

2 in the 3500–3600-cm⁻¹ region as compared to the 2800–2900-cm⁻¹ region strongly suggest the presence of 2b. Finally, it is possible that HF prefers the 2b structure and that DF prefers 2a, since DF preferentially bonds to HF rather than the reverse.²⁶

The bands identified as 3 in these experiments are due to higher aggregates. In the methyl and ethyl sulfide experiments, the broad, strong absorptions in 3300-cm⁻¹ region could be due to a dimer of dimers, i.e. two 1:1 complexes or some higher polymer such as a 1:3 complex. In the thiol experiments, the third hydrogen could participate in higher clusters, but the clear trend in H–F modes coming just below the 1:1 complex and 1:2 complex values suggest a chain type 1:3 complex following a chain type 1:2 complex.

(26) Hunt, R. D.; Andrews, L. *J. Chem. Phys.* 1985, 82, 4442.

Conclusions

Dialkyl sulfide and alkanethiol complexes with HF have been prepared by condensing the reagents with excess argon at 12 K. Infrared spectra reveal strong sharp ν_s (H–F stretching) and two separate ν_l (H–F libration) modes for each 1:1 complex. Comparison with spectra of similar oxygen complexes shows weaker sulfide base–acid interactions and predicts weaker HF hydrogen bonding with sulfide bases. Lower librational modes for sulfide–HF complexes indicate less rigid complexes owing to more diffuse lone pairs on sulfur, and smaller separation between ν_l modes shows a more isotropic sulfur lone pair–HF interaction. Higher stoichiometry 1:2 complexes in these experiments appear to be dominated by the chain structure S–H–F–H–F.

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Contribution from the Laboratory of Chemistry, Kagawa Nutrition College, Sakado, Saitama 350-02, Japan, and Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464, Japan

Hydrophobic and Steric Effects on the Ion-Pair Formation of Tris(1,10-phenanthroline)iron(II) and Arenesulfonate Ions. Kinetic Determination of the Formation Constants of the Ion Pairs and a ¹H NMR Study of Their Structures

Satoshi Tachiyashiki*^{1a} and Hideo Yamatera^{1b}

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Ion-pair formation constants (K) for Fe(phen)₃²⁺ and six kinds of arenesulfonate ions were obtained from kinetic studies of the aquation of the complex ion in aqueous sodium arenesulfonate solutions: $K = 5 \pm 1$, 13 ± 2 , 28 ± 5 , 19 ± 3 , 8 ± 2 , and 5 ± 1 mol⁻¹ dm³ for benzene-, 4-methylbenzene-, 4-ethylbenzene-, 2,4-dimethylbenzene-, 1-naphthalene-, and 2-naphthalenesulfonate, respectively. An arenesulfonate of greater hydrophobicity showed a larger formation constant, except that small formation constants were shown by bulky naphthalenesulfonates. The formation constant was smaller for an arenesulfonate than for an alkanesulfonate with the same number of carbon atoms. The ¹H NMR signal of arenesulfonate in the ion pair was found to shift upfield. Comparison of the observed shifts with those calculated on the basis of the current loop model supported a model of the ion pair in which the arenesulfonate ion lies in the hydrophobic cavity between two phenanthroline ligands of the complex ion with the sulfonate group directed outside the cavity.

Hydrophobic interaction plays an important role not only in biological systems but also in systems containing coordination compounds of aromatic nitrogen-donor ligands such as 1,10-phenanthroline and 2,2'-bipyridine.^{2–8} We previously studied the effects of alkylammonium cations⁹ and alkanesulfonate anions¹⁰ on the rate of racemization and aquation of Fe(phen)₃²⁺ (phen = 1,10-phenanthroline). The complex ion was found to form ion pairs not only with alkanesulfonate ions but also with alkyl-

ammonium cations through hydrophobic interaction. In the present study, various arenesulfonate ions have been examined for the effect on the rate of aquation of the complex ion. This has disclosed how the molecular shape of the arenesulfonate ion affects the formation of the ion pair between Fe(phen)₃²⁺ and an arenesulfonate ion. An ¹H NMR study was also carried out in order to clarify the structure of the ion pair.

