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A Liquid Distribution Study of the Hydrolysis of Cd^{2+}

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The distribution of cadmium at 25°C between the liquid amine LA-1 in benzene and 3 M $Na(ClO_4,OH)$ has been measured, as a function of $[OH^-]$, with radioactive cadmium. The distribution data could be explained by Dyrssen and Sillén's[1] two-parameter approximation for the stepwise formation of $Cd(OH)_4^{2-}$ from Cd^{2+}. High-speed refinement of the parameters obtained by curve-fitting gave the following values with the σ-deviations:

$$a = \tfrac{1}{4} \log \beta_4 = 3.012 \pm 0.043$$
$$b = \tfrac{1}{2} \log K_n K_{n+1}^{-1} = 0.429 \pm 0.047$$
$$\log \gamma_2 \beta_2 (20\ \%\ \text{LA-1}) = 10.345 \pm 0.082$$

The value for the formation constant of $Cd(OH)^+$, $\log K_1 = 4.30 \pm 0.18$, agrees very well with the value in 3 M $LiClO_4$ determined by Biedermann and Ciavatta[2].

Some experiments were also carried out with radioactive $Cd(OH)_2$ in a solubility column[3], but the solubility is lower than that predicted from the values of a and b and Schindler's[4] value of the solubility product of $Cd(OH)_2$ in 3 M $NaClO_4$.

Biedermann and Ciavatta[2] have investigated the hydrolysis of Cd^{2+} in the concentration range above 0.1 M by emf titrations. In this connection it seemed worthwhile to study the hydrolysis of cadmium also at low concentrations, where only mononuclear species might be formed. Previously we had carried out both solubility and distribution experiments[3,5,6] to study the hydrolysis of Hg^{2+}, Ag^+ and VO_2^+, and at a present no other methods seem to be more favorable at low metal concentrations.

A previous investigation by Gayer and Woontner[7] of the solubility of $Cd(OH)_2$ as a function of pH ($-\log [OH^-]$, see below and Fig. 4) did not agree with reasonable values of the solubility product[8], and indicated that difficulties could be met in measuring the solubility even if a column with radio

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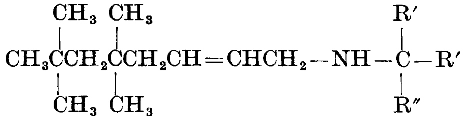
active $Cd(OH)_2$ was used. Some experiments with a solubility column (see below and Fig. 2) confirmed this.

After some preliminary distribution experiments carried out by Mr. John Crabtree, it was found that cadmium(II) could be extracted with benzene (as $Cd(OH)_2$, as was proved later), if the liquid amine Amberlite LA-1 was added to the benzene phase. Similarly Ag^+ is extracted with quinoline in benzene [5], except that in this case $AgClO_4$ is extracted instead of AgOH.

EXPERIMENTAL

Extraction with amine. The amine used was an Amberlite LA-1 product (Rohm & Haas), which is a mixture of highly branched unsaturated, secondary aliphatic amines. A structure formula for the mixture has been indicated as follows:



$$CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2CH{=}CHCH_2{-}NH{-}\underset{R''}{\overset{R'}{C}}{-}R'$$

where $R + R' + R'' = 11-14$ carbon atoms. It is liquid at room temperature. The mean molecular weight of the commercial product is 372 and its molarity at 25°C is about 2.25.

Organic amines may contain more or less carbonate and therefore the 20 % (vol.) amine solutions in benzene (p.a. Merck), were shaken overnight with half their volume of 0.1 M barium chloride or nitrate (barium hydroxide might be more effective) and the two phases then centrifuged. The lighter benzene phase was pipetted off and this amine solution was used in the experiments; lower amine concentrations were obtained by dilution with benzene.

Sodium perchlorate was prepared by dissolving the theoretically needed amount of sodium carbonate (p.a. Merck) in concentrated perchloric acid (p.a. Kebo) and crystallizing the product two times from water. A stock solution (about 6 M) was prepared from this material. The concentration of the sodium perchlorate stock solution was determined by evaporating a 5 ml sample to dryness and weighing.

A dilute perchloric acid solution was titrated against crystallized thallium carbonate using a bromocresol green-methyl red mixture in alcohol as indicator (Ref.[9], p. 83). Sodium hydroxide stock solution was prepared according to Sörensen (Ref.[9], p. 70) in a plastic flask, in which it was kept under an atmosphere of nitrogen. The 1.0, 0.1 and 0.001 M sodium hydroxide solutions were prepared by diluting this stock solution with sodium perchlorate so that the ionic strength of the solutions came to be 3.0 M. The concentrations were determined by means of standard perchloric acid solutions using the same indicator as above.

