Implications of this mechanism for ion-pair chromatography will be reported elsewhere.[9] The relaxation time expression for this mechanism is[10]

$$\mathrm{Tau}^{-1} = k_2([\mathrm{A}^-\mathrm{C}^+] + [\mathrm{S}]\cdot\mathrm{R}) + k_{-2} \qquad (3)$$

with R as a constant term given by $k_1[\mathrm{C}^+]/(k_1[\mathrm{C}^+] + k_{-1})$.

A value for k_2 was obtained, from the slope of a linear Tau^{-1} vs. $[\mathrm{A}^-\mathrm{C}^+]$ plot under conditions of constant [S], of 1.4×10^9 $\mathrm{dm}^3/(\mathrm{mol\ s})$.[7] This is a reasonable order-of-magnitude figure for the (presumably diffusion controlled) sorption step. The single-exponential behavior of the relaxation curve for ODS-I indicates that this material is adequately modeled as a surface with a single type of interaction site.

In contrast, the response for ODS-II is best represented by a continuous distribution of reaction sites. A distribution of first-order rate constants yields an experimental decay curve that is the Laplace transform of the distribution.[11] Thus, Laplace inversion of the decay curve yields the original reaction rate distribution, which in our systems is directly related to the dispersion in the energetics of interaction. The relaxation curve for the ODS-II system is well fit by the function

$$\mathrm{f}(t) = \exp(-ct^{1/2}) \qquad (4)$$

with $c = (6k_0)^{1/2}$, where k_0 is the median rate constant. The inverse Laplace transform of this function yields the following:

$$\mathrm{F}(k,0) = c(4\pi k^3)^{-1/2} \exp(-c^2/4k) \qquad (5)$$

The function $\mathrm{F}(k,0)$ reaches a maximum at $k = k_0 = c^2/6$.[11] The parameter k_0 is in this case the relaxation time mode for the system. A linear plot of k_0 vs. the concentration term in eq 3 will thus yield a mode sorption rate constant. From concentration-dependent measurements of the decay parameter c, such a linear plot yielded a mode sorption rate constant of $2.2 \pm 0.7 \times 10^6$ $\mathrm{dm}^3/(\mathrm{mol\ s})$. (Correlation coefficient = 0.941). This sorption rate constant is dramatically lower than that for ODS-I. Reasons for this reduction are currently under investigation. The value of the equilibrium constant K_2 is 0.88, obtained from Langmuir isotherm measurements using the frontal elution method.[12] By use of the value of k_2 determined above to calculate a mode c value, eq 5 is plotted in Figure 1. From the figure, a value for the dispersion (taken as the width at 10% of peak height) of 2.6×10^7 is obtained. Assuming that the dispersion in K_2 is due to dispersion in k_{-2} (the desorption rate constant: i.e., a fixed sorption rate constant for all sites) and from the relationships $K_2 = k_2/k_{-2}$ and $\Delta G = -RT \ln K_2$, the corresponding dispersion in interaction free energy is 6.23 kJ/mol, relative to a median ΔG of 0.32 kJ/mol.

In summary, the relaxation curves from systems involving heterogeneous surfaces can be modeled as the Laplace transform of the reaction site distribution. Thus, the actual site distribution may be recovered by taking the inverse Laplace transform of the relaxation curves. This represents a direct measure of the degree of heterogeneity of the chemically modified surface, in units of free energy of solute–surface interaction. This dispersion in free energy is the parameter that is most intimately connected with the efficiency of these materials as liquid chromatographic stationary phases. The method should also be useful in other surface adsorptive systems where the surface heterogeneity is important.

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(10) Bernasconi, C. F. "Relaxation Kinetics"; Academic Press: New York, 1976.

(11) Doba, T.; Ingold, K. U.; Siebrand, W. *Chem. Phys. Lett.* **1984**, *103*, 339.

(12) Jacobson, J.; Frenz, J.; Horváth, Cs. *J. Chromatogr.* **1984**, *316*, 53.

