ESR Spectra of the Radical Anions of Nitrobenzene and *p*-Nitrobenzoic Acid Incorporated into Micelles

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The radical anions of nitrobenzene and *p*-nitrobenzoic acid have been prepared chemically for the first time in aqueous solutions with the aid of micelles. The radicals thus prepared are stable and the resulting ESR spectra are unsymmetrical owing to the suppressed rotational diffusion of the radicals due to incorporation into micelles. The environments surrounding the radicals are discussed in terms of the ^{14}N hyperfine coupling constants and the rotational correlation times. For *p*-nitrobenzoic acid radical anion, the temperature dependence of the ESR spectrum has been studied.

Recently molecular assemblies have been studied on their interesting functions and behavior associated with their own structures by many investigators.[1-7] In particular, since micelles as well as cyclodextrins are soluble in aqueous solution and able to incorporate inorganic as well as organic molecules into their nonpolar hydrophobic stages, they provide certain solubilities for compounds insoluble in aqueous solutions.[6,7] Micellar systems have been studied as enzyme-substrate models,[6] for the micellar systems are analogous to enzymes which offer hydrophobic stages to biochemical reactions proceeding in nonpolar environments embedded in polar media such as water.

In this study, the radical anions of nitrobenzene and *p*-nitrobenzoic acid have been prepared chemically, for the first time, in aqueous solutions with the aid of micelles. The radicals thus prepared have been found stable enough to permit variable temperature studies on the ESR spectra, which are unsymmetrical as a result of the suppressed rotational diffusion of the radicals incorporated into micelles.

Hitherto, most of the ESR studies on the micellar systems have been made using the stable nitroxide radicals as spin probes, where the ESR spectrum consists of two components, one due to the radicals in the aqueous phase and the other to those in micellar phase.[8] Thus one component must be separated from the other in studying the behavior of the radicals in the individual phases. In this respect, radicals unstable in bulk water but stable in micelles are valuable as probes for studying micellar structure, simplifying the spectral interpretation. In this paper, the ESR spectra of the radical anions of nitrobenzene and *p*-nitrobenzoic acid incorporated into micellar systems have been studied for investigating the dynamical properties of the radicals in micelles and thereby deducing some aspects of the micellar structures.

Experimental

Nitrobenzene (NB) and *p*-nitrobenzoic acid (NBA) (Tokyo Kasei, GR) were used as received. As the micelle-forming reagents, sodium dodecyl sulfate (SDS), and sodium dodecylbenzenesulfonate (SDBS) (Tokyo Kasei, GR) were used without further purification. Ethanol (Wako, super special grade) and deionized distilled water were used as solvents. The radicals were prepared by reduction with sodium dithionite $Na_2S_2O_2$ (Wako) in aqueous SDS micellar solutions in the presence of a small amount of NaOH under vacuum; the sample solutions were degassed by the freeze-pump-thaw technique. For comparative study, the radical anion of NBA was prepared in 95% ethanol by reduction with glucose in a similar manner.

The ESR spectra were recorded on an X band spectrometer (Echo Electronics) combined with a JEOL JM-360 electromagnet with 100 kHz field modulation. The magnetic fields were measured with a proton NMR gaussmeter (JEOL, JMF-3). The field modulation amplitude and the microwave power were kept as small as possible. Variable temperature measurements were made with a temperature control apparatus (JEOL UTC-2AX/JES-VT-3A). The ESR capillary cells of 3 and 2 mm o.d. were used for 95% ethanol and aqueous micellar solutions, respectively; the former cells were home-made ones, while the latter were commercial ones (JEOL No. 29).

Results and Discussion

The ESR Spectra of Nitrobenzene Radical Anion Incorporated into SDS Micelles. Figure 1(a) shows the ESR spectrum of nitrobenzene radical anion ($NB^{-\cdot}$) observed in aqueous SDS micellar solution at 20 °C; the NB and SDS concentrations were 1.0×10^{-3} and 5.0×10^{-2} mol dm^{-3}, respectively. The spectrum has some characteristic feature, i.e., the high resolution especially in the central-field portion, large ^{14}N hyperfine splitting, and asymmetry in the overall shape. Since the radical could not be generated in aqueous solution in the absence of SDS, it was undoubtedly incorporated into SDS micelles and thereby stabilized. The total number of lines are fifty four as expected.

