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EPR Line Shifts and Line Shape Changes Due to Spin Exchange of Nitroxide-Free Radicals in Liquids 4. Test of a Method to Measure Re-Encounter Rates in Liquids Employing ^{15}N and ^{14}N Nitroxide Spin Probes

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EPR line shifts due to spin exchange of perdeuterated 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (^{14}N−PDT) in aqueous solutions and the same probe isotopically substituted with ^{15}N (^{15}N−PDT) were measured from 293 to 338 and 287 to 353 K, respectively. Nonlinear least-squares fits of the EPR spectra yielded the resonance fields of the nitrogen hyperfine lines to high precision from which the shifts were deduced. The shifts are described by two terms: one linear and the other quadratic in the electron spin-exchange frequency, ω_e. The quadratic term is due to spin exchange that occurs when two spin probes diffuse together and collide. A linear term is predicted for spin exchanges that occur upon re-encounter of the same two probes while they occupy the same "cage" before diffusing apart. The quadratic term has no adjustable parameters, while the linear term has one: the mean time between re-encounters, τ_{RE}. The theory is cast in terms of the spin-exchange-induced line broadening that can be measured from each spectrum independently of the line shifts, thereby removing the explicit dependence of ω_e on the temperature and the spin-probe concentration. In this form, theoretically, the value of the linear term is about a factor of 2 larger for ^{15}N−PDT than for ^{14}N−PDT for all temperatures; however, τ_{RE} must be the same. Experimentally, we find that both of these expectations are fulfilled, providing strong support that the linear term is indeed due to re-encounter collisions. Values of τ_{RE} derived from ^{14}N−PDT and ^{15}N−PDT are of the same order of magnitude and show the same trend with temperature as a hydrodynamic estimate based on the Stokes−Einstein equation.

Introduction

This is a continuation of a series of papers dedicated to extracting as much information as possible from electron paramagnetic resonance (EPR) spectra of nitroxides undergoing spin exchange in liquids. The series was motivated by two facts. First, due to the availability of modern magnetic field sweeps offering superb linearity and personal computers with which nonlinear least-squares fitting could be effected, very high precision could be obtained in measuring the parameters describing the spectra. Second, it was discovered that the rather complex spectra resulting from spin exchange could be described with simple analytical expressions valid to very high spin-exchange frequencies, ω_e.

Spin exchange produces (1) line broadening and (2) shifting of the lines toward the center of the spectra at low to intermediate values of ω_e, followed by (3) merging and narrowing of the spectra at very high values. A monograph[1] published in English in 1980 summarized these well-known properties and theoretical and experimental progress up until that time. Although all three of these spectral manifestations had been studied, the latter two had been critically assessed very little, mostly with limited precision. Thus, in 1980 almost all of the work involved line width studies, even those studies suffered from the lack of a proven method to separate the effects of spin exchange and dipolar broadening effects and often the lack of high precision methods to evaluate ω_e. An important development[2] was the demonstration that spin exchange also induces "dispersion" that can be measured accurately to yield values of ω_e with a precision rivaling the values obtained from line broadening.

In part 1 of this series,[2] we showed that the predictions of the theories summarized in the monograph accurately described the results of experiments on Fremy's salt in water for values of $\omega_e/\gamma A_0 < 0.14$ where A_0 is the hyperfine spacing in the absence of spin exchange and γ is the gyromagnetic ratio of the electron. However, in part 2 we found[3] a significant discrepancy between the line shifts as observed experimentally and the accepted theory, confirming the observations of others.[4−6] The experimental results could be represented as a sum of shifts quadratic in ω_e, as predicted, plus an additional shift linear in ω_e.