Rotation, Solvation, and Hydrogen Bonding of Aqueous Ammonium Ion

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In connection with mechanistic studies on proton exchange in amides, it was concluded[1] that the -NH_3^+ group of solvated $\mathrm{RCONH_3^+}$ rotates with a rate constant of 10^{11} or 10^{12} s^{-1}. This conclusion was derived rather indirectly, and it contrasts with rotation of the -NH_3^+ group of $\mathrm{ArNH_3^+}$, which can be considerably slower.[2,3] We therefore have sought to test this conclusion, but in the simplest analogue, aqueous $\mathrm{NH_4^+}$. This is certainly a fundamental system, whose rate of rotation is of considerable inherent interest. This rate is customarily expressed in terms of a rotational correlation time, τ_c, which is the time required for rotational diffusion through an angle of 33°.[4] For $\mathrm{NH_4^+}$, τ_c can be determined experimentally from the ^{15}N spin–latice relaxation time, T_1, since motion of the attached protons can be the dominant mechanism for that relaxation. (It is essential to use ^{15}N, since quadrupolar relaxation is the dominant mechanism for ^{14}N relaxation in $^{14}\mathrm{NH_4^+}$, despite the high symmetry.)[5] There have been suggestions that T_1 of $^{15}\mathrm{NH_4^+}$ is quite long[6] and that the rotation is quite fast,[7] but no definitive studies have been reported. (Rotation of $\mathrm{NH_4^+}$ in crystals has been studied extensively.)[8] We now report that the rotational correlation time of aqueous $\mathrm{NH_4^+}$ is indeed ca. 10^{-12} s.

Samples were prepared by dissolving $^{15}\mathrm{NH_4NO_3}$ (Prochem 95 or 99% $^{15}\mathrm{NH_4^+}$) or $^{15}\mathrm{ND_4NO_3}$ (prepared by twice exchanging with a 60-fold molar excess of $\mathrm{D_2O}$ and evaporating the solvent) to 1.4 M in 1 M aqueous HCl or $\mathrm{DCl/D_2O}$, respectively, and deoxygenating with Ar or $\mathrm{N_2}$. Samples were contained in 12-mm NMR tubes with an internal 5-mm capillary containing $\mathrm{D_2O}$ when necessary for lock.

^{15}N NMR spectra were run at 20.37 MHz on a Nicolet NT200 wide-bore spectrometer interfaced to a NIC1180E Data Processor. Spin–lattice relaxation times were measured with a saturation–recovery pulse sequence,[9] including homospoil and with narrow-band (low-power) ^{1}H or ^{2}D irradiation, the latter through the lock unit, except at 80 °C, where rapid proton exchange necessitated broad-band irradiation. The data were well fit to a single exponential by a linear least-squares formula or by Nicolet's nonlinear least-squares routine. For nuclear Overhauser enhancement (NOE) measurements, intensities under continuous ^{1}H or ^{2}D irradiation were determined and compared with intensities under decoupling gated on during acquisition to produce singlets. Temperature was monitored both with a thermistor and from the chemical shifts of an ethylene glycol[10] sample subjected to the same irradiation conditions.

Table I lists observed spin–lattice relaxation times, T_1, and NOEs, η. Also listed are the dipole–dipole contributions to T_1, calculated according to eq 1, where $\eta_{\max} = -4.93$ for ^{1}H irradiation

$$T_{1,\mathrm{dd}} = (\eta_{\max}/\eta)T_{1,\mathrm{obsd}} \qquad (1)$$

and −0.76 for ^{2}D irradiation. This correction was reasonably small,

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(1) Perrin, C. L. *J. Am. Chem. Soc.* **1974**, *96*, 5631. Perrin, C. L.; Johnston, E. R.; Ramirez, J. L. *Ibid.* **1980**, *102*, 6299. Perrin, C. L.; Johnston, E. R. *Ibid.* **1981**, *103*, 4697.

(2) Levy, G. C.; Godwin, A. D.; Hewitt, J. M.; Sutcliffe, C. *J. Magn. Reson.* **1978**, *29*, 553.

(3) Lambert, J. B.; Stec, D.; III *Org. Magn. Reson.* **1984**, *22*, 301.

(4) Noggle, J. H.; Schirmer, R. E. "The Nuclear Overhauser Effect"; Academic: New York, 1971.

(5) Randall, E. W. In "Nitrogen NMR"; Witanowski, M., Webb, G. A., Eds.; Plenum: London, 1973; p 64.

(6) Saluvere, T.; Lippmaa, E. T. *Chem. Phys. Lett.* **1970**, *7*, 545.

(7) Rädle, C., Thesis, Karlsruhe. Through: Hertz, H. G. In "Water, A Comprehensive Treatise"; Franks, F., Ed.; Plenum: New York, 1973; Vol. 3, Chapter 7, p 385.

(8) Heidemann, A., et al., , *J. Phys. Soc. Jpn.* **1983**, *52*, 2401 and references cited. Especially: Press, W. *Springer Tracts Mod. Phys.* **1982**, *92*.

