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ESR Studies of the Dynamic Properties of Ion Radicals Captured by Surfactant Micelles

Kosaku SUGA,† Koushi MAEMURA,* Masamichi FUJIHIRA, and Shigeru AOYAGUI
Department of Chemical Engineering, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152
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ESR spectra of duroquinone anion radical (DQ^-), methyl viologen cation radical (MV^+), and 5,10-dimethyl-5,10-dihydrophenazine cation radical ($DMPZ^+$) were measured in various aqueous surfactant solutions. The line width of each peak of the ESR spectra for DQ^- in cationic and anionic surfactant solutions showed a quadratic dependence on the total nuclear quantum number, $M=\Sigma m_i$ (i=1 to 12), of methyl protons of DQ^-. The rotational correlation times, τ_c, of DQ^- determined from these dependences, were 10^{-9}—10^{-8} s in cationic surfactant (dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromide) solutions, and 10^{-10}—10^{-9} s in nonionic surfactant (Triton X-100) solution. ESR spectra of MV^+ and $DMPZ^+$ in anionic surfactant (sodium dodecyl sulfate; SDS) solution showed anomalous patterns as not exhibiting the hyperfine splittings due to the nitrogen nucleus. These anomalies were explained by the more significant broadening of the outer peaks due to nitrogen splitting compared with the broadening of the central peaks corresponding to the nuclear quantum number of nitrogen, $M_N=m_{N1}+m_{N2}=0$. From these results, the rotational correlation time for $DMPZ^+$ in SDS solution was estimated as about 10^{-10} s.

Many nitroxide radicals have been used as spin probes in order to study the dynamic properties of micelles and bilayers.[1-12] ESR spectra of nitroxide radicals solubilized into micelles have unsymmetric hyperfine structure mainly consisting of three peaks due to the nitrogen atom in the nitroxide radical. These unsymmetric properties of spectra are explained by the incomplete averaging of the anisotropic g tensor and the hyperfine coupling tensor. By the analysis of the unsymmetry of these spectra, dynamic properties of micelle and micelle solubilized substances have been determined.[1-12] We are studying the electron-transfer reactions of ion radicals captured by the micelle. In order to study the correlation between the reactivities and the dynamic properties of ion radicals, it is necessary to know the dynamic properties of these ion radicals. However, the ESR spectra of paramagnetic substances solubilized into a micelle other than nitroxide radicals have received little attention. In this paper, we report the characteristics of the ESR spectra of duroquinone anion radical (DQ^-), the 5,10-dimethyl-5,10-dihydrophenazine cation radical ($DMPZ^+$) and the methyl viologen cation radical (MV^+) in several surfactants solutions. Furthermore, we report the dynamic properties, as a rotational correlation time, of ion radicals captured by the micelle obtained from these ESR spectra.

Experimental

Duroquinone (DQ) and methyl viologen dibromide ($MV^{2+}Br_2^{2-}$) used were reagent grade and were used without further purification. 5,10-Dimethyl-5,10-dihydrophenazine (DMPZ) was provide by Dr. Y. Ohsawa in this laboratory. Sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (C_{12}TMAB), tetradecyltrimethylammonium bromide (C_{14}TMAB), hexadecyltrimethylammonium bromide (C_{16}TMAB) and Triton X-100 (TX-100) were reagent grade and used without further purification.

†Present address: Seiko Instruments Inc., Takatsuka, Matsudo, Chiba 271.

Sample solutions of DQ^- and MV^+ were prepared by the reduction of aqueous solutions of DQ and MV^{2+} with sodium dithionite ($Na_2S_2O_4$) in the presence or absence of a surfactant. Sample solutions of $DMPZ^+$ were prepared by the oxidation of aqueous micellar or acetonitrile solution of DMPZ with ceric sulfate ($Ce(SO_4)_2$).

Sample cells for ESR measurements were Pyrex glass capillary cells with about 1 mm inner diameter. ESR spectra were measured by a JEOL-FE3XI ESR spectrometer equipped with a variable temperature adapter. Computer simulation of ESR spectra were carried out with the Hitachi M-280H computer system at the Computer Center of Tokyo Institute of Technology.

