

ESR Studies of Heisenberg Spin Exchange. II. Effects of Radical Charge and Size*

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The Heisenberg spin exchange behavior of several radical-solvent systems has been studied. This work has shown that k , the second-order rate constant for bimolecular encounters, and $|J|\tau_1$ (where $|J|$ is twice the exchange integral and τ_1 is the lifetime of the collision pair) depend markedly on the ionic strength of the solution and upon the size and charge of the radical. For the peroxyamine disulfonate radical in a $5 \times 10^{-2} M$ solution of 1:2 electrolyte, our simple analysis yields $|J|\tau_1 \sim 0.95$ and $k = 2.0 \times 10^{10} M^{-1} \cdot \text{sec}^{-1}$ at 24°C ; increasing the electrolyte concentration to $6.1 \times 10^{-1} M$ gives $|J|\tau_1 \sim 1.3$ and $k = 3.2 \times 10^9 M^{-1} \cdot \text{sec}^{-1}$. These changes in k and $|J|\tau_1$ are attributed to screening by the electrolyte of the charge of the dianion radical; this is discussed in terms of the Debye theory. The di-tertiarybutyl nitroxide (DTBN) radical undergoes apparent strong exchange ($|J|\tau_1 \gg 1$) in pure water ($k = 2.4 \times 10^9 M^{-1} \cdot \text{sec}^{-1}$ at 24°C). The dependence of the exchange frequency (ω_{HE}) on added 1:2 electrolyte is of the form $\omega_{\text{HE}} = \omega_{\text{HE}}(0) \exp(-C_B/C')$, where C_B is the molar electrolyte concentration and $\omega_{\text{HE}}(0)$ the exchange frequency in pure water; for a $2.4 \times 10^{-2} M$ DTBN solution $C' = 0.23 \pm 0.02 M$. This reduction of exchange frequency with electrolyte concentration is attributed to the formation of DTBN aggregates. The durosemiquinone radical undergoes strong exchange in dimethoxyethane ($k = 2.9 \times 10^9 M^{-1} \cdot \text{sec}^{-1}$ at 15°C). The closeness of k to the diffusion-controlled limit indicates that ion pairing takes place in solution. The tetraphenyl arsonium peroxyamine disulfonate radical undergoes apparent weak exchange ($|J|\tau_1 < 1$) in dimethyl sulfoxide. However, rapid radical decay made quantitative study of exchange impossible for this radical.

I. INTRODUCTION

In Part I of this series we have presented a careful ESR linewidth and saturation study of Heisenberg spin exchange in the TCNE⁻ radical.¹ It was found to undergo strong exchange, characterized by the exchange frequency $\omega_{\text{HE}} = \tau_2^{-1} \propto T/\eta$, where τ_2 is the mean time between the successive bimolecular encounters of identical radicals. The theoretical analyses given for this phenomenon have shown that more generally¹⁻⁴

$$\omega_{\text{HE}} = \tau_2^{-1} [1 + J^2 \tau_1^{-2}]^{-1}, \quad (1.1)$$

where J is twice the exchange integral and τ_1 is the mean lifetime of an exchanging radical pair. Strong exchange thus requires $(J\tau_1)^2 \gg 1$. To date, there has only been one radical studied, di-tertiarybutyl nitroxide (DTBN), which has exhibited, in very low viscosity solvents, significant deviations from strong exchange behavior.^{5,6} Plachy and Kivelson have analyzed the results in terms of a modified form of Eq. (1.1).⁶

While we have shown in I how the strong exchange values for $\tau_2^{-1}/C = k$ (where C is the molar concentration of radical and k the associated bimolecular rate constant) can yield useful information on bimolecular diffusion processes between radicals,⁷ studies involving intermediate exchange ($|J|\tau_1 \sim 1$) have the additional feature of supplying information about the interacting pair, since $|J|\tau_1$ can also be measured. Because most common radical-solvent systems appear to exhibit strong exchange, one is led to consider certain modifications to reduce the magnitude of $|J|\tau_1$. These include utilizing (1) very low viscosity solvents to reduce τ_1 ; (2) radicals with bulky sur-

rounding groups to increase the separation of the interacting radical pairs and thus reduce $|J|$; and/or (3) radicals with large and identical charge, so the distance of closest approach is increased, thus reducing $|J|$ and probably τ_1 as well. While the work on DTBN indicated the effects of (1) [and probably (2)], we have conducted experiments to try to emphasize (2) and (3).

A good example of large repulsive charge is found in aqueous solutions of the dianion peroxyamine disulfonate (PADS). Jones has already reported on a study of the concentration dependence of the ESR widths for this system,^{8a} but this is not sufficient for determining whether the exchange is strong or weak.¹ He did report that the higher concentration widths deviate somewhat from a linear dependence on concentration, which he suggested may be due to viscosity changes caused by changes in the radical concentration or to the presence of buffer.^{8a} In the course of our work we have been able to analyze such observations in terms of Debye's theory of ionic-strength effects on reaction rates, while we have found viscosity effects to be rather unimportant.

It is to be noted that Pearson and Buch^{8b} in a study concentrating mainly on the effects of paramagnetic-complex ions on PADS also looked at the effects of the PADS concentration on linewidth as well as the effect of inert electrolyte concentration. The general qualitative results of their work agree with the results of Jones and with the present work. However, Pearson and Buch obtain a minimum linewidth for PADS of 0.345 G. This is considerably larger than that obtained by Jones and by us. It is likely that this large

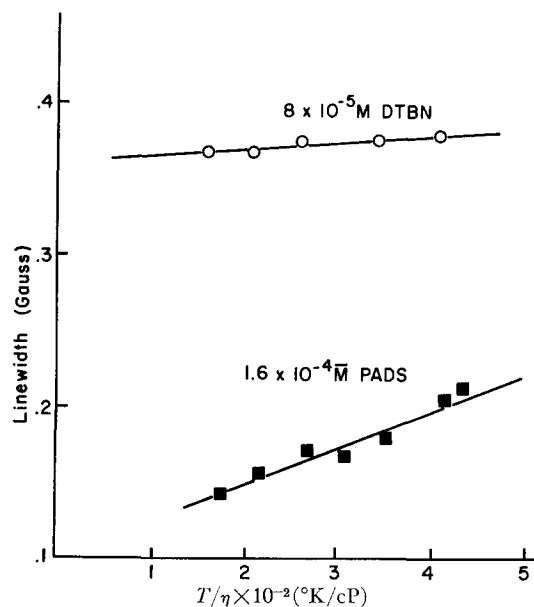


FIG. 1. Derivative width of the $\bar{M}=0$ line as a function of T/η for $1.6 \times 10^{-4} M$ aqueous, deoxygenated PADS solution and $8 \times 10^{-5} M$ aqueous, degassed DTBN solution.

value is due to the presence of oxygen. Also we note that Pearson and Buch did not analyze their results in terms of an appropriate theory of Heisenberg spin exchange, [e.g., Eq. (1.1)].

Because of the poor solubility of PADS in non-aqueous solvents, we were also interested in exploring substituted forms of PADS: e.g., tetraphenylarsonium peroxyamine disulfonate (APADS) and the Sb substituted form (SPADS) which are soluble in a range of solvents.⁹ APADS and related radicals would have the added advantage of large, bulky blocking groups. In fact, a comparatively small value for $|J|$ is expected from our observations on the polycrystalline spectra of SPADS and APADS. Thus, while they each consist of a single line, they are very broad: 91 G and 76 G, respectively.¹⁰ These widths are considerably greater than those obtained from other polycrystalline radicals such as diphenylpicrylhydrazyl, which yields a single-line spectrum about 1.9 G wide. The broad lines may be due to the fact that there is little or no exchange narrowing of the dipolar interactions in the SPADS and APADS spectra, so they are strongly dipolar broadened.

