Neutron Diffraction Studies of Structure in Aqueous Solutions of Urea and Tetramethylammonium Chloride and in Methanol

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Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

Neutron diffraction measurements on aqueous 2–14 molal urea solutions have been made using nitrogen isotope substitution on the urea and hydrogen isotope substitution on the water. In addition, the hydration region of the tetramethylammonium ion in 2.0 m urea solution has been investigated by nitrogen isotope substitution on the TMA at 0.5 m and 2.0 m concentration of TMACl. The N-water correlation functions are very similar across the concentration range, and the H–H correlation function in concentrated urea solution is little changed from that of pure water. In the TMACl solutions the hydration peak is unchanged by the addition of 2.0 m urea. Thus urea appears to fit into the water network without causing significant perturbation of the average water structure or of the hydration region of another solute. In addition to the study of urea we have also made preliminary measurements to test the feasibility of carbon isotope substitution in liquid methanol.

1. Introduction

The structural implications of the addition of urea to aqueous solutions have been a matter of active debate since the original suggestion by Frank and Franks that urea increases the total entropy by mixing only with a denser ("less ordered") species of water, being unable to take part in tetrahedral hydrogen-bonding because of its planar geometry, and hence decreasing the mole fraction of "more ordered" water in the system [1, 2]. In spite of this, very little direct information on structure in urea solutions is available. The X-ray diffraction study of aqueous urea solutions by Adams, Balyuzi and Burge [3] illustrates the problems of interpreting total pair correlation functions $G(r)$ by tentative modelling. The measurements were made at 0.8 to 16.8 molal. Although there seemed to be some evidence of disruption of the water structure by urea at low concentrations, no unequivocal interpretation was possible because of the large number of pair correlations contributing to $G(r)$. We report here direct measurements of this structure using neutron diffraction with isotope substitution.

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This technique yields partial pair correlation functions [4, 5]. The differential scattering cross-section per atom in a liquid can be written

$$\frac{d\sigma}{d\Omega} = \sum_i c_i \bar{b}_i^2 + F(Q), \tag{1}$$

where $F(Q)$, the weighted total structure factor, is

$$F(Q) = \sum_{ij} c_i c_j \bar{b}_i \bar{b}_j [S_{ij}(Q) - 1]. \tag{2}$$

c_i is the atomic concentration of atom i, whose coherent neutron scattering length is b_i, and the sum is taken over all nuclear types. $S_{ij}(Q)$ is the partial structure factor relating to atom types i and j and is the Fourier transform of the partial pair correlation function (PCF) $g_{ij}(r)$. $Q = (4\pi/\lambda)\sin\theta$ is the amplitude of the usual scattering vector, θ is half the scattering angle and λ is the neutron wavelength.

Consider two solutions of identical solute concentration, in one of which atom M has been substituted by the isotope M′. The difference between the $F(Q)$ for the two solutions is

$$\Delta_M(Q) = \sum_i A_{Mi}[S_{Mi}(Q) - 1], \tag{3}$$

where

$$A_{Mi} = 2 c_M c_i b_i (b_M - b_{M'}) \quad \text{for} \quad i \neq M$$

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and

$$A_{MM} = c_M^2(b_M^2 - b_{M'}^2),$$

and the Fourier transform of the difference $\Delta_N(Q)$ is

$$G_M(r) = \sum_i A_{Mi}\, g_{Mi}(r). \tag{4}$$

$G_M(r)$ is a linear combination of just those pair correlations $g_{Mi}(r)$ involving the atom M, weighted by concentration and scattering length. It therefore gives us direct structural information on the environment of the atom M. Using three isotopically distinct solutions, $G_{MM}(r)$ can be obtained as a second difference, from a linear combination of the three measured differential cross-sections [6]. If two isotopes are mixed to make a third, using a proportion x of the isotope M, so that

$$b_{M''} = x\, b_M + (1-x)\, b_{M'} \tag{5}$$

then it can be shown that

$$x\left(\frac{d\sigma}{d\Omega}\right)_M + (1-x)\left(\frac{d\sigma}{d\Omega}\right)_{M'} - \left(\frac{d\sigma}{d\Omega}\right)_{M''} = \left(\frac{N_M}{N}\right)^2 x(1-x)(b_M - b_{M'})^2\, S_{MM}(Q). \tag{6}$$

It can be seen from (3) that the magnitude of the difference function $\Delta_M(Q)$ depends on c_M and b_M, and these put a lower limit on the concentration that can be used in practice. We used nitrogen isotope substitution and D_2O to look at aqueous solutions of urea at 2.0 molal, 7.0 molal and 14.0 molal concentration (approximately 25, 7 and 3.5 water molecules per solute molecule, respectively). The aim was to look at the intermolecular structure in the vicinity of the nitrogen atoms of urea. Since urea can hydrogen bond to water (or to urea) at the NH_2 group and the C=O group, the near neighbour structure in dilute solution would relate to water molecules bonded to the NH_2 group and possibly also those associated with the C=O group. To attempt to distinguish between contributions from hydrogen and oxygen atoms in the water and so get information on the water molecule orientations, we repeated the 2.0 m and 7.0 m measurements in mixtures of light and heavy water. This reduces the average scattering length for hydrogen in the water and should indicate the regions of $G_N(r)$ where hydrogen atoms are concentrated. The proportions of light water chosen were between 20% and 40%; a 40% hydrogenated solution reduces the hydrogen scattering length by 60% while avoiding the high incoherent scattering from ^1H which would result from using a larger proportion of light water. The solute urea will also be 40% hydrogenated since the amide hydrogen atoms are exchangeable.

