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Aquation of First Row Transition Metal Perchlorates in Acetic Acid

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Solubilities of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) perchlorates in acetic acid were measured at 25 °C as a function of the water concentration. The solubilities of these perchlorates in anhydrous acetic acid were determined as: Mn(II), 0.0151; Fe(II), 0.0089; Co(II), 0.0034; Ni(II), 0.00125; Cu(II), 0.0082; Zn(II), 0.0093 mol kg^{-1}*.Equilibria of aquation of the perchlorates are written as follows:*

$$M(ClO_4)_2 + H_2O \xrightleftharpoons{\beta_1} M(ClO_4)_2(H_2O)$$

$$M(ClO_4)_2 + 2H_2O \xrightleftharpoons{\beta_2} M(ClO_4)_2(H_2O)_2$$

Logarithmic overall formation constants of the aquated species, log β_1 *and log* β_2*, were determined as 1.26 and 2.23 for Mn(II), 1.36 and* 2.3_4 *for Fe(II), 1.53 and* 2.9_3 *for Co(II), 1.62 and* 3.2_3 *for Ni(II), 2.09 and* 3.5_5 *for Cu(II), and 1.52 and* 2.9_5 *for Zn(II), respectively. The formation constants of monoaqua complexes are compared with the values estimated from crystal field stabilization energy.*

Introduction

Solubilities of many inorganic compounds in acetic acid have been measured qualitatively and classified by Davidson [1]. Quantitative measurements of solubilities of acetates, nitrates, halides, *etc.* have also been carried out [2–11]. The effect of a second component, such as water and acetates, on the solubilities of electrolytes has also been surveyed [8–11]. Generally, the solubility of electrolytes in acetic acid increases with increasing concentration of a second component. This may be interpreted by the reaction of the solute with a second component.

The solubility of transition metal salts increases considerably in the presence of water in acetic acid [12]. It is impossible to remove water completely from acetic acid, so that the solubility measured in the usual way is subject to a considerable uncertainty, that is, the solubility so far reported is often considerably larger than the true value.

In the present paper, the solubilities of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) perchlorates in acetic acid were measured as a function of the water concentration to obtain the solubilities of the perchlorates in anhydrous acetic acid and to investigate the aquation of the perchlorates. The formation constants of monoaqua complexes are compared with the values estimated from crystal field stabilization energy (c.f.s.e.).

Experimental

Reagents

Acetic acid

Acetic acid was prepared by the method described previously [13].

Metal perchlorates

Iron(II), nickel(II), copper(II) and zinc(II) perchlorates were prepared by dissolving pure metal (99.99%) in hot aqueous perchloric acid solution. Manganese(II) acetate was added to an aqueous perchloric acid solution and heated to expel acetic acid. Cobalt(II) perchlorate was prepared from cobalt(II) chloride in a manner similar to the manganese(II) perchlorate. The hydrates of perchlorates thus obtained were recrystallized from water. The crystals were dissolved in acetic acid and acetic anhydride equivalent to water was added dropwise. Anhydrous perchlorates precipitated were washed twice with anhydrous acetic acid. These perchlorates have been formulated as $M(ClO_4)_2 \cdot 6HOAc$ [14], where HOAc refers to acetic acid.

Experimental Procedure

Several grams of perchlorates were shaken with 30 cm^3 of acetic acid containing various concentra-

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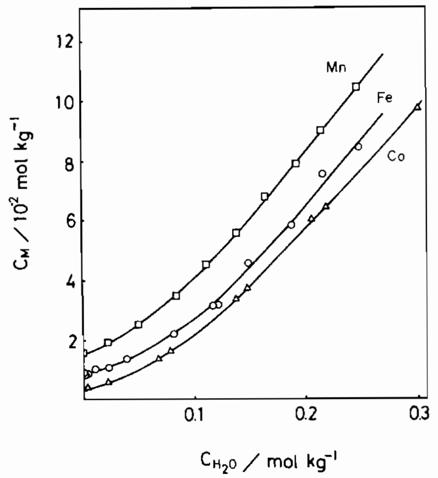


Figure 1. Solubilities of manganese(II), iron(II) and cobalt(II) perchlorates in acetic acid as a function of water concentration. □, manganese(II) perchlorate; ○, iron(II) perchlorate; △, cobalt(II) perchlorate.

