BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3116—3121 (1970)

The Electron Spin Resonance of the Mn^{2+} Ion in Aqueous Surfactant Solutions[*1]

Akinori HASEGAWA, Yasuyoshi MICHIHARA and Masaji MIURA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

(Received June 8, 1970)

The ESR spectrum of the Mn^{2+} ion in an aqueous solution of a surfactant is affected by its concentration. Sodium dodecyl sulfate and sodium decyl sulfate were employed as surfactants in this study. The linewidth of the Mn^{2+} ion is independent of the concentration of the surfactant in the low-concentration range, but it increases over a certain concentration range and then becomes constant. Two values of CMC were observed by measurements of the conductivity corresponding to the concentrations, where the linewidth of Mn^{2+} changed abruptly with the concentration of the surfactant. The linewidth broadening above the first CMC was interpreted as being due to the formation of an outer-sphere complex of the Mn^{2+} ion with a surfactant micelle. The interaction between the counterion and micelle was also investigated on the basis of the ESR spectra of the Mn^{2+} ion with regard to the effects of the kind of surfactant, the temperature, foreign electrolytes, *etc.*

The manganese ion is a typical paramagnetic ion, and a number of ESR studies of this ion have been published.[1-3] Most of them have dealt with it in solid; trace amounts of cations in a solid are displaced by Mn^{2+} ions, and information with regard to the crystal field, the bond character, *etc.* can be obtained from the ESR spectrum of the Mn^{2+} ion. The method of the spin label of the cation with the Mn^{2+} ion is expected to be informative not only for solids but also for electrolytic solutions.

On the other hand, the formation of a complex ion between the Mn^{2+} ion and halogen ions, SO_4^{2-} ions, or $S_2O_4^{2-}$ ions has been studied by means of the ESR spectra of the Mn^{2+} ion.[4-6] In these studies, a two-step coordination model was proposed to explain the broadening of the ESR spectra of the Mn^{2+} ion and several parameters were estimated for the formation and dissociation of an inner- or outer-sphere complex. The electron-spin relaxation of the Mn^{2+} ion in a liquid solution has been investigated in terms of the solvent fluctuation model[7] and the ESR linewidths of the Mn^{2+} ion have been studied in various solvents.[8,9]

It is well-known that a counterion plays an important role in the formation of a surfactant micelle. In this paper, Mn^{2+} ion was added to an aqueous solution of a surfactant and the ESR spectra of the Mn^{2+} ion were observed. The interactions between the counterion and the surfactant micelle were discussed.

By the magnetic resonance technique, several attempts have been made to investigate the surfactant micelle. Some of them have been NMR studies using a hydrogen[10,11] or a fluorine[12-14] nucleus in a surfactant molecule, and others, ESR studies made by spin-labeling the micelle with a monoradical[15] or a biradical.[16] All of these methods

---

[*1] Briefly communicated by M. Miura, A. Hasegawa and Y. Michihara, This Bulletin, **41**, 534 (1968).

1) M. Miura, A. Hasegawa and M. Watanabe, *ibid.*, **41**, 1035 (1968).

2) R. A. Servay, *Phys. Lett.*, **A 26**, 642 (1968).

3) B. V. R. Chowdari, *J. Phys. Chem. Solids*, **30**, 2747 (1969).

4) R. G. Hayes and R. J. Myers, *J. Chem. Phys.*, **40**, 877 (1964).

5) D. C. McCain and R. J. Myers, *J. Phys. Chem.*, **72**, 4115 (1968).

6) L. Burlamacchi and E. Tiezzi, *ibid.*, **73**, 15 (1969).

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

8) C. C. Hinckley and L. O. Morgan, *ibid.*, **44**, 898 (1966).

9) S. I. Chan, B. M. Fung and J. Lutje, *ibid.*, **47**, 2121 (1967).

10) T. Nakagawa and K. Tori, *Kolloid Z.*, **194**, 143 (1964).