Information on the water structure can also be obtained by using hydrogen/deuterium substitution in the water to measure the H–H and H–(O, C, N) correlation functions by the second difference method (6). We did this for 10 molal urea (5.5 water molecules per urea) using a prototype of the SANDALS liquids diffractometer at ISIS [7]. At this concentration any disruption of the bulk H-bonded network by urea would be evident in comparison with the H–H and O–H correlation functions from pure water.

We also made a preliminary investigation of the effect on the hydration structure of adding urea to aqueous solution of tetramethylammonium chloride (TMACl), $(CH_3)_4N^+.Cl^-$, for which we had previously characterised the hydration structure in pure water using nitrogen isotope substitution on the central nitrogen of the ion [8]. It was therefore of interest to see if addition of urea to the solution resulted in the hydration peak becoming broadened or otherwise changed in ways that suggested the water structure had been perturbed. For this we used N isotope substitution on the TMA ion in 0.5 m and 2.0 m TMACl in 2.0 m urea.

In addition to the work on solutions we tested the feasibility of carbon isotope substitution in pure liquid methanol (CD_3OD). The carbon-centred partial pair correlation function would clearly be of great interest in many chemical and biological studies. However, the difference between the scattering lengths for neutrons of the two stable isotopes ^{12}C and ^{13}C is less than 20% that between ^{14}N and ^{15}N and is not accurately known. With a high concentration of carbon (1/6 in methanol) in a well-characterised sample it should nevertheless be possible to measure the partial structure factor. We expected to be able to judge the success of the method from the three intramolecular peaks in $G_C(r)$ corresponding to C–D(Me), C–O and C···D.

2. Method

1. N substitution. The ^{15}N-enriched urea, $(^{15}NH_2)_2CO$, was bought from MSD Isotopes (Merck Frosst, Canada) or from Amersham International, at between 99% and 99.9% ^{15}N (manufacturer's specifications).

The D_2O was bought from Aldrich Chemical Co. ($\geqq$99.8% D). For the samples in pure D_2O the amide hydrogen atoms were deuterated by dissolving the urea in D_2O to allow exchange, followed by freeze-drying. The isotopically distinct solutions were made up in pairs using a dry glove-box for the manipulation of all deuterated materials to minimize contamination by atmospheric light water. An IR measurement of the O–H absorption was made to check that the residual light water content was adequately well matched in pairs of samples. The samples were as follows:

A) 2.0 m urea containing (i) ^{15}N and (ii) ^{14}N in (a) D_2O, (b) 20% H_2O, 80% D_2O and (c) 40% H_2O, 60% D_2O.

B) 7.0 m urea containing (i) ^{15}N and (ii) ^{14}N in (a) D_2O and (b) 30% H_2O, 70% D_2O.

C) 14.0 m urea containing (i) ^{15}N, (ii) ^{14}N D_2O and (iii) a 50:50 mixture of ^{14}N and ^{15}N.

TMACL in 2.0 m deuterated urea solution containing (i) ^{15}N TMACl and (ii) ^{14}N TMACl at (a) 0.5 m and (b) 2.0 m concentration of TMACl.

2. H/D substitution. 10.0 m ^{14}N aqueous urea solution in (a) H_2O, (b) 64% H_2O, 36% D_2O and (c) 36% H_2O, 64% D_2O.

3. Carbon isotope substitution. ^{13}C and deuterated methanol was bought from Aldrich Chemical Co. (99% ^{13}C, $\cong$99.5% D). The samples used were (i) $^{13}CD_3OD$ and (ii) CD_3OD. The deuteration of the two samples differed by less than 0.3% (manufacturer's specification).

The measurements on 2.0 m urea, on TMACl in urea solution and on methanol were made on the diffractometers D4 and D20 at the Institut Laue-Langevin, Grenoble; the measurements on 7.0 m urea were made on the 7C2 diffractometer at CEN-Saclay (Laboratoire Brillouin). The measurements on 14.0 m urea were made on the time-of-flight diffractometer SEPD at IPNS, Argonne National Laboratory, and those on 10.0 m urea on the time-of-flight diffractometer SANDALS (in development) at ISIS, Rutherford Appleton Laboratory. The measurement times ranged from 12 hours to 30 hours per sample, depending on count-rate and availability of time. The samples were contained in thin-walled cylindrical cells of Ti-Zr alloy, an incoherent scatterer, of diameters between 11 and 5 mm; the narrow (5 mm) cell was used for samples containing a high proportion of ^1H. For the H/D substitution experiment only, the samples were contained in flat-plate Al cells of thickness between 1 and 4 mm, depending on the concentration of ^1H in the sample. Up to 5 cm^3 of sample was typically used. For the measurements on reactor sources the scattering angle 2θ was varied over a maximum range of 1.8–130°, using a wavelength of either 0.70 Å or 0.94 Å, to give a range in Q up to a maximum of 14–16.5 $Å^{-1}$. The time-of-flight measurements covered a useful Q-range of up to 25–30 $Å^{-1}$. The lowest useful Q value obtained was 0.3–0.5 $Å^{-1}$. Measurements were made on the contained samples, the empty cell, background and a vanadium standard for the intensity calibration in units of barns (1 barn = 10^{-24} cm^2). The diffraction measurements were corrected for absorption and multiple scattering in the sample and cell and the total weighted structure factors $F(Q)$, (2), and partial structure factors, (3) and (6), calculated. The method used to invert the diffraction data to real space was found to be important for the small and often noisy partial structure factors obtained. Since the direct Fourier transformation of noisy and incomplete data can result in spurious features in the PCF, we have used the Monte Carlo method to calculate the PCFs for the urea data. This method aims to minimize spurious structure due to noise or truncation of the data by requiring the minimum information in the resulting PCF consistent with the input data [9].