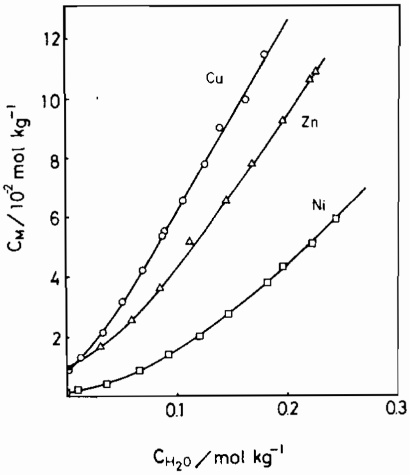


Figure 2. Solubilities of nickel(II), copper(II) and zinc(II) perchlorates in acetic acid as a function of water concentration. □, nickel(II) perchlorate; ○, copper(II) perchlorate; △, zinc(II) perchlorate.

tions of water and 0.02 mol kg^{-1} perchloric acid in a 50 cm^3 centrifuge tube at 25.0 ± 0.5 °C. Perchloric acid is added to suppress solvolysis of perchlorates:

$$M(ClO_4)_2 + HOAc \rightleftharpoons M(OAc)(ClO_4) + HClO_4$$

$$M(ClO_4)_2 + 2HOAc \rightleftharpoons M(OAc)_2 + 2HClO_4$$

In the case of iron(II) perchlorate, the shaking was performed in a sealed tube filled with nitrogen gas to prevent the oxidation of iron(II). After the dissolution equilibrium was established, the remaining crystals were separated by centrifugation. The concentrations of metal and water in the supernatant solution were determined by the compleximetric titration and Karl Fischer aquametry, respectively. It was confirmed that the composition of the solid phase remained constant as anhydrous perchlorate under these conditions.

Results

In Fig. 1 and 2, the solubilities of manganese(II), iron(II) cobalt(II), nickel(II), copper(II) and zinc(II) perchlorates in acetic acid are plotted as a function of the concentrations of water. The solubility of the perchlorate, C_M, increases with increasing concentration of water, C_{H_2O}. This is interpreted in terms of the formation of hydrated species or aqua complexes. As the perchlorates exist as monomeric forms [15, 16], the equilibrium of aquation is written as follows:

$$M(ClO_4)_2 + nH_2O \xrightleftharpoons{\beta_n} M(ClO_4)_2(H_2O)_n \quad (1)$$

By the same treatment of the solubility data as in the acetate system [12], we obtain the formation constants of aquated species, β_n. Solubility *i.e.* the total concentration of metal perchlorate, C_M, is given by eqn. (2).

$$C_M = [M(ClO_4)_2] + \sum_1 [M(ClO_4)_2(H_2O)_n] \quad (2)$$

or

$$\{C_M - [M(ClO_4)_2]\}[M(ClO_4)_2]^{-1}[H_2O]^{-1} = \sum_1 \beta_n [H_2O]^{n-1} \quad (3)$$

where $[M(ClO_4)_2]$ corresponds to the solubility of the perchlorate in pure anhydrous acetic acid. As the nonhydrated species, $M(ClO_4)_2$, is in equilibrium with the solid phase (perchlorate solvated by acetic acid), $[M(ClO_4)_2]$ remains constant even in the presence of water.

The plots in Fig. 1 and 2 being concave, the formation of aqua complexes higher than monoaqua complex is anticipated. As a first approximation to obtain the constants, β_1 and β_2, we calculated $[H_2O]$ on the assumption that the increase in C_M is solely attributable to the formation of monoaqua complex, *i.e.*, $[M(ClO_4)_2(H_2O)] = C_M - [M(ClO_4)_2]$. Here the decrease in $[H_2O]$ caused by the reaction of water with perchloric acid (eqn. (4)) was also taken into consideration ($[H_2O] = C_{H_2O} - [M(ClO_4)_2(H_2O)] - [H_2O \cdot HClO_4]$).

$$H_2O + HClO_4 \xrightleftharpoons{K_f} H_2O \cdot HClO_4 \quad (4)$$

where the formation constant of $H_2O \cdot HClO_4$ has been estimated as $K_f = 68$ [17]. $[M(ClO_4)_2]$ can be obtained by extrapolation of C_M to $C_{H_2O} = 0$ in Figs. 1 and 2. Using the values thus obtained, we plotted the left-hand side of eqn. (3) against $[H_2O]$. From

TABLE I. Overall Formation Constants of Mono- and Diaqua Complexes and Solubilities of Metal Perchlorates in Anhydrous Acetic Acid.

