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Interactions between the Tris(1,10-phenanthroline)iron(II) Cation and Anionic Surfactants: Diffusion and Conductance Studies

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Tracer diffusion coefficients for the $[Fe(phen)_3]^{2+}$ cation (phen=1,10-phenanthroline) have been measured in aqueous solutions of sodium 1-hexane-, 1-octane-, 1-decane-, and 1-dodecanesulfonate (NaDSO) in concentration ranges below the critical micelle concentrations of the surfactants and at 298.2 K. The diffusion coefficient decreases with an increase in the concentration of the surfactants. At a fixed concentration, the diffusion coefficient decreases with an increase in the carbon number of the surfactants. The results are compared with our previous results in sodium dodecyl sulfate (NaDS) solutions. The conductivities of the NaDSO and NaDS solutions were also measured at 298.2 K in the presence and absence of $[Fe(phen)_3]SO_4$. In the presence of $[Fe(phen)_3]SO_4$, the molar conductivities of the surfactants first decrease, then increase, and finally decrease again with an increase in the concentration of the surfactants.

Metal chelate ions of 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy) are known to be hydrophobic.[1,2] When counter ions are hydrophobic, such ions are extracted into water-immiscible organic solvents. Particularly, the red-colored chelate ions of iron(II) have been used extensively in analytical chemistry.[3] In recent years, there has been considerable interest in the reactions of these ions in aqueous surfactant media, i.e., racemization and dissociation reactions,[4] photochemical reactions,[5–8] and electron-transfer or electrochemical reactions.[9]

The elucidation of the solute-solute interactions between these metal chelate ions and other hydrophobic ions is important for an understanding of the reactions of these ions. Our previous study of the tracer diffusion of $[Fe(phen)_3]^{2+}$ in aqueous solutions showed that the hydrophobic interaction between $[Fe(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ reduced the translational diffusivity of $[Fe(phen)_3]^{2+}$.[10] Furthermore, we found that the tracer diffusion coefficient of $[Fe(phen)_3]^{2+}$ in water decreases greatly in the presence of sodium dodecyl sulfate (NaDS), even when the concentration of the latter is below its critical micelle concentration (cmc).[11]

We wish to report here the tracer diffusion coefficients for $[Fe(phen)_3]^{2+}$ in aqueous solutions of sodium 1-hexane-, 1-octane-, 1-decane-, and 1-dodecanesulfonate (NaHSO, NaOSO, NaDeSO, and NaDSO respectively), and the results will be compared with those in NaDS solutions. We also wish to report the conductivities of the $[Fe(phen)_3]SO_4$–NaDSO and $[Fe(phen)_3]SO_4$–NaDS systems.

Experimental

Materials. Reagent-grade Mohr's salt $[FeSO_4(NH_4)_2SO_4 \cdot 6H_2O]$, 1,10-phenanthroline monohydrate, $NiSO_4 \cdot 6H_2O$, $NaClO_4 \cdot H_2O$ (Wako Pure Chemicals), NaHSO, NaOSO, NaDeSO, (Tokyo Chemical Industry), and NaDS (BDH)[12,13] were used as received. The NaDSO (Tokyo Chemical Industry; ion-pair-chromatography grade) was recrystallized from an ethanol-methanol (5:1) mixture. The water was distilled twice. A stock solution of $[Ni(phen)_3]SO_4$ was prepared by mixing $NiSO_4 \cdot 6H_2O$ and phen$\cdot H_2O$ in water. A stock solution of $[Fe(phen)_3]SO_4$ was prepared by mixing $[Fe(phen)_3](ClO_4)_2$ with the sulfate form of an anion exchanger in water, after $[Fe(phen)_3](ClO_4)_2$ had been prepared from Mohr's salt, phen$\cdot H_2O$, and $NaClO_4 \cdot H_2O$.[10]