A stock solution of 0.04 M borax (Merck, p.a.) in 2.92 M sodium perchlorate was also prepared.

Cadmium oxide was prepared by dissolving cadmium metal (p.a.) in conc. nitric acid (Merck, p.a.), evaporating the solution to dryness in a platinum crucible, and heating the residue to about 600°C for about half an hour. A part of this product was irradiated in the Swedish reactor R1. The cadmium isotope used was ^{115m}Cd with the half-life of 43 days; ^{115}Cd (2.3 days) with its daughter ^{115m}In were allowed to die out, in most experiments. The active cadmium oxide was dissolved into 3 M perchloric acid and diluted with 3 M sodium perchlorate.

Equal total volumes (10 or 15 ml) of the aqueous and organic phases were equilibrated in 50 ml Pyrex stoppered centrifuge tubes. The phases were mixed by repeated slow inversion of the tubes at 25°C in a thermostated room. The acidity (or basicity) of the aqueous phase was varied, but the ionic strength was always kept at 3 M with sodium perchlorate. Equilibrium was obtained in 2 h, but in many cases the samples were shaken overnight. No time-dependent differences between the samples were observed.

After shaking, the samples were centrifuged and 5 ml of the aqueous phase taken to measure its pH (or $-\log [OH^-]$) and 2 ml to measure the γ-activity or 10 ml to measure the β-activity. Activity measurements were also made with the organic phase. The measurements of the γ-activity of the solutions, which were contained in plastic tubes, were made with a Tracerlab Versa/Matic II spectrometer connected with a Tracerlab SC-57 low background well scintillation counter. The β-activity measurements were made with a Tracerlab SC-18 Superscaler or SC-19 Utility Scaler connected with SC-31 Interval Timer and a Century Electronics M6 GM-tube for liquid samples. The results reported are mainly based on γ-activity measurements.

The measurements of $-\log [OH^-]$ were made with a Radiometer pH meter Type 4 using a Beckman glass electrode type E and a "Wilhelm" reference bridge of the type:

$$|3\ M\ NaClO_4|\ 2.9\ M\ NaClO_4 + 0.1\ M\ AgClO_4|\ AgCl,Ag$$

The reference buffer solution was 2.99 M with respect to sodium perchlorate and 0.01 M with respect to sodium hydroxide ($-\log [OH^-] = 2.00$). The value $pK_w = 14.22$ for the ionic product [10] of water in 3 M sodium perchlorate at 25°C was used to calculate $-\log [H^+]$ (pH).

Solubility column. The crystalline cadmium hydroxide used in the solubility measurements was prepared from cadmium nitrate by the ammonia method (*cf.* Schindler [4]). $Cd(NO_3)_2(H_2O)_4$ (Merck) was dissolved in water to give 0.5 liter of about 0.6 M solution, which was heated under reflux in an all-ground glass system. So much concentrated ammonia (p.a. Merck) was added to the solution that the cadmium hydroxide first precipitated redissolved again. The solution was refluxed as slowly as possible so as to reduce the rate of loss of ammonia. After refluxing overnight crystals of cadmium hydroxide (diameter about 1 mm) were found in the bottom of the flask. The refluxing was continued until no more crystals seemed to be formed. The crystals were then filtered under an atmosphere of nitrogen, washed with a little water and dried in a desiccator which contained ascarite.

About 1.5 g of the prepared cadmium hydroxide, enclosed in a quartz ampoule, was irradiated at Harwell, England for two months in a strong neutron flux. The short-lived isotope was allowed to die out, before the product was placed in the solubility column (about 1.3 g). A standard reference solution from the radiated product was also prepared. This had the composition: 9.438×10^{-3} M $Cd(ClO_4)_2$, 1.112×10^{-2} M $HClO_4$ and 2.97 M $NaClO_4$, and in the beginning of the experiments gave 119 400 cpm/ml in the β-tube (see above).

The solubility column and method used have been described previously by Dyrssen and Tyrrell [3]. The solution circulated in the column was 0.005 M in borax and the pH was varied by changing the sodium hydroxide concentration. The ionic strength of the solution was kept constant at 3 M with sodium perchlorate. One sample was taken per day and after this the solution in the column was changed. The pH and β-activity of the samples were measured as in extraction experiments above.

All experiments were performed at 25°C.

