The existence of quadruplet ketyl is well known[24] and the existence of the intermediate Fl$^-$(Na$^+$)$_2$I$^-$ seems to be quite reasonable. The slow rate constant in the case of ion pair, Na$^+$BPh$_4^-$, is probably due to the inability of forming quadruplet in this case. The existences of intermediate triple ion and ion quadruplet in cation-transfer reactions have been confirmed recently in our laboratory in the case of semiquinones.[25]

Acknowledgment. Financial support from the National Science Foundation is greatly appreciated.

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Nuclear Magnetic Resonance Studies of Aqueous Urea Solutions

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Contribution from the Unilever Research Laboratory Colworth/Welwyn,
The Frythe, Welwyn, Herts, England. Received October 26, 1971

Abstract: There has been some controversy about the nature of urea solutions, which are important because of their well-known (but as yet unexplained) effects on the conformational properties of a wide range of water-soluble polymers. There are two theories which fit the thermodynamic data: one postulates that urea associates in solution to form a range of aggregates, while the other suggests that urea induces a shift in the equilibrium between the ordered "bulky" and nonordered "dense" species postulated to exist in water, favoring the dense species for statistical reasons (the model excludes specific urea–urea or urea–water interactions). The present work reports nmr relaxation and chemical shift measurements designed to reveal the nature of the species and interactions present in urea solutions. The data show that the long-range order which is characteristic of pure water is destroyed. Correlation times for tumbling of urea molecules show that there is no urea self-association in solution. Urea–water hydrogen-bonded interactions exist, but are only very short-lived, and do not give rise to any extensive ordered arrangement of urea and water molecules. These results rule out the urea association model and are consistent with urea inducing a change in the water equilibrium without taking part in any specific interactions. Such a change would be expected to influence the conformation of water-soluble polymers (*e.g.*, proteins) by changing the nature of polymer–water interactions.

Although aqueous solutions of nonelectrolytes have not, in general, received the same attention as ionic solutions, much effort has been devoted to gaining an understanding of the molecular interactions responsible for the observed properties of urea–water mixtures. It has been recognized for some time that in its aqueous solutions urea possesses some remarkable properties, *e.g.*, it enhances the solubility of hydrocarbons,[1] inhibits micellar aggregation of surfactants,[2] and affects the conformational properties of a wide range of water-soluble polymers; in particular, there is a large and still rapidly expanding literature on the subject of protein denaturation by urea.[3] Most of the published data on aqueous urea solutions describe their thermodynamic properties. This work has been reviewed and supplemented by Stokes,[4] and more recent determinations of heats and heat capacities of solution[5,6] have filled in some of the few remaining gaps.

The thermodynamic properties of aqueous urea solutions provide a framework into which any interpretation of the properties on the molecular level must fit. Urea is characterized by its surprisingly high solubility (>20 *M* at 25°)[7] and by the almost ideal solutions it forms with water.[4,7] This observation, coupled with the similarity of the limiting heat of solution and the heat of fusion of urea, indicates that urea–water interactions in solution are energetically similar to those of urea–urea in the fused state and to water–water interactions in pure water. The heat capacity of solution[5] is only 6 ± 3 cal mol^{-1} deg^{-1} (*cf.* values of 66 and 50 cal mol^{-1} deg^{-1} for ethane and ethanol, respectively), showing that urea does not promote a temperature-sensitive structure in solution. Further indication of the lack of solvent structuring is provided by the only slight increase in apparent molal volume ϕ_v with concentration and the lack of indication of a sharp minimum, such as is characteristic of monofunctional solutes.[8] Urea solutions also show behavior opposite to that of solutions of alcohols, ethers, amines, and ketones in that the temperature derivative $\partial \ln \phi_v/\partial T$ is large and positive, becoming smaller at higher temperatures.

Two different formalisms have been employed to account for the observed physical properties of urea–water mixtures.[9] Stokes has adopted the model of urea association, first considered by Schellman[12a] and

(1) D. B. Wetlaufer, S. K. Malik, L. Stoller, and R. I. Coffin, *J. Amer. Chem. Soc.*, **86**, 509 (1964).

(2) M. J. Schick, *J. Phys. Chem.*, **68**, 3585 (1964).

(3) H. A. McKenzie and G. B. Ralston, *Experientia*, **27**, 617 (1971).

