

## The Complex Formation in the Cadmium Ethoxyacetate and the Cadmium (Ethylthio)acetate Systems

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The complex formation in the cadmium ethoxyacetate and the cadmium (ethylthio)acetate systems in aqueous solution has been studied by measuring the free central ion concentration at 25.0°C in a perchlorate medium at an ionic strength of 1.0 M. The stability constants of the mononuclear complexes have been evaluated both graphically and by a computer method.

The complex formation between the copper(II) ion and the ethoxy- and (ethylthio)acetate ions, respectively, has been investigated earlier and reported<sup>1</sup> by the present author. It was found that the copper(II) ion showed (*b*)-character in the classification of acceptors in (*a*)- and (*b*)-type according to Ahrlund *et al.*<sup>2</sup>

This investigation has now been extended to the cadmium complexes of the ligands mentioned, mainly to find out if chelate formation occurs which should enable a classification of cadmium with respect to the coordination of oxygen and sulphur.

A preliminary experiment indicated that the complexity was weak. In such a case it is favourable to measure directly the concentration of free central ion in the complex solutions. With cadmium this can be done with high accuracy by means of a cadmium amalgam electrode. Thus the main investigation was performed by this method.

### SUMMARY OF THE PRINCIPLES FOR CALCULATION OF THE STABILITY CONSTANTS

Only a short summary is given here. The graphical method of Fronæus is more fully treated in Refs. 1 and 3.

The cumulative stability constant  $\beta_n$  for the mononuclear complex  $MA_n$  is defined by

$$\beta_n = \frac{[MA_n]}{[M][A]^n} \quad (1 \leq n \leq N)$$

where M and A denote the central ion and the ligand, respectively.

Introducing  $X = 1 + \sum_{n=1}^N \beta_n [A]^n$  and  $X' = dX/d[A]$  and assuming only mononuclear complexes to be formed, we obtain for the total concentrations of central ion ( $C_M$ ) and ligand ( $C_A$ )

$$C_M = [M] \times X \quad (1)$$

$$C_A = [A] + [M] \times [A] \times X' \quad (2)$$

Defining the ligand number  $\bar{n}$  by

$$\bar{n} = (C_A - [A])/C_M \quad (3)$$

we get

$$\bar{n} = [A] \times X' / X \quad (4)$$

In the measurements an emf  $E_M$  is determined, defined by

$$E_M = \frac{RT}{\nu F} \ln \frac{C_M}{[M]} \quad (5)$$

Keeping  $C_M$  constant and varying  $C_A$  within an experiment gives us  $C_A$  as a function of  $E_M$ . Repeating this operation with other  $C_M$ -values results in a set of curves on plotting  $C_A$  against  $E_M$ .

From these curves we obtain a set of corresponding values ( $C_M$ ,  $C_A$ ) for every chosen value of  $E_M$ . As  $E_M$  is constant within a set, it follows from eqns. (5), (1), and (4) that  $X$ ,  $[A]$ , and  $\bar{n}$  are also constant. For every  $E_M$ , eqn. (3) is the equation of a straight line from which  $[A]$  can be determined by extrapolation to  $C_M=0$ . Thus corresponding values of  $[A]$  and  $X$  have been obtained.

The determination of the stability constants is carried out by successive extrapolations to  $[A]=0$  of the functions

$$X_j = (X_{j-1} - \beta_{j-1})/[A]; \quad (1 \leq j \leq N; X_0 = X; \beta_0 = 1)$$

The results of the graphical determination of the stability constants have been checked by numerical calculation according to the following principles.

$X$  is a polynomial in  $[A]$ . If  $X_x$  is defined by  $E_x = E_0 + E_M = (RT/\nu F) \ln X_x$ , then  $X_x = \exp(\nu F E_0 / RT) \times X = \kappa X$ . Here  $E_x$  is the emf of the cell (11) when  $C_A \neq 0$  and  $E_0$  is the emf when  $C_A = 0$ . If the complexes are weak, some polynomial

$$\kappa \left( 1 + \sum_{n=1}^Z c_n (C_A)^n \right)$$

should represent a good approximation of  $X_x$  even at a comparatively small degree  $Z$ .