Experimental Section

The sodium arenesulfonates were of reagent grade from Tokyo Kasei Kogyo Co., Ltd., except sodium 4-methylbenzene- and 2,4-dimethylbenzenesulfonate, which were synthesized from the sulfonic acids (Tokyo Kasei) and sodium carbonate. They were recrystallized three times from ethanol–methanol (5:1) solution and dried at 70 °C in vacuo after 5 h. First-order rate constants for the aquation of Fe(phen)₃²⁺ were obtained at 25 °C from the changes in the absorbance at 510 nm of the solution containing 5×10^{-5} mol dm⁻³ [Fe(phen)₃](ClO₄)₂ and a sodium arenesulfonate. Nickel(II) perchlorate (5×10^{-4} mol dm⁻³) was added as a scavenger of liberated phenanthroline. In measuring the ¹H NMR spectra tetramethylammonium bromide (0.002 mol dm⁻³) was used as the internal reference. The other chemicals and procedures were the same as those described in a previous paper.¹¹

Results

Kinetics of the Aquation of Fe(phen)₃²⁺. The observed rate constants of the aquation are shown in Figure 1 as a function of

- (1) (a) Kagawa Nutrition College. (b) Nagoya University.
- (2) Mitchell, P. R. *J. Chem. Soc., Dalton Trans.* 1979, 771–6.
- (3) Sigel, H.; Naumann, C. F. *J. Am. Chem. Soc.* 1976, 98, 730–9. Fisher, B. E.; Sigel, H. *J. Am. Chem. Soc.* 1980, 102, 2998–3008. Sigel, H. *Experientia* 1981, 37, 789–98. Sigel, H. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 389–400.
- (4) Miyoshi, K.; Sakata, K.; Yoneda, H. *J. Phys. Chem.* 1975, 79, 1622–4. Miyoshi, K.; Shimada, K.; Yoneda, H. *Bull. Chem. Soc. Jpn.* 1975, 48, 3403–4. Miyoshi, K.; Kuroda, Y.; Takeda, J.; Yoneda, H.; Takagi, I. *Inorg. Chem.* 1979, 18, 1425–9.
- (5) Iwamoto, E.; Yamamoto, M.; Yamamoto, Y. *Inorg. Nucl. Chem. Lett.* 1977, 13, 399–402. Iwamoto, E.; Tanaka, Y.; Kimura, M.; Yamamoto, Y. *J. Solution Chem.* 1980, 9, 841–8.
- (6) Pramauro, E.; Pelizzetti, E.; Diekmann, S.; Frahm, J. *Inorg. Chem.* 1982, 21, 2432–6.
- (7) Tachiyashiki, S.; Yamatera, H. *Chem. Lett.* 1981, 1681–4.
- (8) Gayley, G. R.; Margerum, D. W. *J. Chem. Soc., Commun.* 1974, 1002–4.
- (9) Tachiyashiki, S.; Yamatera, H. *Bull. Chem. Soc. Jpn.* 1982, 55, 759–63.
- (10) Tachiyashiki, S.; Yamatera, H. *Bull. Chem. Soc. Jpn.* 1984, 57, 1061–6, 1067–9.

- (11) Tachiyashiki, S.; Yamatera, H. *Bull. Chem. Soc. Jpn.* 1982, 55, 1014–21.

