THE EFFECT OF PRESSURE ON THE COMPLEX FORMATION OF COBALT(II) AND NICKEL(II) BROMIDES IN ACETONE SOLUTION

BY IZUMI ISHIHARA

In acetone solution of $CoBr_2$ alone, the species of $CoBr_2S_2$ is predominant in the concentration range higher than *ca.* 10^{-4} mol/*l* at atmospheric pressure and room temperature, where S denotes an acetone molecule. With increasing pressure, the following two equilibria become detectable;

$$CoBr_2S_2+4S \rightleftharpoons CoS_6^{2+}+2Br^-, \quad (I)$$

$$CoBr_2S_2+Br^- \rightleftharpoons CoBr_3S^-+S. \quad (II)$$

In acetone solution of $CoBr_2$ containing LiBr in large quantity, there exists the following equilibrium;

$$CoBr_3S^-+Br^- \rightleftharpoons CoBr_4^{2-}+S, \quad (III)$$

and $NiBr_2$ has the correspondieg equilibrium under the same condition;

$$NiBr_3S^-+Br^- \rightleftharpoons NiBr_4^{2-}+S. \quad (IV)$$

The pressure effect on these equilibria up to 5000 kg/cm²* at 25°C was studied by measuring the absorption spectra in the visible region and calculating the equilibrium constants at each pressure. The volume changes for the stepwise equilibria (I), (II) and (III) were obtained to be -109 ± 10, -5.2 and -0.8 cm³/mol and for (IV) -4.3 cm³/mol, respectively. The largely negative value for equilibrium (I) would be reasonable from the consideration of the electrostrictive effect.

Introduction

The pressure chromism of metal complexes in solution has been studied by a number of authors for the past decades. The pressure chromism of various kinds of metal complexes in aqueous solution was observed first by Wick[1], who gave only qualitative observations. The color change from blue to pink of cobalt(II) chloride in isopropanol with increasing pressure has been attributed to the increase in the coordination number of cobalt(II) ion from four to six by Hamann and his coworker[2]. Lüdemann *et al.*[3,4] measured the visible absorption spectra of the aqueous solution of cobalt(II) and nickel(II) halides with and without adding halides in a wide range of temperature and pressure. They suggested the appearance of some species under the extreme condition, and discussed qualitatively the influence of temperature and pressure on the equilibria and the molar absorption coefficient. Continuously they investigated copper(II) ions in aqueous solutions

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* 1 kg/cm² = 0.9807×10^5 Pa

1) F. G. Wick, *Proc. Amer. Acad. Arts Sci.*, **56**, 557 (1923)

2) A. H. Ewald and S. D. Hamann, *Austr. J. Chem.*, **9**, 54 (1956)

3) H. -D. Lüdemann and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, **71**, 455 (1967); **72**, 514 (1968)

4) H. -D. Lüdemann and W. A. J. Mahon, *High Temperatures-High Pressures*, **1**, 215 (1969)

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with and without chloride in excess[5]. Kitamura[6] discussed a correlation between the pressure chromism and the molecular structure of the solvent alcohols considering a single equilibrium between the complex ion coordinated by four ligands and that by six ligands. Rodriguez and Offen[7] worked on cobalt(II) chloride in water and in ethanol, and they threw doubt upon the highly negative volume change accompanying the ionization reaction reported by Kitamura and suggested that it would be insufficient to obtain the volume change supposing a single common equilibrium in various alcohols. Considering such a large discrepancy, the present author decided to study the pressure effect on the absorption spectra of complex ions in acetone, where the complex-formation equilibria have been established more reliably at atmospheric pressure[8]. In acetone solutions of $CoBr_2$ in the presence and the absence of LiBr there exist three equilibria which have different characters with respect to the ionic valence and the coordination number. In the present paper the equilibrium constant and the volume change for each reaction are determined and the effect of pressure is considered. Further, by examining the equilibrium of nickel(II) bromide with LiBr in excess in acetone and by studying the difference of the pressure dependencies, the effect of the metal ion on the volume changes is discussed.

Experimental

Materials

Pure anhydrous cobalt(II) bromide was prepared by recrystallizing the commercial $CoBr_2 \cdot 6H_2O$ (C. P. grade) three times from pure acetone solution (G. R. grade) and drying it at 140～150°C in a vacuum until a constant weight was reached. The ultra pure reagent $LiBr \cdot (1 \sim 2)\ H_2O$ supplied by Merck was heated to 130～140°C for about 8 hours to make this salt completely anhydrous. Anhydrous nickel(II) bromide of the C. P. grade was dried in a vacuum oven at 130°C prior to use. The solution of this salt was prepared by diluting the supernatant fluid of the concentrated one, and its concentration was determined by the gravimetric analysis with dimethylglyoxime.

Acetone of the spectroscopic grade was used without further purification. The water content was 0.06～0.1 wt% by gas chromatographic and Karl-Fischer analyses by Kyoto Electronics Manufacturing Co. Ltd.

Spectroscopic measurements

Two pairs of quartz cells with the path length of 1 and 5 cm were employed for the measurements at atmospheric pressure. Spectra were measured at atmospheric pressure on a Shimadzu UV-200S spectrophotometer and at high pressure on a Union SM-401 spectrophotometer.

An oil pump with a hand and a screw was used for the generation of the primary pressure,

5) B. Sholz, H. -D. Lüdemann and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, **76**, 406 (1972)
6) Y. Kitamura, *This Journal*, **39**, 1 (1969)
7) S. Rodriguez and H. Offen, *Inorg. Chem.*, **10**, 2086 (1971)
8) D. A. Fine, *J. Amer. Chem. Soc.*, **84**, 1139 (1962)

which was multiplied by an intensifier (piston ratio, 20 : 1). Silicone oil was employed as the pressure transmitting medium. The primary pressure measured by a Bourdon gauge was checked by means of a manganin wire gauge which was calibrated by a free piston gauge. The high pressure optical vessel is shown in Fig. 1. It has two optical windows made of sapphire and the jacket

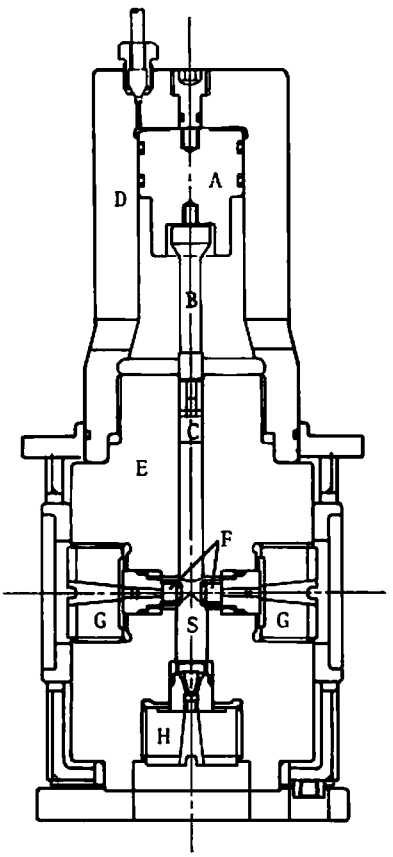

Fig. 1 High pressure vessel for the optical measurements
A: Low pressure piston
B: High pressure piston
C: Piston rod
D: Low pressure cylinder
E: High pressure cylinder
F: Sapphire window
G: Window plug
H: Closure plug
S: Sample solution

through which liquid paraffin is circulated to maintain the temperature at 25±0.02°C. All measurements were carried out at this temperature unless stated otherwise. The spectroscopic data of two or three runs were averaged and the experimental error was ±0.8%.

