J. Am. Chem. Soc. **1980**, *102*, 5187–5191

in the calculation of the orbital term J^{1b}.

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Appendix

This appendix is concerned with evaluating integrals of the form $\langle\chi(\mathrm{A},\alpha_1,l_1,m_1,n_1)|\mathrm{O_C}|\chi(\mathrm{B},\alpha_2,l_2,m_2,n_2)\rangle$ where the operator $\mathrm{O_C}$ associated with center C is one of the "diagonal" operators such as $(3z_\mathrm{C}^2 - r_\mathrm{C}^2)r_\mathrm{C}^{-5}$ or a "cross-term" operator such as $3x_\mathrm{C}y_\mathrm{C}r_\mathrm{C}^{-5}$. For the diagonal operators we use eq 25 of Matsuoka with his denominator corrected to read $t!w!(k - 2t - 2w + 2)!$. Also, in eq 24 π/γ should be changed to $\pi/2\gamma$.

For the cross-term we use the identity

$$3x_\mathrm{C}y_\mathrm{C}r_\mathrm{C}^{-5} = -(2\pi^2)^{-1}\int k_xk_yk^{-2}e^{i(\mathbf{k}\cdot\mathbf{r}_\mathrm{C})}\,\mathrm{d}k$$

Following procedures similar to those of Matsuoka we obtain

$$\langle\chi_\mathrm{A}|3x_\mathrm{C}y_\mathrm{C}r_\mathrm{C}^{-5}|\chi_\mathrm{B}\rangle = \sum_{I,J,K} G_IU_JU_K\pi(2\gamma)^{-1}e^{-\alpha_1\alpha_2AB^2/\gamma}$$

where the *U*'s are defined by Matsuoka and the remaining quantities by ref 22.

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(22) H. Taketa, S. Huzinaga, and K. O-ohata, *J. Phys. Soc. Jpn.*, **21**, 2312 (1966).

EPR Studies of the Molecular Motion of Nitroxide Radicals in Poly(vinyl alcohol) Gels

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Abstract: Rotational diffusion of several nitroxide radicals in aqueous solution and in poly(vinyl alcohol) (PVA) gels has been studied by the analysis of line width of EPR spectra based on the axially symmetric rotational diffusion model proposed by Freed et al. The pore size dependence of the motion of nitroxide in PVA gel is made clear, that is, (1) the correlation time of rotational diffusion of the solute molecule sharply increases in the limited space of the solution smaller than 50 times the volume of solute molecule, (2) the rotational diffusion is more anisotropic in a smaller pore, (3) the anisotropy of the interaction of the solute molecule with the surrounding molecules also increases in a smaller pore, and (4) the interaction is mainly due to weak hydrogen bonding between the solute molecule and the hydroxy group of the PVA lattice. In general, the physical nature of the system represented by the volume ratio of the space of solution or the pore to the solute molecule primarily determines the rotational motion in a limited space, though the chemical nature of the solute molecules also affects the rotational motion considerably, especially its rate.

Introduction

Molecular motion of solute and solvent molecules in solution has been extensively investigated by various methods of spectroscopy. However, most of those investigations were done under the condition that the solute and the solvent molecules were in free motion in the bulk media. The purpose of the present investigation is to investigate the molecular motion of the solute molecule which is confined in a small pore, which is of current interest in biological reactions and catalytic reactions.[1,2] Recently, it has been shown by one of the present authors (S.F.)[3] that a certain minimum volume of solution is required for the maintenance of the free motion of the solute molecule in the solution, and this minimum volume has been referred to as the critical volume, V_c. The value of V_c for a solute molecule of relatively simple structure, such as the hydrated Cu^{2+} ion or the 2,2,5,5-tetramethyl-3-carbamoylpyrrolidin-1-oxy radical, was found to be about $(20 \pm 5\ \text{Å})^3$. As a matter of course, the size of V_c is expected to depend on the nature of the solute molecules, particularly on the size or on the chemical properties of the solute molecules. Thus, in this paper measurements of the V_c's were carried out for nitroxide radicals of similar size, but with different functional groups. As the media for limiting the space of the solution, different kinds of gel are applicable. for example, the gels of silica, poly(vinyl alcohol) (PVA), polystyrene, and so on. Several spectroscopic investigations can be referred to as the works which have been carried out on the solutions in those media.[1,4-6] In the present investigation PVA gels have been chosen as the media which control the space of the solution. The analysis of EPR spectra based on the model of axially anisotropic rotational diffusion proposed by Freed et al. was carried out.[7,8]

