

Studies on the Hydrolysis of Metal Ions

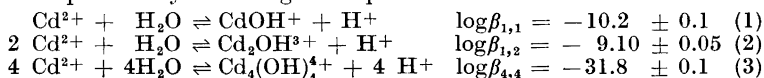
Part 41. The Hydrolysis of the Cadmium Ion, Cd^{2+}

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The hydrolysis equilibria of the Cd(II) ion have been studied at 25°C by measuring the hydrogen ion concentration of a series of cadmium perchlorate solutions, using a glass or a quinhydrone half-cell. The $[\text{Cd(II)}]_{\text{tot}}$ has ranged from 0.1 to 1.45 M. For each $[\text{Cd(II)}]_{\text{tot}}$ the $[\text{H}^+]$ was increased from a value corresponding to a solution saturated with Cd(OH)_2 , until the hydrolysis became negligible. All solutions studied were made to contain 3 M ClO_4^- by adding LiClO_4 .

The emf data, which show that only a small part of the Cd^{2+} ions can be transformed to hydrolysis products without precipitation, may be explained by assuming the equilibria



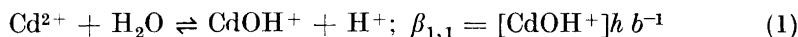
It may be deduced on the basis of the equilibrium constants (1), (2) and (3) that for $[\text{Cd(II)}]_{\text{tot}} \geq 0.1$ M the principal product of hydrolysis is the species $\text{Cd}_2\text{OH}^{3+}$.

Symbols often used in the text

- h = equilibrium concentration of hydrogen ions
- H = analytical excess of hydrogen ions = $[\text{ClO}_4^-] - 2[\text{Cd(II)}] - [\text{Li}^+]$
- b = concentration of Cd^{2+}
- B = total concentration of cadmium
- Z = $(h-H)B^{-1}$ = average number of hydrogen ions set free per cadmium atom
- K_p = formation constant for all species containing p OH groups
- $\beta_{p,q}$ = formation constant of the species $\text{Cd}_q(\text{OH})_p$
- p = number of OH groups bound to the hydrolysis products
- q = number of cadmium atoms present in the hydrolysis products

A number of methods have been used to study the reactions between the Cd^{2+} ion and water. In 1904 Kullgren¹, the pioneer investigator in this field,

determined the hydrogen ion concentration at 100°C of several carefully purified cadmium chloride solutions containing sucrose by measuring the rate of inversion. Kullgren explained his data by assuming the equilibrium



with $\log \beta_{1,1} = -9.5$.

In 1919 Löfman² studied the hydrolysis of Cd(II) by Vesterberg's method³. Löfman equilibrated cadmium acetate solutions at 20°C with ether, and measured the acetic acid concentration of the ether phase. On the basis of the distribution and dimerization constants of acetic acid Löfman was able to calculate for each $[\text{Cd(II)}]_{\text{tot}}$ the ratio $[\text{HAc}]_{\text{aq}}[\text{Cd(II)}]_{\text{tot}}^{-1}$, which under his experimental conditions is very nearly equal to the average number of OH groups bound per cadmium ion. By taking the value 2×10^{-5} for the dissociation constant of acetic acid and by neglecting complex formation between Cd^{2+} and acetate, we have calculated from Löfman's data $\log \beta_{1,1} = -9.2$.

In 1957 Marcus⁴ titrated a series of cadmium perchlorate solutions at 25°C with NaOH, using a glass electrode. The $[\text{Cd(II)}]_{\text{tot}}$ ranged from 0.011 to 0.910 M and all the solutions were made to contain 3 M ClO_4^- by adding NaClO_4 . Marcus interpreted the potentiometric data by assuming equilibrium (1) with $\log \beta_{1,1} = -9.2 \pm 0.2$. He encountered difficulties in obtaining accurate experimental results. The considerable scatter of the $Z (\log h)_B$ data (see Fig. 1 of Ref.⁴) was ascribed by Marcus to the presence of a weak protolyte in the NaOH solutions used, and further, to the slow establishment of the hydrolysis equilibria. We believe that the latter complication was due to the transient precipitation of Cd(OH)_2 caused by a local excess of OH^- . This is hard to avoid when a strong base is added to a poorly buffered cadmium solution.

The solubility of Cd(OH)_2 in dilute HClO_4 and NaOH solutions at 25°C was studied by Gayer and Woontner⁵ in 1957. These investigators explained the variation of the $[\text{Cd(II)}]_{\text{tot}}$ in the saturated solutions, in the $\log h$ region -7 to -9.4 , by postulating the equilibrium



with $\log K = 4.51$ *. This implies that in the $\log h$ range studied, the dissolved cadmium would exist predominantly as CdOH^+ . However, the results of other investigations^{1,2,4} including the present work, indicate that for $\log h = -9.4$ the ratio $[\text{CdOH}^+][\text{Cd}^{2+}]^{-1}$ is at most equal to 0.5 and that it is reduced below 0.01 when $\log h$ tends to -7 . Gayer and Woontner's data, which were obtained in solutions with small buffer capacity, may have been influenced by minute amounts of impurities, such as substances dissolved from glass (*cf.* Ref.⁶).

* Marcus⁴ considered that Gayer and Woontner⁵ calculated from their solubility measurements $\log \beta_{1,1} = -9.3$. He probably derived this result by combining K of (2) with Feitknecht and Reinmann's value⁷ for the solubility product of Cd(OH)_2 , $\text{p}K_s = 14.21$, which is based on the assumption that in the saturated solution $[\text{Cd}^{2+}] = [\text{Cd(II)}]_{\text{tot}}$.

METHOD OF INVESTIGATION

In the present work the hydrolysis equilibria have been studied by measuring the hydrogen ion concentration of a series of cadmium perchlorate solutions at 25°C, using a glass or a quinhydrone electrode. The value of B ranged from 0.1 to 1.45 M, and the test solutions were made to contain 3 M ClO_4^- by adding LiClO_4 . Some arguments have been given earlier⁸ for preferring LiClO_4 to NaClO_4 , and a quantitative study⁹ now being made in this laboratory has yielded further evidence in support of this preference of LiClO_4 .

The cadmium amalgam electrode was not used in this study, because it could be inferred from the h measurements that, at most, only 2 % of B may be transformed to the hydrolysis products before a precipitate forms. A decrease of the $[\text{Cd}^{2+}]$ by 2 % corresponds to a change of 0.25 mV in the potential of the cadmium half-cell; we have never been able, however, to measure the emf of cells containing liquid junctions with an uncertainty lower than ± 0.02 mV.

Preparation of the test solutions. Since the solubility product of $\text{Cd}(\text{OH})_2$ has a low value ($\text{p}K_s \sim 14$) and the Cd(II) ion proved to be a rather weak acid clear, precipitate-free, cadmium solutions containing an appreciable amount of hydrolysis products are very poorly buffered. The preparation and preservation of such solutions represented the most serious problem in this investigation.

We were confronted with a similar situation when the hydrolysis of Ag^+ and of La^{3+} were studied in this laboratory^{8,10}. The experience gained in connection with the studies of these ions was of great value to adopt a suitable method of preparation for cadmium solutions.