Measurements. The diffusion measurements were made by the Taylor dispersion method.[14] In this method, a small amount of a solution is injected into a solvent flowing through a capillary tube. The solute is dispersed along the tube as a result of a combination of convection and molecular diffusion. By detecting the concentration profile at the end of the stream, we can calculate the diffusion coefficient. The solvent contained a specified amount of a surfactant plus 0.1 mM (1 M=1 mol dm^{-3}) $[Ni(phen)_3]SO_4$, while the solution contained the same amount of the surfactant plus 0.1 mM $[Fe(phen)_3]SO_4$. The concentration profile of $[Fe(phen)_3]^{2+}$ was detected by the absorption at 510 nm using a spectrophotometric detector for HPLC (either Japan Spectroscopic Co., Model UVIDEC-100-IV or Waters, Model 490). The other details have been described elsewhere.[10,11,15]

The conductivities of the solutions were measured at 5 kHz by means of a linear-bridge conductometer[16] (Huso, Model 360B) in an oil thermostat controlled to ±0.005 K. Two conductivity cells were used: either a 500-cm^3 Kraus-type cell[17] with a cell constant of 0.3575 cm^{-1} or a 10-cm^3 cell with a cell constant of 2.464 cm^{-1}. Most of the measurements were made with the 500-cm^3 cell. A solvent was introduced into the cell, nitrogen gas was bubbled through when the solvent was pure water, and the cell with a solvent was weighed. A weighed amount of a solid solute was added after each resistance measurement under a nitrogen atmosphere. Some of the measurements on the concentrated solutions were, however, made by using the 10-cm^3 cell, where solutions were prepared by weight separately and transferred into the cell. The densities of some of the solutions were measured by means of a single-neck pycnometer to calculate the molar concentrations.

Results

Table 1 shows the diffusion coefficients of the $[Fe(phen)_3]^{2+}$ ion in sodium 1-alkanesulfonate solutions. Each value is the average of more than five measurements. The diffusion coefficients we measured are the interdiffusion coefficients between $[Fe(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$. If we assume that the diffusion coefficients of $[Fe(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ are essentially the same, the results may be taken as the intradiffusion coefficients[18] of $[M(phen)_3]^{2+}$, M being Fe or Ni. Because the concentration of the $[M(phen)_3]^{2+}$ ions (0.1 mM) is low compared to those of the surfactants, the results obtained can be considered as the tracer diffusion coefficients.

In Fig. 1, the diffusion coefficient is plotted as a function of the surfactant concentration. Our previous results in NaDS solutions[11] are included in the figure. As the surfactant chain length increases, the diffusion coefficient decreases, reflecting the interactions between $[Fe(phen)_3]^{2+}$ and the surfactant anions. Note that the concentrations of the surfactants are no greater than their cmc values except for the two solutions of NaDS (10 and 20 mM).[19,20] Figure 2 shows the Stokes radius, which was calculated from

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

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.[21] Many workers have studied the NaDS diffusion coefficient using different techniques; the Stokes radius for the micelles at cmc is 2.2—2.5 nm.[22] Although we do not have data for NaDeSO, the Stokes radius for sodium decyl sulfate (NaDeS) micelles at the cmc has been reported to be 1.98 nm in 0.1 M NaCl.[23] Thus, even in the premicellar concentration range, in NaDS and NaDSO solutions, the Stokes radius of $[Fe(phen)_3]^{2+}$ is larger than that of the NaDS micelles; in 30 and 40 mM NaDeSO solutions, the Stokes radius of $[Fe(phen)_3]^{2+}$ is close to that of the NaDeS micelles.

In order to obtain more information, we measured the conductance of solutions. The molar conductivities of NaDSO and NaDS in water and $[Fe(phen)_3]SO_4$ solutions were calculated from

Table 1. Tracer Diffusion Coefficients of $[Fe(phen)_3]^{2+}$ in Aqueous Sodium 1-Alkanesulfonate Solutions at 298.15 K

