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Solubility of Transition Metal Complexes in Aqueous Salt Solutions. I. Tris(1,10-phenanthroline)iron(II) Perchlorate

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Solubility of tris(1,10-phenanthroline)iron(II) perchlorate was determined at 25 °C by spectrophotometry in aqueous solutions of sodium halides, sulfate, acetate, and trichloroacetate up to ionic strength of 0.5. It was found that the solubility is higher in the presence of water-structure breaking anions but is lower in the presence of water-structure making anions than is expected from the change in activity coefficients with ionic strength. This was interpreted in terms of compatibility and incompatibility of the influence of the complex cation on the water structure with that of added anions, and the hydrophobic nature of the complex cation was noted.

According to Gurney1) or Frank,2) ions in aqueous solution are classified into three groups on the basis of their interaction with water.1–4) The first group consists of so-called electrostrictive water-structure makers, which attract surrounding water molecules so tightly through ion-dipole interaction that their co-spheres1) cause a local increase in the viscosity. Typical examples are provided by Li^+, F^-, SO_4^{2-}, and other highly charged ions. The second group consists of water-structure breakers, which render the motion of water molecules more vivid around them than that of bulk ones (so-called negative hydration5)). K^+, Rb^+, I^-, and other ions with low charge-to-radius ratio belong to this group and lead to a decrease in the viscosity of the solution. The last one consists of hydrophobic water-structure makers and is quite unique in that, when they are dissolved in water, though hardly soluble in general, water-water interaction is strengthened, *i.e.*, "iceberg" is formed in the vicinity of their hydrophobic parts (hydration of the second kind6) or hydrophobic hydration) and sometimes so-called hydrophobic bonding7) may take place. This behavior is characteristic of aqueous solutions and has attracted the attention of biochemists in recent years. Tetraalkylammonium homologues8) and some organic ions including surfactants belong to this group.

As for coordination compounds, however, the above classification has not been well established,3) though they can be permitted to have a variety of physical and chemical properties by substituting metal ions or coordinated ligands. In a series of our study on the solubility of transition metal complexes, we intend to focus our attention on the nature of their interaction with water and also with coexisting ions and to try to classify them into some groups.

Recently Steigman and Dobrow,9) and Desnoyers *et al.*4,10) succeeded in interpreting most excess thermodynamic functions of aqueous electrolyte solutions on the following assumptions: ions belonging to the first group are antagonistic with those belonging to the second and third groups with respect to their influence on the water structure, while those belonging to the second and third groups are cooperative with each other. On the basis of the above assumptions, it follows that electrolytes composed of cooperative ion pairs tend to have lower activity coefficients in water and the reverse holds for antagonistic pairs.2,11) This phenomenon is often called a mutual or structural salting-in and -out, respectively and has been recently discussed quantitatively by Friedman *et al.*12)

In our recent study on the Pfeiffer effect,13) it was proposed that $[Zn(phen)_3]^{2+}$ (phen=1,10-phenanthroline) is classified into the third group in spite of its relatively high charge. However, the complex is so labile that it is not easy to examine its hydrophobic nature by usual techniques such as electrolytic conductance or viscosity measurements.14) Since $[Zn(phen)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ are closely matched in many respects, particularly with regard to their interaction with water in which we are interested and the latter is extremely stable, the solubility of $[Fe(phen)_3](ClO_4)_2$ was measured in place of $[Zn(phen)_3](ClO_4)_2$ in various aqueous salt solutions as a function of the total ionic strength of these solutions. These data are expected to provide a valuable information on the hydrophobic nature of $[Fe(phen)_3]^{2+}$ as well as $[Zn(phen)_3]^{2+}$ if the concept of compatibility and incompatibility of the water structure influenced by ions,9,10) is suitably applied.

Experimental

Preparation. Tris(1,10-phenanthroline)iron(II) perchlorate monohydrate was prepared by dissolving Mohr's salt, $FeSO_4(NH_4)_2SO_4\cdot 6H_2O$ and 1,10-phenanthroline monohydrate in a mole ratio of 1 : 3 in hot water containing *ca.* 10% of methanol, followed by adding sodium perchlorate monohydrate. The resulting crystal was washed with water and recrystallized from water. Its purity was checked by elemental analysis.

Reagents. Added salts were sodium halides, sulfate, acetate, and trichloroacetate, all of which were of reagent grade and used without further purification.

Procedure. Solution equilibration was attained in a small glass bottle (100 ml) dipped in a water bath kept at 25±0.1 °C with a mercury-in-glass thermoregulator. The salt solution to which solid $[Fe(phen)_3](ClO_4)_2$ had been added, was continuously stirred in the water bath by a magnetic stirrer for 5 to 6 hours. Then an aliquot of the solution was pippetted out through a glass filter and was diluted appropriately in a volumetric flask with water. After 1 or 2 hours, an aliquot of the same solution was again pippetted out and diluted as before. $[Fe(phen)_3]^{2+}$ in the two diluted solutions was determined with a Shimadzu UV-200 spectrophotometer by use of its charge-transfer band with the maximum absorption at 510 nm. When the solution equilibration proved incomplete within experimental error, a similar procedure was done again after 1 to 2 hours. The time taken to reach solution equilibrium was usually from 5 to 6 hours. The molar absorption coefficient of $[Fe(phen)_3]^{2+}$

at 510 nm was 11100 and was not affected at all by added salts.