Uncertainties in ω_e arise due to uncertainties in both the spin-probe concentrations and the temperature. Fortunately, both of these uncertainties may be largely eliminated by writing the theory in terms of the spin-exchange-induced broadening, B_e, that may be measured independently of the line shifts. The shifts that vary quadratically with B_e describe spin-exchange interac-

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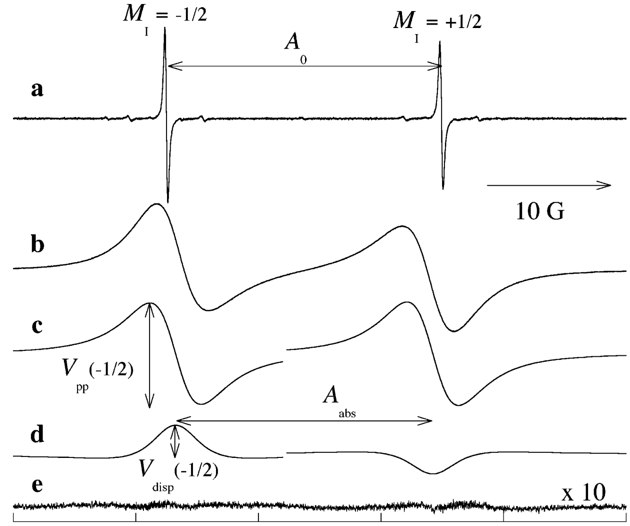

Figure 1. Experimental EPR spectra of ^{15}N−PDT in water at 310 K at (a) 0.038 mM and (b) 37.6 mM. Least-squares fit to (c) absorption and (d) dispersion lines. Ten times the difference in the experimental spectrum (b) and the sum of the theoretical lines in (c) and (d).

tions between nitroxides that diffuse together, collide once, and diffuse apart.[1,2] However, it is well known that bimolecular collisions in liquids are not that simple. The concept of a "cage" within which two molecules re-encounter a number of times before finally diffusing apart evolved[7] due to the work of Noyes[8] and others.[9,10]

In part 3,[11] we proposed that the additional linear shift was due to re-encounter spin exchanges. The effect of re-encounter collisions was not treated in the monograph[1] but was revisited by Salikhov[12] who showed that re-encounters would lead to linear shifts (in addition to the normal quadratic shifts) provided that the spin exchange was strong, that is, that spin exchange effectively occurs upon collision.

The proposal was reasonable because the values of the mean times between re-encounters, τ_{RE}, deduced from experimental line shifts were comparable to hydrodynamic estimates.[11] Part 3 also treated[11] five-line spectra due to a nitrone, where there are two differing shifts. The relative magnitudes of the two shifts were consistent with Salikhov's theory[12] without any adjustable parameters, providing further support for the proposal; however, the difference between the shifts was small. The theory[11,12] predicted a substantial difference in the additional linear shifts that would be observed in ^{15}N and ^{14}N nitroxide spin probe providing the motivation for this work. Here, we study perdeuterated 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (^{14}N−PDT) and the same probe isotopically substituted with ^{15}N (^{15}N−PDT) in water. Although the means now exist to separate spin exchange and dipolar interactions, we work at high temperatures to avoid the problem altogether, reserving for a future paper a detailed study of the separation procedure.

Theory

The theory has been presented in detail for three-line ^{14}N nitroxide spin probes[3] and for five-line nitrone spin probes.[11] Nothing new enters into the theory for the two-line spectra pertinent to ^{15}N−PDT; in fact, several simplifications result. Thus, we summarize the essentials and refer the reader to earlier work for further detail and discussion.[2,3,11] For two, three, or five lines, each line is accurately represented by the sum of an absorption line and a line having the form of a dispersion. The amplitude of the dispersion component, V_{disp}, is defined in Figure 1d. Part of the dispersion line is due to spin exchange[2] and part due to an imbalanced microwave bridge as discussed below.

As ω_e increases, the lines broaden, the spin-exchange induced dispersion increases, and the two lines spaced by A_0 at $\omega_e = 0$, shift toward the center of the spectrum.

