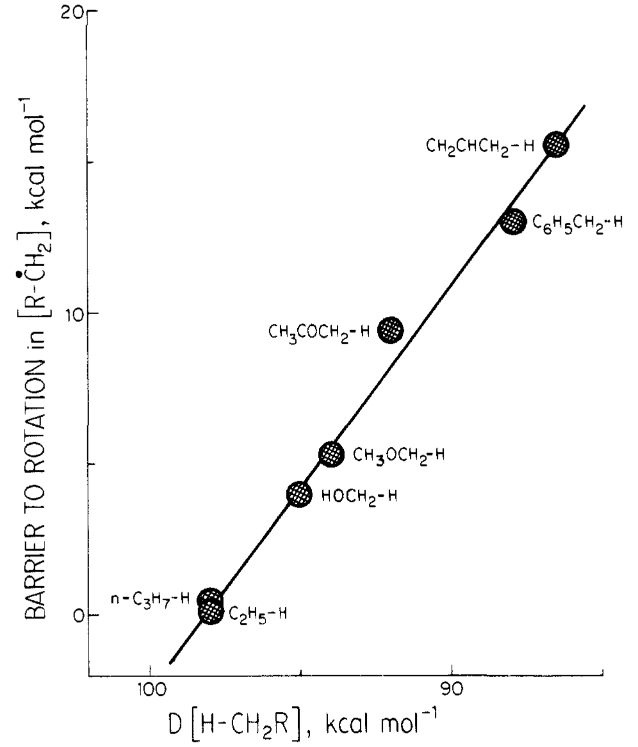

Figure 1. Plot of barrier to internal rotation in radicals $[R\text{-}\dot{C}H_2]$ vs. homolytic bond dissociation energy $D[H\text{-}CH_2R]$. Points from ref 8 or as given in text.

two recent values of our own[2] for $\dot{C}H_2OCH_3$ and $\dot{C}H_2OH$.[3] The correlation is excellent and the new value removes the discrepancy for $\dot{C}H_2COCH_3$.

Acknowledgment. J.L.H. thanks the Natural Sciences and Engineering Research Council of Canada for continuing financial support. J.L.H. and J.K.T. thank the NATO Scientific Affairs Division for a collaborative research award.

Determination of the Interaction Free Energy Dispersion in Sorptive Systems by Relaxation Kinetics Methods

David B. Marshall,* James W. Burns, and David E. Connolly

Department of Chemistry, University of Idaho
Moscow, Idaho 83843

Received November 19, 1985

We report here the direct measurement of sorption–desorption kinetics in a liquid chromatographic system. The sorption rate constants for an ion pair with homo- and heterogeneous octadecylsilicas have been determined by using the pressure-jump relaxation kinetics technique. The results indicate that the relaxation response curve is the Laplace transform of the distribution of first-order relaxations from the heterogeneous surface. Inversion of the relaxation curve permits determination of the mode in the sorption rate constant and a measure of the dispersion in interaction free energy of the solute with the surface.

For heterogeneous sorptive systems, there is a distribution of interaction energies. The particular width and form that this distribution takes may play an important if not critical role in determining the static and dynamic behavior of a sorptive system. For instance, it is known that the surface of chemically modified silica, as used as a stationary phase in HPLC, is heterogeneous with respect to surface silanol groups[1] and the local distribution of surface-bound molecules.[2,3] A heterogeneous surface may give rise to a phase where the kinetics of sorption–desorption are the dominant contributor to the overall chromatographic performance (bandwidth).[4] The kinetic contribution to band broadening may be as high as 70% or higher of the total elution bandwidth.[5] Chemical modification of silica yields a more energetically homogeneous surface.[6] This results in a reduction in peak dispersion and tailing in the chromatographic experiment, yielding a phase with higher "efficiency". Direct measurements of sorption–desorption kinetics in a chromatographic system show that differences in chromatographic efficiency are directly related to differences in sorption–desorption dynamics of test solutes on octadecylsilica stationary phases ("reversed-phase" HPLC).[7]

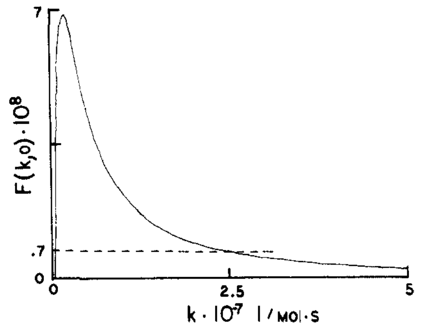

Figure 1. Function of eq 5 plotted for ODS-II, showing the dispersion (width at 10% of peak height) in the value of the desorption rate constant k_{-2}.

