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Potentiometric Studies of Cadmium- and Zinc-Halide Complexes in Acetonitrile

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The overall formation constants of cadmium- and zinc-halide complexes in acetonitrile were determined by potentiometric titration using a saturated metal amalgam indicator electrode. The effect of ion-pair formation was taken into consideration to elucidate the free halide ion concentration in the experiments. The values of log β_3 and log β_4 for cadmium-halide complex were found to be: I^-, 22.4 and 26.5; Br^-, 25.3 and 29.8; Cl^-, 29.2 and 34.0. The values for zinc-chloride complex were 20.1 and 23.4.

Cadmium-, zinc- and manganese(II)-iodide complexes were studied polarographically in acetonitrile and the overall formation constants of these complexes were evaluated.[1] The formation of some halide complexes in non-aqueous solvents was studied potentiometrically by a number of investigators, too.[2-4] As acetonitrile has the donor number of 14.1, many ligand-exchange reactions have been studied in this solvent.[5]

In this work, cadmium-, and zinc-halide complexes have been studied potentiometrically in acetonitrile. The overall formation constants of the halide complexes were determined and the free halide ion concentration was corrected for the effect of ion-pairing. The data obtained were compared with those previously reported by polarography.

Experimental

Materials. Tetraethylammonium halides (Et_4NX) were prepared, purified several times and dried at 60 °C *in vacuo*. Other reagents were prepared as described previously.[1]

Apparatus. Potentials were measured by YOKOGAWA 2802 digital voltmeter with a manual impedance converter. The cell for potentiometric titration had a stopper of silicone rubber which had openings for a microburet tip, nitrogen inlet and outlet tubes and an SCE.[1] The SCE was isolated from the solution by a bridge of 0.1 M Et_4NClO_4 in acetonitrile with ultrafine sintered-glass membranes. The indicator electrode was a saturated metal amalgam,

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[2] S. E. Manahan and R. T. Iwamoto, *Inorg. Chem.*, **4**, 1409 (1965).

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[4] J. K. Senne and B. Kratochvil, *Anal. Chem.*, **43**, 79 (1971).

[5] V. Gutmann, "Coordination Chemistry in Non-aqueous Solutions," Springer-Verlag, Wien (1968).

prepared by warming pure piece of reagent grade metal with thrice-distilled mercury under a stream of nitrogen.

Procedure. Potentiometric titration curve was obtained by the titration of 0.50 mM metal(II) ion with 0.05 M Et_4NX in acetonitrile. The titrant contained the same concentration of metal(II) ion as that in the cell. The concentration of Et_4N^+ was kept constant (0.1 M) for each solution of metal(II) ion and Et_4NX.

Et_4NClO_4[6] and Et_4NCl[7] were assumed to be completely dissociated in acetonitrile and the K_a values of the association constants used were 4.7 for Et_4NBr[6] and 5 for Et_4NI.[8]

The solution in the cell was deaerated by nitrogen gas presaturated with acetonitrile. All the potential measurements were made at 25.0±0.1 °C.

Results and Discussion

The potentiometric titration curves for cadmium-halide system are shown in Fig. 1. $\varDelta E$ is the potential difference between cell potentials when halide is present and when it is absent. C_X and C_M are the total concentrations of halide and of metal(II), respectively. Each titration curve has an inflection point at $C_X/C_M=3$. Inflection at $C_X/C_M=4$ becomes larger in the order of iodide, bromide and chloride. The formation of CdX_3^- and CdX_4^{2-} (X=I, Br and Cl) was found to occur in acetonitrile.

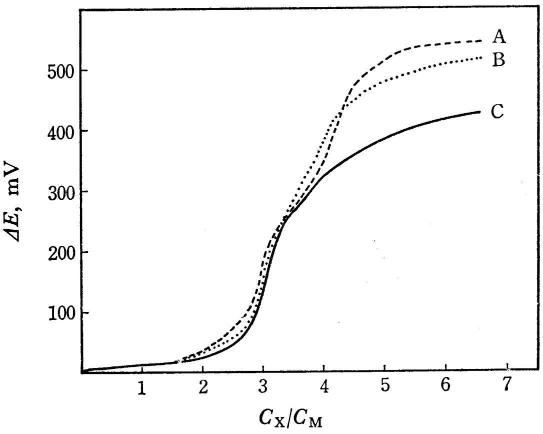

Fig. 1. Potentiometric titration curves for the titration of 0.5 mM Cd(II) with 0.05 M Et_4NCl (curve A), Et_4NBr (curve B) and Et_4NI (curve C).

The formation constants for cadmium- and zinc-halide complexes could not be calculated by Leden's method[9] because of the large inflection of titration curve but were determined in the following way.

