

Metal Complexes with Mixed Ligands. 21. A Potentiometric Study of Cadmium(II) Imidazoles and Cadmium(II)–OH[−] Imidazoles in 3.0 M (Na) ClO₄

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Equilibria between cadmium(II), imidazole (C₃H₄N₂,L) and OH[−] have been studied in 3.0 M (Na)ClO₄ medium at 25 °C by means of potentiometric titrations. In the measurements, glass- as well as Cd(Hg)-electrodes were employed. The total concentrations of cadmium, *B*, and imidazole, *C*, varied through the ranges 0.001–0.090 M and 0.005–0.300 M, respectively, and 0.5 ≤ *C/B* ≤ 16. At the highest *C/B* ratios, data can be explained solely with stepwise metal complexes CdL_{*n*}²⁺, *n* = 1, 2, 3 and 4, with log β₁ = 3.093 ± 0.006, log β₂ = 5.50 ± 0.01, log β₃ = 7.29 ± 0.02 and log β₄ = 8.51 ± 0.03. These data can also be well explained with the two parameter approximation.

At lower *C/B* ratios a ternary hydroxo-imidazole complex, Cd(OH)L⁺ with log *K* (Cd²⁺ + L + H₂O ⇌ Cd(OH)L⁺ + H⁺) = −6.59 ± 0.08 is formed. Data have been analyzed with the least-squares computer program LETAGROPVRID.

In a current project at this department, aqueous three-component systems are systematically investigated using equilibrium as well as structural methods. Equilibrium analysis in the systems H⁺–M–imidazolium (C₃H₅N₂⁺,HL⁺) with M = Ni²⁺,¹ Cu²⁺,² Zn²⁺,¹ Ag⁺,³ and Hg²⁺² have been completed. The results have shown that besides pure binary ML_{*n*} complexes, mononuclear as well as polynuclear M–L–OH[−] species are formed.

The aim of the present paper is to give and discuss the results obtained in the corresponding cadmium(II) system. Although this system has been the subject of several investigations (*cf.* Table 1), no mixed Cd²⁺–L–OH[−] complexes have been reported. Usually the measurements have been

performed with excess imidazole, where the stepwise formation of a series of CdL_{*n*}²⁺ (*n* = 1...6) complexes is predominant. In the present investigation special efforts are made to study possible hydrolysis of the different Cd²⁺–L species. By using glass and cadmium amalgam electrodes equilibrium concentrations of H⁺ and Cd²⁺ can be measured. This will enable us to compare equilibrium constants related to the different electrodes. In this way possible systematic or occasional errors can be detected and the reliability of the results is increased.

EXPERIMENTAL

Chemicals and analysis. Stock solutions of sodium perchlorate were prepared and analyzed as earlier described by Sjöberg.¹⁴ Furthermore, the sodium perchlorate solutions were analyzed for protolytic impurities (HX) as described in Ref. 3.

The dilute perchloric acid and the sodium hydroxide solutions as well as stock solutions of imidazolium (C₃H₅N₂⁺) were prepared and standardized as described earlier.³ Stock solutions of Cd(ClO₄)₂ were prepared by dissolving CdO in a small excess of dilute HClO₄. CdO was made by heating recrystallized Cd(NO₃)₂·4H₂O (Merck p.a.) gradually to 400 °C. Finally the CdO thus formed was ignited overnight at 800 °C. The method is described in detail by Biedermann.¹⁵ The Cd(II) content in the stock solution was determined by direct titration with EDTA, using xylenol-orange as indicator, and gravimetrically by precipitating Cd(NH₄)PO₄·H₂O.¹⁶ The agreement between these two methods and the amount CdO weighed was within 0.4%. The excess of H⁺ was determined

Table 1. Earlier studies of the cadmium(II)-imidazole system, carried out at 25 °C.