11) H. Inoue and T. Nakagawa, *J. Phys. Chem.*, **70**, 1108 (1966).

12) N. Muller and R. H. Birkhahn, *ibid.*, **71**, 957 (1967).

13) R. Haque, *ibid.*, **72**, 3056 (1968).

14) R. E. Bailey and G. H. Cady, *ibid.*, **73**, 1612 (1969).

15) A. S. Waggoner, O. H. Griffith and C. R. Christensen, *Proc. Nat. Acad. Aci. U. S.*, **57**, 1198 (1967).

16) S. Ohnishi, T. J. R. Cyr and H. Fukushima, This Bulletin, **43**, 673 (1970).

give information concerning the inner part of the micelle. In contrast to these investigations, the present study offers information with regard to the interactions between the counterion and surfactant micelle.

Theoretical

The theory of the ESR linewidth of the Mn^{2+} ion in a liquid solution has been developed in terms of the relaxation induced by the solvent fluctuation.[7] An outline of the theory will be given here.

The ESR spectra of the aqueous solutions of the Mn^{2+} ion exhibit six hyperfine components due to the electron spin, $S=5/2$, and the nuclear spin, $I=5/2$. Each of the hyperfine components also consists of five transitions for $m_s-1\leftrightarrow m_s$.

The linewidths for these transitions have been investigated in terms of the relaxation induced by solvent fluctuation. The theory was developed from the time-dependent spin-orbit interaction, using the spin density matrix. The resultant linewidths for the five transitions, $m_s-1\leftrightarrow m_s$, are:

$$\begin{aligned} \Delta H_{3/2,5/2} &= \Delta H_{-5/2,-3/2} = 2.633Z \\ \Delta H_{1/2,3/2} &= \Delta H_{-3/2,-1/2} = 2.312Z \qquad (1) \\ \Delta H_{-1/2,1/2} &= 1.971Z \end{aligned}$$

with

$$Z = C^2\tau_c/\boldsymbol{h}^2$$

where C is the trace of the perturbation Hamiltonian; τ_c, the perturbational correlation time, and $\boldsymbol{h}$, Planck's constant.

The spreads theoretically expected for these transitions, $m_s-1\leftrightarrow m_s$, were also demonstrated to depend upon the magnetic quantum number of nuclear spin by the calculation by means of the perturbation theory. The spread is the smallest, *ca.* 5 gauss, for $m_I=+1/2$ and the largest, *ca.* 30 gauss, for $m_I=-5/2$.

The apparent linewidth of $m_I=1/2$, therefore, is proportional to τ_c:

$$\Delta H_{m_I=1/2} \propto \tau_c \qquad (2)$$

Thus, the correlation time of the solvent fluctuation for the Mn^{2+} ion can be estimated from the linewidth of $m_I=1/2$.

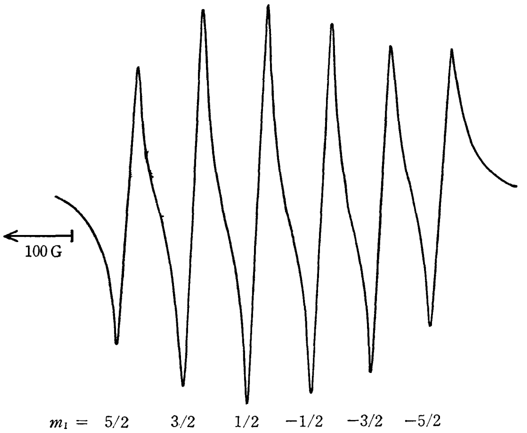
In the present system, the linewidth of the Mn^{2+} ion may also result from the relaxation due to the modulation of zero-field splitting induced by the tumbling motion of the complex.[17-19] The linewidth of $m_I=1/2$ can, any event, be a measure of the correlation time, τ_c.

