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The Complexity Constants of Cadmium Chloride and Bromide

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In a previous article [1] it was shown that ligand concentrations and hence consecutive complexity constants can be determined polarographically with the aid of suitable indicator ions even though the complex itself is not reduced at the electrode. It is, of course, necessary that the indicator ion is reversibly reducible; according to the literature, only a few ions — *e.g.* cadmium, lead, thallium — fulfill this condition. Fortunately, these metal ions are reduced at relatively low negative potentials, and it is therefore possible to use them in the investigation of the complex compounds of most other metals which are reducible at higher negative potentials.

When using the indicator method, it is very important to know accurately the values of the equilibrium constants of the complexes formed by the indicator ion, and in polarographic measurements it seems most appropriate to use polarographically determined values of the constants. Therefore, series of measurements have been started in order to determine the equilibrium constants of various cadmium complexes; in this article the results of measurements of the complexity constants of cadmium chloride and cadmium bromide are reported. A redetermination of these constants also seemed desirable in view of the fact that the values reported in literature differ greatly.

EXPERIMENTAL

A manual apparatus was used. The voltage applied to the cell circuit was regulated by means of a rheostat (total resistance 1 000 ohms) and was accurate to $\pm$ 0.1 mV. The rather high bridge resistance did not cause any appreciable errors (*cf.* Kolthoff and Lingane [2]), since only potential *differences* were measured and the currents were very small. The sensitivity of the "Multiflex" galvanometer used was $5.65 \cdot 10^{-8}$ A/scale unit.

The polarographic cell was connected to the calomel reference electrode by a 3 C sodium perchlorate — 3 C sodium chloride bridge. The resistance of the galvanic cell was *ca.* 1 000 ohms. All the experiments were performed at a temperature of 25° C $\pm$ 0.03°. Purified nitrogen containing less than 0.1 % oxygen was used to remove oxygen from the solutions.

Sodium perchlorate was added to maintain constant activity conditions. All measurements were conducted with a constant ionic strength of 3. The procedure followed in the

Table 1. The cadmium-chloride system at an ionic strength of 3.0. Series A and B: $c_{Cd^{2+}} = 1$ *mC;* $E_{\frac{1}{2}} = -549.6$ *mV (SCE) for* $c_{Cl^-} = 0$. *Series C and D:* $c_{Cd^{2+}} = 0.3$ *mC;* $E_{\frac{1}{2}} = -546.9$ *mV (SCE) for* $c_{Cl^-} = 0$. *The difference in the* $E_{\frac{1}{2}}$ *values is due to the high internal resistance of the cell.*

		$c_{Cl}-$ mC	$-\Delta E_{\frac{1}{2}}$ mV	(4) $[Cl_0^-]$ mC	(3) $\bar{n}$	(6) $\frac{c_{oCd^{2+}}}{[Cd_0^{2+}]}$	(10) F_1 1/mole	(10) F_2 (1/mole)^2	(10) F_3 (1/mole)^3	
A	1	11.54	4.4	11.38		1.41	36.1	3 170		
					0.37					
	2	19.62	6.9	19.32		1.71	36.8	1 889		
					0.53					
	3	27.33	9.2	27.05		2.05	38.8	1 433		
					0.57					
	4	36.84	11.4	36.50		2.42	38.9	1 064		
					0.81					
	5	50.00	14.6	49.60		3.11	42.5	858		○
					0.90					
	6	60.00	16.7	59.56		3.67	44.8	752		
					1.02					
	7	77.79	20.1	77.29		4.77	48.8	630	8 150	
					1.02					
	8	100.0	23.4	99.4		6.18	52.1	524	5 265	
					1.24					
	9	150.0	29.9	149.3		10.23	61.8	413	2 765	
B	1	29.7	9.2	29.4		2.05	35.7	1 215		
					0.76					
	2	58.8	15.9	58.4		3.45	42.0	720		
					1.10					
	3	115.4	25.5	114.8		7.26	54.6	475	4 140	
					1.25					
	4	196.2	34.0	195.4		14.09	67.0	343	1 752	
					1.66					
	5	273.3	41.1	272.4		24.4	85.8	314	1 151	
					1.92					
	6	368.4	48.5	367.4		43.5	115.8	315	857	
					2.04					●
	7	500.0	56.5	498.9		81.0	160.6	322	645	
					2.30					
	8	600.0	61.9	598.8		123.2	204.5	341	570	
					2.23					
	9	777.9	69.4	776.7		221	283	364	468	
					2.59					
	10	1 000	77.8	999		425	424	425	425	
					2.78					
	11	1 235	85.3	1 234		760	615	498	403	
					2.78					
	12	1 500	92.2	1 499		1 300	866	577	385	
C	1	11.68	4.5	11.63		1.42	36.1	3 100		
					0.35					
	2	19.62	6.8	19.55		1.70	35.8	1 835		