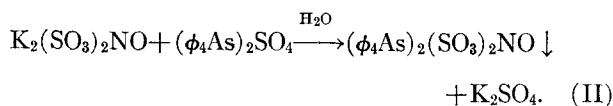
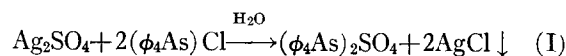
We also included in our study durosemiquinone¹¹ (DSQ) with its moderately bulky methyl groups and single negative charge, and the uncharged DTBN in aqueous solvents for comparison with the work on PADS. We note that the work of Plachy and Kivelson⁶ on DTBN in pentane at 25°C can be interpreted as $J^2\tau_1^2 \cong 4$. When this value is scaled according to the viscosity change (see Sec. IV), one has $J^2\tau_1^2 \cong 64 \gg 1$ for aqueous solvents, i.e., strong exchange is predicted.

II. EXPERIMENTAL RESULTS

A. PADS and Related Radicals

The K_2 (PADS) was obtained from Alfa Inorganics. In most experiments the compound was used as received (75%–88% pure). Batches of compound less than 75% pure were purified by the method of Murib and Ritter.¹² Using this procedure, 89% purity PADS could be obtained without difficulty. The potassium carbonate and the K_2SO_4 was Mallinckrodt analytical grade reagent. Distilled water was used as the solvent in all experiments with PADS.

APADS was synthesized by means of the following reactions:



The silver sulfate was from Eastman Organic Chemicals and the tetraphenylarsonium chloride from Aldrich

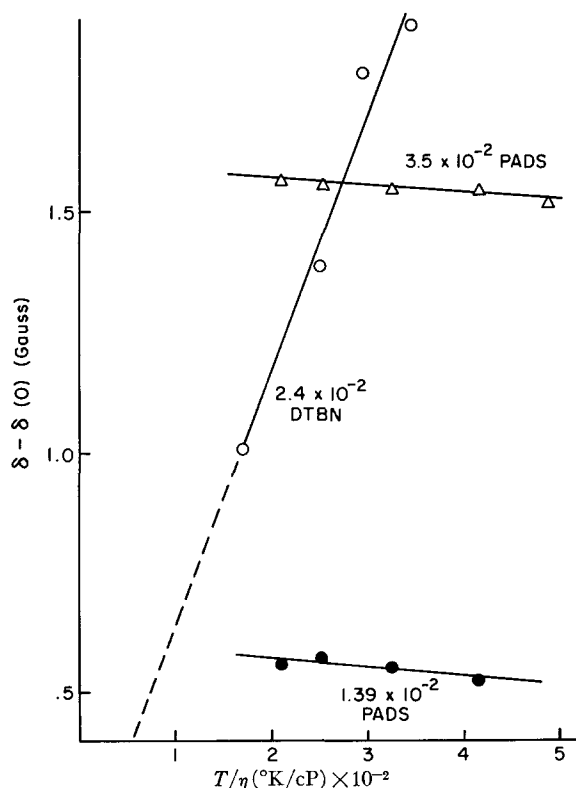
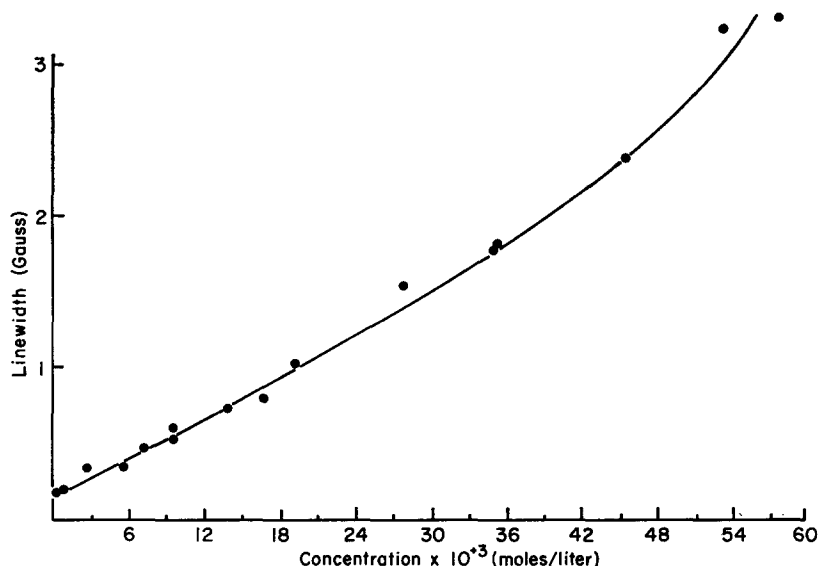


FIG. 2. Derivative width of the $M=0$ line as a function of T/η for three aqueous solutions: $2.4 \times 10^{-2} M$ in DTBN, $1.39 \times 10^{-2} M$ in PADS, and $3.51 \times 10^{-2} M$ in PADS. All were buffered with about 0.05 K_2CO_3 . The very low concentration width (from Fig. 1) has been subtracted out in each case. The values of η have been corrected for the salts present.

FIG. 3. Derivative width of the $\tilde{M}=0$ line as a function of PADS concentration for aqueous, deoxygenated PADS solutions at 24°C and 0.05M in K_2CO_3 .



Chemicals. In Reaction (I) the reagents were mixed in stoichiometric quantities, stirred, and allowed to react in a volume of water such that the final solution of tetraphenylarsonium sulfonate was saturated.¹³ When the reaction was completed, the silver chloride was filtered out of the solution. For Reaction (II) a measured volume of the tetraphenylarsonium sulfonate solution was mixed with a slight excess of PADS. The resulting purple paramagnetic precipitate (APADS)

was stirred, filtered, and washed with water. The APADS was then dried on a vacuum line. When dry, the product was in the form of small purple paramagnetic crystals. No attempt was made to measure the yields of these reactions. The dimethyl sulfoxide (DMSO), which was used as solvent in the APADS experiments, was not purified or specially prepared. The viscosity and density values were taken from standard sources.¹⁴

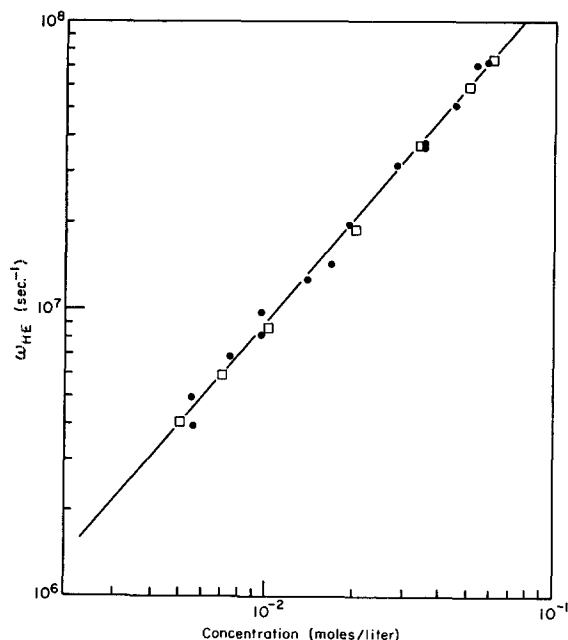


FIG. 4. Logarithmic plot of ω_{HE} as a function of PADS concentration, for aqueous, deoxygenated PADS solutions at 24°C and 0.05M in K_2CO_3 . The (●) points are from Fig. 3, where Eq. (3.0) has been utilized. The (□) points are theoretical estimates for $d=6 \text{ \AA}$ as discussed in Sec. IV.