The broadening is defined by

$$B = \Delta H^{L}_{pp}(\omega_e) - \Delta H^{L}_{pp}(0) \qquad (1)$$

where $\Delta H^{L}_{pp}(\omega_e)$ is the peak-to-peak Lorentzian line width in the first-derivative presentation of the spectrum. A similar expression applies to three-line spectra; however, the broadening is slightly different for the central and outer lines. In general, the total broadening is a sum of contributions from spin exchange and dipolar interactions $B = B_e + B_{dipolar}$.[13] For conditions in which dipolar broadening may be neglected, the spin-exchange frequency may be calculated from broadening as follows:

$$B_e = \frac{2I}{2I+1}\,\frac{2\omega_e}{\gamma\sqrt{3}} \qquad (2)$$

where $I = 1/2$ and 1 are the nuclear spins for ^{15}N and ^{14}N, respectively. For ^{14}N, the value of B_e averaged over the three lines must be used.[3]

A value of ω_e may be obtained from the amplitude of the exchange dispersion, $V_{disp}{}^{ex}$, as follows:

$$\frac{\omega_e}{\gamma A_0} = \frac{3\sqrt{3}}{4}\left|\frac{V^{ex}_{disp}}{V_{pp}}\right|\left[1 - 0.707\left(\frac{V^{ex}_{disp}}{V_{pp}}\right)^2\right] \qquad (3)$$

where V_{pp} is the peak-to-peak height of the absorption component. Equation 3 is valid for both ^{14}N and ^{15}N. The leading term in eq 3 is predicted by perturbation theory[1,2] and second corrects[11] $\omega_e/\gamma A_0$ to within 0.5% for $\omega_e/\gamma A_0 \leq 0.43$, well beyond the range of values in this work. [The correction term was obtained by fitting spectra computed from the rigorous theory, eq 1 of ref 3.]

The dispersion component of a line is made up of a sum of spin-exchange-induced dispersion, amplitude V^{ex}_{disp}, and dispersion due to an imbalance in the microwave bridge, V^{inst}_{disp}

$$V_{disp}(M_I)/V_{pp}(M_I) = V^{inst}_{disp}/V_{pp}(M_I) + V^{ex}_{disp}(M_I)/V_{pp}(M_I) \qquad (4)$$

The value of V^{inst}_{disp} is independent of M_I while $V^{ex}_{disp}(M_I)/V_{pp}(M_I) = -V^{ex}_{disp}(-M_I)/V_{pp}(-M_I)$.[2] For the central line of ^{14}N, $V^{ex}_{disp}(0)/V_{pp}(0) = 0$, thus $V_{disp}(0)/V_{pp}(0) = V^{inst}_{disp}/V_{pp}$ giving a direct measure of V^{inst}_{disp}. Therefore,

$$V^{ex}_{disp}(M_I)/V_{pp}(M_I) = V_{disp}(M_I)/V_{pp}(M_I) - V_{disp}(0)/V_{pp}(0) \quad {}^{14}\mathrm{N} \qquad (5)$$

which provides two independent values of $V^{ex}_{disp}(M_I)/V_{pp}(M_I)$, $M_I = \pm 1$, from which values of ω_e/γ may be computed using eq 3. For ^{15}N, it is straightforward to show from eq 4 that

$$V^{ex}_{disp}/V^{*}_{pp} = \frac{1}{2}\,[V_{disp}(-1/2)/V_{pp}(-1/2) - V_{disp}(+1/2)/V_{pp}(+1/2)] \quad {}^{15}\mathrm{N} \qquad (6)$$

where the reduced peak-to-peak absorption height, V^{*}_{pp}, is given by

$$V^{*}_{pp} = 2V_{pp}(+1/2)V_{pp}(-1/2)/[V_{pp}(+1/2) + V_{pp}(-1/2)] \qquad (7)$$

For ^{15}N−PDT, only one independent value of $V_{\mathrm{disp}}^{\mathrm{ex}}/V_{\mathrm{pp}}^{*}$ is available for use in eq 3. For both probes, we eliminate the parameter ω_e using eq 2.

