August, 1988] © *1988 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 61, 2981—2983 (1988)* 2981

Potentiometric Study of Cadmium(II) Halide and Thiocyanate Complexes in Methanol. Determination of Thermodynamic Stability Constants of Third and Fourth Complexation Step

Khin Nwe Soe, Hidekazu Doe, and Toyokichi Kitagawa*
Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558

(Received October 19, 1987)

Synopsis. The stability constants, K_3 and K_4, of $[\mathrm{Cd^{II}X}_n]^{2-n}$ ($\mathrm{X^-=Cl^-, Br^-, I^-, NCS^-}$) complexes in methanol have been determined by $\mathrm{X^-}$ ion measurements with Ag-AgX and $\mathrm{NCS^-}$ ion selective electrodes at 25 °C.

With the confirmation of the structural postulation, the formation of cadmium halide and thiocyanate complexes at any consecutive step accompanying the conformational change was earlier investigated by Ahrland and his co-workers in dimethyl sulfoxide.[1-3] Those investigations were performed at high ionic strength. We have previously studied the formation of mono- and dihalide and thiocyanate complexes in methanol at an ionic strength of 0.05 M (1 M=1 mol dm^{-3}).[4] The thermodynamic stability constants of mono- and dihalide and thiocyanate complexes, K_1 and K_2, have been studied. In this extended study, we aimed to determine the thermodynamic stability constants of tri- and tetrahalide and thiocyanate complexes, K_3 and K_4. In the present study, all potentiometric measurements were carried out at low ionic strength because it was extremely difficult to evaluate an ion activity coefficient at high ionic strength. The octahedral structure of both aquocadmium and solvated cadmium ion in dimethyl sulfoxide solution was postulated from an X-ray diffraction analysis.[5,6] Moreover, the tetrahedral structure postulation of cadmium tetrahalide complexes in aqueous solution were confirmed by X-ray diffraction studies.[5,7] Recently, the ambidentate coordination of N and S with cadmium at the formation of tri- and tetrathiocyanate complexes in aqueous solution has been postulated as $[\mathrm{Cd(SCN)(NCS)_2}]^-$ and $[\mathrm{Cd(SCN)_2(NCS)_2}]^{2-}$,[8,9] For these reasons, a conformational change will take place at any consecutive step of the formation of cadmium(II) halide and thiocyanate complexes.

Experimental

Materials. Cadmium(II) perchlorate hexahydrate was prepared by neutralizing cadmium carbonate (Nakarai, Guaranteed Grade) with perchloric acid.[10] This hexahydrate salt was purified by triple recrystallization from distilled water and was then dried on a vacuum line over diphosphorus pentaoxide for three days in order to obtain a dihydrate salt. The preparations of the other reagents were described in previous papers.[11,12]

Instrumentation. Outlines of the instrumentation and measurement procedure were described previously.[11,12] In the present study, the sensor for $\mathrm{I^-}$ was a Horiba iodide ion-selective electrode 8005-06T. All measurements were carried out in a closed cell thermostated at 25.0±0.1 °C. The cell contained 40 cm^3 of sample solution before titration.

Data Treatment and Results

In general, the following equilibria are established in methanol:

$$[\mathrm{CdX}_{n-1}]^{3-n}+\mathrm{X}^- \rightleftharpoons [\mathrm{CdX}_n]^{2-n}\ (K_n;\ n=1\text{—}4) \qquad (1)$$

$$\mathrm{Cd^{2+}}+\mathrm{ClO_4^-} \rightleftharpoons [\mathrm{CdClO_4}]^+\ (K_{1\mathrm{A}}) \qquad (2)$$