As the starting material 2 M cadmium perchlorate stock solutions, containing 0.001 M hydrogen ions, have been employed. At such a high acidity (where the hydrolysis is quite negligible) CO_2 can be easily expelled with N_2 , and no reaction with pyrex glass could be detected. By diluting a weighed amount of the stock solution with 4 M LiClO_4 , and NH_3 - and CO_2 -free water, solutions with the composition B' M Cd(II), H'_0 M H^+ , $(3.000 - 2B' - H'_0)$ M Li^+ , 3.000 M ClO_4^- = solution S'_0 were prepared. B' had values ranging from 0.1 to 1.45 M, and H'_0 varied from 10^{-4} to 10^{-3} M, depending on B' . In order to saturate S'_0 with $\text{Cd}(\text{OH})_2$, and thus to attain the maximum Z , a small excess of freshly ignited CdO was added to S'_0 and the mixture was stirred for 12 to 16 h. The dark brown CdO preparation used was, within a couple of hours, transformed completely into white $\text{Cd}(\text{OH})_2$ which is the stable phase at 25°C¹¹. The excess of $\text{Cd}(\text{OH})_2$ was removed by filtration and the resulting clear, saturated solution was sucked into a stoppered burette in which it was preserved. All these manipulations were carried out under an atmosphere of purified nitrogen in the apparatus shown in Fig. 1, the operation of which will be described in the section "Materials and Analysis".

A part of the saturated solution, S_0 , was used to determine the $[\text{Cd}(\text{II})]_{\text{tot}} = B$, which was found to exceed B' by 0.5 to 2 %, depending on B' . Since the solubility of $\text{Cd}(\text{OH})_2$ in solutions S'_0 proved to be low, the volume changes

caused by its dissolution may be neglected. The saturated solutions thus had the general composition

B M Cd(II), H_0 M H⁺, $(3.000 - 2B' - H'_0)$ M Li⁺, 3.000 M ClO₄⁻ = solution S₀ where $H_0 = H'_0 - 2(B - B')$ denotes the analytical excess of hydrogen ions. Because B has always been very near to B' , and H'_0 has been known with an uncertainty of a few percent, an accurate value for H_0 had to be determined by emf measurements (see below). H_0 proved to be negative for each value of B studied.

In the course of the emf measurements, which were carried out as potentiometric titrations, the hydrogen ion concentration of the test solutions was varied by starting with V_0 ml of S₀ and adding to it successively increasing volumes, V_T ml, of another solution, T, which had the composition B M Cd(II), H_T M H⁺, $(3.000 - 2B - H_T)$ M Li⁺, 3.000 M ClO₄⁻ = solution T. A high value was chosen for H_T , such that the hydrolysis in T could be neglected ($H_T = h > -H_0$). Thus all the solutions studied by emf measurements had the general composition

B M Cd(II), H_s M H⁺, $(3.000 - 2B - H_s)$ M Li⁺, 3.000 M ClO₄⁻ = solution S where

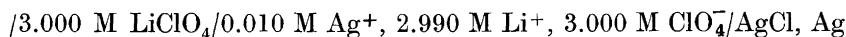
$$H_s = (H_0V_0 + H_TV_T)(V_0 + V_T)^{-1} \quad (3)$$

It is important to note that with this technique, a fresh saturated solution was prepared for each series of measurements. Thus, the reproducibility of the $Z(\log h)_B$ data gives some idea of the effectiveness of our efforts to prevent contamination. The three sets of acceptably agreeing data obtained for solutions with $B = 0.1$ M, which have the lowest buffer capacity, seem to show (see Fig. 2) that the amount of protolysing impurities could be kept at so low a value that they had no appreciable influence on emf data of the present accuracy.

Determination of h by emf measurements. The hydrogen ion concentration of solution S was determined by measuring the emf of the cell



where GE denotes a glass electrode and SE represents the reference half-cell



The emf of cell (A) at 25°C may be written

$$E = E'_0 - 59.15 \log h - 59.15 \log f(\text{H}^+) + E_j(h, B) \quad (4)$$

In (4), E'_0 is a constant, $f(\text{H}^+)$ denotes the activity factor of hydrogen ions and $E_j(h, B)$ represents the liquid junction potential of the junction solution S/3 M LiClO₄. The standard state is defined so that the activity factors of all reacting species tend to unity as the composition of the solution approaches 3 M LiClO₄.

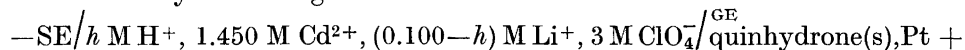
In each series of measurements B was kept constant while $\log h$ was successively increased from about -7.5 to -2.3 . Since Z never exceeded 0.02, the composition of solution S changed only slightly in the course of acidifica-

tion. Consequently, we may regard it as a good approximation to assume that for $B = \text{constant}$, $f(\text{H}^+) = \text{constant}$. Thus (4) may be simplified to

$$E = E_0 - 59.15 \log h + E_j(h, B) \quad (5)$$

where E_0 is a function of B .

The liquid junction potential of the junction $h \text{ M H}^+$, $(3-h) \text{ M Li}^+$, $3 \text{ M ClO}_4^-/3 \text{ M LiClO}_4$ was found in a previous work⁸ to be closely approximated for $h \leq 0.1 \text{ M}$ by the equation $E_j(h, 0) = -15.8 h \text{ mV}$. $E_j(h, 1.45)$ has been determined by measuring the emf of the cell

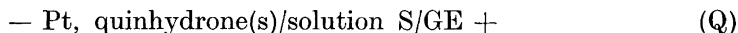


as a function of h in the region 0.01 to 0.1 M. The data could be well described with the linear formula $E_j(h, 1.45) = -22.4 h \text{ mV}$. Since 0.005 M was the highest hydrogen ion concentration measured with cell (A), we could use in the whole B range the $E_j(h, 0)$ function to calculate h from (5). The maximum error introduced by this approximation is much below the uncertainty of the E measurements, $\pm 0.1 \text{ mV}$.

In order to calculate h and Z from the E data the constants E_0 and H_0 need to be known. These were ascertained by determining at the end of each series of measurements a sequence of E values in the h range 0.5 to $5 \times 10^{-3} \text{ M}$, where the hydrolysis is negligible. H_0 was computed from the E data obtained at these high acidities by constructing a Gran¹² plot. E_0 was then calculated for each point employed to find H_0 . In all cases E_0 proved to be constant within $\pm 0.1 \text{ mV}$.

The main part of each series of experiments was devoted to the study of solutions in which $\log h < -5$, where the hydrolysis becomes appreciable. With the known E_0 and H_0 values, and using (5) and (3), h and Z could be calculated for each point of the extensive series of E data obtained in the low acidity range. The family of functions $Z(\log h)_B$ serves as the basis for the calculations presented in later sections.

Comparison of the glass and the quinhydrone half-cells. In order to check the glass electrode, a few series of measurements have been made with the cell



In the $\log h$ range -2 to -6.5 , the emf of cell (Q) was found to be constant within $\pm 0.2 \text{ mV}$ for each value of B studied. This result demonstrates the important point that the dependence on h of the emf of cell (A) is accurately described by eqn. (5).

Decomposition of quinhydrone and its dissociation products prevented us from extending the measurements with cell (Q) to lower acidities. It is worthwhile to note that, although air was carefully excluded from the cell, the decomposition could not be entirely inhibited.

Supplementary emf measurements. To enable us to estimate the influence of impurities introduced with the solvent salt, LiClO_4 , a series of measurements was carried out in $0.21 \text{ M (Li}^+)\text{ClO}_4^-$ solutions. B was kept constant at 0.1 M , while $\log h$ was increased stepwise from -7.3 (= the acidity of the saturated solution) to -3 . The $Z(\log h)_B$ data obtained in the medium $0.21 \text{ M (Li}^+)\text{ClO}_4^-$

could be satisfactorily interpreted in terms of hydrolysis products containing the same number of OH groups as those found to be present in solutions in which $[\text{ClO}_4^-] = 3 \text{ M}$ and $B = 0.1 \text{ M}$. Moreover, the logarithms of the monoligandic equilibrium constant, $\log K_1$, determined in 0.21 M and 3M media differ only by 0.1 unit (see Table 2). We may thus conclude that the amount of impurities in our LiClO_4 preparations do not appreciably affect the results derived from the emf data.

