

EPR Studies of Spin-Spin Exchange Processes

A Physical Chemistry Experiment

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The study of electron paramagnetic resonance (EPR) linewidths has provided information about molecular motions, electron distributions in paramagnetic species, ion pair interactions, and the rates of a variety of chemical reactions. Unfortunately, it has not been easy to conduct EPR linewidth studies in the undergraduate physical chemistry laboratory. There are a number of reasons for this: suitable samples are often difficult to prepare, high performance EPR spectrometers are required in many studies, and expensive and fragile equipment is involved in studies where the temperature must be closely controlled.

The purpose of this experiment is to provide the undergraduate physical chemistry student with an EPR linewidth study which can be accomplished in a relatively short time with a minimum amount of equipment. The source of the line broadening observed in these experiments is a spin-spin exchange process between the radicals formed in aqueous solutions of potassium peroxyamine disulfonate (PADS). In the course of the analysis, a number of basic concepts in magnetic resonance, in solution kinetics, and in the theory of ionic solutions are covered.

Theoretical Background

Solutions of PADS yield a well-defined, three-line EPR spectrum with a hyperfine splitting constant of 13.05 Gauss (1, 2). This hyperfine splitting arises from the interaction of the unpaired electron with the nitrogen nuclear spin of 1. An explanation of the origin of hyperfine splitting and the theory of EPR is presented in several introductory texts (3-5). Figure 1 shows the EPR spectrum of a $1.6 \times 10^{-4} M$ solution of PADS.

When diffusion brings two free radicals with oppositely directed electron spins so close to one another that the wave functions for the two unpaired electrons overlap, there is a probability that these electrons will exchange their spin coordinates. This exchange of spin coordinates is generally referred to as spin-spin or Heisenberg exchange. It has been shown that the exchange interaction is formally equivalent to a direct coupling of spins and that it contributes a term $J S_1 S_2$ to the Hamiltonian for the spin system. Here, S_1 and S_2 are the spin operators for the two unpaired electrons and J , a measure of the strength of the exchange interaction, is twice the exchange integral.

Spin exchange in solution can be considered a random, time-dependent process which leads to a lifetime for a spin state which has a dependence on the exchange rate. Thus, an increase in the exchange rate leads to a reduced lifetime for a given spin state. It is this change in lifetime which leads to the linewidth effects studied in this experiment.

The rate of spin exchange, ω_{ex} , is dependent on two factors, the time between radical-radical collision, τ_2 , and the probability, P , of spin exchange taking place during collisions. That is

$$\omega_{ex} = P/\tau_2 \quad (1)$$

In general, $P = 1$ when exchange takes place during each collision and $P < 1$ when some fraction of the collisions do not result in exchange. A detailed treatment of the dependence of P on the lifetime of the collision pair and on the strength of the exchange interaction can be found in the literature (6).

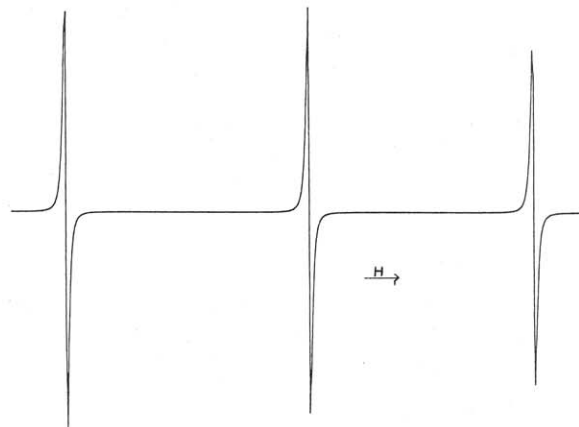


Figure 1. The 1st derivative EPR spectrum of a solution of $1.6 \times 10^{-4} M$ PADS and $5 \times 10^{-2} M$ K_2CO_3 .

