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HYDROPHOBIC INTERACTION BETWEEN TRIS(1,10-PHENANTHROLINE)-METAL(II) ION AND HEXANESULFONATE ION IN AQUEOUS SOLUTION

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The structure of the ion pair of $[M(phen)_3]^{2+}$ and the hexanesulfonate ion was investigated by ^{13}C NMR techniques. The importance of hydrophobic interaction was suggested.

Recently, attention has been aroused to the catalytic effect of ionic surfactants on the reactions of metal complexes.$^{1)}$ Especially, when metal complexes have large hydrophobic ligands, the hydrophobic interaction is considered to play an important role in the catalytic reactions. For example, it is known that racemization and dissociation of $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) are accelerated by anionic surfactants, presumably due to hydrophobic interaction between $[Fe(phen)_3]^{2+}$ and the anionic surfactants;$^{2,3)}$ however, no direct evidence has been presented.

In the present study, the nature of the interaction between $[M(phen)_3]^{2+}$ (M = Fe(II), Ni(II)) and the hexanesulfonate ion ($C_6H_{13}SO_3^-$) was examined from the structural point of view by NMR techniques. Although the catalyses of ionic surfactants in the reactions of metal complexes were usually investigated in micellar solutions, we thought that the interaction between a metal complex ion and a monomeric surfactant ion is more fundamental. Thus, we have made a study of the interaction between the $C_6H_{13}SO_3^-$ monomer and $[M(phen)_3]^{2+}$ in aqueous solution; the hexanesulfonate ion is known to form no micelles in the range of the hexanesulfonate concentrations studied here.$^{4)}$

The crystals of $[M(phen)_3](C_6H_{13}SO_3)_2$ for the preparation of sample solutions were obtained as follows. The chloride of each complexes was first prepared,$^{5,6)}$ and converted to the sulfate by the ion-exchange technique. The addition of $Ba(C_6H_{13}SO_3)_2$ to the sulfate solution yielded a solution of $[M(phen)_3](C_6H_{13}SO_3)_2$. Evaporation of the solution gave the crystals, which were recrystallized from water.

^{13}C NMR spectra were obtained on a JEOL FX-60 Fourier-transform spectrometer operating at 15.04 MHz with the D_2O solutions of $[M(phen)_3](C_6H_{13}SO_3)_2$ at 34.5 ±0.5 °C. The chemical shifts were measured in ppm up-field from the central peak of the triplet resonance of the tetramethylammonium ion (0.01 mol dm^{-3}) as the internal reference.$^{7)}$ The spin-lattice relaxation time (T_1) of ^{13}C NMR for

$C_6H_{13}SO_3^-$ was obtained by the inversion-recovery method. The samples for measuring T_1 had been bubbled with argon gas for ten minutes to remove oxygen gas from the solutions.

Figure 1 shows the ^{13}C chemical shifts of $C_6H_{13}SO_3^-$ observed at various concentrations of $[Fe(phen)_3](C_6H_{13}SO_3)_2$ relative to those for $C_6H_{13}SO_3Na$ in D_2O.

Now, we assume that only two kinds of hexanesulfonate ions with different ^{13}C chemical shifts exist in the solution: the free ion and the 1:1 ion pair with $[Fe(phen)_3]^{2+}$. Then, the observed ^{13}C chemical shift for each carbon atom of the hexanesulfonate ion is given by:

$$\delta_{obs} = P_{MX}\delta_{MX} + (1 - P_{MX})\delta_X \qquad (1)$$

or

$$\delta_{obs} - \delta_X = P_{MX}\Delta\delta_{MX} \qquad (\Delta\delta_{MX} = \delta_{MX} - \delta_X) \qquad (1)'.$$

Here, δ_{obs} is the observed chemical shift, δ_{MX} and δ_X are chemical shifts for the ion-paired and the free anion, respectively, and P_{MX} is the molar ratio of the ion-paired to the total of hexanesulfonate ions.

The δ_X value for each carbon atom of the hexanesulfonate ion was measured with a sodium hexanesulfonate solution in D_2O. The value of P_{MX} was calculated with the known association constant (15 $mol^{-1}dm^3$) for the $[Fe(phen)_3]^{2+}$-$C_6H_{13}SO_3^-$ ion pair.[3] The value of $\Delta\delta_{MX}$ for each carbon atom was obtained from the measured δ_{obs} value by the use of Eq. 1. Figure 2 shows the values thus obtained. Ion-pair formation caused up-field shifts of ^{13}C signals of $C_6H_{13}SO_3^-$; the shift was smallest in the β-position of the alkyl chain and increased in going toward the tail.