Results and Discussion

ESR Spectra for DQ^- in Various Surfactant Solutions. Figure 1 shows the ESR spectra for DQ^- in various solutions. The ESR spectrum for an aqueous solution of DQ^- without surfactant was symmetric and the relative intensity of each peak agreed reasonably with those calculated theoretically. The observed hyperfine coupling constant for twelve equivalent methyl protons of DQ^- in this spectrum was 1.90 G (1G=10^{-4} T) and agreed well with the value for DQ^- in C_2H_5OH[13] and in CH_3OH-H_2O mixture.[14] The ESR spectrum for the DQ^- in 0.5 M (1 M=1 mol dm^{-3}) SDS solution was similar to that mentioned above. On the other hand, the ESR spectra for DQ^- in the nonionic and cationic surfactant solutions were unsymmetrical and the degree of dissymmetry was larger for those in the cationic surfactant solutions than that in the nonionic surfactant solution. Furthermore, for the cationic surfactant solutions, the longer the carbon chain of the surfactant molecule, the larger the degree of dissymmetry.

ESR Spectra of $DMPZ^+$ and MV^+ in SDS Solution. Figure 2 (a) shows the ESR spectrum of $DMPZ^+$ in 0.1 M SDS solution at 40 °C. This spectrum was analyzed as the hyperfine structure with A_1(6H)=6.15 G, A_2(4H)=1.68 G, and A_3(4H)=0.66 G. In fact, as shown

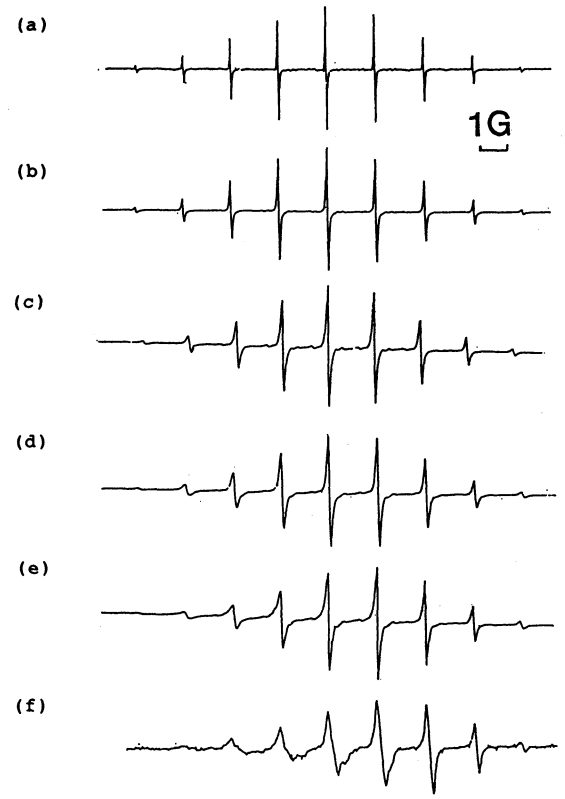

Fig. 1. The ESR spectra of DQ^- in aqueous solutions in the presence or absence of various surfactants at 20°C. (a) Without surfactant; (b) 0.5 M SDS; (c) 0.3 M TX-100; (d) 0.5 M C_{12}TMAB; (e) 0.5 M C_{14}TMAB; (f) 0.5 M C_{16}TMAB.

in Fig. 2 (b), the computer simulated spectrum with these parameters well-reproduced the experimental spectrum. Evidently, this spectrum appeared to have no hyperfine splitting due to the nitrogen nucleus in a $DMPZ^+$ ion. On the other hand, the ESR spectra of $DMPZ^+$ in AN and in aqueous solution without surfactant showed the hyperfine splittings due to the nitrogen nucleus.

