The Effects of Added Electrolytes on Mn²⁺-ion Mobility in Micellar Solutions Studied by the ESR Method

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Synopsis.   The effects of added electrolytes on manganese-ion mobility in manganese dodecyl sulfate solutions $(Mn(DS)_2)$ were measured by means of the ESR method. The addition of aluminum chloride results in line-narrowing and an increase in the signal intensity in the ESR spectra at the concentrations above CMC of the $Mn(DS)_2$ solutions, while the addition of sodium chloride does not affect the ESR spectra.

To obtain information on counterion mobility in the interface between a micelle and the intermicellar solution, some investigations employing the manganese ion as an ESR probe of metal binding to sodium dodecyl sulfate (SDS) micellar solutions have been made by several groups of workers in recent years.[1,2] Above the CMC, it has been found that linewidth-broadening or signal-intensity loss in the ESR spectrum of the Mn^{2+} ion was caused by the Mn^{2+} ion in two environments surrounding the micelle: the manganese ion may be free in the intermicellar solution, or it may be attached to the micelles formed. In the hope of obtaining further corroborating evidence for this postulate, the present study, based on measurements of the linewidth and relative intensity of the Mn^{2+} ion, was performed for $Mn(DS)_2$ solutions, with and without added electrolytes.

The manganese dodecyl sulfate used was prepared by adding an excess of $MnSO_4$ to a SDS solution and by then cooling the solution in a dry ice–water bath. The SDS was synthesized according to the method of Dreger et al.[3]

The surface tensions on $Mn(DS)_2$ and SDS aqueous solutions were measured for the determination of the CMC by means of Kyowa Tensiometer. Surface-tension measurements in the redistilled water at 30 °C indicated no minima and CMC values of 8 mmol dm^{-3} for SDS and 1 mmol dm^{-3} for $Mn(DS)_2$, all in good agreement with those in the literature.[4] The inorganic electrolytes added, sodium and aluminum chlorides, were those of extra-pure reagents and had been purified by recrystallization.

For the preparation of the solution investigated, different amounts of the salts were dissolved in the $Mn(DS)_2$ solution at a given concentration above the CMC. For the concentrations below the CMC, the addition of the Al salt made precipitates, and so the measurements were made for solutions containing 5 mmol dm^{-3} and 10 mmol dm^{-3} $Mn(DS)_2$. The solutions thus obtained were directly inserted into a capillary tube 1.5 mm in o.d. and then sealed in the presence of air for the ESR measurements.

The ESR spectra were recorded with a Japan Electron Model JES-ME-3X spectrometer operating at the X band with 100-KHz field modulation.

In each measurement, six typical hyperfine lines were completely resolved. The linewidth (ΔH) was

directly measured as the peak-to-peak distance of the fourth line from the low-field side.[5] For a Lorentzian resonance line, the intensity is proportional to the product of the height of the derivative curve and the square of the linewidth. The relative intensity was obtained by comparing the (height) × (linewidth)² product with that of the reference sample in the cavity. A sample of 0.01 wt % DPPH dispersed homogeneously in solid KCl was used as the reference standard.[2,6] All the intensity measurements were made with the same sample volume in order to obtain a good reproducibility. In addition, identical microwave power, crystal biasing current, field-scanning rate, and modulation amplitude were used. Figure 1 shows the dependence of the linewidth (ΔH) and the increment
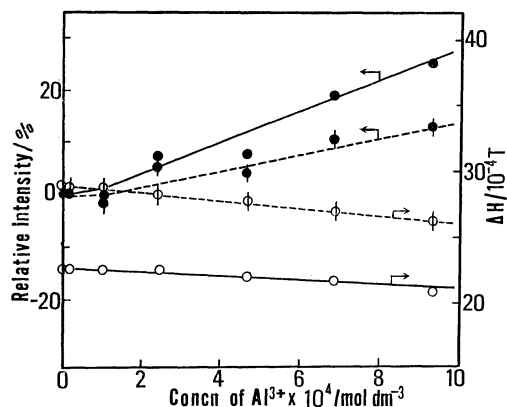

