential.[24] The DMSO molecules, on the other hand, were constrained to be fully rigid using the SHAKE version of the Verlet algorithm. A rough estimate shows that the error in the quadrupole coupling constant due to this approximation is negligible.

As transfer of energy between translational, rotational, and vibrational motions is slow, the simulation was started with the correct proportion of energy in each degree of freedom, and during equilibration each corresponding temperature was scaled individually. Monitoring the individual temperatures during the sampling showed the correct equipartition of energy.

The mixture was simulated within a microcanonical or NVE ensemble (constant number of particles, volume, and internal energy), using molecular dynamics simulations with a time step of 0.25 fs and 500 molecules in a periodically repeating cubic unit cell. Long-range forces were approximated by the Ewald summation. The equilibration was carried out over a period of 20000 steps (5 ps) followed by 50000 (12.5 ps) simulation steps. During the first 15000 steps of the equilibration the individual temperatures were rescaled, while the remaining 5000 steps of equilibration were performed without rescaling. At every 1000th step (0.25 ps) a snapshot of the simulation was taken. From each of these 50 snapshots we selected two clusters for the quantum chemical calculation. As in the experimental work, six mole fractions of water x_{water} were considered, with their densities ρ set to the experimental density at ambient conditions (0.101 MPa and 298 K). Two runs, at $x_{water} = 0.3$ and 0.8, were performed for 500000 and 1 million steps, respectively, to study slow reorganization of the liquid (see below). Table 1 contains the input data.

b. Selection of the Clusters. To undertake quantum chemical calculations which represent the liquid, clusters of a reasonable size have to be selected from the simulation cell. Two problems arise: how to determine the closest neighboring molecules within a site−site interaction model, and the choice of an appropriate cluster size.

Several tests led us to choose the intermolecular distance between the deuterium of interest and the nearest oxygen as the criterium for the definition of a neighbor. As we have a mixture of quite different sized molecules, it turned out to be better to use a fixed radius for the cluster size rather than a fixed number of molecules in the cluster as used previously.[19] Hence, we define a cluster as the central water molecule containing the deuterium of interest and the collection of neighbor molecules lying within a cluster radius. On the basis of previous work calculating QCC's in pure water[19] as well as some further convergence tests, we elected to use a cluster radius $r_{cluster} = 500$ pm. This results in clusters containing an average of 8 molecules for

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$x_{water} = 0.3$ and 17 molecules for pure water. This gives an ample level of confidence in the convergence of the QCC with cluster size, considering that in the previous study the clusters each contained only 5 molecules, and it was demonstrated that even with these smaller clusters the QCC was well converged.[19]

c. Quantum Chemical Calculations. As the simulation treats the methyl groups of DMSO as single sites, these had to be replaced by real methyl groups in the construction of the supermolecular cluster. The carbon atoms were located at the exact position of the methyl sites, and the six hydrogen atoms were arranged so as to reproduce the equilibrium structure of DMSO. This was done using standard published structural values, and should not be critical for the value of the QCC for a deuterium on a neighboring water molecule.

For the ab initio calculations, we used the same basis set for water as in ref 19, as it was specially developed for the determination of the deuterium QCC. A high-quality uncontracted (6s4p4d) basis of Huzinaga was used for the deuterium of interest. For the oxygen atom that is directly bonded to that deuterium, the (9s5p) basis by Dunning[25] was enhanced with two polarization functions and contracted to give a [4s2p2d] basis. A smaller basis was located on all other nuclei: the Dunning[25] (4s)/[2s] basis for D or H, and basis sets by Roos and Siegbahn (7s3p)/[4s2p] for O and C, and (10s6p)/[6s4p] for S.[26] This scheme of employing basis sets of high local quality was developed in the authors' group in the early 1980s, and has since been successfully applied by many other authors for the determination of a range of different properties.

