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

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Synopsis. Solubility of tris(1,10-phenanthroline)-iron(II) perchlorate in water was found to be much increased by the addition of hydrophobic ions. This was interpreted in terms of hydrophobic interaction of the complex cation with hydrophobic ions added.

It is generally accepted that ions in aqueous solutions are classified into three groups according to the nature of their interaction with water; structure-maker, structure-breaker, and hydrophobic structure-maker.[1–3] In our preceding paper of this series,[4] we proposed that $[Fe(phen)_3]^{2+}$ (phen=1,10-phenanthroline) belongs to the last group despite its relatively high charge. In order to ascertain our proposal, solubility of $[Fe(phen)_3](ClO_4)_2$ was measured at 25 °C in aqueous solutions of various hydrophobic salts as a function of total ionic strength.

$[Fe(phen)_3](ClO_4)_2 \cdot H_2O$ was prepared in the same manner as before.[4] Sodium alkane carboxylates (formate to octanoate) were prepared and purified in a similar manner to that described by Sakurai[5] and Tamaki *et al.*[6] Tetraalkylammonium bromides (methyl to *n*-butyl) were dried at 100 °C. Solubility measurements were carried out at 25±0.1 °C in the same manner as before.[4] Usually it took 7 to 8 h to attain solution equilibrium.

In Fig. 1 is plotted the solubility ratio S/S_0, *i.e.*, the ratio of solubility (mol/l) of the complex in aqueous salt solutions to that in pure water, against square root of total ionic strength I for sodium alkane carboxylate solutions. Also drawn are theoretical curves estimated by the Debye-Hückel approximation with a=8 and 9 Å.[4,7] It is seen that S/S_0 is more and more increased as the number of methylene groups in alkane carboxylates is increased,[8] *i.e.*, as the added anions bear more hydrophobic character,[9] and that higher carboxylates[10] (hexanoate to octanoate) show an increasingly positive curvature contrary to the prediction from the Debye-Hückel theory.

S_0 is so low (8.99×10^{-4} mol/l) as compared with the concentration of added salts that the co-sphere[2] of $[Fe(phen)_3]^{2+}$ overlaps predominantly with that of added anions rather than that of ClO_4^-. As a result, it follows that the increment in S/S_0 depends on whether the complex cation is cooperative or antagonistic with added

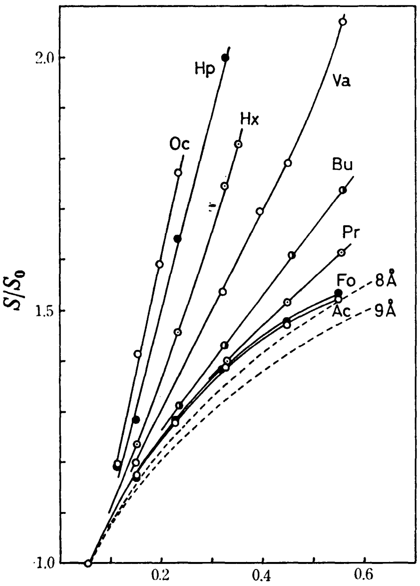

Fig. 1. Dependence of the solubility ratio S/S_0 on square root of ionic strength I for sodium alkane carboxylate solutions. Fo, Ac, Pr, Bu, Va, Hx, Hp, and Oc refer to sodium formate, acetate, propionate, butyrate, valerate, hexanoate, heptanoate, and octanoate solutions, respectively. Dotted lines represent theoretical values estimated by the Debye-Hückel approximation