Ref.	Medium	Method	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log \beta_5$	$\log \beta_6$
4	?	pol	2.79	4.45	5.96	7.03		
5	0.15	pot (gl)	2.80	4.90	6.45	7.58		
6	0.1 M KNO ₃	pol	3.03	5.14	6.48	7.27		
7	0.1 M KNO ₃	pot (Cd(Hg))	2.71	4.71	6.06			
8	0.15 M KNO ₃	pol		5.07	6.46	7.48		
9	0.5 M KNO ₃	pot (Ag)	2.67	4.87	6.01	7.14		
10	0.5 M NH ₄ NO ₃	pot (Ag)	2.64	4.73	5.88	7.13		
10	0.5 M NH ₄ NO ₃	pol	3.01	5.04	6.34	7.20		
11	0.25 M NaClO ₄	pot (gl)	2.699	4.735				
11	0.5 M NaClO ₄	pot (gl)	2.718	4.740				
12	0.5 M NaClO ₄	pot (gl)	2.76	4.87	6.32	7.49		
11	1 M NaClO ₄	pot (gl)	2.768	4.757		8.415		
13	1 M NaClO ₄	pol	2.70	5.08	6.65	7.60	8.18	8.95
11	2 M NaClO ₄	pot (gl)	2.892	5.047	6.996			
11	4 M NaClO ₄	pot (gl)	3.090					
Present work	3 M (Na)ClO ₄	pot (gl,Cd(Hg))	3.093	5.50	7.29	8.51		

potentiometrically, and the ClO₄⁻ content was obtained from the sum $[H^+] + 2[Cd^{2+}]$.

Cadmium amalgam was prepared by dissolving cadmium metal (Merck *p.a.*) in mercury. The cadmium metal was carefully washed with dilute hydrochloric acid, to remove CdO from the surface, and finally the metal was repeatedly rinsed with distilled water. Mercury (GAB, twice distilled) was washed with perchloric acid before use. The concentration of cadmium in the amalgam was varied between 2 and 0.1%. The amalgam was stored under ~300 mM HClO₄.

Apparatus. The cell arrangement and experimental details of the emf measurements are fully described in Ref. 3. During the experiments a stream of argon was bubbled through the solution for stirring and for maintaining an inert atmosphere. The argon was first led through a solution of vanadium(V(III)/V(IV)), in order to remove oxygen.

Electrodes. Glass electrodes (Ingold type 201-NS) were tested against the hydrogen electrode. With $\log h \gtrsim -8.5$ they were found to give constant and reproducible potentials within ± 0.2 mV. In order to check the reliability of the glass electrode, two electrodes were always used, and the difference in the measured emf values was not allowed to exceed 0.2 mV. The *amalgam electrode* consisted of a pool in the bottom of the titration vessel with a mercury-coated platinum electrode¹⁷ in very good contact with the amalgam. Before the amalgam was added, a stream of argon was led through the titration vessel to remove oxygen. The amalgam electrode gave constant potential within a few minutes and the potential remained constant within 0.05 mV for several hours.

As it was impossible to immerse more than one Cd(Hg) electrode in each titration several of the titrations were repeated to check the reliability of the measurements. The electrode gave reproducible potentials within 0.05 mV. A *cadmium ion selective electrode* (Orion, model 94-48A) was also used in some titrations. The electrode was somewhat slow and each point normally took about half an hour for stabilizing. The potential then remained constant within 0.1 mV for several hours. To control the reliability and the reproducibility, the electrode was tested against a cadmium amalgam electrode within the concentration range $0.02 \leq [Cd^{2+}] \leq 0.0001$ M.

The potential was reproducible within 0.4 mV, but did not follow the amalgam electrode. It was found necessary to change the slope from theoretical 29.58 mV to 30.24 ± 0.15 mV (*cf.* eqn. 2b below). This slope was valid in solutions with $-\log [H^+] \gtrsim 3$ and the electrode was calibrated in slightly acid solutions ($[H^+] \leq 0.001$ M).

Solid phases. All the titrations were ended by precipitations. For lower quotients the solid phases were amorphous and not examined further. For higher quotients with $\bar{n} \geq 2.5$ a crystalline phase was obtained. This compound was found to be CdL₆(ClO₄)₂ and powder X-ray investigations showed this phase to be isostructural with NiL₆(ClO₄)₂, determined by Ivarsson and Forsling.²⁰

The cell symmetry is monoclinic with space group $P2_1/n$ and the cell-parameters $a = 16.505(1)$, $b = 7.243(1)$, $c = 11.840(1)$ Å, $\beta = 90.00^\circ$. The cell contains two formula units. $V = 1415.566$ Å³ and $D_x = 1.69$, $D_m = 1.69$ Mg m⁻³.

METHOD

The present investigation has been carried out through a series of titrations in which $[H^+] = h$ and/or $[Cd^{2+}] = b$ were measured using a glass electrode and a cadmium-amalgam electrode, respectively.

