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Spin-Probe Study of Aqueous Soap and Polysoap Solutions

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Poly(2-vinylpyridine) partially quaternized with 1-dodecylbromide, a "polysoap," sodium dodecyl sulfate (SDS), and dodecylpyridinium bromide (DPBr) in their micellar solutions were investigated by the spin-probe technique. It was found that the alkyl side chains in polysoap micelles associate more rigidly than in low-molecular surfactant micelles. This fact is attributed to the surface active groups covalently connected to long polymer chains in the polysoap molecule. By a recently developed method, the rotational correlation times of 2,2,6,6-tetramethyl-4-benzoyloxypiperidin-1-oxyl radical in SDS and DPBr micelles were found to be 5.9×10^{-10} and 3.5×10^{-10} s/rad, respectively. From the values of the isotropic hyperfine splitting constants, it was estimated that the DPBr micelle solubilizes the probe molecule at a more inner site of the hydrophobic portion than does the SDS micelle.

In the aqueous solutions of amphiphile substances, some intermolecular and/or intramolecular structures are formed by the "hydrophobic interaction." Surfactant molecules form the ordered aggregates known as micelles, so that their aqueous solutions manifest such properties as solubilization of hydrophobic compounds and hydrolysis of ester bonds. In the case of amphiphile macromolecules, their hydrophobic portions tend to an intramolecular association which contributes to stabilize the conformation of the macromolecules.

Strauss and coworkers[1] have studied polysoap, which is defined as an amphiphile macromolecule with a surface active side chain. According to the results of the measurement of viscosity, solubilization of hydrophobic compounds, scattering of light, and surface tension, the polysoap molecules dissolve with a relatively compact structure and can solubilize more hydrophobic compounds than low-molecular surfactant molecules corresponding to the monomer units of the polysoap molecule can. These properties, which differ from those of ordinary polyelectrolytes, result from the formation of polysoap micelle, as in the case of low-molecular surfactant micelles.

Thus the hydrophobic interaction plays an important role in the properties of such aqueous amphiphile solutions. But details of the interaction have not yet been sufficiently clarified with respect to energy and structure.

Recently, the spin-probe or spin-label technique developed by McConnell and coworkers[2] has become available for the study of various systems[3] such as polymeric materials, aqueous micellar solutions, and natural or artificial membranes. In these studies one could obtain information about the microscopic environment of the stable radical molecules; the molecular motion and structure of the host materials can thus be uncovered.

In this paper, the authors present some results obtained from the application of the spin-probe technique to aqueous polysoap solutions. Some results about the structure of the inner hydrophobic portion of polysoap micelles, by comparison with that of low-molecular surfactant micelles are also given. The authors finally examine the manner in which the hydrophobic probe is solubilized in micelles.

Experimental

Polysoap (Fig. 1(a)) derived from poly(2-vinylpyridine) (PVP) was synthesized according to the method of Inoue.[4] PVP was obtained by radical polymerization and its elemental analysis was as follows. Found: C, 80.01; H, 6.73; N, 13.22%. Calcd for $(C_7H_7N)_n$: C, 79.97; H, 6.71; N, 13.32%. From viscosity measurements in 95% ethanol solution the molecular weight and the degree of polymerization of PVP were found to be 3.0×10^5 and 2.8×10^3, respectively. Polysoap was prepared by heating a DMF solution of PVP with excess (*ca.* 2 mol) 1-dodecylbromide in an ampoule at 100 °C for 41.5 h. The partially quaternized PVP was precipitated with ether and dried under vacuum. Then the product was dissolved into water and purified by dialysis using a cellophane tubing. The degree of quaternization was estimated to be 32.2% from elemental analysis.

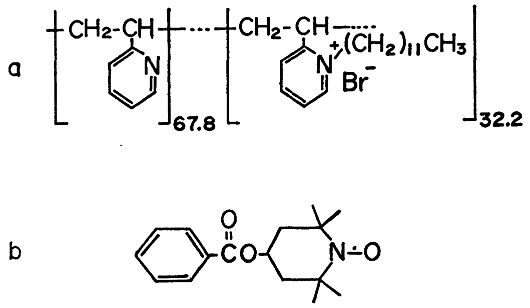

Fig. 1. (a) Polysoap, (b) BzONO.

