Thermochemical Studies on Metal Complexes

VI. The Formation of Some Cadmium(II) Complex Systems at Different Ionic Strengths

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The complex formation between cadmium(II) ions and iodide, thiocyanate, and acetate ions, respectively, has been studied by a potentiometric central ion method at 25.00°C. The investigation has been carried out with a cadmium amalgam electrode in aqueous sodium perchlorate media, the total equivalent concentration of all ions being constant, $I' = 0.25$, 0.50, 1.00, and 2.00 (M), respectively, and for the thiocyanate system also 3.00 (M). The stability constants were calculated with a least squares method, and were found to vary in the same way with the ionic strength for all three systems.

By calculations from calorimetric data obtained at different C_M at ionic strength 3.00 (M) of the cadmium(II) iodide and acetate systems it was shown that this method can be used to determine stability constants for weak complex systems.

The influence of ionic strength on complex formation of the copper(II) acetate system in aqueous solution, reported in a previous paper,[1] was found to be similar to that reported for the lead(II) acetate system in a compilation made by Gobom.[2] The same type of dependence was also reported for the cadmium(II) chloride system by Vanderzee and Dawson[3] and for the cadmium(II) bromide system by Kivalo and Ekari.[4] The variation of the stability constants with ionic strength was qualitatively that given by the expected variation in activity factors. The investigation of the chloride system[3] was performed both at different ionic strengths and at different temperatures and from these measurements it was possible to calculate not only the values of ΔG but also of ΔH and ΔS for the stepwise formation of complex species. To obtain a still better wiew of the relation between complex formation and ionic strength a systematic study of a number of systems has to be carried out and especially the division of the free energy change into one enthalpy and one entropy term as Vanderzee and Dawson[3] have done at each ionic strength would be of interest.

The investigation reported in this and following papers[5,6] is an extension of earlier studies of some cadmium(II) complex systems[7-9] made in order to

compare their stability dependence on ionic strength and to ascertain how the free energy change is built up by the enthalpy and entropy terms. Four systems have been chosen, viz. cadmium(II) chloride, iodide, thiocyanate, and acetate. The measurements were carried out at a temperature of 25.00°C in aqueous sodium perchlorate media, the total equivalent concentration of all ions being constant, I' (see below) = 0.25, 0.50, 1.00, 2.00 (M), and for the potentiometric measurements of the thiocyanate system also 3.00 (M). Earlier results were used to complete the investigation at 3.00 (M).[7-10]

Except for the chloride system, where the β_j-values of Vanderzee and Dawson[3] were used, the stability constants were determined by the potentiometric titration method designed by Leden[10] using a cadmium amalgam electrode, the results reported in this paper, and from these values the free energy changes can be obtained. The calculations of the stability constants from the potentiometric measurements were performed by two least squares methods using the computer SMIL in Lund with programs developed by Ekström[11] and Sandell.[12] Some of the series were checked by graphical extrapolations using the method of Leden.[10] The determination of the enthalpy and entropy changes will be reported in the two following papers.[5,6]

For the cadmium(II) acetate and iodide systems data from calorimetric measurements were used to determine stability constants at 25.00°C and ionic strength 3.00 M in order to compare these results with those from potentiometric measurements.[10] The constants were calculated with a method of corresponding solutions similar to that elaborated by Bjerrum,[13] Olerup,[14] and Fronæus[15] for potentiometric and spectrophotometric measurements of complex systems.

CALCULATIONS OF STABILITY CONSTANTS

1. *Calculation from potentiometric measurements of the free central ion concentration.* The methods of calculation are developed from the equations elaborated by Leden[10] and Fronæus.[15] In this paper only a short summary of the equations used are given. A list of symbols is given in Ref. 7.

Assuming only mononuclear complexes MA_1, MA_2, . . . , MA_N to be formed, we obtain equilibria of the type

$$M + jA \rightleftharpoons MA_j \qquad j = 1, 2, \ldots, N \qquad (1)$$
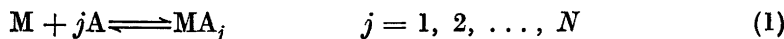
and we can define the functions

$$X([A]) = \frac{C_M}{[M]} = 1 + \sum_{j=1}^{N} \beta_j \times [A]^j \qquad (2)$$

$$X_1([A]) = \frac{X([A]) - 1}{[A]} = \sum_{j=1}^{N} \beta_j \times [A]^{j-1} \qquad (3)$$

or, in the general case

$$X_k([A]) = \frac{X_{k-1}([A]) - \beta_{k-1}}{[A]} = \sum_{j=k}^{N} \beta_j \times [A]^{j-k} \qquad (4)$$

START

Read data: N, C_M, n, $(E_m)_i$, $(C_A)_i$, $i = 1, 2, ..., n$

$(C_A)_i \longrightarrow [A]_i$ $e^{\nu F \cdot (E_m)_i / RT} \longrightarrow X_i$

