The intramolecular OH bond length of water in a concentrated poly(ethyleneoxide) solution. An NMR relaxation study

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The proton relaxation rates of normal as well as ^{17}O-enriched water and the deuterium relaxation rate in ^2H-enriched water were measured in 10 monomolal poly(ethyleneoxide) solutions. The $^{17}O-^1H$ intramolecular dipolar contribution to the proton relaxation rate was determined. From these experimental parameters the intramolecular OH-bond distance in the water molecule was calculated. It was found that this distance is increased by a small (1%) but significant amount compared to the pure water value. The results indicate that the solvent shows increased hydrogen bonding at the hydrophilic as well as the hydrophobic interface.

1. Introduction

The solute–solvent interaction, necessarily present for solvation, may induce changes in the molecular structure of both the aforementioned entities. When water is the solvent, the intramolecular OH bond length (r_{OH}) and to a lesser extent the bond angles are subject to change. These variations will generally depend on the type and amount of solute added. comparison of the values of r_{OH} of pure water in its three basic states (i.e. ice, liquid, and gas) clearly illustrates how the extent of hydrogen bonding, i.e. the intermolecular structure, is reflected in r_{OH} [1]. The aim of the present study is to establish the average intramolecular water OH distance within the hydration sheath of poly(ethyleneoxide) (PEO).

The determination of the intramolecular ^{17}O induced proton relaxation, R_{OH}^{intra}, is extremely useful in this matter since the magnitude of the nuclear interaction is extremely sensitive to the intramolecular OH bond length ($R_{OH}^{intra} \sim r_{OH}^{-6}$). R_{OH}^{intra} is determined by measuring the solvent–proton relaxation rate R_H^{exp} as a function of the ^{17}O mole fraction and determining the slope from data:

$$R_H^{exp} = R_{HH} + p_{^{17}O} R_{OH} . \tag{1}$$

A small correction for the intermolecular contributions to R_{OH} has to be applied. In pure water the ratio $R_{OH}^{inter}/R_{OH}^{intra}$ was estimated to be 0.02 [1]. In PEO solutions this contribution is unknown, but is taken to be the same as in pure water. The rate R_{HH} represents all other contributions to the proton relaxation such as inter- and intra-molecular $^1H-^1H$ dipole–dipole coupling in the solvent and cross relaxation between protons on the polymer and solvent.

However, due to rapid tumbling of molecules, the nuclear coupling constant and correlation time τ_{OH} determining R_{OH}^{intra} cannot be directly determined. The realization that τ_{OH} and the correlation time τ_D of the deuterium quadrupole interaction (χ_D) are basically equal (vide infra), irrespective of the details of the molecular motion, has provided the experimentalist with a useful additional source of information. Furthermore, a semi-empirical equation relating r_{OH} and the deuterium coupling constant χ_D has previously been proposed by this group [2], and facilitates the determination of r_{OH}, χ_D, τ_{OH}, and τ_D in an internally consistent manner.

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2. Molecular motion and structural properties of water studied with NMR

Nuclear magnetic relaxation is possible when the NMR-sensitive nucleus experiences a fluctuating interaction. The strength of this interaction is commonly referred to as the coupling constant. If molecular motions modulate the coupling on a timescale much shorter than $1/\omega_0$, ω_0 being the Larmor frequency, a special case arises called the extreme narrowing limit [3]. This case is usually encountered in liquids, and relaxation formulae are now reduced to relatively simple expressions. In the extreme narrowing limit deuterium (D) and oxygen (^{17}O) quadrupolar nuclear magnetic relaxation rates are given by

$$R_D = \tfrac{3}{8}(2\pi\chi_D)^2(1+\tfrac{1}{3}\eta_D^2)\tau_D \qquad (2)$$

and

$$R_O = \tfrac{3}{125}(2\pi\chi_O)^2(1+\tfrac{1}{3}\eta_O^2)\tau_O, \qquad (3)$$

where χ_D and χ_O are the corresponding quadrupole coupling constants. The modulation of the quadrupolar interaction is characterized by the effective correlation times τ_D or τ_O, respectively. The extent to which the electric field gradient deviates from axial symmetry is expressed by the asymmetry parameter η. For the determination of the OH bond distance only η_D is relevant. The gas values ($\eta_D = 0.135$) and ice values ($\eta_D = 0.12$) differ only slightly [1]. Although the corresponding values for liquid water are expected to be intermediary to those presented above, recent ab initio calculations [4] suggest that η_D may in fact be larger (0.164). Whatever the case, η_D has but a negligible influence on eq. (2), and will be discarded for reasons described below. For ^{17}O the gas values will be adopted $\eta_O = 0.75$.