The shift of the lines toward the center of the spectrum as a function of ω_e is conveniently written in terms of B_e as follows:[11]

$$\frac{A_{\mathrm{abs}}}{A_0} = 1 - \kappa\frac{B_e}{A_0} - \Gamma\left(\frac{B_e}{A_0}\right)^2 \qquad (8)$$

where $\Gamma = 9/32$ for ^{14}N−PDT and 3/2 for ^{15}N−PDT without any adjustable parameters. For Fremy's salt, eq 8 accurately describes the experimental results with $\kappa = 0$ without any adjustable parameters.[2] For other nitroxides and a nitrone, $\kappa \neq 0$.[3−6,11] The premise of this work is that nonzero values of κ are due to spin exchanges that occur in re-encounter collisions.

Applying Salikhov's[12] results to nitroxides, we showed that[11]

$$^{14}\kappa = \frac{\sqrt{3}}{8}(1+\sqrt{2})\sqrt{\gamma A_0^{14}\tau_{\mathrm{RE}}/2} \qquad (9a)$$

$$^{15}\kappa = \frac{\sqrt{3}}{2}\sqrt{\gamma A_0^{15}\tau_{\mathrm{RE}}/2} \qquad (9b)$$

for ^{14}N and ^{15}N nitroxide spin probes, respectively, where the superscript on A_0 indicates the isotope. Note that from the known magnitude of the ratio of the two nuclear magnetic dipole moments

$$A_0^{15} = 1.403\,A_0^{14} \qquad (10)$$

in the same solvent at the same temperature.

Experimental Section

^{14}N−PDT (lot number A559P2, perdeuterated 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl, 97 atom % D) and ^{15}N−PDT (lot number A91BP2, 99 atom % D, 99 atom % ^{15}N) were purchased from CDN Isotopes and used as received. Stock solutions of ^{14}N−PDT and ^{15}N−PDT of concentrations 19.9 and 5.96 mM, respectively, were prepared in MilliQ water by weight and diluted. Another run with ^{15}N−PDT beginning with a 113 mM mother solution was carried out to explore very high values of ω_e. Only low (<8 mM) concentrations were employed in the present work where the linear and quadratic terms are comparable, except to prepare Figures 1 and 2. The accuracy of the concentrations is estimated to be ± 3% and the relative concentrations ± 1%. The temperature, accurate to ± 1 K, was measured with a thermocouple placed just above the active portion of the microwave cavity. During each spectrum, the temperature was stable to ± 0.1 K. EPR spectra were acquired with a Bruker 300 ESP X-band spectrometer interfaced with Bruker's computer. Three spectra, taken one after the other, were acquired for each sample at each temperature. A sweep time of 41 s, time constant of 10 ms, microwave power of 5 mW; sweep width of 50.2 G, and modulation amplitude (MA) of 0.2 G were employed. We routinely set MA to near the narrowest line width in a study to increase the signal-to-noise ratio of low concentrations samples, exploiting the fact[14] that MA does not contribute to the Lorentzian component of the line. The magnetic field sweep width was measured with Bruker's NMR Gaussmeter operating in the 1 mG resolution mode and was averaged over a day's run. At low concentrations, the line shapes were accurately described by Gaussian−Lorentzian sum functions, which are excellent approximations to the Voigt shape.[15] Least-squares fits of the spectra were carried out as detailed previously.[2,3,11] The Gaussian components, due to unresolved hyperfine couplings and the effect of field modulation, yielded line widths as follows: $\Delta H_{\mathrm{pp}}^{\mathrm{G}} = 0.133 \pm 0.005$ G and 0.118 ± 0.007 G for ^{15}N−PDT and ^{14}N−PDT, respectively. After correcting for field modulation,[14] unresolved hyperfine structure contributed 0.064 and 0.088 G to $\Delta H_{\mathrm{pp}}^{\mathrm{G}}$ for the two probes, respectively.