[Surfactant]/mM	$D/10^{-10}m^2s^{-1}$
In $NaC_6H_{13}SO_3$	
4	4.31±0.05
10	4.24±0.02
20	4.13±0.05
In $NaC_8H_{17}SO_3$	
4	4.12±0.06
10	3.92±0.02
20	3.69±0.04
In $NaC_{10}H_{21}SO_3$	
4	3.83±0.04
10	2.99±0.02
20	1.79±0.02
30	1.37±0.01
40	1.23±0.03
In $NaC_{12}H_{25}SO_3$	
2	1.420±0.030
3	0.961±0.010
4	0.841±0.012
5	0.790±0.015
6	0.754±0.010
7	0.755±0.029

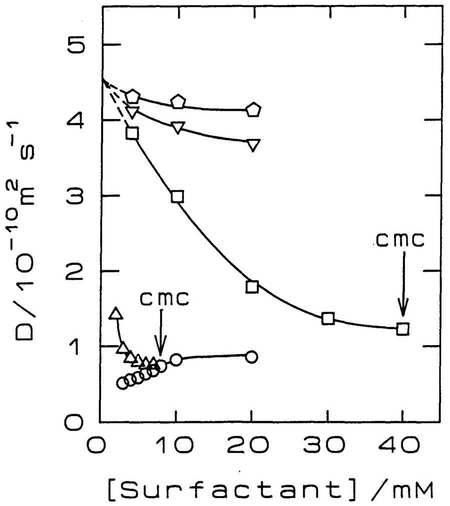

Fig. 1. Tracer diffusion coefficients of $[Fe(phen)_3]^{2+}$ in aqueous surfactant solutions. ⬠, In NaHSO; ▽, in NaOSO; □, in NaDeSO; △, in NaDSO; ○, in NaDS.[11] Arrows indicate cmc's for NaDeSO and NaDS.

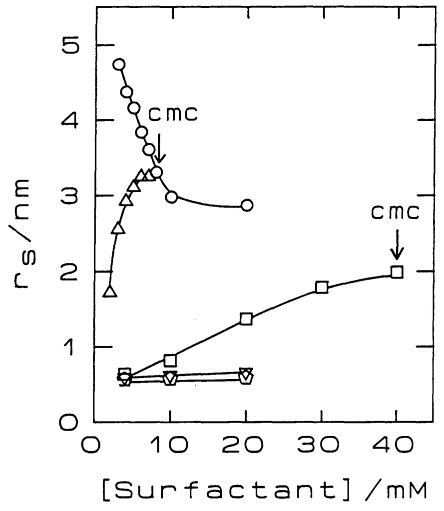

Fig. 2. The Stokes radii of $[Fe(phen)_3]^{2+}$ in aqueous surfactant solutions. Symbols are the same as in Fig. 1.

Table 2. Molar Conductivities of Sodium 1-Dodecanesulfonate in Water and in Aqueous $Fe[(phen)_3]SO_4$ Solutions at 298.15 K

C/mM	Λ/S cm^{2}mol^{-1}	C/mM	Λ/S cm^{2}mol^{-1}
In water		6.241	55.31
($10^6\kappa_0$/S cm^{-1}=0.21)		6.994	55.45
0.857	69.84	7.739	55.68
1.785	68.84	8.505	55.32
2.776	68.08	9.180	55.21
3.878	67.39		
5.148	66.63	In 1.0 mM $[Fe(phen)_3]SO_4$	
6.064	66.27	($10^6\kappa_0$/S cm^{-1}=204.47)	
7.089	65.82	0.389	50.68
8.018	65.57	0.771	49.21
		1.166	42.68
In 0.21 mM $[Fe(phen)_3]SO_4$		1.560	40.00
($10^6\kappa_0$/S cm^{-1}=45.75)		1.928	39.11
0.386	63.50	2.339	38.64
0.776	63.83	2.712	38.98
1.164	62.85	3.157	39.57
1.535	60.68	3.517	40.93
1.927	59.92	3.991	42.11
2.315	59.83	4.696	44.13
2.689	60.03	5.499	45.92
3.072	60.30	6.249	47.32
3.784	60.85	7.017	48.03
4.538	61.15	7.825	48.55
5.355	61.31	8.768	49.04
6.144	61.57	9.530	48.94
6.860	61.18		
7.567	60.97	In 2.0 mM $[Fe(phen)_3]SO_4$	
8.342	60.71	($10^6\kappa_0$/S cm^{-1}=391.65)	
9.103	60.31	0.401	41.41
9.878	59.70	0.790	37.43
		1.198	34.19
In 0.5 mM $[Fe(phen)_3]SO_4$		1.611	31.64
($10^6\kappa_0$/S cm^{-1}=106.87)		2.000	31.52
0.414	57.81	2.416	30.71
0.827	57.60	2.794	30.59
1.208	51.90	3.197	30.89
1.665	49.21	3.620	31.27
2.043	48.85	4.425	31.32
2.408	49.33	5.213	32.45
2.757	50.12	6.010	33.85
3.147	51.04	6.772	35.76
3.930	52.75	7.528	37.39
4.692	54.03	8.360	38.40
5.471	54.78	9.184	39.66