Experimental Section

Nitroxide Radicals. Five nitroxide radicals with different active groups have been used: 2,2,6,6-tetramethylpiperidinyl-1-oxy (Tempo) (I), 2,2,6,6-tetramethylpiperidinolyl-1-oxy (Tempol) (II), 2,2,6,6-tetramethylpiperidonyl-1-oxy (Tempone) (III), and 2,2,5,5-tetramethyl-3-carboxypyrrolidinyl-1-oxy (IV) were synthesized by the methods shown in the literature,[9] and 2,2,5,5-tetramethyl-3-carbamoylpyrrolidinyl-1-oxy (V) was purchased from Aldrich Chemical Co.

PVA Gel. PVA gels were produced by γ-ray irradiation to PVA aqueous solutions. The average distance between the end terminal of PVA molecules, $\langle l\rangle$, may be expressed by eq 1, which has been semi-

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(1) S. L. Regen, *Macromolecules*, **8**, 689 (1975).

(2) K. J. William, D. Marsh, C. S. Sunderland, B. J. Sutton, S. Wain-Hobson, R. A. Dwek, and D. Givol, *Biochem. J.*, **165**, 199 (1977).

(3) S. Fujiwara, K. Nagashima, H. Morita, and Y. Kanaoka, *Bull. Chem. Soc. Jpn.*, **50**, 2851 (1977).

(4) S. L. Regen, *J. Am. Chem. Soc.*, **97**, 3108 (1975).

(5) F. M. Menger, G. Saito, G. V. Sanzero, and J. R. Dodd, *J. Am. Chem. Soc.*, **97**, 909 (1975).

(6) T. Watanabe, K. Furuya, T. Yahagi, and S. Fujiwara, submitted for publication.

(7) S. A. Goldman, G. V. Bruno, C. F. Polnaszek, and J. H. Freed, *J. Chem. Phys.*, **56**, 716 (1972).

(8) J. S. Hwang, R. P. Mason, L. P. Hwang, and J. H. Freed, *J. Phys. Chem.*, **79**, 489 (1975).

(9) E. G. Rozantsev, "Free Nitroxy Radicals", Plenum Press, New York, 1970.

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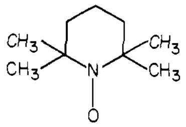

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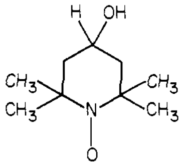

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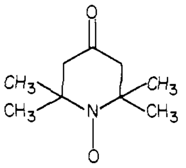

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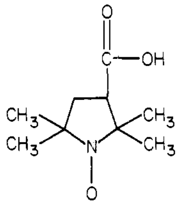

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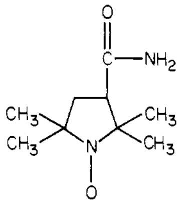

V

empirically derived under the assumptions of random cross-linking and infinitely long chains of PVA.[10a]

$$\langle l\rangle = 2.5[(5.1 \times 10^8 + 1.37 \times 10^8 C)/R]^{1/2} \quad (1)$$

Here C is the concentration of PVA in g/100 mL of H_2O and R is the total dose of γ-rays in radians. As the distribution of $\langle l\rangle$ has not been known precisely, it is presumed to be within the range of ±15% from the experimental data on the gel formation dosage. The width of distribution is larger for a smaller $\langle l\rangle$.[10] Even when the distribution of $\langle l\rangle$ takes the maximum value, ±15%, the uncertainties of $\langle l\rangle$ are ±1.7, ±2.3, ±3.0, and ±4.8 Å for gels ⟨11⟩, ⟨15.5⟩, ⟨20⟩, and ⟨32⟩, respectively.[10b] As is shown later in Figure 3, the distribution of $\langle l\rangle$ for gels ⟨20⟩ and ⟨32⟩ almost does not affect the analysis of line width. The correlation times in the gels ⟨11⟩ and ⟨15.5⟩ are sensitive to $\langle l\rangle$ and the distribution of $\langle l\rangle$ should be taken into consideration. Authors think, however, that the superposition of spectra for various $\langle l\rangle$ is meaningless under the present condition that both the distribution of $\langle l\rangle$ and the typical spectra of nitroxide for the specific $\langle l\rangle$ are unknown. So, in the present paper, $\langle l\rangle$ calculated from eq 1 is taken as a convenient parameter which represents the average size of pore of the solution, and the pore size in gel is assumed to be uniform. The actual procedure of the production of PVA gel was as follows: 20 g of PVA, with a degree of polymerization of 2000, was dissolved in 100 mL of hot water and irradiated by ^{60}Co γ-rays at room temperature in glass tubes 10 mm in diameter and 30 cm in length. PVA gels with different values of $\langle l\rangle$ (11, 13, 15.5, 18, 20, 22, 24, 26, 29, 32, 35, and 41 Å) were produced by changing R from 6×10^7 to 2.9×10^6 rad. The ^{60}Co source of the University of Tokyo was utilized. The homogeneity of the gel was confirmed experimentally by comparing the EPR spectra of the spin-labels loaded into different positions of the gels.