By considering these equilibria, a function, $\bar{n}$, defined as the average number of ligands, $\mathrm{X^-}$, attached to the metal, $\mathrm{M^{2+}}$, is written as:

$$\begin{aligned}\bar{n} &= (C^\circ_\mathrm{X}-[\mathrm{X^-}])/C^\circ_\mathrm{M}\\ &= (y_1\beta_1[\mathrm{X^-}]+2y_2\beta_2[\mathrm{X^-}]^2+3y_3\beta_3[\mathrm{X^-}]^3+4y_4\beta_4[\mathrm{X^-}]^4)/\\ &\quad (1+y_1K_{1\mathrm{A}}[\mathrm{ClO_4^-}]+y_1\beta_1[\mathrm{X^-}]+y_2\beta_2[\mathrm{X^-}]^2+\\ &\quad y_3\beta_3[\mathrm{X^-}]^3+y_4\beta_4[\mathrm{X^-}]^4). \qquad (3)\end{aligned}$$

C°_M and C°_X are the total concentrations of $\mathrm{Cd(ClO_4)_2}$ and NaX respectively, and β_n is the overall stability constant ($\beta_n=\prod_{i=1}^{n} K_n$). It has been assumed that ions with an identical absolute value of charge have the same ion activity coefficient at I=0.05 M.[12] Thus, this assumption leads to $y_1=y_{2+}$, $y_2=y_3=y_{2+}y_\pm^2$, and $y_4=y_\pm^4$, where $y_\pm$ and y_{2+} are the ion activity coefficients of mono- and divalent ions, respectively. By rearranging Eq. 3, the following equation is obtained:

$$\begin{aligned}\bar{n}(1+y_1K_{1\mathrm{A}}[\mathrm{ClO_4^-}]) &= \beta_1(1-\bar{n})y_1[\mathrm{X^-}]+\\ &\quad \beta_2(2-\bar{n})y_2[\mathrm{X^-}]^2+\beta_3(3-\bar{n})y_3[\mathrm{X^-}]^3+\\ &\quad \beta_4(4-\bar{n})y_4[\mathrm{X^-}]^4. \qquad (4)\end{aligned}$$

Here, $\bar{n}$ and $[\mathrm{X^-}]$ are measurable and $K_{1\mathrm{A}}$ has already been determined by conductometric measurements.[13]

Now, in consideration of the equilibria 1—3, the concentration of $\mathrm{Cd^{2+}}$ is:

$$\begin{aligned}[\mathrm{Cd^{2+}}] &= C^\circ_\mathrm{M}/(1+y_1K_{1\mathrm{A}}[\mathrm{ClO_4^-}]+\\ &\quad y_1\beta_1[\mathrm{X^-}]+y_2\beta_2[\mathrm{X^-}]^2+y_3\beta_3[\mathrm{X^-}]^3+y_4\beta_4[\mathrm{X^-}]^4). \qquad (5)\end{aligned}$$

In order to calculate the y_1, y_2, y_3, and y_4 values, the Debye-Hückel second approximation has been used:

$$\ln y = -Az_i^2I^{1/2}/(1+BaI^{1/2}). \qquad (6)$$

Data processing started with initial values of $[\mathrm{ClO_4^-}]=2C^\circ_\mathrm{M}+C^\circ_\mathrm{I}$ and of y_1, y_2, y_3, and y_4 values at I=0.05 M. By the use of these values, β_n were initially estimated by a multiple regression analysis with weighted terms according to Eq. 4. Those n values were used to calculate $[\mathrm{Cd^{2+}}]$, $[\mathrm{CdX}_n^{2-n}]$, and $[\mathrm{ClO_4^-}]$. Then, I was calculated by the use of $[\mathrm{Cd^{2+}}]$ and $[\mathrm{CdX}_n^{2-n}]$. Since this calculated I value was slightly different from 0.05 M, $[\mathrm{X^-}]$ was corrected by a $y_\pm$ value since the calibration

Table 1. Thermodynamic Stability Constants of Cadmium Halide and Thiocyanate Systems in Methanol at 25 °C