In acetonitrile, the concentration of halide ion must be corrected for ion-pair formation. The total concentrations of metal(II) ion and halide are given by Eqs. (1) and (2).

$$C_M = [M^{2+}] + \sum_1^p [MX_p{}^{2-p}] \tag{1}$$

$$C_X = [X^-] + [Et_4NX] + \sum_1^p p[MX_p{}^{2-p}]$$
$$= [X^-] + K_a[Et_4N^+]_t[X^-] + \sum_1^p p[MX_p{}^{2-p}] \tag{2}$$

The total concentration of Et_4N^+, $[Et_4N^+]_t$ was kept to be 0.1 M by addition of the appropriate amount of Et_4NClO_4.

Assuming that the concentration of MX^+ and MX_2 to be negligible at $C_X/C_M \geqq 3$, Eqs. (3) and (4) are derived from Eqs. (1) and (2).

$$YK_4[X^-]^2 + (Y+Y'K_4)[X^-] - Y'' = 0 \tag{3}$$

$$[MX_4{}^{2-}] = Y'' - Y[X^-] \tag{4}$$

where $Y=1+0.1K_a$, $Y'=4C_M-C_X-4[M^{2+}]$, $Y''=3[M^{2+}]+C_X-3C_M$ and $K_4=[MX_4{}^{2-}]/[MX_3{}^-][X^-]$

The potential shift ($\varDelta E$) by addition of halide is given by Eq. (5)

$$\varDelta E = \frac{0.0591}{2} \log \frac{C_M}{[M^{2+}]} \tag{5}$$

and the overall formation constant β_4 is

$$\beta_4 = \frac{[MX_4{}^{2-}]}{[M^{2+}][X^-]^4} \tag{6}$$

A series of values was assumed for K_4 and corresponding values of β_4 were calculated by using Eqs. (3), (4), (5), and (6). The resulting values of log β_4 were plotted against the assumed value of log K_4. The different lines obtained from different points on the titration curve intersect at one point. For example, there can be seen the intersection point as shown in Fig. 2 for cadmium-iodide system. The value of β_3 was calculated from β_4 and K_4.

The plots for the other systems also intersect at one point.

The values of the formation constants for metal(II)-halide systems obtained by potentiometry and polarography[1] are summarized in Table 1.

The agreement between the values of the formation constant obtained for tetraiodocadmium(II) ion by potentiometry and by polarography is quite satisfactory.

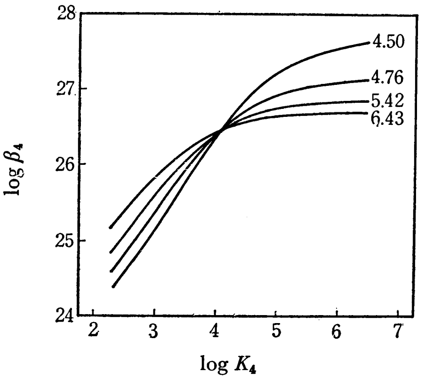

Fig. 2. Graphical solution of the formation constants (β_4 and K_4) for cadmium-iodide system.
Numbers on curves indicate mole ratio, C_I/C_{Cd}.

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TABLE 1. LOGARITHMS OF THE OVERALL FORMATION CONSTANTS β_n FOR CADMIUM- AND ZINC-HALIDE SYSTEMS

System	β_n	Potentiometric data	Polarographic data
Cd(II)-I$^-$	β_3	22.4	
	β_4	26.5	26.2
-Br$^-$	β_3	25.3	
	β_4	29.8	29
-Cl$^-$	β_3	29.2	
	β_4	34.0	
Zn(II)-I$^-$	β_4		18.4
-Cl$^-$	β_3	20.1	
	β_4	23.4	

In the case of the cadmium-bromide system, β_3 and β_4 were obtained by potentiometry, whereas only a crude value of β_4 was obtained by polarography. The stability of metal-chloride complex in acetonitrile follows the natural order of stability, that is, Ni(II) < Cu(II) > Zn(II).[2,10]

These data indicate increasing stability of tri- and tetra-halogeno complexes in the order I<Br<Cl.

The values of β_4 obtained for cadmium- and zinc-halide systems in acetonitrile (donor number,[5] DN=14.1) were compared with those in other solvents such as dimethyl sulfoxide (DN=29.8), methanol (DN=33.8) and formamide (DN=39.1).

In the cadmium-chloride system, the stability (log β_4) decreases in the order acetonitrile (34.0)$\gg$methanol (6.1)[11]>formamide (5.5).[12] In the zinc-chloride system, the value of log β_4 is larger in acetonitrile (23.5) than that in dimethyl sulfoxide (16.25).[13] The stability for other systems decreases with increasing donor number of the solvent, too.

Thus, a solvent of low donor number such as acetonitrile was confirmed to be effective for the formation of halide complexes.

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