Sample for EPR Measurement. Each PVA gel with different $\langle l\rangle$ was soaked in a 1.0×10^{-3} mol/L aqueous solution of nitroxide radical for several days. The PVA gel was then removed from solution, cut into a rectangular sample about 1 × 1 × 7 mm, and sealed into a glass capillary of 2-mm diameter. The PVA gels with larger than 26 Å $\langle l\rangle$ are soft and not easy to pack in the capillaries. The EPR measurements were carried out at various temperatures using a JES-FE1X (JEOL) type spectrometer with 100-kHz modulation.

Results

Nitroxide radicals in dilute aqueous solution produce three hyperfine lines as the result of coupling of the electron spin with ^{14}N nuclei. The relative intensities of these lines can serve as a probe for the examination of the freedom of the molecular motion. In Figure 1, the intensity ratio, R, of the highest field line ($M_z = -1$) to the central line ($M_z = 0$) is presented as a function of $\langle l\rangle$.

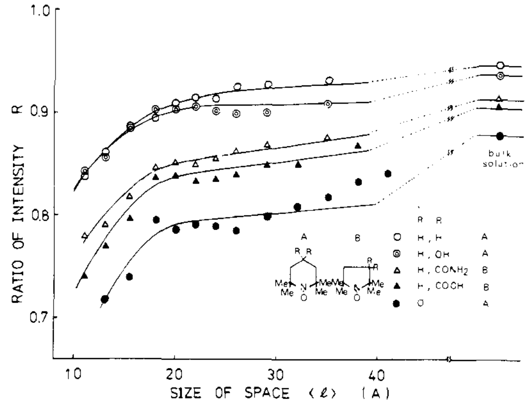

Figure 1, The size dependence of the ratio of signal intensity of the high-field line to the central line, R. R are plotted against the average size of space of solution, $\langle l\rangle$. Data are observed at room temperature.

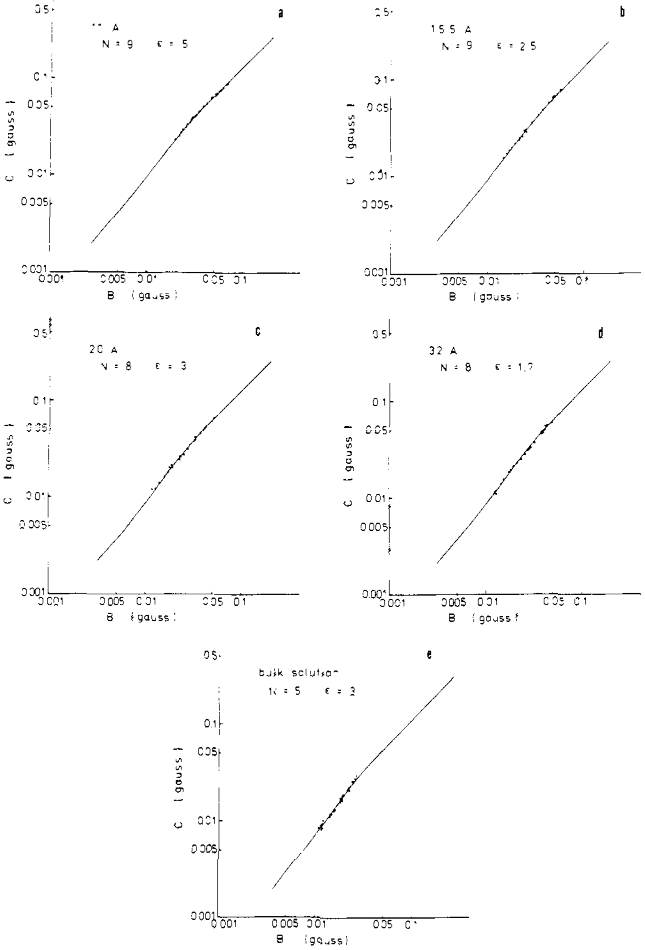

Figure 2. Experimental and calculated values of C vs. B for Tempone in (a) PVA⟨11⟩, (b) PVA⟨15.5⟩, (c) PVA⟨20⟩, (d) PVA⟨32⟩, and (e) bulk aqueous solution, respectively. Solid lines are calculated from eq 3 and 4 by using parameters shown in Table II.