X^-	K_1/M^{-1}	K_2/M^{-1}	K_3/M^{-1}	K_4/M^{-1}	K_3K_4/M^{-2}	β_4/M^{-4}
Cl	$(1.83\pm0.01)\times10^6$	$(9.4\pm3.4)\times10^2$				
Br	$(3.5\pm0.2)\times10^6$	$(4.4\pm0.7)\times10^3$			$(7.9\pm3.5)\times10^3$	$(1.2\pm0.5)\times10^{14}$
I	$(7.8\pm0.2)\times10^6$	$(2.5\pm0.2)\times10^4$	$(1.1\pm0.2)\times10^3$	$(2.2\pm0.6)\times10^2$	$(2.3\pm0.5)\times10^5$	$(4.5\pm1.0)\times10^{16}$
NCS	$(7.2\pm0.1)\times10^5$	$(1.7\pm0.1)\times10^3$			$(5.3\pm3.2)\times10^3$	$(6.5\pm3.9)\times10^{12}$

Table 2. Concentration Stability Constants of Cadmium Halide and Thiocyanate Systems in Methanol at 25 °C: I=0.05 M

X^-	$y_{2+}K_1/M^{-1}$	$y_\pm^2K_2/M^{-1}$	K_3/M^{-1}	$(y_\pm^2/y_{2+})K_4/M^{-1}$	$(y_\pm^2/y_{2+})K_3K_4/M^{-2}$	$y_\pm^4\beta_4/M^{-4}$
Cl	$(1.5\pm0.01)\times10^5$	$(2.5\pm0.9)\times10^2$				
Br	$(2.9\pm0.2)\times10^5$	$(1.1\pm0.2)\times10^3$			$(2.5\pm1.1)\times10^4$	$(8.2\pm3.4)\times10^{12}$
I	$(6.5\pm0.2)\times10^5$	$(6.6\pm0.6)\times10^3$	$(1.1\pm0.2)\times10^3$	$(6.9\pm1.9)\times10^2$	$(7.2\pm1.6)\times10^5$	$(3.0\pm0.9)\times10^{14}$
NCS	$(5.94\pm0.05)\times10^4$	$(4.5\pm0.3)\times10^2$			$(1.7\pm1.0)\times10^4$	$(4.4\pm2.6)\times10^{11}$

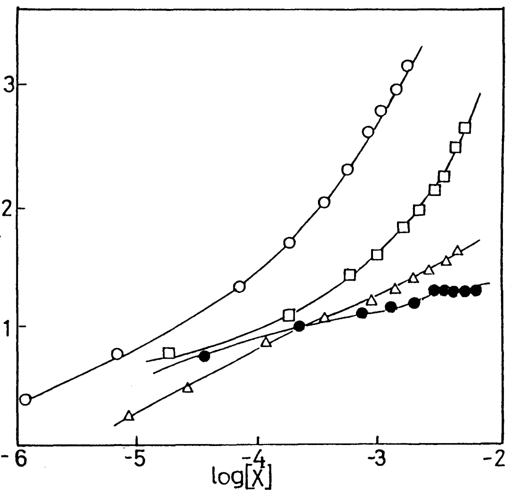

Fig. 1. Average coordination numbers, $\bar{n}$, as a function of log[X^-]: ● chloride; □ bromide; ○ iodide; △ thiocyanate. Dashed line: experimental line.

was made at I=0.05 M.[4)] Here, we could return to Eq. 4 with new values of I, [ClO_4^-], and [X^-]. This series of processing was repeated until β_n values became constant.

Table 1 shows the stepwise stability constants, including K_1 and K_2. The y_{2+} and $y_\pm$ values at I=0.05 M are 0.08285 (a=5° A)[4)] and 0.5110. The concentration stability constants are summarized in Table 2. The products of K_3K_4 are shown in Table 1.

