Potentiometric Study of Mixed Cadmium Halide Complexes in Aqueous Solution

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The stability constants of the binary and mixed cadmium halides in aqueous solution were measured by the specific ion electrode method. Graphic and computer computational methods were compared.

The study of equilibria in aqueous solutions indicates (*17*) that, in general, mixed complexes tend to be formed when two or more ligands are present in a solution. For a discussion of whether and when mixed complex formation would be preferred over the binary compounds, see ref. *17*.

Mixed and binary complex formation in cadmium II halide aqueous solutions has been the subject of several investigations. For a summary of earlier work on the binary compounds, see refs. *3* and *14*. A number of studies deal with specific mixed cadmium halides (*4, 10, 26, 29*), but a general study of the CdXY system where *X* and *Y* are different halides is still lacking. This is the purpose of the present investigation, and to properly compare the formation of binary and mixed complexes, a study under the same conditions was also made of the corresponding binary system.

Previous measurement methods have included spectrophotometry, polarography, ion exchange, solubility, radiotracer, thermochemical, and other analytical methods (*13, 27*). A potentiometric method using specific ion electrodes was applied to some binary systems under varying conditions (*6, 7, 20, 21*). We have now applied it in a systematic manner to the binary halides and extended the method to mixed halides.

For a review of the methods used previously to compute the stability constants, see refs. *15 and 22*. Discrepancies have been reported in the stability constants calculated from the same experimental data with different computational methods, and possible uncertainties arising from application of models describing the experimental situation have been discussed (*5, 8, 23, 25*). We have tried to use the present measurements to examine these problems.

Experimental

All chemicals were of analytical grade and were used without further purification. Triply distilled water was used for all solutions. Stock solutions of sodium halides were prepared after drying the salts at 100°C for 24 hr. The cadmium perchlorate stock solution was prepared by dissolving cadmium carbonate in an excess of perchloric acid sufficient to maintain the pH at 4.5–5.5 and avoid hydrolysis of the cadmium ions (*1*). The concentrations of all standard solutions were determined by classical analytical methods in parallel to the potentiometric measurements.

The measurements were carried out at 25 ± 0.05°C with an "Orion" digital pH/mV meter, Model 801. Its accuracy is ±0.2 mV. The pH range was 4.5–5.5, and the pH was kept constant (±0.01) during each series of measurements. The free ion concentrations were measured with "Ionalyzer" model specific ion electrodes, and calibration curves were constructed for each ion measured. The reference electrode was the "Orion" double-junction Model 90-02-00. The factory-recommended outer filling solution, 10% KNO_3, was unsuitable for the present work, as the supporting electrolyte used was 3*M* $NaClO_4$ with resultant $KClO_4$ precipitation during the measurements. Taking account of the mobilities and chemical reactions of the ions involved in the present measurements, a 10% $NaNO_3$ solution was tried. This led to a general change in the readings obtained, but the change was directly proportional to the concentrations measured and the original readings, so that the accuracy of the measurements was not reduced. The readings were usually taken 5 min after addition of the titrating solution. The time interval between addition of the titrating ion and the instrument reading had to be controlled because of the (known) time needed for the specific electrodes to react to the concentration changes (*19*).

The measurements can be carried out in solutions in which the initial (total) metal ion concentration is either constant or variable. According to Fronaeus (*11*), the mode of measurement affects the values obtained for the constants. Therefore, both modes of work were tried on binary systems and gave the same final results. The first mode was chosen as being more convenient for computation purposes for both binary and mixed systems.

As to the ligands, one method used was to measure the system with the ratio of the two ligands kept constant. A second method was to keep the concentration of one ligand constant during each titration and change only the concentration of the second ligand. The concentrations used were in the range 10^{-1}–10^{-3} molar. The concentration taken into consideration corresponded to the accuracy limits of the appropriate specific electrodes (*7, 20*).