The total concentrations of Cd^{2+} , B , and HL^+ , C , were varied within the limits $0.001 \leq B \leq 0.090$ M and $0.005 \leq C \leq 0.300$ M respectively. h and b were usually varied by adding hydroxide or hydrogen ions. Owing to the formation of precipitates, the available $-\log h$ range was restricted to an upper limit of 7–9. In general, most of the titrations were performed at constant C/B ratio. When C exceeded 0.08 M the titrations were performed with constant C . The following C/B ratios were studied: 0.5, 1, 2, 3, 3.5, 4, 4.5, 6, 8 and 16.

The reversibility of equilibria were tested by performing both forward (increasing $-\log h$) and backward (decreasing $-\log h$) titrations. h and b were determined by measuring the emf of the cell (1),



where ME denotes the measuring electrode (glass electrode and Cd(Hg)-electrode) and RE = Ag, AgCl/0.01 M Cl^- , 2.99 M ClO_4^- , 3.00 M Na^+ || 3.00 M $NaClO_4$.

$$E_H = E_{OH} + 59.16 \log h + E_j \quad (\text{glass electrode}) \quad (2a)$$

$$E_B = E_{OB} + 29.58 \log b + E_j \quad (\text{Cd(Hg) electrode}) \quad (2b)$$

Assuming the activity coefficients to be constant, the expressions (2a) and (2b) are valid for the measured emf. E_{OH} and E_{OB} are constants determined in acid (H^+ , Cd^{2+} , HL^+) solutions of known compositions, where complex formation can be neglected ($-\log h \leq 3$).

For the liquid junction potentials (E_j) we have used $E_j = (-16.7h + 8.0 k_w h^{-1})$ mV, where $k_w = 6.03 \times 10^{-15} M^2$ ¹⁸ is the ionic product of water in 3.0 M $NaClO_4$.

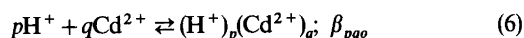
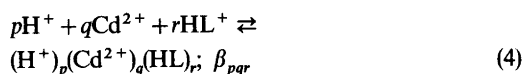
It has been found that E_{OH} is dependent of the cadmium (b), imidazolium (c) and imidazole ($k_a ch^{-1}$) content. Investigations^{2,19} show that the change in E_{OH} , due to changes in b , c and $k_a ch^{-1}$ could be described by the linear function (3), where $\Delta E_{(Cd^{2+})} =$

$$\Delta E_{OH} = \Delta E_{Cd^{2+}} + \Delta b + \Delta E_{HL^+} + \Delta c + \Delta E_L \Delta(k_a ch^{-1}) \quad (3)$$

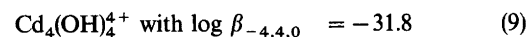
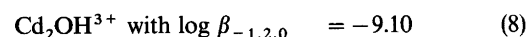
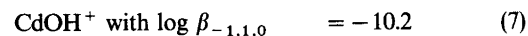
16.0 mV M^{-1} , $\Delta E_{HL^+} = -5.8$ mV M^{-1} and $\Delta E_{(L)} = -5.0$ mV M^{-1} .

The magnitude of ΔE_{OH} caused by concentration changes during the titrations used in the final calculations, was estimated. ΔE_{OH} did not exceed 0.2 mV, which will hardly cause any changes in the equilibrium model.

Data treatment. We will assume the presence of three-component equilibria with the general form (4) besides the two two-component equilibria (5) and (6). For reaction (5) Sjöberg¹⁴ reported $\log(k_a \pm 3\sigma) = -7.913 \pm 0.002$.



Concerning equilibrium (6) Biedermann and Ciavatta¹⁵ found the hydrolytic species (7)–(9).



These results on the two-component equilibria will, in the following, be considered as known and no attempts will be made to adjust their equilibrium constants.

The search for a model (pqr) and corresponding equilibrium constants β_{pqr} that best fit the experimental data was carried out using the least-squares program LETAGROPVRID²¹ (version ETITR).²² The different standard deviations given were defined and calculated according to Sillén.²³ The computations were performed on a CD 6600 computer.

CALCULATIONS AND RESULTS

The analysis of data was started by making $\bar{n}(\log(L))$ and $\eta(\log(L))$ plots, (E_H data) and ($E_H + E_B$ data) respectively, which are given in Figs. 1 and 2.