(9) McDonald, G. G.; Leigh, J. S., Jr. *J. Magn. Reson.* **1973**, *9*, 358.

(10) Ralford, D. S.; Fisk, C. L.; Becker, E. D. *Anal. Chem.* **1979**, *51*, 2050.

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Table I. Spin-Lattice Relaxation Times, Nuclear Overhauser Enhancements, and Rotational Correlation Times for Aqueous Ammonium-N_{15} Ion

T, °C	$T_{1,\text{obsd}}$, s	η	$T_{1,\text{dd}}$, s	τ_c, ps
3.3	35.2	−4.80	36.2	1.41
21	44	−4.67	46.5	1.10
21[a]	46.4	−4.78	47.9	1.07
36	59.5	−4.26	69	0.74
48	78.5	−4.66	83	0.62
80	86.2	−4.16	102	0.50
21	409[b]	−0.57	544	1.50

[a] For 0.7 M NH_4NO_3 in 0.5 M HCl. [b] For ND_4^+ in DCl/D_2O.

in contrast to previous studies at higher temperature, where spin-rotation relaxation is dominant.[6,11] The correction is slightly larger for ND_4^+, owing to diffusional effects and chemical exchange with incompletely deuterated solvent. The rotational correlation time for the ammonium ion was then calculated according to eq 2, with $\langle r_{NH}^{-3}\rangle^{-1/3} = 1.03$ Å[13] $= \langle r_{ND}^{-3}\rangle^{-1/3}$, and

$$\frac{1}{T_{1,\text{dd}}} = 4\,\frac{\frac{4}{3}I(I+1)\gamma_N^2\gamma_{H\text{ or }D}^2\hbar^2}{r_{NH\text{ or }ND}^6}\,\tau_c \qquad (2)$$

the values are listed in Table I. Since τ_c is independent of concentration, we may conclude that ion pairing does not contribute to the observed values, which are characteristic of solvated NH_4^+.

The correlation times in Table I are indeed ca. 10^{-12} s, which is shorter than the 9×10^{-12} s for H_2O in liquid water[14] and remarkably close to the 0.2×10^{-12} s for CH_4 in liquid methane.[15] So rapid a rotation is perhaps surprising, inasmuch as the protons of NH_4^+ are hydrogen-bonded to solvating water molecules, and rotation requires breaking and remaking those hydrogen bonds. There are reasons to suppose that those hydrogen bonds are both strong and directional: In the gas phase, the enthalpy of hydration of NH_4^+ is 10.6-20.6 kcal/mol per water molecule,[16a] and hydrogen bonding is estimated[16b] to contribute up to 20 kcal/mol to the binding of crown ethers to ammonium ions. Also, it has long been known[17] that NH_4^+ fits into the H_2O lattice, and NH_4Br in 18-crown-6 shows protons in directional hydrogen bonds.[18] Moreover, according to MO calculations on $NH_4^+{\cdot}OH_2$,[19] 5.5 kcal/mol is required to create even one bifurcated hydrogen bond, where the H_2O is located midway between two NH protons. Finally, according to a simple electrostatic model,[20] with 11%[21] of a positive charge on each H interacting with water dipoles in a medium of dielectric constant 1, the barrier to rotation of NH_4^+ is >6 kcal/mol. Yet any such barrier would reduce the rate of rotation to a value well below what we observe.

Nor can the protons be tunneling[22] through such a barrier, since the τ_c for $^{15}ND_4^+$, given in Table I, shows that rotation of this ion is retarded only by a factor of $\sim 2^{1/2}$. This is the classical value for k_H/k_D due to the increased moment of inertia. (For comparison with a process known to involve tunneling, the inversion rate of ND_3 is only 1/14 that of NH_3.[23])

Therefore we conclude that there is no substantial barrier to rotation of aqueous NH_4^+. By comparing the observed τ_c with the value expected for a free rotor of this moment of inertia, we estimate that this barrier is only 1.6 kcal/mol. On the other hand, from the temperature dependence of the correlation times in Table I, an apparent activation E_A of 2.76 ± 0.32 kcal/mol and a $\log_{10} A$ of 14.04 ± 0.23 can be calculated. We cannot exclude the possiblity that the discrepancy between these two estimates of the barrier is due to a slight increase of the apparent E_A, owing to the temperature dependence of density.[24] However, the experimentally determined τ_c is characteristic of the average environment of the NH_4^+ ion, averaged over a long time ($T_1 \sim 10^2$ s). If any appreciable fraction (>10%) of the ions are in "disordered" environments—temporarily desolvated or with bifurcated hydrogen bonds—that favor rotation, these can dominate the average. Then the observed E_A would represent the temperature dependence of this fraction. Moreover, since the observed log A is too large for a free rotor of this moment of inertia ($\log_{10} A = 13.1$), we conclude that 1.6 kcal/mol is a better estimate of the barrier to rotation.

