

ESR Spectra of Mn(II) Ions in Reversed Micellar Systems

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Synopsis. ESR spectra of hexaaqua complex of Mn(II) in a hexadecyltrimethylammonium bromide (HTAB)/chloroform reversed micellar system are studied. The structure of the Mn(II) complex is distorted at low water concentrations because of the dehydration due to the lack of water molecules available for the complexes. The effect of dehydration of metal ions on their catalysis for ATP hydrolysis is discussed.

In our previous papers,^{1,2)} we have attempted to characterize the water in reversed micellar systems primarily by near infrared spectra and nuclear magnetic resonance spectra. The water in micelle cores is less polar¹⁾ and more strongly immobilized²⁾ than the ordinary bulk water. A great deal of investigation has been made on the catalytic effects of reversed micellar systems.³⁾ For instance, the hydrolysis of adenosine 5'-triphosphate (ATP) is greatly enhanced with metal ions in a dodecylammonium propionate (DAP)-water-hexane system.¹⁾ In this paper, we intend to clarify the relationship between the nature of water in and the catalytic effect of reversed micelles by the ESR measurement of Mn(II) ions.

The ESR line width of Mn(II) ions in aqueous solutions has been studied by several workers. The relaxation of the ESR spectrum has been interpreted in terms of several mechanisms; Garrett and Morgan⁴⁾ proposed that the relaxation is principally due to solvent fluctuation around the solvated ions, and that at high temperatures the solvent-ligand exchange effect is not negligible in determining the ESR line width. The relaxation due to the spin-spin interaction is neglected in Mn(II) solutions of concentrations lower than 0.01 mol dm⁻³.⁵⁾ Therefore, if suitable conditions are chosen, the effect of spin-spin interaction and solvent-ligand exchange could be neglected in order to examine exclusively the effect of distortion of the solvent coordinated to metal ions. Thus, the ESR spectra of Mn(II) ions solubilized in the water pools of reversed micelles are expected to give valuable information on the nature of the water.

Experimental

ESR spectra at X band (9.4 GHz) were measured on a JEOL model JES-ME 3X spectrometer at a room temperature (22 °C ± 1 °C). Analytical grade MnCl₂·4H₂O was used without further purification. The purification of hexadecyltrimethylammonium bromide (HTAB), hexadecyltrimethylammonium chloride (HTAC), and chloroform was described previously.²⁾ Reversed micellar solutions were prepared according to the procedure in the literature.⁶⁾

Results and Discussion

The forth line ($m_l = +1/2$) of the ESR spectrum of Mn(II), which has six hyperfine lines, is the most

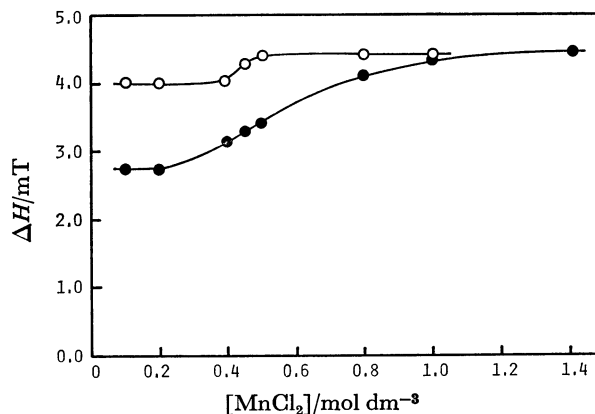


Fig. 1. Line width of Mn(II) as a function of MnCl₂ concentration in HTAB/CHCl₃ (○) and in aqueous (●) system.

[HTAB] = 0.20 mol dm⁻³ and [H₂O] = 0.444 mol dm⁻³.

suitable for line width measurements, since it is least affected by inhomogeneous broadening.⁷⁾ Figure 1 shows the line widths of Mn(II) in aqueous solutions and HTAB/chloroform reversed micellar solutions as a function of concentration of MnCl₂. As the Mn(II) ions hardly exist in the chloroform phase, the line widths for both systems are reasonably compared to each other at the same ratio of [Mn(II)]/[H₂O]. It is estimated in these systems that 0.2 mol dm⁻³ of MnCl₂ corresponds to 125 of the ratio of [HTAB]/[Mn(II)] and at most one Mn(II) ion per micelle by considering the aggregation number of HTAB. Therefore, the broadening arising from the spin-spin interaction is almost negligible below this concentration. The observed ESR parameters of hyperfine coupling constant (A) and line width (ΔH) in the reversed micellar system ($A=9.2$ mT and $\Delta H=4.0$ mT) are similar to those of [Mn(H₂O)₆]²⁺ ($A=9.2$ mT and $\Delta H=3.07$ mT)⁸⁾ and not to those of [MnCl₄]²⁻ ($A=7.9$ mT and $\Delta H=0.96$ mT) nor [MnBr₄]²⁻ ($A=7.5$ mT and $\Delta H=8.0$ mT).⁸⁾ Moreover, no spectral change was observed in HTAC compared to HTAB system, excluding the possible halogen coordination. Consequently, the ESR line broadening of hexa-aquamanganese(II) complex in the reversed micellar system under consideration is thought to be attributable to fluctuations in arrangement of six water molecules in the solvation sphere.