3. Results

3.1. N Isotope Substitution on Urea

Figure 1 shows the weighted partial structure factors $\Delta_N(Q)$ obtained over the range of concentrations. The data from the solutions containing H_2O are noisier than the fully deuterated ones because of the high incoherent scattering from ^1H. The $\Delta_N(Q)$ have been scaled relative to each other by division by the sum of the weighting factors $\sum A_{N,i}$, (3). Figure 2 shows the partial PCFs $G_N(r)$ calculated from the data in Fig. 1a–c. For urea in D_2O, using two samples containing ^{14}N and ^{15}N, (4) becomes

$$G_N(r) = 2c_N(b_{N14}-b_{N15})[c_C b_C g_{NC}(r)+c_O b_O g_{NO}(r) + c_N/2(b_{N14}+b_{N15}) g_{NN}(r)+c_D b_D g_{ND}(r) + c_{O_W} b_{O_W} g_{NO_W}(r)+c_{D_W} b_{D_W} g_{ND_W}(r)] ,$$

where O_W and D_W denote oxygen and deuterium atoms of water molecules. $G_N(r)$ thus contains intramolecular distances N–D, N–C and N···O (Table 1)

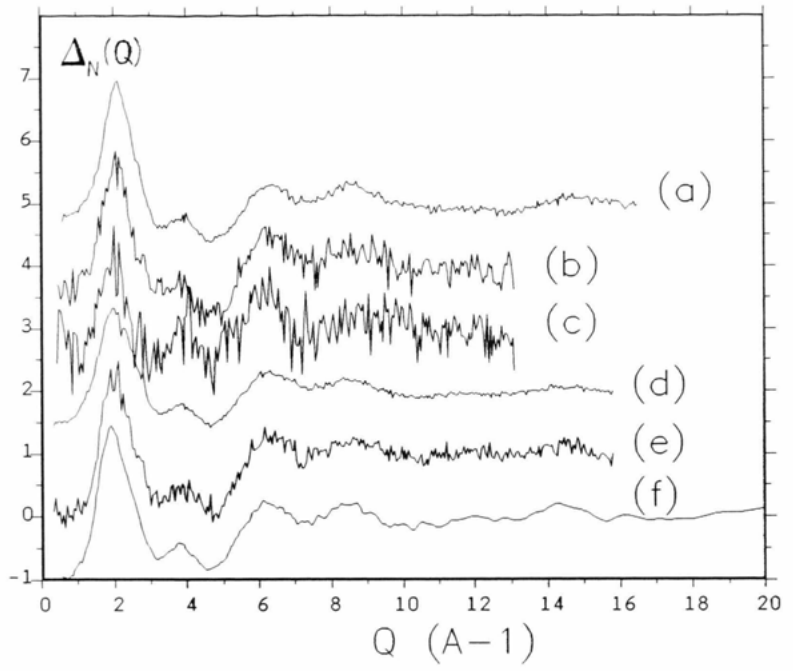

Fig. 1. Partial structure factors from nitrogen isotope substitution, translated on the y axis for clarity: (a) 2.0 m urea in D_2O, (b) 2.0 m urea in 20% H_2O, 80% D_2O, (c) 2.0 m urea in 40% H_2O, 60% D_2O, (d) 7.0 m urea in D_2O, (e) 7.0 m urea in 30% H_2O, 70% D_2O, (f) 14.0 m urea in D_2O.