The aqueous solutions of PADS were buffered with $5 \times 10^{-2}M$ potassium carbonate and were deoxygenated by bubbling water-saturated nitrogen gas through them. The concentration of PADS in the solutions was measured spectrophotometrically with a Cary model 14 spectrophotometer. The absorption spectrum of PADS has been previously reported.¹² The maxima in this spectrum are at 2480 Å ($\epsilon=1690$) and 5450 Å ($\epsilon=20.8$). After the PADS concentration was measured, small aliquots of the solution were taken and used to rinse and fill 1 mm (maximum o.d.) capillary tubes. Previous to being filled these capillary tubes had been washed with distilled water and carefully dried. For ease of handling, the filled capillary tubes were then placed in 3 mm-o.d. Pyrex tubes. The intensity and linewidth of the PADS resonance at the beginning and end of the experiments on a sample were compared to ensure that no appreciable radical decay had taken place. The above procedure gave easily reproducible results. It is estimated that the concentration values quoted for the PADS ESR samples are good to a precision of at least $\pm 10\%$.

The spectrometer system, temperature control system, and experimental techniques have been described in I. The methods employed for DTBN are also discussed in I. Spectrophotometric techniques were used to determine the DTBN concentrations in the different buffered solutions.¹⁵

TABLE I. Least-squares slope and intercept for fit of low-concentration widths to $\delta(0) = g(T/\eta) + \delta(T/\eta=0)$.^a

Radical/solvent	C (moles/liter)	\tilde{M}	$g(\text{G}\cdot\text{cP})/^\circ\text{K}\times 10^4$	$\delta(T/\eta=0)\text{G}$
DTBN: water	8×10^{-5}	0	0.39 ± 0.08	0.363 ± 0.002
PADS/ $0.05M\text{K}_2\text{CO}_3$	1.6×10^{-4}	0	2.5 ± 0.3	0.097 ± 0.010

^a $\tilde{M}=0$ line. Error limits represent standard deviation in least-squares fit to the data.

B. Durosemiquinone

The duroquinone (DQ) was obtained from Aldrich Chemical Company. It was purified by two recrystallizations from 95% ethanol followed by a vacuum sublimation. Samples prepared in this way were determined to be polarographically pure. The DME was Eastman White label and was purified by usual methods.¹⁶ The polarograph-grade tetrabutylammonium perchlorate (TBAP) was from Southwestern Analytical Chemical Company and was purified by repeated recrystallization from 50% (by volume) methanol, 50% water solutions. After recrystallization, the compound was dried at 100°C in a vacuum oven.

The DSQ radical was generated electrochemically using a cell similar to that described by Johnson and Chang.¹⁷ The cell was operated in the manner described by these authors. No reference electrode was used in the experiments. Care was taken to perform the electrolysis close to the first wave. The reduction was terminated when the cell current approached zero, which gave a yield of 60% DSQ. In these experiments the supporting electrolyte was TBAP at a concentration of 0.05 to 0.1M. Samples prepared in this manner were stable for about one year at room temperature. It was possible to heat these samples to 100°C for several minutes with no obvious signs of decomposition.

The sample tubes employed in the experiments to measure the radical molar extinction coefficient ϵ were like that described in Part I. In order to obtain ϵ the

radical concentration was first determined using the dual sample cavity and pitch standard sample.^{1,18} Once ϵ was determined the radical concentrations could be measured by less time-consuming uv techniques. The linewidth studies were carried out using a sample tube equipped with a Pyrocell No. 6008 rectangular quartz cell and a 3 mm Pyrex sidearm which could be closed off from the rest of the system by the use of a Fisher and Porter No. 795-500 Teflon needle valve. The purpose of the needle valve was to prevent distillation of solvent from the 3 mm sidearm when the EPR spectrum was being determined at higher than room temperatures. The Pyrocell quartz cell was used in spectrophotometer measurements of radical absorbance. In these experiments, the absorption peak at 4400 Å [$\epsilon=(7\pm 1)\times 10^3$]¹⁸ was used to determine the radical concentration.

III. EXPERIMENTAL RESULTS

A. Aqueous Solutions of PADS

The T/η dependences of the widths of the $\tilde{M}=0$ line for a $1.6\times 10^{-4}M$ aqueous PADS solution and for an $8\times 10^{-5}M$ aqueous DTBN solution are shown in Fig. 1. The PADS solution was deoxygenated and the DTBN solution was degassed. The PADS solution was buffered with $5\times 10^{-2}M$ potassium carbonate. Unfortunately a wider range of temperatures could not be investigated for PADS because at temperatures above 40°C the

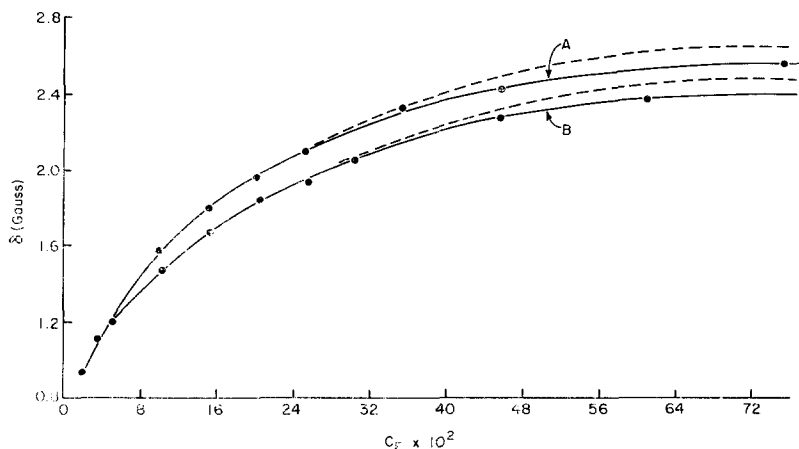


Fig. 5. Derivative width of the $\tilde{M}=0$ line for $2.46\times 10^{-2}M$ deoxygenated aqueous solutions of PADS at 24°C as a function of electrolyte concentration. Curve A corresponds to K_2CO_3 as electrolyte; curve B to $0.05M\text{K}_2\text{CO}_3$ plus K_2SO_4 . The solid curves are not corrected for the viscosity changes due to electrolyte; the dotted curves are corrected by interpolation from Fig. 6. The data have been adjusted for slight differences in initial PADS concentration according to Eq. (3.1).

TABLE II. Least-squares slope and intercept for fit of higher concentration widths to $\delta - \delta(0) = g(T/\eta) + \delta(T/\eta=0)$.^a

A. PADS				
C (moles/liter)	C_E (moles/liter) ^b	$g(\text{G}\cdot\text{cP}/^\circ\text{K})\times 10^4$	$\delta(T/\eta=0)\text{G}$	
0.0139	0.050	-1.8 ± 0.8	0.61 ± 0.02	
0.0351	0.050	-1.4 ± 0.4	1.60 ± 0.01	
0.0243	0.30	10.1 ± 0.6	1.53 ± 0.02	
0.0244	0.61	$22.\pm 1$	1.55 ± 0.03	
B. DTBN				
C (moles/liter)	C_E (moles/liter) ^b	$g(\text{G}\cdot\text{cP}/^\circ\text{K})\times 10^4$	$\delta(T/\eta=0)\text{G}$	$k\times 10^{-9}M^{-1}\cdot\text{sec}^{-1}$ at 24°C
0.024	0	83 ± 1	0.15 ± 0.02	2.4
0.022	0	76 ± 3	0.09 ± 0.05	2.4
0.022	0.050	52 ± 1	0.17 ± 0.02	1.64
0.024	0.060	53 ± 7	0.12 ± 0.1	1.53
0.022	0.30	17.5 ± 0.5	0.17 ± 0.02	0.55
0.022	0.40	8.0 ± 0.3	0.13 ± 0.01	0.25

^a $\tilde{M}=0$ line. $\delta(0)$ is from the least-squares fits in Table I. Error limits represent standard deviation in least-squares fit to the data.