	3	27.33	8.7	27.24	0.44	1.97	35.6	1 304	
	4	36.84	11.3	36.74	0.68	2.41	38.4	1 044	
	5	50.00	14.6	49.88	0.84	3.11	42.4	851	
	6	69.24	17.8	69.10	0.76	3.99	43.2	625	9 040
	7	100.0	23.2	99.8	1.15	6.08	50.9	510	5 100
	8	150.0	29.5	149.8	1.23	9.91	59.6	398	2 656
D	1	29.7	9.0	29.6		2.01	34.1	1 152	
	2	58.8	15.3	58.7	0.71	3.29	38.4	641	
	3	115.4	24.6	115.2	1.04	6.77	50.1	434	3 760
	4	196.2	34.4	196.0	1.44	14.51	69.0	352	1 796
	5	273.3	41.4	273.0	1.64	25.0	87.9	322	1 179
	6	368.4	48.5	368.1	1.85	43.5	115.2	313	850
	7	500.0	57.4	499.7	2.28	86.8	171.9	344	687
	8	692.4	66.6	692.0	2.19	177.8	255	368	531
	9	931.0	76.1	930.6	2.49	373	399	429	460
	10	1 235	85.7	1 235	2.66	785	635	514	416
	11	1 500	92.5	1 500	2.76	1 330	885	590	394

experiments was analogous to that used by Leden [3] in his potentiometric measurements. The polarographic vessel was filled with a solution containing cadmium and sodium perchlorate. The cadmium concentration was usually very low, 1 mC or less. The ligand solution, which contained cadmium perchlorate in the same concentration as the sample solution and sodium perchlorate in such a concentration that the ionic strength was 3, was added from a burette.

The results of the measurements are presented in Tables 1 and 2. The figures above the columns refer to the equations used in the calculation of the values given in the columns.

THE CALCULATION OF THE COMPLEXITY CONSTANTS

The calculations were essentially analogous to those given by Leden [3]. In the derivation of the equations the fundamental differences between potentiometric and polarographic methods must, however, be taken into account.

The symbols used are the same as those employed in the previous paper [1]. The subscript o always refers to concentrations at the electrode surface. The constants are calculated as follows:

1. From polarograms taken at various ligand concentrations, values of ΔE, the difference between the potential of a cadmium perchlorate solution

Table 2. The cadmium-bromide system at an ionic strength of 3.0. Series A and B: $c_{Cd^{2+}} = 1$ *mC;* $E_{\frac{1}{2}} = -549.6$ *mV (SCE) for* $c_{Br^-} = 0$. *Series C:* $c_{Cd^{2+}} = 0.3$ *mC;* $E_{\frac{1}{2}} = -546.9$ *mV (SCE) for* $c_{Br^-} = 0$. *The difference in the* $E_{\frac{1}{2}}$ *values is due to the high internal resistance of the cell.*