Results

Cobalt(II) bromide

In acetone solution of $CoBr_2$, there are two equilibria (I) and (II) as follows:

$$CoBr_2S_2 + 4S \rightleftharpoons CoS_6^{2+} + 2Br^- \qquad (I)$$

and

$$CoBr_2S_2 + Br^- \rightleftharpoons CoBr_3S^- + S, \qquad (II)$$

where S denotes an acetone molecule. At atmospheric pressure and room temperature, it is sufficient to take into account only the equilibrium (I) which can be considered to shift extremely to the left-hand side[8]. As seen in Fig. 2, the pressure promotes so much the ionization reaction (I) that the

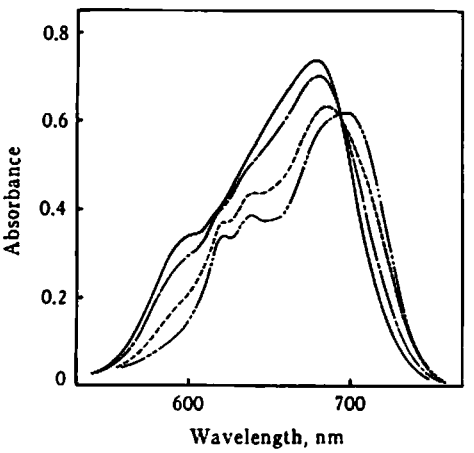

Fig. 2 $CoBr_2$ in acetone at high pressure and 25°C
Conc.: 1.856×10^{-3} mol/l
Path length: 0.959 cm
————: 1 kg/cm²
——·——: 880 kg/cm²
- - - - - - -: 2910 kg/cm²
——- - -——: 5630 kg/cm²

equilibrium (II) should be taken into account at high pressure. This is similar to the effect of temperature on cobalt(II) halide complexes in water and other organic solvents; the visible absorption spectra lose their intensity with lowering temperature, suggesting that the coordination number of cobalt(II) ion varies from four to six[9~12]. The equilibrium (I) indicates that the ionic species having the higher coordination number is formed from the neutral ones. In the equilibrium (II), on the other hand, the coordination number does not change but the kind of the ligand alters.

Equilibrium constants K_1 and K_2 for the corresponding equilibria (I) and (II), respectively, are defined by the following equations:

$$K_1=\frac{[CoS_6^{2+}][Br^-]^2}{[CoBr_2S_2]}f_\pm^3, \tag{1}$$

and

$$K_2=\frac{[CoBr_3S^-]}{[CoBr_2S_2][Br^-]}, \tag{2}$$

where [ ] denotes the molar concentration of each species and $f_\pm$ is the mean ionic activity coefficient given by the Debye-Hückel equation,

$$\ln f_\pm=-\frac{A_f|z_+ z_-|\sqrt{I}}{1+B_f\mathring{a}\sqrt{I}}, \tag{3}$$

where

$$A_f=4.202\times10^6(DT)^{-3/2}, \tag{4}$$

9) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, **1959**, 3997 (1959)
10) W. C. Niewpoort, G. A. Wesselink and E. H. A. M. van der Wee, *Recueil*, **85**, 397 (1966)
11) D. E. Scaife and K. P. Wood, *Inorg. Chem.*, **6**, 358 (1967)
12) K. Mizutani and K. Sone, *Z. Anorg. Allg. Chem.*, **350**, 216 (1967)

and

$$B_f = 50.29\ (DT)^{-1/2}. \qquad (5)$$

In the above equations, z_+ and z_- are the electronic charges of the cation and the anion, respectively, I is the ionic strength, $\mathring{a}$ which has been taken as 10 Å is the average closest approach distance of the ions involved, D is the dielectric constant, and T is the absolute temperature.

In Fig. 2, the increase of the concentration with pressure was corrected by using the interpolated compression data of acetone by Bridgman[13]. With increasing pressure, the peak at 677 nm attributed to $CoBr_2S_2$ is reduced and a new peak appears at longer wavelength. This indicates that the diminishing species $CoBr_2S_2$, which exists in a large amount at atmospheric pressure, is transformed into a new species.

The molar absorption coefficient of $CoBr_2S_2$ at atmospheric pressure and 25°C, $\varepsilon_2(1)$, and that of $CoBr_3S^-$, $\varepsilon_3(1)$ were determined by the following method. Since the species $CoBr_2S_2$ exists predominantly at atmospheric pressure above 10^{-4} mol/l[8] (see Fig. 3), the value of $\varepsilon_2(1)$ is obtained by

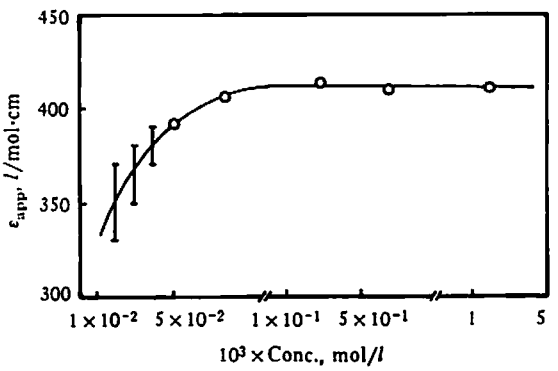

Fig. 3 The concentration dependence of the apparent absorption coefficient ε_{app} at 677 nm of $CoBr_2$ in acetone at atmospheric pressure and room temperature

means of Beer's law. By the mole ratio method adding LiBr step by step to the $CoBr_2$ solution, $\varepsilon_3(1)$ is determined, where the dissociation of $CoBr_3S^-$ is negligible at mole ratio $[Br^-]_t/[Co]_t=3$ (where t means the total concentration) in the range of wavelength 550~800 nm (Fig. 4)[8,14]. In another way, the value is also obtained with the error ±2% from the intercept, $1/(\varepsilon_4(1)-\varepsilon_3(1))$, of the plot of $l\,[Co]_t/([Co]_t\,\varepsilon_4(1)\,l-\text{Abs.})$ *vs.* $[Br^-]$[15] by using the dissociation constant of LiBr[16], where l is the path length, $\varepsilon_4(1)$ is the molar absorption coefficient of $CoBr_4^{2-}$ at atmospheric pressure mentioned later and Abs. is the absorbance. The molar absorption coefficients $\varepsilon_2(1)$ and $\varepsilon_3(1)$ by the mole ratio method are shown in Fig. 5 and those values at the maxima of peaks are given in Table 1. These quantities at wavelength λ and pressure P designated by $\varepsilon_2^{\lambda}(p)$ and $\varepsilon_3^{\lambda}(p)$ are assumed to differ little from those at atmospheric pressure except for the correction of band shifts at high pressure. If the absorption of the species i at pressure P has the shift $\Delta\lambda$ at wavelength λ relative to the atmospheric

