Studies of Spin-Labeled Sodium Dodecyl Sulfate. II. Effect of Sodium Chloride on ESR Line Width

Takeo YAMAGUCHI,* Akira YAMAUCHI,† Eiji KIMOTO, and Hideo KIMIZUKA†
Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-01
†Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812

(Received April 11, 1986)

The ESR spectra of spin-labeled sodium dodecyl sulfate were examined by changing the concentration, temperature, and ionic strength. The broadening of ESR lines due to a monomer surfactant could be explained in terms of an electron-spin exchange and a monomer-micelle exchange. The spin-exchange rate increased with increasing temperature and decreased with increasing ionic strength, i.e., the spin-exchange frequency was closely related to the viscosity of the medium. On the basis of an analysis of the line width above the critical micelle concentration, it was found that the aggregation number of the micelle of this compound and the monomer-micelle exchange frequency were dependent on the ionic strength.

Recent investigations on the micelle have stressed its dynamic properties. The diffusion coefficients of the micelles have been obtained by means of quasi-elastic light-scattering spectroscopy.[1,2] Kinetic studies of micellar systems by pressure-jump, temperature-jump, and ultrasonic absorption have shown that there are two relaxation processes for micelle formation.[3] The slow process, which is characterized by a relaxation time of the order of 10^{-3} s, represents the fluctuation of the total number of the micelles. On the other hand, the fast relaxation process of the order of 10^{-6} s corresponds to the association/dissociation equilibrium of monomeric ion to/from micelles. The NMR and ESR spectra also give useful information regarding the monomer-micelle exchange frequency. NMR data showed that its exchange frequency was below 10^{-5} s.[4] Nakagawa and Jizomoto[5] demonstrated that the lifetime of the spin probe molecules solubilized into micelle was 10^{-6} s. However, there are only a few reports on the dynamic properties of micelles composed of spin-labeled surfactants. Of these, Fox[6] studied the monomer-micelle exchange using cationic surfactant spin-labeled at polar head group and reported that the line broadening due to the monomer-micelle exchange was not observed. On the other hand, Schmidt et al.[7] have investigated the kinetics on micellization of spin-labeled lecithin and correlated the line broadening above the critical micelle concentration (cmc) to the monomer-micelle exchange reaction.

Here, it would be important to confirm the existence of the monomer-micelle exchange by the ESR spectra and, furthermore, to obtain information regarding the dynamic behavior of surfactant molecules in micellar solutions. From such a standpoint, we synthesized the spin-labeled sodium dodecyl sulfate (SL-SDS) labeled with a nitroxide radical.[8,9] Using this spin-labeled surfactant, we studied the properties of an aqueous SL-SDS solution in the absence of salt on the basis of its ESR spectra and conductivity data.[9] In the present work, the effect of added salt on the spin-exchange interaction and the micelle formation of SL-SDS is described.

Experimental

Materials. SL-SDS, sodium salt of 2-ethyl-2-[9-(hydroxysulfonyloxy)nonyl]-4,4-dimethyl-3-oxazolidinyloxyl, was synthesized by the procedure previously described.[8,9]

Viscosity. The viscosity of the medium containing NaCl was calculated according to the Othmer rule.[10,11]

Measurement of ESR. The samples were carefully deoxygenated by the repetitive freeze-thaw technique and then substituted by a dry nitrogen gas. ESR measurements were carried out with a JEOL FE-1X spectrometer equipped with a variable temperature accessory. The temperature control was checked with a copper-constantan thermocouple and was found to be stable within ±0.5°C. The usual spectrometer settings were 100 KHz modulation amplitude, 0.5 G; microwave power, 1 mW; scan range, 200 G; scan speed, 8 min.

Results and Discussion

As we have already noted regarding the properties of an aqueous SL-SDS solution without added salt, the three sharp ESR lines due to nitroxide radicals become broad and eventually coalesce into a single broad line with increasing radical concentration. Such spectral changes have been interpreted in terms of an electron-spin exchange.[9,12] On the basis of the conductivity data, it has been determined that the cmc of SL-SDS is 21.6 mmol $\mathrm{kg^{-1}}$ at 25 °C and its aggregation number is about 6.[9] Because of a small aggregation number and its high cmc, such superimposed ESR signals due to monomer and micellar surfactants as seen above cmc in other spin-labeled surfactants[6,7] were not observed. Figure 1 shows the ESR spectra of 50 mmol $\mathrm{kg^{-1}}$ SL-SDS solutions containing various concentrations of NaCl (0.1—1.0 mol $\mathrm{kg^{-1}}$). The ESR signal in the absence of NaCl was considerably distorted with an increased number of collisions between surfactant molecules. With an increasing NaCl concentration, however, the triplet lines due to monomer surfactant became sharp and a single broad line ascribed to the micelles gradually appeared at the central field. This suggests that, with increasing the amount of added salt, the aggregation number of the micelles increases and the monomer concentration decreases.