		c_{Br^-} mC	$-\Delta E_{\frac{1}{2}}$ mV	(4) $[Br_o^-]$ mC	(3) $\bar{n}$	(6) $\frac{c_{oCd^{2+}}}{[Cd_o^{2+}]}$	(10) F_1 l/mole	(10) F_2 (l/mole)^2	(10) F_3 (l/mole)^3	(10) F_4 (l/mole)^4	
A	1	2.97	2.0	2.89		1.17	58.8	20 350			
					0.18						
	2	5.88	3.9	5.74		1.36	62.7	10 930			
					0.34						
	3	11.54	6.9	11.32		1.71	62.6	5 530			
					0.48						
	4	19.62	10.2	19.32		2.21	62.6	3 240			
					0.74						
	5	27.33	13.4	26.97		2.84	68.2	2 530	93 800		
					0.86						□
	6	41.36	18.0	40.90		4.06	74.9	1 831	44 800		
					1.04						
	7	60.00	23.0	59.44		6.00	84.2	1 419	23 900		
					1.30						
	8	85.72	29.0	85.01		9.56	100.9	1 184	13 920		
					1.66						
	9	100.0	32.3	99.2		12.35	114.2	1 151	11 610		
					1.55						
	10	123.5	36.5	122.6		17.2	132.1	1 078	8 800	71 900	
					2.01						
	11	150.0	41.5	149.0		25.4	163.9	1 099	7 380	49 500	
B	1	29.7	13.5	29.3		2.86	63.5	2 165	73 900		
					1.03						
	2	58.8	22.6	58.2		5.80	82.5	1 416	24 300		
					1.37						
	3	115.4	34.5	114.5		14.70	119.6	1 043	9 120	79 600	
					2.04						
	4	222.2	51.7	220.9		56.0	249	1 126	5 100	23 100	
					2.86						
	5	391.3	72.6	389.7		285	729	1 872	4 805	12 330	■
					3.37						
	6	600.0	91.1	598.3		1 205	2 015	3 370	5 630	9 410	
					3.50						
	7	857.2	107.1	855.4		4 195	4 900	5 720	6 690	7 810	
					3.68						
	8	1 235	124.4	1 233		16 140	13 090	10 600	8 590	6 960	
					3.61						
	9	1 500	133.5	1 498		32 720	21 800	14 580	9 730	6 500	
C	1	29.7	13.9	29.6		2.95	65.9	2 225	75 200		
					0.95						
	2	58.8	22.2	58.6		5.64	79.0	1 347	22 950		
					1.43						
	3	142.9	38.6	142.6		20.2	134.9	945	6 640	46 550	
					2.49						
	4	275.2	59.5	274.8		102.9	370	1 348	4 900	17 820	◪
					3.11						
	5	500.0	83.4	499.5		662	1 328	2 660	5 320	10 650	
					3.53						
	6	692.4	98.1	691.9		2 082	3 005	4 340	6 260	9 050	
					3.36						
	7	1 000	114.0	999		7 155	7 160	7 170	7 175	7 180	
					3.62						
	8	1 500	132.8	1 499		31 050	20 750	13 820	9 230	6 155	

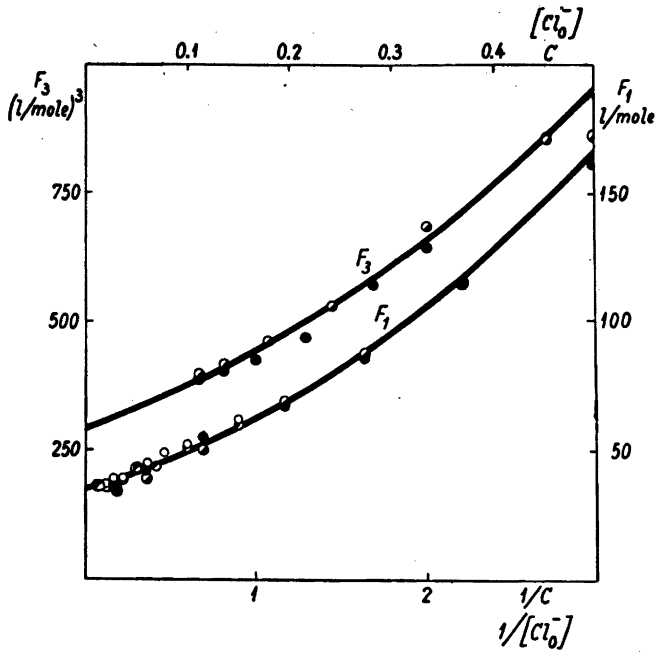

Fig. 1. F_1 as a function of $[Cl_0^-]$ and F_3 as a function of $1/[Cl_0^-]$. The curves have been drawn according to the graphically determined β values. The points are measured values.

containing ligand and the potential of a solution without any ligand, are read; the potentials refer to a selected current, expressed as a relative current $\frac{i}{i_d}$ (i_d = diffusion current). Usually the half-wave current $\frac{1}{2}i_d$ is used.