Experimental

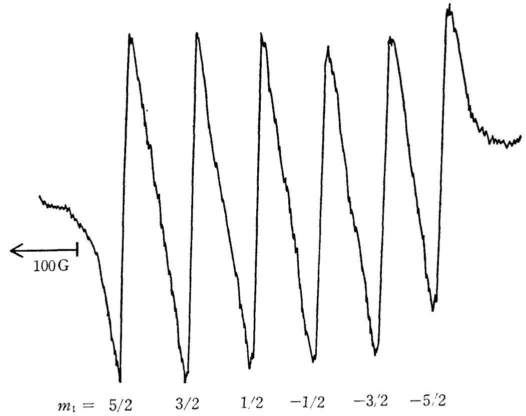
Sodium dodecyl sulfate (SDS) and sodium decyl sulfate (NaDS) were used as surfactants in this study. The former was synthesized and purified by Nippon Yushi Co. Ltd., and the latter, in our laboratory. Different amounts of surfactants were added to an aqueous solution of 1×10^{-3}M $Mn(NO_3)_2$. The solution thus obtained was sealed in a capillary of glass, and the ESR spectra were measured at different temperatures by using a spectrometer described elsewhere.[20] The conductivity measurements were carried out at 50°C or 25°C. To investigate the effect of electrolytes, 1×10^{-2}M $NaNO_3$ or KNO_3 was added to a surfactant solution containing the Mn^{2+} ion.

Results and Discussion

The ESR spectrum of the Mn^{2+} ion in the aqueous solution was remarkably affected by the con-



(a)
Fig. 1 (a)



(b)

Fig. 1. ESR spectra of the aqueous solutions of (a) 1×10^{-3}M and (b) 2×10^{-2}M SDS containing 1×10^{-3}M $Mn(NO_3)_2$ at 50°C.

---

[17] B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957).

[18] A. Carrington and G. R. Luckhurst, *Mol. Phys.*, **8**, 125 (1964).

[19] A. Hasegawa, *J. Chem. Phys.*, to be published.

[20] A. Hasegawa and M. Miura, This Bulletin, **40**, 2553 (1967).

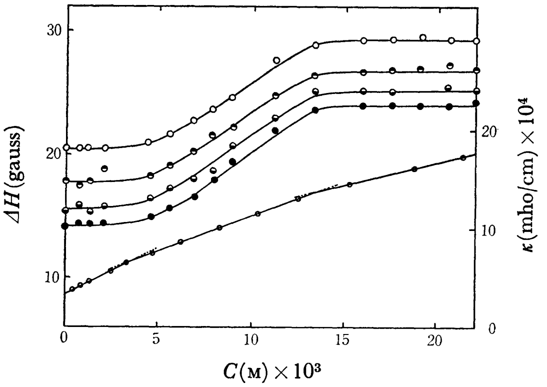


Fig. 2. The dependences of the linewidths (m_I: ○ $-5/2$, ◓ $-3/2$, ◒ $-1/2$ and ● $1/2$) and the conductivity (○) on the concentration of SDS at 50°C. The concentration of Mn^{2+} ion is 1×10^{-3}M. Symbols in the following figures have the same meaning as those in this figure except for Fig. 6.

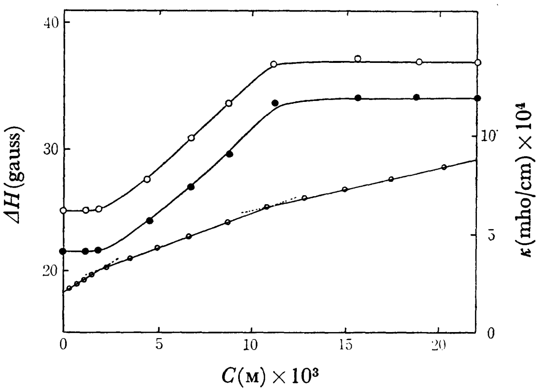


Fig. 3. The dependences of the linewidths and the conductivity on the concentration of SDS at 25°C. The concentration of Mn^{2+} ion is 1×10^{-3}M.

centration of the surfactant, as is shown in Fig. 1. The spectrum consists of six hyperfine structures, corresponding to the states of $m_I=-5/2$, $-3/2$, $-1/2$, $1/2$, $3/2$ and $5/2$ respectively, counting from the side of the lower magnetic field.