The proton (^1H) relaxation resulting from the intramolecular dipolar coupling with ^{17}O is given by

$$R_{OH}^{intra} = \frac{35\hbar^2\gamma_H^2\gamma_O^2\tau_{OH}}{3r_{OH}^6}, \qquad (4)$$

where γ_H and γ_O are the proton and oxygen-17 gyromagnetic ratios respectively, $\hbar$ is Planck's constant divided by 2π, τ_{OH} is the correlation time for the reorientation of the ^1H–^{17}O internuclear vector and r_{OH} is the intramolecular O–H distance.

The principal axes of the D quadrupolar and ^{17}O–

^1H dipolar interaction tensors in the water molecule coincide; both lie along the O–H bond. If the small asymmetry parameter η_D is neglected, the correlation times τ_D and τ_{OH} are similar, irrespective of the details of the motion. To relate τ_D and τ_{OH}, there remains a small but unavoidable solute isotope correction. In pure water one has [1]

$$\tau_D(HDO)/\tau_{OH} = 1.05 \pm 0.02, \qquad (5)$$

a relationship which is assumed to be valid in binary solutions too.

The coupling constant χ_D and the OH bond distance r_{OH} are related by the expression [2]

$$\chi_D = \frac{595(\pm 11)}{r_{OH}^3} - 390(\pm 9)r_{OH}$$

$$(\chi_D \text{ in kHz}, r_{OH} \text{ in Å}). \qquad (6)$$

This relation is based on experimental as well as theoretical results. Recently Eggenberger et al. [4] showed that ab initio calculations of χ_D in liquid water could also be adequately described by eq. (6). The authors do however present an alternative empirical formula suggesting an intermolecular contribution to the D quadrupolar coupling constant χ_D.

Experimental determination of the rates R_D and R_{OH}^{intra}, and subsequent use of eqs. (2), (4)–(7), yields τ_D ($\approx \tau_{OH}$), χ_D and the intramolecular OH bond length r_{OH}. Additional information regarding molecular motion, namely τ_O, may be obtained from the ^{17}O quadrupolar relaxation rate (eq. (3)). For this purpose, the corresponding coupling constant is determined from an empirical relationship between χ_O and χ_D [5] based on coupling constant values from ice, water and solid hydrates

$$\chi_O = (38.214 \pm 1.293)\chi_D - (1650 \pm 302) \quad (\text{kHz}). \qquad (7)$$

Since the deuterium and oxygen-17 quadrupolar interaction tensors have different orientations in the H_2O molecule, the symmetry of the motion may be investigated by comparing the relative changes in correlation times τ_D and τ_O [6].

3. Experimental

Isotopically enriched water was purchased from

Monsanto Research Corp. (Miamisburg) and contained 9.9 (by weight) % ^{16}O, 51.1% ^{17}O, and 39.0% ^{18}O. All natural water was distilled, deionized and filtered with a Milli-Q water purification system (Millipore Corp.) fitted with a 0.22 μm filter. Chemicals were used without further purification unless stated otherwise. PEO ($M_w = 20000$ g mol^{-1}; $M_w/M_n = 1.4$) was obtained from Merck and was dialyzed against water to remove low molecular weight impurities. The solution was freeze-dried after which 10.3 monomol/kg H_2O (isotopically enriched) solutions were prepared. This was done in a cold room (4°C) to minimize exchange with atmospheric humidity. After flushing with nitrogen, samples were sealed and ample time (three days) was allowed for equilibration. Solutions were stored in the dark at 4°C to minimize biological and (photo)chemical degradation. The NMR tubes were home-made and fitted with a glass stopper. All laboratory utensils were cleaned prior to use by heating them in $NaHCO_3$ and EDTA solutions, respectively and subsequently rinsing with water.

Relaxation rates were determined on two different home-built pulse spectrometers at two magnetic field strengths (2.1 and 6 T). No field dependence in relaxation rates exceeding 2.5% was observed, the reason for this difference probably being a slight tem-

perature difference in sample temperature. Spin-lattice relaxation rates (R_1) were determined using the phase alternating inversion recovery method ($\pi-\tau-\pi/2$). Transverse relaxation rates (R_2) were obtained by the spin-echo method ($\pi/2-\tau-\pi$). Data sets consisted of 100 points which were fitted using a nonlinear least-squares procedure. In cases of ^1H relaxation, biexponential relaxation is observed since both polymer and solvent are present in their hydrogenated form. Biexponential fits were performed in a least-squares manner, the weight of the exponents being known, $N_{PEO}/N_{H_2O} = 0.37$, N_x being proportional to the number of spins of type x present in the system. Polymer and solvent relaxation rates differed by an order of magnitude, and could easily be separated in the fit.