Sodium dodecyl sulfate (SDS) was supplied from Nakarai Chemicals Ltd., and dodecylpyridinium bromide (DPBr) was obtained by ion-exchange of guaranteed grade dodecylpyridinium chloride.

The hydrophobic nitroxide radical used as the spin probe, 2,2,6,6-tetramethyl-4-benzoyloxypiperidin-1-oxyl(BzONO, Fig. 1(b)) was synthesized by Rozantzev's method.[5] Its melting point was 105.6 °C (lit, 105 °C) and its elemental analysis was as follows. Found: C, 69.63; H, 8.13; N, 4.91%. Calcd for $C_{16}H_{22}NO_3$: C, 69.53; H, 8.02; N, 5.07%; mol wt 276.4.

The concentration of the spin probe, BzONO, was 1.06×10^{-4} mol/dm^3 in all sample solutions. Besides these solutions, those saturated with BzONO were also prepared for comparison.

ESR spectra were recorded on a JEOLCO model ME-3X spectrometer equipped with a variable temperature accessory.

Results and Discussion

ESR spectra of BzONO in water are shown in Fig. 2. The three main lines of the spectra result from the contact hyperfine interaction between electron spin ($S=1/2$) and ^{14}N nuclear spin ($I=1$), corresponding to nitrogen nuclear spin quantum numbers $M_I=+1$, 0, and -1, respectively, toward the high field direction. One finds out that a less resolved hyperfine structure appears in each line, due to some protons in the BzONO molecule. In Fig. 2(b) (full line), the magnified spectrum of the central line ($M_I=0$), the proton hyperfine structure is observed clearly. Thus, the previous analysis[6] which neglected the proton hyperfine structure of nitroxide radicals cannot be applicable to our systems.

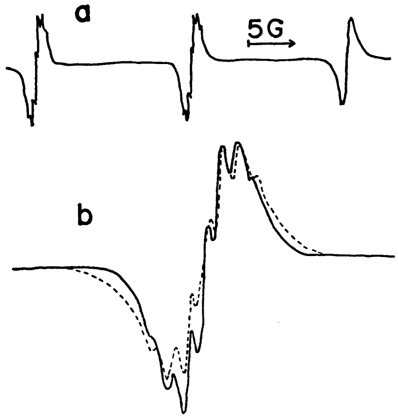

Fig. 2. (a) ESR spectrum of 1.06×10^{-4} mol/dm^3 BzONO in water at 30 °C. (b) The magnified spectrum of central line ($M_I=0$) (full line) and the simulated spectrum (dashed line).

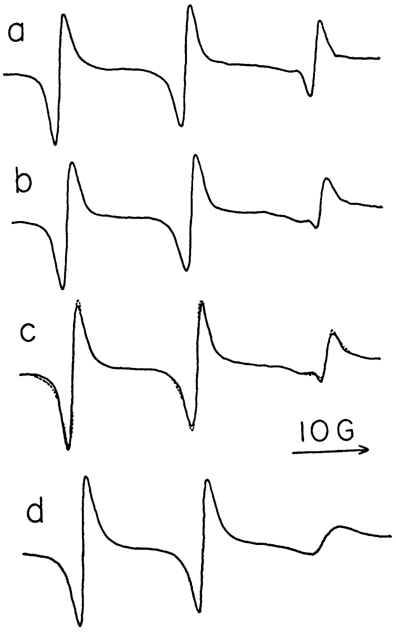

Fig. 3. ESR spectra of 1.06×10^{-4} mol/dm^3 BzONO in aqueous polysoap solutions at 30 °C and the simulated spectrum of BzONO in polysoap micelle. Polysoap concentration: (a) 1.02%, (b) 2.99%, (c) 3.94%. (d) The simulated spectrum in polysoap micelle.

ESR spectra of the aqueous polysoap solutions are shown in Fig. 3. The resolved hyperfine structure in Fig. 2 disappears here, owing to a broadening of each proton hyperfine line. From the shape of the high field line ($M_I=-1$), however, it is clear that two different components are superposed. The changes in line shape with increase in polysoap concentration indicate that the broad component is due to BzONO in the polysoap micellar environment and that the sharp one is due to BzONO in bulk water. The fact that the two different components of BzONO from two media are simultaneously observed indicates that the exchange rate of BzONO molecules between the two media is relatively low. In order to separate the broad component from the sharp one, the experimental spectra were simulated by two sets of three Lorentzian lines. As a sharp component, a spectrum with $T_2^{-1}(M_I)$ of 1.06×10^{-4} mol/dm^3 BzONO in water is used after wiping out the proton hyperfine structure. The dashed line in Fig. 3(c) is a simulated spectrum and Fig. 3(d) is the broad component used in the simulated spectrum.

