The Spin Exchange of Nitroxide Radicals with Ni^{2+} Ions in SDS Micellar Solutions

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The spin-exchange rate of three kinds of hydrophobic nitroxide radicals with paramagnetic ions, Ni^{2+} ions, was measured in an aqueous sodium dodecyl sulfate (SDS) micellar solution at 30 °C. In the presence of SDS micelles, two of the three radicals had their spin-exchange rates accelerated, whereas the rate of the other radical was deaccelerated. These strange results were interpreted on the basis of a different solubilized location of the radicals in SDS micelles. The translational mobility of the Ni^{2+} ions on a micellar surface was estimated from the spin-exchange rate in the accelerated systems.

In preceding studies,[1–3] my coworkers and I investigated the molecular motion of hydrophobic nitroxide radicals solubilized in surfactant micelles by means of the ESR method. The translational mobility of the radicals in micelles[3] was estimated from the magnitude of the spin-exchange rate between the radicals.

The spin-exchange interaction[4] is one of the intermolecular magnetic interaction, occurring upon an intermolecular collision between paramagnetic particles. Due to this fact, the spin-exchange rate is proportional to the rate of intermolecular collisions. One can, therefore, calculate the translational diffusion coefficient from the spin-exchange rate constant if an appropriate model is applied for the diffusion process.

In the present study, the spin-exchange rate of nitroxide radicals with Ni^{2+} ions in micellar solutions was measured in order to investigate how the presence of surfactant micelles affects the collisions between ions and organic molecules in water. If the information on the collisional process in micelles can be obtained, it will be utilized for understanding the mode of ion-binding to the micellar surface and the reaction mechanism of a micellar catalysis.

Experimental

Three kind of nitroxide radicals (Fig. 1) were used as solubilizates. The synthesis of the two of them, 2,2,6,6-tetramethyl-4-benzoyloxy-1-piperidinyloxyl (BzONO, Fig. 1(a)) and 2,2,6,6-tetramethyl-4-myristoyloxy-1-piperidinyloxyl (MyONO, Fig. 1(b)), has been reported elsewhere.[1,3] The other nitroxide radical, 2,2,6,6-tetramethyl-4-(1-naphtoyloxy)-1-piperidinyloxyl (NpONO, Fig. 1(c)), was synthesized by the reaction of the corresponding acid chloride with a nitroxide alcohol, and was purified in a way similar to that described in the literature.[5] The results of an elemental analysis of NpONO was as follows: Found: C, 73.52; H, 7.38; N, 4.26%. Clcd for $C_{20}H_{24}O_3$: C, 73.59; H, 7.41; N, 4.29%; mol wt 326.4.

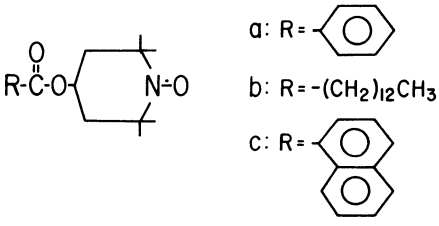

Fig. 1. (a) BzONO, (b) MyONO, and (c) NpONO.

Sodium dodecyl sulfate (SDS) of a specially prepared reagent and nickel nitrate of a guaranteed grade were purchased from Nakarai Chemicals Ltd. The SDS was recrystallized several times from ethanol–water solutions and was further purified by the method of Harrold.[6] The paramagnetic salt was used without further purification.

ESR spectra of the nitroxide radicals solubilized in SDS solutions with various amounts of Ni^{2+} ions were recorded on a JEOL model FE1X spectrometer at 30±0.5 °C.

The concentration of Ni^{2+} ions in sample solutions was determined by chelatometric titration.

Results and Discussion

As is well known, the usual ESR spectrum of nitroxide radicals in solutions consists of three lines owing to the contact interaction between an electron spin ($S=1/2$) and a ^{14}N nuclear spin ($I=1$). The three lines correspond to the ^{14}N nuclear spin quantum numbers, $M_I=+1$, 0, and -1, toward the high-field direction.

In the present study, the three lines broaden their linewidths (in the same manner) with an increase in the concentration of Ni^{2+} ions. I, therefore, will discuss the behavior of the lowest field line ($M_I=+1$) as a representative line.

