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Temperature Dependence of Hydrophobic Ion Association of Tris(1,10-phenanthroline)iron(II) Ion with Arenedisulfonate Ions in Water

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The ion-association constants(K) of $[Fe(phen)_3]^{2+}$ with o- and m-benzenedisulfonate, 2,6- and 2,7-naphthalenedisulfonate ions, determined by conductivity measurements at 0—50 °C, were considerably larger than the electrostatic prediction: K(25 °C) = 99 ± 3, 204 ± 5, 1021 ± 29, and 792 ± 6 $dm^3 mol^{-1}$, respectively. Their hydrophobic behavior was apparently similar to that of alkanesulfonate ions. However, the significant enthalpy contribution was found to the hydrophobic ion association.

Hydrophobic ion association of $[Fe(phen)_3]^{2+}$ with alkylammonium, alkanesulfonate, and arenesulfonate ions has been well investigated through kinetic and NMR studies.1-3) However, its temperature dependence is not clarified though of interest in connection with the nature of the interaction. In the present study, electric conductivities of o-benzenedisulfonate(o-BDS), m-benzenedisulfonate(m-BDS), 2,6-naphthalenedisulfonate(2,6-NDS), and 2,7-naphthalenedisulfonate(2,7-NDS) of $[Fe(phen)_3]^{2+}$ in water were measured at temperatures from 0 to 50 °C in order to obtain the detailed thermodynamic information of the ion association and examine the nature of the interaction.

The salts of $[Fe(phen)_3]^{2+}$ were prepared by adding a potassium salt of o-BDS^{2-} (Aldrich) and sodium salts of m-BDS^{2-}, 2,6-NDS^{2-}, and 2,7-NDS^{2-} (Wako, recrystallized from water)4) to aqueous solutions of the sulfate prepared from iron(II) sulfate and 1,10-phenanthroline(Wako, reagent grade). The complex salts obtained were recrystallized twice from water and air-dried at room temperature; the salt of 2,7-NDS^{2-} was further dried in a silica gel desiccator. The numbers of water of crystallization were determined by the Karl-Fischer method4,5) to be 8.2, 5.3, 12.2, and 1.2 for the salts of o-BDS^{2-}, m-BDS^{2-}, 2,6-NDS^{2-}, and 2,7-NDS^{2-}, respectively. The molar extinction coefficients at $\lambda = 510$ nm in water ($c = 6 \times 10^{-5}$ mol dm^{-3}) were in agreement with one another: $\varepsilon_{max} = 11,110 \pm 20$ $mol^{-1} dm^3 cm^{-1}$.

Conductivity measurements were carried out by using an AG-4311 LCR-meter of Ando Electric Co. with which the resistance of the solution was directly read with an accuracy of ±0.05 %, checked by a precision decade resistance box.6) The temperature measurements were made with a thermistor connected to a Fuso 362 bridge. The other procedures have been described previously.5,6) The reproducibility of the conductivity measurements was about ± 0.2%. The accuracy of temperature was ±0.01 °C.

The observed molar conductivities[7] were analyzed on the assumption of the ion association (ion-pair formation) by the use of the 1970 Fuoss-Justice equation[5,8] where the obstruction effect was considered.[6] The ion-association constants (K) were determined with the limiting molar conductivities in the usual way[5,6] by assuming the values of the closest distance of approach of ions (*a*) which were estimated to be 8.30, 8.35, 8.71, and 8.70 Å for the salts of o-BDS^{2-}, m-BDS^{2-}, 2,6-NDS^{2-}, and 2,7-NDS^{2-}, respectively, from the effective ionic radii of the anions[4] and $[Fe(phen)_3]^{2+}$.[9]

As shown in Table 1 and Fig. 1, the ion-association constants obtained increase in the order of o-BDS^{2-} < m-BDS^{2-} < 2,7-NDS^{2-} < 2,6-NDS^{2-} and are larger than those predicted from the electrostatic theory of ion association.[10] The feature of the temperature dependence is characteristic of each anion. Although the ion-association behavior of o-BDS^{2-} is similar to the theoretical prediction on the assumption of $a = 5.7$ Å,[10] that of the other anions can not be electrostatically explained.

