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EFFECT OF PRESSURE ON THE DISSOCIATION OF ELECTROLYTIC SOLUTION

II Effect of Pressure on the Migration of Hexammine Cobalt (III) Ion in Water

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The pressure coefficients of the limiting ionic conductivity of $[Co(NH_3)_6]^{3+}$, SO_4^{2-}, Cl^- and K^+ in water at 25°C have been obtained over the pressure range $1\sim600\,kg/cm^2$. The results are used to evalute the volume of activation, $\Delta V^{\neq}$, for ionic migration derived by applying the theory of transition state to the migration of an ion. For each ion $\Delta V^{\neq}$ is negative and becomes less negative with increasing pressure, which may be due to the nature of water as solvent.

Introduction

The equivalent conductivity Λ of an electrolyte in various solvents has been widely studied with a high degree of precision. The dissociation equilibrium has been studied using the Onsager equation and its modifications which describe the relation between Λ and the composition of solution. Applying the Onsager equation, it is possible to extrapolate Λ of an electrolyte at a finite concentration to the corresponding value Λ^0 at infinite dilution. The limiting transport numbers then lead to the values of the individual limiting ionic conductivity λ^0_+ and λ^0_-. A large number of such values, especially for aqueous ions, have been determined experimentally.

It is of interest to discuss the mechanism of the migration of an ion in solution. Generally λ^0 has derived theoretically by the theory of transition state1), but little has been discussed about the experimental data with this theory.

In the previous paper2), we reported the effect of pressure on dissociation equilibrium of ion-pair by measuring the equivalent conductivity of aqueous solution of hexammine cobalt (III) chloride under high pressure. Using the limiting conductivity of the chloride reported as well as of the sulphate which has been determined under the same experimental conditions, the variation of limiting ionic conductivity with pressure has been obtained and discussed on the mechanism of migration of ions by the theory of transition state.

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1) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes" p. 552 (1941) McGraw-Hill

2) K. Shimizu, H. Takizawa and J. Osugi, *This Journal*, 33, 1 (1963)

As for the theory of transition state on the migration of an ion, the basic assumption is made that an ion in solution migrates by a series of jumps from one equilibrium position to another and that each jump has a characteristic free energy of activation, $\Delta G_0^{\neq}$. Now an ion having electronic charge $Z\cdot e$ jumps from one equilibrium position to another at the distance L, and then λ^0 is

$$\lambda^0=\frac{ZeF}{h}\cdot L^2\, exp(-\Delta G_0^{\neq}/RT), \tag{1}$$

where h is the Planck constant and F is the Faraday constant,

$$\therefore\ \ln\lambda^0=\ln\frac{ZeF}{h}+2\ln L-\frac{\Delta G_0^{\neq}}{RT}. \tag{1'}$$

By differenciating with pressure at constant temperature,

$$\left(\frac{\partial\ln\lambda^0}{\partial P}\right)_T=2\left(\frac{\partial\ln L}{\partial P}\right)_T-\frac{\Delta V^{\neq}}{RT}, \tag{2}$$

$$\therefore\ \Delta V^{\neq}=-RT\left\{\left(\frac{\partial\ln\lambda^0}{\partial P}\right)_T-2\left(\frac{\partial\ln L}{\partial P}\right)_T\right\}, \tag{2'}$$

where $\Delta V^{\neq}$ is the volume of activation. Now the compressibility β is $-(\partial\ln V/\partial P)_T$, and then $(\partial\ln L/\partial P)_T=1/3(\partial\ln V/\partial P)_T$, so we can express $\Delta V^{\neq}$ as follows,

$$\Delta V^{\neq}=-RT\left\{\left(\frac{\partial\ln\lambda^0}{\partial P}\right)_T-\frac{2}{3}\left(\frac{\partial\ln V}{\partial P}\right)_T\right\}. \tag{3}$$

Thus the volume of activation $\Delta V^{\neq}$ can be estimated from the pressure coefficient of λ^0 and the compressibility of the system which can be displaced in terms of the solvent without any serious error.

Experimental

Hexammine cobalt (III) sulphate 5-hydrate, $[Co(NH_3)_6]_2(SO_4)_3\cdot 5\,H_2O$, was prepared with the same method as hexammine cobalt (III) chloride $[Co(NH_3)_6]Cl_3$ described in the previous paper²⁾ after the method of Bjerrum and McReynolds³⁾, and was heated at 150～180°C till the constant weight was attained as the result of complete dehydration⁴⁾. The high pressure conductivity cell was described in the previous paper²⁾. The conductivity was measured at 25°C, at pressures up to 600 kg/cm², and at concentrations of aqueous solution from 1×10^{-4}N to 10×10^{-4}N. In order to calculate the equivalent conductivities of these solutions under high pressure, it is necessary to know their compressibilities. No such data are available, however, for these solutions and thus the approximation was made using the compressibility of pure water⁵⁾, which was used in calculating the right hand side of Eq. (3) as mentioned before.

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

4) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," XIV. p. 790 (1935) Longmans Green & Co.

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

Result and Discussion

The limiting conductivity Λ^0, which is obtained by extrapolating the plot of Λ against the square root of equivalent concentration, $C^{1/2}$, is shown in Table 1. The limiting ionic conductivity, λ^0, is estimated as follows; the limiting ionic conductivity of Cl^- ion under high pressure is calculated from Λ^0 and the transport number of KCl reported by Wall and Gill[6], and applying the law of the independent migration of ions by Kohlrausch, the limiting ionic conductivity of other ions are calculated successively.

