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# EFFECT OF PRESSURE ON THE DISSOCIATION OF ELECTROLYTIC SOLUTION

## I. Electrical Conductivity of Hexammine Cobalt (III) Chloride at High Pressures

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From the equivalent conductivity, $\Lambda$, of dilute solution ($1.0\times10^{-4}\sim1.0\times10^{-3}N$) of $[Co(NH_3)_6]Cl_3$ at 25°C under high pressure up to 600 kg/cm$^2$, the degree of dissociation, $\alpha$, and the dissociation constant, $K$, of $[Co(NH_3)_6]Cl^{2+}$ formed between $[Co(NH_3)_6]^{3+}$ and $Cl^-$ have been determined. $\Lambda$ increases with increasing pressure. $\alpha$ and $K$ have the minimum values at about 400 kg/cm$^2$ and the volume change, $\Delta V$, caused by dissociation, are 17 cm$^3$/mole at 300 kg/cm$^2$ and $-13$ cm$^3$/mole at 500 kg/cm$^2$. The equivalent conductivity at infinite dilution, $\Lambda_0$, increases from 183.3 to 189.0 under pressure. This may be due to the increase of the ionic mobility which is related with the viscosity of water. The increase of $\Lambda$, therefore, may be mainly ascribed to the increase of ionic mobility under pressure.

### Introduction

It was shown by Hamann and Strauss¹⁾ that the ionization of the simple electrolytes were enhanced at high pressures. From the equivalent conductivities, $\Lambda$, of the dilute solutions under high pressures, the variations of the degree of dissociation, $\alpha$, the dissociation constant, $K$, and the equivalent conductivity at infinite dilution, $\Lambda_0$, are determined, and also it is possible to estimate the amount of the volume change, $\Delta V$, due to the dissociation of the electrolytes. The authors have studied the ionic conductivity of the water solution of a complex, $[Co(NH_3)_6]Cl_3$, at 25°C up to 600 kg/cm$^2$ and examined the pressure effects on $\alpha$, $K$ and $\Lambda_0$.

### Experimentals

Hexammine cobalt (III) chloride, $[Co(NH_3)_6]Cl_3$, was prepared from the water solution of cobaltous chloride, ammonia, ammonium chloride and decolorizing charcoal as a catalyst by the method of Bjerrum and McReynolds²⁾. The crystals were thoroughly washed with conductivity water and absolute alcohol, then dried to a constant weight at 80～100°C.

As shown in Fig. 1, the conductivity cell made of teflon, of capacity 25 ml and cell constant 0.322 cm$^{-1}$, was mounted in a high pressure vessel containing a thermocouple of chromel-alumel as in the previous paper³⁾. The solution, which was isolated with mercury in a glass cup from

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1) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955)

2) W. C. Fernelius, *Inorganic Syntheses*, **II**, p. 216 (1946) McGraw-Hill

3) K. Shimizu, *This Journal*, **30**, 73 (1960)

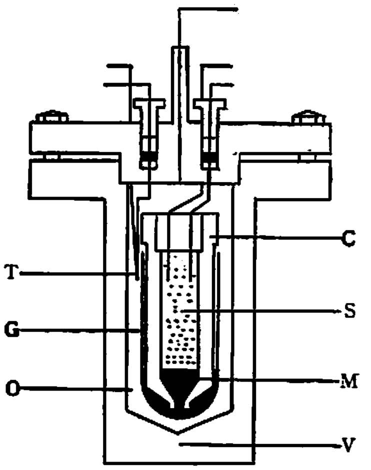

Fig. 1 High pressure conductivity cell
V : high pressure vessel
M : mercury
S : solution
C : teflon cell
O : silicone oil
G : glass cup
T : thermocouple

a silicone oil, was compressed by an oil injector. The pressures were measured by a calibrated Bourdon-type gauge. The pressure vessel was immersed in a temperature bath of liquid paraffin. The conductivity was measured at a temperature 25°C, at pressures 1~600 kg/cm$^2$ and at concentrations of solution $1.0\times10^{-4}\sim1.0\times10^{-3}\,N$. In order to calculate the equivalent conductivity of solutions under high pressures, it is necessary to know their compressibility. No such data are available for the hexammine cobalt (III) chloride solutions and thus the calculations were made in terms of the compressibility of water[4].