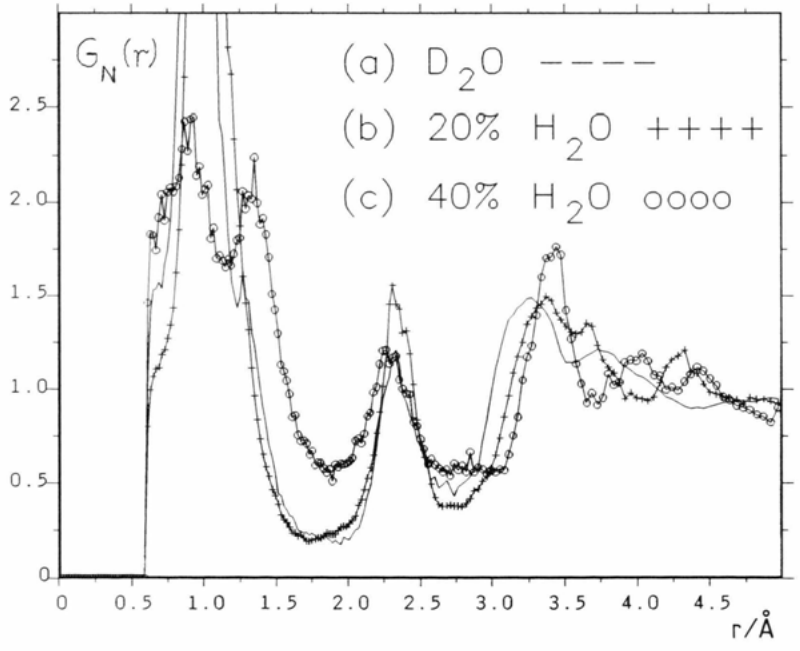

Fig. 2. Partial pair correlation functions from nitrogen isotope substitution:
(a) 2.0 m urea in D_2O (line), (b) 2.0 m urea in 20% H_2O, 80% D_2O (crosses), (c) 2.0 m urea in 40% H_2O, 60% D_2O (circles).

Table 1. Urea: intramolecular distances from nitrogen (123 K) [14].

Atom pair	ND	NC	NO	NN	ND	ND
Separation	1.00, 1.01	1.34	2.27	2.29	2.49	3.21

as well as the N · · · O_W and N · · · D_W distances and for a concentrated solution may include intermolecular urea · · · urea contributions. Table 2 shows the weights of the partial pair correlations contributing to $G_N(r)$. Comparing the weights of the partial pair correlations

with the total weight in the last column, it is seen that for the solutions in D_2O the urea-urea terms become relatively more important and the urea-water terms relatively less important as the solute concentration is increased. In Fig. 2a the region from about 2.5 to 4.5 Å corresponds to the water structure in the vicinity of the urea nitrogen atom. The lower region of r from about 0.75 Å to 2.5 Å corresponds to intramolecular structure and agrees with the known structure of urea to within better than 10%. Because of the asymmetry of the urea molecule about the nitrogen atom, there is some overlapping of intramolecular and intermolecular peaks in $G_N(r)$ in the region 2.5 to 3.2 Å. The structure in Fig. 2b, c should be the same and the curves should differ from Fig. 2a only because of the change in the weights of the N–D and N–D_W terms as the value of b_D and b_{D_W} is reduced due to an increase in concentration of ^1H in the sample (Table 2). It can be seen that there are also oscillations due to increased noise in the data, especially at higher values of r.

The $G_N(r)$ shown in Fig. 2 are normalised by division by the sum of the weighting factors $\sum A_{N,i}$. Consequently peaks corresponding to hydrogen/deuterium atoms are reduced in magnitude as the concentration of ^1H increases, while peaks corresponding to all other atoms are relatively increased in magnitude. Thus in Fig. 2c (40% H_2O) the peak at 1.0 Å corresponding to N–D_2 is much reduced in magnitude compared to Fig. 2a, but the N–C peak at 1.3 Å is relatively increased. The most interesting region of these data is from 3.0 to 3.5 Å, where a consistent trend with H_2O concentration can be seen. The edge of the intermolecular peak moves to higher r values as the concentration of H_2O is increased, while the height of the peak at approximately 3.4 Å from the nitrogen atom increases. This suggests that there is a higher concentration of hydrogen/deuterium atoms than of oxygen atoms in the region 2.8 Å to 3.3 Å and a higher concentration of oxygen atoms than of hydrogen/deuterium atoms at a distance of about 3.4 Å. At higher values of r there is no consistent trend with H_2O concentration and the oscillations are not thought to be significant.

Figure 3 shows $G_N(r)$ for 7.0 m urea in D_2O and in 30% H_2O, and for 14.0 m urea in D_2O. Three differences, which can be denoted $G_{14\text{-}15}$, $G_{14\text{-mix}}$ and $G_{\text{mix-}15}$, were calculated from the three $S(Q)$ obtained from the 14.0 m solutions. Only the best determined, $G_{14\text{-}15}$, is shown in Figure 3c. Comparing the 7.0 m solution in D_2O with that in 30% H_2O (Fig. 3a, b), the region between 3.0 Å and 3.5 Å may show the same trend with increasing hydrogen concentration as was seen in the 2.0 m data, but the effect is considerably less marked. The D_2O data also show some spurious peaks in the 4.0 Å region. Figure 4 shows the superimposed $G_N(r)$ for 2.0 m, 7.0 m and 14.0 m urea in D_2O in the intermolecular region. The comparison is not entirely straightforward because the relative weights of urea-water and urea-urea correlations depend on solute concentration. However, the intermolecular peak at 2.0 m and 14.0 m is very similar. There appears to be somewhat less structure at 7.0 m but we believe that this difference is not significant; the three $G_N(r)$ obtained from the measurements on 14.0 m urea showed approximately the same level of uncertainty. We conclude that no significant changes in intermolecular structure can be seen across the concentration range, in spite of the fact that at 7.0 m and 14.0 m urea $\cdots$ urea hydrogen-bonds (N–H $\cdots$ C=O) must be contributing in the near neighbour distance range.

3.2. *H/D Substitution*

The $g_{HH}(r)$ and $g_{H\text{-(O, C, N)}}(r)$ are shown in Figure 5. These functions do not correspond only to H–H and H–O distances between water molecules, but contain

Table 2. Weights of pair correlations: urea solutions; 1 barn = 10^{-24} cm^2.