^b Concentration of added electrolyte.

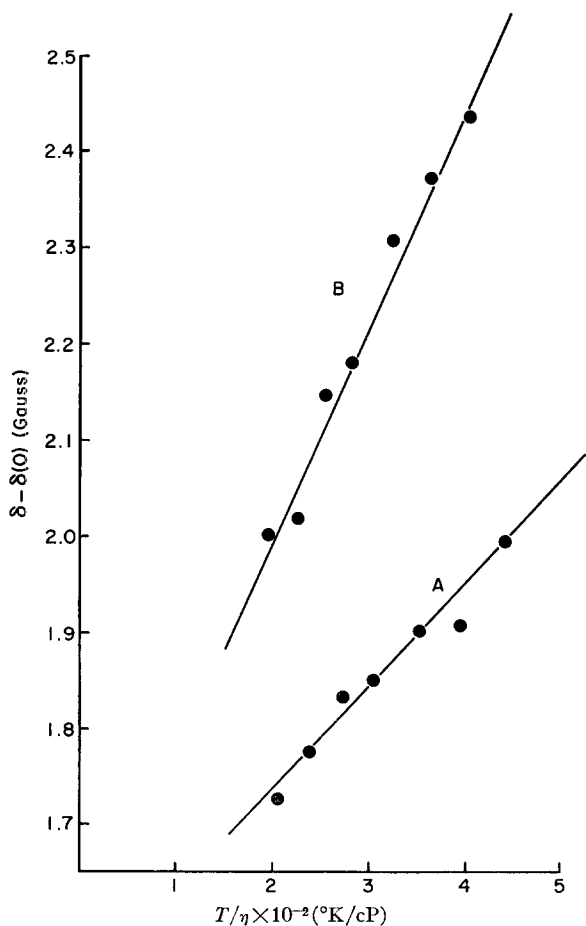


FIG. 6. Derivative width of the $\tilde{M}=0$ line as a function of T/η for deoxygenated aqueous solutions $2.44\times 10^{-2}M$ PADS. Line A corresponds to $0.30M$, Line B to $0.61M$ electrolyte [K_2CO_3 ($0.05M$) + K_2SO_4]. The very low concentration width (from Fig. 1) has been subtracted out in each case. The values of η have been corrected for the salts present.

radical decomposed too rapidly, and below about 10°C PADS and potassium carbonate began to precipitate from the solutions. The least-squares slopes and intercepts for these lines are in Table I. The slight increase in linewidth with T/η for these samples, is probably due to spin rotational interactions. This point has been discussed in I for DTBN, and by Kooser, Volland, and Freed^{19a} and also by Kooser^{19b} for PADS.

The width of the $\tilde{M}=0$ line as a function of T/η for two more concentrated solutions of PADS is shown in Fig. 2. Also included in this figure is the width of the $\tilde{M}=0$ line for a $2.4\times 10^{-2}M$ solution of DTBN. In these plots the $\delta(0)$ as determined from Fig. 1 (and the least-squares fits in Table II) has been subtracted and the viscosities have been corrected for the presence of electrolyte (see below). (The PADS solutions were deoxygenated and the DTBN solution was degassed. All of the solutions including the DTBN were about $5\times 10^{-2}M$ in potassium carbonate.) The results in Fig. 2 can be interpreted in terms of an exchange frequency according to:

$$\begin{aligned}\omega_{\text{HE}} &= \frac{3}{4}\sqrt{3} |\gamma_e| [\delta - \delta(0)] \\ &= 2.28\times 10^7 [\delta - \delta(0)] \text{sec}^{-1},\end{aligned}\quad (3.0)$$

where the statistical factor, discussed in I, has been included. The linewidth observed for the DTBN solution increases linearly with T/η as is expected for the case of strong exchange. The PADS linewidths, however, vary only slightly with temperature, although the variation appears to be linear. The slopes and intercepts for these lines are included in Table II. The negative values for the slopes of the PADS lines suggest that the PADS radicals are undergoing weak exchange.

The dependence of the width of the $\tilde{M}=0$ line on

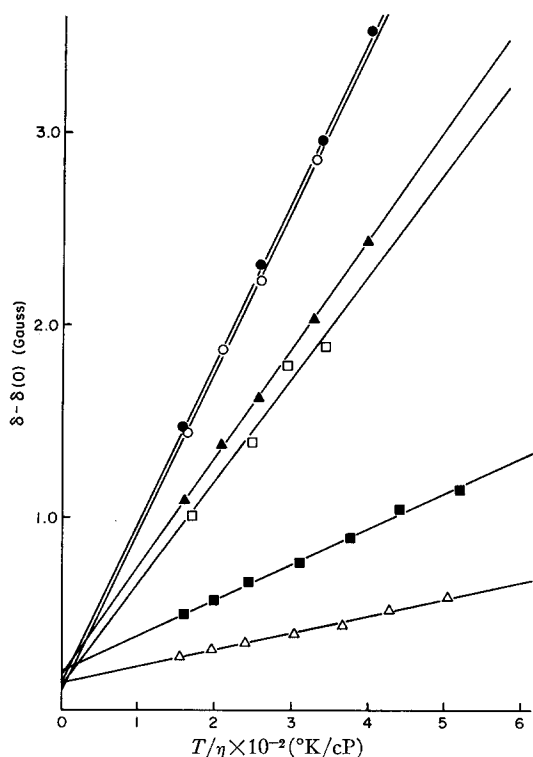


FIG. 7. Derivative width of the $\tilde{M}=0$ line as a function of T/η for degassed aqueous solutions $2.4 \times 10^{-2}M$ DTBN. The lines correspond to different concentrations of K_2CO_3 ; \bullet and \circ —No K_2CO_3 ; \blacktriangle — $0.05M$; \square — $0.06M$; \blacksquare — $0.30M$; \triangle — $0.40M$. The very low concentration width (from Fig. 1) has been subtracted out in each case. The data have been corrected for small differences in initial DTBN concentration and for changes in η due to the K_2CO_3 .

the PADS concentration at $24^\circ C$ is shown in Fig. 3. As reported earlier by Jones,^{8a} this dependence is found to be nonlinear. He has shown that one may write:

$$\omega_{HE} = bC^m, \quad (3.1)$$

where b and m are constant. A logarithmic plot of the data in Fig. 3 is shown in Fig. 4, from which a least-squares fit yields $m = 1.17 \pm 0.03$ and $b = 1.96 \times 10^9$. The uncertainty in m represents the sample deviation from the least-squares fit. This is to be compared with Jones' results of $m = 1.07 \pm 0.02$ and $b = 1.84 \times 10^9$, or a moderately good agreement.

The deviation of m from unity is discussed in Sec. IV in terms of effects of ionic strength. To test our belief that the ionic strength of the solution has an important effect on the spin exchange, a series of solutions $2.5 \times 10^{-2}M$ in PADS were prepared with amounts of combined concentrations of K_2CO_3 and K_2SO_4 ranging from $2 \times 10^{-2}M$ to $0.75M$. (At concentrations of $K_2CO_3 < 2 \times 10^{-2}M$ the PADS tends to be unstable.) The results, given in Fig. 5, show a marked increase in PADS linewidth with increasing ionic concentration, but the effect appears to be leveling off to an asymptotic limit. It was also of interest to see how

the ionic concentration affected the linewidth behavior as function of T/η . These results are shown in Fig. 6 for two solutions of $2.5 \times 10^{-2}M$ PADS, with combined concentrations of $K_2SO_4 + K_2CO_3$ of $0.3M$ and $0.61M$, respectively. The concentration-independent widths have again been subtracted out. The slopes have now become *positive* with the greater slope for the more concentrated solution (cf. Table II). We note that the intercepts for both solutions are comparable. While Fig. 6 illustrates the best linear fits of the data, there appears to be a slight curvature (concave to the right) of the experimental points, especially for the more concentrated sample.