Table I. Calculated C/B as a Function of N

N	$z' = z$	$z' = y$	$z' = x$
10	0.80	1.39	0.56
7	0.80	1.23	0.59
5	0.80	1.11	0.62
3	0.80	0.97	0.68
1	0.80	0.80	0.80
0.5	0.80	0.75	0.85
0.1	0.80	0.72	0.91

The EPR spectra of nitroxides in the various PVA gels indicate that the molecular motion of these nitroxides is in the typical fast rotational or motional narrowing region. A careful line-width study was performed for the radical III on the theory of Freed et al. about an anisotropic rotational reorientation.[7,8] The peak-to-peak derivative line width, δ, is expressed in terms of

$$\delta = A + B\tilde{M} + C\tilde{M}^2 \quad (2)$$

where $\tilde{M}$ is the spectral index number.[11] The B and C values can be experimentally obtained from the peak heights of three hyperfine lines and the line width of the central line in the observed

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(10) (a) A. Danno, *J. Phys. Soc. Jpn.*, **13**, 722 (1958). (b) For example, gel ⟨20⟩ means PVA gel with 20 Å of $\langle l\rangle$.

Table II. Parameters Used for the Analysis of Molecular Motion of Nitroxides in PVA Gels

⟨*l*⟩, Å	*N*	ϵ
11	9	5
15.5	9	2.5
20	8	3.0
32	8	1.7
bulk	5	3.0

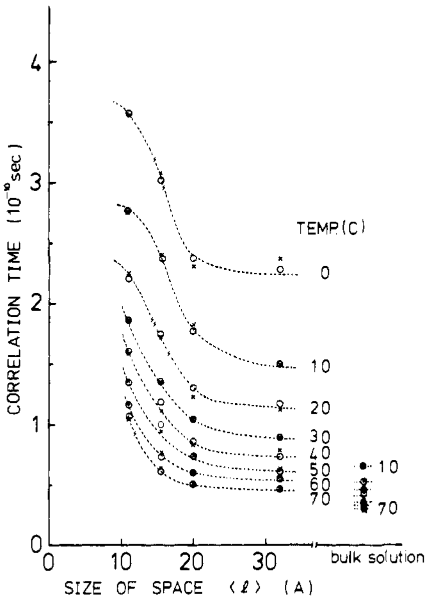

Figure 3. Correlation time of the radical III plotted against the size of pore, ⟨*l*⟩, at each temperature. Observed values from *B* and *C* are plotted by the open circles and the cross marks, respectively. The dotted lines are drawn along the points.

EPR spectra. The experimental *B* and *C* values for Tempone in the gels ⟨11⟩, ⟨15.5⟩, ⟨20⟩, and ⟨32⟩ and in bulk solution are plotted in Figure 2a–e. The *B* and *C* values are theoretically expressed as follows, under the assumption that the rotational-diffusion tensor is axially symmetric:[7]

$$B = (\pi/10)\omega_0\xi[g^{(0)}D^{(0)}\tau(0)\{{}^{16}\!/_3 + 4/(1 + \omega_0{}^2\tau(0)^2)\} + 2g^{(2)}D^{(2)}\tau(2)\{{}^{16}\!/_3 + 4/(1 + \omega_0{}^2\tau(2)^2)\}] \quad (3)$$

$$C = (4\pi^2/5)\xi^2[(D^{(0)})^2\tau(0) \times \{{}^8\!/_3 - 1/(1 + \omega_a{}^2\tau(0)^2) - 1/3(1 + \omega_0{}^2\tau(0)^2)\} + 2(D^{(2)})^2\tau(2)\{{}^8\!/_3 - 1/(1 + \omega_a{}^2\tau(2)^2) - 1/3(1 + \omega_0{}^2\tau(2)^2)\}] \quad (4)$$

where all symbols have the same meanings as in ref 7.