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(9) Other attempts have been made to explain the observed behavior of urea–water mixtures, but they are purely qualitative, and at times highly speculative (*e.g.*, ref 10) and/or confusing, as has been made abundantly clear by Holtzer and Emerson.[11]

(10) M. Abu-Hamdiyyah, *J. Phys. Chem.*, **69**, 2720 (1965).

(11) A. Holtzer and M. F. Emerson, *ibid.*, **73**, 26 (1969).

(12) (a) J. A. Schellman, *C. R. Lab. Carlsberg, Ser. Chim.*, **29**, 223

subsequently extended by Kresheck and Scheraga.[12b] It was originally postulated that in dilute (<1.0 *M*) solutions, urea dimerization is the dominant process and that at higher concentrations stepwise addition of urea

$$U_n + U \rightleftharpoons U_{n+1}$$

must be taken into account. Using volume fraction statistics to evaluate the entropy of mixing, Stokes was able to fit the activity, heat of dilution, and ϕ_v data and to describe the polymerization process by only two equilibrium constants, of which one refers to the dimerization process and the other to all subsequent urea additions. The other model was developed concurrently by Frank and Franks[13] and deals with the urea–water system on a basis radically different from that of Stokes. While the latter author has commented[4] on the problem of why the association model works so well in spite of ignoring the fact that the solvent water is also an associated substance, the Frank and Franks model actually uses this property of water as a starting point. It is assumed that water can be described as a mixture of distinguishable species, coexisting in equilibrium and mixing ideally. Urea, because of its geometry, is barred from being incorporated into the tetrahedrally hydrogen bonded bulky species but is allowed to mix with the dense species, and this mixture obeys the laws which govern regular solutions. This formalism therefore excludes specific urea–urea or urea–water interactions. Two parameters, adjustable within narrow limits, are required for fitting the model to the thermodynamic properties of aqueous mixtures, namely $\Delta G_w{}^\circ$ and $\Delta H_w{}^\circ$ for the equilibrium

$$(H_2O)_{\text{bulky}} \rightleftharpoons (H_2O)_{\text{dense}}$$

By assigning suitable values to these quantities it can be shown, by the application of standard statistical thermodynamical methods, that the presence of urea shifts the water equilibrium from left to right; *i.e.*, urea reduces the degree of water–water hydrogen bonding *without* replacing these interactions by strong urea–water hydrogen bonds. In addition to providing a satisfactory fit for urea–water mixtures, the Frank and Franks model can also account for the influence of urea on the solubility of the lower paraffins.[1]

As Stokes has pointed out,[4] the borderline between physical and chemical association is diffuse, but for the urea association model to be realistic, the enthalpy of aggregation $\Delta H_u{}^\circ$ must be negative and several times larger than *RT*. Urea-urea bonds, therefore, are likely to have a lifetime which is considerably longer than the lifetime normally ascribed to a hydrogen bond, and this in turn would lead to rotational correlation times (nmr or dielectric) $>10^{-11}$ sec. On the other hand, the Frank and Franks formalism predicts that the main effect of urea would be the perturbation of water–water interactions and that urea–urea and urea–water associations would be minimal. Since thermodynamics alone cannot discriminate between the two models, we decided to investigate the interactions and motions of the molecular species in urea–water mixtures by nmr spectroscopy, using information from ^{14}N and ^{15}N for the urea and ^{17}O for water and ^1H for both species. In addition, other limited spectroscopic information is available for these mixtures and this will be discussed in relation to our own results.

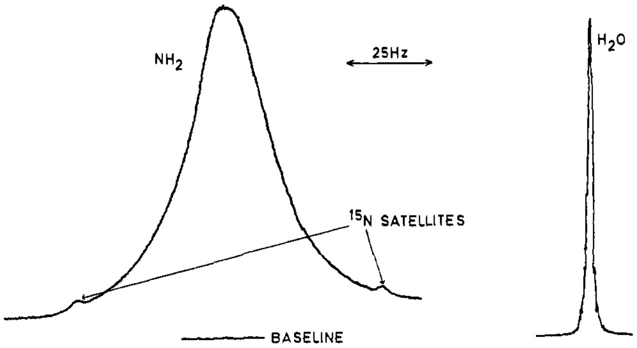

Figure 1. 220-MHz proton spectrum of 6 *M* urea (9°). An offset has been introduced between the urea and water peaks, and the former is recorded with an expanded intensity scale.