It is important to consider the effects of the salts on the viscosity of the solutions. Unfortunately, no information has been found on the effect of PADS and K_2CO_3 on the viscosity of water, although that for K_2SO_4 has been extensively studied.^{20,21} In view of the fact that K_2CO_3 and $K_2(PADS)$ should be similar electrolytes to K_2SO_4 , we would expect them to have a similar effect on the viscosity. Thus at $25^\circ C$ one has²⁰

$$\eta/\eta_0 = 1 + (1.41 \times 10^{-2} C_E^{1/2}) + 0.194 C_E, \quad (3.2)$$

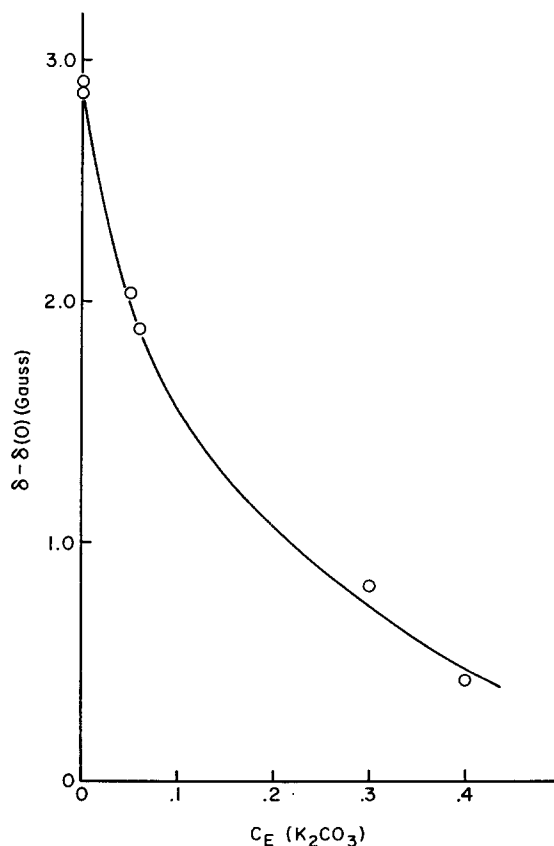


FIG. 8. Derivative width of the $\tilde{M}=0$ line as a function of concentration of K_2CO_3 for degassed aqueous solutions $2.4 \times 10^{-2}M$ DTBN. The curve corresponds to a value of $T/\eta = 333^\circ K/cP$. The data points are from the linear least-squares fits of Fig. 7.

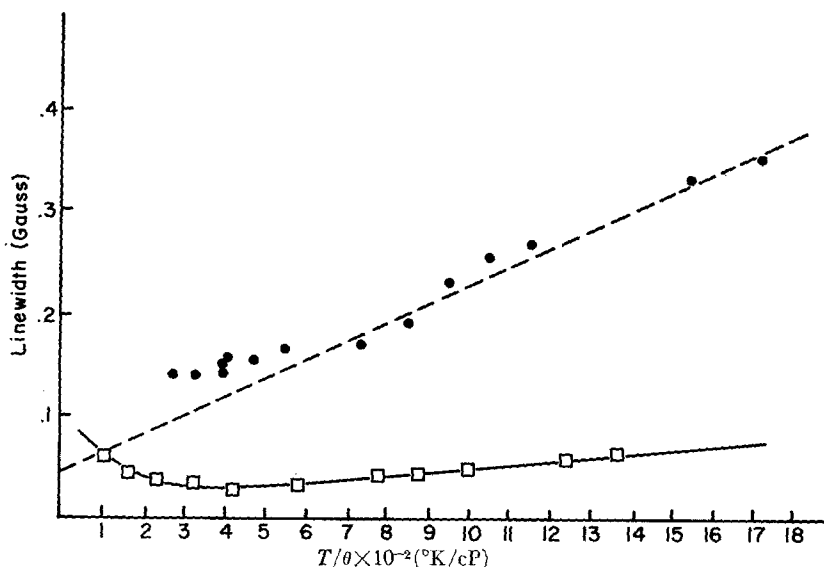


FIG. 9. Derivative width of the $\tilde{M}=0$ line as a function of T/η for solutions of DSQ in DME. The \bullet points corresponds to a DSQ concentration of $0.64 \times 10^{-3} M$ (and $0.51 \times 10^{-3} M$ in DQ), while \square are for $3 \times 10^{-5} M$ DSQ.

where C_E is the electrolyte molar concentration, η_0 is the viscosity of pure water, and η the viscosity of the electrolyte solution. In general, viscosity effects are small, e.g., a $0.1 M$ solution has $\eta/\eta_0 \approx 1.03$, but at $0.61 M$ $\eta/\eta_0 \approx 1.145$. The dotted curves in Fig. 5 give estimated viscosity-corrected results.²² It is seen that the significant linewidth effects in Figs. 3 and 5 are only slightly affected by such corrections. In Figs. 2 and 6, we have used the T/η values appropriate for the electrolyte concentrations.^{20,21}

Lineshape analysis were made for the PADS solutions at a number of concentrations. It was found that at PADS concentrations of $7 \times 10^{-3} M$ or greater the lines were Lorentzian (within experimental error) to a distance of five first-derivative half-widths from the center of the line. This observation was found to be independent of the concentrations of K_2CO_3 and K_2SO_4 . For more dilute solutions small deviations from Lorentzian character have been noted at three or greater half-widths.^{8a,19a,19b} We have neglected such deviations for the dilute solutions since no serious error should result from this^{19a,19b} [i.e., in obtaining ω_{HE} from Eq. (3.0), concentrations were used such that $\gamma(0)$ is only a small correction compared to δ . Also, the least-squares fit of Fig. 4 employed only solutions whose concentrations were $\geq 5 \times 10^{-3} M$.]

B. Aqueous Solutions of DTBN

We have also studied the effects of electrolyte on the spin-exchange linewidths of DTBN. These are shown as a function of T/η in Fig. 7 for several concentrations of K_2CO_3 ranging from 0 to $0.4 M$ while the DTBN concentration is nearly constant at $2.4 \times 10^{-2} M$.²³ The intercepts, which are almost zero, are unchanged,²⁴ but the slopes decrease markedly with an increase in ionic strength. (The linear least-squares

fits appear in Table II.) This effect is the opposite of that for PADS. The variation of the spin-exchange linewidths as a function of K_2CO_3 concentration for a single value of T/η is given in Fig. 8. Similar results are obtained for other T/η values. The shapes suggest an exponential dependence on electrolyte according to:

$$\omega_{HE} = \omega_{HE}(0) e \exp(-C_E/C') \quad (3.3)$$

A least-squares fit of $\log[\omega_{HE}/\omega_{HE}(0)]$ vs C_E yields: $C' = 0.23 \pm 0.02 M$ with an intercept of -0.06 ± 0.06 or essentially zero.