## Results and Considerations

The equivalent conductivity, $\Lambda$, increases with increasing pressure as shown in Fig. 2. As the equivalent conductivity is proportional to ionic mobility and the degree of ionization, the effects of pressure on the ionic mobility and degree of ionization should be examined.

Fig. 3 shows the plots of the equivalent conductivity, $\Lambda$, against square root of equivalent concentration, $C^{1/2}$, which follows Kohlrausch's empirical low. The experimental conductivity curves lie slightly below Onsager's theoretical lines. This slight difference may be attributed to ion-pair $[Co(NH_3)_6]Cl^{2+}$ formed between $[Co(NH_3)_6]^{3+}$ ion and $Cl^-$ ion as pointed out by Linhard and Monk[5]. Then, the ion-pair $[Co(NH_3)_6]Cl^{2+}$ would be in equilibrium with $[Co(NH_3)_6]^{3+}$ and $Cl^-$:

$$\underset{(1-\alpha)m}{[Co(NH_3)_6]Cl^{2+}} \rightleftharpoons \underset{\alpha m}{[Co(NH_3)_6]^{3+}} + \underset{(2+\alpha)m}{Cl^-}$$

where $\alpha$ is the degree of dissociation and $m$ is molar concentration. The equivalent conductivity

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[4] R. E. Gibson and O. H. Loeffler, *J. Am. Chem. Soc.*, **63**, 898 (1941)

[5] V. M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944)
I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, **1951**, 68

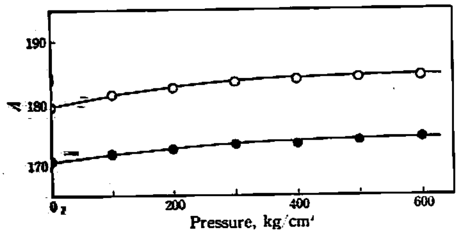

Fig. 2 Pressure dependence of equivalent conductivity of $[Co(NH_3)_6]Cl_3$
-○-: $1.0\times10^{-4}$ N
-●-: $1.0\times10^{-3}$ N

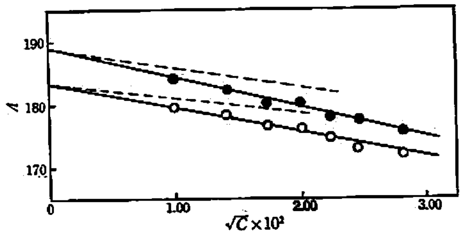

Fig. 3 Equivalent conductivity of $[Co(NH_3)_6]Cl_3$ at two pressures
-○-: 1 kg/cm²
-●-: 600 kg/cm²
- - -: Onsager's theoretical line

is as follows,

$$\Lambda C = 10^3\kappa = \sum_i Z_i m_i \lambda_i ,$$

where $\kappa$ is the solvent-corrected specific conductivity, $Z_i$ the ion valency of $i$th ion, $m_i$ the concentration (g ion/l) and $\lambda_i$ the ionic conductivity.

Then,

$$\Lambda C = 3\alpha m(\lambda_{[Co(NH_3)_6]^{3+}} + \lambda_{Cl^-}) + 2(1-\alpha)m(\lambda_{[Co(NH_3)_6]Cl^{2+}} + \lambda_{Cl^-}).$$

$$\therefore\quad \Lambda = \alpha\Lambda^{31} + \frac{2}{3}(1-\alpha)\Lambda^{21} = \alpha\left\{\left(\Lambda_0^{31} - \frac{2}{3}\Lambda_0^{21}\right) - \left(b^{31} - \frac{2}{3}b^{21}\right)I^{1/2}\right\}$$
$$+\frac{2}{3}(\Lambda_0^{21} - b^{21}I^{1/2}), \qquad (1)$$

where

$$\lambda_{[Co(NH_3)_6]^{3+}} + \lambda_{Cl^-} = \Lambda^{31} = \Lambda_0^{31} - b^{31}I^{1/2},$$
$$\lambda_{[Co(NH_3)_6]Cl^{2+}} + \lambda_{Cl^-} = \Lambda^{21} = \Lambda_0^{21} - b^{21}I^{1/2}$$

and ionic strength, $I$, is equal to $C(1+\alpha)$.