Experimental Section

Urea was obtained from B.D.H. (Analar grade). Solutions (in distilled and deionized water) were prepared not more than a few hours before spectra were obtained. High-resolution proton spectra were run on Varian HR-220 and Perkin-Elmer R10 spectrometers, operating at 220 and 60 MHz, respectively. Accurate values of the base line for line shape measurements were obtained by introducing large field offsets. Chemical shifts were measured as the average of several runs, sweeping in both directions, using precalibrated paper on the HR-220 and audiofrequency modulation side bands on the R10. Spectra were referenced for chemical shift measurements by two techniques: (i) using three internal references in very small quantities (dioxane, acetonitrile, and sodium 1-trimethylsilyl-*n*-propane-3-sulfonate (DSS)), and assuming the chemical shifts of any two were constant if their separation did not change as concentration or temperature was changed; (ii) using an external reference in a Wilmad precision bore coaxial tube and correcting for bulk susceptibility changes.[14] The two methods gave the same results.

Some ^{14}N relaxation times were measured directly on a Bruker Physik B-KR 3229 pulsed nmr spectrometer, operating at 6.5 MHz and using 180°–τ–90° pulse sequences. Pulse lengths were 20 μsec for a 90° pulse.

For ^{17}O nmr measurements, a Varian wide line (VF 16B) spectrometer with the radiofrequency locked to a Schlumberger FS 30/7 signal generator was used in the side-band mode with 400-Hz modulation. Line width measurements were made from upfield and downfield scans to minimize any error due to magnetic field drift. The magnetic field inhomogeneity was monitored at regular intervals with a sample of D_2O of the same volume as the ^{17}O solutions, by adjusting the frequency for dmr measurements. The temperature was measured with a copper–constantan thermocouple placed at the center of a water sample. ^{17}O solutions were prepared from 5% enriched water, distilled under vacuum into weighed quantities of urea and sufficient *p*-hydroxybenzoic acid to give a pH <5 in order to eliminate line broadening due to $J_{^{17}O-^1H}$.

Results

A typical high-resolution proton magnetic resonance spectrum of a solution of urea, $CO(NH_2)_2$, in H_2O (pH 7) is shown in Figure 1. The exchange of protons between urea and water is slow enough for two peaks to be observed. Exchange is greatly enhanced by small changes in pH, which cause collapse of the two peaks into a singlet; thus the exchange process is acid–base catalyzed. The rate constant at pH 7 is <1 sec^{-1} at room temperature, as may be deduced from the sharpness (width at half height, $\Delta\nu_{1/2} \sim 1$ Hz at 220 MHz) and constant separation of the ^{15}N satellites (separation $|^1J_{^{15}NH}| = 89.0$ Hz) and the constant width of the water

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[13] H. S. Frank and F. Franks, *J. Chem. Phys.*, **48**, 4746 (1968).

[14] C. Lussan, *J. Chim. Phys. Physicochim. Biol.*, **61**, 462 (1964).

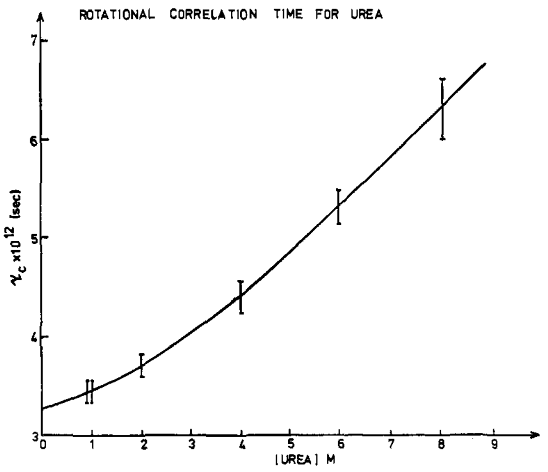

Figure 2. ^{14}N rotational correlation time τ_c as a function of urea concentration in water (17°).

peak with concentration ($\Delta\nu_{1/2}$ varies by <0.2 Hz). These findings are in agreement with other recent observations[15] regarding the exchange process, where a rate constant of 1.5 ± 0.5 sec^{-1} at pH 7 and 35° was quoted.