It is seen that with $C/B \geq 6$ or higher values of B ($B \geq 0.020$ M) \bar{n} as well as η are independent of B and C , thus indicating the formation of a series of mononuclear complexes CdL_n^{2+} . Data fulfilling

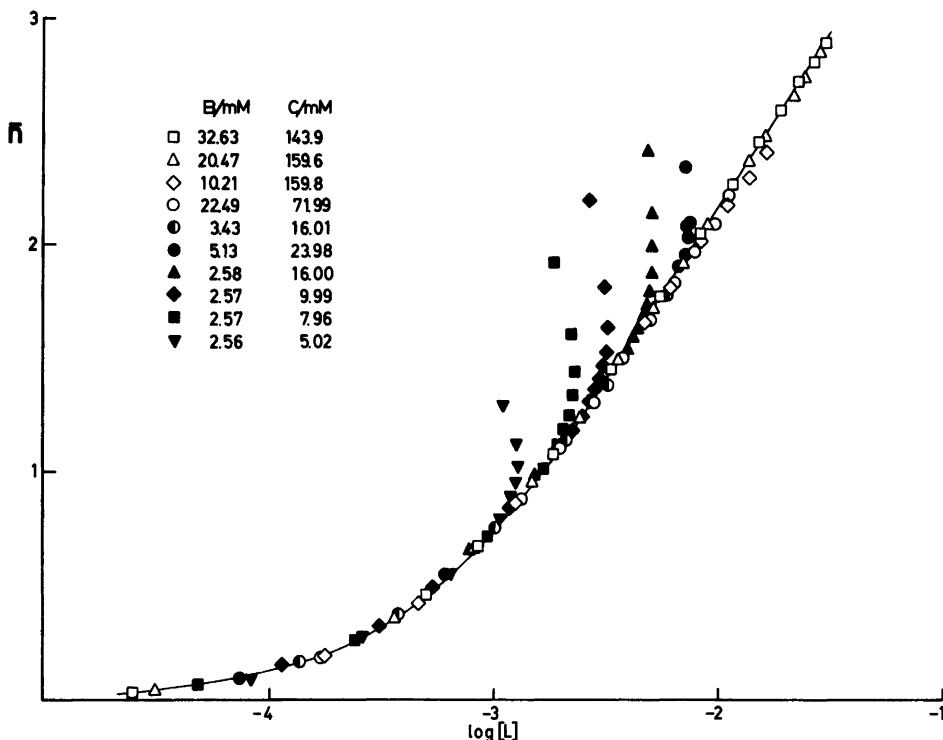


Fig. 1. Experimental data plotted as curves $\bar{n} \log[L]$. Half filled symbols denote a back-titration. In order to make the figure clear, only a few titrations have been plotted. The full drawn curve has been calculated with the set of proposed constants for CdL_n^{2+} , $n=1, \dots, 4$.

these conditions were treated separately and will in the following be denoted Data 1.

For data with quotients $C/B \leq 0.010$ systematic deviations from the mononuclear \bar{n} and η curves were observed. This could indicate that ternary hydrolytic species were formed. These data will be treated separately and denoted Data 2.

In the LETAGROP calculations different data sets were used (cf. Table 2). This will enable us to compare the results obtained from different calculations and thus give information about the reliability of the different electrodes as well as the analytical determinations of H and B . In the different calculations corrections due to a protolytic impurity (HX) in the ionic medium were made as earlier described.³

Data 1. A LETAGROP analysis showed that E_H , E_B as well as $E_H + E_B$ data could be well explained with the complexes CdL^{2+} , CdL_2^{2+} , CdL_3^{2+} and CdL_4^{2+} (cf. Table 2). According to this table, the agreement in $\beta_{-1,1,1}$, $\beta_{-2,1,2}$, $\beta_{-3,1,3}$ and $\beta_{-4,1,4}$,

independent of data sets and minimizing functions, is very good, the difference between the highest and the lowest value being less than 0.02, 0.02, 0.03 and 0.09 in log units, respectively.