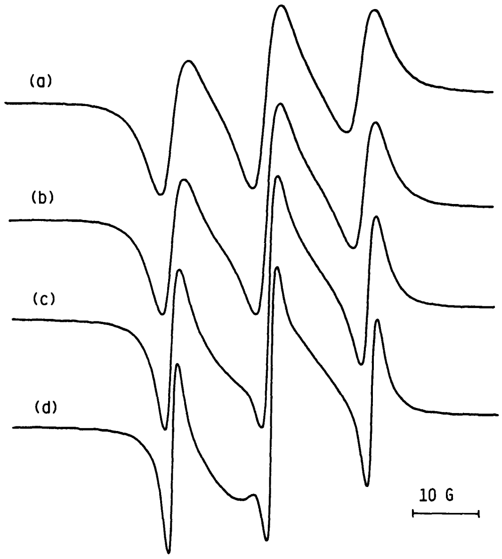

Fig. 1. ESR spectra of 50 mmol kg^{-1} SL-SDS solution containing a) 0, b) 0.1, c) 0.5, and d) 1.0 mol kg^{-1} NaCl, respectively, at 19 °C.

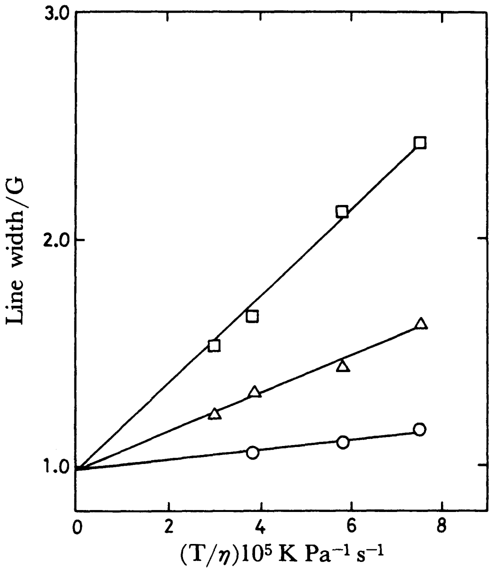

Fig. 3. Width of the $M=+1$ line vs. T/η for SL-SDS solution containing 1 mol kg^{-1} NaCl in 1 (○), 4 (△), and 8 mmol kg^{-1} (□), respectively.

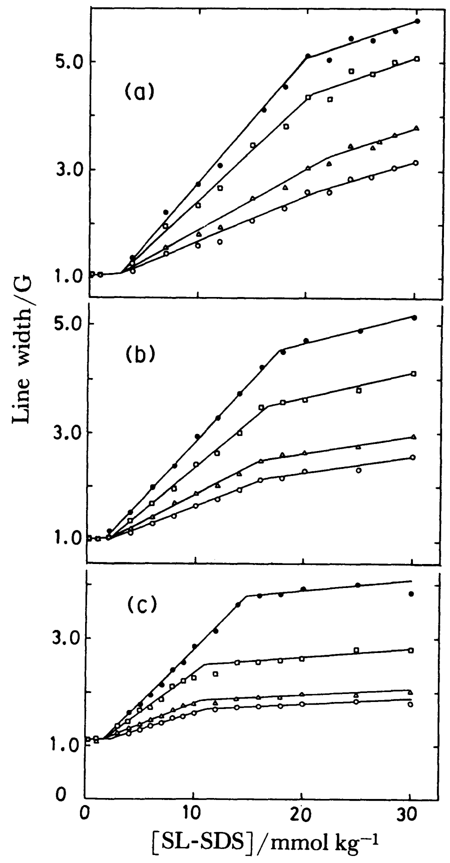

Fig. 2. Width of the $M=+1$ line vs. concentration of SL-SDS at 25 (○), 35 (△), 55 (□), and 70 °C (●) in the presence of 0.1 (a), 0.5 (b), and 1.0 mol kg^{-1} NaCl (c).