Relaxation Studies. The slow exchange rate of the urea protons with water indicates that the exchange process contributes negligibly to the observed width of the urea peak ($\Delta\nu_{1/2}$ typically 40 Hz). This allows determinations of the spin–lattice relaxation time T_1^N of the urea ^{14}N to be made from line shape measurements.[16,17] The breadth of the line arises from the scalar $\{^{14}N, {}^1H\}$ coupling, which gives a 1:1:1 triplet which is only partly washed out by the rapid quadrupolar relaxation of the nitrogen, and T_1^N can thus be calculated if $^1J_{^{14}NH}$ is known. The latter is related to $^1J_{^{15}NH}$ by the ratio of the magnetogyric ratios of ^{14}N and ^{15}N, which is 0.713.

$$|{}^1J_{^{14}NH}| = |{}^1J_{^{15}NH}| \times \gamma_{^{14}N}/\gamma_{^{15}N} = 63.5 \text{ Hz} \qquad (1)$$

The relationship[16,17] used to obtain T_1^N is

$$(T_2^H)^{-1} = (^8/_3)\pi^2 T_1^N({}^1J_{^{14}NH})^2 \qquad (2)$$

where T_2^H is the contribution by this relaxation mechanism to the observed spin–spin relaxation time (T_2^{obsd}) of the urea proton resonance.

$$(T_2^{obsd})^{-1} = (T_2^H)^{-1} + (T_2^*)^{-1} \qquad (3)$$

The last term in eq 3 represents the contribution to the relaxation from magnetic field inhomogeneities and exchange broadening. The use of eq 2 instead of the more complicated formula given in ref 16 assumes that the proton line shape is Lorentzian, *i.e.*, obeys the equation

$$I(\nu)/I(0) = \{1 + 4\pi^2(T_2^{obsd})^2\nu^2\}^{-1} \qquad (4)$$

Here $I(\nu)$ is the intensity at frequency ν, measured from the center of the resonance. The Lorentzian nature of the urea peak was demonstrated by the excellent linear fit obtained by plotting $1/I(\nu)$ against ν^2. Measurement of $\Delta\nu_{1/2}$ then gives T_2^{obsd}, since

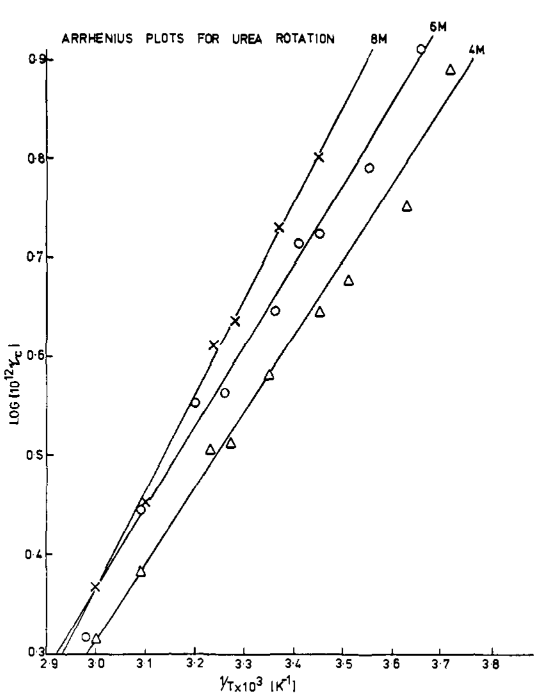

Figure 3. Arrhenius plots of τ_c for 4 *M* (Δ——Δ), 6 *M* (O——O), and 8 *M* (*X*——*X*) urea solutions.

$$\Delta\nu_{1/2} = (\pi T_2^{obsd})^{-1} \qquad (5)$$

The contribution $(T_2^*)^{-1}$ was estimated by measuring the line width of the water and ^{15}N satellite resonances. Values of T_1^N varied between 0.6 and 2.5 msec, increasing with decrease in urea concentration and increase in temperature. Direct measurement of T_1^N by a pulse technique gave results in excellent agreement with those obtained by the above method.