Assuming that the association number of the SDS micelles remains unaffected by the presence of $Na_2S_2O_4$ and NaOH, and that the parent compound is completely converted into the radical, the mean number of radicals in a micelle is estimated to be 1.61. According to the Poisson statistics, the fractions of the micelles with no, one, and two radicals are 20, 32, and 26%,

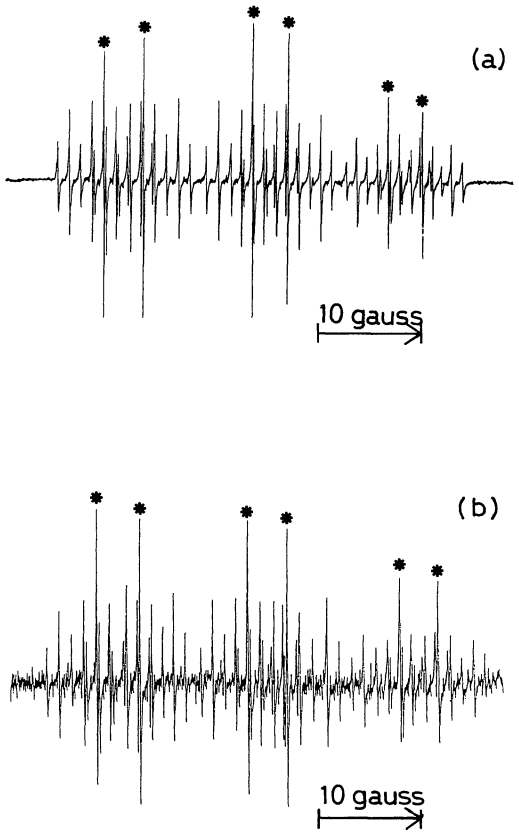

Fig. 1. ESR spectrum of $NB^{-\cdot}$ in aqueous SDS micellar solution observed at 20 °C. The lines marked with asterisks are dependent on the nitrogen nucleus and para proton, but independent of the ortho and meta protons. [NB]/mol dm^{-3}: (a) 1.0×10^{-3}; (b) 3.0×10^{-3}. [SDS]/mol dm^{-3}: 1.0×10^{-1}.

respectively. Since the fraction of the micelles with more than two radicals is small, the intramicellar spin dipole and spin-exchange interactions are unimportant and hence the observed ESR line widths are narrow. The ^{14}N hyperfine coupling constant a^N is affected by the solvent polarity, e.g., the constant is increased from 10.00 to 14.00 G (1 G=10^{-4} T) with increasing fraction of water in *N,N*-dimethylformamide–water mixture;[9] the a^N was observed to be 14.25 G in this work, indicating that $NB^{-\cdot}$ is located in the water-abundant region in micelles.

The ESR line widths of radicals in aqueous micellar solutions are expressed as the sum of the reciprocals of the transverse relaxation times associated with several different sources.[8] Among them, the contribution from the rotational modulation of the anisotropic *g* and hyperfine *A* tensors gives rise to the unsymmetrical spectral features. Since the line widths are dependent predominantly on the nitrogen nuclear spin quantum number, as will be described later on, we restrict the discussion to the lines marked with asterisks in Fig. 1(a) which are independent of the ortho and meta protons, i.e., associated with the smallest possible number of nuclei. The line widths ΔH of these asterisked hyperfine lines are represented as,[10]

$$\Delta H = A + Bm_I^N + C(m_I^N)^2 + Dm_I^H + E(m_I^H)^2 + Fm_I^N m_I^H, \quad (1)$$

where m_I^N and m_I^H are the nuclear spin quantum numbers of the nitrogen nucleus and para proton, respectively, and *B* and *C* involve the rotational correlation times as parameters. For any value of m_I^N, the line widths of the doublet due to the para proton are almost equal. From the three asterisked doublets, we obtain the following values: $A+(1/4)E=0.110$, $B=-0.0.19$, $C=0.019$, $D=1.00\times10^{-3}$, and $F=1.00\times10^{-3}$ G. The *B* and *C* values are much greater than the *D* and *F*, indicating that the line widths are predominantly governed by m_I^N. Thus, we can estimate the rotational correlation time τ from the *B* and *C* values, respectively, through Eqs. 3 and 4 in Ref. 11(a); the τ values associated with *B* and *C* will be referred to as τ_B and τ_C, respectively.[11] For evaluation of the τ values, the $g_{\parallel}$, $g_{\perp}$, $A^N{}_{\parallel}$, and $A^N{}_{\perp}$ values reported by Flockhart et al.[12] can be used; the anisotropic *g* and A^N tensors have not been determined fully yet. Actually, we assume that the rotational diffusion of $NB^{-\cdot}$ is isotropic so that Kivelson's formula is applicable,[10] and $\delta g=(g_{xx}-g_{yy})/2$ and $\delta A^N=(A^N{}_{xx}-A^N{}_{yy})/2$ can be neglected.