As shown in Fig. 2, the relationship between the line width of the signal ($M=+1$ line, where M is the nuclear spin quantum number) at low field and SL-SDS concentration was examined at various temperatures (25, 35, 55, and 70 °C) and NaCl concentrations (0.1, 0.5, and 1.0 mol kg^{-1}). The plots of the line width vs. the SL-SDS concentration show two inflection points. At low concentrations of SL-SDS (0.5 and 1.0 mmol kg^{-1}), the line widths were almost independent of both the temperature and the ionic strength. This indicates that the contribution of spin rotational relaxation[12] to the line width is negligibly small, regardless of the added salt. At a constant temperature and NaCl concentration, the line width became broader with increasing radical concentration. Generally, in free nitroxide radical molecules, the line broadening observed with increasing radical concentration can be attributed to either an electron-spin exchange or an electron spin-electron spin dipole interaction. The relaxation process due to the spin-exchange interaction is dependent on T/η, while that due to dipole-dipole interaction depends on η/T, where η is the viscosity of the medium and T is the absolute temperature.[13] Therefore, the relation of the line width vs. T/η was examined at various concentrations of SL-SDS in the presence of 1 mol kg^{-1} NaCl. As shown in Fig. 3, the line width varied linearly as a function of T/η. This indicates that spin exchange is predominant relaxation process in the range of this concentration. Thus, the line broadening observed between the two inflection points is attributed to the spin-exchange interaction. In the absence of NaCl, the plots of the line width vs. the SL-SDS concentration deviate from a straight line above about 20 mmol kg^{-1}.[9] However, this inflection point shifted to a lower concentration of SL-SDS with increasing NaCl concentration, i.e., it changed from 20 to 11 mmol kg^{-1} by an addition of 1 mol kg^{-1} NaCl. The line-width variation with the SL-SDS concentration above the higher inflection point is small compared with

Table 1. Effects of Temperature and Ionic Strength on Second-Order Rate Constant [a)]

	$k_2 \times 10^{-9}$/kg mol^{-1} s^{-1}			
Temp/°C	Added NaCl/mol kg^{-1}			
	0[b)]	0.1	0.5	1.0
25	2.2 (3.6)	1.9 (3.6)	1.8 (3.5)	1.4 (3.3)
35	2.7 (4.7)	2.4 (4.6)	2.3 (4.5)	1.8 (4.2)
55	4.0 (7.2)	4.0 (7.1)	3.9 (6.7)	3.1 (6.4)
70	5.0 (9.3)	5.1 (9.2)	5.0 (8.8)	4.4 (8.3)

a) Calculated k_2' values are shown in parentheses. b) Data from Ref. 9.

that below its inflection point. For micellar solutions, it is well known that the cmc decreases upon adding salts and the monomer concentration remains constant above cmc.[14)] Taking these facts into account, it is considered that the inflection point at higher concentrations corresponds to the cmc of the surfactant molecules.

The spin exchange between SL-SDS molecules is regarded as a second-order reaction.[13)] The second-order rate constants (k_2) are obtained from the slope of the line width vs. the radical concentration by

$$k_2 = \frac{3\sqrt{3}}{4}|\gamma_e|h, \tag{1}$$

where γ_e is a magnetogyric ratio of a free electron, and h is the slope of the line width-surfactant concentration plots. The obtained values of k_2 are given in Table 1. The values of k_2 decreased upon adding salts at each temperature. The values of k_2 in all cases were of the order 10^9 kg mol^{-1} s^{-1}, indicating that the spin exchange of SL-SDS is a diffusion-controlled process.[12,13)] For such a reaction, the reaction rate is greatly influenced by the viscosity of the solvent. Using the theory of Smoluchowski,[15)] we could obtain the rate constant (k_2') for the bimolecular encounters:

$$k_2' = \frac{N_A}{1000\rho}\frac{4kT}{3\eta}, \tag{2}$$

where N_A is Avogadro's number and ρ, the density of the solution. The values of k_2' are also given in Table 1. The values of k_2' are in agreement with those of $2k_2$. Similar results, i.e., $2k_2$, is equal to k_2', have also been reported by other workers.[12,16—18)] The frequency of the spin exchange is markedly dependent on the charge and size of the radical. For example, the spin-exchange rate of anion radicals with a large repulsive charge increases due to the offset of a coulombic repulsion between these radicals with increasing ionic strength.[19)] Eastman et al.[19)] demonstrated that the spin-exchange rate of the di-*t*-butyl nitroxide radical decreased markedly with increasing ionic strength. In order to explain such a phenomenon, they have proposed that aggregates of the radicals are caused by the hydrophobicity of the *t*-butyl groups. In the present work, the spin-exchange rates of SL-SDS obtained in the presence and absence of NaCl were closely dependent on the viscosity of the medium, suggesting that neither the polar head group nor the hydrocarbon chain of SL-SDS molecule play any significant role in the spin-exchange interaction.