In Fig. 2, the peak-to-peak linewidth, $W(+1)$, of the three nitroxide radicals in 5.2wt% SDS solutions are

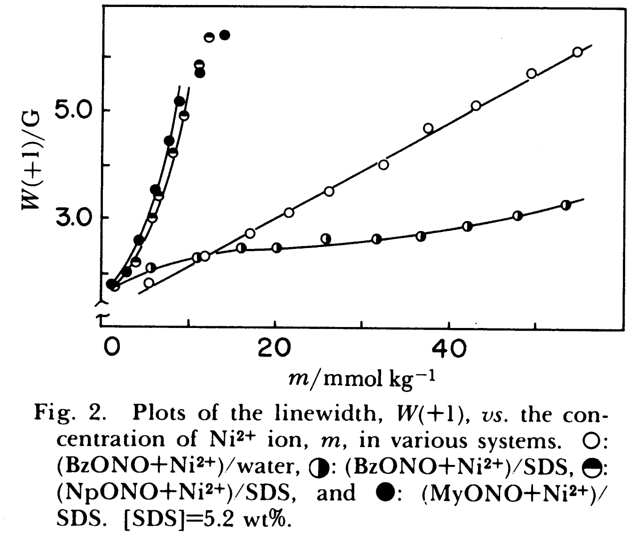

Fig. 2. Plots of the linewidth, $W(+1)$, *vs.* the concentration of Ni^{2+} ion, m, in various systems. ○: ($BzONO+Ni^{2+}$)/water, ◑: ($BzONO+Ni^{2+}$)/SDS, ◓: ($NpONO+Ni^{2+}$)/SDS, and ●: ($MyONO+Ni^{2+}$)/SDS. [SDS]=5.2 wt%.

plotted as a function of the concentration, m, of Ni^{2+} ions. A similar plot of BzONO in water is also shown in the same figure; because of low solubility in water, the spectrum of the other two radicals, NpONO and MyONO, could not be measured.

In the presence of the spin-exchange interaction, $W(+1)$ (that is, the spin-spin relaxation rate, $T_2^{-1}(+1)$) is theoretically described by the spin-exchange rate constant, k_e, and the concentration of the paramagnetic ion, m, in the following expression;

$$W(+1) = (2/\sqrt{3})T_2^{-1}(+1) = (2/\sqrt{3})\{T_{20}^{-1}(+1)+k_e m\} \tag{1}$$

where $T_{20}^{-1}(+1)$ is the spin-spin relaxation rate when no spin-exchange interaction occurs. Thus, it can be predicted that the $W(+1)$ increases linearly with the m.

As can be seen from Fig. 2, the prediction is valid only in the case of BzONO in water. The $W(+1)$-m plots of NpONO and MyONO in the SDS solutions curve upwards steeply, and that of BzONO exhibits little dependence on m.

Most of the SDS molecules in the 5.2wt% SDS solutions dissolve as micelles and the nitroxide radicals are solubilized into micelles. The nonlinear plots in the cases of SDS solutions may be related to this fact.

Comparing these plots with each other, it can be seen that the spin-exchange rates of NpONO and MyONO with paramagnetic ions are accelerated, whereas that of BzONO is deaccelerated in the presence of SDS micelles. The spin-exchange interaction occurs upon collisions between paramagnetic particles. This finding indicates that the SDS micelle affects the collision process between the nitroxide radical and the Ni^{2+} ion.

I will consider why such inverse effects are brought about in the same SDS solutions. There are three possible ways to explain this.

The first possibility is that the retarding effect in the $(BzONO+Ni^{2+})/SDS$ system is an apparent phenomenon caused by the superposition of the signal of BzONO in the bulk solution onto that in the micellar phase. From the solubility value of BzONO into the SDS solution,[7] however, it can be estimated that the more than 99% of the BzONO molecules exist in the micellar phase in the case of the 5.2wt% SDS solution. Thus, the above possibility is implausible.

The second possibility is that the mobility of BzONO in SDS micelles is very low in comparison with the other two radicals. The BzONO molecule, however, has the smallest value of the rotational correlation time, τ_c, in the SDS micelle among the three radicals used (*cf.* Table 1). The values of τ_c were calculated according to a well-known formula.[8] This implies that the BzONO molecule is most mobile in its rotational mode; a similar phenomenon holds also in the translational mode.

The third possibility is that the solubilized location of BzONO in the SDS micelle is not available for an effective collision with paramagnetic ions. It is well known that the isotropic hyperfine splitting constant, a_N is a parameter which reflects the polarity of the microscopic environment where the nitroxide group exists: The value of a_N increases with the polarity.[9] From the a_N values given in Table 1, it can be seen that the BzONO molecule is located in the more polar region of the SDS micelle than is the NpONO or MyONO molecule.