$0 \rightarrow \Delta$

By the least square method appr. β_j -values are calculated from: $X_i = \sum\limits_{j=0}^{N} \beta_j \cdot [A]_i{}^j$

$1 \rightarrow i$

$-\dfrac{\sum\limits_{j=1}^{N} j \cdot \beta_j \cdot [A]_i{}^j}{\sum\limits_{j=0}^{N} \beta_j \cdot [A]_i{}^j} \longrightarrow \bar{n}'$

$(C_A)_i - \bar{n}' \cdot C_M \longrightarrow [A]_i$

$|\bar{n}' - \bar{n}_i| - 0.001$ ≥ 0 $1 + \Delta \rightarrow \Delta$

< 0 $\bar{n}' \rightarrow \bar{n}_i$

$1 + i \rightarrow i$ < 0 $i - n$

$\neq 0$ ≥ 0 Δ

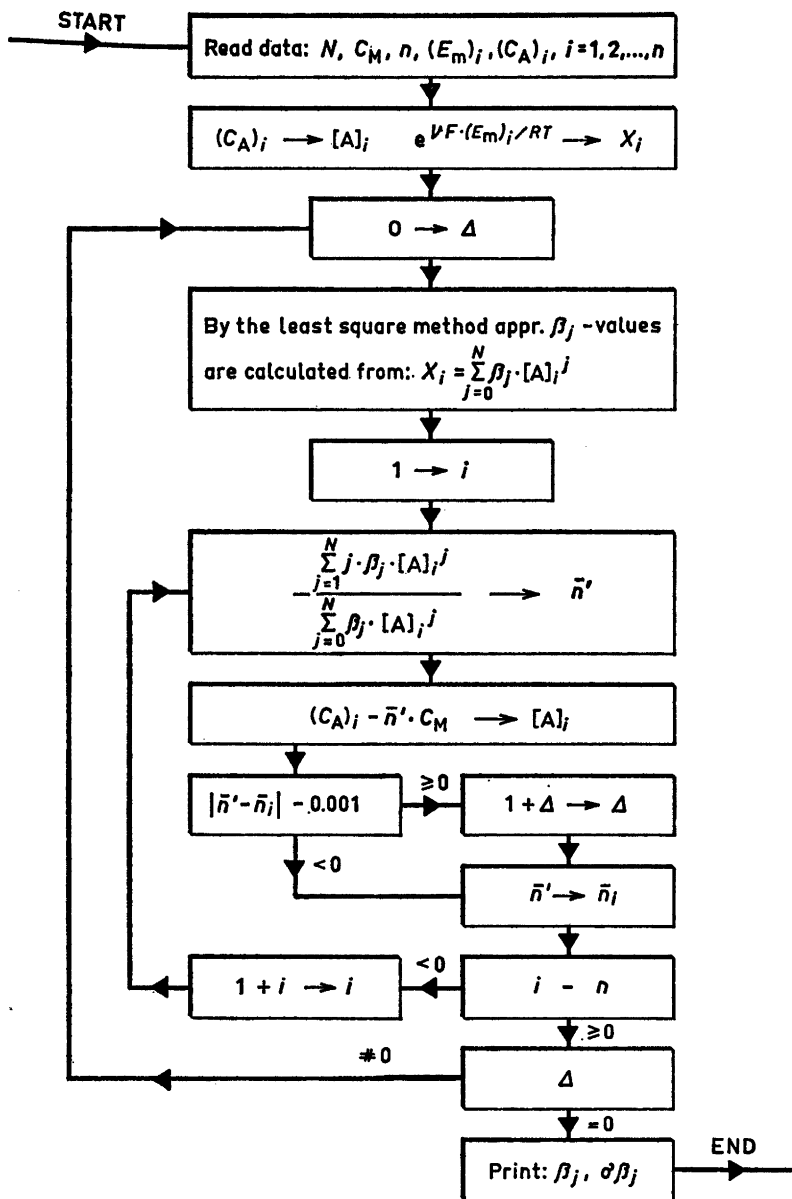$= 0$ Print: β_j, $\sigma \beta_j$ END

Fig. 1. Block scheme of the program developed by Ekström, and used for the calculations of stability constants.

In potentiometric measurements of the free central ion concentration, E_m is determined and $X([A])$ can be caculated according to

$$E_m = \frac{RT}{\nu F} \ln \frac{C_M}{[M]} = \frac{RT}{\nu F} \ln X([A]) \qquad (5)$$

E_m is the difference of the emf, E, of an element of the type (9) and the emf, E_0, of the same element with $C_A = 0$. The stability constants can now be determined by graphical extrapolations of $X_k([A])$-functions *versus* [A] to [A] = 0, first with approximate [A]-values, then with better estimated values. The calculations, however, are best performed using a computer and a least squares program. Such a program has been developed by Ekström [11] (Fig. 1) and used for the potentiometric measurements performed here. Another program, described by Sandell,[12] has been applied as a check for the thiocyanate system at $I' = 3.00$ (M). The results were also checked by graphical extrapolations for some titration series, and in all cases, except for the iodide system at $I' = 2.00$ (M), the methods gave the same constants.

