Electron Spin-Spin Interaction and Translational Diffusion of Nitroxide Radicals in Sodium Dodecyl Sulfate Micelles

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(Received August 9, 1978)

The line width measurements of ESR spectra of 2,2,6,6-tetramethyl-4-benzoyloxypiperidinyl-1-oxyl (BzONO) in sodium dodecyl sulfate (SDS) micelles have been carried out at various concentrations of BzONO. The plot of the line width against the concentration of BzONO shows a line with a break at mole fraction *ca.* 0.05, as opposed to the theoretical prediction that the plot would give a straight line. In order to explain this anomalous behavior, three models for the solubilization of BzONO are considered. On the basis of two of these models, spin exchange rates of BzONO in the micelles are estimated. Translational diffusion coefficients of BzONO in the SDS micelles at 20, 31, and 38.5 °C are calculated by using the spin exchange rate constants and an appropriate diffusion model. The obtained values are of the order of 10^{-7} cm²/s.

Magnetic resonance methods have been used to study both microscopic and dynamical aspects of the solubilization of hydrophobic substances into surfactant micelles.

In the NMR method,[1] the change in chemical shifts caused by aromatic solubilizates is utilized to know a solubilizing site and its environment. Fendler and coworkers[2] have reported that benzene is mainly solubilized in the interior of sodium dodecyl sulfate (SDS) micelles, but it is located near the surface of hexadecyltrimethylammonium bromide (CTAB) micelles.

By means of another NMR technique utilizing the line broadening caused by paramagnetic counter ions, Fox and coworkers[3] have found that *p*-xylene as a solubilizate is distributed uniformly throughout the hydrophobic region of SDS micelles.

By the ESR method, besides the solubilizing site and its environment,[4] dynamical quantities such as rotational correlation times[4,5] in micelles and exchange rates[6] between micellar environment and bulk water have been obtained for nitroxide radical molecules as hydrophobic solubilizates. The values reported so far are of the order of 10^{-10} s/rad for the former and 10^4—10^5/s for the latter.

Recently, the measurement of spin exchange interaction has been applied to the study of translational diffusion in fluid media,[7] and has given very interesting results. In a fluid medium, the spin exchange is accompanied by the molecular collision between dissolved radicals. The exchange rate, therefore, can be connected with their translational diffusion coefficient.[8]

By means of this technique, McConnell and coworkers[9] have estimated that the translational diffusion coefficient of spin-labeled phospholipid molecules in lipid membranes is 6×10^{-8} cm²/s at 37 °C. Ablett and coworkers[10] have studied the hydrophobic interaction by the measurement of spin exchange rate of nitroxide radicals in both water and various organic solvents.

The purpose of the present study is to determine the translational diffusion coefficients of solubilizates in surfactant micelles by this technique, which utilizes the electron spin exchange broadening. The information about this quantity may lead to a further understanding of the solubilization phenomena and the chemical reaction in micellar environments.

Experimental

The synthesis of 2,2,6,6-tetramethyl-4-benzoyloxypiperidinyl-1-oxyl (BzONO, Fig. 1) was reported elsewhere.[11] Sodium dodecyl sulfate (SDS) of specially prepared reagent was recrystallized several times from ethanol-acetone solutions. Its CMC is 8.3×10^{-3} mol/dm³ at 25 °C.

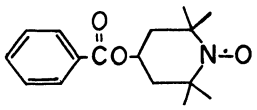

Fig. 1. BzONO.

ESR spectra were recorded on a JEOL model ME-3X spectrometer equipped with a variable temperature accessory. The accuracy of temperature measurements is ±1 K.

The concentration of aqueous SDS solutions ranges from 4 to 7 wt %. In this concentration range, the ESR spectra come only from BzONO in SDS micelles; the fraction of BzONO in bulk water is very small.

