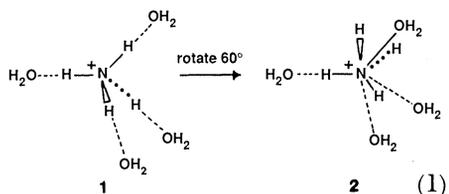


Rotation and Solvation of Ammonium Ion

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From nitrogen-15 spin-lattice relaxation times and nuclear Overhauser enhancements, the rotational correlation time τ_c for $^{15}\text{NH}_4^+$ was determined in a series of solvents. Values of τ_c range from 0.46 to 20 picoseconds. The solvent dependence of τ_c cannot be explained in terms of solvent polarity, molecular dipole moment, solvent basicity, solvent dielectric relaxation, or solvent viscosity. The rapid rotation and the variation with solvent can be accounted for by a model that involves hydrogen bonding of an NH proton to more than one solvent molecule in a disordered solvation environment.

RECENT NUCLEAR MAGNETIC RESONANCE (NMR) measurements (1) have shown that the rotational correlation time τ_c of aqueous ammonium ion is 1.1×10^{-12} second. This is the time required for the NH_4^+ to rotate within its solvation shell by an angle of 33° about any axis (2). So fast a rotation was rather surprising, since NH_4^+ is strongly solvated (heat of solvation $-\Delta H^0 = 86.8$ kcal/mol for solvation in aqueous solution and -62.5 kcal/mol for solvation by four water molecules in the gas phase) (3), and rotation requires the partial breaking of hydrogen bonds. The NH_4^+ ion fits (4) into the water ice lattice (1), with four directional NH-O hydrogen bonds (5). To create the transition state (2) for rotation, it seems that three of those hydrogen bonds must be partially broken before the new hydrogen bonds are formed (Eq. 1),



In order to probe the solvation of NH_4^+ and to understand why its rotation is so fast, we have determined τ_c for NH_4^+ in an extensive series of solvents (6).

The τ_c values were determined at 22°C from the observed spin-lattice relaxation times $T_{1,\text{obsd}}$ of ^{15}N , corrected to the dipole-dipole contribution $T_{1,\text{dd}}$ via the nuclear Overhauser enhancement (NOE) η , according to Eq. 2 (7),

$$\frac{1}{T_{1,\text{dd}}} = \frac{\eta}{\eta_{\text{max}}} \frac{1}{T_{1,\text{obsd}}} \quad (2)$$

$$= 4 \frac{\gamma_{\text{N}}^2 \gamma_{\text{H}}^2 \hbar^2}{r_{\text{NH}}^6} \tau_c$$

where $\eta_{\text{max}} = -4.93$, γ is the magnetogyric

ratio, $2\pi\hbar$ is Planck's constant, and r_{NH} is the NH bond length, 1.03 \AA (8). Equation 2 describes the relaxation of the ^{15}N magnetic dipole by motion of the magnetic dipoles of the attached protons. All NMR spectra were obtained at 20.37 MHz on a Nicolet NT200 spectrometer interfaced to a NIC 1180E data processor.

Spin-lattice relaxation times (Table 1) were measured with a saturation-recovery pulse sequence (9), including homospoil (1). The correction for the contribution of non-dipole-dipole relaxation, η/η_{max} , is usually small. Also, only the attached protons and not the solvent protons are effective in relaxing the ^{15}N , since the near-maximal NOE was observed with selective saturation of the NH protons under conditions such that chemical exchange was slow enough that saturation was not appreciably transferred to solvent. The standard deviation of the data from replicate determinations is 5 to 10%. Values of τ_c in H_2SO_4 and H_3PO_4 are less certain, since the NOE is appreciably weaker than the maximum because of the incursion of unknown relaxation mechanisms other than dipole-dipole relaxation, even with distilled NH_3 . In water, ethylene glycol, dimethyl sulfoxide, glycerol, or ethanol, τ_c is independent of a twofold change in the concentration of NH_4NO_3 , so that the interaction with the NO_3^- counterion does not determine the rotation. In pyridine, τ_c is also independent of NH_4NO_3 concentration, although ion-pairing is complete under all experimental conditions.