Figure 3 (a) shows the ESR spectrum of MV^+ in 0.1 M SDS solution at 30 °C. This spectrum also appears to have no hyperfine splittings due to the nitrogen nucleus, as shown by the comparison with the computer simulated spectrum with A_1(6H)=3.99 G, A_2(4H)=1.57 G, and A_3(4H)=1.33 G in Fig 3 (b). On the other hand, the ESR spectrum of MV^+ in aqueous solution agreed well with the computer simulated spectrum with A(2N)=4.23 G, A_1(6H)=3.99 G, A_2(4H)=1.57 G, and A_3(4H)=1.33 G.

Theoretical Basis for Line-Width Analysis. In order to simplify the analysis of the line width of the ESR spectrum, we assume that the g tensor and the hyperfine coupling tensor have cylindrical symmetry. Under this assumption, from the theory of Kivelson,[15] the line width of each hyperfine lines for an ESR spectrum of a free radical in a doublet state (S=1/2) is given by the following equation:

$$T_2^{-1} = \tau_c[(4/45)(\Delta\gamma H)^2+\sum(3/8)\sigma_{ii}^2[<J_i(J_i+1)>_{M_i}-M_i] + \sum\sigma_{ij}M_iM_j-(4/15)(\Delta\gamma H)b_iM_i] \quad (1)$$

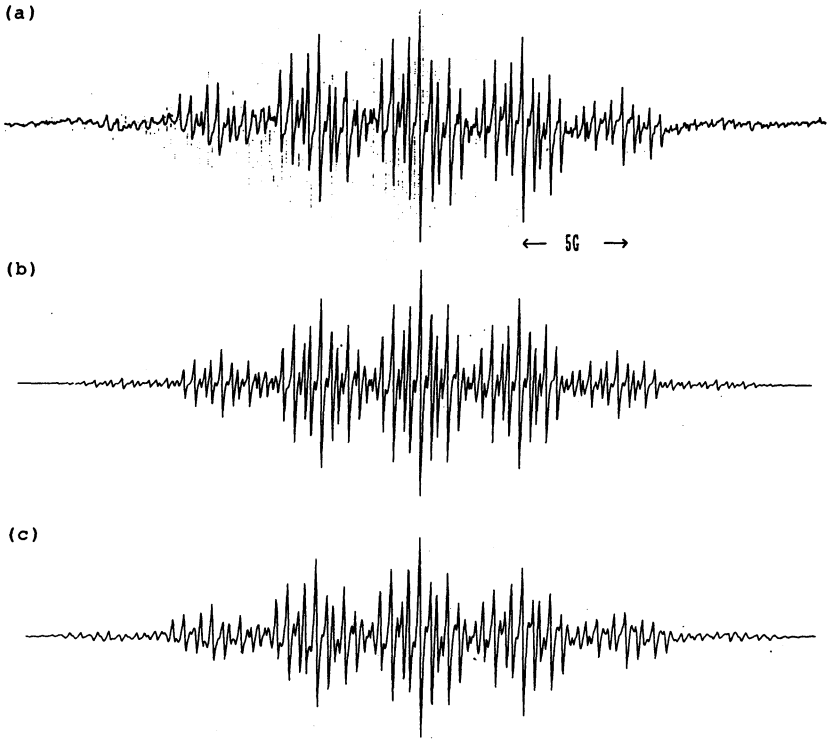

Fig. 2. The ESR spectra of $DMPZ^+$ (a) observed in 0.1 M SDS solution at 40°C; (b) simulated with A_1(6H)=6.15 G, A_2(4H)=1.68 G, A_3(4H)=0.66 G, and ΔH_{pp}(all peaks)=0.120 G; (c) simulated with A(2N)=6.63 G, A_1(6H)=6.15 G; A_2(4H)=1.68 G, A_3(4H)=0.66 G, $\Delta H_{pp}(M_N=\pm2)$=0.570 G, $\Delta H_{pp}(M_N=\pm1)$=0.256 G, and $\Delta H_{pp}(M_N=0)$=0.120 G.