Now remains the choice of which calculation is the most accurate one. Because it must be an advantage to measure both h and b and while H is determined in every titration, it seems reasonable to assume that the data set H, h, b, C , provides the most reliable results. This gives the constant values ($\log \beta_{-1,1,1} = -4.820 \pm 0.006$, $\log \beta_{-2,1,2} = -10.327 \pm 0.011$, $\log \beta_{-3,1,3} = -16.451 \pm 0.020$ and $\log \beta_{-4,1,4} = -23.14 \pm 0.03$).

Though the cadmium ion selective electrode was not as accurate as the Cd(Hg)-electrode, formation constants for the different $\text{Cd}^{2+} - \text{L}$ complexes were calculated (cf. Table 2). The agreement between these constants and those obtained from the other data sets is satisfactory as the differences are less than 0.05 in $\log \beta_{-111} - \log \beta_{-313}$ and 0.1 in $\log \beta_{-414}$.

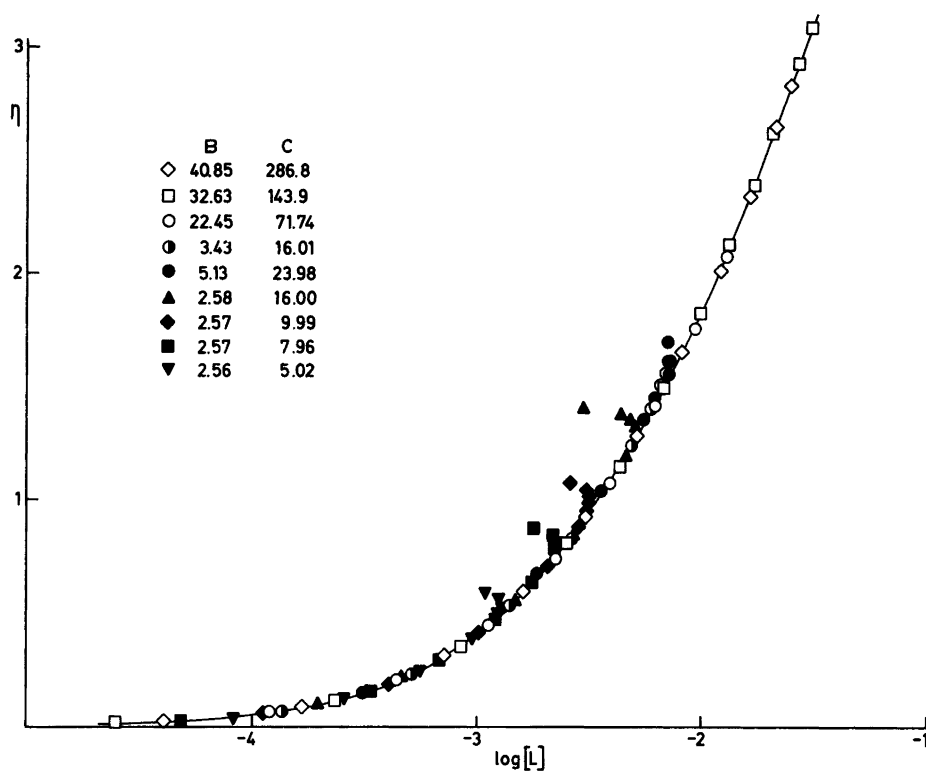


Fig. 2. Experimental data plotted as curves $\eta \log[L]$.