13) P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **49**, 3 (1913)
14) A. S. Meyer and G. H. Ayres, *J. Amer. Chem. Soc.*, **79**, 49 (1957)
15) D. A. Fine, *Inorg. Chem.*, **4**, 345 (1965)
16) I. Ishihara, *This Journal*, **47**, 102 (1977)

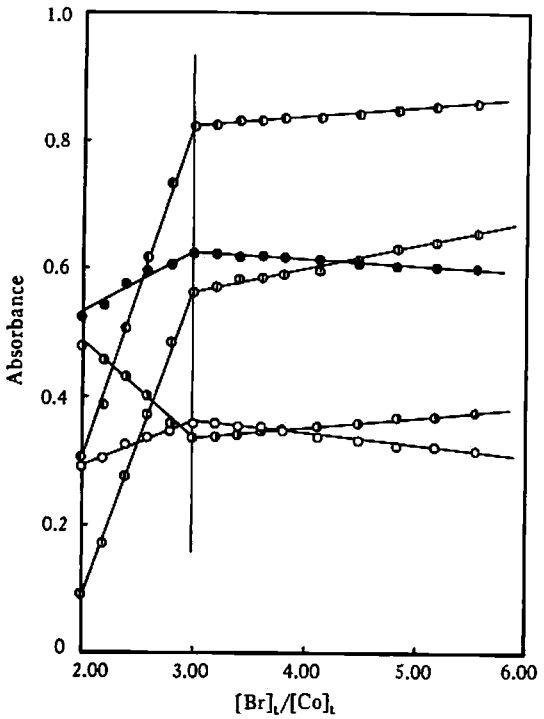

Fig. 4 Examples of mole ratio plots for solutions of ($CoBr_2$+LiBr)
$[Co]_t = 1.242 \times 10^{-3}$ mol/l
Path length : 1 cm
○: 618 nm, ◑: 660 nm, ●: 680 nm
◐: 702 nm, ⓘ: 723 nm

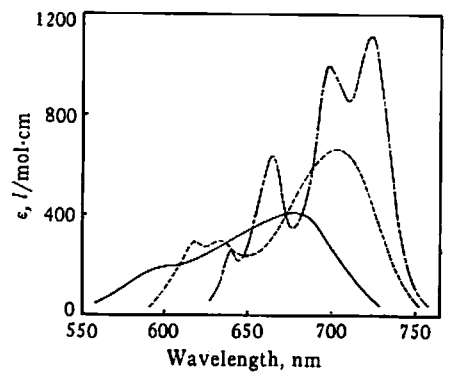

Fig. 5 ε of cobalt(II)-bromide complexes at atmospheric pressure and 25°C
———: $CoBr_2S_2$
– – – – –: $CoBr_3S^-$
——·——: $CoBr_4^{2-}$

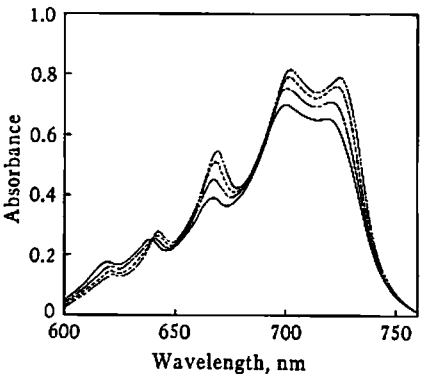

Fig. 6 ($CoBr_2$+LiBr) in acetone at high pressure and 25°C
$[Co]_t = 9.293 \times 10^{-4}$ mol/l
$[Br]_t/[Co]_t = 17.0$
Path length: 1.002 cm
———: 1 kg/cm²
——·——: 880 kg/cm²
– – – – –: 2910 kg/cm²
——··——: 4970 kg/cm²

Table 1 λ_{max} and $\varepsilon_{max}(1)$ of Co–Br complexes in acetone at atmospheric pressure and 25°C

Species	Molar absorption coefficient	λ_{max} (nm)	$\varepsilon_{max}(1)$ (l/mol · cm)
$CoBr_2S_2$	ε_2	~590 (sh)	172
		~635 (sh)	283
		677	410
$CoBr_3S^-$	ε_3	618	291
		633.5	297
		702	662
$CoBr_4^{2-}$	ε_4	639.5	257
		664.5	635
		698	988
		723	1113

value, we can assume,

$$\varepsilon_1^{\lambda}(p)=\varepsilon_1^{\lambda-\Delta\lambda}(1). \tag{6}$$

The assumption in determining $\Delta\lambda$ for the estimation of $\varepsilon_2^{\lambda}(p)$ and $\varepsilon_3^{\lambda}(p)$ will be explained later. The equilibrium constants K_1 and K_2 at high pressure can be calculated by using the concentration of each species given as follows. In the range of the present measurements, 550~750 nm, CoS_6^{2+} has no absorption[17]. Therefore, at wavelength λ,

$$l[CoBr_2S_2]\varepsilon_2^{\lambda}+l[CoBr_3S^-]\varepsilon_3^{\lambda}=Abs^{\lambda}. \tag{7}$$

According to the law of the mass balance, we have

$$[CoBr_2S_2]+[CoBr_3S^-]+[CoS_6^{2+}]=[Co]_t, \tag{8}$$

and

$$2[CoBr_2S_2]+3[CoBr_3S^-]+[Br^-]=2[Co]_t. \tag{9}$$

At high pressure, the simultaneous equations of Eq. (7) at two different wavelengths, Eqs. (8) and (9) can be solved to give the concentration of each species by applying Eq. (6) to the spectroscopic data obtained at high pressure. Then K_1 and K_2 are calculated by Eqs. (1)~(5). The absence of $CoBr_4^{2-}$ was examined by using the molar absorption coefficient of $CoBr_4^{2-}$ mentioned in the next section.

By neglecting the equilibrium (II), the approximate value of K_1 at atmospheric pressure is given as follows:

$$K_1=\frac{4[Co]_t^2\,\alpha^3}{1-\alpha}f_{\pm}^3, \tag{10}$$

where α is the degree of the dissociation of $CoBr_2S_2$ and obtained by the following equation,

$$\alpha=1-\frac{\varepsilon_{app}}{\varepsilon_2}, \tag{11}$$

where ε_{app} is the apparent absorption coefficient as given in Fig. 3.

17) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York (1962)

Cobalt(II) bromide and nickel(II) bromide with excess lithium bromide

On addition of excess LiBr to acetone solution of $CoBr_2$, another type of equilibrium,

$$CoBr_3S^- + Br^- \rightleftharpoons CoBr_4^{2-} + S, \qquad (III)$$

appears, which has no change in the coordination number of the complex ion but alteration of the charges of the ionic species.