The data. In Fig. 1 the extraction data are given in the form of the logarithm of the distribution ratio $q = [Cd]_{tot,org}/[Cd]_{tot,aq}$ *versus* $-\log (OH^-]$. In Fig. 2 the solubility data are given in the form of the logarithm of the total cadmium concentration in solution, $[Cd]_{tot}$ *versus* $-\log [OH^-]$. The points in Fig. 1 represent the mean of six distribution experiments at different initial concentrations of cadmium(II) in the aqueous phase (3.9×10^{-5} to 3.9×10^{-4} M). The two sets of points in Fig. 2 represent two runs with the solubility column starting from each side of the solubility minimum.

Equilibrium constants

General equilibria:

$$\log K_w = \log [H^+][OH^-] = -14.22 \pm 0.02 \text{ (Ref.}^{10})$$
$$\beta_n = [Cd(OH)_n][Cd]^{-1}[OH]^{-n}$$
$$K_n = [Cd(OH)_n][Cd(OH)_{n-1}]^{-1}[OH]^{-1}$$

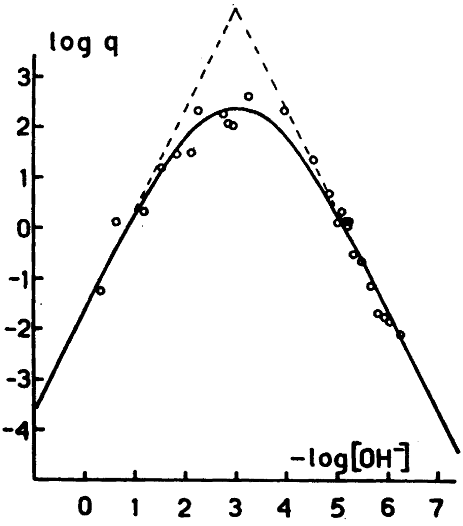


Fig. 1. Distribution of radioactive Cd(II) between benzene with 20 % Amberlite LA-1 and 3 M Na(OH,ClO$_4$) at 25°C. Each point is the mean value of six measurements. The curve is calculated with three parameters: a = 3.01, b = 0.43 and log $\beta_2\lambda_2$ = 10.35 (see text). The equations for the asymptotes (dashed lines) to the distribution curve are given in the text.

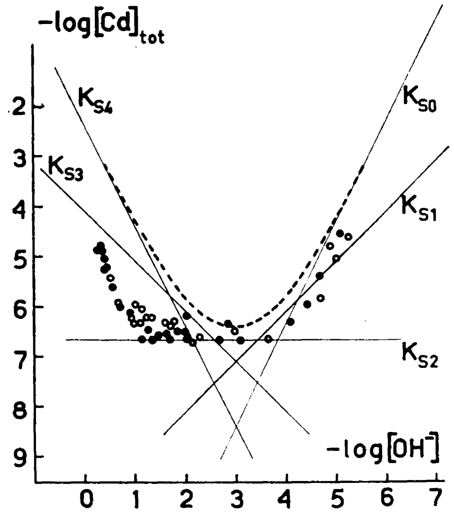


Fig. 2. Solubility of radioactive Cd(OH)$_2$ in 3 M Na(OH,ClO$_4$) at 25°C. The two different sets of points represent two different runs. The thin straight lines represent the equations log [Cd]$_{tot}$ = log K_{sn} + $(n-2)$ log [OH$^-$]. The dashed curve has the same form as in Fig. 1 and is calculated with a = 3.01, b = 0.43 and log K_{s0} = −14.41 (Schindler [4]); K_{sn} are also calculated from these constants.

Two-parameter approximation [1]:

$a = \frac{1}{4}\log\beta_4$
$b = \frac{1}{2}\log K_nK_{n+1}^{-1}$
$\log\beta_n = na - nb\,(4-n)$
$\log K_n = a + b\,(5-2n)$

Distribution constant:

$\lambda_2 = [\mathrm{Cd(OH)_2}]_{\mathrm{org}}[\mathrm{Cd(OH)_2}]^{-1}$:

Solubility equilibria:

$K_{s0} = [\mathrm{Cd^{2+}}][\mathrm{OH^-}]^2$
$K_{s1} = [\mathrm{CdOH^+}][\mathrm{OH^-}] = \beta_1K_{s0}$
$K_{s2} = [\mathrm{Cd(OH)_2}] = \beta_2K_{s0}$
$K_{s3} = [\mathrm{Cd(OH)_3^-}][\mathrm{OH^-}]^{-1} = \beta_3K_{s0}$
$K_{s4} = [\mathrm{Cd(OH)_4^{2-}}][\mathrm{OH^-}]^{-2} = \beta_4K_{s0}$
$[\mathrm{Cd}]_{\mathrm{tot}} = K_{s0}([\mathrm{OH^-}]^{-2} + \beta_1[\mathrm{OH^-}]^{-1} + \beta_2 + \beta_3[\mathrm{OH^-}] + \beta_4[\mathrm{OH^-}]^2)$

