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Tracer Diffusion of Tris(1,10-phenanthroline)iron(II) Cation in Aqueous Sodium Dodecyl Sulfate Solutions. Strong Premicellar Interactions

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Tracer diffusion coefficient of $Fe(phen)_3^{2+}$ (phen = 1,10-phenanthroline) has been determined in aqueous sodium dodecyl sulfate (NaDS) solutions at 298.2 K using Taylor dispersion technique. Below the critical micelle concentration (cmc) of NaDS (3 - 8 mM††), the diffusion coefficient is remarkably low, and increases with increasing concentration of NaDS.

Metal chelate ions of 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy) show hydrophobic property.[1,2] Such ions either stay in aqueous phase or are extracted into water-immiscible organic solvents depending upon the hydrophobicity of the counterions.[3] Our previous study on the tracer diffusion of $Fe(phen)_3^{2+}$ ion in aqueous NaBr, Na_2SO_4, Bu_4NBr (Bu = $n\text{-}C_4H_9$), and $Ni(phen)_3SO_4$ showed that the hydrophobic interaction between $Fe(phen)_3^{2+}$ and $Ni(phen)_3^{2+}$ reduced the diffusion coefficient of $Fe(phen)_3^{2+}$.[4] The degree of interaction is expected to be magnified when hydrophobic ions of different charges are involved. Reaction rates for racemization and dissociation of $M(phen)_3^{2+}$ (M=Fe or Ni),[5] and for fluorescence quenching of $Ru(bpy)_3^{2+}$ [6,7] have been reported to increase significantly when anionic surfactants are added; the accelerations start well below the cmc's of the surfactants, and the existence of the premicellar aggregates has been proposed. We report here the tracer diffusion coefficient of $Fe(phen)_3^{2+}$ cation in NaDS solutions, which is unusually low and shows unusual concentration dependence.

The diffusion coefficient was determined by Taylor dispersion technique.[8] The solvent flowing through the capillary tube contained a specified amount of NaDS plus 0.1 mM $Ni(phen)_3SO_4$, and the solution injected contained the same amount of NaDS plus 0.1 mM $Fe(phen)_3SO_4$. The concentration profile of $Fe(phen)_3^{2+}$ was detected by the absorption at 510 nm using a spectrophotometric

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††1 mM = 1×10^{-3} mol dm^{-3}.

Table 1. Tracer diffusion coefficients and Stokes radii for the diffusion of $Fe(phen)_3^{2+}$ ion in sodium dodecyl sulfate solutions at 298.15 K

[NaDS]/mM	$[Na_2SO_4]$/mM	$D/10^{-11}m^2s^{-1}$	r_S/nm
3.0		5.17 ± 0.12	4.74
4.0		5.61 ± 0.17	4.37
5.0		5.90 ± 0.27	4.16
6.0		6.39 ± 0.31	3.84
7.0		6.80 ± 0.24	3.61
8.0		7.41 ± 0.17	3.31
10.0[a]		8.22 ± 0.11	2.98
20.0[a]		8.56 ± 0.18	2.87
3.0	5.0	6.26 ± 0.15	3.92
3.0	10.0	6.72 ± 0.23	3.65
3.0[a]	20.0	7.47 ± 0.13	3.29
3.0[a]	100.0	8.05 ± 0.18	3.05

[a] These are solutions where normal micelles of NaDS exist.[15)]

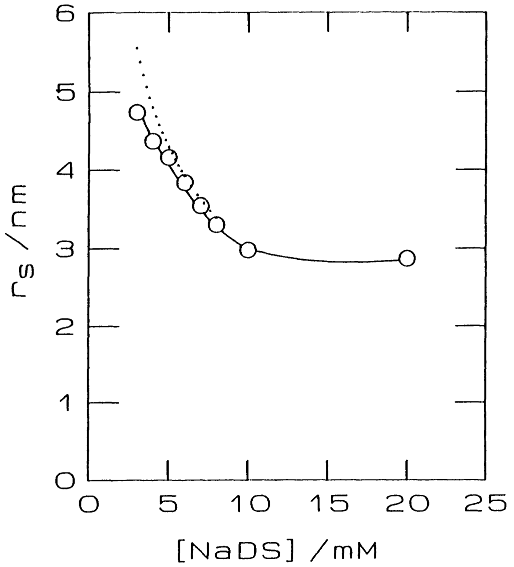

Fig. 1. Stokes radius as a function of NaDS concentration. Dotted line shows the Debye screening length in the premicellar concentration range.