It is worth noting that the difference in log K between m-BDS^{2-} and 2,6- or 2,7-NDS^{2-} is near to that between the experimental and theoretical ones for m-BDS^{2-}. This feature is similar to the dependence of log K on the alkyl-chain length for alkylammonium and alkanesulfonate ions.[1] The increments of $-\Delta G°$ (25 °C) per an aromatic carbon atom from m-BDS^{2-} to 2,7-NDS^{2-} and 2,6-NDS^{2-} were 0.87 and 1.03 kJ mol^{-1}, respectively, in agreement with (0.9 ± 0.1) kJ mol^{-1} for alkanesulfonate ions.[1]

The contact ion pairs formed by the ion association of m-BDS^{2-} with $[Fe(phen)_3]^{2+}$ is presumed to have a similar structure to the ion-pair model proposed for benzenesulfonate ion (BS$^-$):[3] the aromatic ring of m-BDS^{2-} is laid on those of the 1,10-phenanthroline ligand while the sulfonato groups are directed outside the complex ion. Relatively strong ion association for m-BDS^{2-} compared to BS$^-$ ($K = 5 \pm 1$ dm^{3}mol^{-1})[3] is attributed mainly to the difference in the electrostatic attraction. The contact ion pairs of 2,6-NDS^{2-} and 2,7-NDS^{2-} with $[Fe(phen)_3]^{2+}$ are also

Table 1. Ion-Association Constants, K/dm^{3}mol^{-1}

	o-BDS^{2-}	m-BDS^{2-}	2,6-NDS^{2-}	2,7-NDS^{2-}
t/°C	K	K	K	K
0	92.2 ± 2.7	234.1 ± 5.0	1294 ± 37	997 ± 14
5	93.4 ± 2.6	228.2 ± 5.0	1259 ± 44	958 ± 13
10	94.6 ± 2.6	222.2 ± 5.0	1191 ± 35	920 ± 12
15	95.8 ± 2.6	215.8 ± 5.1	1134 ± 34	879 ± 10
20	97.0 ± 2.6	210.0 ± 5.1	1078 ± 32	837 ± 8
25	98.5 ± 2.8	204.2 ± 4.8	1021 ± 29	792 ± 6
30	100.7 ± 2.9	199.6 ± 4.6	969 ± 26	747 ± 5
35	104.3 ± 3.6	195.8 ± 3.9	924 ± 22	703 ± 4
40	108.6 ± 4.3	192.2 ± 3.3	881 ± 18	659 ± 5
45	113.0 ± 4.7	188.4 ± 2.6	841 ± 19	616 ± 8
50	115.8 ± 5.0	184.0 ± 2.4	791 ± 20	578 ± 9

presumed to have similar structures to that for m-BDS^{2-}. Considering that the K values for 1- and 2-naphthalenesulfonate ions are small and similar to that for BS^{-},$^{3)}$ the effective contact of the two aromatic rings of the anion on the ligand surface seems to be required for the stronger ion association. The relatively large K values for 2,6-NDS^{2-} compared to 2,7-NDS^{2-} are thought to be due to the difference in the effective contact, dependent on the relative position of the two sulfonato groups within the anions.

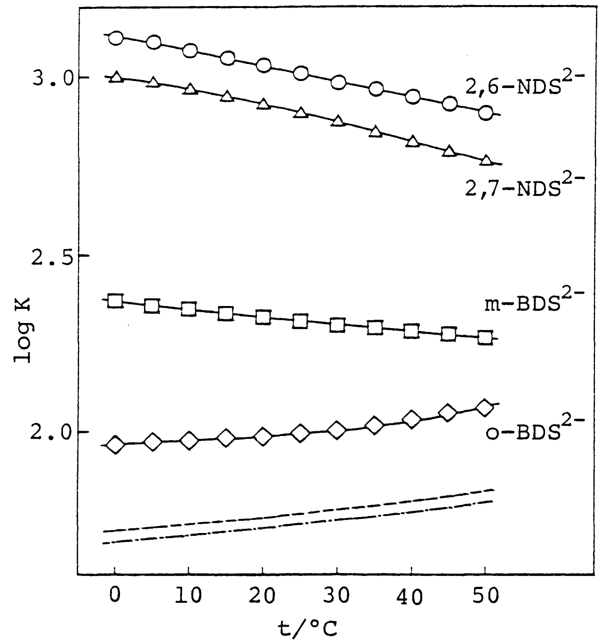

Fig. 1. The temperature dependence of log K. (---) and (--•--) are theoretical curves estimated by assuming $a = 8.3$ and 8.7 Å, respectively.$^{10)}$