The rotational correlation time[18] τ_c of the ^{14}N relaxation mechanism is related to T_1^N by the equation[19]

$$(T_1^N)^{-1} = (^3/_8)(1 + \eta^2/3)(2\pi e^2qQ/h)^2\tau_c \qquad (6)$$

Here (e^2qQ/h) is the quadrupolar coupling constant and η is the asymmetry parameter of the electric field gradient. Values for these quantities in solid urea are available from nuclear quadrupole resonance;[20] the former is 3.425 MHz at 0° and is reduced by only 0.01 MHz for a 20° rise in temperature, while the latter is 0.313 from 0 to 20°. These quantities have not been measured in solution, but it is normally assumed that values of the quadrupolar coupling constant are about 5% higher in solution than in the solid.[21,22] A 5% uncertainty in (e^2qQ/h) leads to a 10% error in τ_c, whereas a 5% error in η leads to only 0.3% error in τ_c. We calculated values of τ_c from T_1^N assuming $(e^2qQ/h) = 1.05 \times 3.425$ MHz $= 3.596$ MHz and $\eta = 0.313$. Equation 6 then becomes

$$\tau_c = 0.00509/T_1^N \times 10^{-12} \text{ sec} \qquad (7)$$

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(15) R. L. Vold, E. S. Daniel, and S. O. Chan, *J. Amer. Chem. Soc.*, **92**, 6771 (1970).

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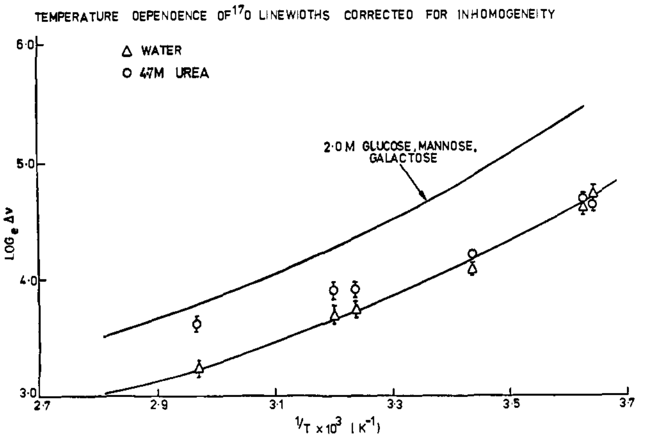

Figure 4. Temperature dependence of ^{17}O line widths (corrected for inhomogeneity) in $H_2{}^{17}O$ solutions: water (Δ——Δ), 4.7 *M* urea (O——O), 2.0 *M* glucose, mannose, or galactose (——).

giving values of τ_c which are plotted as a function of concentration in Figure 2 and of temperature in Figure 3. Error bars in Figure 2 give estimates based on errors of ± 1 Hz in urea line width measurements and on observed differences between line widths of water and ^{15}N satellites. An error in the quadrupolar coupling constant will affect the absolute values of τ_c but not its trends (provided that (e^2qQ/h) is concentration independent). Errors in the absolute value of τ_c are unlikely to be >25%.

Continuous wave proton variable temperature measurements of $T_1{}^N$ were complicated by the increased urea-water proton exchange rate at higher temperatures, producing a noticeable broadening of the ^{15}N satellites above ~55° and a distortion of the urea line shape above ~65°. Pulsed nmr measurements are not subject to this limitation and have an estimated error of ±5%. Figure 3 shows Arrhenius plots for τ_c of urea in 4, 6, and 8 *M* solutions. The plots are reasonably linear and certainly do not show a pronounced increase in slope at low temperatures, unlike water.[23] Average apparent activation energies are 3.4 ± 0.3, 3.7 ± 0.6, and 4.4 ± 0.3 kcal mol^{-1}, respectively.

The ^{17}O line widths of labeled water in 6 *M* urea increase with time due to decomposition of urea. The decomposition is known[24,25] to proceed through two stages in acid or alkaline solution

$$CO(NH_2)_2 \rightleftharpoons NH_4^+ + OCN^- \qquad (8)$$

$$OCN^- + H_3O^+ \longrightarrow NH_3 + CO_2 \qquad (9)$$

The second step buffers the solution against changes in pH. Thus the pH of solutions used, although initially 4.4, was found to increase slowly to a pH >5 on standing. An increase in the ^{17}O line width results because the proton exchange rate is lowered to such an extent that $J_{^{17}OH}$ coupling is observed, as it is[26] with pure water for 5 < pH < 9.