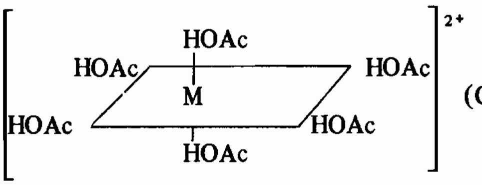
	Mn	Fe	Co	Ni	Cu	Zn
$\log \beta_1$	1.26	1.36	1.53	1.62	2.09	1.52
$\log \beta_2$	2.2_3	2.3_4	2.9_3	3.2_3	3.5_5	2.9_5
$[M(ClO_4)_2]$, 10^{-2} mol kg^{-1}	1.51	0.89	0.34	0.12_5	0.82	0.93

the intercept and slope of the plots, we obtain β_1 and β_2, respectively.

Then using these values of β_1 and β_2 we calculated again $[H_2O]$ from the total concentration of water as a second approximation. The plot of the left-hand side of eqn. (3) against $[H_2O]$ was performed again with the second value of $[H_2O]$. By means of such a successive approximation, we estimated the formation constants of mono- and diaqua complexes, β_1 and β_2, from the intercept and the limiting slope at lower $[H_2O]$, respectively. The plot according to eqn. (3) being concave, formation of higher aqua complexes is anticipated at high water concentration. However we did not try to determine the formation constant of higher aqua complex because of considerable error. The formation constants of aqua complexes, β_1 and β_2, and the solubility of non-hydrated species, $[M(ClO_4)_2]$, thus obtained are listed in Table I.

Discussion

Visible and infrared spectra and X-ray powder diagrams of the crystals of divalent transition metal perchlorates solvated by acetic acid, $M(ClO_4)_2 \cdot 6HOAc$, have been reported, and it has been established that the central metal ions are octahedrally coordinated by the six acetic acid molecules [14]. The acetic acid solution of the perchlorates also exhibit a coloration characteristic of the divalent ion with the octahedral configuration, hence it is considered that the metal perchlorate has the following structure:



The color of the solution scarcely changes by the addition of water. This may indicate that the octahedral structure is preserved in the hydrated species. Thus we may write the formation reaction of monoaqua complex as follows:

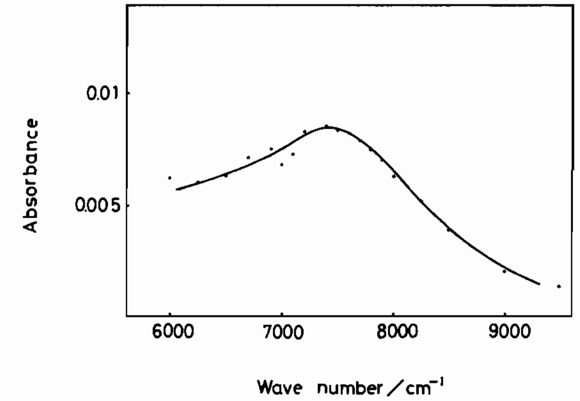
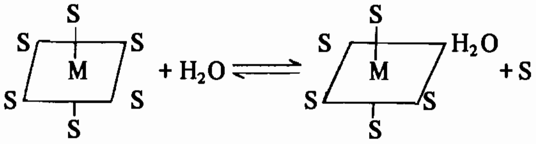


Figure 3. Near infrared spectrum of cobalt(II) perchlorate in anhydrous acetic acid. $C_{Co} = 3.00 \times 10^{-3}$ mol kg^{-1}.



where S refers to acetic acid molecule. The counter ion, ClO_4^-, and charges are omitted for simplicity. The diaqua complex is formed by the substitution of one of the acetic acid molecule remaining in the monoaqua complex with a water molecule.