In order to estimate the diffusion parameter, *N*, and the experimental adjustment parameter into nonsecular spectral densities, ϵ, which are used in standard manners for analysis of line width,[7,8,12] *B* and *C* values are calculated from eq 3 and 4 for various *N* and ϵ values. When g_x, g_y, g_z, A_x, A_y, and A_z values are taken as 2.0104, 2.0074, 2.0026, 6.5 G, 6.7 G, and 33.0 G, respectively,[13] calculated *C*/*B* values are varied as a function of *N* for each axially symmetric rotational diffusion in the region where nonsecular terms are negligible, as is shown in Table I. The observed *C*/*B* values are in the range from 1.0 to 1.3, which indicates that the symmetry axis of the diffusion tensor, *z*′, equals a molecular fixed axis, *y*. Hence, the analysis of experimental line width is carried out as the axial rotational diffusion about *y* axes. The best fitted curves can be obtained by using parameters listed in Table II, and they are drawn as solid lines in Figure 2. If observed *B* or *C* values and these parameters are put into eq 3 or 4, correlation times τ_B or τ_C are estimated. τ_B and τ_C values in each case are shown in Figure 3. The estimated τ_B and τ_C in each case are almost equal to each other as shown in Figure 3, which means that the estimations of *N* and ϵ are correct. Hereafter, the correlation time, τ, is taken as an averaging value of τ_B and τ_C.

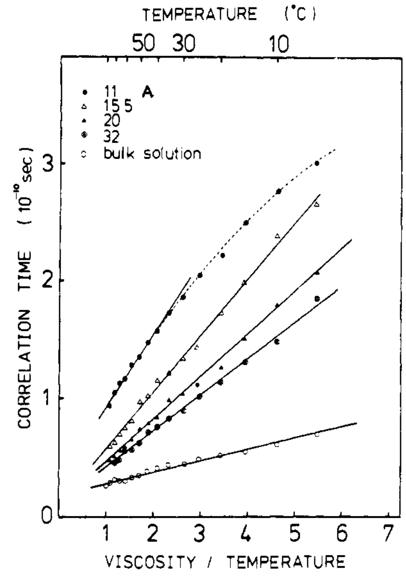

Figure 4. τ vs. η/T for Tempone in PVA gels and in aqueous solution, where η is the temperature-dependent viscosity of the pure water solution. τ is plotted as an averaging value of τ_B and τ_C: open circle (○) for in bulk solution, double circle (◉), closed triangle (▲), open triangle (△), and closed circle (●) for in PVA⟨32⟩, -⟨20⟩, -⟨15.5⟩, and -⟨11⟩, respectively.

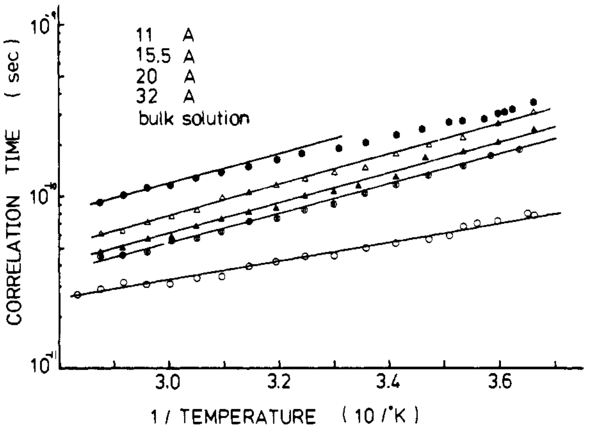

Figure 5, Arrhenius plot of τ. Symbols are the same as those of Figure 4.

If they are plotted vs. η/T, where η means the viscosity of water, the linear relations are obtained as shown in Figure 4, except in the case of gel ⟨11⟩. The relations of τ values to $1/T$ are plotted in Figure 5.

Discussion

Under the assumption that the concentration of the solute is uniform in the PVA gel and the same as that in the bulk solution, we can evaluate the distribution of the solute molecules in a PVA gel for a certain value of ⟨*l*⟩. If ⟨*l*⟩ is 11, 20, 30, or 40 Å, the distribution of the solute molecule in the lattice is equal to the case that only one solute molecule is embedded in a cluster of 1250, 208, 62, or 26 spaces of PVA gel, respectively. These figures suggest that solute–solute interactions are negligible, and, furthermore, that any solute molecule does not encounter the others as it moves through pores in the gel.

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(11) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 1815 (1964).

(12) S. A. Goldman, G. V. Bruno, and J. H. Freed, *J. Chem. Phys.*, **59**, 3071 (1973).

(13) N. Snipes, J. Cupp, G. Höhn, and A. Keith, *Biophys. J.*, **14**, 20 (1974).