Concentration	Solvent	A_{Ni} (mbarns)							$\sum A_{Ni}$ (mbarns)
		c_N	NC	NO	NN	ND	NO_W	ND_W	
2.00 m	D_2O	0.024	0.1094	0.0954	0.2594	0.4375	2.3846	5.4682	8.7545
2.00 m	20% H_2O	0.024	0.1094	0.0954	0.2594	0.3020	2.3846	3.7751	6.9259
2.00 m	40% H_2O	0.024	0.1094	0.0954	0.2594	0.1691	2.3846	2.1133	5.1312
7.00 m	D_2O	0.068	0.8754	0.7635	2.0739	3.4964	5.4537	12.4871	25.1500
7.00 m	30% H_2O	0.068	0.8754	0.7635	2.0739	1.8856	5.4537	6.7344	17.7865
14.00 m	D_2O	0.107	2.1498	1.8750	5.0982	8.5993	6.6966	15.3559	39.7748

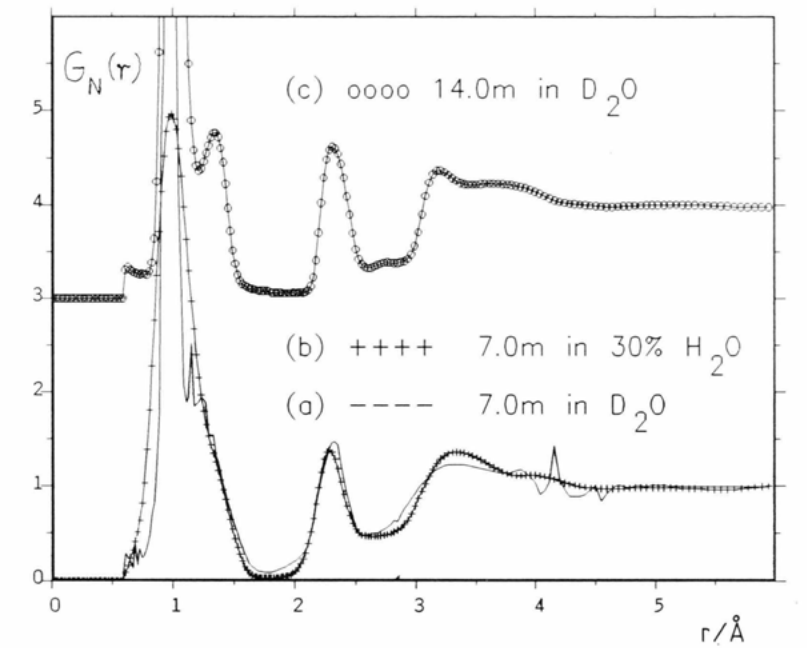

Fig. 3. Partial pair correlation functions from nitrogen isotope substitution:
(a) 7.0 m urea in D_2O (line), (b) 7.0 m urea in 30% H_2O, 70% D_2O (crosses), (c) 14.0 m urea in D_2O (circles); translated 3.0 units along the *y* axis for clarity.

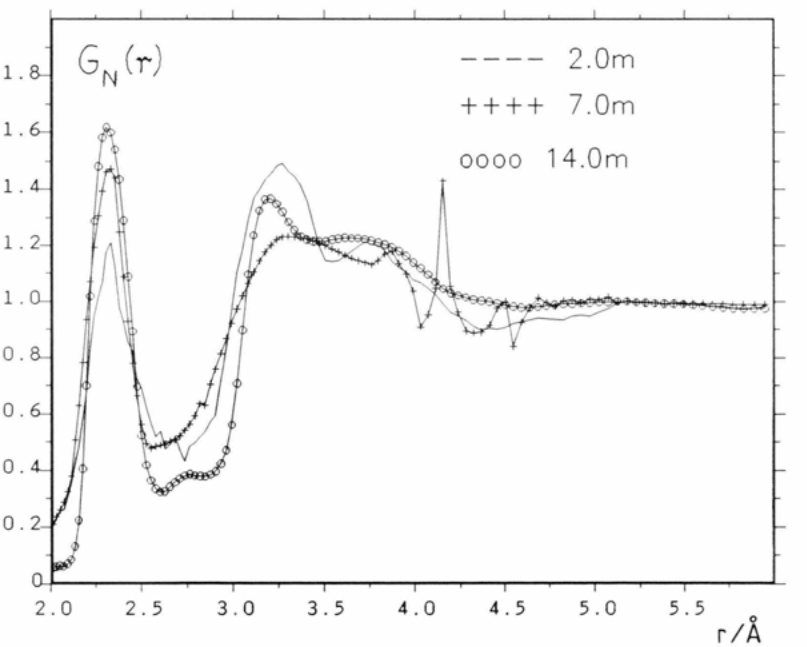

Fig. 4. Partial pair correlation functions from nitrogen isotope substitution for 2.0 m urea (line), 7.0 m urea (crosses) and 14.0 m urea (circles) in D_2O.

also urea-water and possibly urea-urea correlations. $g_{H\text{-}(O,C,N)}(r)$ was calculated from the difference of the $S(Q)$ obtained from the 100% H_2O and 36% H_2O solutions, after subtraction of $S_{HH}(Q)$. The dominant term is $g_{HO}(r)$; there are also less strongly weighted contributions from H–C and H–N correlations [7]. Because the amide hydrogens are exchangeable, $g_{HH}(r)$ also contains contributions from water molecules hydrogen-bonded to urea (N–H···O–H bonds). In spite of this, the H–H function obtained from 10.0 m urea is very similar to that for pure water [5]. The peaks in $g_{HH}(r)$ at 2.4 Å and 3.9 Å in bulk water are