The values of τ_B and τ_C thus obtained are 2.4×10^{-11} and 3.3×10^{-11} s, respectively. The rotational correlation time can also be determined with the following equation,[13] derived from Kivelson's formula,[10]

$$\tau = A_\tau \Delta H(+1)[(I(+1)/I(-1))^{1/2} - 1], \quad (2)$$

where $\Delta H(+1)$ is the peak-to-peak line width of the low-field first derivative line of $m_I^N=+1$, and $I(+1)$ and $I(-1)$ are the peak-to-peak heights of the lines of $m_I^N=+1$ and -1, respectively, all averaged over the para-proton doublets. The constant A_τ is related to the anisotropies in the *g* and A^N tensors. With the *g* and A^N values of Flockhart et al.,[12] we obtain a τ value of 3.5×10^{-11} s in good agreement with the above τ_B and τ_C.

The Brownian rotational correlation time of SDS micelles, τ_{mic}, in aqueous solution is estimated with the Debye–Stokes–Einstein relation to be 0.83×10^{-8} s at 20 °C for the SDS micellar radius of 20 Å. The relative correlation time of $NB^{-\cdot}$ referred to the micellar coordinate system, τ_{rel}, is practically the same as τ on the basis of the following equation of Gutowsky et al.,[14,15]

$$\tau^{-1} = \tau_{rel}^{-1} + \tau_{mic}^{-1}, \quad (3)$$

showing that the $NB^{-\cdot}$ is moderately bound in the water-abundant region near the micellar surface.

Figure 1(b) shows the ESR spectrum of $NB^{-\cdot}$ in

aqueous SDS micellar solution observed at 20 °C with an increased NB concentration of 3.0×10^{-3} mol dm^{-3}. The mean number of radicals in a micelle is estimated to be 4.83 in the above-mentioned manner, and the fractions of the micelles with two, three, four, and five radicals are 9, 15, 18, and 18%, respectively, according to the Poisson statistics. Thus, the spin dipole and spin-exchange interactions are expected to increase as compared with the case of Fig. 1(a); actually the width of the $m_I{}^N=0$ line is 0.125 G, which is 1.1 times as large as that in Fig. 1(a).

The ESR Spectra of *p*-Nitrobenzoic Acid Radical Anion Incorporated into SDS Micelles. Figure 2 shows the ESR spectra of *p*-nitrobenzoic acid radical anion ($NBA^{-\cdot}$) in aqueous SDS micellar solution observed at different temperatures. The NBA and SDS concentrations were 1.0×10^{-2} and 1.0×10^{-1} mol dm^{-3}, respectively. No evidence was found for formation of the radical in aqueous solution in the absence of SDS, confirming that the radical is incorporated into SDS micelles just as in the case of $NB^{-\cdot}$. Although the ESR spectrum of $NBA^{-\cdot}$ has been studied by many investigators,[16–18] the preparation of the radical in aqueous solution by means of chemical reduction has never been reported. The radical is very unstable in aqueous solution in the absence of SDS, similarly to $NB^{-\cdot}$; it cannot be generated even in 70% aqueous ethanol, but is fairly stable in 95% ethanol. As can be seen from Fig. 2, the ESR spectra observed at 10 and 15 °C are unsymmetrical in line shape, and the amplitudes of the high-field lines are considerably small, showing marked line broadening of the lines for $m_I{}^N=-1$; the rotational motion of the radical is largely suppressed at these temperatures. The spectral asymmetry is lower at 20 °C and the spectrum is nearly symmetrical at 25 °C, indicating the thermal activation of the rotational motion.

