October, 1981] © 1981 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 54, 3205—3206 (1981) 3205

The Splitting of the ESR Signal of Di-*t*-butyl Nitroxide Solubilized by Micellar Solutions

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(Received January 20, 1981)

Synopsis. In a hexadecyltrimethylammonium bromide solution containing the stable micelle, a solubilized di-*t*-butyl nitroxide facilitated the partial resolution of the high-field line of the ESR spectrum, which can be associated with the radical in aqueous and micellar phases. Further analysis of the lineshape was made as a function of the surfactant concentration or the temperature.

Stable nitroxide radicals have been widely used as molecular probes or labels in order to study the dynamic effects in a variety of micellar and related membrane-like systems.[1-4] In the present study, the investigation of the ESR lineshapes of di-*t*-butyl nitroxide was made for various types of ionic micellar solutions, with the purpose of further establishing the motional contribution to the ESR linewidths in micellar systems.

Sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), hexadecyltrimethylammonium bromide (CTAB), and sodium 1,2-bis(2-ethylhexyloxycarbonyl)-ethanesulfonate (AOT) were chosen as the surfactants in this study. SDS and STS were synthesized according to the conventional method. Both CTAB and AOT were specially purified reagents. Surface-tension measurements for the surfactant solutions indicated no minima at 30 °C. The nitroxide probe, di-*t*-butyl nitroxide (DTBN), was synthesized by the method of Hoffman *et al.*[5,6] Prior to the ESR measurements, all the solutions were prepared by adding DTBN to the surfactant solutions and stirring them magnetically for several hours. The concentration of DTBN added was always 4.5×10^{-4} mol dm^{-3}. All the ESR spectra were recorded on a Japan Electron Optics Laboratory JES-ME-3X spectrometer operating at the X band.

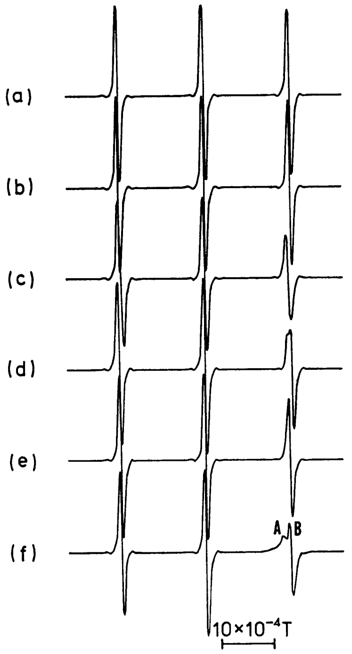

Fig. 1. Representative ESR spectra of 4.5×10^{-4} mol dm^{-3} DTBN at 30 °C.
(a): H_2O, (b): 5.5 mmol dm^{-3} SDS, (c): 33 mmol dm^{-3} SDS, (d): 14 mmol dm^{-3} STS, (e): 33 mmol dm^{-3} AOT, (f): 36 mmol dm^{-3} CTAB.