2. The average ligand number $\bar{n}$ of the system defined by

$$\bar{n} = \frac{\text{number of bound ligands}}{\text{total number of metal atoms}} \tag{1}$$

is computed from the equation of Bodländer

$$\bar{n} = -\frac{dE}{d\ln A} \cdot \frac{mF}{RT} \tag{2}$$

which, when cadmium polarograms taken at 25°C are considered, takes the form

$$\bar{n}_0 = -\frac{d\Delta E}{d\log A_0} \cdot \frac{1}{29.58} \tag{3}$$

$\bar{n}_0$ can be determined from this equation by using differences instead of differentials. As, however, A_0 is not known, the value of c_A is used as a first

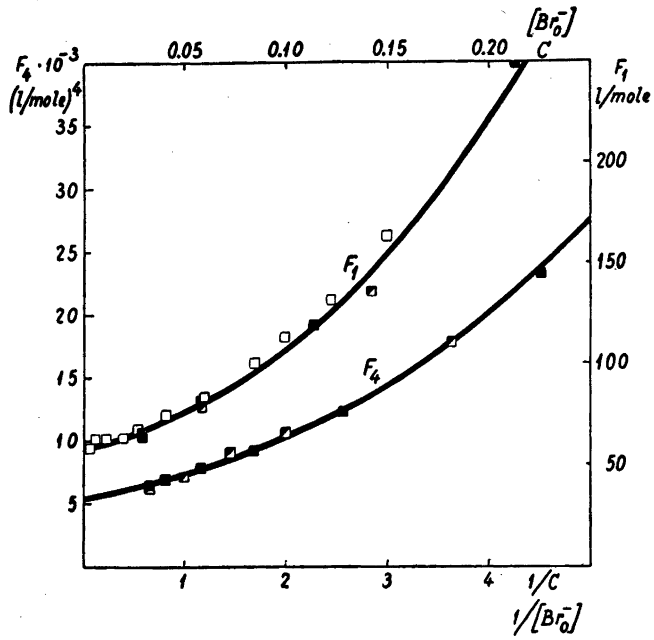

Fig. 2. F_1 as a function of $[Br_0^-]$ and F_4 as a function of $1/[Br_0^-]$. The curves have been drawn according to the graphically determined β values. The points are measured values.

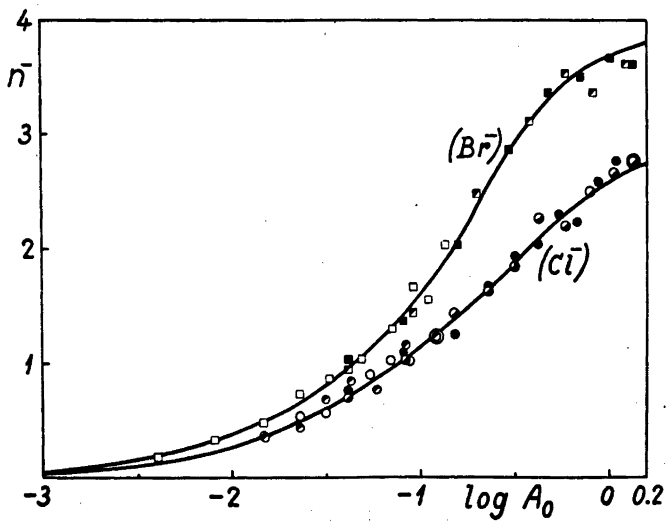

Fig. 3. $\bar{n}$ as a function of the ligand concentration. The curves have been drawn according to the graphically determined β values. The points are measured values.

approximation instead of A_0. When determining complexity constants of cadmium chloride and bromide, the differences between c_A and A_0 are very small.

3. Using these approximate $\bar{n}_0$ values, values of A_0 are then calculated from the equation

$$A_0 = c_A - \bar{n}_0 \cdot \frac{i_d - i}{i_d} \cdot c_M \tag{4}$$

Employing these approximate A_0 values, new $\bar{n}_0$ values are computed using equation (3) and more accurate A_0 values from equation (4).