Estimates of the polynomial coefficients are obtained by minimizing the sum of squares

$$S = \sum_{i=1}^P w_i [(X_x)_i - \alpha(1 + \sum_{n=1}^Z c_n (C_A)_i^n)]^2$$

where  $w_i$  are weights and  $P$  is the number of corresponding values ( $C_A$ ,  $X_x$ ) at a constant value of  $C_M$ . From the definition of  $X_x$ , it follows that

$$dX_x = \text{constant} \times dE_x \times X_x$$

From the measurements it has been established that the scatter  $dE_x$  in the measured emf  $E_x$  is practically constant. If the standard deviation of  $X_x$  is considered to be proportional to  $dX_x$ , we get estimates of the variances according to

$$\sigma^2(X_x)_i \simeq \text{constant} \times (X_x)_i^2$$

and hence

$$w_i = \text{constant} \times (X_x)_i^{-2}$$

The different approximation polynomials are solved for suitable  $X$ -values. The set of pairs ( $C_M$ ,  $C_A$ ) for each  $X$  should be connected by a linear relationship (3). The best regression line is calculated according to the least squares criterion. The weights are put equal to unity. For every value of  $X$  this calculation gives estimates of  $[A]$ , the slope  $k$  (which should be equal to  $\bar{n}$ ) of the regression line, and the variance of  $[A]$ .

The final calculation of estimates of  $\beta_n$  are performed by application of the least-squares principle to the polynomial  $X-1 = \sum_{n=1}^N \beta_n [A]^n$ . Here the

values of  $X-1$  are free from error but the  $[A]$ -values are not. Nevertheless it should be possible to obtain the regression curve if the weights are appropriately chosen. According to Guest<sup>4</sup> they should in this case be

$$w_i = (X')_i^{-2} \times \text{var}([A])_i^{-1}$$

Of course we use the calculated estimate of the variance of  $[A]$  instead of  $\text{var}([A])$ . Since the values of  $(X')_i$  are not known, the calculation of the  $\beta_n$ -values is performed iteratively. The initial value of  $X'$  is obtained from eqn. (4) with  $\bar{n}$  approximated by  $k$ . The estimates of  $\beta_n$  are used in computing better approximations of  $X'$ . Better estimates of the weights are thus obtained. The procedure is repeated until the difference between consecutive sets of  $\beta_n$  is negligible.

If both mononuclear and dinuclear complexes ( $M_2A$ ,  $M_2A_2$ , ...  $M_2A_L$ ) are formed, the total concentrations of  $M$  and  $A$  will be

$$C_M = [M] \times X + 2[M]^2 \times Y \quad (6)$$

$$C_A = [A] + [M] \times X' \times [A] + [M]^2 \times Y' \times [A] \quad (7)$$

where  $Y = \sum_{n=1}^L \beta_{n,2} [A]^n$ ,  $Y' = dY/d[A]$ , and  $\beta_{n,2} = \frac{[M_2A_n]}{[M]^2[A]^n}$ .

Plotting  $C_A$  against  $C_M$  at constant  $E_M$  will not give a straight line in this case since

$$E_M = \frac{RT}{\nu F} \ln(X + 2[M]Y)$$

and  $[A]$  will not be constant at constant  $E_M$ . However, extrapolation of the curve to  $C_M=[M]=0$  will give corresponding values of  $[A]$  and  $X$ .

If  $E_M$ =constant, then  $X + 2[M]Y$ =constant. From this expression and eqns. (6) and (7), the slope  $k_0$  of the curve for  $C_M=[M]=0$  is found to be

$$k_0 = \left( \frac{\partial C_A}{\partial C_M} \right)_0 = \bar{n}_1 - \frac{2Y}{XX'} \quad (8)$$

When the stability constants of the mononuclear complexes have been determined, it is possible utilizing eqn. (8) to consider the formation of dinuclear complexes and even determine  $\beta_{n_2}$ -values from the  $Y$ -function. In practice, however, it is difficult to obtain reliable values of  $k_0$  in the extrapolations.