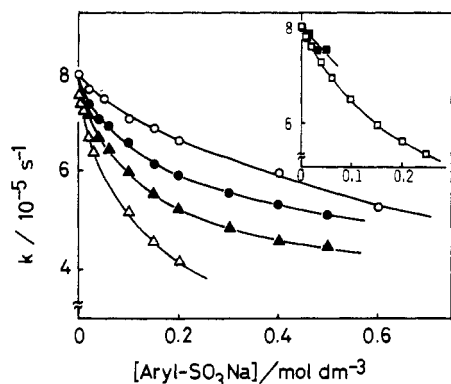


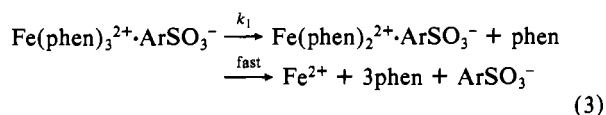
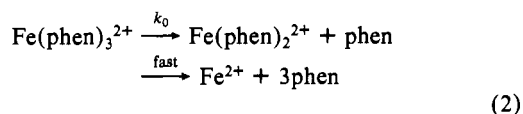
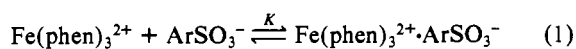
Figure 1. Rate constants of the aquation of $\text{Fe}(\text{phen})_3^{2+}$ in sodium arenesulfonate solutions at 25.0 °C plotted against the arenesulfonate concentration: (O) benzenesulfonate; (●) 4-methylbenzenesulfonate; (Δ) 4-ethylbenzenesulfonate; (▲) 2,4-dimethylbenzenesulfonate; (□) 1-naphthalenesulfonate; (■) 2-naphthalenesulfonate.

Table I. Rate Constants for the Aquation of $\text{Fe}(\text{phen})_3^{2+}$ in the Ion Pair with Arenesulfonate Ions and the Formation Constants of the Ion Pair at 25 °C

sulfonate	$k_1/10^{-5} \text{ s}^{-1}$	$K/\text{mol}^{-1} \text{ dm}^3$
none	$(8.0 \pm 0.2)^a$	
benzene-	3.7 ± 0.3	5 ± 1
4-methylbenzene-	4.2 ± 0.2	13 ± 2
4-ethylbenzene-	2.9 ± 0.3	28 ± 5
2,4-dimethylbenzene-	3.7 ± 0.2	19 ± 3
1-naphthalene-	2.8 ± 0.7	8 ± 2
2-naphthalene-	$2.8-4.2^b$	5 ± 2
<i>n</i> -butane-	1.8 ± 0.4^c	3 ± 1^c
<i>n</i> -hexane-	1.7 ± 0.5^c	18 ± 3^c
<i>n</i> -octane-	1.6 ± 0.3^c	64 ± 8^c
<i>n</i> -decane-	1.8 ± 0.4^c	156 ± 27^c

^a k_0 . ^b The values were assumed on the basis of the values obtained for the other arenesulfonates. ^c Reference 10.

the concentration of sodium arenesulfonates (ArSO_3Na). The changes in the rate of aquation of the complex ion with the changes in the concentration of the sulfonate can be accounted for in terms of an ion-pair formation of the complex ion with an arenesulfonate ion in analogy with the complex-alkanesulfonate system.¹⁰ The aquation in sodium arenesulfonate solutions is assumed to proceed as follows:



Then, the thermodynamic ion-association constant, K , for reaction 1 and the aquation rate constant, k , are given by

$$K = \frac{[\text{Fe}(\text{phen})_3^{2+} \cdot \text{ArSO}_3^-]}{[\text{Fe}(\text{phen})_3^{2+}][\text{ArSO}_3^-]} \left(\frac{\gamma_1}{\gamma_2\gamma_1} \right) \quad (4)$$

and

$$k = \frac{k_0 + k_1 K \gamma_2 [\text{ArSO}_3^-]}{1 + K \gamma_2 [\text{ArSO}_3^-]} \quad (5)$$

where k_0 and k_1 are the rate constant for reactions 2 and 3, respectively. The activity coefficient, γ_z , of an ion with a charge of $\pm z$ was estimated by using the extended Debye-Hückel equation as reported previously.¹² The kinetic results given in Figure 1

Table II. Shifts of ^1H NMR Signals of the Arenesulfonate Ion Caused by the Formation of an Ion Pair with $\text{Fe}(\text{phen})_3^{2+}$ ^a

sulfonate	upfield shifts/ppm		
	ortho	meta	para
benzene-	2.2 ± 0.4 (0.40)	3.1 ± 0.5 (0.55)	3.1 ± 0.5 (0.55)
4-methylbenzene-	1.9 ± 0.3 (0.36)	2.7 ± 0.4 (0.50)	2.5 ± 0.4^b (0.47)
4-ethylbenzene-	1.5 ± 0.3 (0.32)	2.4 ± 0.4 (0.50)	2.3 ± 0.4^c (0.49) 2.2 ± 0.4^b (0.47)