Only the measurements made with a minimum of delay (about 30 min) have therefore been collected in Figure 4. The lower temperature results are thought to be the most reliable because the removal of acid by reaction 9 is proceeding more slowly.[25] From 2 to 18° it can be seen that the ^{17}O line widths in 4.7 *M* urea solutions and $H_2{}^{17}O$ are identical within experimental error. The ^{17}O line widths in water agree within 5% with literature values.[27]

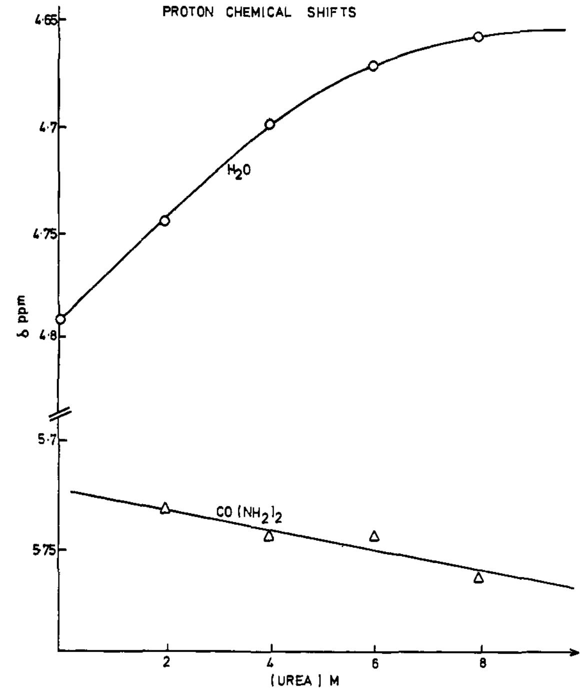

Figure 5. Urea (Δ——Δ) and water (O——O) proton chemical shifts as functions of urea concentration (20°).

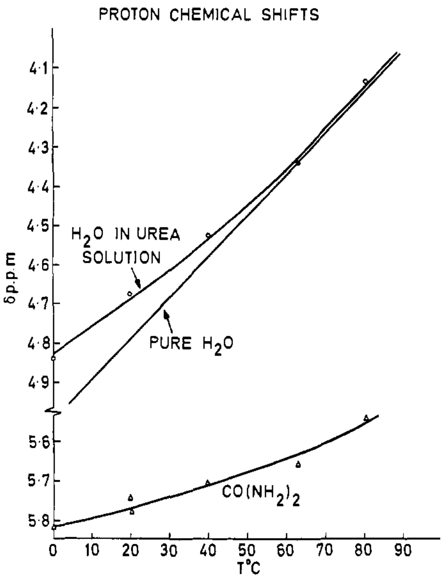

Figure 6. Urea (Δ——Δ) and water (O——O) proton chemical shifts as functions of temperature (6 *M* urea). The chemical shift of pure water is also shown (——).

Chemical Shift Studies. Chemical shifts of the urea and water resonances, δ_u and δ_w, are plotted in Figures 5 and 6 as functions of concentration and temperature, respectively. The change of pH of water on dissolving 8 *M* urea was less than 0.2 and therefore had no measurable effect on δ_w. The pairs of internal references with constant chemical shift separation were DSS and

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dioxane for the concentration run and DSS and acetonitrile for the temperature run.[28] The temperature variation of the chemical shift of pure water is also plotted in Figure 6; values are taken from ref 29 and adjusted to the δ scale using our measurement for water at 20° (Figure 6).