Figure 3 shows the ESR spectra of $NBA^{-\cdot}$ in 95% ethanol observed at different temperatures; at any temperature, the spectrum is more unsymmetrical and the a^N value is smaller than those in aqueous SDS micellar solution. The ESR spectrum of the radical formed in ethanol by reduction with glucose was reported by Ayscough et al.[16]

Every ESR spectrum in Figs. 2 and 3 is composed of three main envelopes due to ^{14}N nucleus. The total number of lines is twenty seven as expected when the carboxyl proton is neglected. The line widths are remarkably smaller in aqueous SDS micellar solution than in 95% ethanol, indicating incorporation-induced reduction of spin dipole and spin-exchange interactions. The a^N was found to be 13.01 and 12.42 G

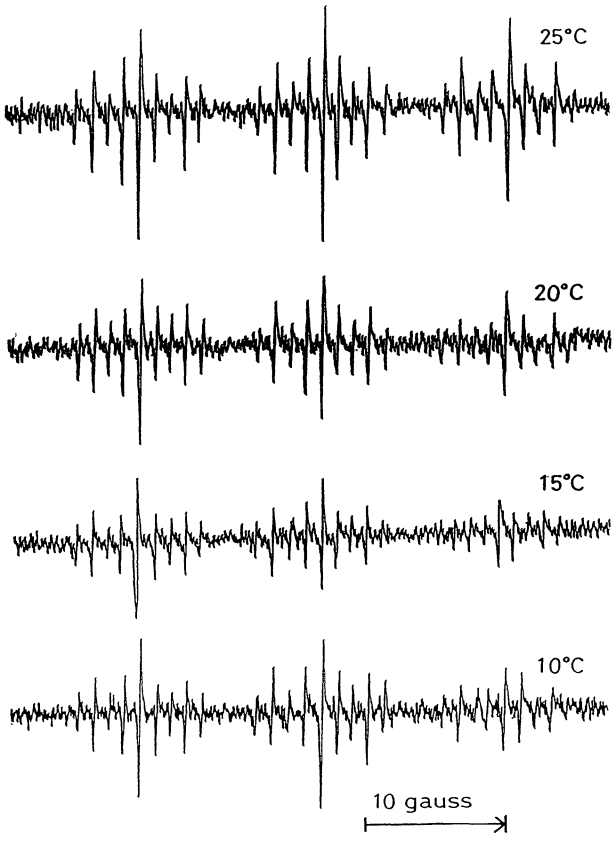

Fig. 2. ESR spectra of $NBA^{-\cdot}$ in aqueous SDS micellar solution observed at different temperatures. [NBA]/mol dm^{-3}: 1.0×10^{-2}. [SDS]/mol dm^{-3}: 1.0×10^{-1}.

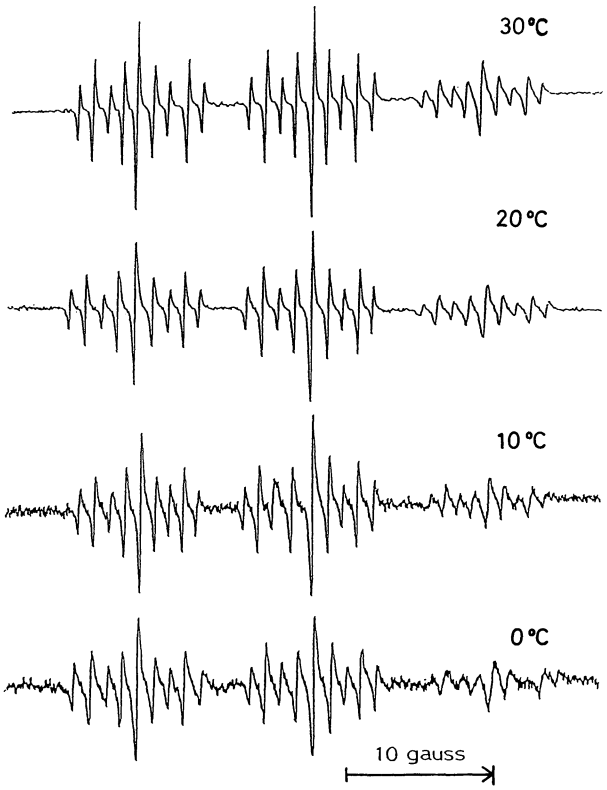

Fig. 3. ESR spectra of $NBA^{-\cdot}$ in 95% ethanol observed at different temperatures. [NBA]/mol dm^{-3}: 1.0×10^{-2}.