The volume of the titrated solution (A) was 50 ml. The total metal concentration was in the range 10^{-2}–10^{-3} molar. The ionic strength was kept constant at 3.00 by use of sodium perchlorate. The metal concentration in the titrating solution (B) was constant and adjusted to that of solution A, whereas the ligand concentration varied or was kept constant depending on the mode of measurement as mentioned above. When the ligand concentration ratio was kept constant, it was adjusted to correspond to the ratio of the appropriate binary constants. The reversible electrode is limited as to the measurements which can be carried out in the presence of certain ions by the value of the specific constant of the electrode. This gives the maximum concentration of an ion at which it will not affect the accuracy of the measurement

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of the concentration of the ion measured. Therefore, when X was kept constant and Y varied, X was chosen as the ion which could not be measured by the appropriate electrode when Y was present (*7, 20*). When neither ion interfered with the other, the ligand measured was the one giving a larger change in the instrument readings.

In the runs on the formation of binary complexes, solution (A) did not contain ligand ions, and solution B contained only one ligand.

Calculations

Binary systems. The equilibrium constants in the binary systems can be obtained by several methods (*2, 11, 18, 23, 25, 28*). The methods used in the present work were chosen to fit the behavior of the constants in question, i.e., $k_1 > k_2 > k_3$ (where k is the stepwise formation constant), and the absolute value of the constants is relatively small.

The overall equilibrium constant for the reaction $M^{2+} + nX^- \rightleftarrows MX_n{}^{2-n}$ is given by $\beta_n = [MX_n][M][X]^n$; the total metal concentration is given by $[M_T] = [M] + [MX] + \ldots + [MX_n]$. Substitution of the values for the concentrations of the various complexes in the expressions for the equilibrium constants for each complex gives the mass-balance equations (*16*):

$$[M_T] = [M]\sum_{n=0}^{N}\beta_n[X]^n \tag{1}$$

and

$$[X_T] = [X] + [M]\sum_{n=0}^{N}n\beta_n[X]^n \tag{2}$$

Initially, Leden's method (*16*) was appropriate for calculation of the first constant only. From Equation 1, we obtain the relation $1/(1 - \bar{n}) = f([X])$ where $\bar{n} = ([X_T] - [X])/[M_T]$ is the mean number of ligands bound to one metal ion. The method entails drawing curves with $[X]$ as the abscissa and $1/(1 - \bar{n})$ as the ordinate. Later, he developed together with Persson a more general method (*15*) permitting calculation of higher constants.

Several other methods were tried during the present work (*2, 11, 18, 23, 28*); the most appropriate was that of Rossotti (*23*) according to which a curve is drawn with $X_1 = (2 - \bar{n})[X]/(1 - \bar{n})$ as abscissa and $Y_1 = \bar{n}/\{(1 - \bar{n})[X]\}$ as ordinate. The equation for β_n is

$$\frac{\bar{n}}{(1 - \bar{n})[X]} = \beta_1 + \beta_2\frac{2 - \bar{n}}{1 - \bar{n}}[X] + \sum_{n=3}^{N}\beta_n[X]^{n-1} \tag{3}$$

After β_1 is obtained, β_2 is calculated from $Y_2 = \{\bar{n} - (1 - \bar{n})\ \beta_1[X]\}/\{(2 - \bar{n})\ [X]^2\}$ and $X_2 = (3 - \bar{n})\ [X]/(2 - \bar{n})$ and so on till β_n.

In addition to the above, the equilibrium constants were calculated with a least-squares program (NLSQ). This is based on a polynomial function, the parameters of which are the equilibrium constants. The program calculates the constants fitting best the experimental values with repeated integrations for the parameters nearest the experimental curve. The NLSQ program was incorporated into a so-called METALAK program which calculated all the concentrations, functions, and curves from the experimental measurements.

Mixed complexes. Here, we have to introduce the appropriate mixing equilibrium constants. To do this, we tried three methods. The Yalman method (*30*) gave good results but can give only the β_{11} constant and is applicable only to measurements at constant ligand concentration ratio. A stoichiometric method was tried in which the total metal concentration was kept constant, as well as the concentration of ligand X. Again, good results were obtained for β_{11} but not for higher complexes. The most useful method was a modification of that of Leden and Persson (*15*) which uses the function

$$F_{00}(X, Y) = \frac{[M_T]}{[M]} = \sum_{i=0}^{M}\sum_{j=0}^{N}\beta_{ij}[X]^i[Y]^j \tag{4}$$