To calculate the electric field gradient we used the Gaussian- 98 program suite.[27] The calculations were performed at the SCF level, which yields good results for water, as has previously been shown.[19,28] A few reference calculations were made with second-order Møller–Plesset perturbation theory (MP2) to ensure that the neglect of correlation was reasonable. In its principal axis system the field gradient tensor is diagonal, the largest element corresponding to the quadrupole coupling constant after application of the conversion factor 672.0 kHz/au. This factor is based on a deuteron quadrupole moment of $Q = 286.0$ fm^2.[29]

Results and Discussion

a. Mole Fraction of the Clusters. When 100 deuterium atoms were selected randomly and the mole fractions of the clusters around each of these deuterium atoms were determined, an interesting observation was made. The average water mole fraction for the 100 selected clusters $x_{100,500\text{pm}}$ (x_{N,r_c} represents an average over N clusters, each with radius r_c, and the central water molecule is excluded) was consistently found to be elevated with respect to the entire system. The difference is large for systems with high DMSO concentrations, and small for those with low DMSO concentrations. This is an indication that the water molecules are aggregating in domains, as might be expected in mixtures involving hydrophobic substances. A less fascinating reason could have been poor selection of the clusters.

To further investigate this matter, we selected all deuterium atoms in the simulation box rather than just the 100 used for the quantum chemical calculations, and extracted clusters around each with $r_{cluster} = 500$ pm, to see whether the average mole fraction $x_{all,500\text{pm}}$ over all clusters was well represented by the hundred clusters in our sample. Table 2 shows in the first column the macroscopic mole fraction, in the second column the enhanced mole fraction averaged over the clusters in the sample, and in the third column the mole fraction averaged over all clusters. As is seen, there is an excellent agreement between the latter two, confirming that the 100 clusters are a good representation of the mixture, and that the deviation between the "local" mole fraction and the macroscopic, or system-wide, mole fraction is a characteristic of the model system rather than an artifact introduced by the sampling technique. As a further test, we extracted clusters from 100 randomly generated molecular arrangements (i.e. starting configurations, sampled prior to the commencement of the simulation) using the same procedure. This yielded a mole fraction equal to the macroscopic one, showing that our procedure for evaluating the cluster mole fractions was valid. It is hence clear that aggregation of water molecules in domains does in fact take place. The typical time evolution of this aggregation is shown in Figure 1. The numbers in parentheses of Table 2 are the results of long time runs, in which averaging was commenced only when the mole fraction stabilized. The plot in Figure 1 is from a run at $x_{water} = 0.8$, where the mole fraction appears stable after about 100 ps. For $x_{water} = 0.3$ it took only about 30 ps. As we will see, however, the QCC is not influenced by these local changes in concentration.

Table 2. Local Water Mole Fractions Obtained by Averaging over Different Total Numbers of Clusters and Different Cluster Radii, Compared with the Macroscopic Mole Fraction

x_{macro}	$x_{100,500\text{pm}}$	$x_{all,500\text{pm}}$	$x_{all,260\text{pm}}$
1.00	1.00	1.00	1.00
0.95	0.95	0.96	0.96
0.80	0.85 (0.85)[a]	0.84 (0.86)[a]	0.86 (0.88)[a]
0.65	0.72	0.70	0.75
0.50	0.56	0.57	0.63
0.30	0.38 (0.48)[a]	0.37 (0.45)[a]	0.44 (0.54)[a]

[a] Long time runs in parentheses, see text.

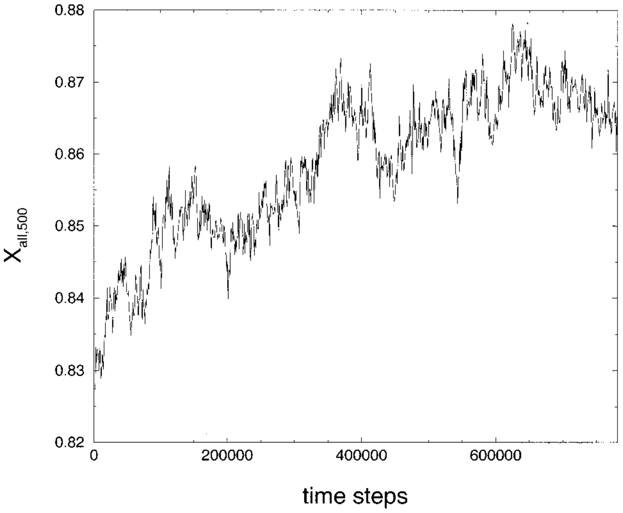

Figure 1. Local mole fraction, averaged over all clusters, during a long time run with a macroscopic mole fraction of $x_{water} = 0.8$.