The reorientational correlation times of water molecules can be expected to be influenced by small solvent viscosity effects between the different isotopic forms of water. The ^1H-, ^2H-, and ^{17}O-relaxation rates presented in table 1 have been corrected according to a linear correction formula originally presented in ref. [1].

Table 1
Longitudinal relaxation rates (R_1) of solvent nuclei (^1H, D and ^{17}O) in a 10.3 monomolal PEO solution, at various isotopic solvent compositions at 298 K. All relaxation data are corrected for solvent viscosity effects and therefore refer to H_2O dynamics. Deuterium R_1 values resulting from the DMSO/H_2O system at various solvent/solute ratios are also included [a]

	x_{H_2O}	p_{17O}	p_{18O}	R_H (1/s)	R_O (1/s)	R_D (1/s)
PEO	0.84	*	*	0.73		4.89 [b]
	0.84	0.090	0.069	0.81	393	
	0.84	0.230	0.176	0.91	386	
	0.84	0.301	0.230	0.97	386	
	0.84	0.395	0.302	1.03	386	
	0.84	0.511	0.390	1.16	384	
DMSO [c]	1	*	*			1.75
	0.95	*	*			2.47
	0.8	*	*			5.53
	0.65	*	*			7.95
	0.5	*	*			7.74
	0.3	*	*			6.49

[a] An asterisk implies natural abundance.
[b] Mole fraction D_2O is 0.024.
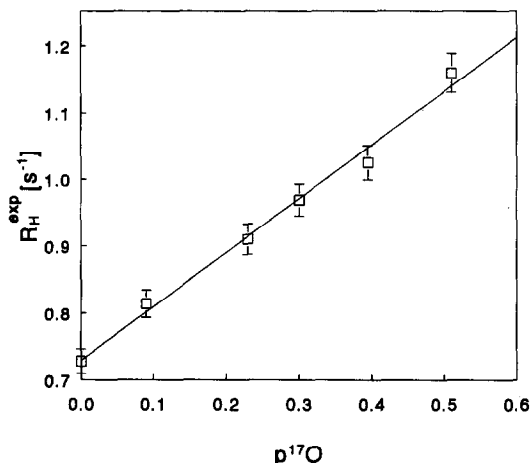[c] Taken from ref. [15]. Different procedures are used [21] to determine R_D in the limit $x_{H_2O} \to 1$.

Fig. 1. Solvent proton relaxation rates in 10.3 monomolal poly(ethyleneoxide) solutions prepared with ^{17}O-enriched water. Relaxation rates are shown as a function of the ^{17}O mole fraction $p_{^{17}O}$.

4. Results and discussion

Proton relaxation rates R_{HH}^{exp} at various ^{17}O mole fractions $p_{^{17}O}$ (corrected for solvent viscosity effects) are collected in table 1. In fig. 1 R_{HH}^{exp} has been plotted versus $p_{^{17}O}$. Linear least-squares analysis (eq. (1)) gives the intercept $R_{HH}=0.73$ s^{-1} and the slope

$R_{OH}=0.81$ s^{-1}. Correction for a 2% intermolecular contribution to R_{OH} yields $R_{OH}^{intra}=0.79$ s^{-1} [7]. Values for R_{OH}^{intra} and R_D established in the PEO/water, DMSO/water, and pure water samples are collected in table 2. Using these experimental parameters together with eqs. (2)–(7), the coupling constants χ_D and χ_O, the correlation times τ_{OH} ($\approx\tau_D$) and τ_O, and the intramolecular O–H bond distance r_{OH} are calculated. These results are also collected in table 2.

In the derivation of r_{OH} a number of assumptions/approximations have been made. Cross relaxation between polymer and solvent [8] contributes to the background rate R_{HH} only, and, hence, does not affect the ^{17}O-induced contribution (R_{OH}). The deuterium asymmetry parameter η_D has been neglected. It has been checked that a small value of η_D, as observed in gas and ice, has but a small influence on r_{OH} (<0.4%). The intermolecular ^{17}O-induced contribution to the ^1H relaxation is unknown, but is taken to be the same as in pure water. The neglect of this interaction gives an immaterial increase in r_{OH} of the order of 0.1%. The solute D isotope effects on the water reorientational dynamics is taken to be 5%, as is the case in pure water. Neglect of these effects results in a 0.4% increase in r_{OH}. since R_{OH} depends on the inverse 6th power of the OH bond distance, r_{OH} can be estimated with an accuracy of the order of 1%.