All emf measurements considered hitherto were performed by increasing gradually the acidity of the test solutions. Doubts may therefore arise whether the true equilibria could be attained in this way. To furnish some light on this essential question a series of measurements was made, employing the glass electrode, by starting with a partially hydrolyzed solution in which $B = 0.7 \text{ M}$ and $\log h = -7.1$, and adding to it increasing volumes of another solution containing 3 M LiClO_4 and 0.736 mM HClO_4 . At the end of the series B had decreased to 0.2 M and $\log h$ to -7.4 . The set of $Z(\log h, B)$ data calculated from these measurements could be accurately described with the same equilibrium constants as were used to explain the data found for acidified solutions, see Fig. 2. This fact affords evidence that the real equilibria were closely approached when the hydrolysis was successively suppressed, *i.e.* using the technique outlined in the preceding sections.

MATERIALS AND ANALYSIS

Cadmium perchlorate stock solutions were prepared by dissolving CdO in a small excess of dilute HClO_4 . CdO was made by igniting $\text{Cd}(\text{NO}_3)_2(\text{H}_2\text{O})_4$. This salt was chosen because it can be easily purified by recrystallization, and because it decomposes to CdO at around 400°C. Pure $\text{Cd}(\text{NO}_3)_2(\text{H}_2\text{O})_4$ was prepared in two ways: (a) $\text{Cd}(\text{NO}_3)_2(\text{H}_2\text{O})_4$ (Baker, p.a.) was twice recrystallized from 0.01 M HNO_3 , (b) Cadmium rods, Baker p.a., that had been first etched with 8 M HNO_3 , were dissolved in an excess of 16 M HNO_3 . The resulting solution was slowly evaporated and the cadmium nitrate crystals, which formed, were separated by filtration. This product was further purified by two recrystallizations from water. No Fe^{3+} , Pb^{2+} , Cl^- or SO_4^{2-} ions could be detected in either type of preparation. The $Z(\log h)_B$ data obtained in solutions originating from cadmium nitrate of type (a) and (b) have always agreed within the experimental uncertainty ($\pm 0.003 \log h$ units).

The cadmium nitrate must be heated gradually to 400°C, and it must be stirred continuously. If these precautions are not taken, a sintered product is formed, and moreover, the melt or the boiling solution is likely to froth over at the transition temperatures of cadmium nitrate. The melt was kept at 400°C, while being stirred, until no more nitrogen oxide fumes could be detected. Finally, the CdO thus formed was ignited overnight at 800°C to expel the last traces of nitrogen oxides. The resulting powder-like CdO was completely transformed into $\text{Cd}(\text{OH})_2$ within a couple of hours after it was brought into contact with our solutions at 25°C.

The cadmium concentrations of the stock and of the test solutions were determined gravimetrically by precipitating $\text{CdNH}_4\text{PO}_4\text{H}_2\text{O}$. The analyses were carried out following closely Winkler's prescriptions¹³, in this way an accuracy of 0.1 % could be attained.

The hydrogen ion concentration ($\sim 0.001 \text{ M}$) of the stock solutions was estimated by adding a measured volume of standardized HClO_4 to a weighed amount of the stock solution and titrating this mixture with NaOH using methyl-red as indicator. The uncertainty of the results did not exceed 2 %.

LiClO_4 , AgClO_4 and HClO_4 solutions were prepared and analyzed as described in an earlier publication⁸.

The saturated solutions, S_0 , were prepared using the apparatus shown in Fig. 1. Nitrogen was supplied through the tubes a_1 and a_2 . The gas, which was taken from a cylinder, was purified and presaturated by passing it through 0.5 M NaOH, then water and finally solution S'_0 . The stoppers R_1 , R_2 and R_3 were made from rubber, this material was chosen to attain some flexibility. The stoppers were cleaned by soaking them in boiling 1 M NaOH and then in water. A thin layer of filter paper pulp was placed on the filter surface of the sintered glass filter funnel, g , to retain the smallest $Cd(OH)_2$ particles. One quarter of a "Whatman ashless tablet" was used for each filtration. No acid or alkaline impurities, Cl^- , SO_4^{2-} or heavy metal ions could be detected in the tablets, which were tested as given earlier⁸.

The apparatus was operated as follows. First the three-way stopcock C_1 was turned to the right and C_3 was opened. Then 70 ml of S'_0 was placed in the vessel A_1 and nitrogen was passed through the solution for two hours. R_1 was then lifted for a moment and freshly ignited CdO (taken from a N_2 -filled desiccator) was dropped into S'_0 . This solution was saturated by stirring it, using a teflon covered magnet bar, with the CdO for a night, while a vigorous stream of N_2 was maintained. Next morning the flask A_2 was flushed with N_2 entering at a_2 and leaving at C_4 , this gas current was continued throughout the filtration. A portion of the saturated solution was pressed into the funnel g by turning C_1 to the vertical, then C_1 was returned to the right and thereby N_2 passed through the solution while it was trickling through the filter. Successive portions of S_0 were transferred to g until about 60 ml filtrate was obtained. C_4 was now closed and the burette was flushed with N_2 by turning C_2 to the vertical. Finally the filtrate was drawn up into the burette by connecting it to a water-jet pump. The saturated solution was preserved in the burette under N_2 at atmospheric pressure.

In each case the filtrate was carefully examined for turbidity, but no suspended $Cd(OH)_2$ particles could be detected. No indication of slow precipitation was found in filtrates which were tested for turbidity regularly during a week.

Experimental details of the emf measurements. All emf measurements were carried out at 25°C. The cell arrangement, which was kept in a paraffin oil thermostat, was similar to that described by Forsling, Hietanen and Sillén¹⁴. Air had been displaced with N_2 in the titration vessel before the test solution was introduced and a N_2 stream was maintained throughout the series of measurements. Nitrogen, which was taken from a cylinder, was passed through successively 0.5 M NaOH, H_2O and 3 M $LiClO_4$ for purification and presaturation.

A number of glass electrodes of the type Beckman No 40498 were employed. Ten minutes after each addition of solution T the emf of cell (A) showed a value which remained constant within ± 0.1 mV for many hours. $E - E_0$ values obtained with different glass electrodes agreed always within 0.2 mV. E was measured with a valve potentiometer

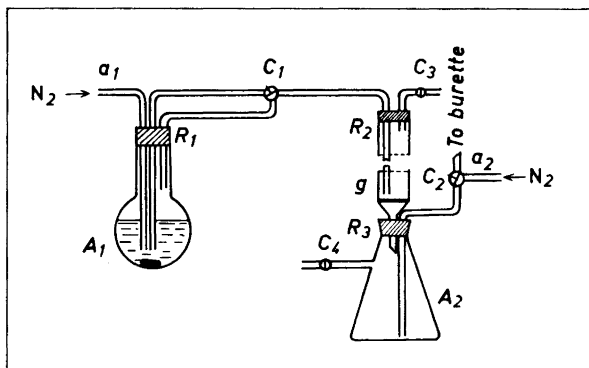


Fig. 1. Apparatus used to prepare saturated solutions.