C. Substituted Peroxylamine Disulfonates in Organic Solvents

Experiments on the APADS:DMSO system were complicated by problems of radical decomposition (slight decomposition can affect linewidths significantly). Thus the results obtained can not be considered as quantitative. The linewidth for a concentrated ($9 \times 10^{-2} M$) APADS sample was found to decrease in a nonlinear manner with increasing T/η . However, $\delta - \delta(0)$ for the $9 \times 10^{-2} M$ sample was found to be linear with η/T {slope $70[(G - ^\circ K)/cP]$ } as expected for a case of weak exchange, but $\delta - \delta(0)$ did not approach zero as η/T approaches zero. Instead, the intercept is large and negative ($\sim -0.2 G$). This latter observation indicates that while weak exchange may be responsible for at least part of the linewidth changes with T/η it is not the only factor affecting the linewidth. But, in order to determine what other factors may be important and to make a quantitative study of the APADS:DMSO system, the problem of radical decay must be solved.

D. Durosemiquinone

In Fig. 9 the linewidth as a function of T/η is displayed for two solutions. The more concentrated is

$0.64 \times 10^{-3}M$ in DSQ and about $0.5 \times 10^{-3}M$ in DQ. The presence of the DQ is due to incomplete electrochemical reduction. The dilute sample, $3 \times 10^{-5}M$ in DSQ, was 85%–90% reduced from DQ. Each of the points in Fig. 9 has been corrected for the effect of density changes on the radical concentration as discussed in I. This figure clearly shows that the linewidth of the concentrated mixture of DQ and DSQ increases with temperature. From earlier work^{7b,25} we expect the rate constant for chemical exchange to be at least 20 times smaller than the rate constant for spin exchange, and it is assumed hereafter that the former contribution to the width is negligible. It is noted that for $T/\eta > 6 \times 10^2 \text{K/cP}$ the linewidths for both solutions increase linearly with T/η ; for the dilute solution presumably due to spin-rotational effects; for the concentrated solution mainly due to exchange. The widths for $T/\eta < 6 \times 10^2 \text{K/cP}$ are no longer linear most likely due to the onset of other relaxation processes dependent on η/T , but also some effects may be due to the TBAP (0.1M in the concentrated solution and 0.05M in the dilute one) which begins to precipitate for $T < -10^\circ\text{C}$ ($T/\eta = 3.9 \times 10^2$) possibly trapping a portion of the radicals.

When the data for $[\delta - \delta(0)]$ vs T/η for values of $T/\eta > 6 \times 10^2 \text{K/cP}$ are fitted to a straight line, then the least-squares value for k is $(2.87 \pm 0.06) \times 10^9 M^{-1} \text{sec}^{-1}$ at 15°C . The error in the concentration measurement is, however, about 10%. The intercept is 22 ± 3 mG or reasonably close to but not quite zero. Some deviation is expected as a result of intermolecular dipolar effects,¹ but there is enough uncertainty in the lower temperature data due to the nonlinear dependence of the widths on T/η so that the deviation is not experimentally significant.

IV. ANALYSIS AND DISCUSSION

A. PADS

The most striking features of our results on PADS are: (1) the large effects of ionic strength on spin-exchange rates as observed by ESR linewidths, and (2) the generally weak T/η dependence of the spin exchange, the nature of which is dependent on ionic strength.

As we have already noted, the solubility of PADS in aqueous solution suggests that the radical exists in the form of a doubly charged hydrated anion. Coulombic repulsion between these anions tends to limit their close approach. But an increase in ionic strength tends to offset these repulsions. Such effects are important for ordinary chemical reactions in ionic solution and one may expect them to play a significant role in spin exchange. We may therefore attempt to analyze this from the point of view of Debye's theory for the reaction rates of charged particles in ionic

solutions.²⁶ The relevant expression for ω_{HE} is given by Eq. (1.1) and for simple Brownian diffusion^{26,27}

$$\tau_2^{-1} = 4\pi d f^* \mathfrak{N} \quad (4.1)$$

$$\tau_1^{-1} = (6D/d^2) f^* \exp[U(d)/kT], \quad (4.2)$$

where the diffusion coefficient in a Stokes-Einstein model is

$$D = kT/6\pi a\eta. \quad (4.3)$$

\mathfrak{N} is the density of radicals, a the molecular radius, and d the "interaction distance" for exchange. The intermolecular potential energy of interaction $U(r)$, for simple like charges in a medium of finite ionic strength is given by²⁸

$$U(r) = [e^{kd}/(1+\kappa d)](Z^2 e^2/\epsilon r) e^{-\kappa r}, \quad (4.4)$$

where

$$\kappa^2 = (4\pi e^2/\epsilon kT) \sum_i \mathfrak{N}_i Z_i^2. \quad (4.5)$$

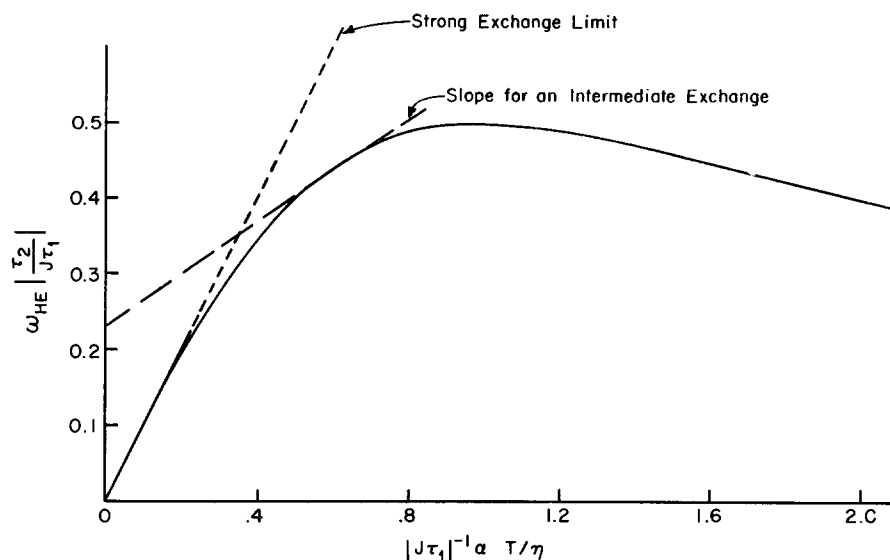
Here ϵ is the dielectric constant of the medium, Z the charge on the radicals, and e an electronic charge. Also \mathfrak{N}_i is the number density of particles of type i and charge Z_i . The parameter κ is known as the reciprocal thickness of the ionic layer. Now²⁶

$$(f^*)^{-1} = d \int_a^\infty \exp\left(\frac{U(r)}{kT}\right) \frac{dr}{r^2}. \quad (4.6)$$

One has $f^* = 1$ in the absence of charge, but $f^* < 1$ for repulsive effects. Equation (4.6), for significant ionic strength (i.e., $\kappa d \gtrsim 1$), must be solved numerically. In our experiments with 0.05M buffer, $\kappa d \sim 1$. However, since Eqs. (4.4) and (4.5) are based on the Debye-Huckel limiting law, they are not really valid for concentrations $> 10^{-2}M$. We therefore must use them only in an instructive or qualitative sense, since our work was performed in a somewhat higher concentration region. We wish to compare such calculations of f^* with Eq. (3.1) to see whether a relationship of this type with $m \sim 0.07$ – 0.17 is a reasonable one, but also we would like to obtain estimates of the relevant parameters in Eqs. (4.2)–(4.6).