The equilibrium constant $K_{3,Co}$ is defined by

$$K_{3,Co} = \frac{[CoBr_4^{2-}]}{[CoBr_3S^-]\,[Br^-]} f_i^2. \qquad (12)$$

The activity coefficient of ionic species i, f_i, is given by the Debye-Hückel equation,

$$\ln f_i = -\frac{A_f\sqrt{I}}{1+B_f\dot{a}\sqrt{I}}. \qquad (13)$$

The absorption spectra of the ($CoBr_2$+LiBr) solution at several pressures are shown in Fig. 6. The diminution of the absorption peak around 630 nm corresponds to the decrease of $CoBr_3S^-$ and the gain around 720 nm to the increase of $CoBr_4^{2-}$. The molar absorption coefficient of $CoBr_4^{2-}$, $\varepsilon_4(1)$, was obtained from the limiting spectra of the acetone solution of $CoBr_2$ with LiBr added in excess at atmospheric pressure[8] as shown in Fig. 5 (see Fig. 7). And the values at the peak maxima

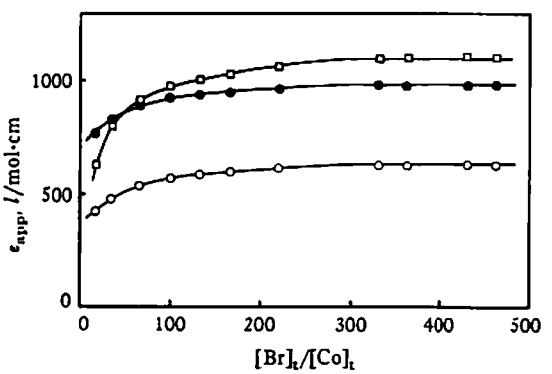

Fig. 7 The change of ε_{app} by adding LiBr to the acetone solution of $CoBr_2$
$[Co]_t = 6.916 \times 10^{-4}$ mol/l
○: 665 nm
●: 698 nm
□: 723 nm

$\varepsilon_{4,max}(1)$ are given in Table 1. By applying Eq. (6), ε_4 at wavelength λ and pressure P, $\varepsilon_4^{\lambda}(p)$, was estimated from $\varepsilon_4^{\lambda}(1)$. The assumption in determining $\Delta\lambda$ in Eq. (6) for the estimation of $\varepsilon_4^{\lambda}(p)$ will be explained in the later section. The concentrations of the species $[CoBr_3S^-]$ and $[CoBr_4^{2-}]$ are obtained by solving the following simultaneous equations.

$$l[CoBr_3S^-]\varepsilon_3^{\lambda} + l[CoBr_4^{2-}]\varepsilon_4^{\lambda} = Abs^{\lambda}, \qquad (14)$$

$$[CoBr_3S^-] + [CoBr_4^{2-}] = [Co]_t. \qquad (15)$$

The values of $[CoBr_3S^-]$ and $[CoBr_4^{2-}]$ are obtainable in another way by applying Eq. (14) at two different wavelengths. The resultant concentrations of these species were in good agreement with those determined by the former method, so the absence of other cobalt complexes was confirmed. In the calculation of $K_{3,Co}$, the concentrations of bromide ion, $[Br^-]$, and that of lithium ion, $[Li^+]$, are also necessary, which can be determined as mentioned below from the dissociation constant of LiBr,

K_d, obtained by the electrical conductivity method[16]. The dissociation constant of LiBr is expressed by the following equations,

$$K_d=\frac{[Li^+]\,[Br^-]}{[LiBr]}f_\pm^2, \tag{16}$$

$$[Li^+]=\alpha'\,[Li]_t, \tag{17}$$

and

$$[LiBr]=[Li]_t-[Li^+]=(1-\alpha')\,[Li]_t, \tag{18}$$

where α' denotes the degree of dissociation and $[Li]_t$ the total concentration of added LiBr. From the law of mass balance,

$$[Br^-]=\alpha'\,[Li]_t+2[Co]_t-3[CoBr_3S^-]-4[CoBr_4^{2-}]. \tag{19}$$

Substituting Eq. (15) in Eq. (19),

$$[Br^-]=\alpha'\,[Li]_t-[Co]_t-[CoBr_4^{2-}]. \tag{20}$$

Since $[CoBr_4^{2-}]$ is already known from the spectral data, $[Br^-]$ can be calculated if α' is known. From Eqs. (3), (17), (18) and (20), Eq. (16) is rewritten as;

$$\ln\frac{\alpha'\,(\alpha'\,[Li]_t-[Co]_t-[CoBr_4^{2-}])}{1-\alpha'}=\ln K_d+\frac{2A_f\sqrt{\alpha'\,[Li]_t+[CoBr_4^{2-}]}}{1+B_f\mathring{a}\sqrt{\alpha'\,[Li]_t+[CoBr_4^{2-}]}}. \tag{21}$$

The quantity α' is determined by solving Eq. (21) by the successive approximation method. Thus, $[Li^+]$ and $[Br^-]$ are obtained by Eqs. (17) and (20), respectively, for the calculation of $K_{3,Co}$ by Eqs. (12) and (13).

The absorption spectra of $NiBr_2$ with a large amount of LiBr at high pressure are shown in Fig. 8. This solution has an equilibrium similar to the case of ($CoBr_2$+LiBr) solution[15],

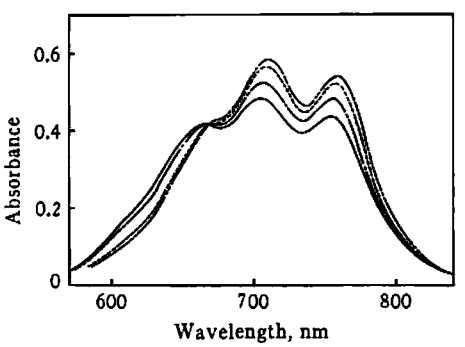

Fig. 8 ($NiBr_2$+LiBr) in acetone at high pressure and 25°C
$[Ni]_t=2.234\times10^{-3}$ mol/l
$[Br]_t/[Ni]_t=32.6$
Path length: 0.963 cm
————: 1 kg/cm²
—·—·—: 880 kg/cm²
- - - - - - - -: 2910 kg/cm²
—··—··—: 4970 kg/cm²

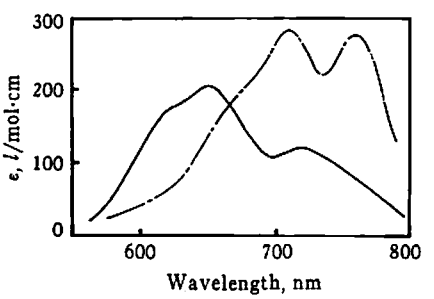

Fig. 9 ε of $NiBr_3S^-$ and $NiBr_4^{2-}$ at atmospheric pressure and room temperature
————: $NiBr_3S^-$
—·—·—: $NiBr_4^{2-}$

Table 2 λ_{max} and $\varepsilon_{max}(1)$ of Ni-Br complexes in acetone at atmospheric pressure and room temperature

Species	λ_{max} (nm)	$\varepsilon_{max}(1)$ (l/mol · cm)
$NiBr_3S^-$	~610 (sh)	
	645	200
	712	115
$NiBr_4^{2-}$	~665 (sh)	
	703	279
	753	273

$$NiBr_3S^- + Br^- \rightleftharpoons NiBr_4^{2-} + S, \qquad (IV)$$

where the equilibrium constant is defined by

$$K_{3,Ni} = \frac{[NiBr_4^{2-}]}{[NiBr_3S^-][Br^-]} f_i^2, \qquad (22)$$

which is calculated just in the same way as in the case of ($CoBr_2$+LiBr) solution by using the molar absorption coefficients of $NiBr_3S^-$ and $NiBr_4^{2-}$ shown in Fig. 9 and Table 2.