$$\Lambda = \frac{1000(\kappa - \kappa_0)}{C}, \tag{2}$$

where κ is the conductivity of the solution, κ_0 is the conductivity of the solvent (i.e., either water or a $[Fe(phen)_3]SO_4$ solution without surfactant), and C is the molarity of the surfactant. The molar conductivities of NaDSO and NaDS are listed in Tables 2 and 3 respectively; they are plotted as a function of the surfactant concentration in Fig. 3.

Table 3. Molar Conductivities of Sodium Dodecyl Sulfate in Water and in Aqueous $[Fe(phen)_3]SO_4$ at 298.15 K

C/mM	Λ/S cm^{2}mol^{-1}	C/mM	Λ/S cm^{2}mol^{-1}
In water		12.051	48.09
($10^6\kappa_0$/S cm^{-1}=0.10)		13.102	46.70
1.575	69.48		
3.083	68.41	($10^6\kappa_0$/S cm^{-1}=102.19)	
4.498	67.67	9.387	51.13
5.101	67.39	10.915	49.25
6.059	67.03	12.566	47.09
8.110	64.67	14.261	44.85
9.276	61.04	16.322	42.50
10.642	56.78	18.257	40.67
11.858	53.58	20.575	39.23
12.623	52.01		
13.213	50.61	In 1.0 mM $[Fe(phen)_3]SO_4$	
		($10^6\kappa_0$/S cm^{-1}=198.91)	
($10^6\kappa_0$/S cm^{-1}=0.55)		4.811	42.14
8.480	64.35	5.482	43.85
10.814	56.66	6.109	44.69
14.388	48.58	6.780	45.23
14.477	48.30	7.445	45.52
		8.178	45.53
($10^6\kappa_0$/S cm^{-1}=1.5)		8.958	45.37
10.109	58.22[a]	9.609	45.22
19.181	42.10[a]	10.848	44.48
29.845	35.81[a]	12.095	43.66
39.218	33.28[a]		
		($10^6\kappa_0$/S cm^{-1}=196.07)	
In 0.20 mM $[Fe(phen)_3]SO_4$		12.161	44.04
($10^6\kappa_0$/S cm^{-1}=42.10)		13.852	42.85
2.662	59.30	15.632	41.27
3.687	60.32	17.119	40.08
4.922	60.70	18.867	38.89
5.531	60.40	20.399	37.95
6.664	59.80	22.382	36.81
7.944	58.84	23.867	36.02
9.287	56.82		
10.502	54.35	In 2.0 mM $[Fe(phen)_3]SO_4$	
11.797	51.59	($10^6\kappa_0$/S cm^{-1}=391.43)	
13.093	49.11	8.133	36.54
14.660	46.55	8.882	37.52
16.217	44.42	9.621	37.65
18.057	42.27	10.348	38.04
		11.125	38.15
In 0.50 mM $[Fe(phen)_3]SO_4$		11.993	38.20
($10^6\kappa_0$/S cm^{-1}=105.26)		14.504	37.76
3.698	51.01		
4.434	52.28	($10^6\kappa_0$/S cm^{-1}=385.87)	
5.181	52.97	20.280	36.36[a]
5.945	53.30	23.278	35.32[a]
6.714	53.24	26.307	34.40[a]
7.486	52.97	29.627	33.71[a]
8.252	52.44	33.918	32.33[a]
9.011	51.82	36.409	32.31[a]
9.752	51.04	42.894	31.51[a]
10.939	49.56		

a) These measurements were made using a 10-cm^3 cell. See text for more details.