Results and Discussion

If K is defined as a thermodynamic solubility product[15)] for $[Fe(phen)_3](ClO_4)_2$, K in water is expressed as

$$K = [[Fe(phen)_3]^{2+}][ClO_4^-]^2 f_{\pm(0)}^3 = 4S_{(0)}^3 f_{\pm(0)}^3 \qquad (1)$$

where S and $f_\pm$ denote the solubility in mol/l and the mean activity coefficient of the complex salt, respectively, and the subscript (0) refers to water. In salt solutions, on the other hand, K is given by

$$K = 4S^3 f_\pm^3 \qquad (2)$$

In the above two equations, ion association is ignored on the ground that $S_{(0)}$ is so small (8.99×10^{-4} mol/l) that there is little contribution from ion association to the solubility when the amount of added salts is small and if any, it does not differ greatly as long as halide ions are concerned[16)] (the Bjerrum's critical distance[17)] amounts to 7.1 Å for halides). From the identity of Eq. (1) with Eq. (2), it follows that

$$S/S_{(0)} = f_{\pm(0)}/f_\pm \qquad (3)$$

If the Debye-Hückel approximation[18)] for activity coefficients is employed, Eq. (3) is rearranged to

$$\log S/S_{(0)} = 1.018[I^{1/2}/(1+0.329aI^{1/2}) - I_{(0)}^{1/2}/(1+0.329aI_{(0)}^{1/2})] \qquad (4)$$

at 25 °C, where I denotes the total ionic strength of the salt solution in which $[Fe(phen)_3](ClO_4)_2$ is dissolved and a the distance of closest approach in Å. Equation (4) suggests that $S/S_{(0)}$ should be greater than unity, increase with I, and should not be dependent on the kind of added salts.

Figure 1 shows the ratios $S/S_{(0)}$ as a function of square root of I and clearly indicates that they are in fact greater than unity but differ considerably from salt to salt added when they are compared at the same ionic strength. Since the cation (sodium ion) is common to all salt solutions and the concentration of ClO_4^- is much lower than that of added salts, the differences in $S/S_{(0)}$ are attributed to these added anions and the co-sphere of $[Fe(phen)_3]^{2+}$ overlaps predominantly with those of added anions rather than that of ClO_4^-. As a result, it can be concluded to a good approximation that the increase in $S/S_{(0)}$ with I depends on whether the complex cation is co-operative or antagonistic with added anions with regard to their influence on the water structure. In Fig. 1 are also drawn the two curves estimated by Eq. (4) with $a=8$ and 9 Å, which are chosen because the radius of $[Fe(phen)_3]^{2+}$ in water has been determined to be 6.5 and 5.3 Å by viscosity[19)] and conductance[16)] measurements, respectively and that of ClO_4^- to be 2.92 Å.[20)]

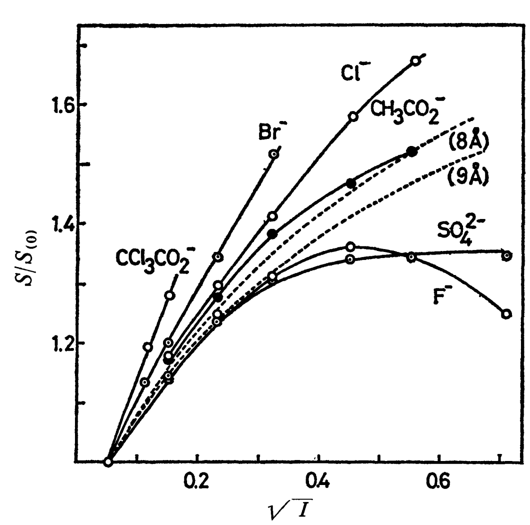

Fig. 1. Dependence of the solubility ratio $S/S_{(0)}$ on square root of ionic strength I. Dotted lines represent the theoretical values estimated by Eq. (4).

A close inspection of Fig. 1 indicates that the deviations of $S/S_{(0)}$ from theoretically estimated values are observed even at low salt concentrations at which the Debye-Hückel approximation is taken valid[18)] and that the order of increasing ratio $S/S_{(0)}$ is $CCl_3COO^- > Br^- > Cl^- > CH_3COO^- > F^- \sim SO_4^{2-}$, which is in good agreement with the order of increasing water-structure breaking power of anions[9)] (NaI could not be examined because of the precipitation of $[Fe(phen)_3]I_2$). Therefore, it is certain that $[Fe(phen)_3]^{2+}$ is cooperative with structure breakers, *i.e.*, it belongs to the third group. It is probably due to the ion association between $[Fe(phen)_3]^{2+}$ and SO_4^{2-} that the curve for sulfate tends to level off at high salt concentration, since the Bjerrum's critical distance amounts to 14.3 Å in this case (the association constant of $[Ru(phen)_3]SO_4$ in water has been reported to be 47 by Yokoyama and Yamatera[21)]). Otherwise, the ratio should begin to decrease like that for fluoride at high salt concentrations.

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