Estimation of molar absorption coefficient at high pressure and calculation of the volume changes

The difference in the molar absorption coefficient of each species between high pressure and atmospheric pressure is considered. In the ($CoBr_2$+LiBr) system, the following facts are found:

(i) The concentration of $CoBr_4^{2-}$ increases with increasing pressure in equilibrium (III), which is confirmed on the basis of the enhancement of absorption maxima around 670, 700 and 720 nm, and diminution around 620 nm due to the decrease of $CoBr_3S^-$ in Fig. 6 (see Fig. 5).

(ii) The absorption maxima at *ca.* 700 nm in Fig. 6 seems to shift to the longer wavelength with increasing pressure, while around 700 nm $\lambda_{max}(CoBr_4^{2-})$ (=698 nm) is shorter than $\lambda_{max}(CoBr_3S^-)$ (=702 nm) at atmospheric pressure (see Table 1 and Fig. 5).

(iii) The enhancement of the absorption maximum around 670 nm due to the increase of $[CoBr_4^{2-}]$ may be in competition with the diminution of the peak at 702 nm due to the decrease of $[CoBr_3S^-]$. While the red shift of the maximum at *ca.* 670 nm also takes place with increasing pressure.

(iv) The falling of the absorption at *ca.* 620 nm with pressure in Fig. 6 is caused by the decrease of $CoBr_3S^-$ and the absorption maximum shifts to the longer wavelength at high pressure. The species of $CoBr_4^{2-}$ has little absorption around this wavelength (Fig. 5). When these facts are taken into account, it can be said that $\lambda_{max}(CoBr_4^{2-})$ at least moves to the longer wavelength on the basis of (i), (ii) and (iii). By the reasons (i) and (iv), it is also concluded for $\lambda_{max}(CoBr_3S^-)$ to cause the red shift. Hence, the shift of the wavelength, $\Delta\lambda$ in Eq. (6), is estimated as written below. By taking into account the red shift and neglecting the change of the intensity with pressure, the molar absorption coefficients of $CoBr_3S^-$ and $CoBr_4^{2-}$ at high pressure were estimated from the shifts of the peaks shown in Fig. 6 as follows. The red shift at *ca.* 670 and 700 nm in Fig. 6 might be smaller than the real shift of $\lambda_{max}(CoBr_4^{2-})$, because it contains the apparent peak shift to the shorter wavelength

side due to the transformation of $CoBr_3S^-$ into $CoBr_4^{2-}$ with pressure. The red shift of the maximum at *ca.* 620 nm in Fig. 6 can be regarded to be caused only by that of $\lambda_{max}(CoBr_3S^-)$ because $CoBr_4^{2-}$ scarcely has absorption at the wavelength. The amounts of the displacements with pressure at the peaks around 620, 670 and 700 nm in Fig. 6 are nearly equal; 0.5 nm per 1000 kg/cm^2. On the other hand, the shift of the peak at *ca.* 720 nm, 1 nm per 1000 kg/cm^2, would be larger than the pressure induced shift, because it contains the apparent peak shift due to the transformation of $CoBr_3S^-$ into $CoBr_4^{2-}$. The former was adopted as the shift of λ_{max} of these species by assuming that the amounts of the shifts with pressure were equal and that their dependency on wavelength could be neglected, but even if the latter was employed, the values of the volume changes mentioned below were not so much affected. Now, $\Delta\lambda$ in Eq. (6) was taken to be 0.5 nm per 1000 kg/cm^2, so $\varepsilon_3^{\lambda}(p)$ and $\varepsilon_4^{\lambda}(p)$ were obtained. Concerning the absorption coefficient of $CoBr_2S_2$, $\Delta\lambda$ was considered to be equal to that in the cases of $CoBr_3S^-$ and $CoBr_4^{2-}$, then $\varepsilon_2^{\lambda}(p)$ was also estimated by Eq. (6).

Now, we can calculate the equilibrium constants at each pressure by using Eqs. (1), (2), (10) and (12). The pressure dependencies of K_1, K_2 and $K_{3,Co}$ are shown in Figs. 10 and 11. The volume changes $\Delta\bar{V}_1^\circ$, $\Delta\bar{V}_2^\circ$ and $\Delta\bar{V}_{3(Co)}^\circ$ accompanying the reactions (I), (II) and (III) are obtained

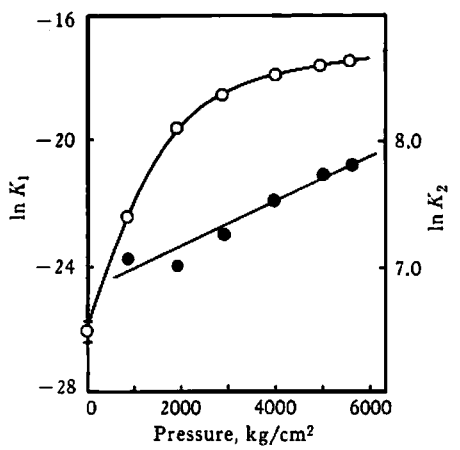

Fig. 10 Pressure dependence of K_1 and K_2 at 25°C
○: K_1
●: K_2

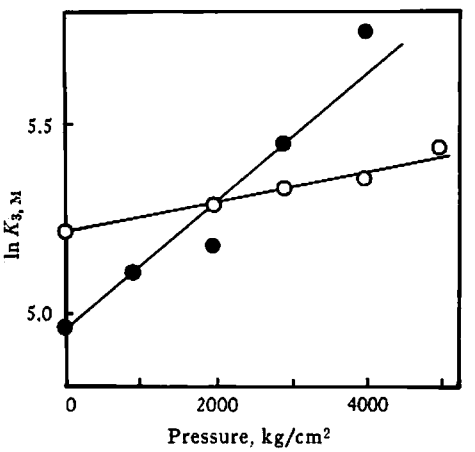

Fig. 11 Pressure dependence of $K_{3,M}$ at 25°C
○: M=Co
●: M=Ni

graphically by the following equation[18],

$$\Delta\bar{V}^\circ = -RT\left(\frac{\partial \ln K}{\partial P}\right)_T + \Delta\nu\beta RT, \tag{23}$$

where R is the gas constant, $\Delta\nu$ is the change in the number of the molecules due to the reaction, and β is the isothermal compressibility of pure acetone calculated by the Tait equation,

$$\beta = -\frac{1}{V_1}\left(\frac{\partial V}{\partial P}\right)_T = \frac{C}{B+P}. \tag{24}$$

18) S. D. Hamann, "Physico-Chemical Effects of Pressure," Chap. 8, Butterworths Scientific Pub., London (1957)

Table 3 Comparison of the values of $\Delta\bar{V}^\circ$

System	$\Delta\bar{V}_1^\circ$ (cm³/mol)	$\Delta\bar{V}_2^\circ$ (cm³/mol)	$\Delta\bar{V}_3^\circ$ (cm³/mol)
Co-Br	-109 ± 10	-5.2	-0.8
Ni-Br	—	—	-4.3

Here V_1 is the molar volume of acetone at atmospheric pressure and 25°C. The numerical values of the constants are B=755.7 bars at 25°C and $C=931\times10^{-4}$ [19]. The former is dependent on temperature while the latter not. The $\Delta\bar{V}^\circ$ values obtained at 1 kg/cm² are summarized in Table 3. The value of $\Delta\bar{V}_1^\circ$ is much smaller than the volume change reported before[20]. The author thinks the value in the present paper is more accurate than the previous one because the equipments had been improved and the equilibrium constant at atmospheric pressure was obtained in this work (the latter was by the extrapolation of K_1 at high pressure). In addition, the equilibrium constant was used in place of the equilibrium quotient and the shift of λ_{max} of each species was taken into account in the present paper.