In this case, the ionic mobility of the bivalent ion-pair is taken as two-thirds of that of the tervalent cation. The degree of dissociation, $\alpha$, is obtained from Eq. (1) and the experimental values of $\Lambda$ under pressures by means of successive approximation.

The dissociation constant, $K$, is represented by the following equation,

$$K = \frac{\{[Co(NH_3)_6]^{3+}\}\cdot\{Cl^-\}}{\{[Co(NH_3)_6]Cl^{2+}\}} = \frac{\alpha(2+\alpha)mf_1f_2}{(1-\alpha)f_3}, \qquad (2)$$

where $f_i$ (1, 2, 3) are the activity coefficients of $[Co(NH_3)_6]^{3+}$, $Cl^-$ and $[Co(NH_3)_6]Cl^{2+}$, which have been calculated from the Debye-Hückel equation,

$$-\log f_i = 0.509 Z_i^2 I^{1/2}, \qquad (3)$$

The results are shown in Table 1, Figs. 4 and 5. As shown in figures, the degree of dissociation of each solution and the dissociation constant have the minimum values at about 400 kg/cm². The pressure coefficient of $\ln K$ gives the volume change, $\Delta V$, due to the dissociation according to the thermodynamical relation as follows,

Table 1 $\Lambda$, $\alpha$ and $K$ under pressures

| $P$ (kg/cm²) | $\Lambda_0$ | $1\times10^{-4}N$ | | | $2\times10^{-4}N$ | | | $3\times10^{-4}N$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $\Lambda$ | $\alpha$ | $K\cdot10^3$ | $\Lambda$ | $\alpha$ | $K\cdot10^3$ | $\Lambda$ | $\alpha$ | $K\cdot10^3$ |
| 1 | 183.3 | 179.5 | 0.9929 | 13 | 177.9 | 0.9896 | 17 | 176.6 | 0.9859 | 18 |
| 100 | 185.8 | 181.3 | 0.9859 | 6.3 | 179.5 | 0.9789 | 8.0 | 178.2 | 0.9754 | 10 |
| 200 | 186.9 | 182.3 | 0.9836 | 5.6 | 180.4 | 0.9767 | 7.3 | 179.0 | 0.9718 | 8.7 |
| 300 | 188.0 | 183.2 | 0.9813 | 4.8 | 181.3 | 0.9743 | 6.6 | 179.8 | 0.9683 | 7.7 |
| 400 | 188.7 | 183.9 | 0.9813 | 4.7 | 181.9 | 0.9731 | 6.3 | 180.3 | 0.9660 | 7.2 |
| 500 | 189.0 | 184.2 | 0.9813 | 4.8 | 182.3 | 0.9742 | 6.6 | 180.8 | 0.9683 | 7.8 |
| 600 | 189.0 | 184.3 | 0.9823 | 5.1 | 182.3 | 0.9740 | 6.6 | 180.9 | 0.9692 | 8.1 |

| $P$ (kg/cm²) | $5\times10^{-4}N$ | | | $8\times10^{-4}N$ | | | $10\times10^{-4}N$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\Lambda$ | $\alpha$ | $K\cdot10^3$ | $\Lambda$ | $\alpha$ | $K\cdot10^3$ | $\Lambda$ | $\alpha$ | $K\cdot10^3$ |
| 1 | 174.7 | 0.9823 | 22 | 172.4 | 0.9768 | 26 | 171.2 | 0.9749 | 28 |
| 100 | 175.8 | 0.9654 | 11 | 173.3 | 0.9572 | 13 | 171.9 | 0.9527 | 15 |
| 200 | 176.7 | 0.9629 | 10 | 174.1 | 0.9535 | 12 | 172.6 | 0.9477 | 13 |
| 300 | 177.3 | 0.9570 | 8.9 | 174.6 | 0.9462 | 11 | 173.0 | 0.9390 | 11 |
| 400 | 177.8 | 0.9546 | 8.4 | 175.0 | 0.9426 | 10 | 173.5 | 0.9367 | 11 |
| 500 | 178.4 | 0.9581 | 9.0 | 175.5 | 0.9449 | 11 | 173.9 | 0.9376 | 11 |
| 600 | 178.7 | 0.9617 | 10 | 175.8 | 0.9483 | 11 | 174.4 | 0.9435 | 12 |