*The graphical representation of the complex systems.* The ligand number  $\bar{n}_1$  for the mononuclear complexes can be calculated according to

$$\bar{n}_1 = \frac{\sum_{n=1}^N n \beta_n [A]^n}{1 + \sum_{n=1}^N \beta_n [A]^n} \quad (9)$$

or by means of the approximate equation

$$\bar{n}_1 \simeq \frac{\Delta E_M}{(RT/\nu F)\Delta \ln[A]} \quad (10)$$

A single  $\bar{n}_1$ -value calculated by eqn. (10) is ascribed to the geometric mean of the two  $[A]$ -values in question.

## EXPERIMENTAL

### Chemicals

*Cadmium perchlorate* was prepared from cadmium carbonate (Matheson Coleman & Bell, Reagent) which was dissolved in ca. 10 % excess perchloric acid (*p.a.*). No foreign ions could be detected in the solution. The stock solution was analysed by titration with EDTA<sup>6</sup> and was found to be 0.336 M.

*Cadmium amalgam*, abt. 8 % by weight, was prepared by heating mercury (*p.a.*) with a calculated amount of cadmium metal (*p.a.*). To prevent cadmium oxide from entering the titration vessel, the amalgam was stored in a special funnel.

*Sodium perchlorate* was prepared as earlier described.<sup>1</sup> A small amount of base (equivalent to  $3.8 \times 10^{-5}$  mole  $H_3O^+$  per mole salt) was found by potentiometric titration with glass electrode.

*Ethoxyacetic acid* and *(ethylthio)acetic acid* were prepared and analysed as described in an earlier paper.<sup>1</sup> The other chemicals used were of *pro analysi* grade.

## Method

To prevent protolysis of the hydrated cadmium ions, the measurements were performed in buffers of the ligand A and its corresponding acid HA (stoichiometric concentrations  $C_A'$  and  $\delta C_A'$ , resp.). The emf  $E_x$  of the cell with the following composition was measured at  $25.00 \pm 0.02^\circ\text{C}$ .



The right hand half cell RE was the same as in (21) in Ref. 1.

For smaller values of  $C_A'$  the solutions in the left hand half-cell were obtained by adding increasing volumes of solution  $S_2$  to a known volume of solution  $S_1$ .

	$S_1$	$S_2$	
$\text{Cd(ClO}_4)_2$	$C_M$	$C_M^0$	M
NaA	0	$C_A^0$	M
HA	0	$\delta C_A^0$	M
$\text{NaClO}_4$	$1.000 - 3C_M^0$	$1.000 - 3C_M^0 - C_A^0$	M

To obtain the highest values of  $C_A'$ , portions of solutions  $S_1$  were added to a known volume of solution  $S_2$ .

$C_A$  was calculated from  $C_A'$  by means of the measured acid constant of HA, with corrections due to the composition of the stock solutions of cadmium perchlorate and sodium perchlorate. The influence of the complex formation upon  $C_A$  was negligible.

The experimental set-up consisted of a titration vessel to which the amalgam storage vessel and other equipment were attached by means of air-tight connexions. A stream of oxygen-free nitrogen, pre-saturated through 1.00 M sodium perchlorate solution, was passed through an aliquot of the initial solution, contained in the titration vessel, for 20–60 min prior to addition of the amalgam. The gas outlet consisted of a cotton-wool plug about 1 cm in length. The nitrogen stream was maintained during the whole titration and ensured adequate mixing of the solution and prevention of oxidation of the amalgam. Every titration series was repeated at least once.

After most titration series the total concentration of cadmium in the solution was determined by complexometric titration.<sup>5</sup> None of the analyses revealed any significant increase in the initial cadmium ion concentration thus indicating that oxidation of the cadmium within the amalgam had been prevented.

The measurements were performed by the aid of a Norma potentiometer with a Kipp en Zonen Galvanometer as a zero instrument specifying a precision of  $\pm 0.01$  mV. In some of the measurements on the ethoxyacetate system a Wulff's potentiometer was used in connexion with a Cambridge Light Spot Galvanometer specifying a precision at  $\pm 0.05$  mV.