2. *Calculation from calorimetric measurements.* Bjerrum,[13] Olerup,[14] and Fronæus [15] have described a method of corresponding solutions which can be used for calorimetric measurements (*cf.* Rossotti [16]). We define the function

$$\Delta h_v = \sum_{j=1}^{N} \sum_{k=1}^{j} \alpha_j \times \Delta H_k = -\frac{1000}{C_M V} \sum_v Q_{corr.} \qquad (6)$$

which is determined for different values of C_M and plotted *versus* C_A. Δh_v is a function of [A] (see Ref. 7) and if the curves are cut at a constant value of Δh_v, the points of intersection would give the corresponding solutions which have the same [A]. (Provided that the function Δh_v is monotonic and the complex system mononuclear.) Now, for selected values of Δh_v, corresponding values of C_A are plotted *versus* C_M and we obtain a number of lines according to the relation

$$C_A = [A] + \bar{n} C_M \qquad (7)$$

The values of [A] are obtained from extrapolation to $C_M = 0$, and of $\bar{n}$ from the slopes of the lines. If the complex system is polynuclear the plot of C_A *versus* C_M is curved and $\bar{n}$ is obtained from the slope of the tangent at [A] = 0. Evaluating the integral [15]

$$\ln X([A]_i) = \int_0^{[A]_i} \frac{\bar{n}}{[A]} \, d[A] \qquad (8)$$

and using the determined pairs of $\bar{n}$ and [A], we obtain a set of corresponding values of $X([A]_i)$ and $[A]_i$ for the system investigated, and the stability constants can be calculated from graphical extrapolations of the functions $X_1([A])$ to $X_N([A])$ *versus* [A] or by corresponding calculations using a high speed computer.
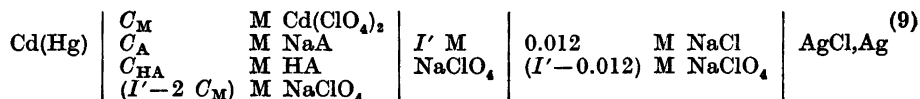
EXPERIMENTAL

Chemicals

Cadmium(II) perchlorate, sodium perchlorate, and *ligand solutions* were prepared and analyzed as previously.[7-9]

Cadmium amalgam, ca. 10 % by weight, was prepared by dissolving sticks of cadmium metal (Baker Analyzed, *p.a.*), cleaned in perchloric acid, into mercury (Merck, *p.a.*) at 60°C and in a nitrogen atmosphere. The amalgam was stored under *ca.* 5 mM perchloric acid.

All solutions were prepared with freshly distilled and demineralized water; reagent grade chemicals were used in all cases and all volumetric apparatus was calibrated before use.

Procedure

1. *The potentiometric measurements.* The complex systems were investigated by central ion measurements, using a potentiometric titration technique. The emf, E (mV), of elements of the following composition was measured:

$$
\text{Cd(Hg)} \left| \begin{array}{ll} C_M & \text{M Cd(ClO}_4)_2 \\ C_A & \text{M NaA} \\ C_{HA} & \text{M HA} \\ (I'-2\ C_M) & \text{M NaClO}_4 \end{array} \right| \begin{array}{l} I'\ \text{M} \\ \text{NaClO}_4 \end{array} \left| \begin{array}{ll} 0.012 & \text{M NaCl} \\ (I'-0.012) & \text{M NaClO}_4 \end{array} \right| \text{AgCl,Ag} \qquad (9)
$$

The right hand half-cell, the reference electrode, was saturated with AgCl and the composition of the left hand half-cell was obtained by adding increasing volumes of a solution T to 20.00 ml of a solution S. The additions were made from an all-glass syringe operated by a micrometer screw with an accuracy of $\pm$ 0.002 ml. T and S contained the same total concentration, C_M (M), of the cadmium ion, which consequently was constant throughout the whole titration series. The ligand can be supplied by either T or S. For the iodide and the thiocyanate systems $C_{HA} = 0$, and for all solutions $4 < \text{pH} < 5$. In this region the hydrolysis of the cadmium ion is negligible.[17]

The connection between the two half-cells consisted of a salt bridge, designed with j-shaped tips to minimize the variations of the diffusion potentials. Both half-cells were jacketed and thermostated at 25.00 $\pm$ 0.05°C with water. The Ag,AgCl-electrode was prepared according to Brown.[18] Good mixing of the solutions was brought about by leading a stream of oxygen-free nitrogen through the solutions in the titration cell both before the amalgam was applied and during the measurements. Before use the nitrogen was passed through an oven containing Cu in order to remove the last traces of oxygen and then bubbled through wash-bottles, one with water and one with a I' M NaClO$_4$ solution, to obtain the correct vapour pressure.