In the case of ($NiBr_2$+LiBr) system, the spectral changes in Fig. 8 around 670, 705 and 755 nm with increasing pressure correspond to the diminution of $NiBr_3S^-$ and the increase of $NiBr_4^{2-}$ (Table 2 and Fig. 9). Those absorption maxima seem to shift to the longer wavelength. The amount of the shift composed of not only the shift in λ_{max} of each species but also that due to the transformation of $NiBr_3S^-$ into $NiBr_4^{2-}$. But it would be reasonable to consider that $\lambda_{max}(NiBr_4^{2-})$ at least would shift to the red, because, when the position of the peak at the longest wavelength at high pressure in Fig. 8 and that of $NiBr_4^{2-}$ at atmospheric pressure in Fig. 9 are compared, the former, 755 nm, appears at longer wavelength than the latter, 753 nm (Table 2). Taking into account the displacement of the λ_{max} around 755 nm at high pressure and assuming the amounts of the red shift of $\lambda_{max}(NiBr_3S^-)$ and of that of $\lambda_{max}(NiBr_4^{2-})$ to be equal, we can estimate the shift in Eq. (6) to be 1 nm per 1000 kg/cm².

The equilibrium constant of (IV), $K_{3,Ni}$ defined by Eq. (22) is calculated by using the dissociation constant of LiBr[16] and the successive approximation method just as in the case of $K_{3,Co}$. The plot of $K_{3,Ni}$ against pressure in Fig. 11 and the application of Eq. (23) give the value of volume change accompanying the reaction (IV), $\Delta\bar{V}_3^\circ{}_{(Ni)}$, which is shown in Table 3.

Discussion

Evaluation of $\Delta\bar{V}_1^\circ$, $\Delta\bar{V}_2^\circ$ and $\Delta\bar{V}_3^\circ{}_{(Co)}$

In the cobalt(II)-bromide system, $\Delta\bar{V}_1^\circ$ is largely negative, while $\Delta\bar{V}_2^\circ$ and $\Delta\bar{V}_3^\circ{}_{(Co)}$ are slightly negative. In reaction (I), the neutral species produce the ionic ones, so that the electrostrictive

19) W. A. Adams and K. J. Laidler, *Canad. J. Chem.*, **45**, 123 (1967)
20) I. Ishihara, K. Hara and J. Osugi, *This Journal*, **44**, 11 (1974)

effect would contribute very much to the negative volume change[21]. In addition, the increase in the coordination number by the formation of CoS_6^{2+} would make $\Delta\bar{V}_1^\circ$ largely negative. In reaction (II) which has small negative volume change, there is no change of the charge of the ionic species and the coordination number. And in reaction (III) which has also small negative volume change, there is no change of the coordination number of the complex ion but the redistribution of charge occurs. The electrostrictive effect described below by Eq. (27) predicts the positive value of $\Delta\bar{V}_2^\circ$ because the species $CoBr_3S^-$ is larger than bromide ion in reaction (II), and also the smaller value of $\Delta\bar{V}_3^\circ{}_{(Co)}$ than the obtained one because the ion with twice negative electronic charge is formed from two ions each of which has a unit electronic charge in reaction (III).

By definition, $\Delta\bar{V}^\circ$ is expressed with the partial molar volume $\bar{V}^\circ$ of each species,

$$\Delta\bar{V}^\circ=\Sigma\bar{V}^\circ, \tag{25}$$

where the summation refers to all products and reactants. Further dividing $\bar{V}^\circ$ as,

$$\bar{V}^\circ=\bar{V}^\circ_{el}+\bar{V}^\circ_{int}, \tag{26}$$

where $\bar{V}^\circ_{el}$ is the part due to electrostriction and $\bar{V}^\circ_{int}$ is that due to intrinsic volume, we can analyze $\Delta\bar{V}^\circ$ more quantitatively.

The electrostrictive term is expressed by Born's equation,

$$\bar{V}^\circ_{el}=-\frac{Nq^2}{2rD^2}\frac{\partial D}{\partial P}, \tag{27}$$

where N is Avogadro's number, r the ionic radius, and q the charge of the ionic species. The dielectric constant of solvent at pressure P, D_p, is calculated by the Owen-Brinkley equation[22],

$$\frac{1}{D_p}-\frac{1}{D_1}=A\log\left(\frac{B+P}{B+1}\right), \tag{28}$$

where A and B are constants; $AD_1=0.2577$[22], $D_1=20.70$[23], B is the same as given in Eq. (24). The intrinsic term is assumed to be expressed by using the radius r of the species.

$$\bar{V}^\circ_{int}=\frac{4}{3}N\pi r^3. \tag{29}$$

The volume change $\Delta\bar{V}_3^\circ{}_{(Co)}$ for reaction (III) is written by using Eq. (25),

$$\Delta\bar{V}_3^\circ{}_{(Co)}=\bar{V}^\circ(CoBr_4^{2-})+\bar{V}^\circ(S)-\bar{V}^\circ(Br^-)-\bar{V}^\circ(CoBr_3S^-) \tag{30}$$

As the value of the radius of Br^- ion, $r(Br^-)$, the ionic crystal radius 1.95 Å by Pauling[24] was used. As $r(CoBr_4^{2-})$ 4.40 Å was taken by summing the bond distance between Co and Br[25] and $r(Br^-)$[24]. The partial molar volume of acetone used as solvent was assumed to be equal to the molar volume

21) S. D. Hamann, "High Pressure Physics and Chemistry," vol. 2, ed. by R. S. Bradley, Academic Press, London, New York (1963)

22) B. B. Owen and S. R. Brinkley, *Phys. Rev.*, **64**, 32 (1943)

23) A. A. Mayott and E. A. Smith, "Table of Dielectric Constants of Pure Liquids," NBC Circular, 514, Aug. 10 (1951)

24) L. Pauling, "The Nature of the Chemical Bonds," 3rd ed., Cornell Univ. Press, Ithaca, New York (1960)

25) D. L. Werz and R. F. Kruh, *J. Chem. Phys.*, **50**, 4313 (1969); *Inorg. Chem.*, **9**, 595 (1970)

of bulk acetone, 74.05 cm^3/mol at atmospheric pressure and 25°C[26]. Then, by using the experimental value of $\Delta\bar{V}_3^\circ(Co)$, -0.8 cm^3/mol, $\bar{V}^\circ(CoBr_3S^-)$ can be estimated by Eqs. (25)~(30). The value of $r(CoBr_3S^-)$, and the electrostrictive and intrinsic terms of $\Delta\bar{V}_3^\circ(Co)$ are obtained. In the same way, $r(CoBr_2S_2)$ can be determined together with $\Delta\bar{V}_2^\circ$, el and $\Delta\bar{V}_2^\circ$, int from $r(CoBr_3S^-)$ mentioned above and experimental value of $\Delta\bar{V}_2^\circ$. Furthermore from the experimental $\Delta\bar{V}_1^\circ$ and $r(CoBr_2S_2)$ given above, $r(CoS_6^{2+})$, $\Delta\bar{V}_1^\circ$, el and $\Delta\bar{V}_1^\circ$, int can be estimated. These values of radii and those of $\Delta\bar{V}^\circ_{el}$ and $\Delta\bar{V}^\circ_{int}$ are given in Tables 4 and 5. The order of the sizes of these complexes seems reasonable,