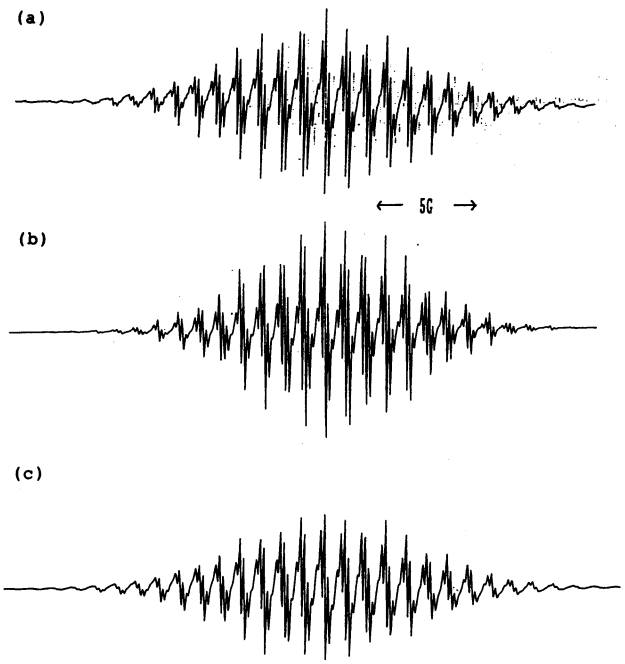

Fig. 3. The ESR spectra of MV^+ (a) observed in 0.1 M SDS solution at 30°C; (b) simulated with A_1(6H)=3.99 G, A_2(4H)=1.57 G, A_3(4H)=1.33 G, and ΔH_{pp}(all peaks)=0.120 G; (c) simulated with A(2N)=4.23 G, A_1(6H)=3.99 G; A_2(4H)=1.57 G, A_3(4H)=1.33 G, $\Delta H_{pp}(M_N=\pm 2)$=0.570 G, $\Delta H_{pp}(M_N=\pm 1)$=0.256 G, and $\Delta H_{pp}(M_N=0)$=0.120 G.

In this equation

$$\Delta\gamma=\gamma_{//}-\gamma_{\perp},$$
$$\sigma_{ij}=(1/5)b_ib_j,$$
$$b_i=(4\pi/3)\{(A_i)_{//}-(A_i)_{\perp}\}$$

and τ_c, H, M_i, and $\langle J_i(J_i+1)\rangle$ are the rotational correlation time, the value of the stationary magnetic field, the quantum number corresponding to the component of the stationary magnetic field of the ith group of equivalent nuclei, and the average value of $J_i(J_i+1)$ for a given value of M_i, respectively. And, $\gamma_{//}$, $\gamma_{\perp}$, $(A_i)_{//}$, and $(A_i)_{\perp}$ are the parallel and the perpendicular components of the principal values of gyromagnetic ratio tensor and hyperfine coupling tensors of the ith nuclear groups.

For one group of equivalent nuclei with I=1/2,

$$\langle J_i(J_i+1)\rangle=(1/2)n_i+M_i^2$$

where n_i is the number of nuclei in the group. When n_i=2 and I=1, $\langle J_i(J_i+1)\rangle$ is 6, 4, and 8/3 for M_i value of 2, 1, and 0, respectively.

Rotational Correlation Times for DQ^- in Micelle. The dissymmetry of the ESR spectra of DQ^- in nonionic and cationic micellar solutions may be explained by the incomplete averaging of the anisotropic g tensor and hyperfine coupling tensor for these radicals due to the restriction of the rotational Brownian motion by the solubilization to a micelle, as explained for nitroxide radicals solubilized into a micelle used as spin probe.

