# RELATION BETWEEN THE PRESSURE EFFECT AND

THE STRUCTURE OF SOLVENT MOLECULE

Pressure Effects on the Various Alcoholic Solutions of Cobaltous Chloride (II) and Cobaltous Bromide (II)

BY YOICHI KITAMURA*

Cobaltous chloride and cobaltous bromide show blue color in alcohols with the carbon number larger than one. Their absorption spectra have the maxima at 660 mμ and 670 mμ, respectively.

At high pressure, these blue colors disappear and the extent of the pressure effect is much dependent on the molecular structure of the solvent.

Considering these phenomena to be caused by the shift of the following chemical equilibria:

$$CoCl_2X_2 + (n-2)X = CoX_n{}^{2+} + 2Cl^-,$$
$$CoBr_2X_2 + (n-2)X = CoX_n{}^{2+} + 2Br^-,$$
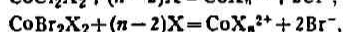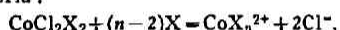
where X represents a solvent molecule and n is 4 or 6, the author has discussed the existence of the above equilibria at normal pressure and concluded that the equilibrium constants are much dependent on the molecular structure of the solvent.

In primary alcohols, the values of ΔV have the same order of magnitude ($-200 \sim -400$ cc/mole) as those expected from a dielectric consideration and increase rapidly with the increase of the pressure, whereas in secondary alcohols they are large and do not change with the variations of the pressure.

The author interprets these tendencies as due to the particular solvation to the Co^{2+} ion by the alcohol molecules.

Introduction

The effect of pressure on the chemical equilibrium in a solution between neutral and ionic species is described as follows[1]:
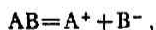
$$AB = A^+ + B^-,$$

$$K = \frac{[A^+][B^-]}{[AB]},$$

$$-\Delta V = RT \frac{d\ln K}{dP}, \tag{1}$$

where ΔV represents the volume change accompanying the shift of the equilibrium.

1) "High Pressure Physics and Chemistry", Vol 2, Chap. 7, ed. by R. S. Bradley, Academic Press, London and New York (1963)

2   Y. Kitamura

Theoretically, the value of ΔV in eq. (1) consists of three parts corresponding to each process as shown schematically,

gaseous state :   AB $\longrightarrow$ A$^+$+B$^-$
                                 ΔV_2
                      $\Delta V_1 \uparrow$ $\downarrow \Delta V_3$
                                 ΔV
solution :   AB $\longrightarrow$ A$^+$+B$^-$,
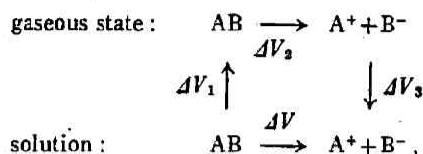
where ΔV_1 refers to the vaporization process of AB molecule from solution to gaseous state, ΔV_2 to the dissociation process of AB molecule in its gaseous state, and ΔV_3 to the dissolution process of the ions of A$^+$ and B$^-$.

The absolute value of the volume change for the dissociation process will be much smaller than that for the dissolution process, since the latter results from the intermolecular volume change of many solvent molecules.

A neutral species attracts its neighboring solvent molecules through the van der Waals force, whereas an ionic species through an electrostatic force in addition. So the absolute value of the volume change for the dissolution of a neutral species will be much smaller than that of an ionic species, hence

$$|\Delta V_1|, |\Delta V_2| \ll |\Delta V_3| \quad \text{and} \quad \Delta V \simeq \Delta V_3 = \sum_i \Delta V_{s,i}. \tag{2}$$

where $\Delta V_{s,i}$ means the volume change by the solvation of the respective ions.

Considering the solvent to be a uniform medium of a dielectric constant of D, the free energy of solvation for a single ion having a charge of q and the radius of r is given by $\Delta G_s = (q^2/2r) (1/D-1)$, and differenciating this with respect to pressure, the volume change by solvation is given by

$$\Delta V_s = (-q^2/2rD^2)\,(\mathrm{d}D/\mathrm{d}P). \tag{3}$$

For the equilibria in aqueous solutions many values of ΔV are known mainly by the measurements of the electrolytic conductivities at high pressure and the values of the same order of magnitude as those expected from eqs. (2) and (3) : $\Delta V \simeq -10 \sim -20$ cc/mole are obtained, which means that the equilibrium constant at 1,000 atm is $1.5 \sim 2.5$ times as large as that at normal pressure.

For equilibria in organic solvents with dielectric constants smaller than that of water, the smaller values of ΔV which lead to more intense pressure effects can be expected from eqs. (2) and (3). For example, in an ethanolic solution ($D \simeq 25$), the absolute value of ΔV will be about ten times as large as that for aqueous solution ($D \simeq 80$), or the equilibrium constant at 1,000 atm will be $63 \sim 4,000$ times as large as that at normal pressure. However, scarecely any measurement has been made in organic solvents.

On the other hand, from the microscopic point of view, a solute species interacts with the individual solvent molecules, so it may well be expected that the molecular feature of the solvent molecule such as the molecular structure might have a prominent influence on the value of ΔV or on the extent of the pressure effect.

The present author has investigated the effect of pressure on various alcoholic solutions of cobaltous chloride and cobaltous bromide and discussed the relation between the extent of the pressure effect and the molecular structure of alcohol.

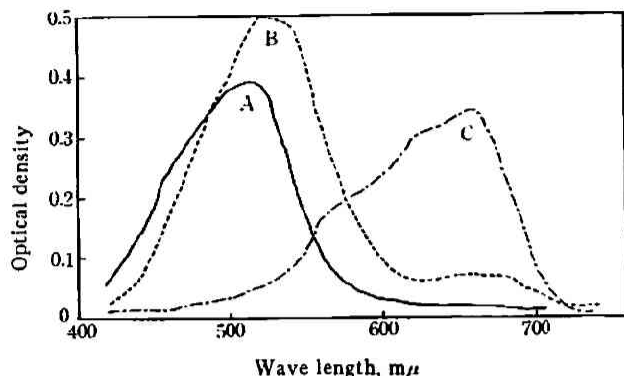Pressure Effect and Structure of Solvent Molecule   3

Fig. 1   Absorption spectra of various solutions of CoCl$_2$
A : Water (8.3×10^{-2}mole/l)
B : Methanol (5.0×10^{-2}mole/l)
C : Ethanol (2.8×10^{-3}mole/l)
Cells of 1cm path length were employed

Anhydrous cobaltous chloride is blue in solid state. In solution it shows different color in various solvents. Some of the visible absorption spectra are shown in Fig. 1. In water it shows pink color and the absorption spectrum has its maximum at 510~520 mμ with the absorption coefficient of about 5 l/mole·cm. In methanol it shows magenta color with two absorption maxima at 530~540 mμ and 660 mμ. The absorption coefficient near 530 mμ is about 10 l/mole·cm. In ethanol it shows blue color and the absorption spectrum has its maximum at 660 mμ with the absorption coefficient of about 160 l/mole·cm.

In other alcohols it shows also blue color and the absorption spectra are almost the same as that in ethanol with absorption coefficient of 200~300 l/mole·cm.

The pink color of the aqueous solution is considered to be due to the hexahydrated cobaltous ion. The colors in alcoholic solution are not yet fully understood.

Groh et al.[2] proposed the existence of the equilibrium:

$$2CoCl_2 = Co^{2+} + CoCl_4^{2-} \qquad\qquad\qquad (I)$$

in ethanol and in propanol, and they attributed the blue color to the complex ion of CoCl$_4^{2-}$.
Wormser[3] proposed the equilibrium :

$$2CoCl_2 = CoCl^+ + CoCl_3^- \qquad\qquad\qquad (II)$$

in ethanol, and attributed the blue color to the complex ion of CoCl$_3^-$.
Katzin et al. and Libus et al. have considered that the molecular complex of CoCl$_2$X$_2$ is the cause of the blue color in ethanol and that the magenta color of methanolic solution is due to the coexistence of CoCl$_2$X$_2$ and CoCl$_2$X$_4$.[4]~[6]

The present author thinks that the explanation by Katzin et al. and Libus et al. is probable, as will be shown in this report.

In each solvent cobaltous bromide shows a similar absorption spectrum to that of cobaltous

2)   J. Groh, Z. Anorg. Allgem. Chem., 146, 305 (1925); J. Groh and R. Schmid, ibid., 162, 321 (1927)
3)   Y. Wormser, Bull. soc. chim. France, 395, (1948)
4)   L. I. Katzin and E. Gebert, J. Am. Chem. Soc., 72, 5464, (1950)
5)   W. Libus, A. Ugniewska and S. Minc, Roczniki Chem., 34, 29 (1960)
6)   Hereafter, X represents a solvent molecule.

4   Y. Kitamura

chloride, and analogous explanations have been made.[5]

Experimentals

Materials

Anhydrous $CoCl_2$ was obtained by drying the Merck's hexahydrated salt $CoCl_2 \cdot 6H_2O$ at about 180~150°C during about 20 hours. The weight decrease of the salt indicated the loss of the six water molecules per one molecule of $CoCl_2$.

Commercial anhydrous $CoBr_2$ of chemically pure grade was used without further purification.

Ethanol was dried by metallic magnesium and then distilled. Other alcohols were dried by calcium sulfate and then distilled. The water content was determined by the Karl Fischer titration. It was below 0.03~0.04 wt% for ethanol used for the measurements at high pressure, below 0.01 wt% for ethanol for the measurements at normal pressure, below 0.05~0.06 wt% for other alcohols for the measurements at high pressure, and below 0.03~0.04 wt% for other alcohols for the measurements at normal pressure.

Measurements of the absorption spectra

A high pressure optical vessel with saphire windows was used for the measurements at high pressure.[7] The measuring process is same as previously reported[8] except for the direct contact of the sample solution with the vessel in the present case. The absorption spectrum of the sample solution after a direct contact for several hours with the vessel was examined and no difference was detected from that of the solution which had not been in contact.

The path length of the light was 2.5~3.0 mm. The maximum error in optical density was smaller than ±0.008. The pressure value was determined at the lower pressure side by means of a Bourdon gauge which was calibrated by a free piston gauge.

At normal pressure four quartz cells with the path length of 0.0336, 1, 5, and 10 cm were used.

A Hitachi EPU-2A type spectrophotometer was used. All measurements were carried out at room temperature (20~25°C).