In some experiments glass electrodes (Beckman 40 495) were used. The emf was then read by a Radiometer PHM 4 potentiometer. The slope of the glass electrodes was shown to be the theoretical (59.2 mV/pH) in the range  $2.4 \leq \text{pH} \leq 4.5$ . The constancy of their asymmetry potentials was checked immediately before and after each titration against a buffer solution of known oxonium ion concentration.

## MEASUREMENTS

*The cadmium perchlorate.* The concentration of free acid in the stock solution of cadmium perchlorate had to be determined analytically. This could of course not be done by a simple acidimetric titration owing to the protolytic

properties of the hydrated cadmium ion. It should be possible, however, to perform the titration in presence of a large excess of iodide ion (which forms fairly stable complexes<sup>6</sup> with the cadmium ion), so that the saturated iodide complex is formed. The determination was performed as a series of potentiometric titrations by the aid of a glass electrode. The titrant was carbonate-free NaOH-solution. In the titrate the total concentration of cadmium ion was 0.2 M and of iodide ion from 2 M to 3 M. Oxygen-free N<sub>2</sub> was led through the titrate during the titration. At the beginning of a titration the pH-value of the titrate solution was about 2. Precipitation occurred at pH  $\approx$  9. The equivalent points were determined according to Gran.<sup>7</sup>

An aqueous solution of the sodium iodide was slightly alkaline. The deficit of free acid was determined by a similar potentiometric titration with HCl.

From the results the quotient  $\alpha$  of the concentration of free acid to the concentration of cadmium in the stock solution was calculated to be

$$\alpha = 0.0989 \pm 0.0005$$

*The cadmium ethoxyacetate system.* In order to determine if complex formation occurred between the free acid and the central ion, the emf of the following cell was measured.

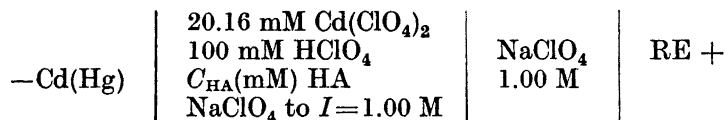


Table 1. Some representative values of C<sub>A</sub> and E<sub>M</sub> for the cadmium ethoxyacetate system.

C <sub>M</sub> =30.24 mM		C <sub>M</sub> =20.16 mM		C <sub>M</sub> =10.08 mM		C <sub>M</sub> =2.016 mM	
C <sub>A</sub> (mM)	E <sub>M</sub> (mV)	C <sub>A</sub> (mM)	E <sub>M</sub> (mV)	C <sub>A</sub> (mM)	E <sub>M</sub> (mV)	C <sub>A</sub> (mM)	E <sub>M</sub> (mV)
14.82	1.54	15.80	1.91	16.77	2.20	16.03	2.25
42.7	4.65	29.95	3.59	44.7	5.71	42.6	5.85
74.0	7.98	43.7	5.21	75.9	9.34	73.8	9.75
107.6	11.44	74.9	8.73	109.6	13.01	107.2	13.45
142.9	14.83	108.6	12.29	144.9	16.54	142.8	17.0
180.9	18.33	143.9	15.77	182.9	20.09	179.4	20.45
222.1	21.85	181.9	19.27	224.1	23.64	221.1	24.1
260.3	24.93	223.1	22.82	262.3	26.72	264.8	27.6
302.4	28.16	261.3	25.90	304.4	29.90	305.6	30.6
339	30.85	303.4	29.13	341	32.57	333	32.65
376	33.44	340	31.79	378	35.07	375	35.5
431	37.08	384	34.81	433	38.7	423	38.65
484	40.4	441	38.54	486	42.0	480	42.2
543	43.9	504	42.40	545	45.4	537	45.55
597	47.0	568	46.1	599	48.5	600	49.05
664	50.7	641	50.2	666	52.1	667	52.5
732	54.2	709	53.7	734	55.5	720	55.2
797	57.5	783	57.45	799	58.7	783	58.3

Table 2. Some values from the graphical determination of [A] in the cadmium ethoxyacetate system.