Results and Discussion

As unpaired electron spin concentration increases in a system, the electron spin-spin interaction becomes more and more important in the electron magnetic relaxation mechanism.[12] This interaction consists of two parts; one is the spin exchange interaction and the other is the dipolar interaction. The former is a contact interaction which occurs only on overlapping of the wave functions of the electron spins. In a solution, therefore, this interaction accompanies the collisional process between paramagnetic species. The latter is a classical magnetic interaction which depends on the distance between paramagnetic species.

From theoretical and experimental studies,[13] both interactions increase linearly with the spin concentration. However, in regard to an increase in T/η where T is the absolute temperature and η is the environmental viscosity, the two interactions behave differently.[14] The spin exchange interaction is proportional to the increase, and, on the other hand, the dipolar interaction is inversely proportional to it. That is to say, the electron spin relaxation rate of spin exchange interaction T_{2E}^{-1} and that of dipolar interaction T_{2D}^{-1} are given by the following formulae, respectively:

$$T_{2E}^{-1} = k_E C \propto T/\eta, \quad (1)$$

$$T_{2D}^{-1} = K_D C \propto \eta/T, \quad (2)$$

where k_E is the second order rate constant for the exchange process, C the spin concentration, and K_D is a proportionality constant.

In the case of nitroxide radicals, the net spin-spin relaxation rate T_2^{-1} takes the following form:

$$T_2^{-1} = T_{20}^{-1} + T_{2E}^{-1} + T_{2D}^{-1}$$
$$= T_{20}^{-1} + (k_E + K_D)C, \quad (3)$$

where T_{20}^{-1} is the relaxation rate when no electron spin-spin interaction occurs. Thus, Eq. 3 predicts that a plot of T_2^{-1} against C will give a straight line.

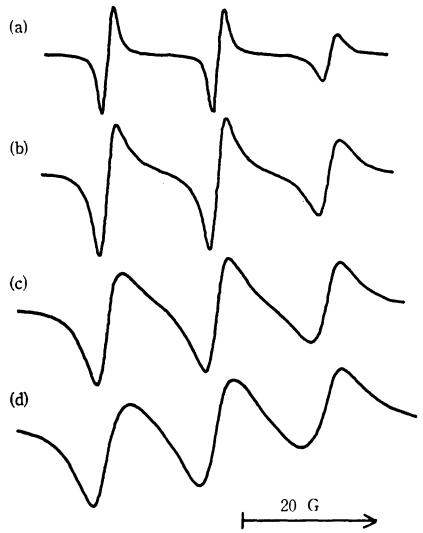

Fig. 2. ESR spectra of BzONO in 4.75 wt % aqueous SDS solutions at 20 °C. Mole fraction of BzONO in micelles: (a) 0.009, (b) 0.037, (c) 0.065, (d) 0.090.

Figure 2 shows ESR spectra of BzONO in 4.75 wt % aqueous SDS solutions at 20 °C. At this SDS concentration, the spectra can be assigned only to BzONO in the SDS micelles. The spectra consist of three lines owing to the contact interaction between an electron spin ($S=1/2$) and an ^{14}N nuclear spin ($I=1$). The three lines correspond to ^{14}N nuclear spin quantum numbers $M_I=+1$, 0, and -1, toward the high field direction. Each line width of the spectra increases with the concentration of BzONO. The broadening is due to the electron spin-spin interaction.

Figure 3 shows the plots of each line width W, equal to $(2/\sqrt{3})T_2^{-1}$, against the mole fraction X of BzONO in micelles. The obtained plots were not represented by straight lines, contrary to the foregoing theoretical consideration. Each line breaks at mole fraction *ca.* 0.05.

Recently, Barratt and coworkers[15] have reported similar results from the study of electron spin exchange of 2,2,6,6-tetramethylpiperidinyl-1-oxyl in glycerol-water mixed solvent; they give no interpretation. We will give our opinion later, though it is an open question whether the nature of their results is the same as in the present study.