4. The concentration M_0 of metal ion at the electrode surface is calculated from the equation

$$\Delta E = -29.58 \cdot \log \left(\frac{i_d - i}{i_d} \cdot \frac{c_M}{M_0} \right) \tag{5}$$

or, if the total metal concentration at the drop surface $\frac{i_d - i}{i_d} \cdot c_M$ is designated by c_{0M}, from the equation

$$\Delta E = -29.58 \cdot \log \frac{c_{0M}}{M_0} \tag{6}$$

In this equation all quantities are known except M_0.

5. The best way of calculating the β constants [1] seems to be a partly graphical method. For this purpose, we introduce functions F_n defined as follows

$$F_1 = \beta_1 + \beta_2 \cdot A_0 + \beta_3 \cdot A_0^2 + \ldots\ldots \tag{7}$$

$$F_2 = \frac{F_1}{A_0} = \frac{\beta_1}{A_0} + \beta_2 + \beta_3 \cdot A_0 + \ldots\ldots \tag{8}$$

or generally

$$F_n = \frac{F_1}{A_0^{(n-1)}} \tag{9}$$

On the other hand, it can easily be shown that

$$F_n = \frac{c_{0M} - M_0}{M_0 \cdot A_0^n} = \frac{\frac{c_{0M}}{M_0} - 1}{A_0^n} \tag{10}$$

As all the quantities on the right side of equation (10) are known, values of F_n corresponding to various values of A_0 can be determined.

F_1 is then plotted as a function of A_0. The point of intersection of the extrapolated curve with the F axis gives β_1 and the slope of the curve at this point β_2.

β_4 and β_3 can be determined in an analogous way by plotting F_4 as a function of $\frac{1}{A_0}$.

The values calculated from the slopes, *i.e.* β_2 and β_3, are, however, not very accurate. They can be more accurately determined on the basis of equations which use A_0 and F values corresponding to minimum values of F_2 and F_3 where the concentrations of MA_2 and MA_3 attain their maximum values. Graphically determined values of β_1 and β_4 have been used in this paper.

The existence of $CdCl_4^{2-}$ complexes has not been proved. F_4 is relatively small and is measured at rather high chloride concentrations which can affect activities of the species.

The F curves used in the calculations of various β values are shown in Figs. 1 and 2. In Fig. 3 the relationship between $\bar{n}$ and ligand concentration is presented graphically. It is assumed that only mononuclear complexes are formed.

COMPARISON OF THE VALUES OF COMPLEXITY CONSTANTS OBTAINED BY DIFFERENT AUTHORS

The cadmium chloride and bromide systems have been investigated by several authors. The papers published before 1943 have been critically reviewed by Leden [3]. In recent years the two systems have been investigated by Robinson and Wallace [4], Davies [5], Korenman [6], King [7], Strocchi [8,9,10], Vasil'ev and Proukhina [11], Korshunov, Malyugina and Balabanova [12], Ermolenko and Makkaveeva [13].

The results of many of these investigations are very approximate, and it seems that the values of Leden [3] and King [7] are the only ones of satisfactory accuracy. In Table 3 the values obtained by three different methods are compared.

Table 3. Complexity constants of cadmium chloride and bromide.

System	Author	Method *	β_1 1/mole	β_2 (1/mole)^2	β_3 (1/mole)^3	β_4 (1/mole)^4
$Cd^{2+}-Cl^-$	Leden [3]	Potent.	38.5	170	260	
	King [7]	Solubility	25	154	250	
	This paper	Polarogr.	35 ± 1	115 ± 5	290 ± 30	
$Cd^{2+}-Br^-$	Leden [3]	Potent.	57	220	2 100	5 000
	This paper	Polarogr.	58 ± 2	275 ± 25	1 600±200	5 400±400

* In all these experiments the ionic strenght was adjusted to 3 by means of sodium perchlorate.

SUMMARY

The consecutive complexity constants of the cadmium chloride and bromide systems have been calculated using polarographic data. The values given in Table 3 were obtained.

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