Table 1. Survey of measurements.

B* = 1.450 *M

$Z \times 10^3$, $-\log h$. Series a. 20.6₈, 7.128; 19.7₈, 7.116; 18.9₃, 7.104; 18.0₆, 7.089; 17.2₃, 7.074; 15.6₀, 7.040; 14.0₃, 7.006; 12.5₂, 6.969; 11.0₇, 6.925; 9.6₇, 6.874; 8.31, 6.818; 7.00, 6.747; 5.73, 6.665; 4.51, 6.565; 3.33, 6.433; 2.18, 6.259; 1.07, 5.953; 0.52, 5.813.

Series b. 20.6₄, 7.121; 19.4₀, 7.106; 18.3₇, 7.092; 17.0₂, 7.069; 15.7₃, 7.043; 14.3₀, 7.011; 13.0₈, 6.982; 11.7₆, 6.950; 10.3₃, 6.903; 8.94, 6.849; 7.61, 6.786.

B* = 1.000 *M

$Z \times 10^3$, $-\log h$. Series a. 17.3₂, 7.221; 16.1₆, 7.200; 15.2₅, 7.185; 13.9₀, 7.155; 12.8₁, 7.128; 11.7₃, 7.102; 10.4₇, 7.065; 9.64, 7.031; 8.43, 6.986; 7.44, 6.937; 6.65, 6.894; 5.88, 6.844; 5.125, 6.785; 4.38, 6.715; 3.82, 6.663; 3.17, 6.599; 2.73, 6.519; 2.19, 6.426; 1.66, 6.310; 1.14, 6.146; 0.62, 5.874.

Series b. 16.0₄, 7.188; 13.7₆, 7.141; 11.5₈, 7.097; 9.47, 7.036; 7.44, 6.952; 6.46, 6.896.

B* = 0.700 *M

$Z \times 10^3$, $-\log h$. Series a. 13.4₂, 7.283; 12.6₈, 7.268; 11.9₀, 7.249; 10.9₁, 7.220; 9.70, 7.178; 8.51, 7.136; 7.34, 7.080; 6.19, 7.014; 5.06, 6.935; 3.96, 6.831; 3.09, 6.725; 2.44, 6.622; 1.81, 6.498; 1.18, 6.319; 0.76, 6.138; 0.35, 5.821.

Series b. 13.7₈, 7.302; 12.5₁, 7.276; 11.2₇, 7.243; 10.0₅, 7.205; 8.86, 7.160; 7.92, 7.118; 6.99, 7.072; 6.08, 7.014; 5.18, 6.952; 4.51, 6.889; 3.86, 6.820; 3.21, 6.742; 2.57, 6.649; 2.14, 6.568; 1.72, 6.475; 1.30, 6.350; 0.88, 6.179; 0.68, 6.054; 0.47, 5.882.

B* = 0.500 *M

$Z \times 10^3$, $-\log h$. Series a. 11.28, 7.342; 10.1₈, 7.309; 9.10, 7.273; 8.04, 7.229; 7.00, 7.175; 6.39, 7.140; 5.58, 7.087; 4.59, 7.004; 3.61, 6.903; 2.66, 6.769; 1.90, 6.629; 1.16, 6.416; 0.61, 6.136; 0.25, 5.726.

Series b. 11.4₆, 7.344; 10.8₀, 7.319; 9.93, 7.297; 9.06, 7.266; 8.01, 7.222; 6.97, 7.170; 6.16, 7.123; 5.55, 7.080; 4.96, 7.031; 4.37, 6.977; 3.79, 6.915; 3.21, 6.847; 2.64, 6.764; 2.26, 6.698; 1.70, 6.577; 1.33, 6.472; 0.96, 6.333; 0.60, 6.122; 0.24, 5.699.

B* = 0.250 *M

$Z \times 10^3$, $-\log h$. Series a. 8.16, 7.493; 7.29, 7.452; 6.43, 7.407; 5.59, 7.347; 5.10, 7.309; 4.44, 7.248; 3.96, 7.200; 3.33, 7.123; 2.70, 7.030; 2.24, 6.945; 1.78, 6.845; 1.33, 6.715; 1.03, 6.594; 0.73, 6.431; 0.44, 6.157.

Series b. 8.38, 7.500; 7.86, 7.476; 6.99, 7.435; 6.14, 7.386; 5.48, 7.337; 4.82, 7.285; 4.34, 7.243; 3.70, 7.173; 3.07, 7.094; 2.60, 7.020; 2.14, 6.933; 1.69, 6.830; 1.38, 6.746; 1.09, 6.639; 0.79, 6.492; 0.35, 6.092.

B* = 0.100 *M

$Z \times 10^3$, $-\log h$. Series a. 5.62, 7.593; 5.20, 7.559; 4.53, 7.505; 3.95, 7.439; 3.55, 7.400; 2.94, 7.309; 2.55, 7.238; 1.94, 7.118; 1.55, 7.003; 1.16, 6.851; 0.97, 6.759; 0.78, 6.641; 0.58, 6.487; 0.40, 6.257.

Series b. 6.80, 7.653; 6.16, 7.608; 5.53, 7.560; 4.91, 7.506; 4.29, 7.440; 3.89, 7.388; 3.49, 7.336; 3.29, 7.305; 2.89, 7.239; 2.50, 7.168; 2.10, 7.084; 1.71, 7.003; 1.33, 6.864; 0.95, 6.676; 0.56, 6.303.

Series c. 7.10, 7.664; 6.46, 7.623; 5.83, 7.579; 5.21, 7.530; 4.59, 7.467; 3.98, 7.401; 3.38, 7.322; 2.98, 7.261; 2.59, 7.190; 2.19, 7.106; 1.81, 7.018; 1.42, 6.884; 1.04, 6.698; 0.56, 6.367.

***B* = 0.100 *M*, $[\text{ClO}_4^-] = 0.21 \text{ M}$**

$Z \times 10^3$, $-\log h$. 2.46, 7.297; 1.85, 7.173; 1.65, 7.121; 1.25, 6.994; 1.05, 6.906; 0.85, 6.837; 0.65, 6.710; 0.45, 6.541; 0.25, 6.283.

Special series of measurements where B was varied

$Z \times 10^3$, *B*, $-\log h$. 8.05, 0.700, 7.116; 7.97, 0.651, 7.143; 7.85, 0.588, 7.182; 7.65, 0.507, 7.229; 7.45, 0.446, 7.266; 7.25, 0.398, 7.298; 6.85, 0.327, 7.342; 6.45, 0.278, 7.358; 5.65, 0.213, 7.405.

Radiometer PHM4, Copenhagen, this instrument was frequently calibrated against a Leeds & Northrup potentiometer of type K3. Ag—AgCl electrodes were prepared according to Brown¹⁵.

The potential of the quinhydrone half-cell was measured by immersing into solution S two platinum foil electrodes. These always agreed within 0.1 mV. The quinhydrone, Merck p.a., had been recrystallized from water, and had been kept for a week in a desiccator over H₂SO₄. No protolyzing impurities or Fe(III) and Cl⁻ ions could be detected in the recrystallized product.

ASCERTAINMENT OF THE COMPOSITION OF THE HYDROLYSIS PRODUCTS

The sets of $Z(\log h)_B$ data, which are summarized in Table 1 and are graphically represented in Fig. 2, form the basis of the following calculations.