Furthermore, we calculated the average mole fraction with $r_{cluster} = 260$ pm, $x_{all,260\text{pm}}$, choosing this radius as it is the summation of the two van der Waals radii of oxygen and hydrogen.[30] The results appear in the last column of Table 2. As expected, the deviation from the macroscopic mole fraction is even larger. This deviation is plotted in Figure 2, where we

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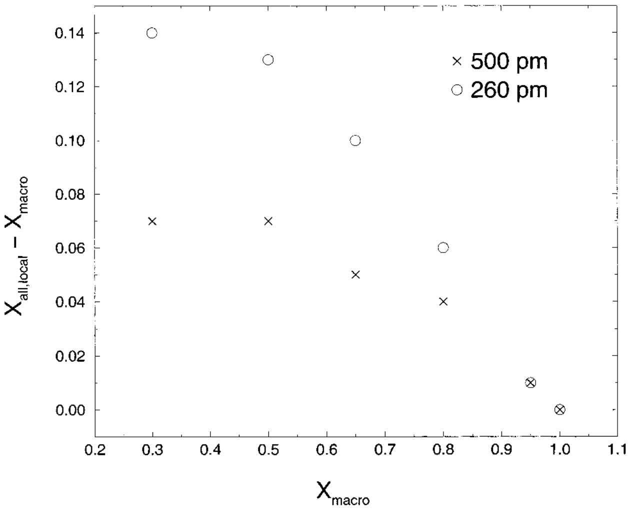

Figure 2. Deviations between the local water mole fraction and the macroscopic mole fraction, for two different cluster sizes. Circles, $r_{cluster} = 260$ pm; crosses, $r_{cluster} = 500$ pm.

Table 3. The Deuterium Quadrupole Coupling Constant and Asymmetry Parameter of Water/Dimethyl Sulfoxide Mixtures[a]

x_{water}	QCC_{avg}	QCC_{rms}	δQCC	QCC_{exp}	η_a	η_b	$\delta\eta$
1.00	253	258	5	255	0.160	0.164	0.004
0.95	266	271	5	213	0.160	0.163	0.003
0.80	274	282	7	242	0.160	0.162	0.003
0.80[b]	269	275	5	242	0.154	0.157	0.003
0.65	275	281	6	264	0.154	0.157	0.003
0.50	261	266	5	293	0.164	0.167	0.004
0.50[c]	269	273	5	293	0.155	0.157	0.002
0.30	273	278	5	317	0.152	0.154	0.002
0.30[d]	266	272	6	317	0.159	0.163	0.004

[a] All QCC values are given in kHz. The values with subscript avg are the arithmetic mean and those with subscript rms the root mean square of the cluster values. δ designates the standard error. [b] Long time run: the clusters were selected between steps 731000 and 780000. [c] A further 100 clusters selected from the same snapshots to see whether the dip in the curve at $x_{water} = 0.5$ is significant. [d] Long time run: the clusters were selected between steps 451000 and 500000.

denote the macroscopic mole fraction as x_{macro}. It is apparent that at lower water mole fractions the deviation becomes greater, and that the smaller the value of $r_{cluster}$, the higher the deviation.

Previous results[19] for pure water, showing that our snapshots are able to reproduce the pair correlation function of the whole system, together with the results in this section, indicate that our samples are representative of the ensemble.

b. Quadrupole Coupling Constants. The main goal of this work is to compare the experimental QCC's obtained by Gordalla and Zeidler[1] with the values from the simulation and, in particular, to see whether the calculated QCC exhibits a marked decrease at a mole fraction of $x_{water} = 0.95$. For consistency with experiment, the liquid state QCC was calculated not only as a simple mean (QCC_{avg}) from the individual clusters but also as the root-mean-square value (QCC_{rms}). The same applies to the asymmetry parameter $\eta = (V_{\alpha\alpha} - V_{\beta\beta})/V_{\gamma\gamma}$, where $V_{\alpha\alpha}$, $V_{\beta\beta}$, and $V_{\gamma\gamma}$ are the diagonal components of the electric field gradient in its principal axes system, the last one being the component with the largest absolute value. The values are provided in Table 3. Only one column of errors is given, as they are similar for the mean and rms values. In Figure 3 we plot QCC_{rms} [kHz] together with the experimental measurements QCC_{exp} [kHz]. The calculated QCC's do not correspond to the experimental values reported by Gordalla and Zeidler.[1] In marked contrast to the experimental results, we do not observe any significant dependence of the deuterium quadrupole coupling constant on the composition at all. This is reasonable, if the simulations correspond to water molecules existing mostly in liquid water-only domains, or if DMSO forms similar hydrogen bonds to water. As discussed earlier, a separation of water molecules from DMSO molecules is consistent with the elevated water mole fractions for the clusters compared to the macroscopic mole fraction.