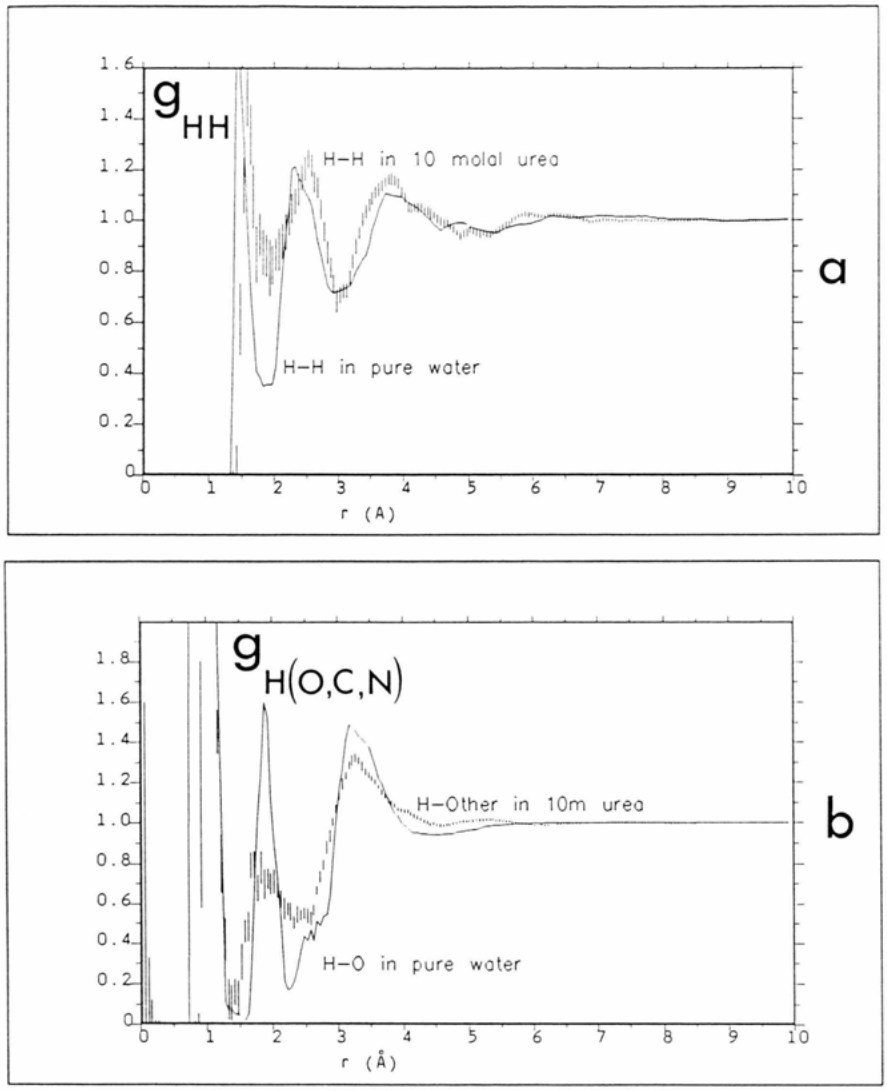

Fig. 5. (a) H–H pair correlation function, (b) H–(O, C, N) pair correlation function in aqueous 10.0 m urea solution (dashes) compared to H–H and H–O correlation function in pure water (line) [5].

characteristic of the hydrogen-bonding geometry, and we would expect these to be broadened if the water structure were significantly disrupted. The H–(O, C, N) function is considerably broadened compared to bulk water, but this could be due to urea-water and urea-urea contributions. There is also a small shift in the first intermolecular peak position compared to pure water of about 0.1 Å in both the H–H and the H–(O, C, N) functions.

3.3. N Substitution on TMA in Urea Solution

Figure 6 shows $G_N(r)$ for the TMA ion in 2.0 m urea solution compared to the result obtained in D_2O solution alone [8]. In this case the first two peaks at 1.5 Å and 2.1 Å correspond to intramolecular structure. The first corresponds to the position of the 4 carbon atoms bonded to the nitrogen and the second, which is a minimum because of the negative scattering length of hydrogen, to the 12 methyl hydrogen atoms at approximately 2.1 Å from the nitrogen. The peak centred at about 4.5 Å from the nitrogen atom corresponds to the hydration region of the TMA ion. In the case where TMA is dissolved in water alone, the peak accounts for about 20 water molecules. It can be seen from Fig. 5 that the hydration peak is unchanged in the urea solution compared to the solution in pure water.