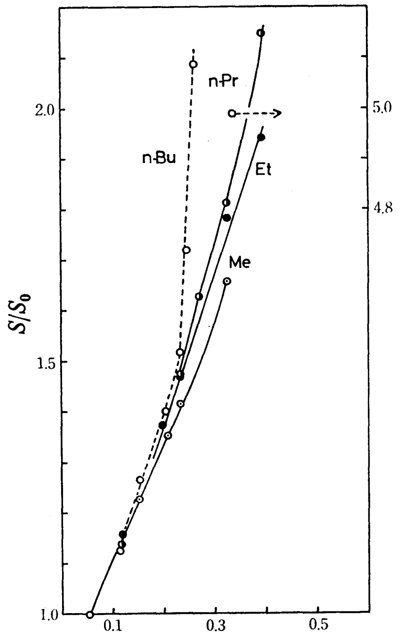

Fig. 2. Dependence of the solubility ratio S/S_0 on square root of ionic strength I for tetraalkylammonium bromide R_4NBr solutions. Me, Et, *n*-Pr, and *n*-Bu refer to Me_4NBr, Et_4NBr, $n\text{-}Pr_4NBr$, and $n\text{-}Bu_4NBr$ solutions, respectively. Only one point in the most concentrated solution of $n\text{-}Bu_4NBr$ corresponds to the right-hand scale.

anions with respect to their influence on the water structure, as pointed out by Steigman and Dobrow,[11] and Desnoyers *et al.*,[12] if ion association is negligible. Since added anions are all singly charged, their electrostatic association with the complex cation is not so extensive, at least at low salt concentrations.[4] Thus, it is confirmed from Fig. 1 that $[Fe(phen)_3]^{2+}$ is cooperative with hydrophobic anions.

Figure 2 shows similar plots for tetraalkylammonium bromide solutions and indicates that S/S_0 does not differ appreciably from salt to salt added when the salt concentration is relatively low. This is to be expected since the co-sphere of the complex cation firstly interacts with that of Br^- ion, which is common to all salt solutions. However, as the salt concentration is increased, S/S_0 begins to diverge; the more hydrophobic the added cation is,[13] the more S/S_0 increases (structural salting-in[3] or cation-cation interaction). In particular for tetra-*n*-butylammonium bromide (n-Bu_4NBr) solutions, S/S_0 suddenly increases greatly at *ca.* 0.05 mol/l. The critical micelle concentration (cmc) of n-Bu_4NBr is reported to be *ca.* 0.04 mol/l at 25 °C by Lindenbaum and Boyd.[14] Thus, this abnormal increase in S/S_0 is attributed to so-called solubilization of the complex cation into micelles composed of n-Bu_4N^+, though the electrostatic repulsion is expected between the complex and the micelles. Therefore, the complex cation is cooperative with hydrophobic cations, too.

In conclusion, $[Fe(phen)_3]^{2+}$ belongs to the hydrophobic structure-maker group and is stabilized by the hydrophobic interaction[15] with added hydrophobic ions in aqueous solutions.

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8) If Gurney's suggestion that formate ion is a weaker structure-maker than acetate ion, is really correct (Ref. 2, p. 201), it is reasonable that S/S_0 for formate solutions is larger than that for acetate solutions, since structure-makers are antagonistic with hydrophobic structure-makers.[4]

9) Hydrophobic nature of some alkane carboxylate ions has been recently examined and discussed by some workers, H. Snell and J. Greyson, *J. Phys. Chem.*, **74**, 2148 (1970); Refs. 5 and 6.

10) The cmc of potassium octanoate is reported to be *ca.* 0.4 mol/l at 25 °C. Thus, all alkane carboxylates examined here do not form micelles under our experimental conditions. See the following references, K. Shinoda, "Colloidal Surfactants," Academic Press Inc., New York, N. Y. (1963); R. M. Diamond, *J. Phys. Chem.*, **67**, 2413 (1963).

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13) Hydrophobic nature of R_4N^+ ion has been reviewed by W.-Y. Wen, "Water and Aqueous Solutions," ed. by R. A. Horne, John Wiley & Sons, Inc., New Yoerk, N. Y. (1972), p. 613; *J. Solution Chem.*, **2**, 253 (1973). In particular, it is noteworthy that Desnoyers *et al.* (*Can. J. Chem.*, **43**, 3232 (1965)), Wirth and LoSurdo (*J. Phys. Chem.*, **72**, 751 (1968)), and Arnett *et al.* (*J. Amer. Chem. Soc.*, **92**, 7039 (1970)) have found the solubility of benzene in water to be much increased by the addition of tetraalkylammonium bromides.

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