respectively in aqueous SDS micellar and 95% ethanol solutions at 20 °C, which are larger than those in other organic solvents.[16-18] Nordio et al. reported a value of 9.65 G in DMF.[18] As compared with the difference of 2.06 G between the a^N values of di-*t*-butyl nitroxide radical in hexane and aqueous solutions,[19] the a^N of $NBA^{-\cdot}$ is slightly more sensitive to solvent. The experimental hyperfine coupling constants, a^{Ho} and a^{Hm}, for the ortho and meta protons are 3.33 and 1.18 G, respectively, in aqueous SDS micellar solution at 20 °C. As can be seen from Figs. 2 and 3, the relative intensities of the individual lines in the central main envelope are, at any temperature, in good agreement with those predicted simply by the statistical weights of the nuclear spin states, in contrast to the observation that the intensity ratios of the hyperfine lines among the three main envelopes differ significantly from those predicted thereby. This shows that the ESR spectrum is unsymmetrical as a whole, due to the line width variations. The line width of $NBA^{-\cdot}$ can be represented by the following relation:[13]

$$\Delta H = (I/I_{st})^{-1/2}\Delta H_{st}, \quad (4)$$

where ΔH and I are the peak-to-peak width and intensity, respectively, and the subscript "st" stands for "standard"; the line of $m_I{}^N=0$ has been chosen arbitrarily as the standard. Within any of the three envelopes, the line widths are scarcely dependent on the proton spin quantum number set ($m_I{}^{Ho}$, $m_I{}^{Hm}$); the variations in line width are characterized predominantly by the nitrogen nuclear spin quantum number $m_I{}^N$. The line widths for $m_I{}^N=0$ observed in aqueous SDS micellar solution at 20 °C are 0.171 G, while those for $m_I{}^N=-1$ are considerably large, amounting to 0.200 G and indicating the suppressed rotational motion of the radical. Since the proton hyperfine coupling is little responsible for the line broadening, Eq. 1 can be simplified as follows:

$$\Delta H = A + Bm_I{}^N + C(m_I{}^N)^2. \quad (5)$$

The mean number of the radicals in an SDS micelle is estimated to be 7.31, on the same assumption as adopted for $NB^{-\cdot}$. The fractions of the micelles with six, seven, and eight radicals are 14, 15, and 14% in the Poisson statistics. This is consistent with the fact that the observed line width of 0.171 G for $m_I{}^N=0$ in $NBA^{-\cdot}$ is considerably larger than the corresponding value of 0.110 G in $NB^{-\cdot}$ in Fig. 1(a). Incidentally, the line width for $m_I{}^N=0$ of $NBA^{-\cdot}$ is 0.151 G in 50% ethanol solution containing β-cyclodextrin at 20 °C,[20] where the 1:1 inclusion complex is formed.

The τ_B and τ_C of $NBA^{-\cdot}$ in aqueous SDS micellar solution have been evaluated from Eq. 1 to be 2.6×10^{-11} and 1.1×10^{-11} s at 20 °C, respectively, by borrowing the anisotropic g and hyperfine tensors, $g_\parallel$, $g_\perp$, $A_\parallel$, $A_\perp$, of $NB^{-\cdot}$, since those of $NBA^{-\cdot}$ are not available. The τ value determined with Eq. 2 is 3.4×10^{-11} s, which is of the same order as the τ_B and τ_C. The rotational correlation time of the radical in the micellar coordinate system, τ_{rel}, is practically the same as τ on the basis of Eq. 3. Judging from the a^N and τ_{rel}, the radical is moderately bound in the water-abundant region near the micellar surface, similarly to the case of $NB^{-\cdot}$. Here, it may be noted that generally in the micellar structure, water penetrates up to the sixth or seventh carbon position along the hydrocarbon chain.[6,7]

The rotational correlation times τ_B, τ_C, and τ of the radical in 95% ethanol at 20 °C are 10.8×10^{-11}, 9.4×10^{-11}, and 11.9×10^{-11} s, respectively. These values are close to each other, and larger than those in the aqueous SDS micellar solution, showing that the rotational diffusion of the radical is more suppressed in 95% ethanol due to hydrogen bonding.