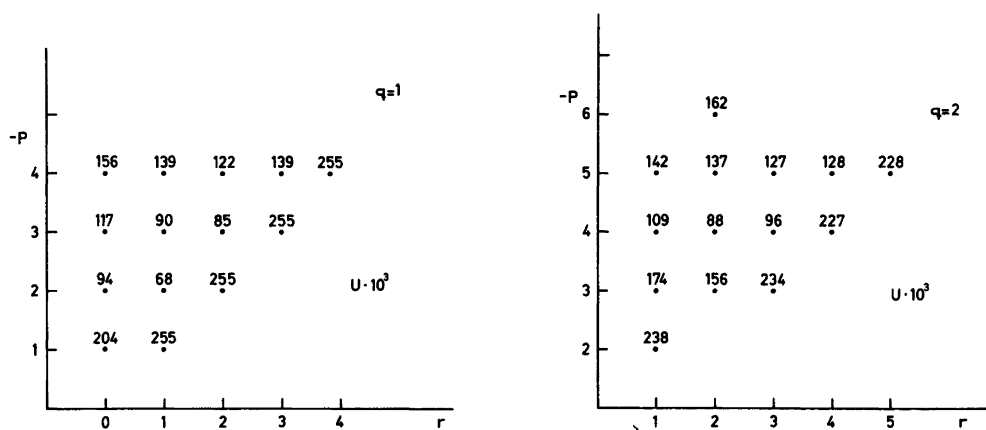


Fig. 3. Letagrop-search for ternary $H_pCd_q(HL)_r^{(p+2q+r)+}$ -complexes. The diagrams give error square sums $U_H(p,r) \times 10^3$ assuming only one complex. In the calculation the hydrolytic species and the binary species CdL_n^{2+} , $n=1, \dots, 4$, have been assumed to be known. The calculation is based on 97 experimental points, chosen to cover as great concentration ranges as possible.

Table 2. Results of LETAGROP calculations on different data sets. The formation constants, $\beta_{p,q,r}$ are defined according to the equilibria $\text{pH}^+ + \text{qCd}^{2+} + \text{rHL}^+ \rightleftharpoons \text{H}_p\text{Cd}_q(\text{HL})_r^{(q+2q+r)+}$. The error $3\sigma(\log \beta_{pqr})$ is given when the corresponding constants are varied. Results are given from the calculations on data 1 (upper part of the table) and data 2 (lower part).

Data	Number of titr/number of points	CdL_1^{2+} $\log(\beta_{-1,1,1})$ $\pm 3\sigma$	CdL_2^{2+} $\log(\beta_{-2,1,2})$ $\pm 3\sigma$	CdL_3^{2+} $\log(\beta_{-3,1,3})$ $\pm 3\sigma$	CdL_4^{2+} $\log(\beta_{-4,1,4})$ $\pm 3\sigma$	$\text{Cd}(\text{OH})\text{L}^+$ $\log(\beta_{-2,1,1})$ $\pm 3\sigma$	$\sigma(Y)/\text{mM}$	Data set used
E_H	11/249	-4.801 ± 0.010	-10.333 ± 0.012	-16.460 ± 0.032	-23.23 ± 0.07		0.002 ^a	<i>h, H, B, C</i>
E_B	12/241	-4.817 ± 0.004	-10.323 ± 0.006	-16.444 ± 0.019	-23.179 ± 0.005		0.061 ^c	<i>b, H, B, C</i>
$E_H + E_B$	11/199	-4.820 ± 0.006	-10.327 ± 0.011	-16.451 ± 0.020	-23.14 ± 0.03		0.073 ^b	<i>h, b, H, C</i>
$E_H + E_B$	11/199	-4.826 ± 0.004	-10.316 ± 0.012	-16.432 ± 0.037	-23.21 ± 0.13		0.064 ^c	<i>h, b, B, C</i>
$E_H + E_B$	11/199	-4.837	-10.316	-16.436	-23.20		0.10 ^b	<i>h, b, H, C</i> ^d
E_B	5/128	-4.794 ± 0.007	-10.320 ± 0.017	-16.40 ± 0.03	-23.07 ± 0.09		0.086 ^c	<i>b, H, B, C</i> ^e
$E_H + E_B$	10/97	-4.820	-10.327	-16.451	-23.14	-14.50 ± 0.08	0.026 ^b	<i>h, b, H, C</i>
$E_H + E_B$						-14.40 ± 0.09	0.025 ^c	<i>h, b, B, C</i>

^a $Y = Z_{\text{CALC}} - Z_{\text{EXP}}$. ^b $Y = H_{\text{CALC}} - H_{\text{EXP}}$. ^c $Y = B_{\text{CALC}} - B_{\text{EXP}}$. ^d β_{n1n} values calculated according to the relation $\beta_{-n1n} = *K_1^n \cdot K^{n(n-1)/2}$, where $\log *K_1 = -4.837 \pm 0.003$ and $\log K = -0.642 \pm 0.003$. ^e Values calculated with data received from measurements with the commercial cadmium ion selective electrode.