The method to be employed for finding the composition of the hydrolyzed species and the corresponding equilibrium constants is mainly determined by the range of B studied. In the present work B values ranging from 0.1 to 1.45 M could be investigated. With more dilute solutions (*e.g.* for $B = 0.05$ M) we have not been able to obtain reliable results, thus, when a series of measurements was repeated, the deviations of the corresponding Z values considerably exceeded one percent, which we set as the highest limit of acceptable uncertainty. This failure can be explained by the slight buffer capacity of dilute cadmium solutions. The buffer capacity is proportional to BZ , and Fig. 2 shows that the accessible range of BZ narrows rapidly as B is decreased. In forthcoming publications, dealing with investigations where hydrolyzed solutions were prepared by electrolysis (using a coulometer), some arguments will

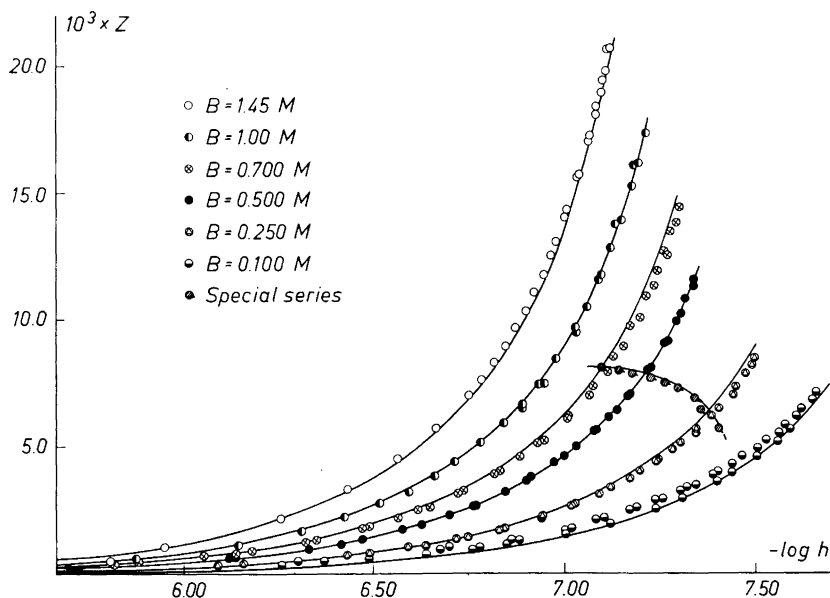


Fig. 2. Z = the average number of hydrogen ions set free per cadmium atom as a function of $-\log h$. The curves were calculated with the $\beta_{p,q}$ values proposed in Table 3.

be presented which make it seem probable that the difficulties arising for $B < 0.1$ M are mainly caused by nephelometrically undetectable amounts ($\sim 1-2$ micromoles/liter of filtrate) of $\text{Cd}(\text{OH})_2$ particles passing through the filter.

The variations of the activity factors of the reacting species, due to the replacement of 2Li^+ by Cd^{2+} , are certainly not negligible in our test solutions containing such high concentrations of cadmium. Consequently, our data cannot be treated by methods worked out for an inert medium. On the other hand the self-medium method proposed by Hietanen and Sillén¹⁶ proved to be of great value (section I). The main idea of this method is that data obtained at each value of B are considered separately. Since only low Z values were accessible and since Cd^{2+} was found to be a weak acid, the changes in composition are small when B is kept constant while the hydrolysis is suppressed by adding dilute HClO_4 to a solution saturated with $\text{Cd}(\text{OH})_2$. Thus the assumption that for $B = \text{constant}$ the activity factors are constants may be regarded as a close approximation. Evidently, by the separate analysis of each set of $Z(\log h)_B$ data only the number of OH groups bound to the hydrolysis products, p , and the corresponding homoligandic equilibrium constants, K_p , can be evaluated, whereas this treatment cannot give any information on the number of cadmium atoms, q , present in the complexes, because B is always very close to b .

A plausible estimate of the probable values of q may be obtained by examining the functions $K_p(B)$. When we disregard the variation of the activity factors K_p represents a power series of the single variable B . If the series contains only one or two terms, reasonable values for the exponents of B , the q 's, can be derived easily (section II). Clearly, this treatment is approximate and the conclusions involve the uncertainty due to the unknown variation of activity factors. Nevertheless some evidence will be given¹⁷ in a work concerned with the hydrolysis of Y(III), covering the yttrium concentration range 0.01 to 1 M, that the values of q and $\beta_{p,q}$ deduced by the method of section II are not likely to be seriously in error.

In sections I and II a number of approximations were introduced and the several groups of data were discussed separately, it was therefore desirable to compare the complete set of data with normalized model functions based on the exact equations. This forms the subject of section III, which moreover contains a treatment according to the generalised least squares method, proposed by Sillén²⁰, to provide an additional check on the consistency of the results of our calculations.

I. Determination of p by the self-medium method

In this section each set of $Z(\log h)_B$ data will be discussed separately.

In a series of solutions, where B is kept constant while Z is varied, the molar concentration of OH groups bound per cadmium, $h-H$, can be expressed by the equation

$$h-H = BZ = \sum_p \sum_q p [\text{Cd}_q(\text{OH})_p] = \sum_p \sum_q p \beta_{p,q} b^q h^{-p} \quad (6)$$

In (6) the variables p and q may assume a series of integral values, and $\beta_{p,q}$ designates the formation constant of the hydrolysis product $\text{Cd}_q(\text{OH})_p^{(2q-p)+}$

$$\beta_{p,q} = [\text{Cd}_q(\text{OH})_p] h^p b^{-q} \quad (7)$$

To find the number of OH groups bound to the hydrolysed species the $Z(\log h)_B$ data will be compared with functions representing different hypotheses concerning the prevailing values of p . For the calculation of these model functions on the basis of (6) some assumptions must be made also about the dependence of b upon h . Since the maximum Z has never exceeded 0.021, b must be always very close to B . Consequently, we have to estimate only an upper and a lower limit for b and then we have to examine how much the deduced values of p are influenced when b varies from maximum to minimum.

The inequality $b < B$ yields B as the upper limit, to estimate the lower one we have postulated that hydrolysis products with $q/p > 2$ do not occur in appreciable concentrations. This postulate is based on the consideration that the formation of species with $q/p > 2$ would involve an accumulation of positive charges which is improbable because of the electrostatic repulsion.

The results of section II strongly support the validity of this postulate. Were complexes with $q/p > 2$ formed in significant amounts, their presence would certainly have been detected by the treatment described in section II.

We may therefore regard the inequality

$$B > b \geq B(1 - 2Z) \quad (q \leq 2p) \quad (8)$$

to provide reasonable limits for b .

On the basis of (6) and (8) two types of model functions, F and Φ , have been constructed to approximate the experimental BZ values:

$$F(h) = \sum_p \sum_q p B^q \beta_{p,q} h^{-p} = \sum_p K_p h^{-p} \quad (> BZ) \quad (9)$$

and

$$\Phi(w) = \sum_p \sum_q p B^q \beta_{p,q} w^p = \sum_p K_p w^p \quad (\leq BZ) \quad (10)$$

where K_p , the homoligandic equilibrium constant, is equal to

$$K_p = \sum_q B^q \beta_{p,q} \quad (11)$$

and

$$w = (1 - 2Z)^2 h^{-1} \quad (12)$$

When a particular hypothesis concerning the p values was tested, both the F and the Φ functions were compared with the data. It should be pointed out immediately that identical numbers were obtained for the most probable values of p when either approximation (9) or (10) was used. Moreover, the $\log K_p$ values calculated with F and Φ never differed more than 0.01 units. These results indicate that the conclusions derived by the self-medium method are not appreciably influenced by the fact that the b values are not known exactly. In the following discussion only the F functions will be given explicitly, the calculations involving Φ were analogous except that w was used instead of h^{-1} as the independent variable.