where M is the maximum number of X ligands, and N is the maximum number of Y ligands (4) for cadmium halides bound to one metal ion ($M + N \leq 4$). According to Schaap and McMasters (*24*), the F_{00} function can be expanded in the form (assuming that $M + N = 4$)

$$F_{00}(X, Y) = A + B[Y] + C[Y]^2 + D[Y]^3 + E[Y]^4 \tag{5}$$

Table I. Binary Stability Constants of $CdX_n{}^{2-n}$

n	β_n, this work	β_n (*16*)[a]
Complexes of Cd–Cl		
1	39.0 ± 0.6	38.5 ± 1
2	178 ± 42	170 ± 10
3	254 ± 53	260 ± 10
Complexes of Cd–Br		
1	58.5 ± 0.5	57.0 ± 2
2	215 ± 25	220 ± 20
3	$2.15 \times 10^3 \pm 100$	$2.00 \times 10^3 \pm 200$
4	$1.24 \times 10^4 \pm 1.0 \times 10^3$	$5.00 \times 10^3 \pm 500$
Complexes of Cd–I		
1	120 ± 1	120 ± 2
2	$1.23 \times 10^3 \pm 100$	708 ± 500
3	$3.25 \times 10^5 \pm 1.1 \times 10^4$	$1.00 \times 10^5 \pm 1 \times 10^4$
4	$1.60 \times 10^6 \pm 1.0 \times 10^6$	$3.00 \times 10^6 \pm 1 \times 10^6$

[a] The results of refs. **28** and **12** are also in good agreement with the values obtained in the present work. For other results, see ref. **3**.

Table II. F_{00} Expansion Parameters Calculated for Constant Concentration of X and Varying Concentration of Y

Mol concn of X	Calculated parameters				
	A	B	C	D	E
1) X = Cl; Y = Br					
0.001	1.51	80	1.82×10^4	2.28×10^5	...
0.002	1.39	175	1.00×10^4	...	...
0.004	1.70	185	1.12×10^3	1.05×10^4	...
0.006	1.03	81	2.35×10^3	...	...
0.010	2.02	520	3.62×10^3	...	...
0.012	2.84	157	9.02×10^2	2.07×10^4	...
2) X = Cl; Y = I					
0.001	1.23	...	5.0×10^4	5.0×10^6	...
0.002	1.02	135	1.5×10^4	2.05×10^7	...
0.004	1.00	128	2.3×10^3	1.2×10^6	...
0.006	1.01	141	4.30×10^3	3.09×10^6	...
0.010	1.00	164	1.15×10^4	9.0×10^5	6.25×10^7
0.012	1.00	175	8.20×10^3	3.55×10^6	...
0.050	1.00	115	1.30×10^4	...	...
0.100	0.998	900	9.65×10^4	1.36×10^6	...
3) X = Br; Y = I					
0.002	1.00	120	1.23×10^3	4.87×10^5	...
0.0049	1.00	150	1.1×10^4	3.3×10^6	...
0.0098	1.00	280	1.2×10^4	3.95×10^7	...
0.0117	1.00	190	4.0×10^3	3.4×10^6	...
0.0147	1.00	210	5.0×10^3	2.5×10^7	...
0.0490	1.00	76.5	2.15×10^3	...	...
0.0980	1.00	100	2.2×10^3	2.05×10^6	...

Table III. Stability Constants of Mixed Ligand Cd(II)-Halide Complexes

Complex	β_{11}	β_{12}	β_{13}	β_{21}	β_{22}
Cd-Cl-Br	1.83×10^4 $\pm 0.10 \times 10^4$	1.10×10^5 $\pm 0.20 \times 10^5$	2.75×10^6 $\pm 0.10 \times 10^6$	2.37×10^6 $\pm 0.50 \times 10^6$	7.4×10^6 $\pm 1.0 \times 10^6$
Cd-Cl-I	3.5×10^4 $\pm 1.0 \times 10^4$	1.65×10^5 $\pm 0.10 \times 10^5$	... ...	2.96×10^6 $\pm 0.20 \times 10^6$	... ...
Cd-Br-I	1.12×10^4 $\pm 0.60 \times 10^4$	1.21×10^4 $\pm 0.30 \times 10^4$	1.42×10^8 $\pm 0.10 \times 10^8$	5.5×10^6 $\pm 0.2 \times 10^6$	1.76×10^5 $\pm 0.90 \times 10^5$