Data 2. In the search for ternary species it was assumed that formation constants for the species CdL_n^{2+} , $n = 1, 2, 3, 4$, had the values proposed above. Furthermore, formation constants for the hydrolysis of cadmium were those given by Biederman.¹⁶

The search for ternary complexes was started with a *pqr*-analysis of the residuals. That is a systematic trial and error procedure testing complexes with different composition $(\text{H}^+)_p(\text{Cd}^{2+})_q(\text{HL}^+)_r$, one by one. The test was carried out with a representative part of data including 10 titrations and 97 experimental points, and with the data set *h,b,H,C*. The result of the analysis is given in Fig. 3. It is seen from these calculations that the lowest error squares sum U_H is obtained for the complex $(\text{H}^+)_{-2}(\text{Cd}^{2+})_1(\text{HL}^+)_1$ with $\log \beta_{-2,1,1} = -14.50 \pm 0.08$ giving $\sigma(H) = 0.03$ mM. For comparison a calculated value from

(*h,b,B,C*) data is also given in Table 2. As can be seen, $\log \beta_{-211}$ varies between -14.50 and -14.40. Because the complex is formed in small amounts (~5% of *B*, cf. Fig. 4b) and with $-\log h \approx 8$, the determination of the complex-constant cannot be carried out with the highest precision.

For the same reason, as discussed under Data 1, the most reliable value of $\log \beta_{-2,1,1}$ is supposed to be the one evaluated from *h,b,H,C*-data. Thus $\log \beta_{-211} = -14.50 \pm 0.08$ is proposed.

DISCUSSION

The present investigation has been carried out by measuring two free concentrations, *h* and *b*. This made it possible to carry out the LETAGROP-calculations by excluding one of the quantities *h, b, H* and *B*, thus yielding four different types of data sets

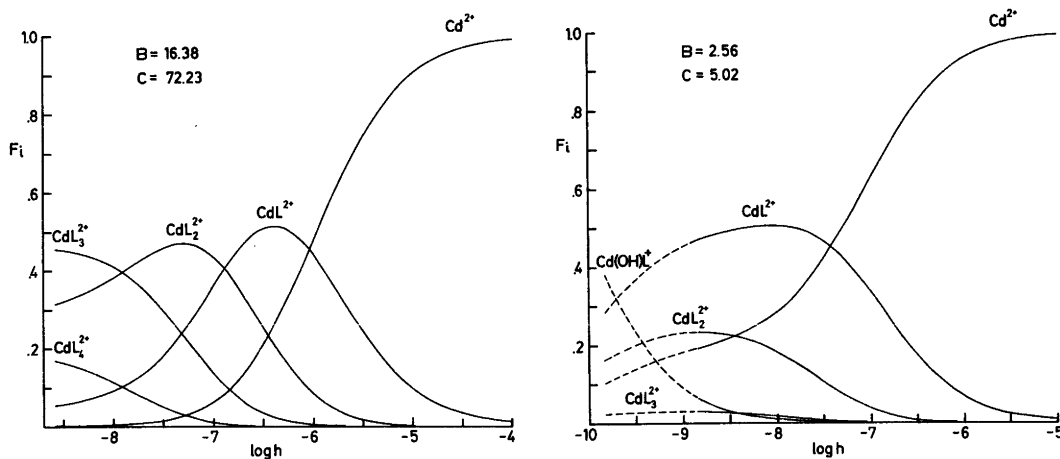
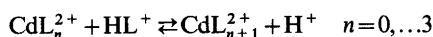


Fig. 4. Distribution diagrams $F_i(\log h)_{BC}$. F_i is defined as the ratio between cadmium(II) in a species and the total cadmium(II). The computer program SOLGASWATER³³ was used for the calculations with the set of proposed constants. Broken lines denote ranges where no measurements have been performed due to precipitation (extrapolated range)

(cf. Table 2).* The results show that the agreement in the evaluated constants is good. Calculations showed that for higher C/B -ratios, data could be well explained with stepwise formed complexes CdL_2^{2+} , CdL_3^{2+} and CdL_4^{2+} . The distribution of these complexes is shown in Fig. 4a.

With regard to the stepwise formation of Cd^{2+} -L complexes, data was also analyzed with the two-parameter approximation of the type given in eqn. (10). The two-parameter approximation gave a good



$$*K_{n+1} = *K_1 K^n = \frac{[\text{CdL}_{n+1}^{2+}][\text{H}^+]}{[\text{CdL}_n^{2+}][\text{HL}^+]} \quad (10)$$

explanation of data with the parameters $\log *K_1 = -4.837 \pm 0.003$ and $\log K = -0.642 \pm 0.002$. From these parameters $\log \beta_{n1n}$ -values can be calculated and the resulting complex constants for CdL_n^{2+} , $n=1, \dots, 4$ are in good agreement with those separately calculated (cf. Table 2). Thus it seems as the stepwise formation of CdL_n^{2+} complexes ($n \leq 4$) almost equally well could be explained with two parameters as with four.