Tables 1 and 2 present the rotational correlation times estimated similarly to the case of $NB^{-\cdot}$. The temperature dependence of the rotational correlation time τ is shown in Fig. 5. In the aqueous SDS micellar solution, the molecular motion is seen to be about 1.5 times slower at 10 °C than at 20 °C, and all the τ values are of the order of 10^{-11} s, indicating that the radical rotates nearly freely. The line widths for $m_I{}^N=0$ in the aqueous SDS micellar solution are 0.166, 0.178, 0.171, and 0.154 G at every 5 degrees from 10 to 25 °C, which

Table 1. Temperature Dependence of the Rotational Correlation Times τ_B, τ_C, τ, and τ_{rel} of $NBA^{-\cdot}$ Incorporated into SDS Micelles[a]

Temp/°C	Rot. correl. times/10^{-11} s			
	τ_B	τ_C	τ	τ_{rel}
10	4.5	3.9	5.3	5.3
15	4.5	1.5	5.4	5.4
20	2.6	1.1	3.4	3.4
25	0.6	1.7	1.0	1.0

a) The SDS concentration is 1.0×10^{-1} mol dm^{-3}. τ_B and τ_C refer to the coefficients B and C in Eq. 1, respectively, and τ to Eq. 2. τ_{rel} refers to the micellar coordinate system.

Table 2. Temperature Dependence of the Rotational Correlation Times τ_B, τ_C, and τ of $NBA^{-\cdot}$ in 95% Ethanol Solution[a]

Temp/°C	Rot. correl. times/10^{-11} s		
	τ_B	τ_C	τ
0	14.4	11.5	15.7
5	14.5	11.9	15.9
10	14.1	11.7	15.3
15	12.6	9.4	14.2
20	10.8	9.4	11.9
25	10.0	8.2	11.0
30	7.0	6.8	7.9

a) See note to Table 1.

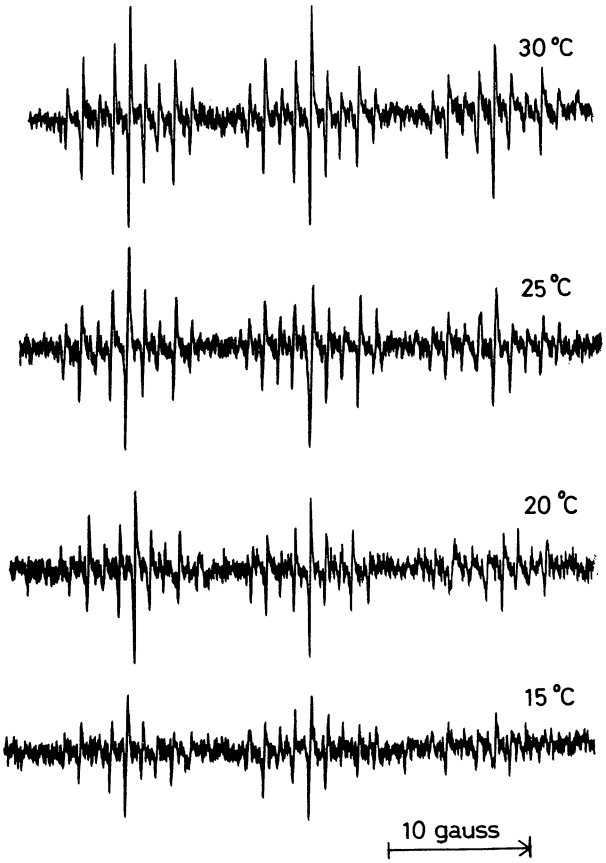

Fig. 4. ESR spectra of $NBA^{-\cdot}$ in aqueous SDBS micellar solution observed at different temperatures. [NBA]/mol dm^{-3}: 1.0×10^{-2}. [SDBS]/mol dm^{-3}: 1.0×10^{-1}.

involve various isotropic contributions. The isotropic contributions cannot be estimated straightforwardly, since many different, both identified and unidentified, types of perturbations are involved, e.g., the temperature-dependent aggregation number can be a perturbing factor.[7] On the other hand, the temperature dependence of the line widths in 95% ethanol can be explained predominantly by the viscosity of water; the widths for $m_I{}^N=0$ in 95% ethanol have been found to be 0.280, 0.235, 0.249, 0.228, 0.217, 0.185, and 0.166 G at every 5 degrees from 0 to 30 °C.