In all of the solvents tested, the rotation of NH_4^+ is quite fast. In contrast, most ions, such as CO_3^{2-} , SO_4^{2-} , SCN^- , and various dyes and metal complexes, rotate more slowly (10-12), and the few exceptions [ClO_4^- ($\tau_c = 0.78$ psec) (11) and NO_3^- ($\tau_c = 1.04$ psec) (12)] do not have the hydrogen-bonding requirements (1) of NH_4^+ . These

should be substantial, since molecular-orbital calculations (13) suggest that 5.5 kcal/mol is required to bifurcate one hydrogen bond in $\text{NH}_4^+\cdot\text{OH}_2$. Yet NH_4^+ often rotates nearly as fast as CH_4 ($\tau_c \sim 0.2$ psec) (14), whose solvation is certainly weak. Indeed, the data in Table 1 show that, relative to a free rotor with the same moment of inertia, solvation of NH_4^+ imposes a barrier of only 1 to 3 kcal/mol. There is substantial variation of τ_c from solvent to solvent, of no immediately apparent pattern. Rotation of NH_4^+ is faster in water than in nearly all other solvents. This is opposite to the behavior of SO_4^{2-} , which rotates more slowly in water than in methanol (11). Further comparisons with other ions are not possible, since no other ion has been studied in so wide a range of solvents.

What feature of the solvent determines τ_c of NH_4^+ , and what is the special feature of water that permits so fast a rotation? We shall consider in turn solvent polarity, molecular dipole moment, solvent basicity, viscosity, dielectric relaxation, and the density of hydrogen-bond acceptors.

1) The high polarity of water does not cause so short a τ_c , since τ_c in Table 1 does not relate linearly to any measure of solvent polarity. The solvents of highest dielectric constant—water, H_2SO_4 , and *N*-methylacetamide—are at the extremes of τ_c . The one nonpolar solvent, pyridine, is intermediate. Unfortunately, a wider range of nonpolar solvents is not possible because of the insolubility of NH_4NO_3 . Pyridine is unusual in this respect, and τ_c is not quite comparable because of ion-pairing. However, ion-pairing would retard rotation, as has been observed (15) for MnClO_4^+ and various $\text{Co}(\text{en})_3^{+3}$ ion pairs (en is ethylenediamine). Yet rotation is faster in pyridine than in the more polar solvents such as dimethyl sulfoxide or *N*-methylacetamide. Thus rotation is not facilitated by solvent polarity.

2) Since hydrogen bonding is predominantly of electrostatic origin (16), an electrostatic model might account for the variation of τ_c . The barrier to rotation would then be proportional to the dipole moment of the solvent molecule. For water, the barrier would be 6 kcal/mol (1) for rotation about a twofold axis or 4 kcal/mol for rotation about a threefold axis (Eq. 1). Yet there is no linear relation (17) between $\log \tau_c$ and molecular dipole moment (18).

3) The linear relation between $\log \tau_c$ and the hydrogen-bond acceptor basicity param-

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Table 1. Rotational correlation times of the ammonium ion (δ).

Solvent	$T_{1,obsd}$ (seconds)	$-\eta$	τ_c (psec)
96% H ₂ SO ₄	57	2.55	0.46
Water	44*	4.67*	1.1*
Water- <i>d</i> ₂ (ND ₄ ⁺)	409*	0.57*	1.5*
85% H ₃ PO ₄	16.6	2.8	1.7
18-Crown-6/ acetone	16.4	4.43	2.8
50% v/v aqueous ethanol	18	4.94	2.8
Methanol	13.6	5.1†	3.8
Ethylene glycol	8.5	5.1†	6
Pyridine	4.97	4.76	10
Glycerol	3.6	4.2	12
Dimethyl sul- foxide	3.96	5.0†	13
Ethanol	3.6	5.1†	14
N-Methyl- acetamide	2.6	4.9	20

*Values from (1). †Taken as 4.93 in Eq. 2, since $-\eta$ cannot exceed $-\eta_{max}$.