Table III. Effective Rotational Radii of Tempone and Parameter κ

$\langle l \rangle$, Å	a, Å	r_e, Å	κ
11	2.68	3.2	0.59
15.5	2.52		0.49
20	2.39		0.42
32	2.16		0.31
aq	1.47		0.10

The following three features result from Figure 1: (i) the molecular motion of solute molecule is more restricted in the PVA gels than in the bulk solution; (ii) the pattern of the restriction is almost the same with respect to all five radicals and the restriction gets especially marked at the pore where $\langle l \rangle$ is less than about 18 Å; (iii) the rate of the molecular motion gets slower in the order of I $\sim$ II $>$ IV $\sim$ V $>$ III. These results suggest that the thermal motion of the solute molecule becomes drastically restricted when the pore size decreases to a nearly equal volume of the solution for all of the nitroxides used, and that the chemical nature of the functional group of the radical affects the correlation time of the rotational motion. The five nitroxide radicals are almost the same in molecular size with a core size of about $(8 \times 6 \times 6)$ A^3, and different with respect to the functional groups and the structure.[14]

Accordingly, it is concluded from the results of the present experiment that the motional pattern of nitroxide in gels is primarily determined by the relative size of the solute molecule to the size of reservoir and that the nature of the functional groups contributes to the rate of rotational motion.

In order to make more detailed comparison of the thermal motion of those molecules in PVA gel, further analysis of the correlation times of anisotropic rotational diffusion has been made as follows.

Anisotropic Rotational Diffusion of Tempone in PVA Gels. If the rotational diffusion of molecules is described by the Stokes–Einstein hydrodynamic equation, correlation time, τ, is written

$$\tau = 4\pi a^3 \eta / 3kT \qquad (5)$$

where a is a molecular hydrodynamic radius and η is a viscosity of the liquid. Although this equation is for the molecules in an infinite medium, the observed τ for nitroxides in PVA gels shows a linear relation to η/T, as shown in Figure 4, except for gel $\langle 11 \rangle$. From the slopes of the graphs, the effective rotational radii, a, can be obtained, which are shown in Table III. It is known that the radius, a, is almost always smaller than the geometrically measured or calculated mean radius, r_e, of the molecule. If we write

$$a^3 = \kappa r_e^{\,3} \qquad (6)$$

the empirical parameter κ is a measure of the anisotropy of the intermolecular potentials.[15] The geometric results are based upon values of $r_x \simeq 4.2$, $r_y \sim 2.7$, and $r_z \simeq 2.2$ Å for Tempone[16] and the geometric radius r_e is estimated at 3.2 Å.[8] Then κ is calculated as shown in Table III. According to Kivelson,[15] κ approaches unity for very anisotropic interactions and zero for hard-sphere interactions. From Table III, it is made clear that the interaction is more anisotropic in a smaller gel space.

The diffusion parameter $N = R_{\parallel}/R_{\perp}$, where $R_{\parallel}$ and $R_{\perp}$ are the components of the rotational diffusion about z' and about x', respectively, is 1 for isotropic rotational motion and becomes larger as anisotropy of motion increases.[7] The observed values for each PVA gel, as shown in Table II, become larger as $\langle l \rangle$ decreases. This result means that the anisotropy of rotational motion is larger as the size of the pore available for the solute becomes narrower. Theoretically, N equals 1.35 for Tempone,[8] which indicates a small asymmetry in the rotational diffusion. In the present experiment, however, N is too large. This result is explained by a strong interaction of nitroxide with the surrounding solvent and PVA gel, and the interaction is stronger in the smaller gel. This conclusion from N agrees with the discussion from κ cited above. Adjustment parameters, ϵ, in Table II are larger than unity, which indicates that the nonsecular spectral densities exhibit significant deviations from Debye-like spectral densities in these experimental cases.

Activation energies of the rotational motion calculated from the slope of Figure 5 are 1.00, 1.71, 1.77, 1.75, and 1.65 kcal/mol in bulk solution and gels $\langle 32 \rangle$, $\langle 20 \rangle$, $\langle 15.5 \rangle$, and $\langle 11 \rangle$, respectively. This increase of activation energy in PVA gels is mainly due to an interaction between radical and the surrounding PVA gel. This interaction is mainly a weak hydrogen bonding. It is generally known that both structured water and free water exist in polymer gel. Thus, water medium in PVA gel is not uniform and the viscosity of water in PVA gel should be slightly higher than that in bulk solution. This may be one of the reasons for the higher activation energy in PVA gel.