The emf was measured to $\pm$ 0.02 mV by a Norma Precision Compensation Bridge type 54, with a Kipp Lightspot Galvanometer AL 2 as zero instrument and a Weston cell as standard cell. After the first point the potentials were stable within 5 min and could, with few exceptions, be reproduced within 0.1 mV. Every titration series was repeated at least once.

In contrast to the earlier measurements [7-9] at 3.00 M the ionic medium is now defined by keeping the number I' constant for the solutions. I' is obtained from the relation

$$
I' = 1/2 \sum_i C_i |z_i| \qquad (10)
$$

which leads to a constant anion concentration if changes caused by the complex formation are neglected. This definition has some advantages and the difference between I' and the formal ionic strength I is so small in the concentration ranges used that comparisons still can be made with the earlier measurements. Where no mistake can be made the term ionic strength is used here in both meanings. As usual in determining stability constants by the method with constant ionic strength, it is assumed that the liquid junction potentials and the activity coefficient factors remain constant throughout a titration series and so may be included as constants in E_0. This approximation leads

to some systematic errors which may be expected to influence especially the values of β_3 and β_4.

2. *The calorimetric measurements* were performed using the titration calorimeter [19] and the methods [7-9] described previously.
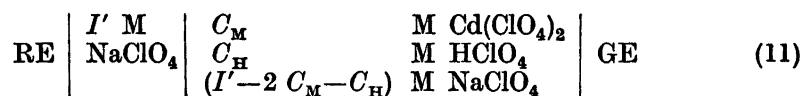
Table 1. The corresponding values of C_A and E_m for the cadmium(II) iodide system at different ionic strengths and $C_M = 0.010$ (M).

$I' = 0.25$ (M) $E_0 = 767.58$ (mV)		$I' = 0.50$ (M) $E_0 = 765.24$ (mV)		$I' = 1.00$ (M) $E_0 = 760.15$ (mV)		$I' = 2.00$ (M) $E_0 = 748.55$ (mV)	
C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)
0.000	0	0.00	0	0.00	0	0.00	0
0.750	0.49	2.00	1.10	4.00	2.17	4.00	2.37
1.600	1.01	3.97	2.21	7.96	4.19	7.96	4.64
2.224	1.37	5.94	3.26	11.88	6.15	11.88	6.79
2.956	1.83	7.88	3.27	15.76	7.96	15.76	8.85
3.67	2.26	9.80	5.27	19.60	9.67	19.60	10.77
4.39	2.65	11.71	6.20	23.41	11.31	23.41	12.63
5.80	3.43	15.45	7.99	30.91	14.39	30.91	16.15
7.17	4.18	19.15	9.63	38.26	17.39	38.26	19.54
8.52	4.93	22.78	11.22	45.45	20.24	45.45	22.91
9.85	5.65	26.28	12.71	52.6	23.09	52.6	26.26
11.15	6.30	29.75	14.16	59.5	25.90	59.5	29.62
12.43	7.00	33.15	15.54	66.3	28.62	66.3	32.99
13.69	7.69	36.50	16.88	73.0	31.40	73.0	36.34
16.14	8.95	43.05	19.41	86.1	36.77	86.1	42.97
18.50	10.10	49.32	21.80	98.6	42.04	98.6	49.32
20.77	11.16	55.41	24.11	110.8	47.04	110.8	55.20
22.96	12.18	61.24	26.36	122.5	51.73	122.5	60.72
25.09	13.15	66.93	28.57	133.8	56.10	133.8	65.60
30.12	15.32	80.30	33.76	160.6	65.61	160.6	76.06
34.73	17.23	92.63	38.56	185.3	73.40	185.3	84.36
39.02	18.88	104.1	43.02	208.1	79.80	208.1	91.13
43.00	20.48	114.7	47.08	229.3	85.14	229.3	96.68
46.7	21.91	124.5	50.72	249.0	89.69	249.0	101.38
50.1	23.23	133.7	54.06	267.5	93.62	267.5	105.49
56.4	25.64	150.5	59.83	301.0	100.19	301.0	112.16
59.8	26.89	165.2	64.60	330.3	105.35	330.3	117.41
61.9	27.77	178.3	68.58	356.5	109.51	356.5	121.62
66.5	29.52	189.9	71.94	379.9	112.94	379.9	125.13
66.8	29.66	200.5	74.81	401.0	115.86	401.0	128.07
71.2	31.35						
74.8	32.77						
75.2	32.89						
83.2	36.06						
93.6	40.13						
99.8	42.43						
115.3	48.36						
124.9	51.99						
136.3	55.94						
150.0	60.50						

MEASUREMENTS AND RESULTS

1. Potentiometric measurements of cadmium(II) systems

The cadmium(II) perchlorate and sodium perchlorate. In order to determine the concentrations of free perchloric acid in the stock solutions, $[H^+]$ was measured by titrations of the salt solutions with $HClO_4$, the potentials being determined with a glass electrode according to Ciavatta [20] using the following cell:

$$\text{RE} \left| \begin{array}{c} I' \text{ M} \\ \text{NaClO}_4 \end{array} \right| \begin{array}{ll} C_M & \text{M Cd(ClO}_4)_2 \\ C_H & \text{M HClO}_4 \\ (I'-2\,C_M-C_H) & \text{M NaClO}_4 \end{array} \left| \text{GE} \right. \tag{11}$$

In the sodium perchlorate stock solutions, pH $\simeq$ 6, an impurity of weak protolytes with a total buffer effect of less than 5×10^{-5} moles per mole of

Table 2. The corresponding values of C_A and E_m for the cadmium(II) thiocyanate system at $I' = 3.00$ (M) and different central ion concentrations.