Figure 3 shows the ^{13}C spin-lattice relaxation rate $((T_1)^{-1})$ of each carbon atom of the hexanesulfonate ion measured in a 0.05 mol dm^{-3} $[Ni(phen)_3](C_6H_{13}SO_3)_2$ solution in D_2O. In this system, the relaxation of the ^{13}C spin is mainly caused by the interaction with the electron spins of $[Ni(phen)_3]^{2+}$. When a nuclear spin intermolecularly interacts with electron spins, the dominant relaxation mechanism is the electron-nuclear dipolar relaxation.[8] When the paramagnetic source is an octahedral nickel(II) complex, $(T_1)^{-1}$ in the fast motion limit is given by:[8,9]

$$(T_1)^{-1} = BT_{1e}r^{-6} \quad (B = 4g^2\gamma^2\beta^2S(S+1)/3) \qquad (2)$$

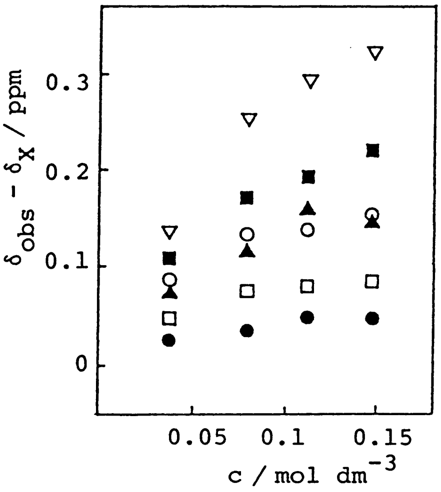

Fig. 1 Relative ^{13}C chemical shifts of hexanesulfonate ion in D_2O solutions of $[Fe(phen)_3]$-$(C_6H_{13}SO_3)_2$: ○, α-; ●, β-; □, γ-; ▲, δ-; ■, ε-; ▽, methyl-carbon. c = concentration of $[Fe(phen)_3](C_6H_{13}SO_3)_2$.

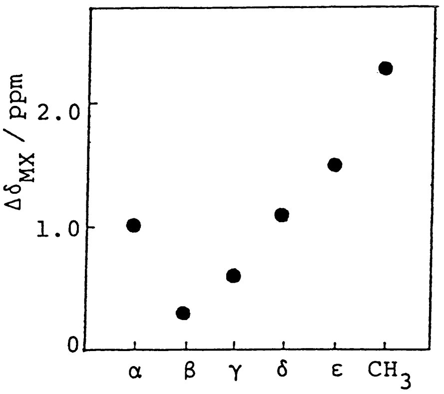

Fig. 2 Change in the ^{13}C chemical shifts ($\Delta\delta_{MX}$) of $C_6H_{13}SO_3^-$ due to fomation of the ion pair with $[Fe(phen)_3]^{2+}$.

where r is the distance between a particular carbon atom of $C_6H_{13}SO_3^-$ and the Ni(II) ion, γ the gyromagnetic ratio of the ^{13}C nucleus, and T_{1e} the electron spin relaxation time; other symbols have their usual meanings. We assume that the observed $(T_1)^{-1}$ can be divided into two parts : $(T_{1(X)})^{-1}$ for the free $C_6H_{13}SO_3^-$ and $(T_{1(MX)})^{-1}$ for the ion pair with $[Ni(phen)_3]^{2+}$.

$$(T_1)^{-1} = P_{MX}(T_{1(MX)})^{-1} + (1 - P_{MX})(T_{1(X)})^{-1} \qquad (3).$$

Here, we assumed that $(T_{1(X)})^{-1}$ can be approximated by the ^{13}C relaxation rate of $C_6H_{13}SO_3Na$ in D_2O, since the relaxation rate falls off quite sharply in proportion to r^{-6} between the associated and further removed ions.[8)] By considering the measured $(T_{1(X)})^{-1}$ values (Fig. 3) and the P_{MX} value (≈ 0.1),[3)] the second term of Eq. 3 can be disregarded. Then, Eq. 3 is approximated by:

$$(T_1)^{-1} \approx P_{MX}(T_{1(MX)})^{-1} \propto T_{1e}r_{MX}^{-6} \qquad (4)$$

where r_{MX} is the distance between a particular carbon atom of $C_6H_{13}SO_3^-$ and the Ni(II) ion in the ion pair. Since P_{MX} and T_{1e} are common to all the carbon atoms, the $(T_1)^{-1}$ value observed for each ^{13}C nucleus should be proportional to r_{MX}^{-6} for the carbon atom. Then, the results in Fig. 3 show that the δ- and ε-carbon atoms of the hexanesulfonate ion are placed closest to the nickel ion in the $[Ni(phen)_3]^{2+}$-$C_6H_{13}SO_3^-$ ion pair. The distance from the nickel ion becomes larger in going toward the α-carbon atom, which showed the smallest $(T_1)^{-1}$ value.