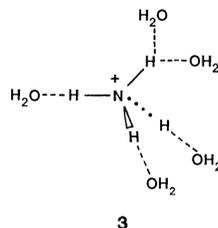
eter β (19) is also poor (17) (for nine solvents whose β values are tabulated or can be modeled by tabulated solvents). Rotation is properly faster in solvents that are poor hydrogen-bond acceptors, but the relation is created largely by the outlying point for water, which is a poor acceptor, whereas H₃PO₄ (modeled by triethyl phosphate) deviates markedly.

4) Viscosity might be important in determining τ_c , inasmuch as the activation energy (2.76 kcal/mol, SE 0.32 kcal/mol) (1) for rotation in water is near the activation energy of 3.8 kcal/mol (18) for viscous flow. Also, the Debye equation (20) is satisfied, in that a plot of τ_c for aqueous NH₄⁺ versus η/T (where η is now viscosity) is linear with a slope near V_{molar}/R (the ratio of the molar volume to the gas constant). Nevertheless, there is no statistically significant linear relation (17) between rotational correlation times in Table 1 and solvent viscosity (18). Viscous solvents such as glycerol, H₃PO₄, H₂SO₄, and ethylene glycol do not retard the rotation, as was inferred previously (21) from an analysis of proton-exchange kinetics of benzamide-¹⁵N.

5) Another possibility is that rotation of the NH₄⁺ is governed by the random motion of the surrounding solvent. If so, $\log \tau_c$ should be linearly related to $\log \tau_D$, where τ_D is the Debye time for dielectric relaxation (22). However, this relation is poor (17). Also, NH₄⁺ rotation is often faster than dielectric relaxation. For example, in water $\tau_c = 1.1$ psec and $\tau_D = 11$ psec.

6) We suggest that NH₄⁺ rotation is so fast, especially in water, because of multiple coordination to the NH protons. The four hydrogen bonds of structure 1 are appropriate for NH₄⁺ in a water ice lattice (4), but

the actual solvation is more disordered. The measured τ_c pertains to an environment averaged over T_1 , which is a long time, ~ 10 seconds. If an additional solvent molecule is available, rotation need not break three hydrogen bonds, as in structure 2, but can occur by breaking one bond while another is forming, as in structure 3:



Simulations of the structure of aqueous NH₄⁺ and methylammonium ions indicate that each NH proton is associated with either 2.0, 1.2, or 1.3 water molecules (23). The special feature of water is that the molecules are so small that many of them can cluster about the NH₄⁺. Both H₂SO₄ and H₃PO₄ are larger molecules, but each can place many hydrogen-bond acceptors adjacent to the NH₄⁺. 18-Crown-6 is similar, with six oxygen atoms that can face toward the NH₄⁺. The rapid rotation within 18-Crown-6 is in contrast to that for a cryptand, for which it was concluded (24) that ND₄⁺ does not reorient rapidly within a cavity of four nitrogen atoms. The slowest rotations are observed with large solvent molecules that have only one oxygen or nitrogen atom that can coordinate to NH₄⁺, since it is difficult to fit more than four molecules about the NH₄⁺. Indeed, the least poor linear relation (17) is between $\log \tau_c$ and the oxygen atom density of the solvent (18). Admittedly, this is too crude a parameter for quantitative application. However, the linearity is significant and supports multiple coordination as largely responsible for the variation of τ_c with solvent. Aqueous ethanol deviates slightly from the linear relation since the solvent in the vicinity of the ion is more aqueous than the bulk solvent mixture.

These data are a sensitive probe of ion-solvent interactions and the structure of the solvation environment about NH₄⁺. Rotation of NH₄⁺ within its solvation shell is remarkably fast. We suggest that rotation is so fast, especially in water, because the disordered environment presents one or more additional solvent molecules that facilitate rotation. This model is consistent with the discrepancy (1) between the observed activation energy for rotation in water and the barrier relative to a free rotor. We present these data as a challenge for simulation of NH₄⁺ rotation, not only in water but also in other solvents.

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