Table 4 The estimated radii of ionic species

Species	Radius (Å)
CoS_6^{2+}	6.10
$CoBr_2S_2$	5.11
$CoBr_3S^-$	4.70
$CoBr_4^{2-}$	4.40
Br^-	1.95[a]
S	3.08[b]

a) From ref. (24)
b) Calculated from the molar volume of acetone 74.05 cm^3/mol at atmospheric presure and 25°C

Table 5 The calculated values of $\Delta\bar{V}^\circ$

$\Delta\bar{V}^\circ$	Experimental value (cm^3/mol)	$\Delta\bar{V}^\circ_{el}$ by Eq. (27) (cm^3/mol)	$\Delta\bar{V}^\circ_{int}$ by Eq. (29) (cm^3/mol)
$\Delta\bar{V}_1^\circ$	-109 ± 10	-83.4	-21.9
$\Delta\bar{V}_2^\circ$	-5.2	$+14.9$	-19.3
$\Delta\bar{V}_3^\circ(Co)$	-0.8	-9.1	$+8.3$

where the more acetone molecules the complexes have, the larger the sizes of the complexes are, because acetone molecule has a larger volume than bromide ion.

In reaction (I), the large negative value of $\Delta\bar{V}_1^\circ$ would be caused mainly by the electrostrictive effect accompanied by the formation of the ionic species from the neutral ones. The increase of the coordination number contributes also to the negative value of $\Delta\bar{V}_1^\circ$. A large pressure dependence of $\Delta\bar{V}_1^\circ$ is interpreted by the change of $\Delta\bar{V}_1^\circ$, el and $\Delta\bar{V}_1^\circ$, int with pressure. Both are negative at atmospheric pressure and increase with pressure resulting from the pressure dependence of the dielectric constant and the partial molar volume of acetone. The value $\Delta\bar{V}_1^\circ$ is much more negative than the volume changes of the ionization of weak acids and bases in water, $-10\sim-30$ cm^3/mol[21]. Rodriguez and Offen[7] reported the volume change $+16$ cm^3/mol of the following inorganic complex

26) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry," vol. 2, Organic Solvents, 3rd ed., ed. by A. Weissberger, Wiley-Interscience, New York etc.

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reaction in water at 25°C,

$$CoS'_6{}^{2+} + nCl^- \rightleftharpoons CoS'_{4-n}Cl_n^{2-n} + (2+n)\,S',$$

where S′ means the water molecule. And they calculated the electrostrictive volume change to be +15 cm³/mol by Born's equation using $n=3$, $r(CoS'_6{}^{2+})=2.2$ Å, $r(Cl^-)=1.8$ Å and $r(CoS'Cl_3{}^{-1})=2.3$ Å. The volume change for the following reaction was obtained by Swaddle and coworkers[27,28] to be −7～−12 cm³/mol,

$$M(NH_3)_5X^{2+} + H_2O \longrightarrow M(NH_3)_5OH_2{}^{3+} + X^-,$$

where M=Co(III), Cr(III) and $X^-=Cl^-$, Br^-. From these reported values of the volume changes in water and the fact that the term $(1/D^2)(\partial D/\partial P)$ in Eq. (27) of acetone is 9.5 times as large as that of water[22,29,30], the large negative value of $\Delta\bar{V}_1^\circ$ in this work seems reasonable which is accountable qualitatively by the electrostrictive effect. In reaction (II), the smaller bromide ion is transformed into the larger ion $CoBr_3S^-$ with pressure without the change of the electronic charge. Then, if only the electrostriction theory is considered, $\Delta\bar{V}_2^\circ$ might be expected to be positive, but $\Delta\bar{V}_{2,\,\mathrm{int}}^\circ\,(<0)$ may contribute to the negative value of $\Delta\bar{V}_2^\circ$ as shown in Table 5. In reaction (III), the ion with $-2e$ (where e is the electronic charge) is formed from two ions each of which has $-e$. Then, if only the electrostrictive term was considered, $\Delta\bar{V}_{3(\mathrm{Co})}^\circ$ might be expected to be largely negative, but the compensation of the positive intrinsic term would make the value of $\Delta\bar{V}_3^\circ$ small negative.

From the consideration above, it may be concluded that the effect of electrostriction makes an important contribution to the volume change in the equilibrium where neutral species produce ionic ones and the large change of the charge occurs as in reaction (I), but in the complicated ionic reactions such as (II) and (III), the change of intrinsic volume should also be taken into consideration.

Comparison of $\Delta\bar{V}_1^\circ$ with that in ethanol

The salt CoX_2 (X is Cl or Br) in ethanol has the equilibrium similar to that in acetone, as given in equilibrium equation (I).

$$CoX_2(Et)_2 + 4Et \rightleftharpoons Co(Et)_6{}^{2+} + 2X^-, \qquad (V)$$

where Et denotes an ethanol molecule and X is Cl or Br. Rodriguez and Offen[7] gave −45 cm³/mol at 25°C and Kitamura[6] −154 cm³/mol at room temperature as for the experimental value of the volume change for $CoCl_2$ in ethanol. The latter author got the volume change of −230.4 cm³/mol for $CoBr_2$ in ethanol. In order to compare $\Delta\bar{V}_1^\circ$ in acetone obtained in this work with the reported value, the present author has been estimated the volume change for $CoBr_2$ in ethanol, $\Delta\bar{V}_1^{\circ(\mathrm{Et})}$, to be −43 cm³/mol using −45 cm³/mol for $CoCl_2$[7] and considering Eq. (27), $r(Cl^-)=1.80$ Å and $r(Br^-)=1.95$ Å[24], but neglecting the difference of the intrinsic term. The constants in Eq. (28) used in the estimation of the pressure dependence of the dielectric constant of ethanol are as follows: $AD_1=$

27) W. E. Jones, L. R. Carey and T. W. Swaddle, *Can. J. Chem.*, **50**, 2739 (1972)
28) G. Guastalla and T. W. Swaddle, *Can. J. Chem.*, **51**, 821 (1973)
29) C. G. Malmberg and A. A. Maryott, *J. Res. nat. Bur. Stand.*, **56**, 1 (1956)
30) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd. ed., Reinhold Publishing Corporation (1958)

0.3039[22], $D_1=24.55$[26], $B=1366.5$ bars[22]. Since the positive value of $(1/D^2)(\partial D/\partial P)$ of ethanol in Eq. (27) is smaller than that of acetone by the factor of 0.55, $\Delta\bar{V}_1^{\circ(Et)}{}_{,el}$ would be larger than $\Delta\bar{V}_1^{\circ}{}_{,el}$ in acetone. Furthermore, at atmospheric pressure and 25°C, the molar volume of ethanol 58.05 cm³/mol is smaller than that of acetone 74.05 cm³/mol[26]. Therefore, $\Delta\bar{V}_1^{\circ(Et)}{}_{,int}$ would be less negative than $\Delta\bar{V}_1^{\circ}{}_{,int}$ in acetone. Thus, $|\Delta\bar{V}_1^{\circ(Et)}|$ would be smaller than $\Delta\bar{V}_1^{\circ}$ in acetone.