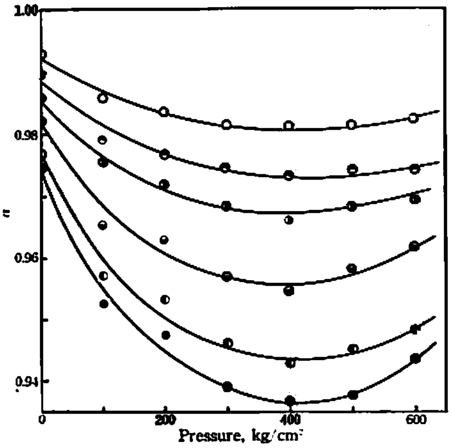

Fig. 4 Pressure dependence of degree of dissociation of $[Co(NH_3)_6]Cl_3$

-○-: $1.0\times10^{-4}$ N
-◓-: 2.0 〃
-◑-: 3.0 〃
-◒-: 5.0 〃
-◐-: 8.0 〃
-●-: 10.0 〃

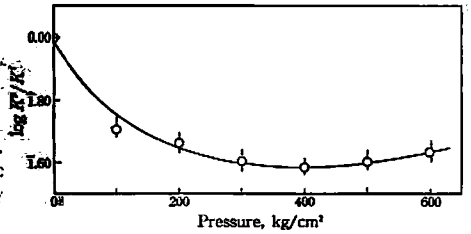

Fig. 5 Pressure dependence of $\log K^p/K^1$ of $[Co(NH_3)_6]Cl_3$

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT}. \qquad (4)$$

$\Delta V$ are 17 cm³/mole at 300 kg/cm² and −13 cm³/mole at 500 kg/cm², the sign of $\Delta V$ changing from positive to negative at about 400 kg/cm². $\Delta V$ may be equal to $\Delta V_1 + \Delta V_2$. $\Delta V_1$ is the volume change of ions themselves and positive in this system. $\Delta V_2$ is the volume change of solvent attracted by ions under pressures and negative because of the increase of ionic valencies. $\Delta V_1$ would be predominant at lower pressure so that $\Delta V$ is positive. At higher pressure, $\Delta V_2$ would take place of $\Delta V_1$, for water, of which the dielectric constant increases with increasing pressure[6], would be attracted much more by ions. Then pressure would favour the dissociation of ion-pair to cation and chloride ion.

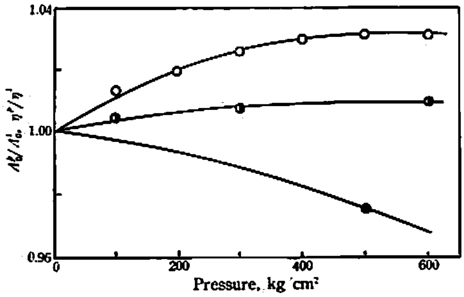

Fig. 6 Pressure dependence of equivalent conductivity at infinite dilution of $[Co(NH_3)_6]Cl_3$ and viscosity of water

-○-: $\Lambda_0^p/\Lambda_0^1$
-◐-: $\eta^p/\eta^1$ at 23°C (Cohen)
-●-: 〃 at 30°C (Bridgman)

The equivalent conductivity at the infinite dilution, $\Lambda_0$, increases from 183.3 to 189.0 with increasing pressure as shown in Table 1. This may be due to the increase of the ionic mobilily, which is related with the viscosity of water, $\eta$. The variation of $\Lambda_0$ and $\eta$ by pressure have similar tendencies as shown in Fig. 6, although Walden's rule is not best obeyed by this electrolyte. The increase of $\Lambda$ by pressure, therefore, may be mainly ascribed to the increase of ionic mobility.

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