Discussion

For the chloride system, K_3 and K_4 were so small that they could not be determined under this experimental conditions (Fig. 1), that $\bar{n}$ does not exceed 2. Similarly, in the bromide system, $\bar{n}$ does not exceed 3 due to the small values of K_3 and K_4. For the iodide system, the complex was formed up to tetraiodide under this experimental conditions and generally, thermodynamic stability constants decrease in the order $K_1 > K_2 > K_3 > K_4$. Besides, the stabilities of halide complexes decrease in the order $I^- > Br^- > Cl^-$, as shown in Fig. 1, since cadmium(II) is a soft acid, preferring to coordinate with soft donor ligands.[14,15)] In a protic solvent like water, the same sequence was found for cadmium(II) halides in various ionic media.[3)]

The existence of $[Zn(MeOH)_6]^{2+}$ and $[Zn(MeOH)_5(ClO_4)]^+$ was postulated from a proton magnetic resonance investigation of the zinc-methanol system.[16)] For this reason, the solvated cadmium ion probably has an octahedral $[Cd(MeOH)_6]^{2+}$ structure in this study. Additionally, according to the structural postulation described above (introduction), it can be obviously seen that the structural change of an octahedral coordination to tetrahedral coordination will certainly occur at any consecutive step of formation of cadmium(II) halide complexes in methanol.

According to the K_2 value, we have discussed earlier[4)] how the steric hindrance of ligands in an octahedrally coordinated structure would suppress the formation of cadmium dihalide complexes; it would cause the value of K_2 to become small, making the ratio of K_1/K_2 extremely large. Therefore, it was impossible for a coordination change to take place at the second step. In other words, it will take place at the subsequent steps.

The coordination change at the subsequent steps was confirmed by a Raman study[17)] on the $C_{3}v$, bent structure of $CdBr_3^-$ in an aqueous solution. For this reason, it is quite possible that $CdBr_3^-$ and CdI_3^- have a tetrahedral structure with a solvent molecule at an apex in methanol. Our results did not clearly indicate the step at which the conformational change occurs viz. the formation of a trihalide complex or the formation of a tetrahalide complex. However, an extremely small K_2 value may support a change at the third step. If data on enthalpy and entropy changes is available, they will be of great help in discussing the conformational change in greater detail.

K. N. S. thanks Professor Dr. Ko Ko Gyi of Rangoon University, Rangoon, Burma, for his kind permission to do research work in Japan.

References

1) S. Ahrland and N. O. Bjork, *Acta Chem. Scand.*, **30A**, 249 (1976).

2) S. Ahrland and N. O. Bjork, *Acta Chem. Scand.*, **30A**, 257 (1976).

3) S. Ahrland, *Pure Appl. Chem.*, **51**, 2019 (1979).

4) H. Doe, K. Wakamiya, C. Yoshida, H. Ozaki, K. N. Soe, and T. Kitagawa, *Inorg. Chem.*, **26**, 2244 (1987).

5) H. Ohtaki, H. Maeda, and S. Ito, *Bull. Chem. Soc. Jpn.*, **47**, 2217 (1974).

6) I. Persson, A. Iverfeldt, and S. Ahrland, *Acta Chem. Scand.*, **A35**, 295 (1981).

7) S. Pocev, R. Trido, and G. Johansson, *Acta Chem. Scand.*, **A33**, 179 (1979).

8) T. Yamaguchi. K. Yamamoto, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **58**, 3235 (1985).

9) S. Isiguro, K. Yamamoto, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **59**, 1009 (1986).

10) "Shin Jikken Kagaku Koza," Maruzen, Tokyo (1976), Vol.8, Chaps. 1—3.

11) H. Doe, A. Shibagaki, and T. Kitagawa, *Inorg. Chem.*, **22**, 1639 (1983).

12) H. Doe and T. Kitagawa, *Inorg. Chem.*, **21**, 2272 (1982).

13) H. Doe and T. Kitagawa, *Bull. Chem. Soc. Jpn.*, **58**, 2975 (1985).

14) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

15) R. G. Pearson, *J. Chem. Educ.*, **45**, 581 (1968).

16) S. A. Al. Baldawi and T. E. Gough, *Can. J. Chem.*, **47**, 1417 (1969).

17) J. W. Macklin and R. A. Plane, *Inorg. Chem.*, **9**, 821 (1970).