Table 1 Λ^0 under pressure

Pressure (kg/cm²)	1	100	200	300	400	500	600
$[Co(NH_3)_6]Cl_3$	183.3	185.8	186.9	188.0	188.7	189.0	189.0
$[Co(NH_3)_6]_2(SO_4)_3$	187.0		191.5		194.1		195.0

Table 2 λ^0 under pressure

Pressure (kg/cm²)	1	100	200	300	400	500	600
K^+	73.52	73.59	73.67	73.73	73.74	73.73	73.71
Cl^-	76.35	76.71	77.08	77.44	77.76	78.08	78.33
SO_4^{2-}	86.05		81.68		83.16		84.33
$[Co(NH_3)_6]^{3+}$	106.95	109.09	109.82	110.56	110.94	110.92	110.67

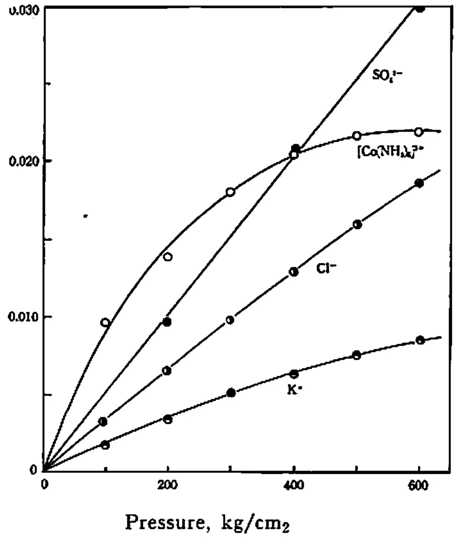

Fig. 1 Variation of $\log(\lambda^0_p/\lambda^0_1)-\frac{2}{3}\log(V_p/V_1)$ with pressure

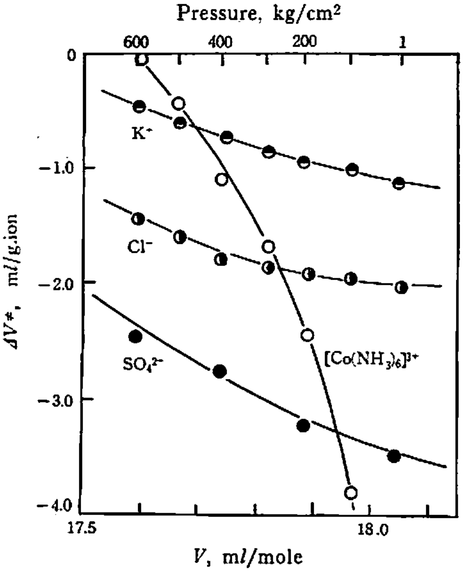

Fig. 2 Variation of $\Delta V^{\neq}$ with molar volume of water and pressure

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6) F. T. Wall and S. J. Gill, *J. Phys. Chem.*, **58**, 740 (1954)

Using these values shown in Table 2, $\ln(\lambda_P^0/\lambda_1^0)-2/3\cdot\ln(V_P/V_1)$, where subscripts P and 1 mean the values at P and 1 kg/cm^2 respectively, is calculated for each ion and plotted against pressure as shown in Fig. 1. From the slope of each curve, $\Delta V^{\ddagger}$ is calculated for each ion using Eq. (3).

As shown in Fig. 2, in which $\Delta V^{\ddagger}$ is plotted against the molar volume of pure water under high pressure as well as against pressure, $\Delta V^{\ddagger}$ is negative and becomes less negative with increasing pressure, which would be due to the nature of water as solvent.

As mentioned before, an ion jumps successively from equilibrium position to another. This eqilibrium position is corresponded to the position of a hole formed in solution. It is uncertain whether an ion migrates bearing its hydration shell or not. However, the hole would have the capacity enough to accomodate the ion, and so this hole would be far larger than holes existing in pure water. Thus $\Delta V^{\ddagger}$ contains the volume change for producing the hole as well as for jumping of an ion from one hole to another. And it will be probable that the greater part of $\Delta V^{\ddagger}$ arises from the volume change for the former process. And moreover the volume change arising from the former process would be devided into two parts; the volume change ΔV_{α} accompanying the destruction of open structure of water and ΔV_{β} accompanying the formation of hole in non-hydrogen bonded water, since the X-ray diffraction or other methods have suggested the local presence of the four coordinated open structure of water at lower temperature[7]. So ΔV_{α} is negative and ΔV_{β} positive. Thus in the case of aqueous solution, $\Delta V^{\ddagger}$ is approximately the sum of ΔV_{α} (<0) and ΔV_{β} (>0). In our experimental condition, so ΔV_{α} will be more predominant than ΔV_{β}, which makes $\Delta V^{\ddagger}$ negative.

The decrease of the degree of open structuce in water with increasing pressure[8] will make $\Delta V^{\ddagger}$ less negative. The remarkable change of $\Delta V^{\ddagger}$ of a larger ion with pressure may be mainly ascribed to a greater degree of destruction of open structure and larger compressibility.

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[8] R. Ginell, *ibid.*, **34**, 1249, 2174 (1961)