In the first instance we have attempted to explain the data in the simplest way by assuming that all the hydrolysis products are homoligandic. The F

function corresponding to the hypothesis, that a single value of $p = P$ occurs, F_p , can be brought to the following normalized form

$$F_p = P K_p h^{-P} = P x^P = F_p(\log x), \log x = P^{-1} \log K_p - \log h \quad (13)$$

A group of F_p functions covering the range of P from 1 to 6 was plotted, and each of them was superimposed on the $BZ(\log h)_E$ data. The complete set of $BZ(\log h)_{0.1}$ data was found to be satisfactorily described by $F_1(\log x)$. No member of the F_p group could, however, be fitted throughout the experimentally accessible $\log h$ range to any set of data obtained in more concentrated cadmium solutions. On the other hand, at each value of $B \geq 0.25$ M the experimental points seemed to approach F_1 as Z decreased, and moreover, the lower the value of B considered the greater was the part of the total range of Z which appeared to agree with F_1 .

We may thus conclude that in solutions where BZ is low the main products of hydrolysis are monoligandic, while species containing several OH groups are formed in increasing amount as BZ tends to the maximum value attainable 0.03. On the basis of the F_p functions no certain information could be gained concerning the composition of the multiligandic species.

The predominance of monoligandic species in the region where $BZ \leq 0.003$ can be clearly demonstrated by calculating the average number of OH groups bound to the hydrolysis products, \bar{p} , as a function of $\log h$. Using approximation (9) \bar{p} is obtained by the equation⁸

$$\bar{p} = \frac{\sum p [\text{Cd}_q(\text{OH})_p]}{\sum [\text{Cd}_q(\text{OH})_p]} = BZ \int_{\log h}^{\infty} BZ \, d \log h)^{-1} \quad (14)$$

When BZ is approximated with Φ the integral in (14) is to be replaced by $\int_{\log w}^{\infty} BZ \, d \log w$. The \bar{p} values calculated with the F and Φ functions were found in each case to coincide within the limits of experimental uncertainty.

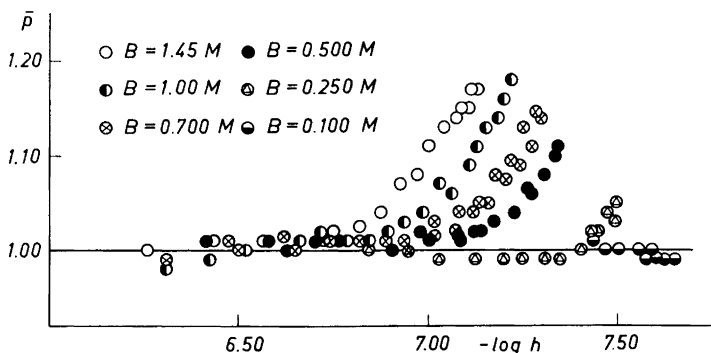


Fig. 3. \bar{p} = average number of OH groups bound to the hydrolysis products as a function of $-\log h$.

The integration was performed using the trapezoidal rule. In order to avoid the arbitrariness associated with smoothed curves the experimental points were taken directly, thus unequal integration intervals were chosen.

The magnitudes of the residual integrals $\int_{-6.5}^{\infty} BZ \, d \log h$ and $\int_0^{-6.5} BZ \, d \log w$ were estimated graphically using the extrapolation method described earlier⁸. For $Z > 0.003$, where the uncertainty arising from the extrapolation becomes negligible, the calculated \bar{p} values may be considered to be reliable within $\pm 2\%$.

The $\bar{p}(\log h)_B$ plots, shown in Fig. 3, indicate that at each value of B a $\log h$ region can be found where \bar{p} remains constant within 1.00 ± 0.02 . For each experimental point falling in this region, which is seen in Fig. 3 to be narrowed as B increases, $\log K_1 = \log (BZh)$ was calculated, these have shown no appreciable trend with h . The most probable values of $\log K_1(B)$ are summarized in Table 2, the uncertainty of the constants was assumed to be equal to the maximum deviation from the mean value.

In order to explain the data from measurements made in solutions where $BZ > 0.003$ it was assumed that besides Cd_pOH another species containing p' OH groups, $Cd_{q'}(OH)_{p'}$, is also formed. It is recalled that in these formulas q and q' denote unknowns which can take several integral values, whereas p' is a constant.

To test the validity of this assumption which may be expressed by the equation

$$BZ = F_{1,p'} = K_1 h^{-1} + p' K_{p'} h^{-p'} \tag{15}$$

the data were recalculated to the form $\log (BZh)$ versus $(\log h)_B$, and a plot of them was constructed. The plot was compared with the following normalized function derived from (15)

$$W_{p'} = \log F_{1,p'} - \log K_1 + \log h = \log (1 + p'u^{p'-1}) = W_{p'}(\log u) \tag{16}$$

$$\log u = (p'-1)^{-1} \log (K_{p'}/K_1) - \log h \tag{17}$$

The advantage of using (16) is that it makes possible to evaluate both $\log K_1$ and $\log K_{p'}$. A group of $W_{p'}$ functions covering the p' range 2 to 8 was calculated and a plot of each was superimposed on the data. All the available sets of $\log (BZh)$ data could be fitted to W_4 , whereas systematic deviations were found

Table 2. Survey of the homoligandic equilibrium constants.

$B \text{ M}$	$-\log K_1$ eqns. (14) and (16)	$-\log K_4$ eqn. (16)	p' $b = B$	$b = \frac{p'}{1-2Z} B$
0.100	10.81 ± 0.02	—	—	—
0.250	10.19 ± 0.01	—	—	—
0.500	9.65 ± 0.01	33.10 ± 0.01	4.5 ± 0.5	4.1 ± 0.5
0.700	9.39 ± 0.01	32.57 ± 0.01	4.1 ± 0.5	3.9 ± 0.5
1.000	9.08 ± 0.01	31.96 ± 0.01	3.8 ± 0.5	3.6 ± 0.5
1.450	8.74 ± 0.01	31.30 ± 0.01	4.0 ± 0.5	3.8 ± 0.5
0.100 *	10.89 ± 0.01	—	—	—

* $[ClO_4^-] = 0.21 \text{ M}$.

in some part of the studied $\log h$ range with any other member of the $W_{p'}$ group. This result indicates that the data of present accuracy can be satisfactorily explained by assuming the formation of Cd_7OH and $\text{Cd}_{q'}(\text{OH})_4$ but no other mechanism involving only two p values is acceptable.

The probable values of the constants $\log K_1$ and $\log K_4$ were obtained by reading off in the position of best fit the difference $W_4 - \log(BZh)$ and $\log u - (-\log h)$. The fit was always found to be satisfactory. The $\log K_1$ values calculated in this way practically coincided with those in Table 2 which were derived on the basis of the $\bar{p}(\log h)_B$ plots. The $\log K_4$ values obtained with (16) are also inserted in this table.