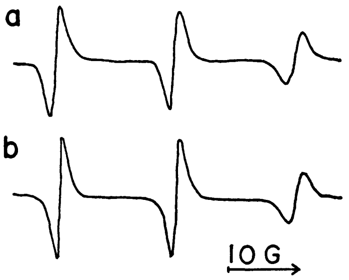

Fig. 4. ESR spectra of 1.06×10^{-4} mol/dm^3 BzONO in (a) 6.3% aqueous SDS solution and (b) 3.0% aqueous DPBr solution at 30 °C.

Figures 4(a) and 4(b) show the spectra of BzONO in the SDS and DPBr solutions, respectively. In the low-molecular surfactant solutions, above CMC which is 0.22 wt% for SDS aqueous solution and 0.37 wt% for DPBr aqueous solution, the spectra are almost independent of surfactant concentration. All over the concentration range of these solutions, the authors cannot distinguish the two different components associated with two media, that is, the micelle and the bulk water. According to the previous studies[7,8] of similar systems, the above finding does not imply that the exchange rate of the probe is too high to be resolved by ESR method, but implies that the g- and A-tensors of the probe radical are only slightly different between the two media, and that the probe is isotropically tumbling in the low-molecular surfactant micelle. By computer simulation employing the modified Bloch equations which take account of both the micelle-water exchange and the spin exchange in the micelle, the exchange rate of BzONO between SDS micelle and bulk water is estimated to be $(2.5-5.0)\times10^4$/s. This value supports the previous interpretation of spectra of probes in low-molecular surfactant micellar solutions.

Comparing the line width of these spectra, one notices that the line width of spectra of BzONO is broader in the polysoap micellar environment than in either the low-molecular surfactant micellar environment or bulk

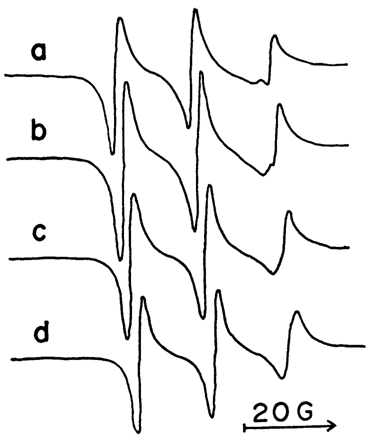

Fig. 5. ESR spectra at various temperatures of BzONO saturated at 30 °C in 4.45% aqueous polysoap solution. Temperature: (a) 30, (b) 40, (c) 50, (d) 60 °C.

water. As the causes of the line width broadening in polysoap micelle, two assumptions are possible; one is the appearance of anisotropy of g- and A-tensors and the other is Heisenberg spin exchange interaction between probe radicals solubilized in polysoap micelle where the local concentration of radicals is extremely high. Here, if the latter occurs, the broadening must decrease with the increase in polysoap concentration at the constant radical concentration, and, on the other hand, it must be intensified with an increase in radical concentration or in temperature. But the present results are not consistent with these suppositions, as shown in Figs. 3 and 5. Therefore, it is quite reasonable that the broadening of the line width in the polysoap micelle results from anisotropy of g- and A-tensors, which depends on nitrogen spin quantum number M_I and is remarkable especially in the high field line ($M_I=-1$). Thus, it is concluded that the probe molecule tumbles more slowly in polysoap micelle than in low-molecular surfactant micelles. From another point of view, the result may reflect the fact that the inner alkyl chains in polysoap micelle form more rigid structures than those in low-molecular surfactant micelles.