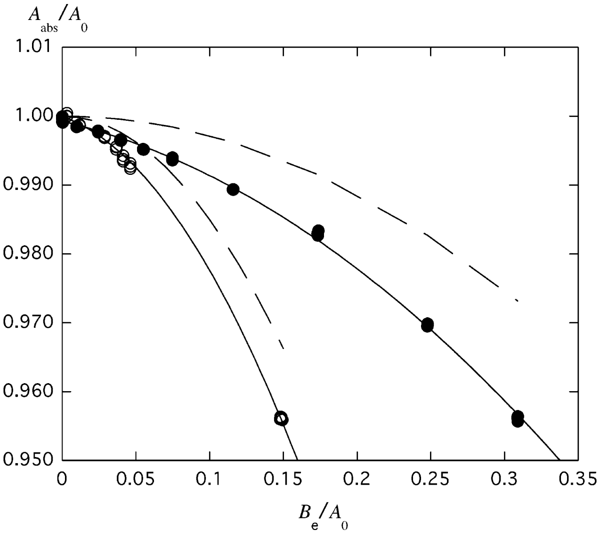

Figure 2. EPR line shifts of ^{15}N−PDT (open circles) and ^{14}N−PDT (filled circles) as a function of the normalized broadening. Values of B_e were measured from broadening of the low-field lines; other values may be obtained from other lines and from spin-exchange induced dispersion yielding two other similar curves for ^{15}N−PDT and four others for ^{14}N−PDT. Results from individual spectra illustrate the reproducibility.

Results

Spectra of ^{15}N−PDT in water at 310 K are shown in Figure 1 at a low (3.8×10^{-5} M, Figure 1a) and a higher concentration (0.0376 M, Figure 1b). The spectrum in Figure 1b shows considerable spin exchange exhibiting broadening and shifting of the lines toward the center of the spectrum as well as a characteristic "sloping" down and to the right. Only data in the range 0.038 to 5.96 mM are utilized in the present paper; the higher concentration was utilized to prepare Figure 1 to better show the effects of spin exchange. The minor lines flanking the main lines in Figure 1a with a splitting of 5.98 ± 0.01 G are due to ^{13}C in natural abundance. Figure 1c shows the absorption components, and Figure 1d shows the dispersion components of the least-squares fit. Figure 1e is 10 times the difference in the fits and the experiment, showing that the fits are excellent. Small correlations evident in the residuals (Figure 1e) are due to ^{13}C because no provision to fit those lines is included in the present version of the software. The parameters V_{pp} and V_{disp} are defined in Figure 1 as well as A_0 in Figure 1a and A_{abs} in Figure 1c. Note that, except for A_0, none of these parameters is available from the spectrum itself (Figure 1b); one must separate the components (Figure 1c,d) by nonlinear least-squares fitting. The overlap of the dispersion components causes the spacing between the lines in the experimental spectrum to be substantially less than A_{abs}.[2] Three-line EPR spectra of ^{14}N−PDT are similar to those already published together with least-squares fits; for example, see Figure 1 of ref 3 where V_{pp}, V_{disp}, and $2A_{\mathrm{abs}}$ are defined. The concentrations of ^{14}N−PDT were limited to ≤7.72 mM.

To provide a sample calculation, the resulting parameters from fitting Figure 1b and four other spectra obtained one after the

TABLE 1: Parameters from Spectra of Figure 1[a] (^{15}N−PDT in Water at 310 K)

[^{15}N−PDT], mM	M_I	ΔH^G_{pp}, G	ΔH^L_{pp}, G	B, G	V_{disp}/V_{pp}	A_{abs}, G
37.6	−1/2	0	4.169 ± 0.003	3.957 ± 0.004	0.287 ± 0.0008	21.071 ± 0.002
	+1/2	0	4.195 ± 0.008	3.967 ± 0.009	−0.188 ± 0.0006	
0.038	−1/2	0.133 ± 0.005	0.212 ± 0.003	0	0	22.530 ± 0.001
	+1/2	0.133 ± 0.004	0.229 ± 0.003	0	0	