$E_M$ (mV)	$C_A$ (mM) for $C_M =$				
	30.24 mM	20.16 mM	10.08 mM	2.016 mM	0
3	27.79	24.90	23.00	21.21	20.70
6	55.1	50.6	47.1	43.7	43.2
9	83.7	77.3	72.9	67.7	67.0
12	113.4	106.0	99.9	94.6	93.4
15	114.6	136.0	129.2	122.8	121.5
18	177.1	167.7	160.3	153.2	151.6
21	212.1	201.4	193.1	185.7	183.6
24	248.6	237.5	228.5	220.0	218.2
27	287.1	275.5	266.0	257.4	255
30	327.5	315.0	306.0	297.5	295.5
33	370	358	348	338	337
36	414	402	392	382	380
39	461	448	437	428	426
42	510	497	486	476	474
45	560	548	538	528	526
48	614	602	590	581	578
51	669	656	645	637	634
54	728	714	703	694	692
57	787	774	763	754	751

The emf of this cell was very stable. When  $C_{HA}$  was increased from 0 to 318 mM, the emf decreased 1.28 mV. Obviously no complex formation occurred since this should have caused an increase of the emf.

The acid constant of ethoxyacetic acid at 25.00°C and ionic strength 1.00 M ( $\text{NaClO}_4$ ) was determined by means of a glass electrode in buffer solutions. With the concentration of the base ranging from 3 mM to 40 mM the acid constant was determined to be  $(3.08 \pm 0.01) \times 10^{-4}$  M.

In the main investigation the emf. rapidly reached stable values. The reproducibility of  $E_M$  was in general better than 0.05 mV except for the highest  $C_A$ -values where a tolerance of about 0.1 mV was found. In the ethoxyacetate buffer used in this investigation  $\delta$  had the value 0.198. The experimental results are collected in Tables 1 and 2.

The stability constants were determined both graphically and numerically with very good agreement (the stated errors are 99.9 % confidence limits obtained by the numerical method).

$$\begin{aligned}\beta_1 &= 11.7 \pm 0.1 \text{ M}^{-1} \\ \beta_2 &= 49 \pm 1 \text{ M}^{-2} \\ \beta_3 &= 35 \pm 4 \text{ M}^{-3} \\ \beta_4 &= 98 \pm 5 \text{ M}^{-4}\end{aligned}$$

*The cadmium (ethylthio)acetate system.* The measurements and the determination of the stability constants were performed in the same way as in the ethoxyacetate system.

No evidence of complex formation could be found between cadmium and the free acid. When  $C_{\text{HA}}$  was increased from 0 to 292 mM the emf decreased 1.39 mV.

The acid constant of (ethylthio)acetic acid at 25.00°C and  $I=1.00$  M ( $\text{NaClO}_4$ ) was determined to  $(2.26 \pm 0.01) \times 10^{-4}$  M.

The reproducibility of  $E_{\text{M}}$  was in general better than 0.05 mV. In the buffer solution  $\delta$  was 0.192.

The experimental results are collected in Tables 3 and 4.

The following stability constants were obtained.

$$\begin{aligned}\beta_1 &= 18.7 \pm 0.2 \text{ M}^{-1} \\ \beta_2 &= 133 \pm 4 \text{ M}^{-2} \\ \beta_3 &= 320 \pm 20 \text{ M}^{-3} \\ \beta_4 &= 520 \pm 40 \text{ M}^{-4}\end{aligned}$$

### DISCUSSION

The complex formation curves for the two systems are reproduced in Fig. 1. The ligand number  $\bar{n}_1$  reaches a value of about 3. The same value is reached, independent of  $C_{\text{M}}$ , if the experimental values of  $C_{\text{A}}$  are used instead of  $[\text{A}]$  in eqn. (10). The steep form of the curves indicates a formation

Table 3. Some representative values of  $C_{\text{A}}$  and  $E_{\text{M}}$  for the cadmium (ethylthio)acetate system.