For simple Brownian diffusion τ_2^{-1} is calculated by means of the expression

$$\tau_2^{-1} = (4\pi dND)f^* \quad (2)$$

In the above, N is the number density of radicals and d is the "interaction distance" for exchange. Typically, this distance is taken as twice the radius of the radicals undergoing exchange. The Stokes-Einstein diffusion constant, D , is determined from the equation.

$$D = \frac{kT}{6\pi a\eta} \quad (3)$$

Here η is the viscosity, a the molecular radius, and kT the product of the Boltzmann constant and the temperature. The correction factor f^* in expression (2) was first introduced by Debye to take account of the effect of coulombic interactions on the collision rate (7). If the species for which τ_2^{-1} is being calculated has no charge, $f^* = 1$; but, for collisions between like-charged ions, $f^* < 1$. The following theoretical expressions can be written for f^* :

$$(f^*)^{-1} = d \int_d^\infty \exp \left[\frac{U(r)}{kT} \right] dr/r^2 \quad (4)$$

where the intermolecular potential energy of interaction $U(r)$, for simple like charges in a medium having finite ionic strength, is (in SI units)

$$U(r) = [e^{\kappa d}/(1 + \kappa d)] \frac{Z^2 e^2}{4\pi\epsilon_0\epsilon} e^{-\kappa r} \quad (5)$$

and

$$\kappa^2 = \left(\frac{e^2}{\epsilon_0\epsilon kT} \right) \sum_i N_i Z_i^2 \quad (6)$$

Here ϵ is the dielectric constant of the medium, ϵ_0 the vacuum permittivity, Z the charge on the colliding radicals, and e an electronic charge. The number density of particles of species i is N_i and Z_i is the charge on species i . In terms of the Debye model κ^{-1} may be considered to be the thickness of the ionic layer. In general, for collisions between like charged ions, f^* increases with increasing ionic strength.

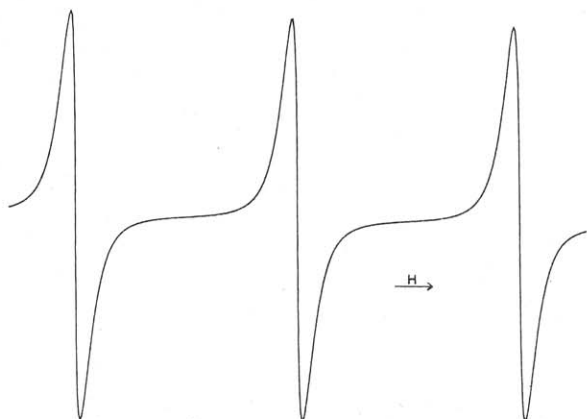


Figure 2. The 1st derivative EPR spectrum of a solution of $1.9 \times 10^{-3} \text{ M}$ PADS and $5 \times 10^{-2} \text{ M}$ K_2CO_3 .

In the linewidth experiments considered here, only well-defined hyperfine lines will be observed. Thus, the increase in linewidth caused by increasing the radical concentration will not lead to appreciable overlap of the three hyperfine lines. This is referred to generally as the slow exchange limit. The PADS spectrum in Figure 2 shows spin exchange broadened hyperfine lines in the slow exchange unit. The derivation of a relation between ω_{ex} and the observed linewidth in the limit of slow exchange is accomplished most conveniently by means of the modified Bloch equations. This derivation is carried out in a number of places and has general applicability to an appreciable number of situations encountered in NMR and EPR (3-5).

In the slow exchange limit

$$\omega_{\text{ex}} = (3/2)(\sqrt{3}/2) \gamma(\Delta H - \Delta H_0) \quad (7)$$

The gyromagnetic ratio of the electron ($1.76 \times 10^{-7} \text{ sec}^{-1} \text{ Gauss}^{-1}$ in angular frequency units) is given by γ . The factor $3/2$ arises because the spin exchange between radicals with the same nuclear spin configuration produces no observable line broadening. The first derivative linewidths (in terms of Gauss) in the presence and absence of exchange are given by ΔH and ΔH_0 respectively. The factor $\sqrt{3}/2$ is included to convert the derivative linewidth to the linewidth of the absorption curve.

Experimental

PADS of high purity is obtained most easily by means of the simple synthesis described by Moser and Howie (8). The purity of the final product can be determined spectrophotometrically using the extinction coefficients ($\epsilon = 20.8$ at 545 nm) given by Murib and Ritter (9). The PADS solutions used in the EPR studies are $5 \times 10^{-2} \text{ M}$ in K_2CO_3 . The purpose of the K_2CO_3 is to increase the pH of the solution and to prevent the decomposition of the PADS. Oxygen, a potential source of linebroadening, can be removed from the solutions by bubbling water saturated nitrogen gas through the solution prior to the EPR measurements. Small aliquots of the deoxygenated solution are used to rinse and fill 1 mm (maximum O.D.) capillary tubes for about 1 cm or less of their length. To avoid accidental breakage of the capillary tubes in the EPR cavity, it is a good idea to place the filled capillaries inside a 3 mm O.D. Pyrex® tube. It should be noted that the radicals formed in solutions of PADS, unlike many radicals, are not destroyed by oxygen.