[a] Mean values and standard deviations from five spectra.

other are given in Table 1 as mean values and standard deviations. At all temperatures, the parameters obtained from the 3.8 × 10^{-5} M sample were within experimental error of those found by extrapolation to zero concentration, indicating negligible spin exchange. The values of $^{14}A_0$ and $^{15}A_0$ are very slightly temperature dependent. For example,$^{15}A_0$ varies from 22.533 G at 290 K to 22.494 G at 350 K giving an average over the range of temperatures in this work of $^{15}A_0 = 22.507 \pm 0.016$ G. For ^{14}N−PDT,$^{14}A_0 = 16.053 \pm 0.004$ G. From line broadening in Table 1, values of $\omega_e/\gamma = 6.854 \pm 0.0007$ G and 6.871 ± 0.014 G are obtained from the low- and high-field lines, respectively, using eq 2. From the value of $[V_{disp}(-1/2)/V_{pp}(-1/2) - V_{disp}(+1/2)/V_{pp}(+1/2)]/2 = 0.237 \pm 0.001$ we find $\omega_e/\gamma = 6.547 \pm 0.0028$ G from eq 3.

Figure 2 shows line shifts for ^{14}N−PDT, filled circles, and ^{15}N−PDT, open circles at 338 K. The dashed lines above the two respective curves are the quadratic terms in eq 8. Points from individual spectra are plotted to illustrate the reproducibility in the measurement of A_{abs}. The solid lines through the data points are the least-squares fit to eq 8 with one adjustable parameter, κ. The abscissa of plots like Figure 2 depends on the method to determine the broadening. To assess the uncertainty in the values of κ due to the uncertainty in the values of B_e, five such plots for ^{14}N−PDT and three for ^{15}N−PDT were prepared, respectively, corresponding to the various independent methods to obtain B_e. These plots were fit to eq 8 to obtain values of κ from which mean values and standard deviations were computed.

Figure 3 gives the resulting values of κ for ^{14}N−PDT, filled circles, and ^{15}N−PDT, open circles. A priori, we expect the ratio $^{15}\kappa/^{14}\kappa$ to be given by the ratio of eq 9b to eq 9a. Forming the ratio, utilizing eq 10, yields $^{15}\kappa/^{14}\kappa = 1.96$ at all temperatures. Figure 3 shows that this ratio is very nearly obtained. Forming the ratio from Figure 3 at the five common temperatures, we find that $^{15}\kappa/^{14}\kappa$ varies from 1.89 ± 0.20 at 293 K to 2.02 ± 0.20 at 338 K with an average value of 1.93 ± 0.11.

Values of τ_{RE} computed from values of κ using eqs 9a and 9b are presented in Figure 4 as functions of T/η, where η is the shear viscosity. The resulting values of τ_{RE} from the two probes are within experimental uncertainty of one another. The Stokes−Einstein prediction[12] for re-encounter times is given by

$$\tau_{RE} = \frac{3\pi b^3 \eta}{2kT} \tag{11}$$

where b is the distance between spin probes at collision and k the Boltzmann constant. Taking b to be the twice the Van der Waals radius of 3.5 Å as computed from the method of Bondi,[16,17] eq 11 yields the solid line in Figure 4.

Discussion and Conclusions

Figure 4 provides strong further support for the proposal[11] that $\kappa \neq 0$ in eq 8 is due to spin exchange that occurs via re-encounter collisions. Despite nearly a factor of 2 differences in the values of $^{14}\kappa$ and$^{15}\kappa$ at all temperatures, Figure 3, the resulting values of τ_{RE} are the same within experimental uncertainty. Furthermore, the values are of the same order-of-magnitude and show the same trend with temperature as the hydrodynamic estimate employing the Stoke−Einstein (SE) equation. Indeed, it is not expected that τ_{RE} would follow the SE exactly because the re-encounters occur after short-range diffusion involving both hydrodynamic and microscopic interactions.[18] Other spin probes in other solvents also show departures from the SE; see, for example, Figure 9 of ref 11. [Note: The slope of the SE line in that figure is a factor of 2 too large due to an error in eq 25 of ref 11.]