Measurements of the electrolytic coductivities

A teflon cell with a pair of platinized platinum electrode was used for measurements at high pressure and the cell constant (about 0.8 cm^{-1}) was determined for each run from the comparison of the specific conductivity with that measured in the cell of a known cell constant. The apparatus and the details of the measurement are shown in other report.[9] A Yanagimoto MY-7 type low frequency bridge was used. All of the measurements were carried out in a thermostat controlled at 25°C unless otherwise stated.

7) J. Osugi and Y. Kitamura, *This Journal*, 35, 25 (1965)
8) J. Osugi and Y. Kitamura, *ibid.*, 36, 88 (1966)
9) J. Osugi, M. Sato and N. Ifuku, *ibid.*, 35, 32 (1965)

Pressure Effect and Structure of Solvent Molecule 5

Results

Part 1   Solutions of Cobalous Chloride

Pressure effects on the absorption spectra

Fig. 2 shows some of the absorption spectra at high pressure.[10]   The absorption intensities of the whole band from 500 mμ to 700 mμ decrease with the increase of pressure. The extent of the decrease by pressure is very much different in each solvent.

Fig. 3 shows the ratios of the optical density at 660 mμ at higher pressure to that at normal pressure. Table 1 shows the ratios for all of the alcohols employed as solvents. Octanol becomes solid at pressure above 3,000 kg/cm^2 and 2-methyl-2-propanol above 240 kg/cm^2. In other alcohols the spectra are measured up to the pressure where the absorption intensities become below one tenth of those at
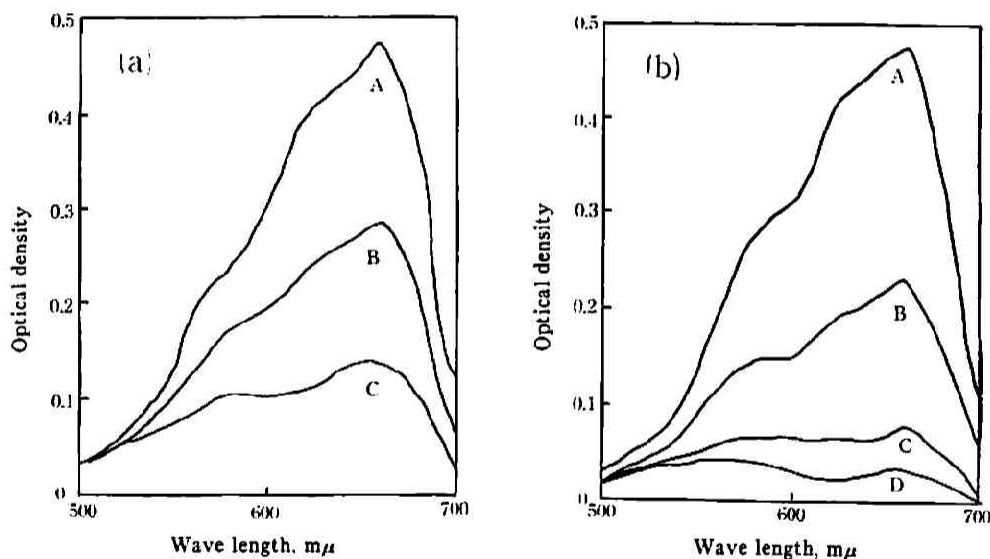

Fig. 2   Absorption spectra of alcoholic solutions of CoCl$_2$ at high pressure

(a) Ethanol solution (8.8 × 10^{-3} mole/l)

A : 1 kg/cm^2,   B : 1,000 kg/cm^2,   C : 2,000 kg/cm^2

(b) 1-Butanol sotution (6.08 × 10^{-3}mole/l)

A : 1 kg/cm^2,   B : 2,000 kg/cm^2,   C : 4,000 kg/cm^2,

D : 5,000 kg/cm^2

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10) All of the data at high pressure are calibrated for the change of the concentration through the contraction of the whole volume of the solution using the volume data at high pressure by P. W. Bridgman.

P. W. Bridgman, "Collected Experimental Papers", Harvard University Press (1964)

6   Y. Kitamura
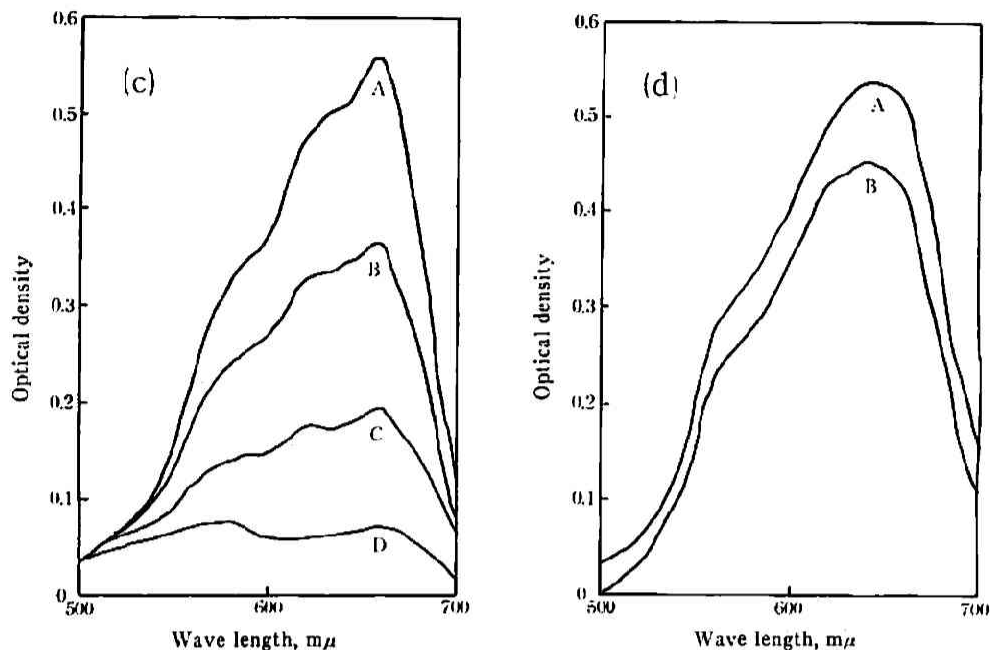
Fig. 2   Absorption spectra of alcoholic solutions of $CoCl_2$ at high pressure

  (c) 2-Methyl-1-propanol solution $(6.06 \times 10^{-3} mole/l)$

    A : 1 kg/cm², B : 2,000 kg/cm²,

    C : 4,000 kg/cm², D : 6,000 kg/cm²

  (d) 2-Butanol solution $(6.25 \times 10^{-3} mole/l)$

    A : 1 kg/cm², B : 10.000 kg/cm²
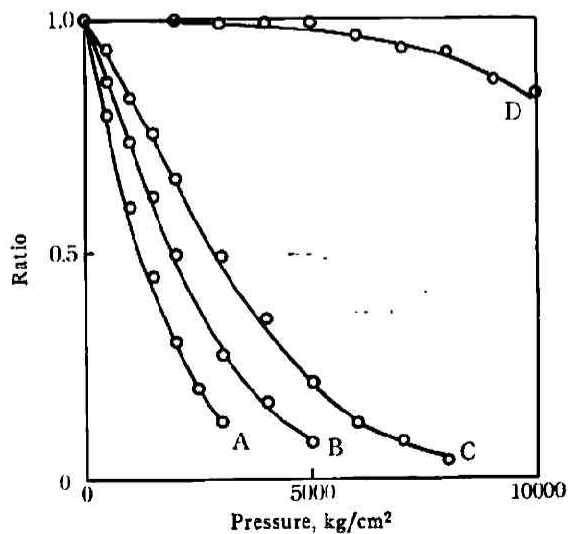
Fig. 3   Ratios of the optical density at 660 mμ at high pressure to that at normal pressure for solutions of $CoCl_2$
Solvent;

A : Ethanol

B : 1-Butanol

C : 2-Methyl-1-propanol

D : 2-Butanol

normal pressure, and the intensities never increase again at pressures higher than that pressure. From Fig. 3 and Table 1 it is obvious that the pressure effects are most remarkable in primary alcohols without a side chain such as ethanol and 1-propanol, and moderate in primary alcohols with a side chain such as 2-methyl-1-propanol and 3-methyl-1-butanol and very small in secondary alcohols.

Fig. 4 shows the absorption spectrum of methanolic solution at high pressure. In this case also the absorption intensity near 660 mμ decreases with increase of pressure and to a less extent that near 530 mμ too.
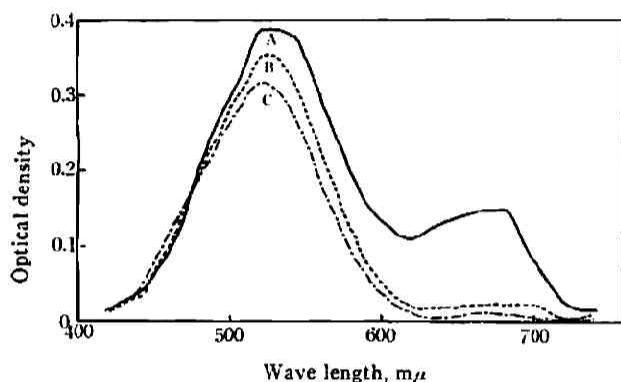

Fig. 4 Absorption spectra of methanolic solutions of CoCl$_2$ at high pressure (0.1mole/l)

A : 1 kg/cm^2,
B : 2,000 kg/cm^2,
C : 4,000 kg/cm^2

The pressure effect is small in 2-propanol as indicated in Table 1, whereas, as shown in Fig. 5, it is sufficiently large in 2-propanol which contains 5 vol % of methanol.

Every absorption spectrum described above comes to the initial one again at normal pressure.