With an increase in water concentration resulting in larger water pools in the micellar cores, the line width of the ESR spectra decreases, gradually approaching to that in aqueous solution ($\Delta H=2.7$ mT in Fig. 2). Figure 3 represents the water concentration dependence of ESR signal intensity, which is proportional to the product of height of the derivative curve and square of its width.⁸⁾ It is interesting to

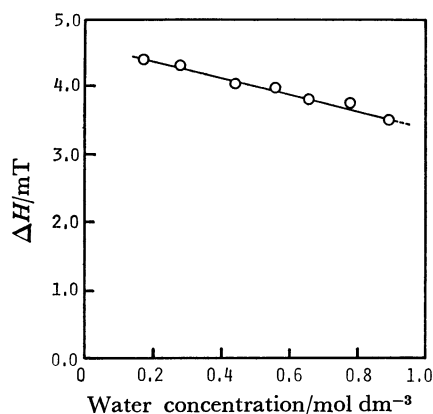


Fig. 2. Effect of water concentration on the line width of Mn(II) at a constant $[\text{Mn(II)}]/[\text{H}_2\text{O}]$ ratio. $[\text{Mn(II)}]=0.20 \text{ mol dm}^{-3}$ of water and $[\text{HTAB}]=0.20 \text{ mol dm}^{-3}$.

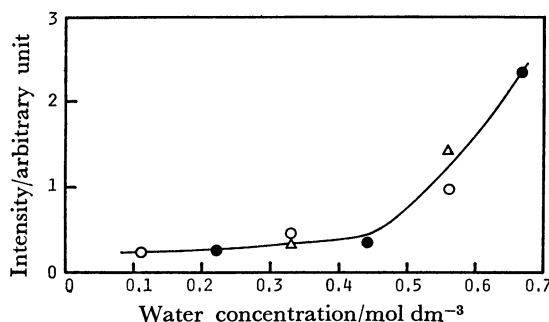


Fig. 3. Effect of water concentration of the ESR intensity of Mn(II). $[\text{HTAB}]=0.20 \text{ mol dm}^{-3}$, $[\text{Mn(II)}]=4.4 \times 10^{-4} \text{ mol dm}^{-3}$ (○), $8.8 \times 10^{-4} \text{ mol dm}^{-3}$ (●), and $13.2 \times 10^{-4} \text{ mol dm}^{-3}$ (△).

note that the intensity remains nearly constant below 0.4 mol dm^{-3} of water concentration irrespectively of the Mn(II) concentration. This indicates that the water of these lower concentrations interacts exclusively with polar head group of HTAB and does not participate in the solvation of Mn(II) ions. As the water concentration increases above 0.4 mol dm^{-3} , the ESR intensity increases even though the ratio of $[\text{Mn(II)}]/$

$[\text{H}_2\text{O}]$ decreases. These results indicate that after completion of the hydration shell of the polar head groups of HTAB molecules, water molecules begin to coordinate to Mn(II) ions. Similar results were obtained by Sunamoto and Hamada⁶⁾ and Wells⁹⁾ by visible spectra of CoCl_2 in the reversed micellar system.

It was reported in the previous paper¹⁾ that the polarity of water estimated from the λ_{max} value of pyridine 1-oxide in the DAP/hexane reversed micellar system decreases with a decrease in $[\text{H}_2\text{O}]/[\text{DAP}]$ ratio, and attains the value between ethanol and chloroform at low water concentrations. The apparent decrease in the polarity is considered to be attributed to the lower degree of hydration of pyridine 1-oxide. This conclusion is supported by the present result that Mn(II) ions are dehydrated in small water pools of reversed micellar cores. The rate enhancement of ATP hydrolysis in the presence of metal ions such as Mg(II) or Mn(II)¹⁰⁾ in the reversed micellar system mentioned above may be accounted as the result of dehydration of metal cations. This could promote the formation of metal-ATP complexes in the reversed micellar system, enhancing the nucleophilic attack of water at condensed phosphate group of ATP.

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