In the presence of $[Fe(phen)_3]SO_4$, the molar conductivity of NaDSO decreases, passes through a minimum, and increases again with an increase in the concentration of NaDSO. This tendency becomes more marked with an increase in the concentration of $[Fe(phen)_3]SO_4$. Measurement in higher concentrations of NaDSO was not possible because the Krafft temperature of NaDSO is high (306 K).[20] In the case of NaDS, when we add the surfactant to a solution of $[Fe(phen)_3]SO_4$, a precipitate of $\{[Fe(phen)_3](DS)_2\}_n$

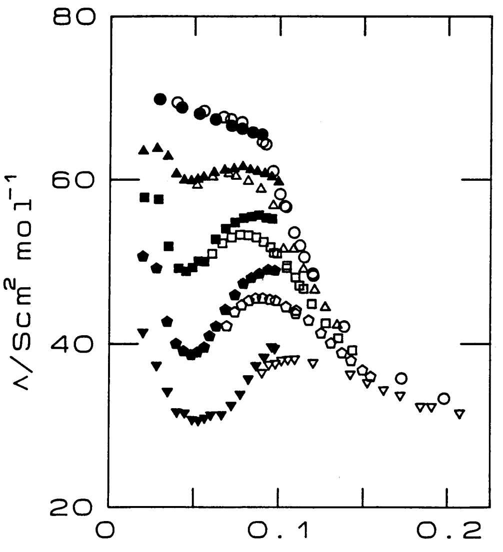

Fig. 3. Molar conductivities of NaDSO (closed symbols) and NaDS (open symbols) in water and aqueous $[Fe(phen)_3]SO_4$. Concentrations of $[Fe(phen)_3]SO_4$ are 0 mM (● and ○), 0.2 mM (▲ and △), 0.5 mM (■ and □), 1 mM (⬟ and ⬠), and 2 mM (▼ and ▽).

appears; this precipitate is then resolubilized by the further addition of NaDS.[24,25] For example, in the case of 0.2 mM $[Fe(phen)_3]SO_4$, we found that a precipitate appears when the NaDS concentration is 0.13 mM and that it is resolubilized when the NaDS concentration reaches 2.1 mM. The results shown in Fig. 3 are in NaDS concentration ranges higher than the resolubilization points. In this case, we made measurements also in the NaDS concentrations above the cmc. With an increase in the concentration of NaDS, the molar conductivity increases, passes through a maximum, decreases, and finally approaches that in pure water.

Discussion

When $[Fe(phen)_3]SO_4$ and a surfactant NaA are mixed, the reaction which takes place may be written as:

$$x[\mathrm{Fe(phen)_3}]^{2+}+y\mathrm{A}^-+z\mathrm{Na}^+ \leftrightarrows \mathrm{Na}_z[\mathrm{Fe(phen)_3}]_x\mathrm{A}_y{}^{(y-2x-z)-}. \tag{3}$$

As we noted earlier, in 3—8 mM NaDS and 3—7 mM NaDSO the Stokes radius of $[Fe(phen)_3]^{2+}$ is larger than that of the NaDS micelles. However, the conductance results do not show the existence of normal micelles in these concentration ranges. As may be seen in Fig. 3, even in 0.2 mM $[Fe(phen)_3]SO_4$ the molar conductivities of NaDS and NaDSO are much higher than that of NaDS above the cmc. (Note that the concentration of $[M(phen)_3]^{2+}$ was 0.1 mM in the diffusion measurements.) A similar conclusion has been reached on the basis of surface-tension and light-scattering measurements.[24]