As is shown in Figure 3, it is clear that the rotational correlation times of nitroxide are almost constant in the PVA gel when $\langle l \rangle$ is larger than 20 Å and become drastically longer in PVA gels when $\langle l \rangle$ gets less than 15.5 Å, although this phenomenon is dependent upon temperature. If the volume of the pore is assumed to be $\langle l \rangle^3$ and that of Tempone is assumed to be $(4/3)\pi r_e^{\,3}$, where r_e equals 3.2 Å, the ratio of these volumes becomes 25 for $\langle l \rangle$ = 15 Å and 58 for $\langle l \rangle$ = 20 Å. So it is thought that the motion of solute molecule is affected in the limited space of the pore, which is less than about 50 times the volume of the solute molecule. When one solute molecule is located in the center of the pore, the distances between the outer sphere of the solute molecule and the lattices of the pore equal 2.2, 4.5, and 6.8 Å for gels $\langle 11 \rangle$, $\langle 15.5 \rangle$, and $\langle 20 \rangle$, respectively. Thus, the interaction of the solute molecule with lattice or PVA gel easily works in the smaller gel.

Molecular Interaction between the Solute and the Lattice of Pore. A strong dependence of the rate of the molecular motion in PVA gel on the species of the radicals is observed as shown in Figure 1. Some anisotropic interactions of radicals with the surrounding molecules are important in smaller PVA gels, as cited above for the case of Tempone. On the basis of these findings, it is concluded that the interaction of the functional groups of the nitroxide radical with the PVA gel affects the motion of the molecule and that the interactions of the solute molecules with the PVA gel occur in the order of carbonic (III) $>$ carboxylic (IV) $\sim$ carbamoyl (V) $>$ alcoholic (II) $\sim$ hydrogen (I). This order is contradictory to the usual order of the electronegativities, since the latter gives the lineup of V $\gtrsim$ IV $>$ III $>$ II $>$ I. It is inferred that the carbonyl group in the radical III is especially heavily polarized and has larger electronegativity than the carbonyl group in usual compounds because of both 1,4-through-space and 1,4-through-bond interactions of the orbitals.[17] This is confirmed from the EPR data of the radical III. Namely, the hyperfine coupling constant due to N nuclei of the radical III is as small as that of the radical V and the line width of the central line is extremely small.[18] This may refer to the fact that the electron density on the NO bond and the 12 methyl groups is low and the carbonyl group is strongly polarized. Thus, the order of the strength of the interaction with PVA gel follows the order of electronegativity of the functional groups, and the interaction of the solute with the PVA lattice is assumed to be predominantly determined by the accessibility of the hydrogen bonding.

Conclusion

The discussion so far given is based on the experimental data of the nitroxide radicals in PVA gels. However, the nature of the finding is general. Hence, it would be reasonable enough to conclude that the rotational diffusional motion is limited when the size of the pore for the solute is reduced. The critical volume

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(14) L. J. Berliner, Ed., "Spin Labeling, Theory and Application", Academic Press, New York, 1976, p 239.

(15) R. E. D. McClung and D. Kivelson, *J. Chem. Phys.*, **49**, 3380 (1968).

(16) R. P. Shibaeva, L. O. Atovmyan, M. G. Neiganz, L. A. Novakovskaya, and S. L. Ginzburg, *Zh. Strukt. Khim.*, 13, 42 (1972).

(17) R. Hoffman, *Acc. Chem. Res.*, **4**, 1 (1971).

(18) Hyperfine coupling constants due to N nuclei are 17.2, 16.8, 15.9, 16.1, and 15.9 G, and the line widths of central line are 1.47, 1.45, 0.37, 1.45, and 1.30 G for the radicals I–V, respectively.

of the pore, at which the rotational motion of the solute molecule is drastically restricted, may be in the range from 25 to 50 times the volume of solute molecule. In the smaller pore, the interaction of solute molecule with the surrounding molecules, that is, solvent or polymer lattice, works more easily and the anisotropy of the interaction becomes larger ($\kappa \rightarrow$ larger), and consequently the anisotropy of rotational diffusion also becomes larger ($N \rightarrow$ larger).

All those results cited above suggest that the rotational diffusion is mainly determined by the size of the solute molecule, i.e., by the physical nature of the latter. However, the data of the present investigation also suggest that the chemical effects also affect the rotational diffusion of the solute molecules by reducing the rate of the rotational motion. In this investigation, nothing was learned about translational diffusion of the solute molecule in PVA gel. However, the translational motion of the solute molecule in PVA gels seems to be inhibited by the chain of PVA gels compared to the bulk solution.