$C_{\text{M}}=20.40$ mM		$C_{\text{M}}=15.00$ mM		$C_{\text{M}}=10.08$ mM	
$C_{\text{A}}$ (mM)	$E_{\text{M}}$ (mV)	$C_{\text{A}}$ (mM)	$E_{\text{M}}$ (mV)	$C_{\text{A}}$ (mM)	$E_{\text{M}}$ (mV)
8.78	1.47	9.30	1.69	9.77	1.97
29.34	5.10	29.87	5.56	30.4	6.00
49.0	8.50	49.5	9.10	50.0	9.64
67.8	11.65	68.3	12.27	68.8	12.97
85.8	14.51	86.3	15.25	86.8	15.97
105.8	17.61	106.3	18.43	106.8	19.17
127.5	20.82	128.0	21.68	128.5	22.45
148.0	23.72	148.6	24.57	149.1	25.31
172.2	26.96	172.8	27.83	173.3	28.55
194.9	29.84	195.5	30.69	196.0	31.43
218.2	32.70	218.8	33.54	219.3	34.25
242.0	35.42	242.6	36.26	243.1	36.94
269.5	38.44	270.1	39.24	270.6	39.96
301	41.76	302	42.50	302	43.20
338	45.44	339	46.11	339	46.79
376	48.89	377	49.55	377	50.20
413	52.16	414	52.8	414	53.37
453	55.52	454	56.1	454	56.68
495	58.78	495	59.3	496	59.88
535	61.81	536	62.3	536	62.85
598	66.30	599	66.7	599	67.26



Table 4. Some values from the graphical determination of [A] in the cadmium (ethylthio)acetate system.

$E_M$ (mV)	$C_A$ (mM) for $C_M =$			
	20.40 mM	15.00 mM	10.08 mM	0
3	17.42	16.25	14.95	12.8
6	34.6	32.3	30.4	26.3
9	52.0	49.0	46.5	41.1
12	70.0	66.7	63.3	56.8
15	88.9	84.8	81.0	73.2
18	108.4	103.6	99.4	90.6
21	128.8	123.4	118.7	109.0
24	150.0	144.6	139.6	129.5
27	172.6	166.5	161.5	150.8
30	196.2	189.9	184.5	173.2
33	220.9	214.3	208.8	197.1
36	247.2	240.3	234.2	222.2
39	274.8	268.0	261.9	249.5
42	303.6	296.8	290.5	278.5
45	334	327	320	308
48	366	359	352	339
51	400	393	386	374
54	435	428	422	409
57	472	466	459	445
60	511	505	498	485
63	551	546	538	526
66	594	588	581	569

of a fourth mononuclear complex in both systems. The determination of the concentration of the free ligand could be done by linear extrapolation, well within the experimental reproducibility. For higher values of [A], however, the slopes  $k$  of the extrapolation lines differed from the  $\bar{n}_1$ -values calculated

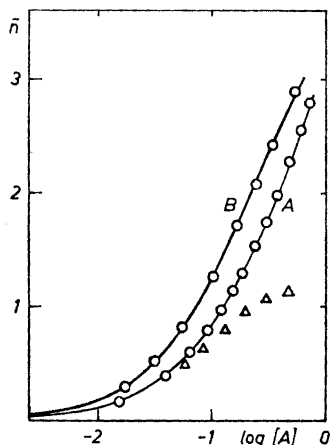


Fig. 1. The mononuclear complex formation curves for the cadmium ethoxyacetate (A) and the cadmium (ethylthio)acetate (B) systems. The fulldrawn curves represent  $\bar{n}_1$  computed by means of eqn. (9) and the sign (O) refers to  $\bar{n}_1$  obtained from eqn. (10). The sign ( $\Delta$ ) refers to  $k$ -values for the former system.