The origin of the pressure effect

General consideration : From the fact that the extent of the pressure effect is much dependent

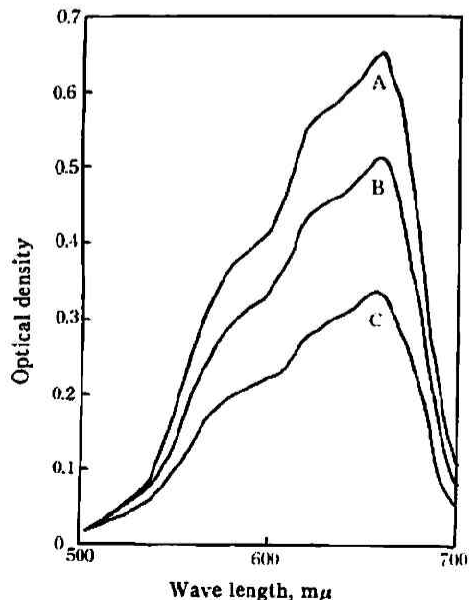Fig. 5 Absorption spectra of 2-propanolic solutions of CoCl$_2$ containing 5 vol% of methanol at high pressure (6.16 × 10^{-3}mole/l)

A : 1 kg/cm^2,
B : 4,000 kg/cm^2,
C : 6,000 kg/cm^2

8   Y. Kitamura

on the molecular structure of the solvent molecule and on the existence of the alcohol molecules which have a molecular structure capable of inducing the pressure effect as shown in Fig. 5, one may consider that the pressure effect is due to the shift of some chemical equilibrium in which the solvent molecules directly participate. In addition the alcohol molecule should participate in the equilibrium through the hydroxyl group, because the relative position of the hydroxyl group in the alcohol molecule is important for the extent of the pressure effect. As the whole band intensity from 500 mμ to 700 mμ decreases without remarkable change of the band shape, the whole band may correspond to one molecular species.

Generally an ionic species attracts its neighboring solvent molecules to a resulting contraction of the whole volume i.e. $\Delta V_\star < 0$; $dD/dP > 0$ in eq. (3). So the equilibrium constant is expected to increase with the increase of pressure, which means that the equiliblium shifts to the ionic species at high pressure.

Hence, one may consider that this pressure effect is caused by the shift of some chemical equilibrium between neutral and ionic species in which the solvent molecule directly participates.

Electrolytic conductivities of ethanolic solutions at high pressure :   Fig. 6 shows the value of the
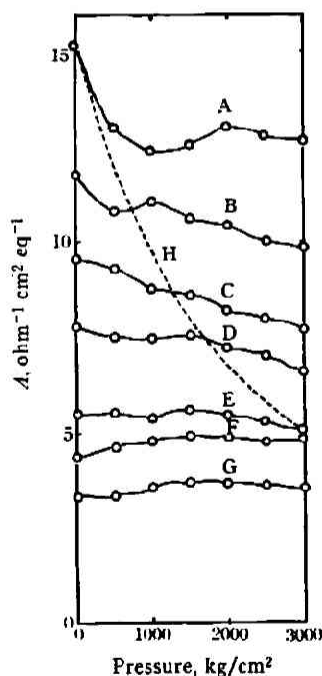
Fig. 6   Equivalent conductivities of ethanolic solutions of CoCl₂ at high pressure

Conc. (mole/l) × 10⁴ ;

    A : 1,   B : 2.5,   C : 5,   D : 10,   E : 25

    F : 50,   G : 100

The dotted line H indicates the decrease due to the viscosity change for 1 × 10⁻⁴ mole/l solution

equivalent conductivities at high pressure for ethanolic solutions of various concentration.[10]   In dilute solutions, the values of Λ decrease with increasing pressure. The rate of the decrease becomes smaller with increasing concentration to a slight increase in the concentration near 0.01 mole/l.

Writing the degree of dissociation as a and the equivalent conductivity of each ion as λ_{0+} and

λ_{0-}, Λ is written by

$$\Lambda \simeq \alpha(\lambda_{0+} + \lambda_{0-}). \tag{4}$$

Three effects of pressure on Λ should be considered:

i) The increase of α at high pressure which can be deduced from the above considerations.

ii) The decrease of λ_{0+} and λ_{0-} through the increase of the viscosity of the solvent at high pressure.

iii) The change of λ_{0+} and λ_{0-} through the deformation of the ions or through the change of the dielectric constant of the solvent at high pressure.

Among these, i) and ii) are important. The dotted line H in Fig. 6 indicates the decrease of Λ for 1×10^{-4} mole/l solution calculated from the values of the viscosity coefficients at high pressure, taking only the effect ii) into account.[11] Practically, as shown by A, Λ does not so much decrease as indicated by H, and this means the posibility of the effect i) or the increase of the degree of dissociation at high pressure. The smaller rate of the decrease for higher concentration can be interpreted through the increasing contribution of the effect i), owing to the decreasing value of α with increasing concentration. Thus one may conclude that the ionic dissociation is promoted in the ethanolic

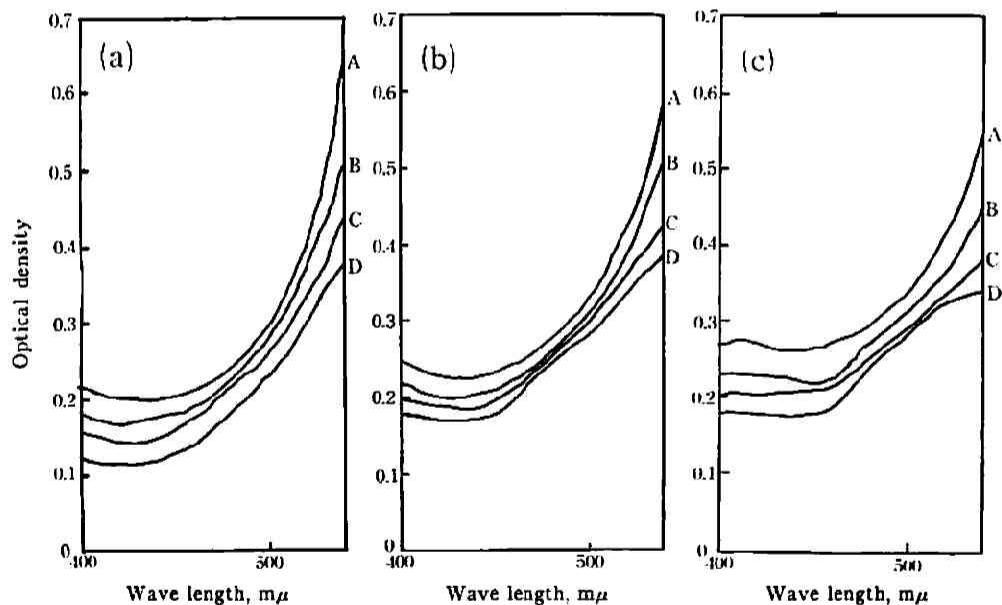Fig. 7 Absorption spectra of ethanolic solutions of CoCl$_2$ containing a little amount of water at high pressure (7×10^{-2}mole/l)

    (a) Water content : 0.1 wt.%

    (b) Water content : 0.4 wt.%

    (c) Water content : 1.5 wt.%

        A : 1 kg/cm^2,   B : 1,000 kg/cm^2,

        C : 2,000 kg/cm^2,   D : 3,000 kg/cm^2

11) P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **61**, 57 (1926)

Y. Kitamura

solution of cobaltous chloride with increasing pressure.

The chemical equilibrium as the origin of the pressure effect: The equilibrium which was proposed by Groh *et al.*[2] or by Wormser[3] will lead to the intensification of the blue color with increasing pressure, which is contradictory to the observed phenomena.

Thus, considering the neutral species corresponding to the blue color to be $CoCl_2X_2$, one may discuss the possibility of the equilibrium between the hexahydrated ion which might be produced through the interaction with the trace of water in the solvent[12] :

$$CoCl_2X_2 + 6H_2O = Co(H_2O)_6^{2+} + 2Cl^- + 2X \qquad \text{(III)}$$
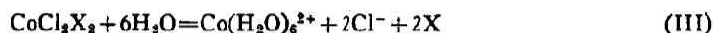
Assuming the pressure effect to be caused by the shift of equilibrium (III), one can expect the increase of the absorption intensity at $520\,m\mu$ simultaneously with the decrease at $660\,m\mu$, since the hexahydrated ion has maximum at $520\,m\mu$ as shown in Fig. 1. In the spectra at high pressure shown above, the concentrations of cobaltous chloride are about 7×10^{-3} mole/l, so the expected increment in optical density when the whole cobaltous ion comes to be the hexahydrated ion through eq. (III) is about 0.01, which is comparable to the maximum error. The spectra of solutions of higher concentration; 7×10^{-2} mole/l are shown in Fig. 7. As indicated in Table 1, in ethanolic solution the maximum at $660\,m\mu$ almost disappears at about $3,000\,kg/cm^2$ and one can expect a quantity of 7×10^{-2} mole/l of hexahydrated ion or an increase of the optical density of 0.1 at $520\,m\mu$, which is sufficiently

Table 1   The ratios of the optical density at $660\,m\mu$ at high pressure to that at normal pressure for the solutions of $CoCl_2$

Solvent		Pressure (kg/cm²)				
		1,000	2,000	3,000	4,000	5,000
Ethanol	CH_3CH_2OH	0.61	0.30	0.13		
1-Propanol	$CH_3(CH_2)_2OH$	0.69	0.38	0.17	0.03	
1-Butanol	$CH_3(CH_2)_3OH$	0.74	0.49	0.26	0.17	0.07
1-Pentanol	$CH_3(CH_2)_4OH$	0.67	0.42	0.23	0.12	0.06
1-Hexanol	$CH_3(CH_2)_5OH$	0.60	0.30	0.16	0.09	
1-Octanol	$CH_3(CH_2)_7OH$	0.66	0.40			

Solvent		Pressure (kg/cm²)				
		2,000	4,000	6,000	8,000	10,000
2-Propanol	$CH_3CH(OH)CH_3$	0.98	0.96	0.89	0.78	0.64
2-Methyl-1-propanol	$(CH_3)_2CHCH_2OH$	0.66	0.35	0.13	0.04	
3-Methyl-1-butanol	$(CH_3)_2CH(CH_2)_2OH$	0.52	0.20	0.06		
2-Butanol	$CH_3CH_2CH(OH)CH_3$	1.01	1.01	0.97	0.92	0.84
4-Methyl-2-pentanol	$(CH_3)_2CHCH_2CH(OH)CH_3$	0.98	0.96	0.93	0.87	0.81
2-Methyl-2-propanol	$(CH_3)_3COH$	1.00*				

*)   This is the value at $240\,kg/cm^2$

12)   A. H. Ewald and S. D. Hamann, *Austral. J. Chem.*, 9, 54 (1956)
      H. D. Lüdemann and E. U. Franck, *Ber. Bunsenges. Physik. Chem.*, 71, 455 (1967)
      M. Kato, T. Katsurai, K. Sone and S. Utsuno, *Z. Phys. Chem.*, 35, 348 (1962)

larger than the maximum error. However, no change can be seen at high pressure other than the uniform decrease with the whole band except in the case of Fig. 7 (c), which contains a rather large amount of water. The pressure effect described above are obtained in solution whose water content is smaller than 0.1 wt%, so one may conclude that they are not caused by the shift of equilibrium (III).