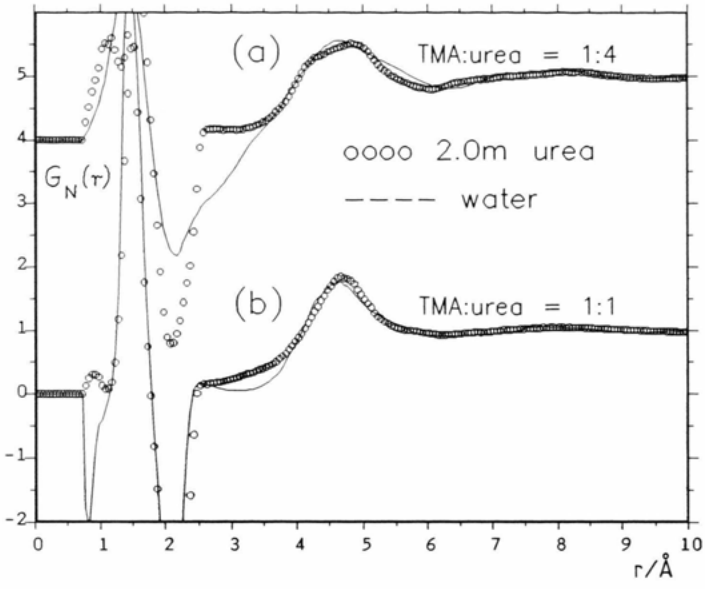

Fig. 6. Partial pair correlation functions from nitrogen isotope substitution on TMA in 2.0 m urea solution (circles) compared to solution in pure water (line): (a) 0.5 m TMACl, (b) 2.0 m TMACl. (a) has been translated along the y axis for clarity.

3.4. Carbon Isotope Substitution

Figure 7 shows $\Delta_C(Q)$ for liquid methanol and $G_C(r)$ calculated by direct Fourier transform. The structure at low r values is the result of the truncation of the Fourier transform and would be eliminated using the iterative method used for the urea data. It can be seen that there is rather little structure in $\Delta_C(Q)$. The positions of the three peaks in $G_C(r)$ at 1.0, 1.4 and 1.8 Å correspond reasonably well to the expected intramolecular distances from carbon. However, the coordination numbers are too low by a factor of more than 2. This error is well outside the 10–20% accuracy we have obtained for the urea and TMACl solutions.

4. Discussion

Using nitrogen isotope substitution on urea the known intramolecular structure is reproduced well in all the experiments. The intermolecular peak, from about 2.7 Å to 4.5 Å accounts for about 8 water molecules at 2.0 m concentration. The peak is broad and shows no well defined structure. Comparison with theoretical models suggests that this lack of structure in the intermolecular region is a consequence of the asymmetry of the hydration structure about the substituted nitrogen atom [10]. To try to understand the interactions in the intermolecular region we have looked for changes in the measured $G_N(r)$ when either the solute concentration or light water concentration is varied.

Figure 4 shows that there is remarkably little change in the intermolecular structure in the concentration range of 2.5 to 3.5 water molecules per urea molecule. There is also no significant structure beyond about 4.5 Å at any concentration, i.e. beyond first molecular neighbour distance. The lack of longer-range structure is also shown by the H–H and H–(O, C, N) correlations in 10.0 m area (and by the H–H and O–H correlations in pure water [5]). Measurements using a proportion of light water were made at 2.0 m and 7.0 m concentration. The 2.0 m data show a trend with increasing light water concentration which seems to show a relative preference for hydrogen/deuterium atoms at around 3.0 Å from nitrogen and a relative preference for oxygen atoms at around 3.4 Å from nitrogen. At 7.0 m concentration (approximately 7 waters per urea) there must be some close urea-urea interactions which would give contributions from N–H···O=C hydrogen bonds in the region up to 4.5 Å. However, the structure changes less with light water concentration in the 7.0 m case than in the 2.0 m case. This is partly due to the fact that the light water content was lower (30% for 7.0 m, 40% for 2.0 m), but it also suggests that the geometry of the N–H···O–H and N–H···O=C bonds (i.e. urea-water and urea-urea bonding) is similar, in spite of the difference in geometry of the molecules. It may also suggest a preference for urea-urea bonding over urea-water bond-