The increasing slopes for the linewidth dependence on T/η as the electrolyte concentration is increased (cf. Table II), can be directly related to an increase in magnitude of the product $|J| \tau_1$ provided Eqs. (1.1), (4.1), and (4.2) are valid. A useful relation is obtained by differentiating ω_{HE} with respect to T/η utilizing these equations. We assume that f^* and $\exp[U(d)/kT]$ are much more slowly varying functions of T than T/η , and this is borne out for the PADS solutions in the calculations discussed below, that is, when T/η changes by a factor of 2 these parameters are found to change by about 2%. One then

FIG. 10. Theoretical plot of ω_{HE} vs $|J\tau_1|^{-1} \propto T/\eta$. J is assumed to be constant, and τ_1/τ_2 is independent of T/η . Thus ω_{HE} is given as the dimensionless ratio with $|J|\tau_1/\tau_2$.



obtains:

$$\bar{\omega}_{\text{HE}} = \frac{T}{\eta} \frac{d\omega_{\text{HE}}}{d(T/\eta)} = \omega_{\text{HE}} \left(\frac{1 - J^{-2}\tau_1^{-2}}{1 + J^{-2}\tau_1^{-2}} \right) \quad (4.7)$$

from which

$$J^{-2}\tau_1^{-2} = [(\omega_{\text{HE}} - \bar{\omega}_{\text{HE}})/(\omega_{\text{HE}} + \bar{\omega}_{\text{HE}})]. \quad (4.8)$$

The values of ω_{HE} may be taken directly from Figs. 2 and 6 utilizing Eq. (3.0), while those of $\bar{\omega}_{\text{HE}}$ are obtained from Table II. Alternatively values for $\omega_{\text{HE}} - \bar{\omega}_{\text{HE}}$ are given by the intercepts in Table II (see Fig. 10). (The value of $\bar{\omega}_{\text{HE}}$ for 0.05 electrolyte is not very sensitive to PADS concentration in the region of interest, so an interpolated result from Table II was used.) The results, including estimates of $|J|\tau_1$ and τ_2^{-1} at 24°C are given in Table III. Since the T/η values differ somewhat for the different electrolyte concentrations, values for these parameters corrected to a common T/η value [utilizing Eqs. (4.1)–(4.3)] are also given. This simple analysis indicates that τ_2^{-1} increases considerably with increasing electrolyte concentration, and, while $|J|\tau_1$ also increases, the extent is less pronounced.

There are several significant points of criticism to be made about this analysis. First the values of T/η used, as well as the correction to a common T/η , involve the questionable assumption that the electrolyte effect on the macroscopic viscosity is roughly the same as that on the “microscopic” viscosity associated with Eq. (4.3). However, the correction factors are not large. Second, in the region where $|J|\tau_1 \sim 1$, Eqs. (1.1), (4.1)–(4.3) predict that the dependence of ω_{HE} (or width) on T/η should not be linear over significant ranges of T/η (see Fig. 10). In our experiments (from 10–40°C) it was possible to change T/η

by only about a factor of 2,²⁹ and small deviations from linearity could be hidden in the uncertainties in the linear least-squares fits although some curvature may be discerned in Fig. 5. However, we note that the values of $|J|\tau_1$ in Table III, if interpreted as the mean values for Figs. 2 and 6, would lead to noticeable curvature. But mean values not very different from these of ~ 0.67 for Fig. 2 and ~ 1.7 for Fig. 6 would not yield much curvature, but would suggest that Eq. (4.2), and hence Eq. (4.7), is not strictly applicable. In this connection the possibility that non-diffusive factors, such as intermolecular interactions between PADS radicals [not as simply given as in Eq. (4.3)], which significantly affects τ_1 , cannot be ruled out. It is possible that the simple two-state model upon which Eq. (1.1) is based¹⁻⁴ could also require modification.

The results in Fig. 5 indicate that the widths at 0.61M electrolyte are probably near an asymptotic limit. It is thus interesting to compare these results with those predicted by Eqs. (4.1)–(4.3) in the absence of charge effects, i.e., $f^* = 1$, etc. Then for $d = 2a = 7 \text{ \AA}$ (our estimate of an effective diameter for the PADS anion from the bond lengths), we obtain $k = 3.5 \times 10^9 \text{ sec}^{-1}$ and $\tau_1 = 1.2 \times 10^{-10} \text{ sec}$ at 24°C in pure water ($T/\eta = 326^\circ\text{K}/\text{cP}$); but corrected to the common $T/\eta = 300$, one has $k = 3.2 \times 10^9 \text{ sec}^{-1}$ and $\tau_1 = 1.3 \times 10^{-10} \text{ sec}$.³⁰ The value of k for the solution 0.61M in electrolyte is thus very close to this theoretical value. However, the results for other radicals are often somewhat less than the calculated values. We note that if $d > 2a$, then k becomes greater than the values calculated for $d = 2a$. It would seem likely that $d > 2a$ for the close approach of two PADS dianions even in the presence of a strong ionic atmosphere.

TABLE III. Estimates of effect of electrolyte concentration on τ_1 and k for aqueous PADS solutions.^a

	Concentration of added electrolyte			Pure water: calculated
	0.05M	0.30M	0.61M	
T/η at 24°C ^b	320	305.1	284.7	326
$ J \tau_1$ at 24°C	0.954	1.18	1.34	...
$k \times 10^{-9}$ at 24°C	1.99	2.98	3.19	3.5
$ J \tau_1$ at $T/\eta = 300$ ^c	1.017	1.20	1.28	...
$k \times 10^{-9}$ at 24°C ^c	1.87	2.94	3.36	3.2

^a $C = 2.4 \times 10^{-2} M$; k in units of $M^{-1} \cdot \text{sec.}^{-1}$.

^b From Refs. 20, 21.

^c From results at 24°C utilizing dependence of D on T/η , cf. Eqs. (4.1)–(4.3).

A series of calculations based on Eqs. (4.4)–(4.6) for the concentrations appropriate to Fig. 3 and for different values of d were performed. The integration of Eq. (4.6) was performed numerically with a modified version of Simpson's rule utilizing a CDC 6600 computer,³¹ and the results for f^* and $r = \{f^* \exp[U(d)/kT]\}^{-1}$ are given in Table IV. Note that f^* varies more rapidly than r with concentration for the smaller values of d . These results were then used to obtain sets of values for k , $|J| \tau_1$, and then ω_{HE} according to Eqs. (1.1), (4.1), and (4.2). The values of $|J| \tau_1$ and k for the 0.05M electrolyte concentrations as given in Table III (for 24°C) were used as the references. The calculated results for $d = 6 \text{ \AA}$ are included in Fig. 4 and are in good agreement with the experimental results. Least-squares fits of the results to Eq. (3.1) are given in Table V and compared with the experimental results. We note first of all, the Eqs. (1.1), (4.1)–(4.6) do not lead directly to a simple relationship of the form of Eq. (3.1). Thus, it is not surprising to find some scatter as evidenced in the sample deviations given for the theoretical results. However, given the approximations inherent in our theoretical and experimental analyses, the comparison is surprisingly good with the best agreement existing between our experimental results and the theoretical value for $d = 6 \text{ \AA}$. In view of the not very large variation in theoretical results with the value of d , as well as the substantial experimental and theoretical uncertainties, this value is probably not too significant, although the over-all agreement is quite encouraging. We have not extended this analysis to the more concentrated electrolyte solutions (0.3–0.6M), since the Debye expressions of Eqs. (4.4)–(4.5) are certainly no longer appropriate.

B. DTBN

The uncharged DTBN radical would not be expected to exhibit any of the above noted ionic-strength-

dependent effects. Indeed, the spin-exchange rate is found to decrease with increasing ionic strength. We think this may be attributed to the formation of aggregates of radicals in aqueous solution, because of the hydrophobic characteristics of the large *t*-butyl groups.³² Such aggregate formation would be enhanced in a manner ultimately equivalent to the well-known salting-out effect as a result of increasing the ionic strength. The net effect of aggregate formation would be to reduce the frequency of bimolecular encounters at a given radical concentration partly because there are always fewer aggregates than individual DTBN molecules.