Table 2
Intramolecular O–H bond length in the water molecule (r_{OH}), the deuterium and oxygen-17 quadrupole coupling constants (χ_D and χ_O, respectively), the correlation time of the intramolecular OH vector (τ_{OH}) and the correlation time of the oxygen quadrupole tensor (τ_O). The solvent mole fraction is indicated by x_{H_2O}. All values are determined at 298 K. The corresponding values in ice and gas are included for the sake of comparison

Solution	x_{H_2O}	R_{OH}^{intra} (s^{-1})	r_{OH} (Å)	χ_D (kHz)	χ_O (MHz)	τ_{OH} (ps)	τ_O (ps)
H$_2$O [a]	1	0.28	0.98	250	8.1	2.0	1.97
PEO	0.85	0.79	0.99	230	7.0	6.1	7.06
DMSO	1	0.28 [b]	0.99	230	7.0	2.2	
	0.95	0.57 [b]	1.01	180	5.6	5.0	
	0.80	1.03 [b]	1.00	210	6.2	8.3	
	0.65	1.13 [b]	0.98	250	7.9	8.1	
	0.5	0.82 [b]	0.95	310	10.3	5.0	
	0.3	0.64 [b]	0.95	330	11.1	3.7	
ice [c]	1		1.01	210	6.4		
gas [c]	1		0.97	310	10.2		

[a] Taken from ref. [2].
[b] Data taken from table 1 in ref. [15] and processed according to eq. (1).
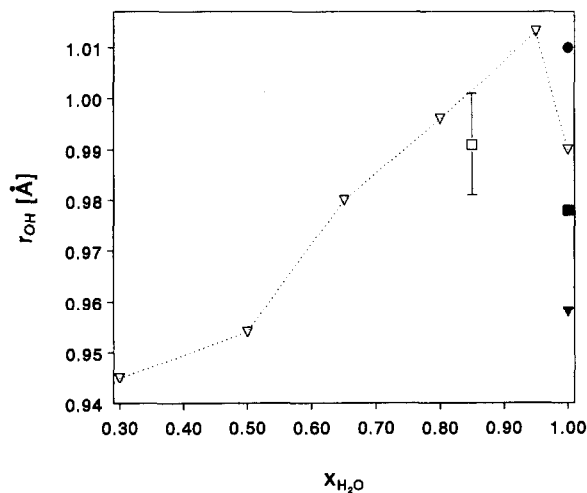[c] Taken from ref. [1].

Fig. 2. Average intramolecular O–H distance (r_{OH} (Å)) in water molecules in an (□) aqueous PEO solution and (▽) DMSO solution as a function of the solvent mole fraction (x_{H_2O}). Pure water (■), ice (●) and gas (▼) values are also displayed.

In a 10 monomolal PEO solution, the monomer-water ratio is about 1:5.5. Cavity surface calculations [9] show that the number of water molecules that can be packed around a PEO monomer lies in the range 5–7 [10]. All the water present in a 10 molal PEO solution must therefore be in contact with the polymer surface and may be typified as hydration water, accordingly. In view of the heterogeneous character of the polymer surface, the hydration water may be decomposed into several classes, reflecting the fact that relaxation rates and related properties of water adjacent to hydrophobic and hydrophilic interfaces cannot be assumed to be identical a priori. Since no attempt shall be made to analyze data in such detail, the results presented in table 2 should be interpreted as effective average quantities.

From the value of r_{OH} displayed in fig. 2 it is clear that addition of the polymer results in an increase of the average intramolecular O–H bond length. The value of r_{OH} increases from 0.978 to 0.991 Å. This may be taken as an indication of an increase in the strength of the average hydrogen bond. The magnitude of the OH bond distance indicates that this elongating effect cannot be *solely* attributed to increased H bonding between the small fraction of water molecules which form a hydrogen bond with the polymer ether atoms. In this picture, the H_2O

molecules which are not bound to the polymer should have a r_{OH} similar to that of pure water. Employing a two-phase model and realizing that only two O–H bonds (at most) are involved in hydrogen bonding with each ether atom, the length of these bonds would have to be approximately 1.05 Å in order to yield the observed average. Since this value is larger than r_{OH} in ice (1.01 Å), it seems likely that the water molecules adjacent to the hydrophobic interface also show an increase in r_{OH}. The latter increase in r_{OH} is probably due to enhanced hydrogen bonding between solvent molecules, since interaction between water and the hydrophobic interface is unlikely to elongate the intramolecular OH bond length. This increased interaction among solvent molecules is reminiscent of hydrophobic hydration [11]. When a hydrophobic entity is solvated in water an entropy reduction is observed. This reduction is claimed to be caused by enhanced solvent correlation at the hydrophobic interface.