From the Eq. 1, the line width of each of the hyperfine lines for the ESR spectrum of DQ^- with equivalent twelve protons is expressed as follows,

$$(T_2)^{-1}=\tau_c\{[(9/20)b^2+(4/45)(\Delta\gamma H)^2]-(4/15)b\Delta\gamma HM+(b^2/5)M^2\}. \quad (2)$$

If the line width due to other relaxation mechanisms is given by ΔH_o, from Eq. 2 the total peak to peak line width, ΔH_{pp}, in the magnetic field unit is expressed as follows,

$$\Delta H_{pp}=a_1+a_2M+a_3M^2+\Delta H_o \quad (3)$$

where $a_1=(2\hbar\sqrt{3}g\beta)[9/20)b^2+(4/45)(\Delta\gamma H)^2]\tau_c$, $a_2=(2\hbar/\sqrt{3}g\beta)(4/15)b(\Delta\gamma H)\tau_c$, and $a_3=(2\hbar/\sqrt{3}g\beta)(b^2/5)\tau_c$.

Figure 4 shows the dependence of the observed line width for each peak of the ESR spectra of DQ^- in 0.5 M C_{12}TMAB solution at 10 and 20°C upon the value of M. These line width values agreed well with the quadratic fitted curves according to Eq. 3, and from these curves the parameters a_1, a_2, a_3, and ΔH_o were determined.

In order to determine the value of τ_c, however, the value of b and $\Delta\gamma$ must be known. Fortunately, as shown in Fig. 5, the ESR spectrum of DQ^- in C_{16}TMAB solution has marked unsymmetrical profile, and is similar to those in a solid matrix, especially at low temperature. The DQ^- molecule does not have exact cylindrical symmetry, but the spectrum in Fig. 5 shows that the principal values of the gyromagnetic ratio tensor and hyperfine coupling tensor of this

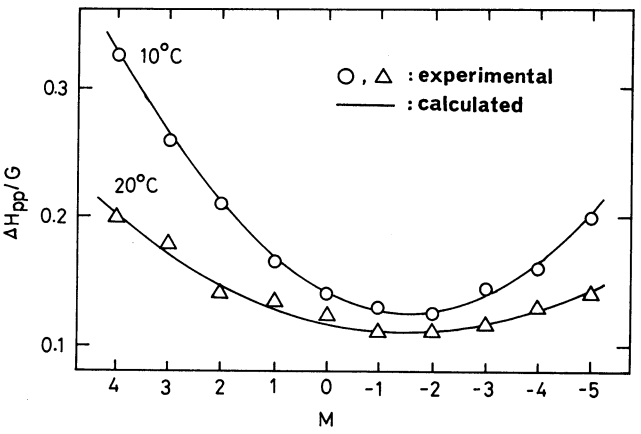

Fig. 4. The dependence of the line width, ΔH_{pp}, of the ESR spectrum of DQ^- in 0.5 M C_{12}TMAB solution on the total nuclear quantum number, M, of twelve hydrogens at 10 and 20°C.

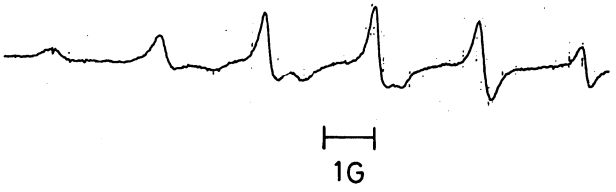

Fig. 5. The ESR spectrum of DQ^- in 0.5 M C_{16}TMAB solution at 10°C.

Table 1. Rotational Correlation Times of the Duroquinone Anion in Various Surfactant Micelles

Surfactant Solution	$\tau_c \times 10^9$/s			
	10°C	20°C	30°C	40°C
0.5 M C_{12}TMAB	3.4	1.5	—	—
0.5 M C_{14}TMAB	—	3.2	2.2	—
0.5 M C_{16}TMAB	>3	>3	>3	2.9
0.3 M TX-100	0.85	0.53	0.37	—