One would expect that an aggregate, consisting of two or more DTBN molecules, would have the hydrocarbon portions of the molecules on the inside and the nitroxides on the outside. Thus the regions of high electron density (i.e., along the NO bond) would be separated by one or more *t*-butyl groups, and therefore may be expected to act essentially independent of one another in a spin-exchange reaction with another DTBN radical or aggregate, i.e., it could be possible that only one radical of each aggregate would be involved in the exchange. This would have the apparent effect of decreasing \mathfrak{R} , the concentration of radicals. (If steric factors are important in the exchange of pairs of single radicals, then they would tend to lead to an offsetting effect upon aggregate formation.) Note also, that if we take d , the interaction distance, to be determined by the exchanging nitroxide groups, its value should not be significantly affected by aggregate formation. On the other hand, τ_1^{-1} , $\tau_2^{-1} \propto$

TABLE IV. Values for f^* and r calculated for different PADS concentrations and interaction distances from Debye's theory.^a

PADS Conc.	d (Å)				
	5	6	7	8	9
	A. f^*				
$5 \times 10^{-3} M$	0.168	0.294	0.417	0.523	0.610
7	0.172	0.300	0.423	0.529	0.616
10	0.177	0.307	0.431	0.537	0.624
20	0.195	0.331	0.458	0.564	0.649
35	0.220	0.364	0.492	0.597	0.680
50	0.243	0.392	0.522	0.625	0.705
60	0.258	0.409	0.539	0.641	0.720
	B. r				
$5 \times 10^{-3} M$	0.192	0.239	0.289	0.338	0.385
7	0.192	0.240	0.290	0.340	0.387
10	0.193	0.242	0.292	0.342	0.390
20	0.195	0.246	0.298	0.349	0.399
35	0.199	0.252	0.306	0.360	0.410
50	0.202	0.258	0.314	0.369	0.421
60	0.205	0.261	0.319	0.375	0.427

^a C_B concentration of 0.05M due to K_2CO_3 is assumed in all cases. In these calculations we have taken account of the almost negligible effects of the hydrolysis reaction: $H_2O + CO_3CO_3^{2-} \rightleftharpoons OH^- + HCO_3^-$. The value of K for this reaction was taken from H. S. Harned and S. R. Scholas, Jr., J. Am. Chem. Soc. **63**, 1706 (1941).

$\frac{1}{2}(D_i + D_j) \propto (a_i^{-1} + a_j^{-1})$, where i and j refer to the two exchanging aggregates. Thus both τ_1 and k^{-1} may be expected to increase as a result of aggregate formation due to slower diffusion coefficients. For strong exchange, increasing τ_1 has no significant effect [cf. Eq. (1.1)], but a decrease in k means that ω_{HE} is decreased beyond that due to the effective decrease in \mathcal{N} [cf. Eq. (4.1)].

We note that the value for k obtained from Table II for DTBN in pure water ($2.4 \times 10^9 \text{ sec}^{-1} M^{-1}$) is about $\frac{2}{3}$ of the value calculated from Eqs. (1.1), (4.1)-(4.3). Thus the proposed aggregation effect does not appear to be very significant in the absence of electrolyte. We also note that the form of Eq. (3.3) is suggested by the form of the Huckel equation for the "salting-out effect" on the activity coefficient γ of a nonelectrolyte: $\log \gamma = C'(\frac{1}{2} \sum_i \mathcal{N}_i Z_i^2)$, where C' is the salting-out constant.³³

It might be possible to detect such aggregates through a study of the colligative properties of DTBN-containing solutions.

C. TCNE⁻ and DSQ⁻

The results of a study of TCNE⁻, which exhibits strong exchange, in low-dielectric DME and THF solvents were given in I. It was shown that the values of k were comparable to those predicted from Eqs. (1.1), (4.1)-(4.3) for neutral radicals (i.e., $f^* \cong 1$) and therefore much greater than those predicted for singly charged radicals. That analysis neglected the effects of ionic strength. We have calculated f^* for these systems neglecting ion pairing effects and find that for $d=6 \text{ \AA}$, $T=15^\circ\text{C}$, f^* ranges from 3.7×10^{-5} for $1 \times 10^{-5} M$ solutions to 8.66×10^{-4} for $3 \times 10^{-3} M$ solutions (the most concentrated solutions). It is quite clear, then, that the ionic strength effect is wholly inadequate to provide the needed shielding of charged radicals. This, therefore, supports the conclusion that ion pairing must be playing a significant role in neutralizing the radical charge. We might also note that the predicted temperature dependence of f^* (neglecting ion-pairing effects) is substantial, ranging from 6.61×10^{-4} at 200°K to 2.26×10^{-4} at 300°K for $1 \times 10^{-3} M$ solutions in DME (or THF).

The results on DSQ⁻ in DME are consistent with those of TCNE⁻ in that solvent, i.e., it appears to undergo strong exchange. The value for k for DSQ⁻ is somewhat less, 2.9 vs $4.1 \times 10^9 M^{-1} \text{ sec}^{-1}$ at 15°C , and this could well be attributed to (1) increased steric factors and/or (2) somewhat weaker charge cancellation by ion pairing of DSQ⁻ with tetrabutyl ammonium ions as compared to $K^+ \text{TCNE}^-$.

V. CONCLUSIONS

It has been possible to analyze the spin-exchange behavior of aqueous solutions of the PADS dianion

TABLE V. A comparison of calculated and experimental dependence of ω_{HE} on electrolyte concentration.^a

Experimental	m	$b \times 10^{-9}$
This work	1.17 ± 0.03	1.96
Jones ^b	1.07 ± 0.02	1.84
Calculated ^c		
$d=5 \text{ \AA}$	1.20 ± 0.02	2.2 ± 0.2
6 \AA	1.17 ± 0.01	1.9 ± 0.1
7 \AA	1.14 ± 0.01	1.73 ± 0.10
8 \AA	1.12 ± 0.01	1.60 ± 0.07
9 \AA	1.11 ± 0.01	1.50 ± 0.06

^a The data were fitted to Eq. (3.1).

^b Reference 8 (a).

^c f^* and r from Table IV. Data for 0.05M electrolyte from Table III served as scaling points for τ_2^{-1} and $|J| \tau_1$.

radical in terms of an intermediate exchange ($|J \tau_1| \sim 1$) model which is very sensitive to ionic strength effects. The results for the more dilute electrolyte solutions are found to be in good agreement with Debye's theory of ionic strength effects on reaction rates. The DTBN radical exhibits strong exchange ($|J| \tau_1 \gg 1$) in aqueous solvents, but the exchange behavior is markedly affected by increasing the ionic strength, presumably because this leads to aggregation of the radicals. It appears that APADS exhibits weak exchange ($|J| \tau_1 \ll 1$), but because of radical decay problems, a quantitative analysis can not be carried out. The DSQ⁻ radical undergoes strong exchange in DME exhibiting results very similar to those observed for the TCNE⁻ radical, which has no bulky methyl groups. Thus, to date, intermediate to weak intermolecular spin exchange has only been observed in nitroxide-containing free radicals.

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- ²⁹ Attempts were made to obtain a greater range of T/η values by using glycerine-water solutions of PADS. However, serious radical decomposition problems were encountered. A wider range of T/η values could be obtained from pressure-dependent studies utilizing high-pressure techniques.
- ³⁰ An order of magnitude estimate of J may be attempted from the data of Table III utilizing the $C_E=0.05M$ solution results, and the estimates of r in Table IV.B ranging from 0.2 to 0.4. One obtains $|J| \sim 3 \times 10^{10} \text{ sec}^{-1}$ or about 1 cm^{-1} .
- ³¹ The upper limit in the integration was set at $31d$ instead of infinity. That this is a good approximation is shown by the fact that the range $21d-31d$ contributes no more than $\sim 1\%$ to the final result.
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