The results of line width measurement with two SDS concentrations were on the same lines, as is shown in

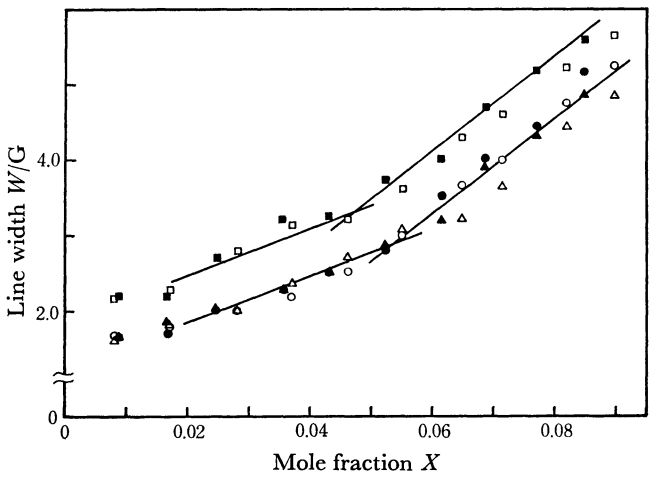

Fig. 3. Plots of W against X at 20 °C in 4.75 wt % aqueous SDS solutions (○: $M_I=+1$, △: $M_I=0$, and □: $M_I=-1$); in 7.01 wt % aqueous SDS solutions (●: $M_I=+1$, ▲: $M_I=0$, and ■: $M_I=-1$).

Fig. 3. This fact guarantees that the ESR spectra observed involve no signal from BzONO in bulk water, and indicates that the presence of the break is not caused by the interaction between electron spins belonging to different micelles.

Figures 4 and 5 show the results at 31 and 38.5 °C, respectively. At these temperatures, it was also observed that the linear plots of W against X fail. The gradients of these lines above and below mole fraction of *ca.* 0.05 are listed in Table 1. It is observed that the gradient decreases with an increase in temperature in the mole fraction range below *ca.* 0.05, whereas it increases in the higher mole fraction range. This finding can be interpreted by suggesting that below *ca.* 0.05 of X the dipolar interaction is predominant and, on the contrary, above *ca.* 0.05 of X the electron spin exchange interaction is predominant. (*cf.* Eqs. 1 and 2)

In order to understand the above-stated anomalous spin concentration dependence of the line width, three models for the solubilized state may be considered, as follows.

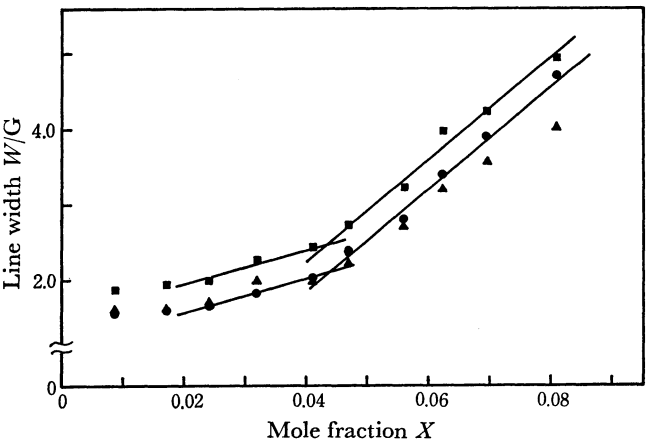

Fig. 4. Plots of W against X in 5.71 wt % aqueous SDS solutions at 31 °C (●: $M_I=+1$, ▲: $M_I=0$, and ■: $M_I=-1$).

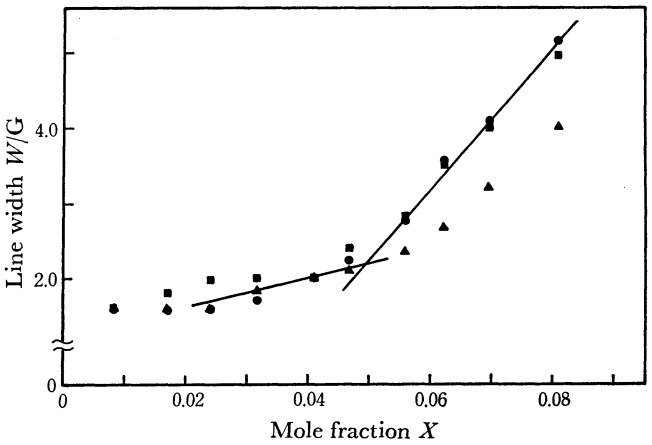

Fig. 5. Plots of W against X in 5.71 wt % aqueous SDS solutions at 38.5 °C (●: $M_I=+1$, ▲: $M_I=0$, and ■: $M_I=-1$).