$C_M = 5.00$ (mM) $E_0 = 745.14$ (mV)		$C_M = 10.00$ (mM) $E_0 = 736.02$ (mV)		$C_M = 20.00$ (mM) $E_0 = 727.98$ (mV)	
C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)
0.00	0	0.00	0	0.00	0
2.00	0.57	4.00	1.06	8.00	1.63
3.98	1.15	7.96	2.09	15.91	3.36
7.88	2.21	15.76	4.00	31.51	6.61
11.71	3.23	23.41	5.84	46.81	9.64
15.45	4.18	30.90	7.53	61.8	12.38
19.13	5.16	38.30	9.13	76.6	14.94
22.78	6.04	45.45	10.61	90.9	17.30
29.75	7.68	59.5	13.42	119.0	21.53
36.50	9.23	73.0	15.90	146.0	25.32
43.04	10.64	86.1	18.15	172.2	28.57
52.4	12.56	104.8	21.19	209.6	33.07
66.9	15.41	133.9	25.49	267.7	39.20
80.3	17.82	160.6	29.08	321.2	44.18
92.6	19.93	185.3	32.13	370.5	48.35
114.8	23.37	229.5	37.10	459	55.08
133.7	26.13	267.5	40.97	535	60.17
150.5	28.40	301.0	44.14	602	64.35
159.5	29.60	319.0	45.96	638	66.49
177.3	31.88	354.5	48.98	709	70.27
178.3	31.92	356.5	49.00	713	70.63
199.5	34.36	399	52.48	798	74.77
200.5	34.51	401	52.54	802	75.18
228.0	37.47	456	56.53	912	79.09
266.3	41.34	533	61.79	1065	86.37
319.8	46.21	640	68.41	1279	94.49
400.0	52.72	800	76.91	1600	105.75

sodium perchlorate was found. This impurity was neglected. In the stock solutions containing cadmium $[H^+]/C_M \simeq 10^{-3}$.

The cadmium iodide system. For this system, as for the others, it was concluded that the amalgam was not effected by the complex solutions since the potentials were well reproducible and remained constant for several hours. The corresponding data of C_A and E_m are collected in Table 1, the E_m-values are averages for two or three titration series. $I' = 0.25, 0.50, 1.00,$ and 2.00 (M). $C_M = 0.010$ (M) for all ionic strengths and $C_{HA} = 0$. In order to obtain the best estimation of E_0, the values of E are plotted *versus* C_A and the curves extrapolated to $C_A = 0$.

Assuming no polynuclear species to be formed,[5,10] four complex species are found and their formation constants in different media are tabulated in Table 7. The errors in the constants for the second step are large especially for $I' = 2.00$ (M).

The cadmium(II) thiocyanate system. This system was investigated also at $I' = 3.00$ (M) with $C_M = 0.005, 0.010,$ and 0.020 (M). For $I' = 0.25, 0.50,$

Table 3. The corresponding values of C_A and E_m for the cadmium(II) thiocyanate system at different ionic strengths and $C_M = 0.010$ (M).

$I' = 0.25$ (M) $E_0 = 767.59$ (mV)		$I' = 0.50$ (M) $E_0 = 765.28$ (mV)		$I' = 1.00$ (M) $E_0 = 760.90$ (mV)		$I' = 2.00$ (M) $E_0 = 749.45$ (mV)	
C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)
0.000	0	0.00	0	0.00	0	0.00	0
0.750	0.18	2.00	0.51	4.00	0.86	4.00	0.90
1.500	0.41	3.98	0.97	7.96	1.73	7.96	1.79
2.956	0.84	7.88	1.87	15.76	3.42	15.76	3.50
4.39	1.21	11.71	2.70	23.41	4.93	23.41	5.13
5.80	1.51	15.45	3.51	30.90	6.27	30.90	6.60
7.17	1.91	19.13	4.24	38.30	7.51	38.30	7.98
8.52	2.21	22.78	4.99	45.45	8.77	45.45	9.19
11.15	2.90	29.75	6.36	59.5	11.04	59.5	11.60
13.69	3.46	36.50	7.71	73.0	13.09	73.0	13.73
16.14	4.11	43.04	8.95	86.1	15.00	86.1	15.74
19.65	4.85	52.4	10.58	104.8	17.54	104.8	18.49
25.09	6.21	66.9	13.01	133.9	21.13	133.9	22.19
30.12	7.15	80.3	15.06	160.6	24.12	160.6	25.47
34.73	8.25	92.6	17.85	185.3	26.64	185.3	28.17
43.00	9.91	114.8	19.78	229.5	30.77	229.5	32.69
50.1	11.27	133.7	22.14	267.5	34.11	267.5	36.11
56.4	12.44	150.5	24.06	301.0	36.78	301.0	39.08
59.8	13.06	159.5	25.08	319.0	38.15	319.0	40.43
66.5	14.25	177.3	27.03	354.5	40.69	354.5	43.18
66.8	14.27	178.3	27.11	356.5	40.80	356.5	43.36
74.8	15.64	199.5	29.27	399	43.71	399	46.38
75.2	15.65	200.5	29.40	401	43.87	401	46.54
85.5	17.30	228.0	31.96	456	47.28	456	50.16
99.8	19.46	266.3	35.27	533	51.71	533	54.85
119.9	22.32	319.8	39.50	640	57.17	640	60.65
150.0	26.15	400.0	45.12	800	64.56	800	68.45