The EPR spectrum is recorded after positioning the PADS solution at the center of the microwave cavity. It is advisable to run the EPR experiments at the lowest microwave powers consistent with a good signal-to-noise ratio on the spectrum and with satisfactory spectrometer operation. This precaution

Values of linewidth (ΔH), exchange frequency (ω_{ex}), and f^* as determined for a series of PADS solutions which were $5 \times 10^{-2} \text{ M}$ in K_2CO_3 . The calculations for f^* were made with $d = 6\text{ \AA}$ and $Z = 2$.

PADS Concentration $\times 10^3$	$\Delta H(\text{Gauss})$	f^*	$\omega_{\text{ex}} \times 10^{-7} \text{ sec}^{-1}$	$\omega_{\text{ex}}/f^* \times 10^{-7} \text{ sec}^{-1}$
5.5	0.387	0.295	0.495	1.68
9.8	0.541	0.306	0.848	2.77
13	0.690	0.315	1.19	3.78
17	0.873	0.325	1.61	4.95
19	1.02	0.329	1.93	5.87
28	1.54	0.349	3.14	8.99
35	1.77	0.364	3.66	10.1
45	2.37	0.383	5.05	13.2
56	3.15	0.402	7.20	17.9

ensures minimum sample heating from microwave absorption and removes saturation broadening from consideration as a line-broadening mechanism. If the temperature of the sample is controlled by means of a variable temperature device, heating of the sample by microwave absorption is no longer a problem. It should be noted that under the conditions of the experiment the linewidths are quite insensitive to temperature variations; for example, a 2°C temperature change leads to less than a 1% linewidth change. In every case the response time and modulation amplitude settings should be reduced until they are a negligible source of line broadening.

Analysis of Experimental Results

The first step in the experiment is to determine the dependence of the ESR linewidth (ΔH) on the radical concentration. Next, eqn. 7 is used to obtain ω_{ex} from the measured linewidth. In this work, all linewidth measurements were made on the center line in the EPR spectrum and ΔH_0 , as determined from $1.6 \times 10^{-4} \text{ M}$ PADS sample, is taken to be 0.170 Gauss. A computer program employing eqns. 5, 6, and 7 can be written to calculate f^* as a function of d and of the ionic strength. The table gives values of f^* calculated as a function of PADS concentration assuming $d = 6\text{ \AA}$. Here d is assumed to be the approximate diameter of a $(\text{SO}_3)_2\text{NO}^{2-}$ ion as determined from a molecular model. However, it should be pointed out that when the ions in the solution vary greatly in size (as is the case here) the identification of d as an ionic diameter is not strictly correct (11).

The experimental data in the table can be used to prepare a plot of ω_{ex}/f^* versus the PADS concentration. Fitting the points with a linear least squares program one obtains a slope of $2.86 \pm 0.09 \times 10^9 \text{ sec}^{-1} \text{ mole}^{-1} \text{ liter}$ and a zero concentration intercept of $0.05 \pm 0.1 \times 10^7 \text{ sec}^{-1}$. As expected, the intercept is zero within the experimental error. Theoretical values of $(\tau_2 f^*)^{-1}$ can be calculated from eqn. 2 as a function of radical concentration at 24°C . A plot of the results of these calculations yields a slope of $3.6 \times 10^9 \text{ sec}^{-1} \text{ mole}^{-1} \text{ liter}$. In the calculations leading to this plot the effect of the dissolved salts on η can be neglected. A comparison of the experimental and theoretical results indicates the following possibilities:

(a) Brownian diffusion does not describe the motion of the radicals in the solution; (b) $P \neq 1$; thus, there is no exchange on every collision; (c) the assumption that $d = 2a$ in the calculation of τ_2 is incorrect; (d) ion pairing may occur in solution. A careful study of this system leads to the conclusion that all of the above effects are potentially significant (2, 10, 11).

The experimental results provide insight into the kinetics of the spin-spin exchange reaction and qualitative verification of the Debye theory for the effect of change on reaction rates. In addition, the experiment can be modified readily to investigate a variety of other effects. For example, uncharged nitroxide radicals ($f^* = 1$) can be substituted for PADS in this experiment or the spin exchange broadening produced by

dissolved oxygen can be studied. Computer calculations of lineshapes and absorption curves can also be included.

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