The Stokes radius may reflect electrostatic interactions as well as the size of the premicellar aggregates. The electrostatic interaction is reduced when a salt is added. Even when Na_2SO_4 was added to 3 mM NaDS, the Stokes radius of $[Fe(phen)_3]^{2+}$ was still larger than that of the NaDS micelles.[11] In a 3 mM surfactant solution, the molar ratio of the surfactant to $[Fe(phen)_3]^{2+}$ is 30. If the size of an aggregate is larger than that of an NaDS micelle which contains 60 monomers, the value of x in Eq. 3 has to be larger than 2. From a luminescence-quenching study, it has been reported that $[Ru(bpy)_3]^{2+}$ forms premicellar "clusters" with NaDS which contain several $[Ru(bpy)_3]^{2+}$.[5]

The fact that there is precipitate-formation between $[Fe(phen)_3]^{2+}$ and DS^-, but not between $[Fe(phen)_3]^{2+}$ and DSO^-, together with the fact that there is a lower diffusion coefficient for $[Fe(phen)_3]^{2+}$ in NaDS than in NaDSO (Fig. 1), suggests a stronger interaction between $[Fe(phen)_3]^{2+}$ and DS^- than between $[Fe(phen)_3]^{2+}$ and DSO^-. Just above those concentrations, where the precipitate $\{[Fe(phen)_3](DS)_2\}_n$ is resolubilized, the molar conductivities of NaDS are only slightly lower than those of NaDSO, as if the system has lost the memory that it has had a precipitate. This is in contrast to the definitely smaller diffusion coefficient of $[Fe(phen)_3]^{2+}$ in NaDS than in NaDSO (Fig. 1). In the case of diffusion, we are looking at the movement of $[Fe(phen)_3]^{2+}$ ions. Because the concentration of $[Fe(phen)_3]^{2+}$ is small almost all $[Fe(phen)_3]^{2+}$ ions are considered to be in premicellar aggregates, and the diffusion coefficient of $[Fe(phen)_3]^{2+}$ is essentially that of the aggregates; thus, it is sensitive to the aggregate size.

In the case of conductivity, the situation is more complicated. Below the cmc of a surfactant NaA, the molar conductivity of the surfactant can be expressed by

$$\begin{aligned}\Lambda(\mathrm{NaA})=\{&[C_t(\mathrm{NaA})-\Delta C(\mathrm{Na}^+)]\lambda(\mathrm{Na}^+)\\&+[C_t(\mathrm{NaA})-\Delta C(\mathrm{A}^-)]\lambda(\mathrm{A}^-)\\&-2[\Delta C([\mathrm{Fe(phen)_3}]^{2+})]\lambda([\mathrm{Fe(phen)_3}]^{2+})\\&+(y-2x-z)[\Delta C(\mathrm{A}^-)/y]\lambda(\mathrm{aggregate})\}/[C_t(\mathrm{NaA})],\end{aligned} \tag{4}$$

where "aggregate" refers to the right-hand side of Eq. 3, $C_t(X)$ means the total molar concentration of X in the solution, $\Delta C(X)$ means the molar concentration of X in the aggregates, and $\Lambda(X)$ or $\lambda(X)$ means the molar conductivity of X, expressed as the (X/valency) molar unit, i.e., the equivalent conductivity. In other words, the molar conductivity of NaA, as calculated from Eq. 2, has contributions from: 1) the free ions of Na^+ and A^-, 2) the $[Fe(phen)_3]^{2+}$ ions which were used to form the aggregate (negative contribution), and 3) the aggregates themselves. In Fig. 3, the initial part of the decrease in Λ of NaDSO may be attributed to aggregate formation, which reduces the concentrations of the free Na^+, DSO^-, and $[Fe(phen)_3]^{2+}$ ions. After passing through the minima, Λ increases because the concentration of $[Fe(phen)_3]^{2+}$ is fixed and the aggregate formation is saturated. This is the concentration region where the precipitate $\{[Fe(phen)_3](DS)_2\}_n$ is resolubilized, and the system has sufficient free ions of Na^+ and DS^-. This is why the conductance results do not differ drastically between NaDS and NaDSO. After passing through the maxima, the conductivities decrease because normal micelles are formed.