So low a barrier might have been anticipated: Bifurcated hydrogen bonds are quite common in crystals.[25] Also, the enthalpy of hydration of NH_4^+, corrected for hydrophobic effects, lies on the plot vs. $1/r$ for hydration of alkali-metal ions.[26] We conclude that solvation of aqueous ammonium ion may involve hydrogen bonds, but these are not strong and directional.

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[11] Lichter, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 3200.

[12] Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution NMR Spectroscopy"; Pergamon: London, 1965; Vol. 1, p 24.

[13] Ibers, J. A.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *28*, 929.

[14] Smyth, C. P. "Dielectric Behavior and Structure"; McGraw-Hill: New York, 1955.

[15] McClung, R. E. D. *J. Chem. Phys.* **1971**, *55*, 3459.

[16] (a) Meot-Ner, M. *J. Am. Chem. Soc.* **1984**, *106*, 1265; (b) *Ibid.* **1983**, *105*, 4912. But see: Sharma, R. B.; Blades, A. T.; Kebarle, P. *Ibid.* **1984**, *106*, 510.

[17] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 102.

[18] Nagano, O.; Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 790.

[19] Kollman, P. *J. Am. Chem. Soc.* **1977**, *99*, 4875.

[20] Perrin, C. L., unpublished calculations. After: Condon, F. E. *J. Am. Chem. Soc.* **1965**, *87*, 4481.

[21] Ishida, K.; Kadowaki, S.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 967.

[22] Bell, R. P. "The Tunnel Effect in Chemistry"; Chapman and Hall: London, 1980.

[23] King, G. W. "Spectroscopy and Molecular Structure"; Holt Rinehart and Winston: New York, 1964; p 360.

[24] Wilbur, D. J.; Jonas, J. *J. Chem. Phys.* **1975**, *62*, 2800.

[25] Taylor, R.; Kennard, O.; Versichel, W. *J. Am. Chem. Soc.* **1984**, *106*, 244. Jeffrey, G. A.; Mitra, J. *Ibid.* **1984**, *106*, 5546.

[26] Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 318.

Molecular Recognition through the Exact Placement of Functional Groups on Rigid Matrices via a Template Approach[1]

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Molecular recognition of polymers prepared by imprinting with templates has been intensively studied in recent years.[2,3] In this way progress has been made in building specific binding sites into polymers as models of biological receptors and enzymes. Imprinting during the preparation of cross-linked polymers in most cases has been used for the preparation of chiral cavities containing functional groups. The selectivity observed in racemic resolution then is a result of the combination of the exact cavity-shape fitting

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[1] Enzyme-Analogue Built Polymers. 20. For Part 19, see: Wulff, G.; Poll, H.-G.; Minarik, M. *J. Liquid Chromatogr.*, in press.

[2] (a) Wulff, G.; Sarhan, A.; Zabrocki, K. *Tetrahedron Lett.* **1973**, 4329–4332. (b) Wulff, G.; Vesper, W.; Grobe-Einsler, R. Sarhan, A. *Makromol. Chem.* **1977**, *178*, 2799–2816. (c) Wulff, G.; Kemmerer, R.; Vietmeier, J.; Poll, H.-G. *Nouv. J. Chim.* **1982**, *6*, 681–687. (d) Wulff, G.; Best, W.; Akelah, A. *React. Polym. Ion Exch., Sorbents* **1984**, *2*, 167–174. (e) For a comprehensive review, see: Wulff, G. *ACS Symp. Ser.*, in press.

[3] (a) Shea, K. J.; Thompson, E. A. *J. Org. Chem.* **1978**, *43*, 4253–4255. (b) Shea, K. J.; Thompson, E. A.; Pandey, S. D.; Beauchamp, P. S. *J. Am. Chem. Soc.* **1980**, *102*, 3149–3155. (c) Damen, J.; Neckers, D. C. *J. Am. Chem. Soc.* **1980**, *102*, 3265–3267. (d) Andersson, L.; Sellergren, B.; Mosbach, K. *Tetrahedron Lett.* **1984**, *25*, 5211–5214. (e) Fujii, Y.; Matsutani, K. *J. Chem. Soc., Chem. Commun.* **1985**, 415–417.

0002-7863/86/1508-1089$01.50/0