TABLE 1. GRADIENTS OF W-X LINES IN TWO MOLE FRACTION RANGES

Temp (°C)	Gradient/G	
	$X<0.05$	$X>0.05$
20	30.4	62.4
31	22.4	67.2
38.5	19.2	92.8

Model 1. In this model it is considered that one SDS micelle consists of several clusters containing some SDS molecules. It is, moreover, assumed that a solubilizate molecule is bound in one of these clusters and cannot transfer from one to another. In a cluster, however, a solubilizate molecule can move easily. On this assumption, the occurrence of a break in the W-X plot can be explained as follows.

With an increase in the concentration of BzONO in SDS micelles, the number of BzONO in each cluster increases. When the number of BzONO in one micelle exceeds one, the dipolar interaction takes place, and as long as the number of BzONO in each cluster does not exceed one, only this interaction is present. The reason for this is that BzONO molecules in different clusters cannot collide with each other. When the number in one cluster exceeds one, the spin exchange interaction is superimposed to the dipolar interaction.

Thus, in the plot of line width against BzONO mole fraction, a break may occur and this point corresponds to the concentration where one cluster solubilizes just one BzONO molecule.

Since the values of mole fraction at the break in Figs. 3, 4, and 5 are almost equal to 0.05, the number N^c_{mo} of the SDS molecules constituting one cluster is estimated to be 19, satisfying $1/(1+N^c_{mo})=0.05$. Considering that the aggregation number of the SDS molecules in one SDS micelle is equal to 62,[16] it can be derived that three clusters exist in one SDS micelle.

Accoridng to the studies[17] concerning the micellar structure of ionic surfactants, the micelles at low concentration have spherical or ellipsoidal shape with a single hydrophobic core and a continuous surface. On the other hand, at high concentration (more than 10 wt %), some surfactants form a bilayer structure. Since the concentration of SDS solutions used in the present study ranges from 4 to 7 wt %, it is supposed that the micellar structure in the solutions is similar to that at low SDS concentration. In these micellar models, a continuous structure is assumed in the micelle. Therefore, the nature of the cluster proposed in this model 1 remains unexplained.

Model 2. In this model, the occurrence of spin exchange interaction above the mole fraction *ca* 0.05 is explained by a structural change in micelles caused by the solubilization of BzONO. The structural change assumed here is one which makes the hydrophobic portion of micelles more fluid-like. As was stated above, the dipolar interaction predominates over the spin exchange interaction at lower radical concentration, so that the change into fluid-like structure weakens the former and strengthens the latter. Thus, the plots of line width against BzONO concentration produce a break at the concentration of the structural change.

In the NMR study[18] on mixed solutions of a nonionic surfactant, hexa(oxyethylene)dodecyl ether, and a fluorescent dye, it was found that the line width of alkyl methylene protons decreases with an increase in the concentration of the dye and remains constant above 0.05 of the mole fraction of the dye. These findings have been explained on the basis of a change in the micelle structure caused by the electrical charge of the dye molecules trapped in the poly(oxyethylene) shell of the micelle.

Fendler and coworkers[2] found that plots of chemical shifts of a zwitterionic surfactant, 3-(*N*,*N*-dimethyldodecylammonio)-1-propanesulfonate, against the concentration of solubilizate, benzene, or nitrobenzene, exhibit a break in the region of mole fraction from 0.04 to 0.12. This break has been ascribed to an alteration in the micelle structure.

These results may support this model 2, if one assumes that the aromatic solubilizates including BzONO cause the structural change in micelle.