detector for HPLC. Other details have been described elswhere.[4,9)] NaDS (BDH, specially pure) was used as received.[10)]

Table 1 shows the diffusion coefficients and the Stokes radii which were calculated by

$$r_S = \frac{kT}{6\pi\eta D} \qquad (1)$$

where k is Boltzmann's constant, T is the absolute temperature, and η is the viscosity of the solvent for which we used the value for pure water. The most striking finding is the fact that the diffusion coefficient of $Fe(phen)_3^{2+}$ is remarkably low; in 3 mM NaDS, it is about one tenth that in pure water, i.e., D = 4.64×10^{-10} m^2 s^{-1}.[4)] Furthermore, the diffusion coefficient is smaller when the concentration of NaDS is lower. We measured the conductivity of NaDS solution in the presence (0.2 mM) and absence of $Fe(phen)_3SO_4$. Both the slope and the breakpoint of the conductivity-vs.- concentration curve change only slightly in the presence of 0.2 mM $Fe(phen)_3SO_4$, which means that the normal micelles are not formed below 7-8 mM of NaDS. The similar results have been reported by other workers.[11,12)] Such a low diffusion coefficient of $Fe(phen)_3^{2+}$, however, suggests the existence of premicellar aggregates. In accord with previous workers who studied the systems containing $Ru(bpy)_3^{2+}$ and NaDS,[6,11)] we believe that almost all $Fe(phen)_3^{2+}$ ions are in the aggregates.

Tachiyashiki and Yamatera explained their results by 1:m (m=3 or 4) and 1:8 premicellar aggregates of $Fe(phen)_3^{2+}$ or $Ni(phen)_3^{2+}$ and DS^-.[5)] Baxendale and

Rodgers, who studied the fluorescence quenching in NaDS solutions using $Ru(bpy)_3^{2+}$ as an emitter and 9-methylanthracene as a quencher, showed that there exist "clusters" containg several $Ru(bpy)_3^{2+}$ ions below the cmc of NaDS. Another interesting result is that the quenching rate constant is larger in 6 mM than in 3 mM NaDS, which means that the quencher and the emitter are easier to encounter in the 6 mM clusters; they stated that the result "probably reflects the smaller cluster size" in 6 mM solution. Our results are consistent with their observation.

At this stage, however, it is not easy to estimate the cluster size unambiguously because the diffusion coefficient, or Stokes radius, reflects electrostatic interactions as well as the size of the clusters, or the premicellar aggregates. In other words, the Stokes radius can be expressed by

$$r_S = r_a + r_e \qquad (2)$$

where r_a is the radius of the aggregate itself, and r_e is the length reflecting the electrostatic interactions. It is known that, in the case of electrolyte-free monodisperse latex particles, the ordered structures are taken even in dilute solutions. Recently Okubo studied the structural relaxation time for such solutions.[13)] The translational diffusion coefficients for the particles were calculated from the structural relaxation times, and they were found to be much smaller than those estimated from the particle size. When the diffusion coefficcients were estimated for the spheres including the Debye screening length, r_D, however, the estimated and observed diffusion coefficients agreed well.

In Fig. 1, the Stokes radius is plotted as a function of the concentration of NaDS. Dotted line shows the Debye screening length calculated from

$$r_D = (4\pi e^2 \sum_i n_i z_i^2/\varepsilon kT)^{-1/2} \qquad (3)$$

where e is the electronic charge, n_i is the concentration of the free ion of the valency z_i, and ε is the dielectric constant of the solvent.[14)] If the interaction length, r_e in Eq. 2, is replaced by r_D, Stokes radius is equal to $r_a + r_D$. Although the concentration dependence of r_S is very similar to that of r_D in the premicellar range, the Stokes radius is not greater than the Debye screening length; this suggests that the interaction length, r_e, is smaller than r_D in our case. Debye screening length, or the thickness of the electric double layer is reduced when an electrolyte is added. As seen in Table 1, the addition of Na_2SO_4 decreases the Stokes radius. However, even when the highest amount of electrolyte was added, both in premicellar and micellar ranges (10 mM and 100 mM Na_2SO_4, respectively),[15)] the Stokes radius is still larger than that for NaDS micelles determined from tracer or mutual diffusion coefficient close to the cmc.[16)]

In conclusion, the results obtained here suggest strong interactions between $Fe(phen)_3^{2+}$ and DS^-, and the existence of premicellar aggregates. Recognition of such a low diffusion coefficient of $Fe(phen)_3^{2+}$ will help us to explain the effects of surfactants on various kinds of interactions and reactions involving such metal chelate ions.

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