In spin-labeled surfactants, monomer amphiphilic molecules incorporated into micelles undergo a fast spin exchange, causing a line broadening. Therefore, the increase in line width above cmc (Fig. 2) can be ascribed to the monomer-micelle exchange and was examined according to the treatment of Schmidt et al.[7)] On the basis of Aniansson's kinetic theory on the micellization, they have given the following kinetic expression on the monomer-micelle exchange in order to explain the ESR line broadening of the monomer surfactant above cmc.

$$\Delta W = \frac{k^+}{\bar{n}}(C - C_m), \tag{3}$$

where ΔW is the line-width variation in frequency unit, k^+ is the rate constant for the association of monomer to micelle, $\bar{n}$ is the aggregation number of the micelle, C_m is the critical micelle concentration, and C is the total concentration of the surfactant. According to Eq. 3, the slope of plots of the line width vs. the surfactant concentration equals to $k^+/\bar{n}$. As the aggregation number of SL-SDS without NaCl is about 6 at 25 °C,[9)] 1.3×10^9 kg mol^{-1} s^{-1} is obtained as the value of k^+. This is in rough agreement with the value of 1.8×10^9 kg mol^{-1} s^{-1} obtained using Eq. 1 from the relation between the line width and the SL-SDS concentration above cmc. This suggests that the monomer surfactant becomes associated with the micelles as if a bimolecular reaction occurs. The values of the association constant k^+ reported for various surfactants are between 10^8 and 10^9 dm^3 mol^{-1} s^{-1}, which exist in the expected range for a diffusion-controlled reaction.[3,15)] Therefore, it is considered that the values of k^+ characterized with the diffusion-controlled reaction should be approximately independent of ionic strength and hydrocarbon chain length of surfactants.[3,7)] On the other hand, the rate constant (k^-) for the dissociation of one amphiphilic ion from the micelles is strongly dependent on the alkyl chain length of the surfactant and ionic strength.[3,7)] The rate constant k^- is obtained from the following relation developed by Aniansson et al.,[3)]

$$k^- = k^+ \cdot \text{cmc}. \tag{4}$$

The calculated value of k^- for SL-SDS is 2.8×10^7 s^{-1}. The values of k^+ and k^- obtained from the ESR line width for SL-SDS in this study are compared with those, i.e., $k^+ = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1} and $k^- = 1.0 \times 10^7$ s^{-1}, from chemical relaxations for SDS by Aniansson et al.[3)] It seems that the agreement is well satisfied. The temperature and ionic strength dependences of $k^+/\bar{n}$ are given in Table 2. At any temper-

Table 2. Effects of Temperature and Ionic Strength on Association Constant ($k^+/\bar{n}$)

Temp/°C	$k^+/\bar{n} \times 10^{-8}$/kg mol^{-1} s^{-1}			
	Added NaCl/mol kg^{-1}			
	0[a)]	0.1	0.5	1.0
25	2.2	1.7	0.70	0.27
35	2.3	1.9	0.86	0.32
55	2.4	1.9	1.3	0.45
70	2.5	2.0	1.6	0.72

a) Data from Ref. 9.

ature, the values of $k^+/\bar{n}$ decrease greatly with increasing ionic strength. As mentioned above, the changes in k^+ values for the ionic strength are small. On the other hand, the aggregation number of SL-SDS micelles increases drastically with increasing ionic strength (Fig. 1). Therefore, the decreases in $k^+/\bar{n}$ upon adding salt are mainly attributed to an increase in the aggregation number, whereas the change in $k^+/\bar{n}$ with temperature is small compared with that for the ionic strength. With increasing ionic strength, the temperature dependence of $k^+/\bar{n}$ becomes large. This can be interpreted in terms of both the increase in k^+ and the decrease in $\bar{n}$ with increasing temperature. In order to obtain detailed information concerning the effect of NaCl on the micellar kinetics of SL-SDS, it is necessary to examine the aggregation number of SL-SDS micelles in the presence of any added salt.

The authors wish to thank Mr. Toshihiko Kiyohara for his technical assistance.

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