molecule are nearly cylindrically symmetric. From this spectrum, we have estimated the value of $|A_{//}-A_{\perp}|$ and $|g_{//}-g_{\perp}|$ as 0.225 G and 1.49×10^{-3}, respectively. The values of τ_c were determined from the values of a_1, a_2, and a_3 independently, and they agreed well with each other. Table 1 shows the values of τ_c for DQ^- in various micellar solutions. These values of τ_c decrease with the increase of temperature, and increase with the length of the alkyl chain of the surfactants. The τ_c of DQ^- in C_{16}TMAB solution at low temperature can not be determined because of the complexity of the ESR spectrum due to the large anisotropy as shown in Fig. 5. However, these values of τ_c may be nearly 10^{-8} s at 10 or 20 °C, because this large anisotropic character of the spectrum indicates the larger correlation time of DQ^- in this solution. In previous works, almost only the values of τ_c for nitroxide radicals in micellar solutions have been reported. Furthermore, the majority of these values were measured in anionic micellar solutions such as SDS. These values of τ_c for nitroxide radicals in anionic micellar solutions were about 10^{-10} s,[1,3,4,7,12] and those in nonionic micellar solutions were about 10^{-9} s.[6,8,11]

The values of τ_c for DQ^- in the nonionic surfactant solution was smaller than those of nitroxide radicals in nonionic surfactant solutions. This result may be due to the fact that DQ^- is not only in a micellar phase but also in an aqueous phase in the nonionic surfactant solution, because the diffusion coefficient of DQ^- in the nonionic surfactant solution determined by cyclic voltammogram was larger than those of micelle itself. On the other hand, it was shown by cyclic voltammetry that DQ^- in the cationic surfactant solutions was almost completely captured by the micelle. The values of τ_c for DQ^- in the cationic surfactant solutions measured in this experiment are larger by one or more orders than those for nitroxide radicals in anionic surfactant solutions cited in the literatures.[1,3,4,7,12] This result shows that the rotational diffusion of DQ^- in the cationic micelle was more strongly restricted by the micelle than the nitroxide radical in the anionic micelles.

Rotational Correlation Times for $DMPZ^+$ and MV^+ in the SDS Micelle. From the results for the ESR spectra of $DMPZ^+$ and MV^+ in SDS solution, it is suggested that the peaks of the ESR spectra of $DMPZ^+$ and MV^+ split by the hyperfine interaction with the nitrogen nucleus are extremely broadened except for the central peaks corresponding to the zero value of the total nuclear quantum number of nitrogen, $M_N=0$.

If the contribution to the line width of each hyperfine lines due to the anisotropy of the gyromagnetic ratio tensor and the hyperfine coupling tensors other than nitrogen nucleus are neglected, the line width of each peak is determined only by the value of M_N. In such a situation, from Eq. 1, the line width of the hyperfine lines corresponding to the value of M_N, which equals to 0, ±1, and ±2, are $(8/40)b_N^2\tau_c$, $(17/40)b_N^2\tau_c$, and $(38/40)b_N^2\tau_c$, respectively.

Figures 2 (c) and 3 (c) show the computer simulated spectra considering the hyperfine splitting by nitrogen nucleus: $A(2N)=6.63$ G ($DMPZ^+$),[16] $A(2N)=4.43$ G (MV^+),[17] and the contribution to the line width due to the anisotropy of the hyperfine coupling tensor of the nitrogen nucleus described above: $\Delta H_{pp}(M_N=\pm2)=0.570$ G, $\Delta H_{pp}(M_N=\pm1)=0.256$ G, and $\Delta H_{pp}(M_N=0)=0.120$ G. These spectra reproduced the observed spectra (Fig. 2 (a), 3 (a)) more exactly than the simulated spectra obtained by neglecting the hyperfine splitting due to the nitrogen nucleus.

These results show that the ESR spectra of $DMPZ^+$ and MV^+ in 0.1 M SDS solutions appear to have no nitrogen hyperfine splittings because of the larger anisotropy of the nitrogen hyperfine coupling tensor compared with those of the other coupling tensors and the g tensor.