Discussion

Breakdown of Water Structure. The addition of urea to water results in a limited reduction in the degree of water hydrogen bonding, as evidenced by the dependence of δ_w on urea concentration. The effect is greatest at low urea concentrations and low temperatures, as would be expected if the results reflect a breakdown of long-range order in water. This can be regarded as an effective increase in the water "structural temperature,"[30a] and the results, expressed in this way, are in complete agreement with those obtained from infrared measurements.[30b] As an example, addition of 6 *M* urea is, in terms of δ_w, equivalent to raising the temperature of water from 20 to 30°. The use of urea for "isothermal heating" of water, thus providing insight into the dense-bulky water equilibrium, will be dealt with in more detail elsewhere.[31] Raman scattering in the region of the water hydrogen bond stretching frequency ($\sim$175 cm^{-1}) also indicates that urea induces an overall reduction in the degree of water–water hydrogen bonding.[32] Furthermore, ultrasound attenuation measurements covering frequencies of 18–175 MHz and the concentration range 0–8 *M* urea have shown[33-35] that the normal contribution to the ultrasound relaxation from the open packed, probably four-coordinated water is completely suppressed by 8 *M* urea. Long-range order, such as is believed to exist in pure water, can be ruled out in a concentrated solution, since the molar ratio urea:water is high (about 1/4.4 in 8 *M* solution; at 20°, the solubility is about 3 mol of urea/10 mol of water, and at 70° it is about 3 mol of urea/4 mol of water).

The rotational correlation time of water molecules is unaffected or slightly increased by the addition of urea. Figure 4 shows that the ^{17}O line width of labeled water shows no measurable change on the addition of 4.7 *M* urea, indicating no change in the τ_c of the water. Therefore the observation[36] of an enhanced deuteron relaxation rate in D$_2$O solutions of urea should be ascribed to a contribution from the deuterons on the urea molecules, rather than to hydrogen bonding between water and urea. For comparison some results are also given in Figure 4 for monosaccharides at a lower concentration than that used for the urea. These clearly show a relaxation enhancement, which is consistent with the Raman scattering[32] result that sucrose enhances the concentration of tetrahedrally hydrogen-bonded water molecules. Dielectric measurements[37] give a dielectric relaxation time for the water in 8 *M* urea at 25° of 6.97 ± 0.13 × 10^{-12} sec, compared with 8.26 ± 0.04 × 10^{-12} sec obtained under the same conditions for pure water. This reduction should be reflected by a corresponding small change in the ^{17}O line width in Figure 4 (which refers to a lower concentration), but it may be masked by the increased line width due to decomposition of urea.

Absence of Urea Self-Association. The fact that the change in δ_u with urea concentration is only very slight points to a lack of significant urea self-association, as is also indicated by the absence of any structural relaxation observed by ultrasound attenuation.[33,38] This is supported by the measurements of τ_c as a function of urea concentration. If dimers or a distribution of larger aggregates existed in solution for longer than 10^{-11} sec, then the variation of τ_c with concentration would follow an S-shaped curve, and since τ_c is proportional to the viscosity and the volume of the rotating entity (or entities), its value in concentrated (8 *M*) solution would be far more than double its value in dilute solution (a factor of about 1.8 is observed). Furthermore, the magnitude of the observed τ_c indicates that the tumbling species is a urea monomer. A simple calculation based on the Debye equation

$$\tau_c = 0.74\bar{V}n/3N_0kT \qquad (10)$$

where $\bar{V}$ is the molar volume, n is the viscosity, and N_0 is Avogadro's number, gives τ_c = 4.7 × 10^{-12} sec for a dilute solution (n = 0.01 poise) at 17°. This may be compared with a measured value of about 3.3 × 10^{-12} sec in dilute solution. The variation of viscosity with urea concentration is less pronounced than the variation of τ_c, changing by a factor of 1.4 for the concentration range 1–8 *M*. This suggests that there may be weak self-association of urea molecules with a lifetime $\sim$10^{-12} sec. The dielectric relaxation time τ_ϵ for urea in 8 *M* solution[37] is 26.5 ± 0.2 × 10^{-12} sec, giving a ratio τ_ϵ/τ_c = 4.9. This may be composed with a ratio of 3.3 for pure water.[39] If the tumbling entity were a spherical particle, as represented by eq 10, the ratio would be 3.

The Arrhenius plots for τ_c of urea suggest that there is only one type of urea environment in concentrated solutions. This rules out the existence of extended structures in such solutions (*cf.* water).[23] The values of the activation energies may be compared with 3.3 kcal mol^{-1} and about 10 kcal mol^{-1} for water at high and low temperatures, respectively. Clearly the reorientation process is easier than would be expected if urea took part in any long-lived structure in solution. The slight increase with urea concentration is probably due to a tighter packing of molecules in the solution as the "bulky phase" water structure is broken down.