Table 1. The isotropic hyperfine splitting constant, a_N, and the rotational correlation time, τ_c

	[SDS](wt%)	a_N/G	$\tau_c/10^{-10}$ s rad^{-1}
$(BzONO+Ni^{2+})/SDS$	0	17.0	0.35
	5.2	16.8	0.96
	7.6	16.7	
$(NpONO+Ni^{2+})/SDS$	0	16.9	
	5.2	16.4	2.4
$(MyONO+Ni^{2+})/SDS$	1.3	16.6	
	2.6	16.6	
	3.9	16.6	
	5.2	16.6	3.4

Assuming that the SDS micelle is an ordinary spherical micelle with the Stern layer and the diffuse layer being used as the binding regions of the counterions, I think that the nitroxide group of BzONO is in the diffuse layer, whereas that of NpONO or MyONO is near the Stern layer: The nitroxide group of BzONO protrudes from the micellar surface. When Ni^{2+} ions are added to SDS solutions, they will initially become bound to the Stern layer and then, to the diffuse layer with a further increase in their concentration. Consequently, a nitroxide group of BzONO in the diffuse layer cannot collide with the Ni^{2+} ions bound to the Stern layer.

On the basis of the above idea, I can predict that the spin-exchange rate of BzONO increases at higher concentrations of Ni^{2+} ions where the Ni^{2+} ions become bound to the diffuse layer. Figure 3 shows the $W(+1)$-m plots of BzONO for two solutions with different amounts of SDS over a wider range of m. It is

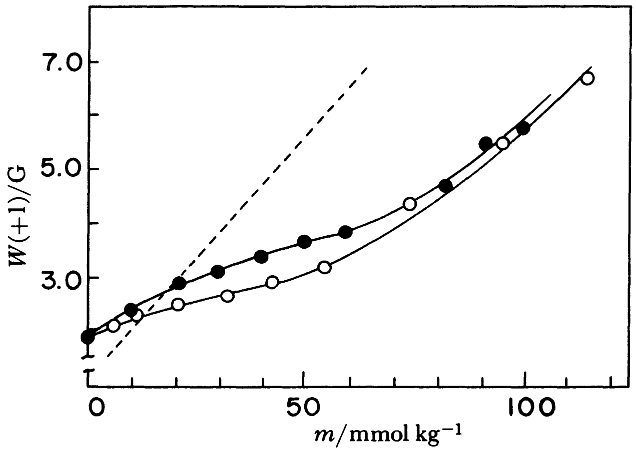

Fig. 3. Plots of $W(+1)$ *vs.* m in $(BzONO+Ni^{2+})/SDS$ systems with the SDS concentrations of 5.2 wt%: (○) and 7.6 wt%: (●). Dashed line is a similar plot of $(BzONO+Ni^{2+})$/water.

noticeable that $W(+1)$ varies consistently with prediction. The concentration where a sharp increase in $W(+1)$ begins, corresponds to a sufficient content to neutralize about 50% of the negative charges of the micellar dodecyl sulfate ions. This finding coincides with Zayev's results[10] regarding proton NMR relaxation studies on a system similar to the present one. Zayev has discovered two binding areas of the Cu^{2+} ion onto SDS micelles. One is an area of complete binding up to a Cu^{2+} ion content of 50—60% with respect to that equivalent to dodecyl sulfate ions. This area corresponds to the Stern layer. The other is the area of weak binding above the Cu^{2+} ion content; this area corresponds to the diffuse layer.

It is additionally noticeable (in Fig. 3) that until the sharp increase in $W(+1)$ begins, the $W(+1)$ in 7.6wt% SDS solutions is greater than that in 5.2wt% SDS solutions. This fact may imply that the BzONO in a micelle interacts with Ni^{2+} ions bound onto the other micelles.

From the above discussion, it is concluded that the deaccelerating effect of SDS micelles on the spin-exchange rate of BzONO with paramagnetic ions results from the solubilized location of BzONO emerging outside from the micellar surface.

In order to investigate the acceleration in the $(NpONO+Ni^{2+})$/SDS or $(MyONO+Ni^{2+})$/SDS system, the $W(+1)$ of MyONO in the solutions with various amounts of SDS was measured as a function of the Ni^{2+} ion concentration. The data obtained are plotted in Fig. 4. In all the solutions, the accelerating effect can be observed (*cf.* the straight dashed line in the figure). A similar plot of MyONO in water will be depicted by a straight line with a smaller slope than of the dashed line.

In this case, the accelerating effect results from the condensation of Ni^{2+} ions on the micellar surface and, moreover, from an appropriate solubilized location of the nitroxide group of MyONO for colliding with the Ni^{2+} ions: Its nitroxide group exists in the Stern layer.