For the calculation of $\Delta\bar{V}_1^{\circ(Et)}{}_{,el}$ the value of $r(Co(Et)_6^{2+})$ 5.50 Å was estimated as

$$r(Co(Et)_6^{2+})=d(Co\text{-}O)+2r(L, Et)-r(O), \tag{31}$$

where d(Co-O) is the bond length between cobalt ion and oxygen atom in the ligand ethanol molecule[25], r(L, Et) the radius of the ligand ethanol molecule, and r(O) the van der Waals radius of oxygen by Pauling[24]. The value r(L, Et) was estimated by assuming that the alcohol molecules coordinated around the Co^{2+} ion would be in a state similar to that at extremely high pressure and its volume would reduced to about 60 % by the coordination process[6]. Then $\Delta\bar{V}_1^{\circ(Et)}{}_{,el}$ is calculated to be -48 cm³/mol by Eq. (27). This value is roughly in accordance with the corrected one -43 cm³/mol obtained by Rodriguez and Offen[7]. By assuming that the contribution of $\Delta\bar{V}_1^{\circ(Et)}{}_{,int}$ would be smaller than $\Delta\bar{V}_1^{\circ(Et)}{}_{,el}$ as in the case of acetone solution, the difference between $\Delta\bar{V}_1^{\circ}$ in acetone and $\Delta\bar{V}_1^{\circ(Et)}$ by them is qualitatively reasonable by considering the difference of the pressure dependences of the dielectric constants of these two solvents. The value obtained by Kitamura[6] seems too small.

Comparison of $\Delta\bar{V}_3^{\circ}{}_{(Co)}$ and $\Delta\bar{V}_3^{\circ}{}_{(Ni)}$

The difference between $\Delta\bar{V}_3^{\circ}{}_{(Co)}$ and $\Delta\bar{V}_3^{\circ}{}_{(Ni)}$ may lead to an interesting discussion on the contribution of the metal ion. By definition, the volume change $\Delta\bar{V}_3^{\circ}{}_{(Ni)}$ for reaction (IV) is written by using the partial molar volume of each species just in the same way as $\Delta\bar{V}_3^{\circ}{}_{(Co)}$ in Eq. (30),

$$\Delta\bar{V}_3^{\circ}{}_{(Ni)}=\bar{V}^{\circ}(NiBr_4^{2-})+\bar{V}^{\circ}(S)-\bar{V}^{\circ}(Br^-)-\bar{V}^{\circ}(NiBr_3S^-) \tag{32}$$

By subtracting Eq. (32) from Eq. (30) we have,

$$\begin{aligned}\Delta\bar{V}_3^{\circ}{}_{(Co)}-\Delta\bar{V}_3^{\circ}{}_{(Ni)}=&\{\bar{V}^{\circ}(CoBr_4^{2-})-\bar{V}^{\circ}(NiBr_4^{2-})\}\\&-\{\bar{V}^{\circ}(CoBr_3S^-)-\bar{V}^{\circ}(NiBr_3S^-)\}\end{aligned} \tag{33}$$

The experimental value of $(\Delta\bar{V}_3^{\circ}{}_{(Co)}-\Delta\bar{V}_3^{\circ}{}_{(Ni)})$ is $+3.5$ cm³/mol. For the detail consideration of this value, the partial molar volume of each species is calculated by using Eqs. (26)~(29). From the discussion above, $r(CoBr_4^{2-})$ was estimated to be 4.40 Å. From references,

$$r_c(Co^{2+})-r_c(Ni^{2+})=0.02\ \text{Å}^{24},$$

$$d_g(Co\text{-}Br)-d_g(Ni\text{-}Br)=0.06\ \text{Å}^{31},$$

where $r_c(M^{2+})$ is the ionic radius of the metal ion M^{2+} in the crystalline state and d_g(M-Br) is the bond length between the metal ion and the bromide ion in gas phase. Then the difference between d_s(Co-Br) and d_s(Ni-Br) is considered to lie between these values, 0.02 Å and 0.06 Å, where

31) L. I. Katzin, "Transition Metal Chemistry," vol. 3 ed. by R. L. Carlin, Marcel Dekker, Inc., New York (1966)

d_s(M-Br) is the bond length in solution. When only the electrostrictive term is taken into account, and the difference between d_s(Co-Br) and d_s(Ni-Br) is assumed to be maximum, 0.06 Å, the value of the first term on the right side of Eq. (33) is $+0.6$ cm^3/mol by Eq. (27). The small second term related only to univalent ion contributes to diminish this value. Although the experimental positivity of $(\Delta\bar{V}_3^{\circ}{}_{(Co)}-\Delta\bar{V}_3^{\circ}{}_{(Ni)})$ can be explained by the electrostrictive term, but the value estimated is too smaller than the experimental value. To obtain the intrinsic volume of $NiBr_4^{2-}$, 4.36 Å is used as the value of $r(NiBr_4^{2-})$, *i. e.*, the difference between d_s(Co-Br) and d_s(Ni-Br) is assumed to be moderate, 0.04 Å. Then the first term on the right side of Eq. (33) is calculated to be $+6.2$ cm^3/mol, where the intrinsic term calculated by Eq. (29) is $+5.8$ cm^3/mol and the electrostrictive one by Eq. (27) is 0.4 cm^3/mol. Then, by using the experimental value $+3.5$ cm^3/mol of $(\Delta\bar{V}_3^{\circ}{}_{(Co)}-\Delta\bar{V}^{\circ}{}_{3(Ni)})$, the second term on the right side of Eq. (33) is $+2.7$ cm^3/mol, where the electrostrictive effect would be small as discussed above. If the electrostrictive term is neglected, from the fact that the positive first term is larger than the positive second one in Eq. (33) and $r(MBr_3S^-)$ is larger than $r(MBr_4^{2-})$, the relation of the magnitude of the radii for those complex species is obtained from Eq. (29),

$$\{r(CoBr_4^{2-})-r(NiBr_4^{2-})\}>\{r(CoBr_3S^-)-r(NiBr_3S^-)\}>0. \tag{34}$$

i. e.,

$$\{r(NiBr_3S^-)-r(NiBr_4^{2-})\}>\{r(CoBr_3S^-)-r(CoBr_4^{2-})\}. \tag{35}$$

These equations show that the species $CoBr_3S^-$ is larger than $NiBr_3S^-$ and, by the replacement of the bromide ion with the acetone molecule in the coordination sphere, the radius of complex species might change more in the smaller Ni-complex than in the larger Co-complex.

As discussed above, it might be concluded that the difference between $\Delta\bar{V}_3^{\circ}{}_{(Co)}$ and $\Delta\bar{V}_3^{\circ}{}_{(Ni)}$ would be explained mainly by the effect of the intrinsic volume.

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