The following one can be considered to be another equilibrium in which solvent molecules directly participate :

$$CoCl_2X_2+(n-2)X=CoX_n^{2+}+2Cl^-, \qquad\qquad (IV)$$

where n is 4 or 6.
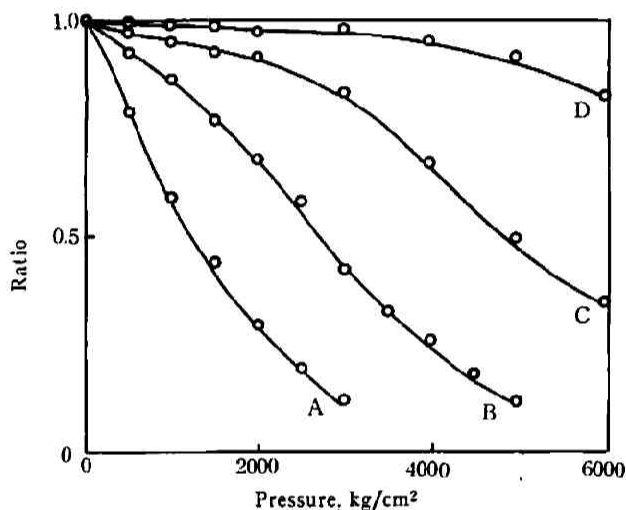
Fig. 8 Ratios of the optical density at 660 mμ at high pressure to that at normal pressure for ethanolic solutions of CoCl$_2$ containing LiCl

Conc. of CoCl$_2$: 8.79$\times10^{-3}$ mole/l
Conc. of LiCl (mole ratio to CoCl$_2$);

A : 0. B : 9.9, C : 51.6, D : 118

Fig. 8 shows the pressure effect for the ethanolic solution of cobaltous chloride with excess of chloride ion. It is obvious that the coexistence of lithium chloride in the solution has an effect to supress the pressure effect, which further supports the view that the pressure effect is attributed to the shift of some chemical equilibrium. There have been several discussions as to the molecular species corresponding to the blue color in the presence of excess chloride ions. Katzin *et al.* have proposed the existence of $CoCl_4^{2-}$ and $CoCl_3X^-$ which have their absorption maxima near 660 mμ. If one neglects the existence of these species, the supressing effect of exess chloride ion is in accordance with the mechanism (IV).

According to the mechanism (IV), cobaltous ion with four or six alcohol molecules attached probably through the hydroxyl group will exist at high pressure. In secondary alcohols, this ion will be rather bulky owing to the mutual repulsion of the carbon chain with the resultant smaller absolute value of ΔV, leading to a small pressure effect as showh experimentally.

The pressure effect in methanolic solution may also de interpreted from the mechanism (IV) for the peak at 660 mμ and from the following one for the peak near 530 mμ :

$$CoCl_2X_4+(n-4)X=CoX_n^{2+}+2Cl^-, \qquad\qquad (V)$$

where n is 4 or 6.

12   Y. Kitamura
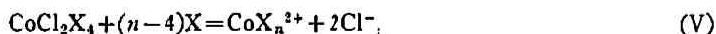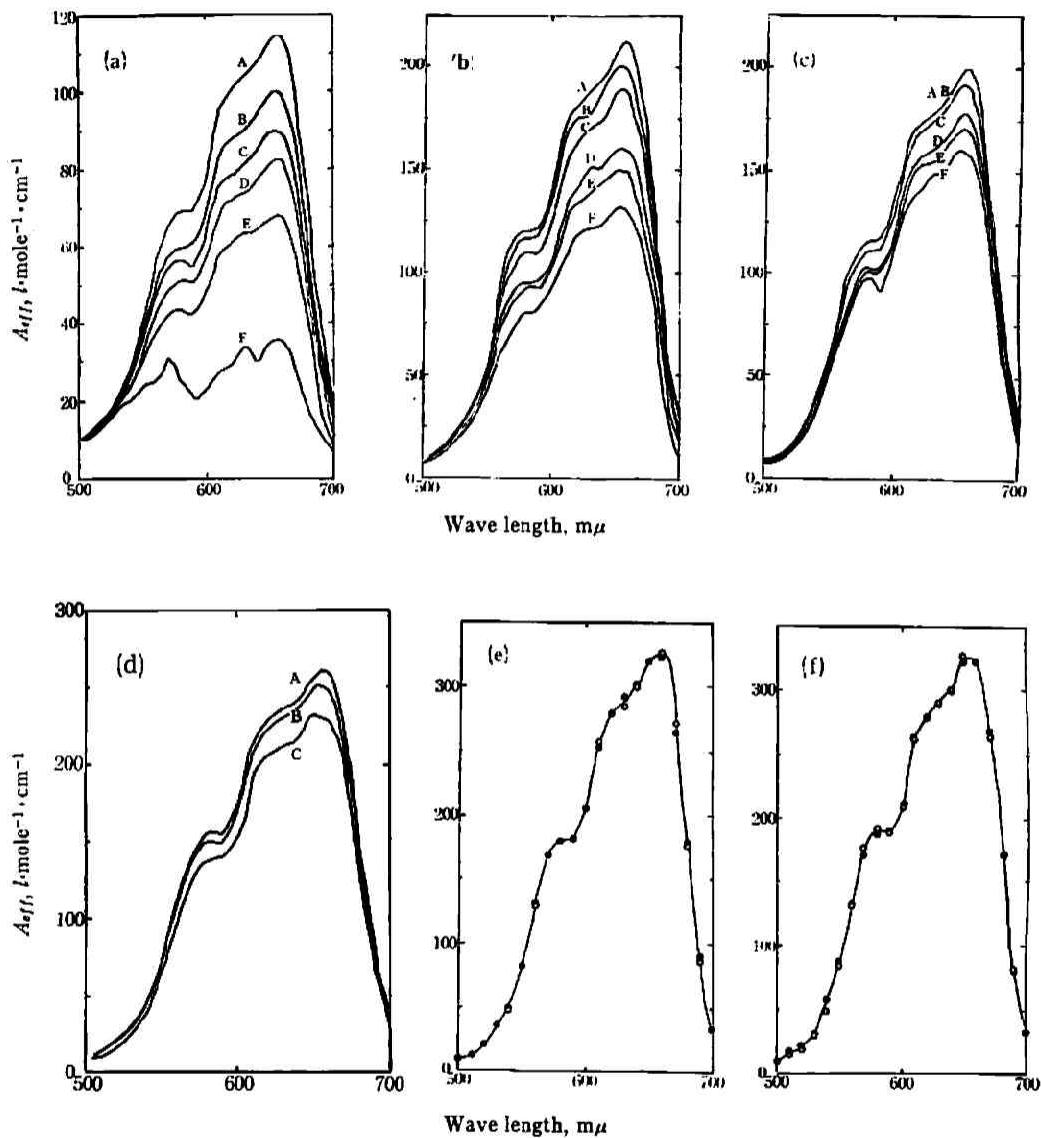
Fig. 9   Absorption spectra of alcoholic solutions of various concentrations of CoCl$_2$

    (a) Solvent: Ethanol

        Conc. (mole/l) $\times 10^4$:   A: 11,   B: 9,   C: 7,   D: 5,   E: 3,   F: 1

    (b) Solvent: 1-Propanol

        Conc. (mole/l) $\times 10^4$:   A: 7,   B: 5,   C: 3,   D: 1,   E: 0.75,   F: 0.5

    (c) Solvent: 1-Butanol

        Conc. (mole/l) $\times 10^4$;   A: 7,   B: 5,   C: 3,   D: 1,   E: 0.75,   F: 0.5

    (d) Solvent: 2-Methyl-1-propanol

        Conc. (mole/l) $\times 10^4$;   A: 5,   B: 1,   C: 0.5

(e) Solvent : 2-Propanol
Conc. (mole/l)×10^4 ; ◯: 0.5, ●: 5.0

(f) Solvent : 2-Butanol
Conc. (mole/l)×10^4 ; ◯: 0.5, ●: 5.0

(g) Solvent : 2-Methyl-2-propanol
Conc. (mole/l)×10^4 ; ◯: 0.5, ●: 50

This existence of the equilibrium (IV) in each solution will be further discussed in the following sections.

Concentration dependences of the absorption intensities

Fig. 9 shows the absorption spectra of each solution. The ordinate represents the effective absorption coefficient; (optical density)/(path length)·(concentration of cobaltous chloride). In primary alcohols the effective absorption coefficient increases with increase of the concentration of cobaltous chloride as indicated in Figs. 9 (a)~(d); the absorption bands do not obey Beer's law in these solvents. On the other hand in 2-propanol, in 2-butanol and in 2-methyl-2-propanol, it is independent on the concentration of the solute, as indicated in Figs. 9 (e)~(g); the bands obey Beer's law in these solvents. Figs. 9 (e)~(g) show the spectra for two concentrations; the obedience to Beer's law are also confirmed for other concentrations; 0.25×10^{-4} mole/l, 1×10^{-4} mole/l and 3×10^{-4} mole/l.

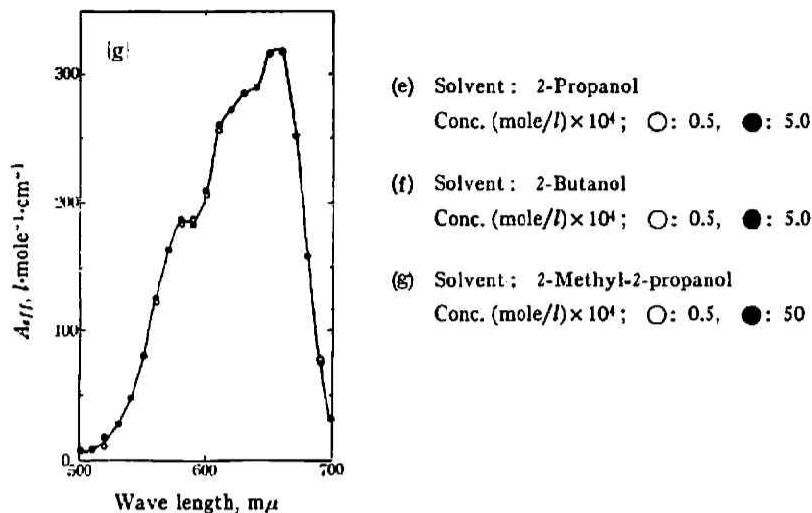These results may be considered to indicate the existence of the equilibrium between the blue complex and some species which do not show blue color with the equilibrium constants whose magnitude is dependent on the molecular structure of the solvent.