The variation in the linewidth is shown in Fig. 2, where the linewidths of four lines in the lower magnetic field are plotted against the concentration of SDS at 50°C. When the concentration of SDS is below 3×10^{-3}M, the linewidth is practically unaffected by the concentration. However, the linewidth increases with the concentration in the range from 3×10^{-3} to 13×10^{-3}M and becomes constant above 13×10^{-3}M. The linewidth of $m_I=1/2$, as is shown in Eq. (2), is proportional to the correlation time, τ_c, of the Mn^{2+} ion resulting from the fluctuation of the solvent shell. In the lower concentration range, the interaction between the Mn^{2+} ion and SDS seems negligibly small, because the correlation time is unaffected by the addition of SDS. The correlation time, however, increases over the concentration range from 3×10^{-3} to 13×10^{-3}M and then takes a constant value, which is 1.7 times that below 3×10^{-3}M.

The conductivity of the aqueous solution of SDS containing Mn^{2+} ions was measured at 50°C; the results are given in Fig. 2. Two broken points were observed, as may be seen in the figure, in the relation between the specific conductivity and the concentration. The concentrations at these broken points, which correspond to the first and the second critical micelle concentrations (CMC) respectively, counting from the lower concentration, are in good agreement with those observed in connection with ESR linewidth of the Mn^{2+} ion.

Similar results were obtained at 25°C, as may be seen in Fig. 3. Both the first and second CMC's decrease with a drop in the temperature, the rate of decrease being larger for the second CMC than for the first. The correlation time of the Mn^{2+} ion takes a higher value at 25°C than at 50°C, and the value below the first CMC at the lower temperature is nearly equal to that above the second CMC at the higher temperature.

A molecule of SDS has a hydrocarbon chain consisting of 12 carbon atoms. The CMC of surfactant generally increases with a decrease in the number of the carbon atom. Thus, sodium decyl sulfate (NaDS), with 10 carbon atoms in a hydrocarbon chain, was investigated. A change in the ESR linewidth of the Mn^{2+} ion was also observed, accompanied by an increase in the concentration of NaDS; the concentrations, where the linewidth abruptly changed, were in excellent agreement with the CMC's determined by the conductivity measurements. The linewidth of $m_I=1/2$ above the second CMC is 22.5 gauss at 50°C, as may be seen in Fig. 4, which is 93% of that in the case of SDS at 50°C. The correlation time, therefore, is short compared with that in the case of SDS.

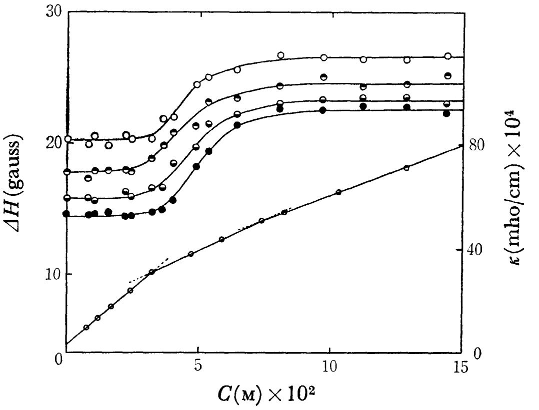


Fig. 4. The dependences of the linewidths and the conductivity on the concentration of NaDS at 50°C. The concentration of Mn^{2+} ion is 1×10^{-3}M.