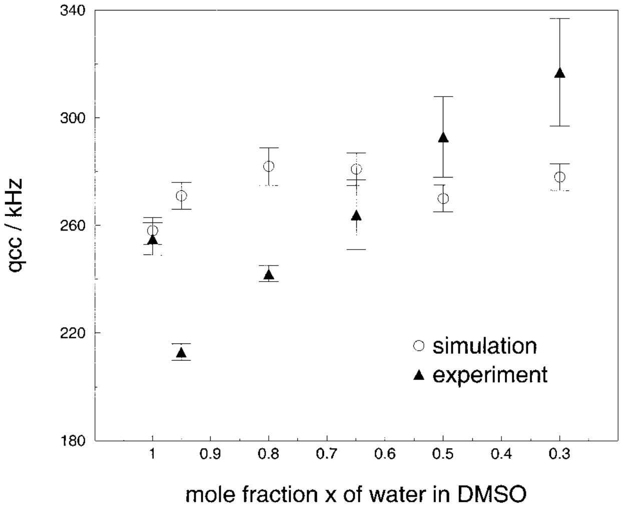

Figure 3. Deuterium quadrupole coupling constant versus the mole fractions of water, comparing the experimental results and those from this study. The experimental results are averages of results at 278, 288, and 298 K, which did not show a clear temperature dependence. Triangles: experiment; circles: simulations.

The simulated QCC values show a dip in the region of $x_{water} = 0.5$. To check whether this is reasonable, we performed calculations for a further 100 snapshots at this composition. The value $QCC_{rms} = 273$ kHz for these snapshots is within the statistical error limits of the former value, $QCC_{rms} = 266$ kHz, but also within that of the values at $x_{water} = 0.3$ and 0.65. This confirms that changing the concentration of DMSO has no effect on the QCC.

We performed additional calculations on the MP2 level for three clusters at $x_{water} = 0.3$, 0.5, and 0.8, respectively, to check whether the neglect of electronic correlation has any significant influence on the intermolecular contributions to the quadrupole couplings. Whereas the inclusion of correlation increased the overall couplings by 4−6%, the change in the intermolecular part was below 1%. Hence, we might safely conclude that inclusion of correlation would not improve the quality of the present results.

As the value for pure water is well reproduced, we assume that there are no serious errors on the technical side of the simulations. All values are also significantly different from the gas-phase value of 307 kHz.

Conclusions

The strong dip of the QCC at small DMSO concentrations in water/DMSO mixtures, as found by Gordalla and Zeidler, could not be confirmed. In fact, we find no significant dependence of the deuteron quadrupole coupling constant of the water on composition. A positive result would have dispelled doubts about the validity of approximations used in the evaluation of the experimental results. The latter are consistent with the existence of the iceberg effect and the hydrophobic interaction (the QCC is strongly dependent on the strength and number of hydrogen bonds, and is quite different for ice and liquid water). However, as the QCC is an average property of the bulk fluid, it cannot be safely concluded from the simulations that there are no microsopic changes in the local structure of the liquid with composition.

From comparison of the data obtained from the computer simulation with the experimental results it seems that the approximations used to obtain the experimental QCC are too crude. However, since a number of approximations are also used in the computer simulation (see Methods and Calculations above), the question of whether the model used in the simulation is too simple or there is an invalid approximation made in the interpretation of the experimental QCC is still open. Therefore, further investigations are in progress in our group to determine, within the same model framework, the electric field gradient time correlation function, which leads directly to the spin−lattice relaxation times. If we are able to reproduce the experimental relaxation times, the disagreement of the QCC will be a strong hint that certain assumptions underlying the evaluation of the experimental data are invalid, and we would hope to be able to show exactly which ones. If, however, we are unable to reproduce the experimental relaxation times, the theoretical model would need to be improved.

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