The proposition (I) by Groh *et al.* will mean the obedience to Beer's law, which is contradictory to the present results in normal alcohols[2] and (II) by Wormser the decrease of the effective absorption coefficient with increase of the concentration, which is also contradictory to the present results[3].

Electrolytic conductivities in each solution

Table 2 shows the values of the equivalent conductivities of each solution. The values are comparatively large in primary alcohols and are very small in secondary alcohols. These results further indicate the existence of ionic species in the solutions in a quantity dependent on the molecular structure of the solvent.

Fig. 10 shows the value of equivalent conductivity against the square root of the equivalent concentration $\sqrt{c}$ (eq./l)$^{1/2}$ for solutions of straight-chained alcohols. For ethanolic solution the value

14   Y. Kitamura

Table 2   The values of the equivalent conductivities in solutions of CoCl$_2$

Condition		Solvent			
		Primary alcohols		Secondary alcohols	
Temperature		25°C		20°C	
Cell constant		0.3182 cm^{-1}		0.053 cm^{-1}	
Specific conductivity of the solvent		$<3 \times 10^{-7}$ ohm^{-1} cm^{-1}		$<5 \times 10^{-8}$ ohm^{-1} cm^{-1}	

Solvent: Ethanol		Solvent: 1-Propanol		Solvent: 1-Butanol		Solvent: 2-Methyl-1-propanol	
Conc.	Λ	Conc.	Λ	Conc.	Λ	Conc.	Λ
0.08	30.0	0.50	4.76	1.56	1.17	12.5	0.127
0.25	21.1	0.75	3.93	3.13	0.818	25.0	0.09
1.00	15.5	1.00	3.43	6.25	0.585	100.0	0.053
5.00	9.95	3.00	2.07	12.5	0.431		
7.00	8.82	5.00	1.62	25.0	0.314		
11.0	7.55	7.00	1.39				

Solvent: 2-Propanol		Solvent: 2-Butanol		Solvent: 2-Methyl-2-propanol	
Conc.	Λ	Conc.	Λ	Conc.	Λ
1	1.23	1	<0.27	1	<0.27
10	0.13	10	0.030	10	<0.027
100	0.043	100	0.014	100	0.005

Concentrations are shown in (mole/l) $\times 10^{-4}$
Equivalent conductivities are shown in (ohm^{-1} cm^2 eq^{-1})
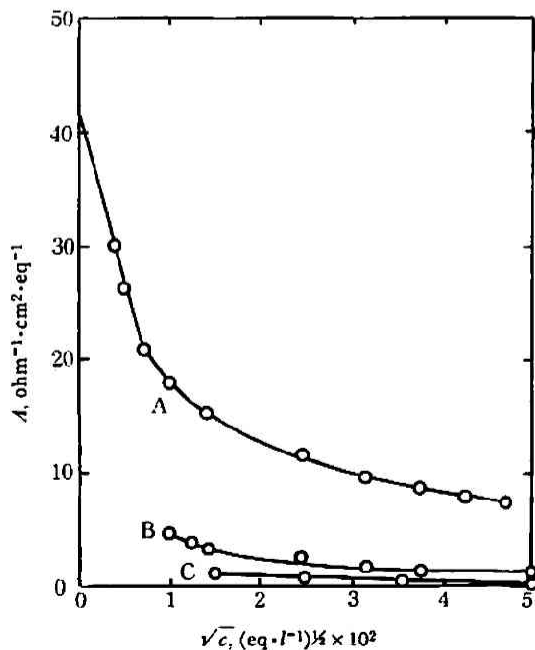
Fig. 10   The equivalent conductivities of solutions of CoCl$_2$ against the square root of the equivalent concentration

A : Ethanol solution,
B : 1-Propanol solution,
C : 1-Butanol solution

Pressure Effect and Structure of Solvent Molecule   15

of Λ at infinite dilution can be obtained by the linear extrapolation: $\Lambda_0 = 41.8$[13]

From the measurements by Barak *et al.*, $\lambda_0(Cl^-) = 24.3$, hence $\lambda_0(Co^{2+}) = \Lambda_0(CoCl_2) - \lambda_0(Cl^-) = 17.5$. According to the Stokes approximation;

$$\lambda_0 = \frac{eF}{6\pi\eta d} \times 10^7,\tag{5}$$

where η: viscosity coefficient

d: kinetic radius of the ion

e: unit charge

F: Faraday constant

The kinetic radius of Co^{2+} ion in ethanol can be calculated from the value of $\lambda_0(Co^{2+})$; $d = 4.30$ Å. The crystal radius of Co^{2+} ion is 0.74 Å and this rather large kinetic radius can be appreciated through the several alcohol molecules moving with the Co^{2+} ion.

Equilibrium constant in each solution

Fig. 11 shows the dependence of the effective absorption coefficient on the concentration at 660 mμ for solutions which do not obey Beer's law. For 1-propanolic, 1-butanolic and 2-methyl-1-propanolic solution, this becomes constant at concentrations higher than 1×10^{-3} mole/l, and for ethanolic solution at concentrations higher than 5×10^{-2} mole/l, which is not shown in the figure.

Fig. 12 (a) indicates the ratios of the effective absorption coefficient to that of 0.1 mole/l solution for each ethanolic solution at each wave length and Figs. 12 (b) and (c) the ratios to that of 0.01 mole/l 1-propanolic and 1-butanolic solution, respectively. For each solution this ratio is almost
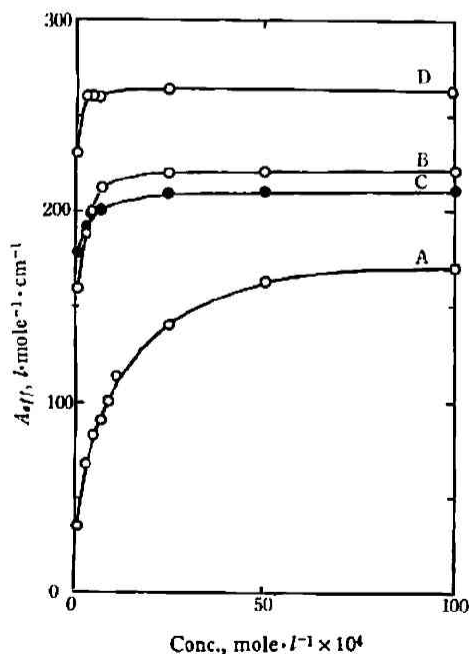

Fig. 11 Dependences of the effective absorption coefficient at the maximum of 660 mμ on the concentrations of $CoCl_2$

A: Ethanol solution,
B: 1-Propanol solution,
C: 1-Butanol solution,
D: 2-Methyl-1-propanol solution

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13) Hereafter, the equivalent conductivities are given in units of ohm^{-1}·cm^2·eq^{-1}.
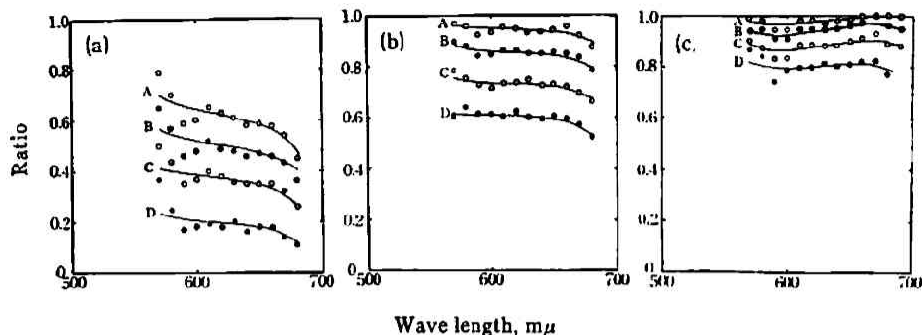
Y. Kitamura

Wave length, mμ

Fig. 12　Ratios of the effective absorption coefficients of alcoholic solutions of CoCl$_2$

(a)　Solvent:　Ethanol

Conc. (mole/l) $\times 10^4$;　A: 11,　B: 7,　C: 3,　D: 1

Ratios are taken to the coefficients of 0.1 mole/l solution

(b)　Solvent:　1-Propanol

Conc. (mole/l) $\times 10^4$;　A: 7,　B: 3,　C: 1,　D: 0.5

Ratios are taken to the coefficients of 0.01 mole/l solution

(c)　Solvent:　1-Butanol

Conc. (mole/l) $\times 10^4$;　A: 7,　B: 3,　C: 1,　D: 0.5

Ratios are taken to the coeffecients of 0.01 mole/l solution

constant over the wave length from 580 mμ to 690 mμ.　This may be considered to indicate that in the rather broad absorption band from 500 mμ to 700 mμ, the band at least from 580 mμ to 690 mμ is due to a single molecular species.

Thus, making the following assumption :

i')　The true absorption coefficient is given by that of 0.01 mole/l solution except for ethanolic solution and by that of 0.1 mole/l solution for ethanolic solution.

ii')　The concentration of the blue complex is proportional to the optical density at the maximum of 660 mμ,

the equilibrium in each solution is treated as (IV) and the equilibrium constants are calculated at each concentration ; the concentration of CoCl$_2$X$_2$ in each solution is given by multiplying the ratio of the effective absorption coefficient at 660 mμ to the true coefficient in each solvent by the total concentration of cobaltous chloride.　The results are shown in Table 3.

The equilibrium constants show a fairly good agreement for different concentrations except for those from 1×10^{-4} mole/l ethanolic solution, from 7×10^{-4} mole/l 1-propanolic solution, and from 0.5×10^{-4} mole/l 2-methyl-1-propanolic solution.

