The Electron Spin Resonance of Mn^{2+} Ion in the Aqueous Solution of Surfactant

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Manganese ion is one of the typical paramagnetic ions and a number of ESR studies on this ion have been published. Most of them have dealt with it in solid; a minute amount of cation in solid is displaced with Mn^{2+} ion, and the magnitude of the crystal field and its symmetry are estimated through the ESR spectrum of Mn^{2+} ion. The method of spin label of cation with Mn^{2+} ion is expected to be applied not only to solid but to electrolytic solution.

It is well-known that cation plays an important role in the formation of surfactant micelle. So Mn^{2+} ion was added to the aqueous solution of surfactant and the effect of counterion in the solution was evaluated through the ESR spectrum of Mn^{2+} ion.

Theory of the ESR spectrum of Mn^{2+} ion in liquid solution has been recently presented by Garrett and Morgan in terms of solvent-fluctuation-induced relaxation.[1] They have shown that each of six hyperfine lines consists of five transitions of $\Delta m_S=1$, the line width of $m_I=-5/2$ is broadest and that of $m_I=1/2$ is narrowest, and that the latter is approximately proportional to the correlation time τ_C for solvent fluctuation.

Sodium dodecyl sulfate (SDS) and sodium decyl sulfate (NaDS) were employed as surfactant in this study. Each of them was added to the aqueous solution of 1×10^{-3} M $Mn(NO_3)_2$. The solution thus obtained was sealed in a capillary of glass and ESR measurements were carried out.

The ESR spectrum of Mn^{2+} ion in the aqueous solution is affected by the concentration of SDS. The variation in the line width accompanied with the concentration of SDS is shown in Fig. 1. When the concentration of SDS is below 3×10^{-3} or above 13×10^{-3} M, the line width is practically unaffected by the concentration. But line width increases with the concentration in the range from 3×10^{-3} to 13×10^{-3} M. As the line width of $m_I=1/2$ is proportional to the correlation time τ_C, τ_C increases up to 1.7 times in this region.

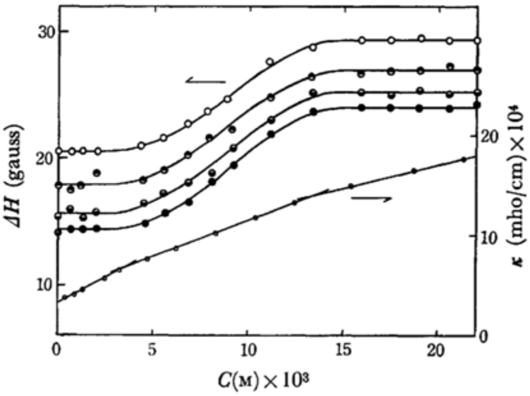

Fig. 1. The dependences of the line width (large circles) and the specific conductivity (smaller circle) on the concentration of SDS at 50°C.
○— $m_I=-5/2$, ◓— $m_I=-3/2$,
◒— $m_I=-1/2$, ●— $m_I=1/2$

Conductivity measurements were carried out in order to determine the CMC (critical micelle concentration). The specific conductivity-concentration curve broke at two points as is seen in Fig. 1. The concentrations corresponding to these two points are the first and second $\mathrm{CMC_s}$ from the side of the lower concentration of SDS, respectively, and agree well with the concentrations at which the line width of ESR of Mn^{2+} changes.

Similar experiments were also done on NaDS. Coincidence between $\mathrm{CMC_s}$ and the concentrations at which ESR line width changes was also found here. The correlation time increases in the range from the first CMC, 3×10^{-2} M, to the second CMC, 7×10^{-2} M, and that at the concentration above the second CMC is about 0.93 times of that in case of SDS.

The increase in the correlation time may be interpreted as that Mn^{2+} ion is bound to the surfactant micelle.

The details of this investigation will be published later.

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[1] B. B. Garrett and L. O. Morgan, *J. Chem. Phys.*, **44**, 890 (1966).