* A complete list of the experimental data is available from this department.

It is also interesting to note that in 0.5 M NaClO_4 medium (Marsicano *et al.*¹²) $\log K_2/K_1 = -0.65$, $\log K_3/K_2 = -0.66$ and $\log K_4/K_3 = -0.28$, i.e. it seems that in this medium the two parameter approximations should be valid too, at least up to the formation of CdL_3^{2+} . In the present investigation $\log K_{n+1}/K_n = -0.64$ ($n=1,2,3$) is in good agreement with the above given values. This is an indication that in NaClO_4 media the ratio between the stepwise constants (K_n) is of the same magnitude regardless of the medium concentration. This hypothesis is also supported by the following values given by Lumme and Virtanen:¹¹ ($\log K_2/K_1$, M NaClO_4) $-0.66, 0.25; -0.70, 0.5; -0.78, 1; -0.72, 2$.

If we compare the values of the stability constants obtained in this investigation with those reported by Marsicano *et al.* and Lumme *et al.* we find that the values increase with increasing medium concentration. Within the range 0.25–3.0 M NaClO_4 the linear equation (11) is valid, where I is the medium concentration, and the errors given corresponding to $\pm 1\sigma$.

By combining eqns. (10) and (11) and assuming the two parameter approximation to be valid, one obtains eqn. (12), where -0.67 is an average value of

$$\log K_1 = 2.66(1) + 0.13(1)I \quad (11)$$

$$\log K_{n+1} = 2.66 + 0.13I - n \cdot 0.67; \quad n=0, \dots, 3 \quad (12)$$

$\log K_{n+1}/K_n$ ratios cited above. Concerning the structure of the different CdL_n^{2+} species it seems reasonable to assume that no change in the coordination is taking place during the complex formation as the two-parameter approximation is applicable. The complexes most probably have an octahedral configuration. This assumption is confirmed by X-ray measurements of the solid phases $\text{Cd}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$,²⁴ $(\text{CdCl}_2)_\infty$,²⁵ $(\text{CdL}_2\text{Cl}_2)_\infty$,²⁶ $\text{CdL}_3\text{SO}_4 \cdot \text{H}_2\text{O}$ ²⁷ and $\text{CdL}_6(\text{ClO}_4)_2$ (see above), where cadmium is reported to have octahedral coordination in these structures.

At low ratios ($C/B < 6$) a ternary complex is formed. The best explanation was given by the -2,1,1 complex, which is formed to an amount of 5% of B, see Fig. 4b. Whether this is a hydroxoimidazole ($\text{Cd}(\text{OH})\text{C}_3\text{H}_4\text{N}_2^+$) or an imidazolate ($\text{Cd}(\text{C}_3\text{H}_3\text{N}_2)^+$) complex is impossible to deduce from potentiometric data.

The existence of imidazolate complexes in solution has been claimed by Morris and Martin²⁸ in the Co^{2+} -system. In highly alkaline solutions (1 M NaOH) with great excess of imidazole they found evidence for the formation of a tetrahedral $\text{CoL}_4\text{H}^+_{-1}$ complex in which an imidazolate ion is coordinated. From spectrophotometric measurements they estimated $\text{p}K_a(\text{CoL}_4^{2+}) \sim 12.5$.

In the present investigation the -2,1,1 complex probably is a CdLOH^+ complex. The complex is formed at low ratios C/B and within a pH range close to the one for pure hydrolysis of the Cd^{2+} -ion. In fact CdL^{2+} is an acid ($\text{p}K_a(\text{CdL}^{2+}) = 9.68$) slightly stronger than the Cd^{2+} -ion ($\text{p}K_a(\text{Cd}^{2+}) = 10.2$). The hypothesis³ that the composition of a mixed hydroxo complex should be related to the binary species (cf. $\text{CdLOH}^+ - \text{CdOH}^+$) seems to be valid in this system too. This relation was also found in the corresponding Ni^{2+} ,²⁹ Cu^{2+} ,³⁰ Zn^{2+} ,³¹ Hg^{2+} ³² and Ag^+ ³ systems, all investigated at this department.

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