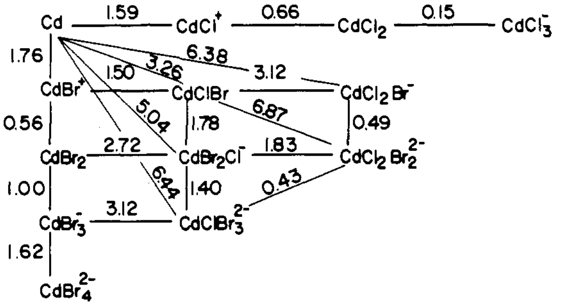

Figure 1. Cd(II)-chloride-bromide system

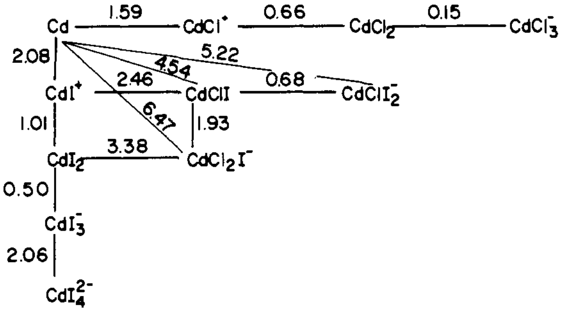

Figure 2. Cd(II)-chloride-iodide system

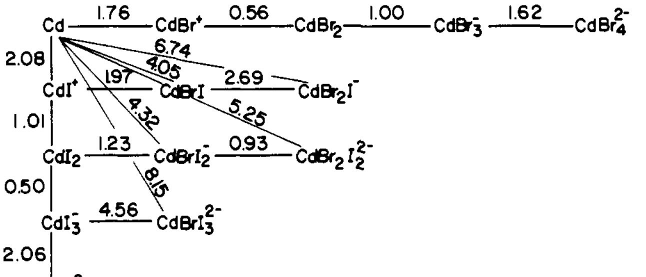

Figure 3. Cd(II)-bromide-iodide system

From Equation 4 the following expressions can be derived for the polynomial parameters of Equation 5:

$$A = \beta_{00} + \beta_{10}[X] + \beta_{20}[X]^2 + \beta_{30}[X]^3 + \beta_{40}[X]^4$$

$$B = \beta_{01} + \beta_{11}[X] + \beta_{21}[X]^2 + \beta_{31}[X]^3$$

$$C = \beta_{02} + \beta_{12}[X] + \beta_{22}[X]^2$$

$$D = \beta_{03} + \beta_{13}[X]$$

$$E = \beta_{04}$$

and corresponding expressions can be obtained for lower $M + N$ values. By use of the binary constant values calculated as described in the previous section, the mixed complex equilibrium constants are obtained. The mean number of ligands ($\bar{n}$) bound to one metal ion gives the number of parameters calculated in Equation 5 and the appropriate complexes existing in the given run.

The most accurate results for the first constants (obtained from extrapolation of the F_{00} function) were obtained for $\bar{n}$ values in the range of 0.2–0.8. These values are little affected by the high complexes formed with increasing ligand concentration (9). The range of $\bar{n} = 1.2$ to 1.8 was used to evaluate the second stepwise stability constants, and so on. The highest complexes were calculated with all the measured data except those for $\bar{n} <$ 0.2.

Results and Discussion

The calculated binary system equilibrium constants, together with the standard errors, are given in Table I, where they are compared with previously determined values. The polynomial parameters obtained in the F_{00} expansion are presented in Table II. With the data in Tables I and II, the mixed complex equilibrium constants were calculated and are shown in Table III. Figures 1–3 summarize and interrelate the results for the Cd(Cl,Br), Cd(Cl,I) and Cd(Br,I) systems, respectively. The results show that the values of the stability constants increase with the number of ligands bound to the metal ion. The highest values are obtained for the symmetrical MX_2Y_2 complexes.

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