The increased water interaction is also reflected by the enhancement of the correlation times τ_D and τ_O. The values are increased by a factor 3.4 with respect to the pure water values (table 2). In PEO solutions the small difference between τ_D and τ_O indicates a slight anisotropy in the water reorientational dynamics. This observation is in accordance with more extensive ^{17}O and D NMR results previously reported by Breen et al. [12]. In the latter work the anisotropy in the reorientational motion was obtained from the ratio of the [17]O and D relaxation rates. It was assumed that the coupling constants χ_O and χ_D are not affected by the polymer. However, the results collected in table 2 show that these constants are in fact decreased with respect to their pure water values (less than 13%). The relaxation rates ratio is, however, not sensitive to this effect because of the similar relative reduction in χ_O and χ_D. Accordingly, the conclusions reached in ref. [12] regarding the anisotropic motion of the H_2O molecule are still meaningful. One may add that in spite of the reduction in χ_O and χ_D, increased relaxation rates are observed. This shows that a reduction in coupling constants can be overcompensated for by an increase in correlation times.

The reorientational rotational correlation times of the aqueous component (τ_{H_2O}) in binary mixtures of water with low molecular weight (nonionic) or-

ganic liquids (acetone [13], DMSO [14] and THF [15]) have previously been reported. The initial addition of the organic component results in an increase in τ_{H_2O}. Further addition of the solute results in a decrease in τ_{H_2O}. Accordingly, a maximum in τ_{H_2O} is observed in the water-rich region. This suggests a reinforcement of the interaction among the water molecules. In contrast, the correlation times of the respective solutes (τ_{solute}) are hardly affected by the solution composition. The maximum in τ_{H_2O} and the insensitivity of τ_{solute} to the solvent mole fraction x_{H_2O} are in contrast with what is observed in the PEO/H$_2$O system. The combined results from refs. [12,16] show that although τ_{H_2O} increases as a function of x_{PEO} in the $0 \leqslant x_{PEO} \leqslant 0.4$ range, there is no sign of an inflection point indicating a maximum. A weak coupling between solute and solvent dynamics may be partly responsible for this difference. Analysis of the polymer deuterium spectral density of [D$_4$]-PEO in H$_2$O [10] shows that the main loss of correlation of the C–D bond orientation occurs in the 10^{-11}–10^{-12} s time regime. In the relevant concentration range, the correlation time characterizing this dynamic process increases by an order of magnitude (from 5 to 50 ps). This strong reduction in solute mobility (not shown by low molecular weight organics) is probably a consequence of the increasing entanglement of the polymer chains.

The dipolar ^{17}O contribution to the proton relaxation R_{OH}^{intra} has been determined in a number of two [15], and three component [2,7,17] (ionic/polyionic) systems. Comparison with the dimethylsulphoxide (DMSO)/water system studied by Gordella and Zeidler [15] is perhaps most meaningful. The reason being that DMSO and PEO are nonionic and feature heterogeneous interfaces, i.e. they both have hydrophobic and hydrophilic surfaces in contact with the solvent. The rates R_D and R_{OH}^{intra} in DMSO/water [15] were determined at various DMSO concentrations ($0.3 \leqslant x_{H_2O} \leqslant 1$) and are collected in tables 1 and 2, respectively. The corresponding values for the intramolecular OH bond lengths were calculated. The results are also shown in fig. 2. It is interesting to note how effective the PEO and DMSO molecules are in altering the internal water structure at their respective interfaces. In view of the dependence of r_{OH} on x_{H_2O}, it is best to compare values of r_{OH} at concentrations where both

species are exactly fully hydrated. Based on cavity surface calculations [9], the hydration numbers of PEO [18] and DMSO [1] are expected to be 6 and 20 [2], respectively. Accordingly, full hydration occurs at $x_{H_2O} = 0.85$ (PEO) and 0.95 (DMSO). Comparison of the data in fig. 2 shows that DMSO induces an increase in hydration water OH bond distance 2.6 times larger than PEO. It should be borne in mind that the DMSO and PEO data were obtained in two different laboratories and slightly different experimental procedures were used [3]. Accordingly, the value of 2.6 should be considered tentatively.