^a The shifts from the positions of the peaks for the arenesulfonate ion in the absence of the complex ion. Values in parentheses are the chemical shifts of the arenesulfonate ($\delta^{\text{obsd}} - \delta_X$; see text) observed in solutions of $[\text{Fe}(\text{phen})_3][\text{ArSO}_3]_2$ of with concentrations of 0.05, 0.05, and 0.03 mol dm^{-3} for benzene-, 4-methylbenzene-, and 4-ethylbenzenesulfonate, respectively. ^b Methyl proton signals. ^c Methylene proton signals.

were analyzed by the use of eq 5 to give the values of k_1 and K (Table I). Those values previously obtained for systems containing alkanesulfonates¹⁰ are also listed in Table I for comparison.

¹H NMR of Arenesulfonates. ¹H NMR was measured for the arenesulfonates of the complex in order to clarify the structures of the $\text{Fe}(\text{phen})_3^{2+}$ -arenesulfonate ion pairs.

In solutions of the arenesulfonate of the complex, the ¹H chemical shifts of the arenesulfonate signals (δ^{obsd}) can be expressed by

$$\delta^{\text{obsd}} = \delta_{\text{MX}} P_{\text{MX}} + \delta_X (1 - P_{\text{MX}}) \quad (6)$$

where δ_{MX} and δ_X are the chemical shift of a proton signal of an arenesulfonate ion in $\text{Fe}(\text{phen})_3^{2+}$ -arenesulfonate ion pairs (MX) and that of the corresponding signal of an unassociated arenesulfonate ion (X), respectively, and P_{MX} is the ratio of the concentration of MX to the total arenesulfonate (MX + X) concentration. Then, the difference ($\Delta\delta_{\text{MX}}$) between the proton chemical shift of MX and that of X can be expressed by

$$\begin{aligned} \Delta\delta_{\text{MX}} &= \delta_{\text{MX}} - \delta_X \\ &= (\delta^{\text{obsd}} - \delta_X) / P_{\text{MX}} \end{aligned} \quad (7)$$

The values of δ_X were measured in sodium arenesulfonate solutions. The values of P_{MX} were calculated from the ion-pair formation constants listed in Table I. The $\Delta\delta_{\text{MX}}$ values calculated from eq 7 are listed in Table II together with the ($\delta^{\text{obsd}} - \delta_X$) values shown in parentheses.

Discussion

Ion-Pair Formation Constants. The formation constant increased in the order benzene- < 4-methylbenzene- < 4-ethylbenzenesulfonate. This is consistent with the tendency previously found for alkanesulfonates that the formation constant increased with increasing length of the alkyl chain of the sulfonate.¹⁰ This suggests that hydrophobic interaction plays an important role in the formation of the ion pairs of the complex ion and the benzenesulfonate derivatives. However, the formation constant for each arenesulfonate is smaller than that of the alkanesulfonate with the same number of carbon atoms (Table I) and is as large as that for an alkanesulfonate with one or two fewer carbon atoms, benzenesulfonate corresponding to butane- or pentanesulfonate. This can be related to the less flexible nature of an arenesulfonate as compared to an alkanesulfonate, which results in a less appropriate geometric condition for efficient hydrophobic interaction with the metal complex ion and/or to a weaker hydrophobicity of aromatic groups; a π -electron system shows an affinity to water to some extent,¹³ and thus the phenyl group has a hydrophobicity comparable to that of the butyl group.¹⁴ The small formation constants for arenesulfonates suggests that charge-transfer interaction is weak between the phenanthroline ligand of the complex

- (12) Tachiyashiki, S.; Yamatera, H. *Polyhedron* **1983**, *2*, 9-12.
 (13) Goldman, I. M.; Crisler, R. O. *J. Org. Chem.* **1958**, *23*, 751-2. Ooki, M.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1960**, *23*, 717-21.
 (14) Rosen, M. J. *J. Am. Oil Chem. Soc.* **1974**, *51*, 461-5. Lin, I. J.; et al. *J. Colloid Interface Sci.* **1973**, *45*, 378-85. Sinoda, K.; Nakagawa, T.; Tamamushi, B.; Isemura, T. *Colloidal Surfactants*; Academic: New York, 1963.