Model 3. In this model the occurrence of the break in the W-X curves is ascribed to a clustering of BzONO themselves in SDS micelles. The clustering, which occurs at some BzONO content, makes its local concentration higher in the micelle. Therefore, the dependence of electron spin-spin interaction on the BzONO concentration changes, producing a break. Recently, in the case of some nitroxide biradicals in lipid membranes, a clustering of radicals was observed by Rey and McConnell.[19] It is a disadvantage of this model that, in the ESR spectra in the present study, there is no signal corresponding to monomeric BzONO molecules which should exist in equilibrium with BzONO clusters.

All three models can explain, in any event, the occurrence of the breaks on the lines in Figs. 3—5. The determination of the most favorable model remains a further problem, and the simulation of the experimental spectra which will serve to solve the question is now being carried out.

On the basis of model 1 and model 2, the spin exchange rate of BzONO in SDS micelles are determined, and then the translational diffusion coefficients of BzONO in the micelles are calculated. The tanslational diffusion coefficient cannot be defined in model 3, since the spin exchange rate in this model does not reflect the diffusion process of BzONO in SDS micelles.

According to studies[20] on the relationship between the spin exchange interaction and the molecular collision process, the rate f_c of the bimolecular collision between radicals has the following relationship with the spin exchange rate T_{2E}^{-1} ($=f_E$) in a relatively viscous medium ($\eta>3$—4 cp):

$$f_c = 3T_{2E}^{-1} = 3f_E. \quad (4)$$

Since $f_E=k_EC$ in Eq. 1,

$$f_c = 3k_EX \quad (5)$$

is derived, if C is defined as the mole fraction X.

On the other hand, assuming that the surfactant molecules and solubilizate, BzONO, constitute a two-dimensional hexagonal structure in the micelle, the average number[8,21] of new solubilizate molecules encountered by a solubilizate molecule in one diffusion step is equal to $3X$, where X is the mole fraction of the solubilizate in micelles. Thus, f_c is represented by

$$f_c = 3nX, \quad (6)$$

where n is an average rate of diffusion step.

A two-dimensional diffusion coefficient D_{tr} can be written as

$$D_{tr} = n\lambda^2/4 \quad (7)$$

where λ is a mean length in one diffusion step. Substituting Eqs. 5 and 6 into Eq. 7, D_{tr} is rewritten as

$$D_{tr} = k_E\lambda^2/4. \quad (8)$$

Therefore, if k_E can be estimated from Figs. 3—5, and an appropriate diffusion model is assumed, the translational diffusion coefficient of BzONO in SDS micelles can be reasonably determined.

In model 1, k_E corresponds to a difference between the two gradients (below and above mole fraction *ca.* 0.05). Strictly speaking, the value does not correspond to k_E, since the magnitude of intra-cluster dipolar interaction may not be equal to that of inter-cluster dipolar interaction.

In model 2, k_E corresponds to the gradient above mole fraction *ca.* 0.05.

λ^2 was estimated to be 5.8×10^{-15} cm^2 from the results[22] of the surface area occupied by one polar head group in SDS micelles.

Substituting the values of k_E and λ^2 into Eq. 8, the translational diffusion coefficients of BzONO in SDS micelles were obtained. The results at 20, 31, and 38.5 °C are listed in Table 2. The increasing tendency of D_{tr} with temperature is more reasonable in model 1 than in model 2.

The translational diffusion coefficient of low-molecular weight substances in ordinary solutions is of the order of 10^{-5} cm^2/s, and that of phospholipid[21] or steroid[23] molecules in lipid membranes is of the order of 10^{-8} cm^2/s. The values obtained in the present system fall between these two.

Table 2. Translational diffusion coefficents of BzONO in sodium dodecyl sulfate micelles

Temp (°C)	Model 1 $D_{tr}/10^{-7}$cm^{2}s^{-1}	Model 2 $D_{tr}/10^{-7}$cm^{2}s^{-1}
20	1.1	2.2
31	1.6	2.4
38.5	2.6	3.3

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