1.00, and 2.00 (M) $C_M = 0.010$ (M). $C_{HA} = 0$ for all series. The corresponding data of C_A and E_M may be seen in Tables 2 and 3. The E_0-values were checked by extrapolations of E versus C_A to $C_A = 0$.

No effects from polynuclear species were found when C_M was varied, either with graphical plots or computer calculations. The assumption of four complex species agreed best with the experimental data. In the calculations two different programs [11,12] were used for the measurements with $I' = 3.00$ (M). One program performed the calculations for each series, while the other used all series in one calculation (the method with corresponding solutions). No systematic difference was observed between the two methods when the same range of ligand concentration was used, and the first program was generally applied. The stability constants for the different media are collected in Table 7.

The cadmium(II) acetate system. To avoid hydrolysis of this system, 1:1 buffers were used in the measurements. $C_M = 0.010$ (M) for all series and $I' = 0.25$, 0.50, 1.00, and 2.00 (M). The corresponding data of C_A and

Table 4. The corresponding values of C_A and E_m for the cadmium(II) acetate system at different ionic strengths and $C_M = 0.010$ (M).

$I' = 0.25$ (M) $E_0 = 766.50$ (mV)		$I' = 0.50$ (M) $E_0 = 764.42$ (mV)		$I' = 1.00$ (M) $E_0 = 759.41$ (mV)		$I' = 2.00$ (M) $E_0 = 748.16$ (mV)	
C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)	C_A (mM)	E_m (mV)
0.000	0	0.00	0	0.00	0	0.00	0
0.750	0.29	2.00	0.32	4.00	0.68	4.00	0.75
1.500	0.42	3.98	0.65	7.96	1.31	7.96	1.46
2.956	0.65	7.88	1.31	15.76	2.54	15.76	2.83
4.39	0.91	11.71	1.95	23.41	3.69	23.41	4.19
5.80	1.23	15.45	2.58	30.90	4.80	30.90	5.49
7.17	1.44	19.13	3.20	38.30	5.90	38.30	6.71
8.52	1.71	22.78	3.77	45.45	6.94	45.45	7.87
11.15	2.23	29.75	4.88	59.5	8.89	59.5	10.05
13.69	2.68	36.50	5.93	73.0	10.66	73.0	12.06
16.14	3.16	43.04	6.92	86.1	12.33	86.1	13.92
19.65	3.82	52.4	8.33	104.8	14.57	104.8	16.43
25.09	4.79	66.9	10.40	133.9	17.90	133.9	20.02
30.12	5.71	80.3	12.25	160.6	20.69	160.6	23.07
34.73	6.67	92.6	13.88	185.3	23.15	185.3	25.72
43.00	8.04	114.8	16.65	229.5	27.16	229.5	29.99
50.1	9.28	133.7	18.95	267.5	30.36	267.5	33.34
56.4	10.33	150.5	20.84	301.0	33.03	301.0	36.06
59.8	10.91	159.5	21.79	319.0	34.24	319.0	37.44
66.5	12.01	177.3	23.72	354.5	36.72	354.5	40.02
66.8	12.04	178.3	23.84	356.5	37.01	356.5	40.20
74.8	13.39	199.5	26.01	399	39.74	399	43.09
75.2	13.40	200.5	26.12	401	39.95	401	43.20
85.5	15.13	228.0	28.83	456	43.33	456	46.70
99.8	17.39	266.3	32.36	533	47.79	533	51.13
119.9	20.39	319.8	36.95	640	53.36	640	56.55
150.0	24.62	400.0	43.20	800	60.84	800	63.75

Table 5. The reaction heats, corrected for dilution, for the cadmium(II) acetate system at different central ion concentrations. C_M is the initial cadmium ion concentration in the S solutions. C_A and C_{HA} are the acetate ion and acetic acid concentration, respectively, in the T solutions.