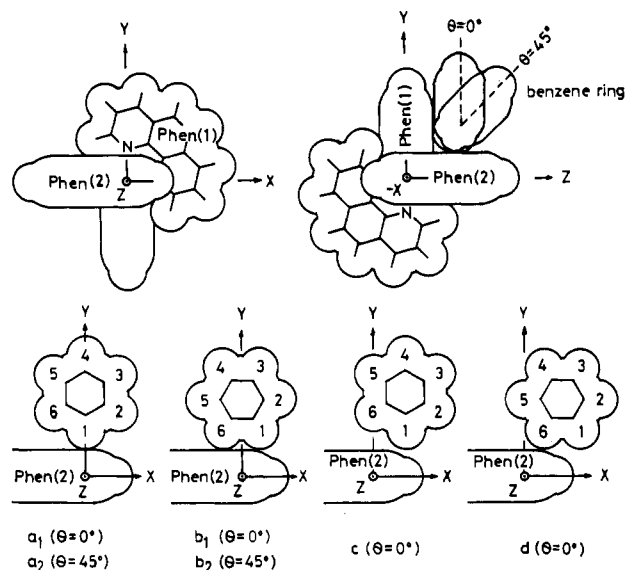


Figure 2. Geometries (a_1 , a_2 , b_1 , b_2 , c , and d) assumed for the $\text{Fe}(\text{phen})_3^{2+}$ -benzenesulfonate ion pair. The origin of the coordinate is placed at the central metal ion, the z axis is perpendicular to the plane of phen(1), and phen(2) lies on the xz plane (the top of the figure). The benzene molecule sits on phen(1) ($\theta = 0^\circ$) in cases a_1 , b_1 , c , and d , and it is placed at 45° with the planes ($\theta = 45^\circ$) of phen(1) and phen(2) in cases a_2 and b_2 (top right). Protons of the benzene molecule are designated by arabic numbers 1–6 (bottom). A sulfonate group is substituted for one of the six hydrogen atoms.

ion and the aryl group of the sulfonate.

The formation constant was smaller for 2,4-dimethylbenzenesulfonate than for 4-ethylbenzenesulfonate. The former may be less hydrophobic than the latter, since the hydrophobicity of the 2-methyl group of the former should be reduced by the nearby polar sulfonate group. The formation constants for 1- and 2-naphthalenesulfonates were much smaller than expected from their hydrophobicity. This is probably due to the large size of the 1- and 2-naphthyl groups; only a part of the group will be effective in the hydrophobic interaction with the complex ion. This was shown to be true from the ^1H NMR study to be described below.

Structure of the Ion Pair. Table II shows that all the proton signals of the arenanesulfonate were shifted upfield when associated with the complex ion. This indicates that the arylsulfonate ion in an ion-pair lies so close to the complex ion as to be affected by the ring current of the phenanthroline ligands of the complex ion.

In order to learn the structure of the ion pair, the shifts of ^1H NMR signals of benzenesulfonate in the ion pair were calculated by the current-loop model,^{15,16} which was recently proved to be effective for estimating the ring current effects of aromatic ligands in metal complexes.¹⁷ In this calculation, parameter values were chosen to be the same as those used for the benzene molecule.¹⁶ The number of π -electrons was assumed to be equal to 6 for each of the three six-membered rings of a phenanthroline molecule. The ring current shifts for the benzenesulfonate proton were calculated as the sum¹⁷ of the shifts caused by each of the nine six-membered rings of the three phenanthroline ligands in the complex for six geometries of the ion pair (a_1 , a_2 , b_1 , b_2 , c , and d of Figure 2).