Fig. 1. Relative intensity (full points) and linewidth (open points) of Mn^{2+} as a function of added $AlCl_3$ concentration in $Mn(DS)_2$ solutions. —●—, —○—; 5 mmol dm^{-3} $Mn(DS)_2$, --●--, --○--; 10 mmol dm^{-3} $Mn(DS)_2$.
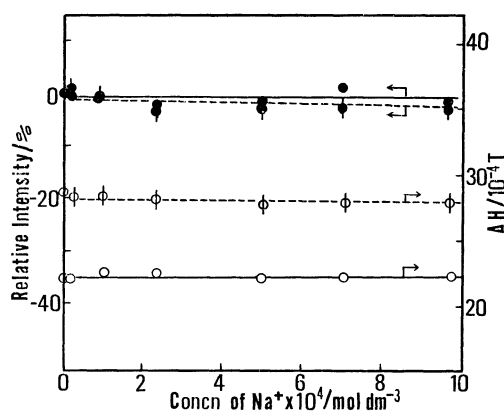

Fig. 2. Relative intensity (full points) and linewidth (open points) of Mn^{2+} as a function of added NaCl concentration in $Mn(DS)_2$ solutions. —●—, —○—; 5 mmol dm^{-3} $Mn(DS)_2$, --●--, --○--; 10 mmol dm^{-3} $Mn(DS)_2$.

in the relative intensity of the Mn^{2+} ion on the concentration of the added $AlCl_3$ at 30 °C, while in Fig. 2 the results for NaCl are presented. Although the figures show some scatter in the relative intensity, the much more pronounced effect of the Al^{3+} ion than that of the Na^+ ion at equimolar concentrations is immediatly obvious. On the further addition of the Al^{3+} ion, the linewidth tends to be appreciably narrower, whereas there is a corresponding increase in the relative intensity. On the contrary, no detectable changes in the ΔH and the intensity were observed upon the addition of NaCl in the range of the concentrations studied. This probably arises in part from the replacement of the Mn^{2+} ion with the more multivalent Al^{3+} ion in the electrical double layer at the micelle surface, followed by the increase in the average number of the free Mn^{2+} ion in the intermicellar solution. This fact was observed upon

the addition of Mn^{2+} or VO^{2+} ion to a SDS solution.[1,7] Some support for this result may also be given by the observation of the ESR spectra for $Mn(DS)_2$ solutions with no added salts, as is shown in Fig. 3. In agreement with the earlier finding,[2] the line-broadening is observed at the CMC, and it increases as the concentration is raised. Simultaneously, the signal intensity seems to increase in proportion to the number of the free Mn^{2+} ion, irrespective of the loss in the intensity due to the micellar-bound Mn^{2+} ion above the CMC, as has been stated by Oaks.[2]

On the basis of these deductions concerning the nature of the Mn^{2+} ion motion, the increase in the line-narrowing and intensity with the increase in the concentration of the added Al^{3+} ion can be explained in terms of a decrease in the amount of Mn^{2+} ions bound to the micelle relative to those "free" in the intermicellar solution.
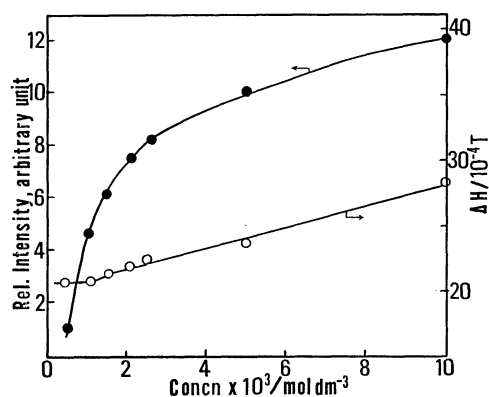

Fig. 3. Relative intensity and linewidth of Mn^{2+} as a function of $Mn(DS)_2$ concentration at 303 K.

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