The ESR Spectra of *p*-Nirtrobenzoic Acid Radical Anion Incorporated into SDBS Micelles. Figure 4 shows the ESR spectra of $NBA^{-\cdot}$ in aqueous 1.0×10^{-1} mol dm^{-3} SDBS micellar solution observed at every 5 degrees from 15 to 30 °C. The radical is stabilized considerably in SDBS micelles; the CMC of SDBS is 1.63×10^{-3} mol dm^{-3} at 25 °C,[6] much smaller than that of SDS, 8.1×10^{-3} mol dm^{-3}. The ESR intensity increases with increasing temperature. Although the ESR spectra observed at 10 and 15 °C are poor in signal-to-noise ratio (S/N), especially at 10 °C, it is clearly seen that the ESR spectra are fairly unsymmetrical at lower temperatures, and tend to be

Table 3. The Temperature Dependence of the Rotational Correlation Times τ_B, τ_C, and τ of $NBA^{-\cdot}$ Incorporated into SDBS Micelles[a]

Temp/°C	Rot. correl. times/10^{-11} s		
	τ_B	τ_C	τ
15	6.4	5.5	7.3
20	5.7	3.7	6.5
25	3.2	0.9	4.0
30	1.9	1.9	2.7

a) The SDBS concentration is 1.0×10^{-1} mol dm^{-3}. See note to Table 1.

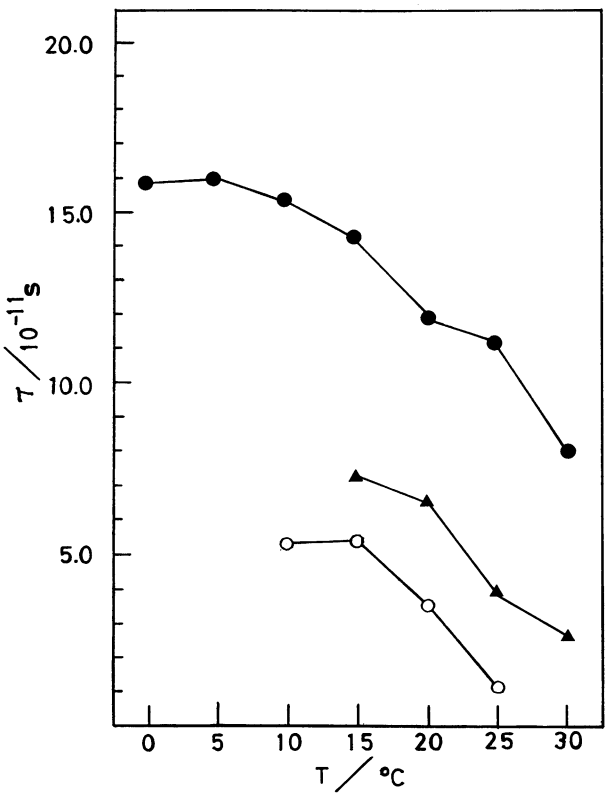

Fig. 5. Temperature dependence of the rotational correlation time τ for $NBA^{-\cdot}$. ○: in SDS micelles, ●: in 95% ethanol, ▲: in SDBS micelles.

symmetrical at higher temperatures. The a^N values obtained at every 5 degrees from 10 to 30 °C are close to each other, similarly to the case of the aqueous SDS micellar solution. In view of the a^N value, the radical is located in the water-abundant region, i.e., the SDBS micelles allow the penetration of water similarly to SDS micelles. The τ_B, τ_C, and τ have been estimated for all the temperatures studied; the values evaluated at 10 °C are less reliable owing to the poor spectral S/N ratio. Table 3 collects the τ_B, τ_C, and τ of the radical in the SDBS micellar solution from 15 to 30 °C. Figure 5 shows the temperature dependence of τ at every 5 degrees from 15 to 30 °C; in the range 15—20 °C, the rotational diffusion is suppressed, while it is nearly

free above 25 °C. The temperature dependence of the dynamical properties of the radical as well as the stabilization of the radical is remarkable in the aqueous SDBS micellar solution.

Concluding Remarks. Since the rotational correlation time of a radical in nonpolar solvent is generally of the order of 10^{-12} s, the rotational motion of the NB and NBA radical anions is seen to be suppressed in micellar solutions. The τ_C values tend to be smaller than the τ_B and τ values in general, as can be seen from Tables 1 to 3.

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