Here, we assume that the δ- and ε-methylene groups are in contact with the chelate cation in the $[Ni(phen)_3]^{2+}$-$C_6H_{13}SO_3^-$ ion pair. The distances from the Ni(II) ion to the δ- and ε- carbon atoms can be estimated at about 6 Å on the basis of crystal structure data.[10)] Then, by reference to Eq. 4, the $(T_1)^{-1}$ values given in Fig. 3 indicate that the carbon atoms of $C_6H_{13}SO_3^-$ in the ion pair are in a narrow range of distances between 6 Å and 7 Å from the Ni(II) ion and accordingly that the alkyl group of $C_6H_{13}SO_3^-$ is extended around the $[Ni(phen)_3]^{2+}$ ion.

In contrast to Fig. 3, Fig. 2 are characterized by the large up-field shift of the methyl-carbon signal due to formation of the $[Fe(phen)_3]^{2+}$-$C_6H_{13}SO_3^-$ ion pair. The up-field shift of the ^{13}C signals of the $C_6H_{13}SO_3^-$, except for α-carbon,[11)] is attributable to the ring-current of the

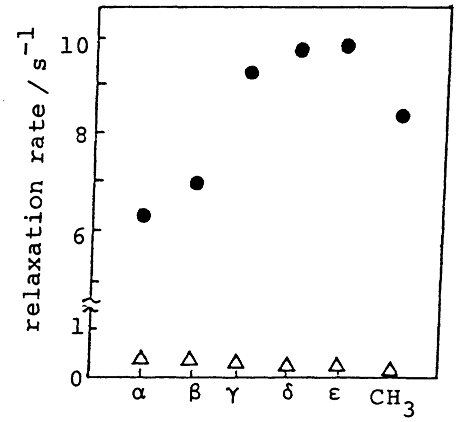

Fig. 3 ^{13}C relaxation rate of the hexanesulfonate ion in the D_2O solutions of 0.05 mol dm^{-3} $[Ni(fhen)_3](C_6H_{13}SO_3)_2$ (●, $(T_1)^{-1}$) and $C_6H_{13}SO_3Na$ (△, $(T_{1(X)})^{-1}$).

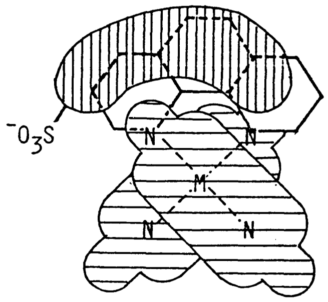

Fig. 4 Probable structure of the $[M(phen)_3]^{2+}$-$C_6H_{13}SO_3^-$ ion pair (▥, alkyl group of hexanesulfonate ion; ▤, phenanthroline ligand).

phenanthroline ligands.$^{12)}$ If the ring-current effect of the phenanthroline ligand is assumed to be the same as that of the benzene molecule, an up-field shift of about +0.8 ppm can be expected for a methylene or methyl carbon atom that is placed just above a phenanthroline ligand.$^{13,14)}$ The larger up-field shift observed for the methyl carbon signal (= +2.2 ppm) may be partly due to a larger shielding effect of phenanthroline than that of benzene, but can also be attributed to the effect of a neighboring phenanthroline ligand. If the latter is an important cause for the large shift, the methyl group can be expected to lie in a pocket between two phenanthroline ligands perpendicularly placed to each other. The trend of the $\Delta\delta_{MX}$ values as observed in Fig. 2 can also be related to the effect of the neighboring phenanthroline ligands, the effective number of which probably decreases in going from the methyl- to the β-carbon. The distance between the nickel and carbon atoms, on the other hand, changes only slightly from a carbon atom to another of the same hexanesulfonate ion. Similarly, the very small change in the β-carbon chemical shift may indicate that the β-carbon atom lies off the phenanthroline ligands.

Figure 4 represents a probable average structure. This, together with other experimental results obtained in our laboratory,$^{2,3)}$ demonstrates that hydrophobic interaction plays an important role in the $[M(phen)_3]^{2+}$-$C_6H_{13}SO_3^-$ ion pair.

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14) The distance from the carbon atom of the methyl group to the plane of the phenanthroline ligand was assumed to be 3.8 Å, which is approximately equal to the sum of the van der Waals radii.

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