Since the structures of the aquated and non-aquated species are both octahedral, we can compare the experimental results with the value estimated from crystal field stabilization energy (c.f.s.e.). Hereinafter we shall discuss the formation constant of monoaqua complex, β_1.

To obtain a ratio of ligand field strength of water and acetic acid for a given metal ion, we measured a near infrared spectrum (ν_1) of cobalt(II) perchlorate in anhydrous acetic acid. The results are shown in Fig. 3 and we obtain $\nu_{1(\mathrm{Co(HOAc)}_6^{2+})} = 7400$ cm^{-1}. Since the value of ν_1 for hexaaqua complex have been reported as $\nu_{1(\mathrm{Co(H_2O)}_6^{2+})} = 8000$ cm^{-1} [18], the ratio of 10Dq is obtained as:

$$\frac{10\mathrm{Dq\ for\ Co(HOAc)_6^{2+}}}{10\mathrm{Dq\ for\ Co(H_2O)_6^{2+}}} = 0.93$$

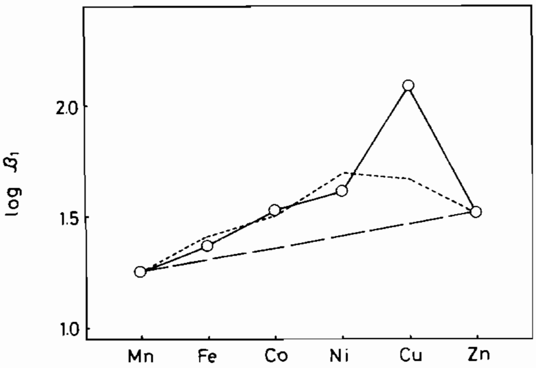


Figure 4. Log β_1 as a function of atomic number of metal. Open circles are experimental results. Dotted line is calculated value. See text.

This ratio will apply to the other metal ions [19], so we can evaluate 10Dq for $M(HOAc)_6^{2+}$ of the other metals from hexaaqua complex, $M(H_2O)_6^{2+}$.

In the case of monoaqua complex, $M(H_2O)(HOAc)_5^{2+}$, the only one molecule of six acetic acid molecules coordinated to metal ion is substituted by a water molecule. Therefore, by means of a law of average environment [19], the following relationship is obtained:

$$\text{c.f.s.e.}\{M(HOAc)_6^{2+} \longrightarrow M(H_2O)(HOAc)_5^{2+}\} = \frac{\text{c.f.s.e.}\{M(HOAc)_6^{2+} \longrightarrow M(H_2O)_6^{2+}\}}{6}$$

The value of c.f.s.e. thus obtained spectrochemically was converted to the equilibrium constant and was plotted in Fig. 4 with dotted line. The observed value is shown by solid line. The observed value is in good agreement with the calculated one. The discrepancy in copper(II) will be interpreted by the distorted octahedral structure of the copper species. In the case of metal acetate [12], the observed value of formation constant of monoaqua species considerably differs from that estimated spectrochemically. Thus, it is considered that in the case of metal perchlorate the complex ion, except for copper(II), has practically an exact octahedral configuration, whereas in metal acetate, in which the acetate ion coordinates directly to the central ion, the symmetry of complex ion will be lower.

The order of the stepwise formation constants of diaqua complexes, K_2 (= β_2/β_1), agrees also with the Irving–Williams series. The ratio of stepwise formation constants of monoaqua complex, β_1, and diaqua complex, K_2, are calculated as log β_1/K_2 = 0.3 for Mn(II), 0.4 for Fe(II), 0.1 for Co(II), 0.0 for Ni(II), 0.6 for Cu(II) and 0.1 for Zn(II). These values differ to some extent from the statistical value, β_1/K_2 = 12/5. This indicates that the coordination of the second water is affected by the first water molecule already coordinated.

The plot of log[$M(ClO_4)_2$] against the atomic number of metal ion exhibits a shape expected from c.f.s.e. This will indicate the presence of highly symmetric complex ion, $M(HOAc)_6^{2+}$ as in solid state, $M(ClO_4)_2 \cdot 6HOAc$ [14].

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