Representative ESR spectra in various types of surfactants at 30 °C are presented in Fig. 1. As was observed from the earlier finding,[1] the spectrum of DTBN in an SDS aqueous solution at concentrations below the CMC was identical with that obtained in pure water (Figs. 1(a) and 1(b)). These normal three-line spectra of nearly equal width are characteristic of a variety of rapidly tumbling nitroxides, suggesting no significant variation that might indicate the formation of premicellar aggregates or DTBN-monomer interactions. On the other hand, the high-field hyperfine line of DTBN in a 33 mmol dm^{-3} SDS micellar solution above the CMC is markedly broadened as a consequence of its interaction with the micelles. The relative magnitude of the tumbling motion of the radical is predicted from the rotational correlation time (τ_c); this value was computed from the linewidth and height of the ESR signals by the method of Martinie *et al.*[7] The values obtained in water and SDS solutions with concentrations above the CMC, where the linewidth was essentially little dependent on the SDS concentrations, were approximately 10^{-11} s and 10^{-10} s respectively. It can be seen that, although the experimental value for pure water agrees roughly with the one calculated (2.9×10^{-11} s) from the Stokes law (assuming the DTBN particle radius of 0.3 nm), the experimental values for the SDS solution are much smaller than that calculated for the radical rigidly adsorbed to a hypothetical rigid micelle (10^{-8} s). As has been stated in connection with other nitroxides,[1,3] the solubilized DTBN is considered to tumble too rapidly to be adsorbed on the micelles. Qualitatively, similar behavior was observed in solutions of the other surfactants studied, although there were some indications of the spectral distortion (or partial resolution) of the high-field line in both STS and CTAB micellar solutions (Figs. 1(d) and 1(f)). In the latter, most notably, the high-field line in a 36 mmol dm^{-3} CTAB micellar solution was replaced by two signals analogous to A and B. In this regard, the spectrum resembles that observed in the membrane-like system.[2] The explanation of the distortion is that signals from the radical molecule in two environments, *i.e.*, in the micelle and in the bulk aqueous solution, can be observed separately, indicating that the exchange of the radical between the two environments is very slow. On the contrary, the single signal of the high-field line observed in AOT and SDS suggests that the radical exchanges rapidly to produce a single symmetric signal, which is a weighted average of the spectra found in the two environments. In these spectra, it seems to be unnecessary to consider the overlapping of two types of spectral lines due to the different environments of the probe. Especially, the very narrow line resulting for AOT suggests a motion which is very rapid compared with those of the other surfactants studied. In contrast with our result at 30 °C, Atherton *et al.*[5] found that the high-field line for SDS micellar solutions was barely resolved at 23 °C for DTBN in two environments. Accordingly, the rate of exchange of the radical probe for the SDS solution at 30 °C is presumed to be relatively slow compared to that of AOT; therefore, a motional behavior similar to that of STS may rather be expected. Therefore, the greater asymmetry of the lineshape, as well as the larger τ_c value, is observed with a longer length of the surfactant alkyl chain. From the ^{1}H NMR study of an SDS micellar solution containing a Tempo radical, Oakes *et al.*[4] showed that the radical-induced proton relaxation occurred preferentially at the α-methylene group of the SDS micelle. Based upon the chemical similarity of DTBN and Tempo, we find a strong indication for a solubilization mainly occurring in the outer region within the SDS micelles. With CTAB, the relative intensities of the A and B signals of the high-field line were strongly dependent upon the CTAB concentration (Fig. 2). As the concentration of CTAB is increased, an increase in Signal A and a concomitant decrease in Signal B are observed, until Signal B, due to the radical in the bulk aqueous phase, is no longer observable. This results from the relative population of the DTBN tumbling rapidly in each phase. Recently, the CTAB micelle has been described as being a more closely packed micelle or having a long-range order, giving it a somewhat solidlike character.[8] This suggestion is advantageous in explaining the above-mentioned incorporation of the DTBN in the CTAB micelle. That is, the small DTBN radical, which is nearly spherical, could rotate rapidly in a relatively rigid micelle; however, it would exhibit a slow chemical exchange of the radical between the micellar and the bulk aqueous phases. In solutions containing the more stable micelles, the DTBN radical can be expected to exhibit two distinct spectra of the high-field line.

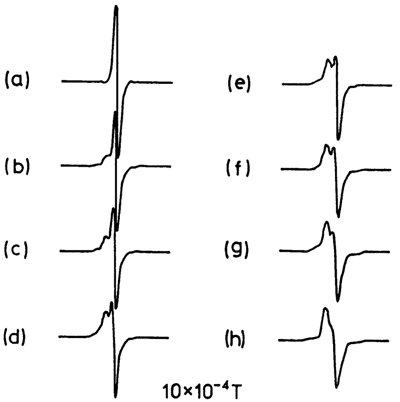

Fig. 2. Concentration dependence for the high-field line of ESR spectra in CTAB solutions at 30°C.
(a): 10, (b): 21, (c): 30, (d): 39, (e): 45, (f): 48, (g): 54, (h): 63 mmol dm^{-3} CTAB.

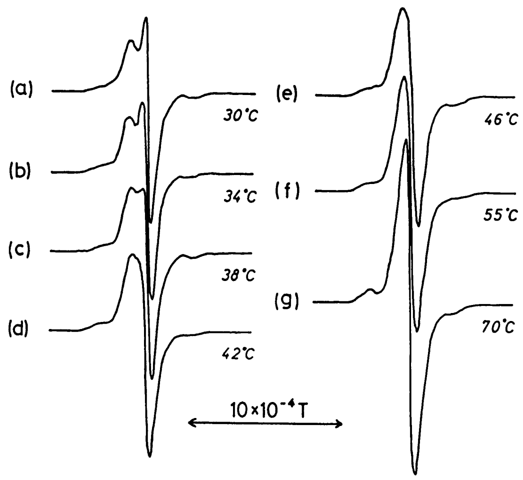

Fig. 3. Temperature dependence for the high-field line in 42 mmol dm^{-3} CTAB.

The spectra for the 42 mmol dm^{-3} CTAB solution have also been studied over the temperature range of 30—86 °C. As the temperature is increased, the two signals of a high-field line progressively coalesce, until a single line is observed at *ca.* 46 °C (Fig. 3). The increase in the amount of solubilized radical in the micellar phase might be accounted for by the change in the micellar structure and in the solubilities of the radical in the aqueous phase. At higher temperatures above 46 °C, it is conceivable that the increase in the temperature could cause a linewidth decrease in the high-field line. This indicates that the narrowing due to the faster exchange rate between the two environments probably dominates in this temperature range. The most likely explanation is that the micelle would become less rigid as a result of the increased flexibility of the alkyl chains and that the above-mentioned packing restrictions would become less important, finally leading to a disruption of the micelles.

We are gratefully indebted to Professor Hiroshi Kato for his very generous hospitality and invaluable advice during the synthesis of di-*t*-butyl nitroxide.

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