Recently, in the measurement of NMR relaxation times of poly(4-vinylpyridine) partially quaternized with 1-octylbromide in methanol, Ghesquire and coworkers[9] have found that the spin-lattice relaxation times T_1 of ^{13}C in the octyl group decrease with the increase in degree of quaternization. This result partly supports the present supposition about the structure of alkyl chains in polysoap micelle, since in a system with dipole-dipole interaction T_1 is inversely proportional to mobility about the spin under consideration. The authors suppose that surface active groups connected covalently into long polymer chains are mainly responsible for the mobility reduction of alkyl chains. Moreover, if the hydrophobic portion of amphiphile macromolecules used as synthetic enzymes has a rigid structure similar to that of the polysoap micelle, the rigidity may partly contribute to the rate of enzyme reactions such as hydrolysis of esters.[10]

For quantitative discussion, the authors determined the rotational correlation time τ_c of probe molecule, BzONO, in SDS and DPBr micelles, respectively, and roughly estimated it in the polysoap micelle. According to the Debye and BPP theory,[11] the rotational correlation time τ_c of a molecule in solution has the following relation to the environmental viscosity η:

$$\tau_c = 4\pi a^3\eta/3kT, \qquad (1)$$

where a is the spherical radius of the molecule, k the Boltzmann constant, and T is the absolute temperature.

The spectra are analyzed by Poggi and Johnson's method[12] taking into account the unresolved proton hyperfine structure of ESR spectra of nitroxide radicals. The main assumptions required for the spectra analysis are as follows:

(1) Each spectra line consists of unresolved hyperfine splitting lines from 12 equivalent methyl protons of a BzONO molecule.

(2) Proton hyperfine lines have Lorentzian shape and an equal splitting constant. Their line widths are equal in the same M_I line.

(3) The g- and A-tensors of ^{14}N are axially symmetric, that is, $A_X=A_Y$ and $g_X=g_Y$.

By a spectral simulation using these assumptions, each line width, $W_H(M_I)$, of the proton hyperfine lines in the three lines is obtained. The dashed line in Fig. 2(b) is the simulated spectrum for the experimental spectrum (full line) of the central line ($M_I=0$) of BzONO in water. The agreement between the two spectra is satisfactory except for the unsymmetry of the experimental spectrum. These $W_H(M_I)$ are substituted into the following equation derived from Kivelson's theory:[13]

$$\tau_c = \frac{T_2^{-1}(-1)+T_2^{-1}(+1)-2T_2^{-1}(0)}{0.25b} = \frac{\frac{\sqrt{3}}{2}\{W_H(-1)+W_H(+1)-2W_H(0)\}}{0.25b}, \qquad (2)$$

$$b = \frac{2}{3}\left\{A_z-\frac{1}{2}(A_x+A_y)\right\},$$

where A_X, A_Y, and A_Z are the three components of the A-tensor.

The obtained rotational correlation times for SDS and DPBr micelles are 5.9×10^{-10} and 3.5×10^{-10} s/rad, respectively. The values of the nitrogen hyperfine splitting constants a_N in SDS and DPBr micelles are 16.7 and 16.3 G, respectively. It should be noted that the values of both τ_c and a_N in SDS micelle are greater than those in DPBr micelle. From the previous study,[14] the nitrogen hyperfine splitting constant a_N is in a proportional relationship to the polarity of environment. By considering that the values of a_N in water and dodecane are 17.1 and 15.4 G, respectively, and that τ_c is proportional to environmental viscosity η, the above findings are interpreted as follows. The SDS micelle solubilizes BzONO in the vicinity of the polar surface of micelle, whereas the DPBr micelle solubilizes in the internal hydrophobic portion where the BzONO molecule is more mobile. The order of τ_c of the present results also indicates that the state of the internal hydrophobic portion in the low-molecular surfactant micelles is not solid-like, but liquid-like, as was reported in the previous papers.[15,16]

The rotational correlation time τ_c of BzONO in the polysoap micelle is roughly estimated to be 9.8×10^{-10} s/rad by a similar procedure, except for employing $T_2^{-1}(M_I)$ evaluated by the peak-to-peak width of the above spectrum (Fig. 3(d)) instead of $T_2^{-1}(M_I)$ obtained by the spectra simulation taking account of the proton hyperfine structure. If τ_c in the low-molecular surfactant micelles are also estimated by the same rough estimation, the values in SDS and DPBr micelles are 4.3×10^{-10} and 2.1×10^{-10} s/rad, respectively. The result confirms quantitatively the preceding suggestion that BzONO tumbles more slowly in the polysoap micelle than in the low-molecular surfactant micelles.

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