An interesting observation made by Gordella and Zeidler [15] is that the deuterium coupling constant χ_D depends strongly on the DMSO concentration. Initial addition of DMSO ($x_{solute} \approx 0.05$) causes a decrease in χ_D. Interestingly, this reduction in χ_D is more pronounced compared to the situation in low molecular weight ionic solutions [2,19]. Further addition of DMSO ($x_{solute} > 0.05$) results in a progressive increase in χ_D. At high solute fractions, χ_D approaches the gas value. The OH bond distance is related to χ_D via eq. (6). In fig. 2 it is seen that, after an initial increase in r_{OH}, the intramolecular OH bond length becomes smaller than the pure water value and, as more DMSO is added, eventually approaches the gas value. These observations indicate a breakdown of the hydrogen bond network at high solute fractions. As a result the internal structure of the water molecule becomes progressively similar to the situation in gas state.

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[1] QUANTA/CHARMm parameters from Release 3.2 were used in this study.

[2] To calculate the hydration number, the solute area necessary to accommodate a single water molecule was estimated to be 12.7 Å^2.

[3] The ^{2}H-relaxation rates at various DMSO/water ratios are presented in table 1, and refer to R_D at $x_{H_2O} \rightarrow 1$. Gordella and Zeidler estimated this limit by measuring R_D in samples with $0 \leqslant x_{H_2O} \leqslant 0.7$–0.8, and through subsequent extrapolation to $x_{H_2O} = 1$. A different approach was taken by our group; R_D values were determined in the $0.975 \leqslant x_{H_2O} \leqslant 0.985$ range and corrected for viscosity effects. Measurements on DMSO/water and pure water in our laboratory were consistently 10%–20% higher. Accordingly slight differences in derived quantities are most likely to be due to extrapolation errors and/or differences in sample temperature.

References

[1] D. Lankhorst, J. Schriever and J.C. Leyte, Ber. Bunsenges. Physik. Chem. 86 (1982) 215.

[2] R.P.W.J. Struis, J. de Bleijser and J.C. Leyte, J. Phys. Chem. 91 (1987) 1639.

[3] A. Abragam, Principles of nuclear magnetism (Oxford Univ. Press, Oxford, 1961) ch. 8.

[4] R. Eggenberger, S. Gerber, H. Huber, D. Searles and M. Welker, J. Phys. Chem. 97 (1992) 5898.

[5] I.J.F. Poplett, J. Magn. Res. 50 (1982) 397.

[6] C.W.R. Mulder, J. Schriever and J.C. Leyte, J. Phys. Chem. 87 (1983) 2336.

[7] J.R.C. van der Maarel, A.K. Jawahier and J.C. Leyte, Macromol. 23 (1990) 959.

[8] B. Benko, V. Buljan and S. Vuk-Pavlovic, J. Phys. Chem. 84 (1980) 913.

[9] M.L. Connolly, Science 221 (1983) 706.

[10] T.W.N. Bieze, J.R.C. van der Maarel, C.D. Eisenbach and J.C. Leyte, submitted for publication.

[11] F. Franks and D.S. Reid, in: Water, a comprehensive treatise, ed. F. Frank (Plenum Press, New York, 1972) p. 323.

[12] J. Breen, D. Huis, J. de Bleijser and J.C. Leyte, J. Chem. Soc. Faraday Trans I 84 (1988) 293.

[13] E. von Goldammer and H.G. Hertz, J. Phys. Chem. 74 (1970) 3734.

[14] E. von Goldammer and M.D. Zeidler, Ber. Bunsenges. Physik. Chem. 73 (1969) 4.

[15] B.C. Gordella and M.D. Zeidler, Mol. Phys. 59 (1986) 817.

[16] H. Tiemessen, J.R.C. van der Maarel, H.E. Bodde, H. Jousma and H.E. Junginger, J. Controlled Release 13 (1990) 73.

[17] J.R.C. van der Maarel, J. Magn. Res. 81 (1989) 92.

[18] T.W.N. Bieze, A.C. Barnes, C.J.M. Huige, J.E. Enderby and J.C. Leyte, submitted for publication.

[19] J.R.C. van der Maarel, D. Lankhorst, J. de Bleijser and J.C. Leyte, J. Chem. Phys. 90 (1986) 1470.