The effects of the concentration of the Mn^{2+} ion on the two CMC's and on the linewidth of the ESR spectrum were investigated by using an NaDS solution containing Mn^{2+} ion in a concentration of 2×10^{-3}M. The increase in the concentration of the Mn^{2+} ion, as may be seen in Fig. 5, gave rise to the decreases in the CMC's and in the linewidth of the ESR spectrum above the second CMC.

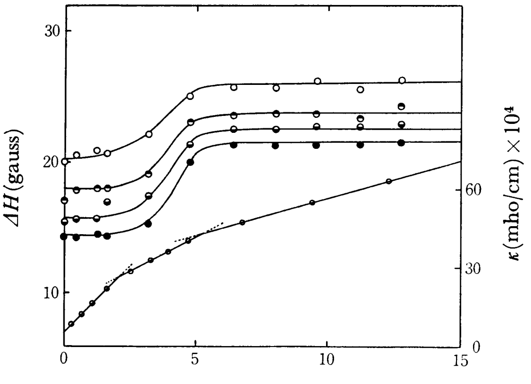


Fig. 5. The dependences of the linewidths and the conductivity on the concentration of NaDS at 50°C. The concentration of Mn^{2+} ion is 2×10^{-3}M.

Frenkel has proposed the following relation with regard to the structural correlation time, τ_c, in terms of the transient lattice model for liquids:[21]

$$\tau_c \propto \rho M/\eta T \qquad (3)$$

where η is the viscosity; M, the apparent molecular weight of fluctuating solvent; ρ, the density, and T, the absolute temperature. This relation has been proved by an investigation of the linewidths of the ESR spectra of the Mn^{2+} ion in kinds of solvents.[7]

The equation of viscosity is shown by:[22]

$$\eta = \boldsymbol{h}N_A/v \exp(\Delta F^{\neq}/\boldsymbol{R}T) \qquad (4)$$

where $\boldsymbol{h}$ is Planck's constant; N_A, Avogadro's number; v, the molar volume, and $\Delta F^{\neq}$, the standard free energy of activation per mole in the elemental process of the viscous flow. From Eqs. (2), (3), and (4), the following relation can be obtained:

$$\ln(\rho T\Delta H_{m_I=1/2}) = \Delta F^{\neq}/\boldsymbol{R}T + \ln K \qquad (5)$$

where K is the constant proportional to M. This equation shows the existence of a linear relation between ln $(\rho T\Delta H_{m_I=1/2})$ and $1/T$. The ESR spectra of the Mn^{2+} ion in the aqueous solutions of the two surfactants were then measured at different temperatures. The results exhibited linear relations, as was to be expected from Eq. (5), and as is shown in Fig. 6. The value of $\Delta F^{\neq}$ could be obtained from the gradient, and the constant, K, from the intercept. The values of $\Delta F^{\neq}$ for SDS and NaDS, both below the first CMC and above the second CMC, were determined to be equal to 2.0 kcal/mol in spite of the differences in the kind and concentration of the surfactant. On the other hand, the constant, K, which involves the apparent molecular weight of the solvent bringing about the fluctuation in the Mn^{2+} ion, changes with the kind and concentration of the surfactant. This may be attributed to the change in the apparent molecular weight of the solvent. From Eqs. (2) and (3), the apparent molecular weight of the solvent can be estimated by:

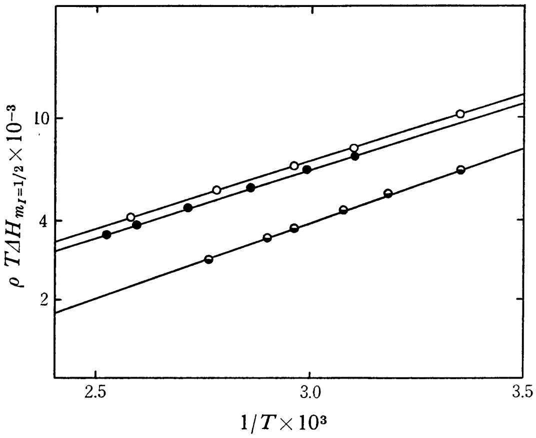


Fig. 6. The relations between $\rho T\Delta H_{m_I=1/2}$ and $1/T$.
◒: below the first CMC for SDS and NaDS
○: above the second CMC for SDS
●: above the second CMC for NaDS