In order to determine the rotational correlation times for $DMPZ^+$ and MV^+ captured by the SDS micelle, it is necessary to know the anisotropy parameter of the nitrogen hyperfine coupling tensors of these cation radical, b_N. Unfortunately, these values have not yet been determined experimentally. Therefore, we must estimate these values from those of nitrogen-containing paramagnetic compounds. Typical principal values of hyperfine coupling tensors for the nitrogen nucleus of nitroxide radicals are about 32, 6, and 6 G.[18] From these values, an anisotropy parameter, and an isotropic coupling constant are obtained: $b_N=26$ G, $A_N=15$ G. The relative anisotropy parameter defined here, $b_N/A_N=1.73$, of nitroxide radical is the largest among those of the nitrogen-containing paramagnetic compounds.[19] If we adopt this value as the relative anisotropy parameter for $DMPZ^+$ and MV^+, the calculated rotational correlation times of these cation radicals may be the lowest limit of these values. Assuming that the values of b_N's for $DMPZ^+$ and MV^+ are $6.63\times1.73=11.5$ G and $4.23\times1.73=7.3$ G, respectively, the rotational correlation times for these cation radicals can be evaluated from the following equation,

$$\Delta H_{pp}(M_N=0)=(2/\sqrt{3})(\hbar/g\beta)(38/40)b_N^2\tau_c. \quad (4)$$

Using the observed line width at 40 °C, i.e. 0.12 G for $DMPZ^+$ and MV^+, the calculated rotational correlation times are 1.4×10^{-11} and 3.4×10^{-11} s. These values are small compared with those for DQ^- in cati-

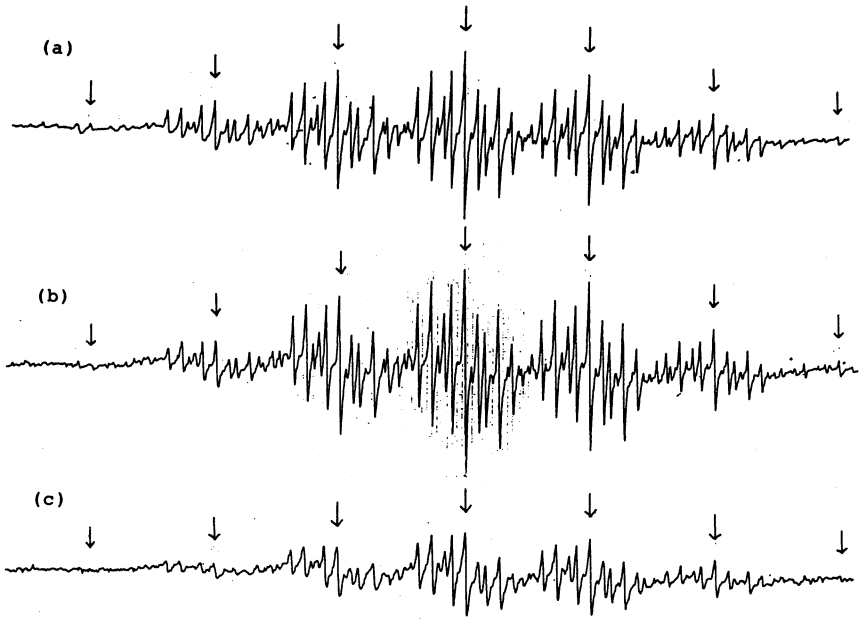

Fig. 6. The ESR spectra of $DMPZ^+$ in 0.1 M SDS solution at (a) 40 °C; (b) 20 °C; (c) 0 °C. Arrows shows the main peaks splitted by the hyperfine interaction of an electron spin with six methyl hydrogens.

onic micelles. However, these values are their lower limit, as described above. Therefore, it is desirable to determine their upper limit by the other method.