Additional evidence can be afforded for the conclusions reached with the curve-fitting by a numerical treatment which enables one to examine systematically how the experimental error and the underlying assumptions affect the estimation of p' . Eqn. (15) may be rearranged to the form

$$\log(BZ - K_1 h^{-1}) = \log p' + \log K_{p'} - p' \log h \quad (18)$$

Thus, provided the hypothesis that only species with $p = 1$ and $p = p'$ are formed is valid, $\log(BZ - K_1 h^{-1})$ should be a linear function of $\log h$ having the slope $-p'$. For each experimental point corresponding to $BZ \geq 0.003$ three values of $\log(BZ - K_1 h^{-1})$ have been calculated by inserting the most probable value of $\log K_1$, and as well as its lower and higher limit, as given in Table 2. In this connection there was no need to take into account the uncertainty of BZ , since it is much lower than that of K_1 . For a particular set of data the most probable value of p' was computed with the formula

$$p' = \frac{\sum_1^n y_i - \frac{2n}{n+1} y_{n+1}}{\sum_1^n x_i - \frac{2n}{n+1} x_{n+1}}$$

where y_i and x_i designate a pair of values of $\log(BZ - K_1 h^{-1})$ and $\log h$. In order to gain an idea on the influence of random experimental error the number of points ($2n$) considered for a particular value of K_1 was varied from 4 to 12. In the final step all the calculations were repeated with approximation (10), in this case instead of (18) the equation

$$\log(BZ - K_1 w) = \log p' + \log K_{p'} + p' \log w \quad (18a)$$

was used.

The results are presented in Table 2, the limits indicate the maximum deviation from the mean of all the p' values obtained by varying K_1 and n . The reasonable constancy of the p' values appears to justify the conclusions deduced graphically. Thus the experiments have been of sufficient accuracy to exclude the hypothesis that besides Cd_7OH and $\text{Cd}_{q'}(\text{OH})_4$ other hydrolysis products may be present in appreciable concentration.

II. Estimation of the probable values of q and q'

If we introduce the approximation that in our solutions of $[\text{ClO}_4^-] = 3 \text{ M}$ the activity factor ratios occurring in the exact expressions for the formation constants

$$\beta'_{p,q} = \beta_{p,q} f(p,q) f^p(\text{H}^+) f^{-q}(\text{Cd}^{2+}) \quad (19)$$

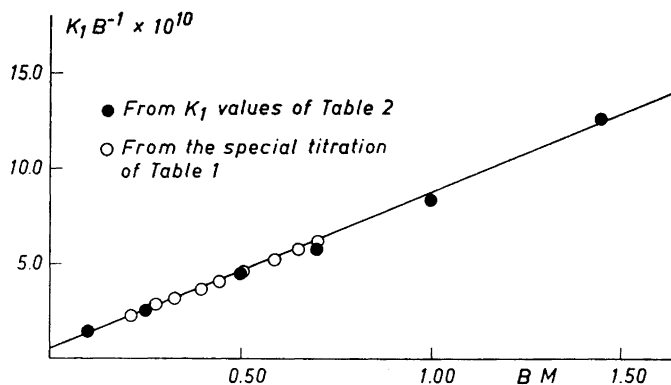


Fig. 4. $K_1 B^{-1}$ (eqn. (20)) as a function of B . The line represents the equation:

$$K_1 B^{-1} = 5 \times 10^{-11} + 8.2 \times 10^{-10} B.$$

vary to a negligible extent, the number of cadmium atoms present in the species Cd_qOH and $\text{Cd}_q(\text{OH})_4$ can be evaluated by analysing the functions $K_1(B)$ and $K_4(B)$.

According to (11) K_1 is equal to

$$K_1 = B \beta_{1,1} + B^2 \beta_{1,2} + \dots \quad (20)$$

A plot of $K_1 B^{-1}$ versus B is shown in Fig. 4. This plot was calculated from the K_1 values of Table 2 (full circles), and as well as from the series of measurements performed by adding 3 M LiClO_4 to a partially hydrolyzed solution of $B = 0.7$ M (circles). It can be inferred from the $\bar{p}(\log h)_B$ functions in Fig. 3 that each point of this series of measurements (recorded in Table 1) falls in the region where the monoligandic species predominate.

All the points of Fig. 4 are seen to fit a straight line within the limits of experimental uncertainty, consequently the data can be explained by assuming the formation of CdOH^+ and $\text{Cd}_2\text{OH}^{3+}$ only. The most probable values of $\beta_{1,1}$ and $\beta_{1,2}$ were estimated using the method of least squares. This yielded the results

$$\log \beta_{1,1} = \log ([\text{CdOH}^+] h [\text{Cd}^{2+}]^{-1}) = -10.3 \pm 0.2$$

and

$$\log \beta_{1,2} = \log ([\text{Cd}_2\text{OH}^{3+}] h [\text{Cd}^{2+}]^{-2}) = -9.10 \pm 0.05$$

In order to find the prevailing values of q' a plot of $\log K_4 = \log (\Sigma B^{q'} \beta_{4,q'})$ against $\log B$ was constructed. The points, taken from Table 2, seemed to fit a line of slope 4, indicating the formation of the single species $\text{Cd}_4(\text{OH})_4^{4+}$. The correctness of this hypothesis is illustrated in Fig. 5 where $\log K_4 - q' \log B$ is plotted as a function of B for the q' values 3, 4 and 5. It is seen from this figure that $\log K_4 - 4 \log B$ shows no appreciable trend with B , while large systematic deviations occur for $q' = 3$ and $q' = 5$. Moreover, the deviations

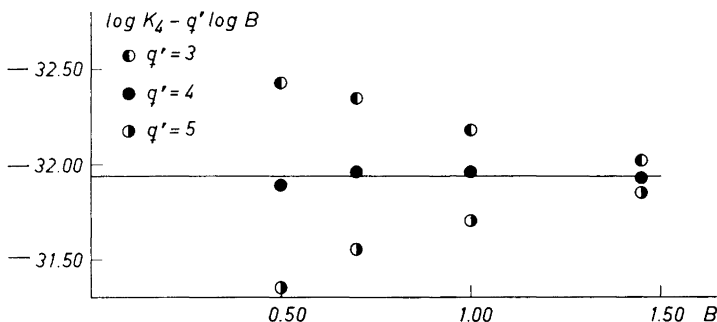


Fig. 5. $\log K_4 - q' \log B$ (eqn. (11)) as a function of B for q' values 3, 4 and 5. For the sake of clarity the points for $q' = 3$ have been shifted vertically by -0.25 units and those for $q' = 5$ by $+0.25$ units.

change sign as q' passes through 4. Thus the data are only compatible with the assumption that $\text{Cd}_4(\text{OH})_4^{4+}$ is formed. Taking the average value of $\log K_4 - 4 \log B$ we can write

$$\log \beta_{4,4} = \log [(\text{Cd}_4(\text{OH})_4^{4+}) h^4 [\text{Cd}^{2+}]^{-4}] = -31.8 \pm 0.1$$

III. Comparison of the complete set of data with normalized model functions

The calculations presented in section II have furnished evidence for the formation of the monoligandic species CdOH^+ and $\text{Cd}_2\text{OH}^{3+}$, and for the presence of a single tetraligandic hydrolysis product $\text{Cd}_4(\text{OH})_4^{4+}$. The numerical values given in section II for the formation constants should be regarded, however, as first approximations and should be refined by direct comparison with the $BZ(\log h)_B$ data.

In order to obtain more trustworthy values of $\beta_{p,q}$ the totality of the experimental data was compared with normalized projection maps. This method, which has been developed by Sillén¹⁸, has proved to be of great value for the investigation of complicated ionic equilibria. It has the essential advantage over many other approaches that the same set of experimental data can be compared with model functions representing different hypotheses, and moreover the method yields a reliable estimate for the uncertainty in the magnitudes of the formation constants. Since the projection maps are calculated with exact equations the results derived on the basis of them provide a check on the magnitude of the errors caused by approximations (9) and (10).