Thus one may conclude that there exists in each solution a chemical equilibrium which at least has the same stoichiometrical relation as (IV).　For solutions which obey Beer's law, the magnitude of the equilibrium constants may be estimated from the values of the equivalent conductivities.　As-

Pressure Effect and Structure of Solvent Molecule 17

Table 3   The equilibrium constants calculated from the effective absorption
coefficient at 660 mμ for solutions of CoCl$_2$

| Solvent ; | Ethanol, | $A_0 = 195$ | | Solvent : | 1-Propanol, | $A_0 = 220$ | |
a	A	b	$K \times 10^7$	a	A	b	$K \times 10^9$
1	35.0	0.18	1.23	0.5	132	0.30	1.06
3	68.0	1.05	2.85	0.75	151	0.515	1.01
5	82.4	2.11	4.56	1.00	160	0.727	1.12
7	90.0	3.23	6.63	3.00	188	2.56	1.33
9	100.0	4.62	7.31	5.00	200	4.55	0.80
11	114.3	6.45	5.85	7.00	212	6.75	0.10
Solvent :	1-Butanol,	$A_0 = 210$		Solvent :	2-Methyl-1-propanol,	$A_0 = 260$	
a	A	b	$K \times 10^{10}$	a	A	b	$K \times 10^{11}$
0.5	160	0.381	1.77	0.5	230	0.442	1.77
0.75	172	0.614	1.64	0.75	250	0.721	0.14
1.00	178	0.848	1.66	1.00	250	0.962	0.23
3.00	191	2.73	2.88				
5.00	199	4.74	1.48				
7.00	200	6.67	2.16				

$$CoCl_2X_2 + (n-2)X = CoX_n^{2+} + 2Cl^-$$
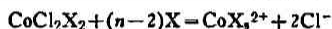
a: Total concentration of CoCl$_2$

b: Concentration of CoCl$_2$X$_2$

$2(a-b)$: Concentration of Cl$^-$

Concentrations are shown in (mole/l) $\times 10^{-4}$

$$K = \frac{4(a-b)^3}{b}$$

K is shown in (mole/l)^2

A_0: True absorption coefficient at 660 mμ

A: Effective absorption coefficient at 660 mμ

A_0 and A are shown in l/(mole·cm)

suming the kinetic radius of the ion in eq. (5) not to be much different in various alcohols, the value of $\Lambda\eta$ will be proportional to α through eq. (4). Table 4 shows the values of α thus obtained and the equilibrium constants calculated from these values of α. The mean ratio of the degree of dissociation from the spectral data to the value of $\Lambda\eta$ for ethanolic, 1-propanolic and 1-butanolic solution is chosen as the ratio for all of the solutions. For 2-propanolic, 2-butanolic and 2-methyl-2-propanolic solutions, the value of Λ and η, hence that of α and K are the values at 20°C. However, these will be sufficient for the discussion of the order of magnitude. On Table 4 a clear correspondence can be seen between the value of the equilibrium constant and the molecular structure of the solvent molecule; it is of the order of 10^{-7} (mole/l)^2 in ethanol, becoming smaller in alcohols with longer straight chain or with a side chain to the smallest value of 10^{-12} (mole/l)^2 in alcohols which have a side chain close to the hydroxyl group.

This correspondence to the structure of the alcoholic molecule should be interpreted to indicate the direct participation of the solvent molecule to the equilibrium.

18   Y. Kitamura

Table 4   The equilibrium constants estimated from the equivalent conductivity
          for solution of CoCl$_2$

Solvent	Λ (ohm^{-1}·cm^2·eq^{-1})	η (centipoise)	a	K (mole/l)^2
Ethanol	7.8	1.10*1)	0.32	2.0×10^{-7}
1-Propanol	1.25	2.00*2)	0.094	3.7×10^{-9}
1-Butanol	0.45	2.56*2)	0.043	3.4×10^{-10}
2-Propanol	0.126	2.40*2)	0.011	6.0×10^{-12}
2-Butanol	0.03	4.21*1)	0.005	4.2×10^{-13}
2-Methyl-1-propanol	0.15	3.32*2)	0.02	2.8×10^{-11}
2-Methyl-2-prpanol	<0.03	6.90*2)	<0.007	$<1.4 \times 10^{-12}$

The concentration is 1×10^{-3} mole/l for each solution
*1) Handbook of Chemistry and Physics 46th edition
      Published by The Chemical Rubber Co. (Ohio, U.S.A.)
*2) International Critical Tables Vol. VII
      Published by McGraw-Hill Co. (New York and London)

Table 5   Equivalent conductivities and the absorption coefficients at 660 mμ of
          higher alcoholic solutions of CoCl$_2$

Solvent	Λ (ohm^{-1}·cm^2·eq^{-1})	conc. (mole/l)	Λ (l/mole·cm)	conc. (mole/l)
1-Pentanol	9.3	1×10^{-4}	195	1×10^{-2}
1-Hexanol	0.41	1×10^{-3}	97.5	1×10^{-2}
1-Octanol	<0.15	1×10^{-3}	164	1×10^{-2}

Furthermore, the dependence of the true absorption coefficient on the molecular structure means the direct participation of the alcohol to the blue complex and the rather large kinetic radius of Co^{2+} ion in ethanol may be interpreted by several alcohol molecules attached. Thus one may conclude the equilibrium is not only stoichiometrically but precisely the same as (IV).

It is confirmed that the band does not obey Beer's law in 1-pentanol, in 1-hexanol, and in 1-octanol, in the concentration range from 0.5×10^{-4} mole/l to 5×10^{-4} mole/l, from 0.75×10^{-4} mole/l to 15×10^{-4} mole/l, and from 0.5×10^{-4} mole/l to 5×10^{-4} mole/l, respectively. The values of the equivalent conductivity and the absorption coefficient at 1×10^{-2} mole/l is shown in Table 5. The small value of Λ in 1-octanol will be due to a rather large value of η ($\eta_{25°C} = 7.21$ c.p.). Thus there will be also in these solutions an equilibrium between the blue complex and the ionic species.

Fig. 13 shows the equivalent conductivity and the effective absorption coefficient at the maximum (520~530 mμ) for dilute methanolic solutions. The effective absorption coefficient decreases with the increase of the equivalent conductivity, which may indicate the existence of the equilibrium (V). However, the change of the effective absorption coefficient with the concentration is not proportional at each wave length for the concentrations below 2.5×10^{-3} mole/l, the maximum is near 520 mμ and above 5.0×10^{-3} mole/l it is near 530 mμ. Hence, the author keeps from further quantitative discussions.
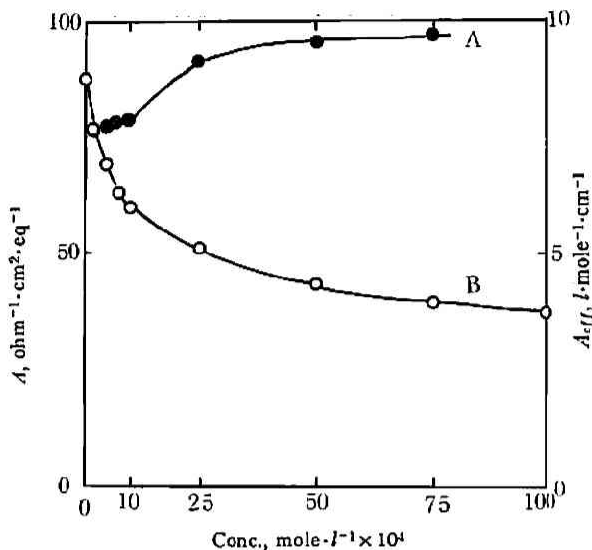
Fig. 13 The effective absorption coefficient at the maximum ($520 \sim 530$ mμ) and the equivalent conductivity of methanolic solution of CoCl$_2$

A: Effective absorption coefficient
B: Equivalent conductivity

Equilibrium constant at high pressure

Thus, considering the pressure effect to be caused through the shift of the equilibrium (IV) and assuming the true absorption coefficient to be independent of the pressure, the equilibrium constants at high pressure can be calculated through the assumptions i') and ii'). The results are shown in Table 6 and Fig. 14.

Table 6 The equilibrium constants and the values of ΔV at high pressure for solutions of CoCl$_2$

Solvent: Ethanol. $a=11.04 \times 10^{-3}$, $d=0.316$,					
Pressure	1	500	1,000	1,500	2,000	2,500
O.D.	0.472	0.376	0.286	0.211	0.141	0.099
A	170	135.4	103.0	76.0	50.8	35.6
K	1.17×10^{-6}	2.01×10^{-5}	9.71×10^{-5}	2.84×10^{-4}	7.54×10^{-4}	1.45×10^{-3}
ΔV	-154	-100	-64.1	-48.3	-38.2	-30.3

Solvent: 1-Propanol, $a=7.16 \times 10^{-3}$, $d=0.32$					
Pressure	1	500	1,000	1,500	2,000	3,000
O.D.	0.406	0.336	0.278	0.212	0.155	0.068
A	220	182.1	150.6	114.9	84	36.8
K	1.7×10^{-9}	1.25×10^{-6}	9.36×10^{-6}	4.30×10^{-5}	1.27×10^{-4}	7.11×10^{-4}
ΔV	-396	-161	-80.9	-57.3	-51.7	-33.7

Solvent: 1-Butanol, $a=7.51 \times 10^{-3}$, $d=0.374$						
Pressure	1	500	1,000	1,500	2,000	3,000	4000
O.D.	0.478	0.415	0.355	0.294	0.233	0.125	0.081
A	210	182.3	156.0	129.2	102.4	55.0	35.6
K	2.90×10^{-10}	5.86×10^{-7}	5.14×10^{-6}	2.09×10^{-5}	6.20×10^{-5}	3.46×10^{-4}	7.58×10^{-4}
ΔV	-497	-183	-82.1	-60.7	-47.2	-35.6	-10.1

Y. Kitamura

Solvent : 2-Methyl-1-propanol, $a=7.53 \times 10^{-3}$, $d=0.353$

Pressure	1	1,000	2,000	3,000	4,000	6,000	8,000
O.D.	0.556	0.465	0.368	0.271	0.195	0.071	0.020
A	260	217.4	172	126.7	91.2	33.2	9.4
K	4.32×10^{-11}	1.20×10^{-6}	1.32×10^{-5}	6.29×10^{-5}	1.77×10^{-4}	1.24×10^{-3}	5.64×10^{-3}
ΔV	-425	-103	-47.2	-33.7	-27.0	-16.9	-37.1

Solvent : 2-Propanol, $a=6.90 \times 10^{-3}$, $d=0.277$

Pressure	1	2,000	4,000	6,000	8,000	10,000
O.D.	0.498	0.490	0.476	0.441	0.389	0.317
A	330	324.7	315.4	292.2	257.8	210.0
K	9.62×10^{-12}	7.92×10^{-10}	1.69×10^{-8}	3.23×10^{-7}	2.55×10^{-6}	1.43×10^{-5}
ΔV	-64.6	-45.0	-36.5	-30.9	-22.5	-16.9