In the present paper, the analysis of line width is carried out by the model of axially symmetric rotational diffusion. Actually, one hyperfine line due to N nucleus is composed of 13 hyperfine structures due to H nuclei, which results in inhomogeneous broadening. In the case of Tempone radical, the hyperfine coupling constant due to H nuclei is very small compared with that in the other radicals I, II, IV, and V, and the effect of inhomogeneous broadening is not considered in the discussion. It is reasonably said, however, that the conclusion obtained in this experiment shows the correct trend of rotational motion in the limited pore. In the case of Tempo radical, which has a larger hyperfine coupling due to H nuclei, similar analysis without an inhomogeneous broadening fails to explain the line width. The analysis of line width for Tempo radical in PVA gels will be discussed separately.

It has been recently noticed[19] that the confinement of water molecules in a small space of polyacrylamide is effective for the promotion of freezing. These phenomena might have relevance to the motion of molecules in limited space.

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[19] S. Katayama and S. Fujiwara, *J. Am. Chem. Soc.*, in press.

Molecular Orbital Theory of the Hydrogen Bond. 22. 4-Monosubstituted Pyridines as Proton Acceptors

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Abstract: Ab initio SCF calculations with the STO-3G basis set have been performed to investigate substituent effects on the hydrogen-bonding ability of 4-R-pyridine bases, with R including the substituents CH_3, NH_2, OH, F, C_2H_3, CHO, and CN. The equilibrium structures of the water-4-R-pyridine dimers are stabilized by a linear hydrogen bond formed through the nitrogen lone pair of electrons, and are similar to the equilibrium structure of the water-pyridine dimer with the plane of the pyridine ring perpendicular to that of the water molecule, with little variation in intermolecular distances. Except for F, substitution of a π donating and σ withdrawing group for H in the 4 position strengthens the hydrogen bond in water-4-R-pyridine dimers, while substitution of a σ and π electron-withdrawing group weakens the hydrogen bond. Primary substituent effects alter the electronic environment at the pyridine nitrogen, and are evident from changes in n-orbital energies upon substitution. These n-orbital energies are linearly related to the hydrogen-bond energies of the water-4-R-pyridine dimers provided that the n orbital is essentially localized at the nitrogen. A comparison of the stabilities of corresponding perpendicular water-2-R-pyridine and water-4-R-pyridine dimers shows that the hydrogen bond in the latter is stronger. However, secondary substitutent effects may further stabilize planar equilibrium structures of particular water-2-R-pyridine dimers to the extent that the 2-R-pyridine may form the more stable complex.

Introduction

Substituent effects on base properties are a major factor determining the behavior of compounds in important chemical and biochemical processes, and have therefore been a subject of interest and investigation in modern chemistry. This interest has intensified recently, owing to developments in chemical ionization mass spectrometry and ion cyclotron resonance spectroscopy which now permit measurements of gas-phase ion-molecule equilibria and the energetics of ion-transfer reactions in the gas phase,[1-4] and by the application of ab initio molecular orbital theory to the study of isodesmic processes.[5] Combined theoretical and experimental data have led to new insights into substituent effects on molecular basicity, and comparisons with solution data have demonstrated the important role which the solvent may play in moderating basicity in condensed media.[6-9]

As part of a continuing investigation of substituent effects on base strength, the hydrogen-bonding ability of a set of 2-monosubstituted pyridines was recently evaluated in this laboratory from ab initio molecular orbital calculations.[10] In that study, the structures and stabilization energies of water-2-R-pyridine complexes (mixed dimers), with R including the isoelectronic saturated groups CH_3, NH_2, OH, and F and the unsaturated groups C_2H_3

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(1) (a) R. W. Taft in "Proton-Transfer Reactions", E. F. Caldin and V. Gold, Eds., Wiley, New York, 1975, pp 31-77; (b) P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977).

(2) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 311 (1976).

(3) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).

(4) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 5920 (1975).

(5) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).

(6) E. M. Arnett in ref 1a, pp 79-101.

(7) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 318 (1976).

(8) E. M. Arnett, B. Chawla, L. Bell, M. Taagepera, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5729 (1977).

(9) W. R. Davidson, J. Sunner, and P. Kebarle, *J. Am. Chem. Soc.*, **101**, 1675 (1979).

(10) J. E. Del Bene, *J. Am. Chem. Soc.*, **101**, 7146 (1979).

0002-7863/80/1502-5191$01.00/0