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Hydration of Perchlorate Anion in Nitrobenzene by Means of Cryoscopic Measurements

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Synopsis. By means of cryoscopic measurements, hydration of the perchlorate anion in nitrobenzene was examined and the value of the first hydration constant was determined.

Tris(1,10-phenanthroline)iron(II) chelate cation is well extracted into nitrobenzene with certain anions.[1] As the size of anions increases, extractability increases. At the same time, a small amount of water was found to be transferred into nitrobenzene accompanied by the anions.[2,3] However, it is not as yet clear whether or not the water molecule transferred with the ion pair is associated with the ions in the organic phase. Cryoscopic measurements were carried out in order to estimate the first hydration constant of the perchlorate anion. The results were compared with those obtained by isopiestic measurements.[4]

Experimental

Preparation of the crystal of tris(1,10-phenanthroline)-iron(II) perchlorate was carried out according to the method reported previously, and its purity was checked by analysis.[4] The crystal was dehydrated by heating at 120 °C for a day just before use. Nitrobenzene was purified by washing with concentrated sulfuric acid and water successively, then dried over anhydrous calcium chloride and filtered with a filter paper. The resulting product was distilled under reduced pressure.

An appropriate amount (85—425 mg) of $Fe(phen)_3(ClO_4)_2$ was added to 20 ml of nitrobenzene solution containing various amounts of water, the freezing point depression being measured with a Beckmann thermometer. Since moisture in the air seriously affects the measurements, the amount of water was checked before and after the cryoscopic measurements and necessary correction made. Stoichiometric concentration of water was determined by means of the Karl Fischer titration.

Results and Discussion

The cryoscopic constant determined by the use of water as a solute is 6.815. The value is similar to that reported previously.[5] Some authors pointed out the occurrence of self-association of water in nitrobenzene,[6,7] but we have ignored it since the concentration of water is very low. The mixture of water and tris(1,10-phenanthroline)iron(II) perchlorate shows a smaller freezing point depression than expected from the additivity, thus indicating the occurrence of association.

From conductivity measurements, the ion pair of tris(1,10-phenanthroline)iron(II) perchlorate is considered to be completely dissociated in nitrobenzene.[8] Moreover, the amount of water co-extracted into nitrobenzene decreased with the increase[2,3] in anion size. The water co-extracted into nitrobenzene is considered to be attached to anions.

Now let us consider the degree of hydration. Since the concentration of water is very low (below 0.05 mol/l), the concentration of highly hydrated species such as di- or tri-hydrated species is assumed to be negligibly small. The mean hydration number $\bar{n}$ is described as follows:

$$\bar{n} = \frac{[ClO_4 \cdot H_2O]}{[ClO_4]+[ClO_4 \cdot H_2O]} = \frac{\beta_1[H_2O]_f}{1+\beta_1[H_2O]_f} = \frac{[H_2O]_{total}-[H_2O]_f}{[M]}$$

or

$$\frac{\beta_1}{1+\beta_1[H_2O]_f} = \frac{[H_2O]_{total}-[H_2O]_f}{[H_2O]_f} \cdot \frac{1}{[M]} \tag{1}$$

where $[M]=2\,[Fe(phen)_3{}^{2+}]=[ClO_4]$, and β_1 denotes the first hydration constant. Strictly speaking, the depression of freezing point at a certain concentration of salt might not be the linear function of the concentration of water. However, as a first approximation, the concentration of free water not associated with the perchlorate ion can be represented by the use of an apparent cryoscopic constant. The approximation is equivalent to the description that the amount of hydrated water is proportional to the stoichiometric concentration of water, and is considered to be valid from the data relating to the change of mean hydration number with free water. $[H_2O]_{total}/[H_2O]_f$ can thus be represented by K_f/K_1, where K_f is the cryoscopic constant of nitrobenzene and K_1 the apparent cryoscopic constant of nitrobenzene containing salts. Substituting the above relation into Eq. (1) we have

$$\frac{\beta_1}{1+\beta_1[H_2O]_f} = \frac{K_f-K_1}{K_1} \cdot \frac{1}{[M]}$$

If we assume that $\beta_1[H_2O]_f$ is negligibly smaller than unity, we get the following equation.

$$\frac{K_f-K_1}{K_1} \cdot \frac{1}{[M]} = \beta_1 \tag{2}$$

The results calculated by means of Eq. (2) are given in Table 1. Measurements were carried out at tem-

TABLE 1. HYDRATION CONSTANTS OF THE PERCHLORATE ION IN NITROBENZENE

M	K_1	β_1
0.00498	6.49 ±0.12	5.1±2.9
0.00999	6.270±0.094	4.5±1.4
0.0151	6.068±0.095	4.2±1.0
0.0257	5.493±0.204	4.7±1.1

peratures near 5.5 °C, the term β_2 being neglected in the treatment of data. The values of β_1 estimated at different concentration of salt are similar to each other, a mean value 4.5 being obtained within experimental errors. The constant β_1 was determined to be 1.5 ± 0.1 from the isopiestic study,4) where the measurements were carried out at 25 °C. The results seem to be reasonable, when we take the difference of conditions of the two experiments into consideration. We can conclude that all the excess water transferred by the solvent extraction of ion pair is hydrated to the anions. This indicates that the water molecule is chemically bound to the perchlorate ion in nitrobenzene phase.

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