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(28) Subramanian, *et al.*,[5,6] have measured δ_w in urea solution with respect to internal acetone. Their results strongly disagree with ours, in that they found that the addition of urea produced very little change in δ_w; *e.g.*, 6 *M* urea produces an upfield shift of 0.01 ppm, compared to our result of 0.12 ppm as shown in Figure 5. We have repeated the measurements using their method but obtain results identical with those shown in Figure 5 obtained using our other two methods (internal and external referencing).

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(37) R. Pottel and D. Adoph, personal communication.

(38) This is in contrast to the conclusion reached by Vold, *et al.*,[15] based on the observation that rate constants for acid- and base-catalyzed protolysis vary with concentration. However, this result could equally well be explained in terms of a variation in the water "structural environment" with concentration.

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Nature of Urea–Water Interactions. Although urea causes a breakdown of long-range order, the water in concentrated urea solutions is nevertheless extensively hydrogen bonded, as evidenced by the fact that δ_w is still strongly temperature dependent (the increase in "structural temperature" is only moderate). That this hydrogen bonding involves the urea molecules is suggested by the upfield shift of δ_u with increasing temperature. The high solubility of urea suggests the existence of some urea–water interactions. Other studies[31] have shown that δ_w contains an appreciable downfield contribution due to urea–water interactions. However, ultrasound attenuation results[33] indicate that there are no extended structures involving urea and water, and the existence of two easily resolvable dielectric relaxations in 8 *M* urea[37] shows that urea and water molecules tumble independently. Urea–water association is therefore short-range and short-lived. Such association slightly retards the tumbling of the urea molecules, as may be seen by comparison of our τ_c results with those[40] for mixtures of water with acetone, which is isoelectronic with and of similar shape to urea. The τ_c of acetone remains roughly constant, *ca.* 1×10^{-12} sec over the whole composition range, while that of the water shows a maximum at about 30 mol % acetone. The latter observation is ascribed to a water structuring process for which there is no evidence in the urea–water mixtures. The linear nature of the Arrhenius plots for the urea τ_c and the values of the activation energies confirm that the tumbling species is not a urea–water complex. The fact that the proton exchange rate is slow also indicates that urea–water hydrogen bonding is only short-lived (*cf.* a rate of *ca.* 10^3 sec^{-1} for water–water proton exchange in pure water). This agrees with observations that in water the presence of structure-breaking ions slows down the exchange rate.[41]

Conclusions

We can draw the following conclusions about the structures and interactions in a concentrated urea solution. (i) The long-range order characteristic of pure water is destroyed and is not replaced by extended structures involving urea molecules. (ii) There are no urea dimers or higher polymers. (iii) There are extensive short-range, short-lived interactions between water and urea, involving hydrogen bonds to the urea NH_2's and possibly to the urea $C{=}O$.

These conclusions fit the model[13] which proposes that urea displaces the water equilibrium from a bulky species involving long-range order to a dense species involving only short-range structure, by resembling water in its capability to form hydrogen bonds but by having the wrong geometry to take part in extended water structures. The resemblance to water explains the high solubility of urea.

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Infrared Studies of Isotope Effects for Hydrogen Adsorption on Zinc Oxide

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Abstract: Kinetic and equilibrium isotope effects were studied for type I hydrogen, deuterium, and hydrogen deuteride adsorption on zinc oxide. At room temperature, there is no equilibrium isotope effect for hydrogen *vs.* deuterium, but the preferred form of adsorption of hydrogen deuteride appears to be ZnH–OD rather than ZnD–OH by a factor of 2–3. Kinetic isotope measurements reveal that hydrogen adsorbs faster than deuterium by a factor of at least 5 at −195°. The kinetic isotope effect for HD at −195° reveals ZnD–OH is the favored form by a factor of 20–100. Approximate computations of these effects based on observed ir frequencies reveal that these effects are explicable provided we assume the bending vibrations for adsorbed species are either very low frequency compared to those observed for simple molecules or that the adsorption is mobile at room temperature.

Hydrogen chemisorption on zinc oxide at or above room temperature occurs in two stages: the first stage is characteristically rapid and is complete in a few minutes; the second stage is characteristically slow and continues for at least 24 hr.[2-4] The nature of these adsorbed species has been the subject of many discussions.[2-8] Pace and Taylor, in a classic paper,[5] examined

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