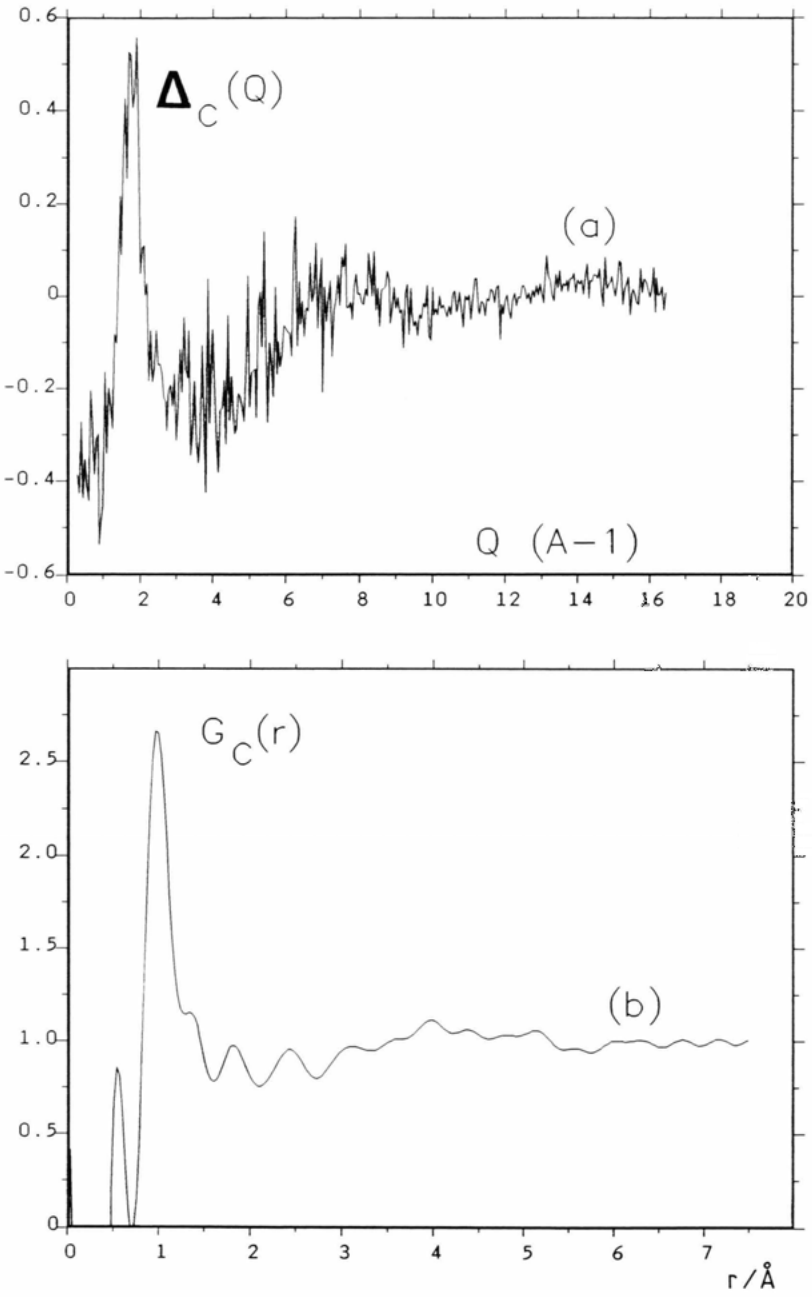

Fig. 7. (a) Partial structure factor. (b) Partial pair correlation function obtained from carbon isotope substitution in liquid methanol.

ing at the light concentration, since peaks due to the N–H···O=C interaction would not be affected by an increase in light water content.

The experiments using H/D substitution in the water also indicate that the change in overall intermolecular structure with urea concentration is small. The H–H pair correlation function from 10.0 m urea is scarcely different from that in pure water, although it contains contributions from N–H···O–H bonds. However, it appears that the first neighbour H–H distance is increased by a small amount (0.1 Å) and the hydrogen-bonding H···O distance has decreased by the same amount. Since the H···O peak may also contain some contributions from urea-water and

urea-urea neighbours, this second apparent change should be interpreted with caution. However, the two changes in nearest H–H and H–O distance taken together are consistent with a shift from tetrahedral to trigonal hydrogen-bonding such as might be expected at a high concentration of urea [7]. There is no indication from the H–H correlation function that the existence of some trigonal bonding has significantly disrupted the usual water-water hydrogen bonding geometry.

The results from the TMACl in urea solution also showed no evidence of significant broadening or other change in the peak shape to indicate a disordering of the TMA hydration region as a result of addition of urea. TMACl was chosen for the experiments because it is symmetric about the substituted nitrogen atom, which considerably simplifies the interpretation of the hydration peak, and because we had previously been able to show that the hydration structure in pure water was characteristic of an apolar solute [8]. Although the present work shows no changes in the hydration with addition of urea, 2.0 m urea is not a high concentration and it would be necessary to repeat the measurements with higher concentration before drawing firm conclusions. However the results so far tend to support the view given above that urea fits into the water structure rather than causing structural perturbation. At the 2.0 m concentration, it seems likely that urea could substitute for water in the TMA hydration region. We have suggested elsewhere that the water molecule orientations are consistent with a disordered cage structure around the TMA ion [8] and it would be possible for the planar urea molecule to fit into such a structure [1]. Recent spectroscopic evidence on the mechanism of solubilisation by urea also suggest that urea-solute interactions are more important than changes in water-solute interactions [12, 13].

The carbon isotope substitution experiment on methanol was intended as a test of the method to see if adequate intramolecular peak positions and coordination numbers could be obtained. Although the expected positions and relative areas of the intramolecular peaks are found, the absolute normalisation of $G_C(r)$ is in error by an amount significantly greater than would be expected from the probable uncertainties in the data analysis, including the errors in the published neutron cross-sections. The source of this discrepancy is not clear at this stage. One possible explanation is that the published value of the neutron scattering legth for ^{13}C is considerably too low. This seems plausible in view of the fact that the peak positions found were satisfactory, but the coordination numbers incorrect by an overall scaling discrepancy. It is nevertheless important to persevere with carbon isotope substitution experiments because of the potential usefulness of such measurements, especially in view of current improvements in the count-rate of neutron diffractometers.

Summary

We have investigated structure in solutions containing urea by determining the partial pair correlation functions centered on nitrogen in the solute and on hydrogen in the water. These measurements show little change in the intermolecular structure over a wide concentration range. This suggests a similarity between urea-water and urea-urea hydrogen bonding structures in spite of the differences in molecular geometry. In addition, we have found no evidence that urea disrupts either the bulk water network or water in the hydration sphere of another solute (the TMA ion). It appears more likely that urea is able to fit into the water network without causing a measurable change in the average water structure. Thus any entropic changes resulting from the addition of urea to water or aqueous solutions appear not to be the result of significant structural disordering, a direct conclusion which has implications for models of urea solvation.

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