$$M \propto \Delta H_{m_I=1/2}\rho T/\eta \qquad (6)$$

By using the ρ and η values of the aqueous solution measured at 25°C, and by assuming that the proportional constant in Eq. (6) is independent of the concentration of the surfactant, the apparent molecular weight of the solvent can be seen to increase over the region from the first CMC to the second CMC, and the ratio of the value above the second CMC to that below the first CMC can be determined to be 1.5 for the aqueous solution of SDS at 25°C.

From the fact that the broadening of the ESR spectrum of the Mn^{2+} ion is observed only above the first CMC, it is expected that the surfactant micelle participates in the solvent fluctuating the Mn^{2+} ion. As the micelle is very large compared with the water molecule, the apparent molecular weight of the solvent in the presence of the micelle might be expected to be much larger than that estimated above. It is, therefore, interesting to speculate about the interactions between the counterion and the micelle; one of the interactions is the ion-binding between them. One possible ion-

---

[21] J. Frenkel, "Kinetic Theory of Liquids," Dover Publications, New York (1955), pp. 188—208.

[22] S. Glasstone, J. Laidler and J. Eyring, "The Theory of Rate Processes," McGraw-Hill Co., New York (1941), p. 484.

binding is the formation of a complex in which the Mn^{2+} ion largely retains its full hydration sphere, an outer-sphere complex. At the other extreme, ion-binding is accomplished by the formation of an inner-sphere complex in which the Mn^{2+} ion is stripped of its hydration sphere.[5] The two-step process for complex ion formation can be shown by the following reaction equations:[5]

$$Mn^{2+}(H_2O)_n + X^{m-} \rightleftarrows Mn^{2+}(H_2O)_nX^{m-} \qquad (I)$$

$$Mn^{2+}(H_2O)_nX^{m-} \rightleftarrows Mn^{2+}X^{m-} \qquad (II)$$

where X^{m-} represents the micelle with negative charges. The two-step process has been proved for the Mn^{2+} ion in an aqueous solution containing an ion such as F^-, Cl^-, Br^-, I^-, SO_4^{2-}, or $S_2O_4^{2-}$.[4–6] In these studies, the first process was observed from a broadening of the ESR spectrum of the Mn^{2+} ion near room temperature, and the second one, from a broadening above 100°C. From these results, and from the fact that another broadening was found in an aqueous solution of surfactant near 130°C, the broadening of the ESR spectrum of the Mn^{2+} ion in a surfactant solution near room temperature is interpreted to be due to the process of the formation of an outer-sphere complex. Water molecules mainly, and surfactant micelles partially, participate in the fluctuation of the Mn^{2+} ion.

Accordingly, the "apparent molecular weight" described above is predominantly dependent on the forward and backward rate constants in the reaction (I) rather than an average size of the micelles. Several thermodynamic values for the reaction (I) could be evaluated on the basis of the broadening by the introduction of several assumptions, but that is far from our present purpose.

The broadening of the ESR spectrum above the first CMC may be interpreted in terms of the model in which the amount of the Mn^{2+} ion bound by the surfactant micelle increases with the amount of the micelle. Above the second CMC, no changes in the interaction between the Mn^{2+} ion and the micelle were observed from the ESR spectrum; this may suggest that practically all of the Mn^{2+} ions in the solution participate in the ion-binding with the micelle in the range from the first CMC to the second CMC.

The strength of the ion-binding or the forward rate constant of the reaction (I) is large for SDS as compared with that for NaDS.