Although DSO^- and DS^- differ from each other by only one oxygen atom, there is a large difference between their behavior when the solid state or a highly condensed state is involved, i.e., 1) DS^- forms a precipitate with $[Fe(phen)_3]^{2+}$ but DSO^- does not, 2) NaDSO is stable in a solid state rather than micelles at 298 K (the Krafft temperature is high) but NaDS forms micelles at the same temperature. Also, there are differences between their premicellar aggregates, as seen in the differences in their diffusion coefficients (Fig. 1).

Comparison with Other Studies. It is of interest to compare the above results with those in the previous work of others. Tachiyashiki and Yamatera have found that the reaction rates for the racemization and dissociation of $[M(phen)_3]^{2+}$ (M=Fe or Ni) increase significantly when anionic surfactants are added.[4] They start increasing below the cmc's of the surfactants: 20, 1—2, and 0.3—0.4 mM for NaDeSO, NaDSO, and NaDS respectively. It is worth noting that, at these concentrations, the diffusion coefficient is significantly lowered, i.e., to ca. 2×10^{-10} m^2 s^{-1} or lower (Fig. 1). Tachiyashiki and Yamatera could explain their results by assuming the formation of $1{:}m$ premicellar aggregates between the metal chelate cations and surfactant anions, i.e., 1 : 8 aggregates for NaDeSO, and 1 : 3 or 1 : 4 plus 1 : 8 aggregates for NaDSO and NaDS. They could also explain the result for $[Fe(bpy)_3]^{2+}$ in NaDS in terms of 1 : 3 or 1 : 4 plus 1 : 8 aggregates.

Baxendale and Rodgers found that the luminescence quenching rate of $[Ru(bpy)_3]^{2+}$ is increased by 9-methylanthracene (MeA) in a NaDS solution, even when the concentration of NaDS is below the cmc.[5] They interpreted this result as being due to the formation of premicellar clusters which incorporate the emitter and quencher molecules. The quenching rate constant is larger in 6 mM NaDS than in 3 mM NaDS (both below the cmc). This led them to state, "The higher value of k_1 (the rate constant) for 6 mM NaDS probably reflects the smaller cluster size which could put quencher and emitter in closer proximity." This is in conformity with the smaller Stokes radius of $[Fe(phen)_3]^{2+}$ in 6 mM than in 3 mM NaDS (Fig. 2). They also found that the quenching rate constant is larger in micellar systems than in premicellar solutions; they stated that this "may arise from a higher mobility of the species on the micelle surface." However, from the data presented in Fig. 2, an alternative interpretation would be that the smaller size of the micelles puts emitter and quencher in closer proximity, thereby increasing the quenching rate. The quenching of $[Ru(bpy)_3]^{2+}$ fluorescence by the 1,1′-dimethyl-4,4′-bipyridinium cation (MV^{2+}) has also been reported to be enhanced in NaDS solutions below the cmc.[6—8]

Bruhn and Holzwarth have found that the rates of electron-transfer reaction between the $[Os(bpy)_3]^{3+}/[Mo(CN)_8]^{4-}$, $[Os(bpy)_3]^{3+}/[Fe(CN)_6]^{4-}$, and $[Ir(CN)_6]^{2-}/[Os(bpy)_3]^{2+}$ ions decrease when NaDS is added; they start decreasing when the NaDS concentration is still below the cmc.[9a] This may be interpreted as a result of the interaction between the $[Os(bpy)_3]^{n+}$ (n=2 or 3) and DS^- ions, which prevents $[Os(bpy)_3]^{n+}$ ions from coming in contact with the hydrophilic anions.

Thus, although there are some exceptions,[9c,25] there are many observations of different kinds which support the formation of premicellar aggregates when $[M(phen)_3]^{2+}$ or $[M(bpy)_3]^{2+}$ cations and anionic surfactants are mixed together. The detailed picture of the aggregates, however, still differs from one observation to another; especially, our finding of a large premicellar aggregate size is unique.

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