Solvent : 2-Butanol, $a=7.74 \times 10^{-3}$, $d=0.256$

Pressure	1	5,000	6,000	7,000	8,000	9,000	10,000
O.D.	0.520	0.515	0.506	0.490	0.480	0.455	0.433
A	325	321.9	316.3	306.3	300	284.4	270.6
K	6.39×10^{-13}	2.41×10^{-10}	5.0×10^{-9}	5.0×10^{-8}	1.18×10^{-7}	5.33×10^{-7}	1.34×10^{-6}
ΔV				-33.7			

d (cm): Path length
O. D. : Optical density at 660 mμ
Other abbreviations correspond to Table 3
Concentration is shown in (mole/kg-solvent)
K is shown in (mole/kg-solvent)^2
Pressure is shown in (kg/cm^2)
The value of ΔV is shown in (cc/mole)
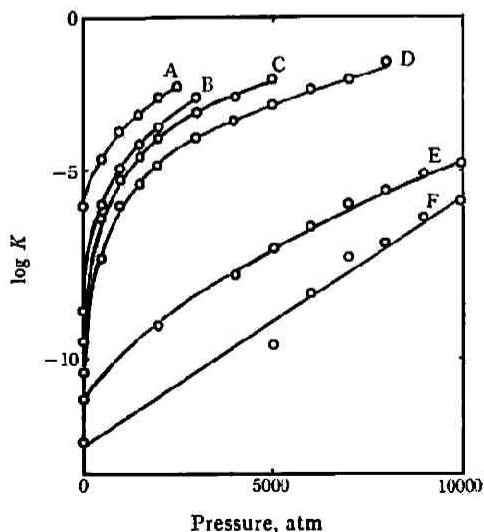The value of T in eq. (1) is chosen to 298°K

Fig. 14   The values of log K at high pressure for solutions of CoCl$_2$

Solvent ;   A : Ethanol,   B : 1-Propanol,
C : 1-Butanol,
D : 2-Methyl-1-propanol,
E : 2-Propanol,   F : 2-Butanol

Part 2   Solutions of Cobaltous Bromide

Pressure effects on the absorption spectra

Fig. 15 shows the absorption spectra of ethanolic solutions of cobaltous bromide at high pressure. The absorption intensity decreases with increase of pressure.

Equilibrium constant in each solution

Fig. 16 shows the absorption spectra of ethanolic solutions of various concentrations of cobaltous bromide.   The existence of some chemical equilibrium will be inferred from the disobedience to Beer's law.   Fig. 17 shows the dependences of the effective absorption coefficient on the concentration at the maximum ($670\,m\mu$) in various solvents. The same tendency as in the case of cobaltous chloride solution can be seen.   From the analogy to the cobaltous chloride solution, assuming the equilibrium as follows;

$$CoBr_2X_2 + (n-2)\,X = CoX_n^{2+} + 2Br^-, \qquad\qquad (VI)$$

where n is 4 or 6, the equilibrium constant for a few concentrations is calculated through the analogous assumptions with i') and ii').   The result is shown in Table 7.   From the comparatively good agreement for different concentrations, one may conclude that there exists an equilibrium described as (VI).   The analogous correspondence between the values of equilibrium constants and molecular structures will be inferred.

Equilibrium constants at high pressure

From the absorption intensity the equilibrium constants at high pressure are calculated through
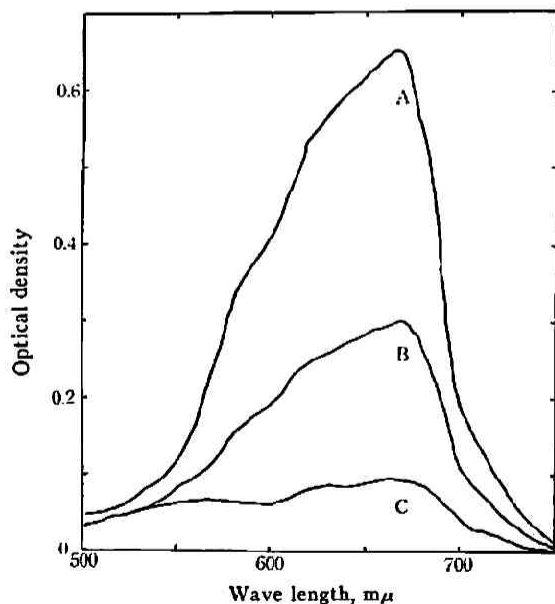

Fig. 15   Absorption spectra of ethanolic
solution of CoBr$_2$ at high pressure
Conc.: 1.6×10^{-2} mole/l
Pressure (kg/cm^2);
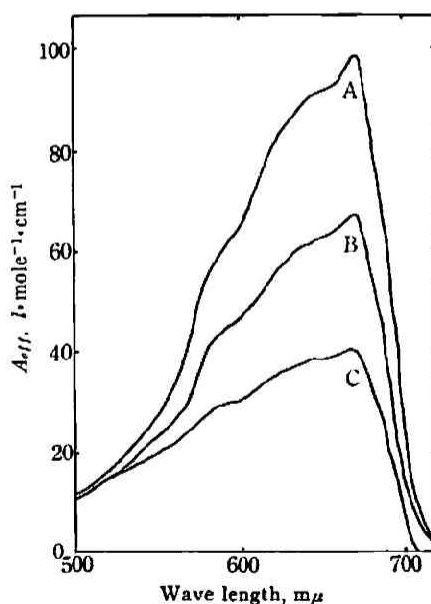A: 1,   B: 1,000,   C: 2,000

Fig. 16   Absorption spectra of ethanolic
solutions of various concent-
rations of CoBr$_2$
Conc. (mole/l)$\times 10^4$;   A : 7.5,
B : 5.0, C : 2.5

Y. Kitamura

Table 7   The equilibrium constants in solutions of $CoBr_2$

Solvent : Ethanol, $A_0 = 244.6$			Solvent : 1-Propanol, $A_0 = 295$			Solvent : 1-Butanol, $A_0 = 292.5$		
$a \times 10^4$	A	$K \times 10^6$	$a \times 10^4$	A	$K \times 10^9$	$a \times 10^4$	A	$K \times 10^{10}$
2.5	40.0	0.895	0.75	134.7	7.9	0.5	190	6.59
5.0	66.8	1.41	1.00	151.0	9.09	0.75	208	7.67
7.5	98.7	1.18	2.5	204.8	10.3	1.0	217	9.26

Solvent : 2-Methyl-1-propanol, $A_0 = 360$				Solvent : 2-Propanol, $A_0 = 410$		
$a \times 10^4$	A	$K \times 10^{11}$		$a \times 10^4$	A	$K \times 10^{13}$
0.5	312.0	2.73		0.5	394	6.16
0.75	326.7	1.96		0.75	400	3.35
1.0	327.0	3.40		1.0	400	5.96

The abbreviations correppond to Table 3
A_0 and A are the values at 670 mμ.

Table 8   The equilibrium constants and the values of ΔV at high pressure for solutions of $CoBr_2$

Solvent : Ethanol, $a = 2.0 \times 10^{-2}$, $d = 0.202$					
Pressure	1	1,000	2,000	3,000	4,000
O.D.	0.645	0.293	0.098	0.030	0.017
A	200	91.6	30.6	9.4	5.3
K	1.82×10^{-6}	1.05×10^{-3}	8.57×10^{-3}	3.71×10^{-2}	6.90×10^{-2}
ΔV	-230.4	-84.3	-39.3	-22.5	-11.2

Solvent : 1-Propanol, $a = 1 \times 10^{-2}$, $d = 0.241$					
Pressure	1	1,000	2,000	3,000	4,000	5,000
O.D.	0.560	0.379	0.204	0.100	0.051	0.029
A	290	199.5	107.4	52.6	26.8	15.3
K	1.42×10^{-8}	2.01×10^{-5}	2.83×10^{-4}	1.25×10^{-3}	3.30×10^{-3}	6.55×10^{-3}
ΔV	-247.3	-94.4	-49.5	-31.5	-19.1	-15.7

Solvent : 1-Butanol, $a = 8.83 \times 10^{-3}$, $d = 0.238$					
Pressure	1	1,000	2,000	3,000	4,000	5,000
O.D.	0.491	0.351	0.220	0.105	0.06	0.039
A	288	206.5	129.4	61.8	35.3	22.9
K	1.2×10^{-9}	1.12×10^{-5}	1.23×10^{-4}	7.26×10^{-4}	1.76×10^{-3}	3.12×10^{-3}
ΔV	-463.1	-100.0	-47.2	-29.2	-20.2	-14.6

Solvent : 2-Methyl-1-propanol, $a = 7.95 \times 10^{-3}$, $d = 0.217$					
Pressure	1	2,000	4,000	6,000	8,000
O.D.	0.500	0.333	0.147	0.064	0.035
A	360	239.8	105.8	46.08	25.2
K	4.17×10^{-11}	1.42×10^{-5}	3.03×10^{-4}	1.31×10^{-3}	2.91×10^{-3}
ΔV	-330.5	-64.6	-28.1	-12.4	-7.3

Solvent : 2-Propanol, $a = 5.70 \times 10^{-3}$, $d = 0.268$			
Pressure	1	6,000	8,000	10,000
O.D.	0.495	0.479	0.445	0.392
A	410	397.2	369	325
K	8.29×10^{-13}	4.0×10^{-9}	1.45×10^{-7}	1.45×10^{-6}
ΔV	-36.5			

Solvent : 2-Butanol, $a = 5.94 \times 10^{-3}$, $d = 0.242$					
Pressure	1	2,000	4,000	6,000	8,000	10,000
O.D.	0.465	0.459	0.455	0.441	0.404	0.341
A	400	394.7	391.2	379.2	347.4	293.2
K		3×10^{-10}	1.5×10^{-9}	2.1×10^{-8}	3.65×10^{-7}	3.67×10^{-6}
ΔV	-29.2				

The abbreviations correspond to Table 6.
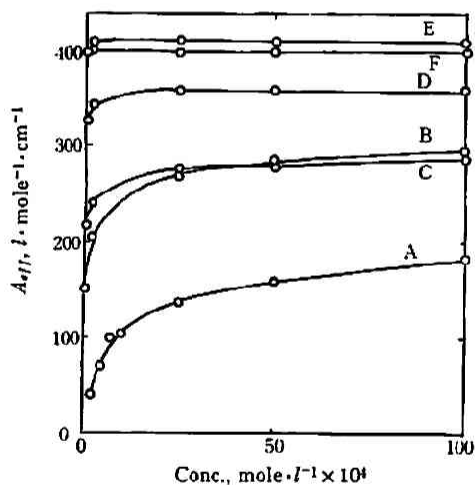O.D., A_0 and A are the values at 670 mμ.