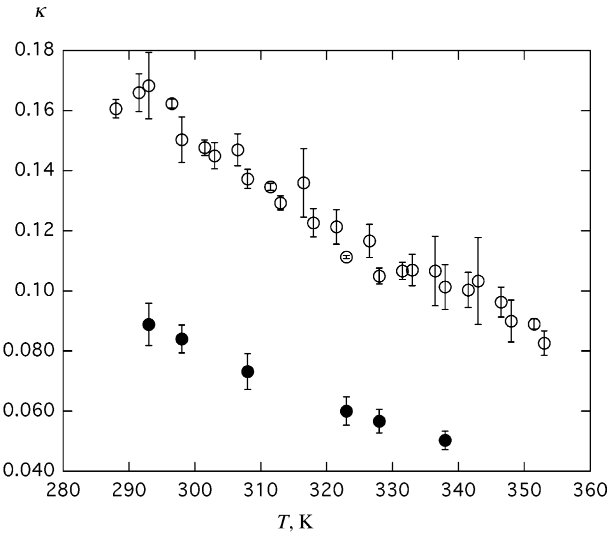

Figure 3. Values of κ from ^{15}N−PDT (open circles) and ^{14}N−PDT (filled circles) as a function of the temperature.

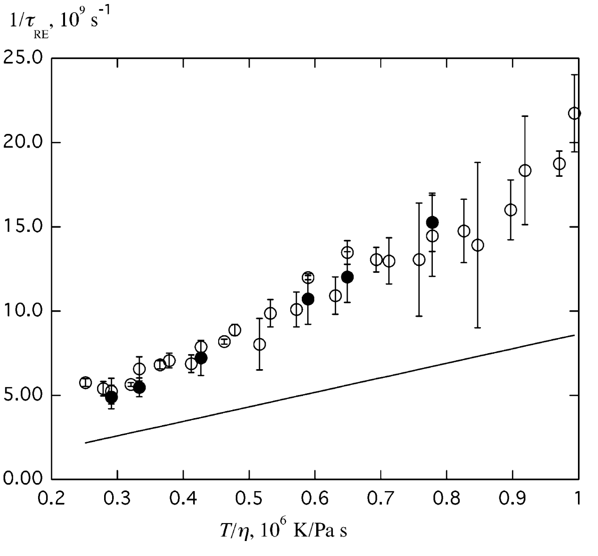

Figure 4. Re-encounter rate of PDT in water as a function of the temperature divided by the shear viscosity as determined from ^{15}N−PDT (open circles) and the ^{14}N−PDT (filled circles). The solid line is the Stokes−Einstein prediction, eq 11.

Although ^{15}N spin probe leads to larger values of κ, τ_{RE} is not obtained with more precision for two reasons: (1) the difference in the linear and quadratic terms is less for ^{15}N and (2) only one value of $V_{\mathrm{disp}}^{\mathrm{ex}}/V_{\mathrm{pp}}^{*}$ and two of line broadening are available rather than two and three values, respectively, for ^{14}N. Therefore, the additional expense in employing ^{15}N spin probes to study re-encounters in liquids is not justified. Also, in Part 2 we showed[3] that spectra severely broadened by unresolved hyperfine structure may be properly analyzed to study τ_{RE}; thus, deuterated spin probes are not needed to study liquids or complex fluids.

In Part 3,[11] we pointed out that $\kappa = 0$ for Fremy's salt could be due to weak spin exchange; however, it has occurred to us that it might also be due to the inhibition of re-encounters by strong Coulombic repulsion while the two doubly charged probes are in close proximity. It could be of interest to study singly charged probes to look for intermediate values of τ_{RE}.

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