Table III. Calculated Differences in the Upfield Shifts for the Ortho, Meta, and Para Protons of the Benzenesulfonate Ion Associated with $\text{Fe}(\text{phen})_3^{2+}$ with Various Geometries

geometry ^a	$\delta_m - \delta_o^b$	$\delta_p - \delta_o^c$	geometry ^a	$\delta_m - \delta_o^b$	$\delta_p - \delta_o^c$
a_1 2	-0.95	-1.43	a_2 2	-1.12	-1.67
3	0.89	0.60	3	1.11	0.69
4	1.34	1.65	4	1.25	3.34
5	0.94	0.91	5	1.11	0.69
b_1 2	0.27	-0.60	b_2 2	0.00	-0.94
3	1.18	2.58	3	1.51	2.73
4	1.54	2.19	4	1.51	2.73
5	-0.27	-0.78	5	0.00	-0.94
c 2	-0.03	-0.72	d 2	0.69	0.81
3	0.93	1.77	3	1.24	2.52
4	1.25	2.03	4	0.78	0.85
5	0.03	0.41	5	-0.69	-1.26

^a The geometries are drawn in Figure 2. The numerical values indicate the position of a sulfonate group. ^b The difference in the upfield shifts between meta and ortho protons. ^c The difference in the upfield shifts between para and ortho protons.

Absolute values of the calculated shifts gave ranges of 0.3–2.2, 0.8–2.3, and 0.3–3.5 ppm, for ortho, meta, and para protons of benzenesulfonate, respectively, depending on the geometry of the ion pair in Figure 2. The larger upfield shifts for meta and para protons, compared with that for the ortho proton (Table II), were obtained when the sulfonate group is directed outside the central metal ion. Thus the arenanesulfonate ion tends to associate with the complex ion with the hydrophobic tail (para position) close to the complex ion and with the sulfonate group far apart from it. On the other hand, none of the geometries with a fixed configuration in Figure 2 accounted for the observed shifts of benzenesulfonate proton signals, probably because of the observed absolute shift values being affected by effects other than ring current.¹⁷ Therefore the calculated and the observed differences in the shifts between protons at different sites were compared to clarify the structure of the ion pair. Such differences are expected to come mainly from the ring current effect.

Table III summarizes the calculated differences in the shifts between the meta and the ortho protons and between the para and the ortho protons of benzenesulfonate for the six geometries with various configurations (with a sulfonate group at various positions). The table shows that the observed difference in the upfield shifts of 0.9 ± 0.13 ppm between ortho and meta protons and between ortho and para protons (Table II) can be reproduced approximately by the calculation if the sulfonate group is at the 5-position of a_1 . The observed differences would also be reproduced as an average shift difference if the benzenesulfonate ion takes several different positions with appropriate probabilities.

For systems containing 4-methylbenzene- and 4-ethylbenzenesulfonate, the observed shift differences were $(0.8\text{--}0.9) \pm 0.13$ ppm between the ortho and the meta protons and $(0.6\text{--}0.8) \pm 0.11$ ppm between the ortho proton and the para alkyl protons (Table II). Although the geometrical conditions in these cases are slightly different from that in the case of benzenesulfonate, the geometry of a_1 with the sulfonate group at the 3- or 5-position approximately reproduces the observed values. The latter geometry seems to be more favorable in the respect that the methyl or ethyl group lies above the phenanthroline ligand, while the sulfonate group lies off the hydrophobic ligand.

All the results indicate that the arenanesulfonate ion lies at the center of the hydrophobic cavity between two phenanthroline ligands (with the most probable geometry of a_1) with its sulfonate group directed outside the cavity (at the 5-position, for example). The results demonstrated that hydrophobic interaction is more important than the electrostatic interaction between the complex cation and arenanesulfonate anions.

(15) Waugh, J. S.; Fessenden, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 846–9.

(16) Johnson, C. E., Jr.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012–4.

(17) Tachiyashiki, S.; Yamatera, H., submitted for publication in *Bull. Chem. Soc. Jpn.*