As shown by solid lines in Fig.1, the experimental log K can be well reproduced by quadratic equations of log K vs. t.$^{5)}$ Standard enthalpies and entropies of ion association (ΔH° and ΔS°) were evaluated by the use of these equations and shown in Tables 2 and 3. Except for o-BDS^{2-}, the values of ΔH° are negative, while those of ΔS° are positive but smaller

Table 2. Standard Enthalpies of Ion Association, ΔH°/kJ mol^{-1}

	o-BDS^{2-}	m-BDS^{2-}	2,6-NDS^{2-}	2,7-NDS^{2-}	Theoretical$^{a)}$
t/°C	ΔH°	ΔH°	ΔH°	ΔH°	ΔH°
5	1.0 ± 0.9	-3.7 ± 0.4	-6.1 ± 0.9	-5.3 ± 0.3	2.6
15	2.1 ± 0.5	-3.7 ± 0.2	-6.7 ± 0.5	-6.6 ± 0.2	3.2
25	3.4 ± 0.4	-3.6 ± 0.2	-7.4 ± 0.4	-8.1 ± 0.2	3.8
35	4.8 ± 0.6	-3.4 ± 0.3	-8.1 ± 0.5	-9.8 ± 0.2	4.4
45	6.5 ± 1.2	-3.2 ± 0.5	-8.8 ± 1.1	-11.6 ± 0.4	5.0

a) Ref. 10; for $a = 8.30$-8.71 Å.

Table 3. Standard Entropies of Ion Association, ΔS°/J K^{-1}mol^{-1}

	o-BDS^{2-}	m-BDS^{2-}	2,6-NDS^{2-}	2,7-NDS^{2-}	Theoretical$^{a)}$
t/°C	ΔS°	ΔS°	ΔS°	ΔS°	ΔS°
5	41.2 ± 3.2	31.8 ± 1.3	37.2 ± 3.0	38.0 ± 1.1	42.1-42.6
15	45.2 ± 1.7	32.0 ± 0.7	35.1 ± 1.6	33.3 ± 0.6	44.0-44.6
25	49.6 ± 1.2	32.3 ± 0.5	32.9 ± 1.2	28.2 ± 0.5	45.9-46.5
35	54.4 ± 1.8	32.8 ± 0.8	30.6 ± 1.4	22.8 ± 0.6	47.9-48.6
45	59.5 ± 3.6	33.4 ± 1.5	28.3 ± 3.5	17.0 ± 1.3	50.0-50.6

a) Ref. 10; for $a = 8.71$-8.30 Å.

than the theoretical ones. With increasing temperature, the ΔH° and ΔS° values for 2,6- and 2,7-NDS^{2-} are further decreased, while those for m-BDS^{2-} are slightly increased but their deviation from the theoretical ones becomes remarkable in analogy with 2,6- and 2,7-NDS^{2-}. From the temperature dependence of ΔH° and ΔS°, the molar heat-capacity changes by the ion association, ΔC_p°, are obviously negative for 2,6- and 2,7-NDS^{2-}. The negative ΔC_p° is attributable to the decrease of the hydrophobic hydration-water molecules around the ions by the contact ion-pair formation. Usually, this expects the relation of $T\Delta S^\circ > \Delta H^\circ > 0$ consistent with the concept of the hydrophobic interaction.[11] However, the present results for ΔH° and ΔS° are not necessarily in accord with this expectation.

The relatively small ΔS° may be owing to the steric restriction on the contact ion-pair formation and the negative ΔH° may indicate the presence of exothermic short-range interactions between the aromatic ring of the anion and that of the ligand of the complex ion. These are consistent with the requirement for the stronger ion association as described above. Consequently, the large ion-association constants for m-BDS^{2-}, 2,6- and 2,7-NDS^{2-} compared to the theoretical one are considered to arise from the cooperative effect of the hydrophobic and exothermic short-range interactions.

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