	$\sum Q_{corr.}$ (cal)							
C_M (M)	0.015		0.030		0.060		0.090	
C_A (M)	3.000		3.000		3.000		3.000	
C_{HA} (M)	0.100		0.100		0.100		0.100	
v (ml)								
1.005	−0.867	−0.902	−1.467	−1.459				
2.009	−1.457	−1.485	−2.544	−2.535	−3.949	−3.964	−4.681	−4.658
4.018	−2.100	−2.119	−3.888	−3.876	−6.499	−6.537	−8.188	−8.105
6.027	−2.409	−2.400	−4.673	−4.637	−8.166	−8.185	−10.664	−10.614
8.036	−2.622	−2.604	−5.113	−5.091	−9.225	−9.224	−12.449	−12.452
10.045	−2.812	−2.750	−5.417	−5.384	−9.925	−9.902	−13.729	−13.708
12.054	−2.920	−2.891	−5.615	−5.587	−10.390	−10.357	−14.596	−14.620
14.063			−5.750	−5.724	−10.684	−10.668	−15.214	−15.203
16.072			−5.839	−5.799	−10.889	−10.861	−15.641	−15.619
18.081					−11.054	−11.045	−15.917	−15.907
20.090							−16.102	−16.097

Table 6. The corresponding values of Δh_v, [A], and $\bar{n}$ and the X-functions obtained by graphical integration of the $\bar{n}/[A]$-functions for the cadmium(II) acetate and iodide systems.

Ligand	$-\Delta h_v$ (kcal/mole)	[A] (mM)	$\bar{n}$	[A] (mM)	$X([A])$	$X_1([A])$ (M^{-1})	$X_2([A])$ (M^{-2})	$X_3([A])$ (M^{-3})
Ac$^-$	−0.25	7.9	0.165	10	1.232	23.2	220	
	−0.50	18.2	0.36	20	1.511	25.6	230	
	−0.75	30.5	0.61	30	1.842	28.1	237	
	−1.00	47	0.91	40	2.232	30.8	245	
	−1.10	56	1.01	50	2.690	33.8	256	
	−1.20	67	1.13	75	4.178	42.4	285	
	−1.30	79	1.26	100	6.263	52.6	316	
	−1.40	92	1.44	125	9.066	64.5	348	
	−1.50	111	1.65					
	−1.60	136	1.81					
I$^-$	0.50	2.9	0.204	5	1.742	148	6 600	220 000
	1.00	6.1	0.466	10	2.929	193	7 800	230 000
	1.50	10.2	0.780	15	4.781	252	9 130	242 000
	2.00	13.0	1.168	20	7.575	329	10 700	260 000
	2.50	17.3	1.526	25	11.64	426	12 440	278 000
	3.00	21.8	1.882	30	17.54	551	14 530	301 000
	3.50	27.6	2.212	40	36.75	894	19 480	350 000
	4.00	33.6	2.542	50	70.75	1395	25 600	402 000
	4.50	41.8	2.840	60	126.1	2085	32 800	456 000
	5.00	53.2	3.096	70	211.4	3005	41 150	510 000
	5.50	67.1	3.386	80	336.0	4190	50 910	568 000
	6.00	95.4	3.692					

Table 7. The stability constants obtained in this work compared to those of Vanderzee and Dawson (Ref. 3) for the chloride system, those of Kivalo and Ekari (Ref. 4) for the bromide system, and those of Leden (Ref. 10) for ionic strength 3.00 M. *Ionic strength 0.75 M. **Calorimetric method.

I'	(M) $j=$	β_j (M^{-j})					
		0.25	0.50	1.00	2.00	3.00	3.00 (Ref. 10)
Cd–Cl	1		23.5	22.3	26.5	34.8	38.5 ± 1
(Ref. 3)	2		63	60	89	160	170 ± 10
	3			26	61	195	260 ± 10
	4						
Cd–Br	1		36.5 *	36.5	38	45	57 ± 2
(Ref. 4)	2		126 *	105	180	250	220 ± 20
	3		145 *	180	600	1900	2000 ± 200
	4		340 *	460	1000	3200	5000 ± 500
Cd–I	1	88 ± 1	77 ± 1	75 ± 1	94 ± 2	115 ± 10 **	120 ± 2
	2	440 ± 100	430 ± 100	450 ± 100	400 ± 200	$(5.5 \pm 3) \times 10^3$ **	700 ± 500
	3	$(2.1 \pm 0.2) \times 10^4$	$(1.9 \pm 0.1) \times 10^4$	$(2.2 \pm 0.2) \times 10^4$	$(5.1 \pm 0.3) \times 10^4$	$(15 \pm 5) \times 10^4$ ***	$(10 \pm 1) \times 10^4$
	4	$(3.2 \pm 0.3) \times 10^5$	$(3.1 \pm 0.2) \times 10^5$	$(4.2 \pm 0.2) \times 10^5$	$(11 \pm 1) \times 10^5$	$(50 \pm 20) \times 10^5$ **	$(30 \pm 10) \times 10^5$
Cd–SCN	1	27.0 ± 0.5	22.6 ± 0.5	20.7 ± 0.5	22.0 ± 0.5	25.5 ± 0.5	24.5 ± 1.0
	2	125 ± 8	109 ± 5	97 ± 5	111 ± 5	175 ± 6	96 ± 5
	3	200 ± 100	120 ± 30	107 ± 20	177 ± 17	300 ± 30	380 ± 20
	4		95 ± 50	75 ± 30	107 ± 25	300 ± 40	
Cd–Ac	1	18.5 ± 1.0	15.5 ± 0.5	15.0 ± 0.5	17.2 ± 0.5	21 ± 2 **	20 ± 1
	2	100 ± 20	80 ± 6	66 ± 4	95 ± 6	210 ± 30 **	190 ± 20
	3	500 ± 200	150 ± 20	110 ± 10	135 ± 10		260 ± 50
	4						100 ± 50