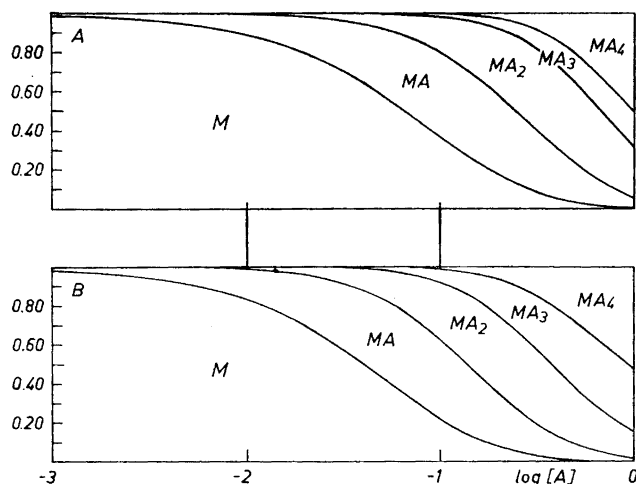


Fig. 2. The distribution of the central ion (see eqns. (11) and (12) in Ref. 1) between the mononuclear complexes with varying  $[A]$  in the cadmium ethoxyacetate (A) and the cadmium (ethylthio)acetate (B) systems.

from eqns. (9) and (10). Probably this effect is mainly due to changes in the activity coefficients upon complex formation and by changing  $\text{NaClO}_4$  against ligand buffer during the titrations.

To check if the discrepancy between  $\bar{n}_1$  and  $k$  could be caused by the formation of dinuclear complexes, the  $Y$ -function was calculated according to eqn. (8) in the region  $50 \text{ mM} < [A] < 400 \text{ mM}$ . The  $Y$ -functions could be well reproduced by the polynomial  $4.7 \times 10^3 [A]^3 + 1.1 \times 10^5 [A]^6$  for the ethoxyacetate system, and by  $4.7 \times 10^4 [A]^3 + 3.4 \times 10^6 [A]^6$  for the (ethylthio)acetate system. With these coefficients considered as estimates of  $\beta_{32}$  and  $\beta_{62}$ , values of  $[A]$  and  $[M]$  were calculated from eqns. (6) and (7). The concentrations of the complexes could then be calculated. It was found that in the region under consideration, the concentrations of the hypothetical complexes  $M_2A_3$  and  $M_2A_6$  did not exceed 3 % of  $C_M$  in the ethoxyacetate system, and 5 % in

Table 5. The stepwise stability constants  $K_n$  ( $M^{-1}$ ) calculated from the determined constants  $\beta_n$ .

Systems	$K_1$	$K_2$	$K_3$	$K_4$
$\text{Cd}^{2+}/\text{Et}\cdot\text{O}\cdot\text{CH}_2\cdot\text{COO}^-$	11.7	4.2	0.7	2.8
$\text{Cd}^{2+}/\text{Et}\cdot\text{S}\cdot\text{CH}_2\cdot\text{COO}^-$	18.7	7.1	2.4	1.6
$\text{Cd}^{2+}/\text{CH}_3\cdot\text{COO}^-$ (at $I=3.0$ according to Leden <sup>8</sup> )	20	9.5	1.4	0.4

the (ethylthio)acetate system. Thus it must be concluded that it is not possible to decide with certainty from these measurements whether polynuclear complexes are formed or not. It can be mentioned, however, that Leden<sup>8,9</sup> has found indications of formation of polynuclear complexes in the cadmium acetate system.

The stepwise stability constants  $K_n = [MA_n]/[MA_{n-1}][A]$  are calculated from the  $\beta_n$ -values and collected in Table 5. For comparative purposes the constants of the cadmium acetate system according to Leden,<sup>9</sup> have been included. A comparison between these constants indicates that the complex formation should occur mainly in the same way in these three systems. There is no clear evidence of chelate formation. The ratio between the  $K_1$ -values are quite in accordance with the ratio between the  $K_a$ -values of the acids in question.

Earlier findings on similar ligands<sup>10,11</sup> indicate that the cadmium ion has a somewhat greater affinity for neutral oxygen than for neutral sulphur. From the investigation reported here it is not possible to draw a similar conclusion since no chelates are formed.

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