The increase in the amount of the added Mn^{2+} ion, as may be seen in Figs. 5 and 6, gave rise to diminutions in both the first and the second CMC's and to a decrease in the correlation time above the second CMC. This may be due to the neutralization of the negative charges of the micelle with Mn^{2+} ions.

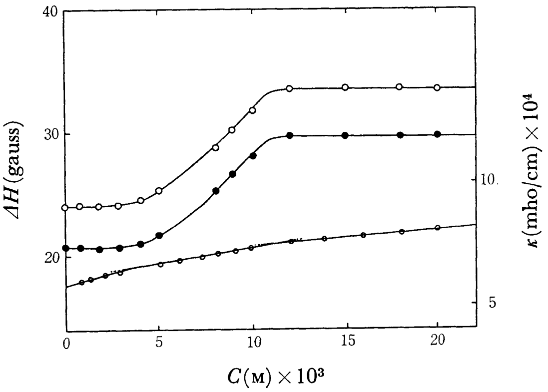


Fig. 7. The dependences of the linewidths and the conductivity on the concentration of SDS in the presence of 1×10^{-2}M $NaNO_3$, at 25°C. The concentration of Mn^{2+} ion is 1×10^{-3}M.

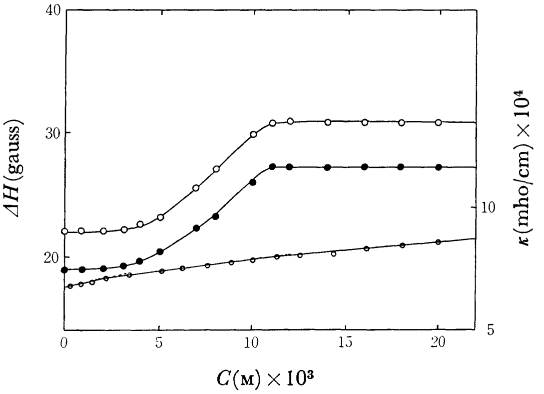


Fig. 8. The dependences of the linewidths and the conductivity on the concentration of SDS in the presence of 1×10^{-2}M KNO_3, at 25°C. The concentration of Mn^{2+} ion is 1×10^{-3}M.

Next, the effect of electrolytes on a surfactant solution containing the Mn^{2+} ion was investigated. Numerous authors have reported that the addition of simple electrolytes lowers the CMC of an ionic surfactant and increases the average size of the micelles.[23] Although alkali halides, *e.g.*, NaCl. KCl, and NaBr, are generally used for this purpose, halogen ions are inadequate for the present study because halogen ions give rise to a broadening of the ESR spectrum of the Mn^{2+} ion by forming outer-sphere complexes with the Mn^{2+} ion. Thus, such nitrates as $NaNO_3$ and KNO_3 were used for the following experiments (Figs. 7 and 8), since the nitric ion has no appreciable effect on the Mn^{2+} ion. By the addition of 1×10^{-2}M $NaNO_3$ or KNO_3, the broadening of the spectrum is diminished and the effect of KNO_3 on the diminution is superior to that of $NaNO_3$. This may be explained as follows: the added electrolytes weaken the bond between the Mn^{2+} ion and the surfactant micelle. The narrowing of the ESR spectrum of the Mn^{2+}

---

[23] M. J. Shik, *J. Phys. Chem.*, **68**, 3585 (1964).

ion arising from the addition of electrolytes observed below the first CMC corresponds to the fact that a linewidth narrowing was observed upon the initial addition of electrolytes to a solution of the Cr^{3+} ion.[24] This narrowing has been interpreted as being caused by a diamagnetic cation, which decreases the effective charge density of the anions in the outer-sphere.

Thus, by using a paramagnetic ion, the Mn^{2+} ion, as an indicator, several pieces of information with regard to the interaction between the counterion and the surfactant micelle were obtained from our measurements of the ESR spectrum of the ion.

---

24) K. M. Sancier, *ibid.*, **72**, 1317 (1968).