Fig. 17 Dependences of the effective absorption conficients at the maximum of 670 mμ on the concentrations of CoBr$_2$
Solvent ;
  A: Ethanol, B: 1-Propanol
  C: 1-Butanol,
  D: 2-Methyl-1-propanol,
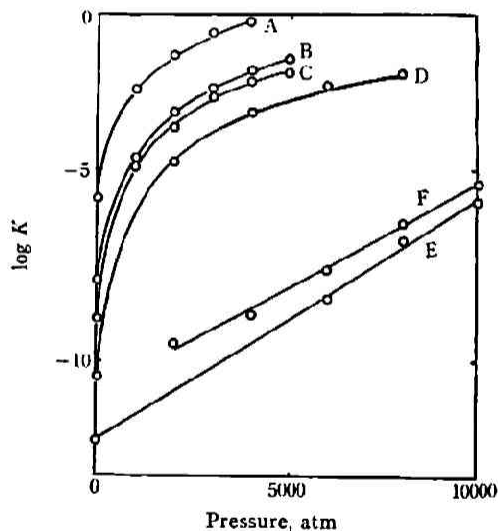 E: 2-Propanol, F: 2-Butanol

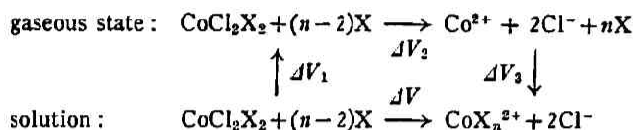Fig. 18 The values of $\log K$ at high pressure for solutions of CoBr$_2$
Solvent ;
  A: Ethanol, B: 1-Propanol,
  C: 1-Butanol,
  D: 2-Methyl-1-propanol,
  E: 2-Propanol, F: 2-Butanol

the analogous assumptions with i') and ii'). The results are shown in Table 8 and Fig. 18.

24   Y. Kitamura

Discussion

As shown in Tables 6 and 8, one will notice that the values of ΔV in primary alcohols are small and increase rather rapidly with increase of the pressure, whereas those in secondary alcohols are large and almost constant against the pressure.

Theoretical estimation of the volume change may be illustrated as follows,

gaseous state : $CoCl_2X_2 + (n-2)X \longrightarrow Co^{2+} + 2Cl^- + nX$

$$\uparrow \Delta V_1 \qquad \overset{\Delta V_2}{} \qquad \Delta V_3 \downarrow$$

$$\overset{\Delta V}{}$$

solution : $CoCl_2X_2 + (n-2)X \longrightarrow CoX_n^{2+} + 2Cl^-$

and the value of ΔV may be approximated by that accompanying the dissolution process of Co^{2+} and $2Cl^-$.

An estimation can be made through eqs. (2) and (3), where the ionic radius would be approximated by the crystal radius of the ion. The results are shown in Table 9.

Table 9   The estimation of ΔV at normal pressure by eqs. (2) and (3)
dD/dP is shown in $(atm)^{-1}$

Solvent	D	$\dfrac{dD}{dP} \times 10^3$	$\Delta V(CoCl_2)$	$\Delta V(CoBr_2)$
Ethanol	24.3	2.0	-134.4	-132.8
1-Propanol	20.1	1.85	-181.7	-179.5
1-Butanol	17.1	1.7	-230.7	-227.9
2-Methyl-1-propanol	17.7	1.7	-241.0	-238.1
2-Propanol	18.3	1.85	-219.2	-216.6
2-Butanol	15.8	1.7	-270.2	-267.0

Regarding the solvation to Co^{2+} ion as a sort of coordination, a more adequate estimation would be as follows. The value of ΔV_3 is divided into three parts $i.e.$ $\Delta V_3 = \Delta V_a + \Delta V_b + \Delta V_c$, where ΔV_a, ΔV_b and ΔV_c mean the volume change through the coordination of alcohol molecules to Co^{2+}, that through the electrostatic attraction by the alcohol coordinated cobaltous ion CoX_n^{2+} and ΔV_c that through the electrostatic attraction by Cl^- or Br^-.

Generally the rate of the volume change of alcohols becomes smaller with the increase of pressure and at pressure higher than 10.000 atm the volume reduces to almost a constant volume of about 60 % of the volume at normal pressure which may be regarded as the true volume of alcohol other than that by the translational motion of the molecules. The alcohol molecules coordinated around the Co^{2+} ion would nearly lose the translational motion and be in a state similar to that at extremely high pressure ; hence the volume would reduce to about 60 % by the coordination process. Considering n in eq. (IV) to be 6 by the analogy to $Co(H_2O)_6^{2+}$, ΔV_a may be given by

$$\Delta V_a \simeq (\text{molecular volume of alcohol}) \times 0.4 \times 6,$$

and the radius of the coordinated ion necessary for the evaluation of ΔV_b would be given by the radius of a sphere whose volume is (molecular volume of alcohol) $\times 0.6 \times 6$ plus that of bare cobaltous

ion (1.7 cc/mole). For ethanolic solution the radius thus obtained is somewhat smaller than the kinetic radius obtained from eq. (4). The results are shown in Table 10.

Table 10   Another estimation of ΔV at normal pressure

Solvent	M.V.	ΔV_a	$r(CoX_n^{2+})$	ΔV_b	$\Delta V(CoCl_2)$	$\Delta V(CoBr_2)$
	cc/mole	cc/mole	angstrom	cc/mole	cc/mole	cc/mole
Ethanol	57.8	−138.7	3.69	−25.1	−189.3	−187.5
1-Propanol	74.7	−179.3	4.01	−31.2	−245	−242.6
1-Butanol	91.5	−219.6	4.30	−36.9	−300.3	−297.2
2-Propanol	76.2	−182.9	4.04	−37.3	−261.9	−258.9
2-Methyl-1-propanol	92.1	−221.0	4.31	−34.4	−296.3	−293.4
2-Butanol	91.7	−220.1	4.30	−43.2	−314.7	−311.0

M.V.   indicates the molecular volume of alcohol

$r(CoX_n^{2+})$ indicates the radius of CoX_n^{2+} ion

In primary alcohols the values of ΔV have the same order of magnitude as those estimated above and the agreements are better with the latter estimation, whereas in secondary alcohols they have not the same order.

Fig. 19 indicates the value of ΔV at high pressure. In primary alcohols the values of ΔV increase with the increase of pressure, whereas in secondary alcohols they do not change with variations of pressure. The dotted lines indicate the value calculated from eqs. (2) and (3) in ethanolic and
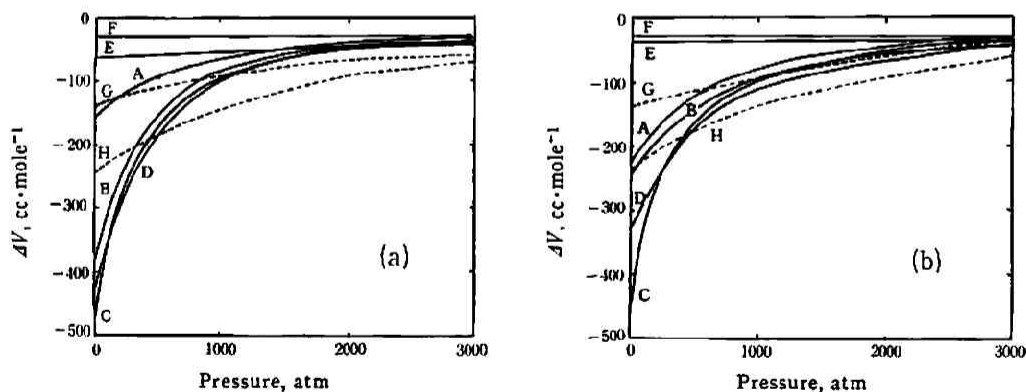
Fig. 19   The values of ΔV at high pressure

(a)   Solute : $CoCl_2$

(b)   Solute : $CoBr_2$

Solvent ;   A, G: Ethanol,   B: 1-Propanol,   C: 1-Butanol,

D, H : 2-Methyl-1-propanol,   E: 2-Propanol,   F: 2-Butanol

The dotted lines indicate the values given in Table 9

26   Y. Kitamura

2-methyl-1-propanolic solution.

The change of ΔV by the latter estimation would be rather smaller than that by eqs. (2) and (3), since the coordinated molecules are considered not to be compressed further.

The dielectric constants at high pressure have been measured for ethanol and for 2-methyl-1-propanol[15]. The values of dD/dP in 1-propanol and in 2-propanol are estimated to be the average value of dD/dP for ethanol and for 2-methyl-1-propanol and those in 1-butanol and 2-butanol to be the same as in 2-methyl-1-propanol, which may be justified by the correspondence of the value of dD/dP with the molecular size in the series of water, methanol, ethanol and 2-methyl-1-propanol.

The author interprets these phenomena as follows. Generally an ionic species is solvated in a solution. The solvation to Cl^- and Br^- may be one only through an electrostatic force owing to the closed shell structure of the ion, whereas the solvation to cobaltous ion will be a sort of coordination through the hydroxyl group of the alcohol molecule, which can be inferred from the existence of $Co(H_2O)_6^{2+}$ and the significant dependence of the values of ΔV arises from this solvation or coordination process. For primary alcohols the solvent molecule can easily arrange around the cobaltous ion to form a complex ion of CoX_n^{2+} to a resulting more effective contraction of the surroundings than that through only the electrostatic force or than that expected from eqs. (2) and (3).

The compressibility of the solvent around the ion which has been already compressed to some extent would be smaller than the bulk compressibilty since the rate of volume change of a liquid generally becomes smaller at high pressure[10] and the absolute value of ΔV is considered to decrease with increasing pressure. At high pressure the bulk compressibility becomes also small and the value of ΔV does not further remarkably change. On the other hand, in secondary alcohols the first solvation shell around the Co^{2+} ion cannot be constructed owing to the mutual repulsion of the alcohol molecules resulting from the close distance between the hydroxyl group and the side chain and the surroundings of the ion does not remarkably differ from that around the neutral species, leading to a larger value of ΔV and to a constancy of ΔV against pressure because both of the surroundings will be almost equally compressed.

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