Two octadecylsilicas were synthesized for this study. Details of the synthetic procedure are reported elsewhere.[7] The two aliquots differ in levels of total carbon coverage, "ODS-I" containing 19.25% carbon and "ODS-II" containing only 12.25%. ODS-I is the more "efficient" of the two materials in terms of the elution peak width for test solutes when the materials are used as liquid chromatographic stationary phases.[7] From the considerations cited above, it is expected that ODS-I would be a more homogeneous material and thus show less dispersion in interaction free energy with solutes. The kinetic indicator for this pressure-jump relaxation experiment is an ion pair system in methanol at 25 ± 0.05 °C, involving a fluorescent sorption indicator, 1-anilino-8-naphthalenesulfonate, or "ANS", and high ("pseudoconstant") concentrations of trimethylhexadecylammonium counterion.[8] Details of the general experiment will be reported elsewhere.[7,9] The relaxation curve observed upon abruptly reducing the pressure from 2500 psi to atmospheric pressure has an initial fast step that is attributable to the primary sorption–desorption process, followed by a slow step that is due to pore intercalation effects.[7]

The relaxation kinetic data for the fast response for ODS-I are consistent with the following kinetic mechanism:

$$[A^-] + [C^+] \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} [A^-C^+] \qquad (1)$$

$$[A^-C^+] + S \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} A^-CS^+ \qquad (2)$$

---

(1) Unger, K. K. "Porous Silica"; Elsevier: Amsterdam, 1979; Chapters 1 and 3.

(2) Lochmüller, C. H.; Marshall, D. B.; Harris, J. M. *Anal. Chim. Acta* **1981**, *131*, 263.

(3) (a) Lochmüller, C. H.; Colborn, A. S.; Hunnicutt, M. L.; Harris, J. M. *Anal. Chem.* **1983**, *55*, 1344; (b) *J. Am. Chem. Soc.* **1984**, *106*, 4077.

(4) Giddings, J. C. "Dynamics of Chromatography"; Marcel Dekker: New York, 1965; Section 6.5.

(5) Horváth, Cs.; Lin, H.-J. *J. Chromatog.* **1978**, *149*, 43.

(6) Horváth, Cs.; Melander, W.; Molnar, I. *J. Chromatogr.* **1976**, *125*, 129.

(7) Marshall, D. B.; Burns, J. W.; Connolly, D. E. *J. Chromatogr.*, in press.

(8) Dowling, S. D.; Seitz, W. R. *Anal. Chem.* **1985**, *57*, 602.

(9) Marshall, D. B.; Burns, J. W.; Connolly, D. E. *Anal. Chem.*, accepted for publication.

0002-7863/86/1508-1087$01.50/0

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

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

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

A value for k_2 was obtained, from the slope of a linear Tau^{-1} vs. $[A^-C^+]$ plot under conditions of constant [S], of 1.4×10^9 dm^3/(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

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

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

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

The function $F(k,0)$ 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 $2.2 \pm 0.7 \times 10^6$ dm^3/(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.

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to NSF (Grant CHE 83-06881) for financial support of this research.

---

(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

Charles L. Perrin* and Robert K. Gipe

Department of Chemistry, D-006, University of
California, San Diego, La Jolla, California 92093

Received June 13, 1985

In connection with mechanistic studies on proton exchange in amides, it was concluded[1] that the -NH_3^+ group of solvated $RCONH_3^+$ 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 $ArNH_3^+$, which can be considerably slower.[2,3] We therefore have sought to test this conclusion, but in the simplest analogue, aqueous 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 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 $^{14}NH_4^+$, despite the high symmetry.)[5] There have been suggestions that T_1 of $^{15}NH_4^+$ is quite long[6] and that the rotation is quite fast,[7] but no definitive studies have been reported. (Rotation of NH_4^+ in crystals has been studied extensively.)[8] We now report that the rotational correlation time of aqueous NH_4^+ is indeed ca. 10^{-12} s.

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

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

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

---

(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.