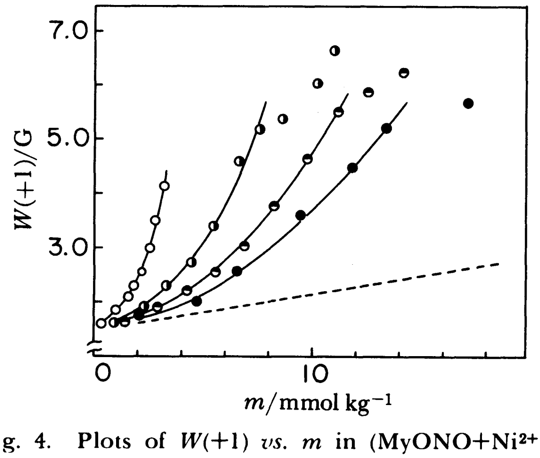

Fig. 4. Plots of $W(+1)$ *vs.* m in $(MyONO+Ni^{2+})$/SDS systems with the SDS concentrations of 1.3 wt%: (○); 2.6 wt%: (◑); 3.9 wt%: (◓); 5.2 wt%: (●). Dashed line is a similar plot of $(BzONO+Ni^{2+})$/water.

If the above idea holds, plots of $W(+1)$ against the mole ratio, X_r, of Ni^{2+} ions on the micellar surface in these solutions will be on the same line. The X_r was defined by the following equation;

$$X_r = n(Ni^{2+})/\{n(DS^-) + n(MyONO)\} \tag{2}$$

where $n(Ni^{2+})$ is the number of Ni^{2+} ions bound onto one micelle on the assumption that all Ni^{2+} ions are bound onto micelles, $n(DS^-)$ the number of dodecyl sulfate ion in one micelle, being equal to the aggregation number=62,[11] and n(MyONO) is the number of MyONO solubilized in one micelle, being equal to unity in the present case. I assumed that $n(DS^-)$ and n(MyONO) are approximately constant. Strictly speaking, they will change with an increase in the concentration of Ni^{2+} ions.

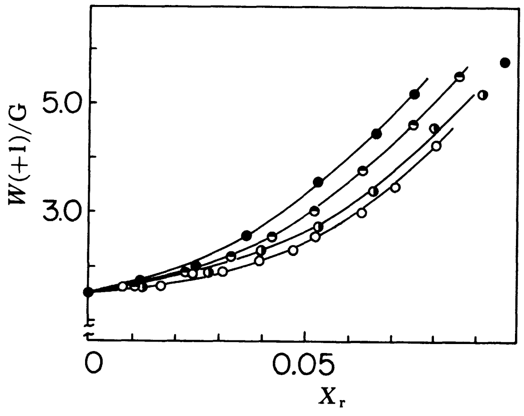

Fig. 5. Plots of the linewidth, $W(+1)$ *vs.* the mole ratio, X_r, of Ni^{2+} ion on the micellar surface in $(MyONO+Ni^{2+})$/SDS systems with the SDS concentrations of 1.3 wt%: (○); 2.6 wt%: (◑); 3.9 wt%: (◓); 5.2 wt%: (●).

Figure 5 shows the obtained $W(+1)$-X_r plots. They are not on a common line, but on upwardly curved lines (their curvatures become greater with the SDS concentration). This fact indicates that the above assumption regarding $n(DS^-)$ and n(MyONO) is inadequate, and/or that there is an intermicellar interaction which induces the spin-exchange with the Ni^{2+} ions bound to other micellar surfaces.

In the plots, the departure from linearity might be a result of the distribution of the number of bound Ni^{2+} ions per micelle. In previous studies,[2,3] my coworkers and I investigated the spin-exchange between BzONO or MyONO molecules solubilized in SDS micelles. We obtained similar curved lines in plots of $W(+1)$ against the mole fraction of radicals in the SDS micelles. The curved lines could be successfully simulated by considering the distribution of the number of radical molecules per micelle. The non-linear behavior of some observed parameters in several other studies regarding micellar solution[12,13] was interpreted using a similar model.

Consequently, in an estimation of the translational diffusion coefficients of Ni^{2+} ions bound to a SDS micellar surface, I will analyze the $W(+1)$-X_r plots in consideration of the distribution of Ni^{2+} ions. The analysis is in progress; the results will be described in my next paper. Qualitatively, in comparison with the previous results of the lateral diffusion of MyONO in the SDS micelle,[3] I can presume that the translational mobility of Ni^{2+} ions on the micellar surface are not extremely different from that of MyONO solubilized in the micelle.

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