The computation procedure described in a previous publication¹⁹ was closely followed. First the $Z(\log h)_B$ data were recalculated to the form $\log B(3 \log B - 4 \log h)_Z$ by graphical interpolation. This did not involve any significant loss of accuracy because the curves fitted to the $Z(\log h)_B$ points had a rather low slope. A plot of the $\log B(3 \log B - 4 \log h)_Z$ data, covering

the Z range 0.002 to 0.015, has been compared with a group of normalized functions

$$\log B^*(X)_{z,\gamma} \tag{21}$$

where $\log B^* = \log B + 1/3 \log \beta_{4,4} - 4/3 \log \beta_{1,1}$ (22)

$$X = 3 \log B - 4 \log h + \log \beta_{4,4} \tag{23}$$

and

$$\log \gamma = \log \beta_{1,2} + 1/3(\log \beta_{1,1} - \log \beta_{4,4}) \tag{24}$$

The $\log B^*(X)_{z,\gamma}$ functions are based on the fundamental equations

$$B = b(1 + \beta_{1,1}h^{-1} + 2 \beta_{1,2} b h^{-1} + 4 \beta_{4,4}b^3 h^{-4}) \tag{25}$$

and

$$Z = (\beta_{1,1}h^{-1} + \beta_{1,2}b h^{-1} + 4\beta_{4,4}b^3 h^{-4})(1 + \beta_{1,1}h^{-1} + 2 \beta_{1,2}b h^{-1} + 4 \beta_{4,4}b^3 h^{-4})^{-1} \tag{26}$$

Introducing the new variables

$$\alpha = \beta_{1,1}h^{-1} \text{ and } u = \beta_{4,4}^{-1/3} \beta_{1,1}^{-1/3} h^{-1}b \tag{27}$$

two of the three constants can be eliminated from (25) and (26) which then will take the form

$$B^* = u \alpha^{-1}(1 + \alpha + 2\gamma u + 4 u^3\alpha) \tag{28}$$

$$Z = (\alpha + \gamma u + 4\alpha u^3)(1 + \alpha + 2\gamma u + 4\alpha u^3)^{-1} \tag{29}$$

Eqs. (28) and (29) show that when Z and γ are kept constant α becomes a function of u only, consequently $\log B^*(X)_{z,\gamma} = \log B^*(3 \log B^* + 4 \log \alpha)_{z,\gamma}$

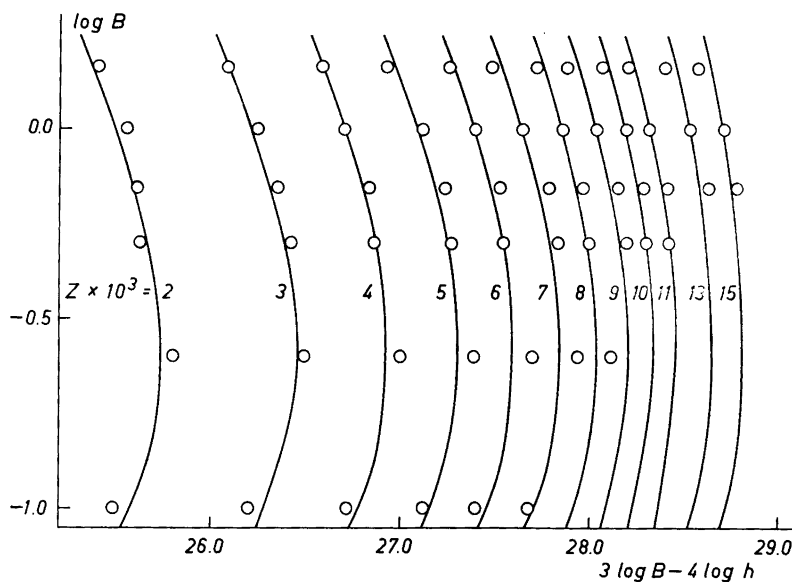


Fig. 6. $\log B$ as a function of $3 \log B - 4 \log h$ in the Z range 0.002 to 0.015. The circles represent the experimental data and the curves were calculated with the formation constants given in the third row of Table 3.

Table 3. Survey of the formation constants estimated using different approaches.

Method	$\log \beta_{1,1}$	$\log \beta_{1,2}$	$\log \beta_{4,4}$
Eqn. (11)	-10.3 ± 0.1	-9.10 ± 0.05	-31.8 ± 0.1
Projection maps	-10.2 ± 0.1	-9.10 ± 0.05	-31.8 ± 0.2
LETAGROP	$-10.2_6 \pm 0.06$	-9.10 ± 0.01	-31.82 ± 0.03
proposed value	-10.2 ± 0.1	-9.10 ± 0.05	-31.8 ± 0.1

can be evaluated by ascribing a series of values to u . The actual calculations were carried out with a Ferranti-Mercury high speed computer employing the "PROKAIS" program of Ingri and Sillén²¹. $\log \gamma$ was varied from -1.75 to -2.75 , and for each value of γ a family of $\log B^*(X)_{Z,\gamma}$ functions, where Z ranged from 0.002 to 0.015, was calculated. Each family of plots representing a particular γ value was superimposed on the experimental points. The best agreement was found with $\log \gamma = -1.90$, but the fit was acceptable throughout the $\log \gamma$ interval -1.85 to -1.95 . By reading off the differences $\log B^* - \log B$ and $X - (3 \log B - 4 \log h)$ in the position of best agreement we have calculated, using (22), (23) and (24), the constants given in Table 3. The fit obtained with these $\beta_{p,q}$ values is illustrated in Fig. 6.

The magnitudes of the formation constants estimated using the projection maps are seen from Table 3 to agree satisfactorily with those derived in section II. Thus the approximate method employed there yielded reliable conclusions in our case.

Finally the data have been treated by the generalized least square method, "LETAGROP", recently proposed by Sillén²⁰. 120 experimental points were chosen and the set of $\beta_{1,1}$, $\beta_{1,2}$ and $\beta_{4,4}$ values making the error square sum $= \Sigma(Z - Z_k)^2$ a minimum were calculated as outlined in Ingri and Sillén's publication²¹. Z_k in the error square sum expression denotes the value of the function (26) for a particular triplet of the constants. The values of $\log \beta_{1,1}$, $\log \beta_{1,2}$ and $\log \beta_{4,4}$ leading to the minimum error square sum are recorded in Table 3, the results are seen to agree well with those deduced by other approaches. The uncertainties given for the constants calculated with "LETAGROP" represent three times the "standard deviations" as defined by the D boundary²⁰, these are of course lower than the maximum errors estimated on the basis of the graphical methods.

As the most important test for the correctness of our calculations let us consider Fig. 2. This shows that the data of present accuracy can be satisfactorily described with the proposed values of the constants given in Table 3. From the $(Z - Z_k)$ values computed with the LETAGROP a quantitative measure of the agreement may be gained. From a total 120 points 69 have shown positive deviations whereas 51 negative ones. The average of the positive deviations $(1 - Z_k Z^{-1})$ amounts to 4% and the average of the negative deviations $(Z_k Z^{-1} - 1)$ equals 2.5%. The magnitude and the sign of the deviations did not exhibit any appreciable trend either with B or $\log h$.

It may be inferred from the values of the formation constants that in the range of B studied the main product of hydrolysis is Cd_2OH^{3+} . The predominance of this highly charged species seems to suggest that short range forces, which can counteract a considerable electrostatic repulsion, are mainly responsible for the formation of the polynuclear cadmium species.

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