In the above discussion, we have neglected the effect of the anisotropy of the hyperfine coupling tensors of the hydrogen atoms. In fact, their anisotropy did slightly affect the ESR spectrum of $DMPZ^+$ at 40 °C, but appreciably more at lower temperatures. Figure 6 shows the temperature dependence of the ESR spectrum of $DMPZ^+$. Peaks indicated by arrows are the main peaks split by the hyperfine interactions of an electron spin with methyl hydrogens. Their intensities became more unsymmetrical with decreasing temperature. The degree of dissymmetry is smaller compared with that of DQ^- in cationic micelle at 20 °C (ref. Fig. 1). The twelve hydrogens of DQ^- is a β hydrogen with respect to an odd electron on the ring carbon atoms. Similarly, the methyl hydrogen of $DMPZ^+$ is also a β hydrogen with respect to an odd electron on the ring nitrogen atoms. The degree of anisotropy of the hyperfine coupling tensor for a β hydrogen is generally smaller compared to an α hydrogen. For DQ^-, the relative anisotropy parameter b_H/A_H is about 0.1. It is reasonable to assume that the relative anisotropy parameter for methyl hydrogens of $DMPZ^+$ is about 0.1. The isotropic hyperfine coupling constant of methyl hydrogens is 6.2 G, and about three times larger than that for the hydrogens of DQ^-. The contribution of an anisotropy parameter to the line width of an ESR spectrum is proportional to its square. Therefore, it is shown that the rotational correlation time (τ_c) of $DMPZ^+$ is at least smaller than a tenth of those for DQ^- in cationic micelles, i.e. about 10^{-9} s. The upper limit of the rotational correlation time of MV^+ in the SDS micelle can not be determined because of the complexity of the ESR spectrum of MV^+.

From the results shown above, it is concluded that the rotational coorrelation times (τ_c) of $DMPZ^+$ in the SDS micelle have a value between 10^{-9} and 10^{-11} s, and probably about 10^{-10} s. The large difference between the rotational correlation times for $DMPZ^+$ in the SDS micelle and DQ^- in a cationic micelle is a remarkable fact. The reason for this is not yet known, but it may be noteworthy that the cationic surfactant has three methyl groups at the positively charged hydrophilic part, $(CH_3)_3N^+$-, while the anionic surfactant (SDS) has only the $-SO_3^-$ group at the hydrophilic part.

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References

1) A. S. Wagoner, O. H. Griffith, and C. R. Christensen, *Proc. Nat. Acad. Sci. U. S. A.*, **57**, 1198 (1967).
2) K. K. Fox, *Trans. Faraday Soc.*, **67**, 2802 (1971).
3) N. M. Atherton and S. J. Strach, *J, Chem. Soc., Faraday Trans. 2*, **68**, 374 (1972).
4) J. Oakes, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1464 (1972).
5) K. K. Fox, *J. Chem. Soc., Faraday Trans. 2*, **72**, 220 (1976).
6) H. Yoshioka, *J. Colloid Interface Sci.*, **63**, 378 (1978).
7) H. Yoshioka, *Chem. Lett.*, **1977**, 1477.
8) H. Yoshioka, *J. Colloid Interface Sci.*, **66**, 352 (1978).

9) C. L. Kwan, S. Atik, and L. A. Singer, *J. Am. Chem. Soc.*, **100**, 4783 (1978).
10) Y. Y. Lim and J. H. Fendler, *J. Am. Chem. Soc.*, **101**, 4023 (1979).
11) H. Yoshioka, *J. Colloid Interface Sci.*, **83**, 214 (1981).
12) M. F. Ottaviani, P. Baglioni, and G. Martini, *J. Phys. Chem.*, **87**, 3146 (1983).
13) B. Venkataraman, B. G. Segal, and G. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959).
14) J. K. Dohrmann, *Ber. Bunsenges. Phys. Chem.*, **74**, 575 (1970).
15) D. Kivelson, *J. Chem. Phys.*, **33**, 1094 (1960).
16) R. F. Nelson, D. W. Leedy, E. T. Seo, and R. N. Adams, *Z. Anal. Chem.*, **224**, 184 (1967).
17) C. S. Johnson Jr. and H. S. Gutowsky, *J. Chem. Phys.*, **39**, 58 (1963).
18) S. Schreier, C. F. Polnaszek, and I. C. P. Smith, *Biophys. Acta*, **515**, 375 (1978).
19) J. R. Rowlands and D. H. Whiffen, *Nature*, **193**, 61 (1962); T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961); J. S. Hyde and E. S. Freeman, *J. Phys. Chem.*, **65**, 1636 (1961); H. Zeldes and R. Livingston, *J. Chem. Phys.*, **35**, 563 (1961).