E_m are collected in Table 4. The E_0-values were checked by extrapolations of E versus C_A to $C_A = 0$. According to Leden [10] no complex formation was found between the cadmium(II) ion and HAc.

The calculations have been performed both assuming three and four complex species. Using ligand concentrations up to 0.2 (M) for $I' = 0.25$ and 0.50 (M) and 0.4 (M) for $I' = 1$ and 2 (M) the agreement between the two sets of stability constants as well as between the calculated and experimental values is excellent. In higher ligand concentration ranges the experimental data are better described with four stability constants. However, the systematic errors of this system, e.g. changes in diffusion potentials, changes in activity coefficient factors, and competing complex reactions of the acetate ion, are greater than for the first two, and therefore only three stability constants are given for each ionic strength. The final values of the stability constants calculated are shown in Table 7.

2. Calorimetric measurements of cadmium(II) acetate and iodide systems

From calorimetric data measured at $I = 3.00$ (M), collected in Table 5 or published earlier,[7] it is possible to calculate stability constants of at least approximative magnitude of the acetate and iodide systems using the method described (see above). The corresponding values of Δh_v, [A], and $\bar{n}$ are collected in Table 6 together with calculated values of the X-functions. For the acetate system the agreement is good between the values of the first and second stability constants obtained with this method and with the potentiometric one,[10] but for the iodide system the differences are much greater.[10] This is due to the abnormally low stability of the second complex species. The values determined are shown in Table 7.

·For the acetate system the plottings of C_A versus C_M for constant Δh_v are not linear which indicates a change in $\bar{n}$. This is possibly due to formation of polynuclear species, but may also be caused by changes in the activity coefficient factors or competing complex reactions of the acetate ion. Errors in the dilution heats may also interfere. However, in the potentiometric measurements reported by Leden [10] a similar deviation was found for this system, and the anomaly could be explained by the formation of polynuclear species. For the iodide system no such deviation from linearity is observed either by Leden [10] or in this investigation.

DISCUSSION

The variation in stoichiometric stability constants with ionic strength is similar for the three cadmium systems investigated here and for the cadmium chloride system investigated by Vanderzee and Dawson [3] (see Table 7). All these systems have a minimum of the β_j-values between the ionic strengths 0.5—1 M. This result is in accordance with qualitative predictions made from discussions of the expected variation in activity coefficient factors. The stoi-

chiometric constants, β_j, can be related to the thermodynamic constants, $\beta_j{}^0$, by activity coefficients, f_X, according to

$$\beta_j = \beta_j{}^0 \ \frac{f_M (f_A)^j}{f_{MAj}} \tag{12}$$

where $\beta_j{}^0$ by definition remains constant, when the ionic strength varies. The activity coefficients, however, normally go through a minimum, and from eqn. (12) the β_j-values here would be expected to do the same, which was experimentally found. The position of the minimum must depend on the individual f_X-values, but no significant change is noticed for the different ligands used (see Table 7).

The calorimetric method of determining the stability constants from corresponding solutions can be used with satisfactory results for systems with suitable values of ΔH_j and β_j. The method may be valuable as a complement to other methods, *e.g.* potentiometric or solubility measurements.

Note added in proof. Through personal communication with Professor C. E. Vanderzee I was informed about unpublished data for the cadmium(II) iodide system obtained by C. E. Vanderzee and R. A. Myers in measurements at different ionic strengths and temperatures. The values at 25°C are:

Ionic strength	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})
0.2	90	770	1.65×10^4	3.6×10^5
0.5	74	600	1.42×10^4	3.3×10^5
1.0	75	550	1.50×10^4	4.7×10^5
2.0	88	1200	3.45×10^4	12.0×10^5
3.0	131	3200	$12.0 \ \times 10^4$	48.5×10^5

Except for the β_2-values, the agreement between these values and those reported in this paper is very satisfactory and mostly within the given errors.

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