TREATMENT OF THE DISTRIBUTION DATA

The data are not accurate enough to allow a treatment which can be accepted without discussion. We shall therefore give several arguments below which support the results obtained by the following treatment:

It is known [2] that at low concentrations of Cd(II), $\mathrm{Cd^{2+}}$ is the main species in 3 M perchlorate solutions below pH 9 (above $-\log[\mathrm{OH^-}] = 5$). For values of $-\log[\mathrm{OH^-}]$ between 4.5 and 6.3 the distribution ratio, q, is approximately proportional to $[\mathrm{OH^-}]^2$, which gives the slope -2 in Fig. 1. This shows that cadmium is extracted as $\mathrm{Cd(OH)_2}$ in this $[\mathrm{OH^-}]$ region. We now make the assumption that this is the only cadmium species extracted into the benzene phase and that the distribution ratio λ_2 is independent of the $\mathrm{OH^-}$ and $\mathrm{ClO_4^-}$ content in 3 M $\mathrm{Na(OH,ClO_4)}$.

By variation of the amine concentration, $[\mathrm{L}]_{\mathrm{org}}$, in the benzene phase between 2 and 20 % we found that $q\,[\mathrm{L}]_{\mathrm{org}}^{-2}\,[\mathrm{OH^-}]^{-2}$ was approximately constant, which indicated that two amine molecules are bound to $\mathrm{Cd(OH)_2}$ and thus that four ligands are attached to Cd(II) in the organic phase.

When $[\mathrm{OH^-}]$ is increased above 0.001 M the distribution ratio decreases which indicates that negative hydroxo complexes are formed in the aqueous phase.

We also found that there was no systematic change of distribution ratio when the initial total concentration of cadmium was varied between 3.9×10^{-5} and 3.9×10^{-4} M. Thus we seem to be dealing only with mononuclear species.

In formulating a quantitative expression for the distribution ratio over the whole $[\mathrm{OH^-}]$ region there is no chemical reason to leave out any of the complexes $\mathrm{CdOH^+}$, $\mathrm{Cd(OH)_2}$, $\mathrm{Cd(OH)_3^-}$ and $\mathrm{Cd(OH)_4^{2-}}$ especially as the curve has a tendency to approach the slope $+2$ in Fig. 1. On the other hand the accuracy is too low to allow the determination of five parameters: β_1, β_2, β_3, β_4 and λ_2 or $\beta_2\lambda_2$. We therefore decided to use the two-parameter approximation given by Dyrssen and Sillén [1], especially as this approximation can very well describe the complex formation of Cd^{2+} with NH_3. In fact it was shown by Dyrssen and Sillén [1] that a curve of the present type should be obtained when an intermediate complex is extracted (case II). Thus

$$q = \frac{[\mathrm{Cd(OH)_2}]_{\mathrm{org}}}{[\mathrm{Cd^{2+}}] + [\mathrm{CdOH^+}] + [\mathrm{Cd(OH)_2}] + [\mathrm{Cd(OH)_3^-}] + [\mathrm{Cd(OH)_4^{2-}}]}$$

or

$$q = \frac{\beta_2\lambda_2[\mathrm{OH^-}]^2}{1 + \beta_1[\mathrm{OH^-}] + \beta_2[\mathrm{OH^-}]^2 + \beta_3[\mathrm{OH^-}]^3 + \beta_4[\mathrm{OH^-}]^4}$$

The asymptotes of the log q (—log $[OH^-]$) curve in Fig. 1 are

$$\log q = \log \beta_2\lambda_2[\mathrm{OH^-}]^2 = \log \lambda_2 + 2a - 4b + 2 \log [\mathrm{OH^-}]$$
$$\log q = \log \beta_2\lambda_2\beta_4^{-1} [\mathrm{OH^-}]^{-2} = \log \lambda_2 - 2a - 4b - 2 \log [\mathrm{OH^-}]$$

and they intersect at the point

$$-\log [\mathrm{OH^-}] = a$$
$$\log q = \log \lambda_2 - 4b$$

The point on the curve below this point has

$$\log q = \log \lambda_2 - 4b - \log (2 \times 10^{-3b} + 10^{-4b})$$

Approximate values of a, b and $\log \lambda_2$ could then be obtained by curvefitting [1,11].

These constants were then refined by high-speed computing using a Ferranti-Mercury computer and the LETAGROP program [12,13] with the following SP:

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1) Title; cadmiumdistr 3 par weight log $q$; newline; jump 2
3) $X = 0$; $K = P$; $i = 1(1)N$; print $(e_i)$ 1,3; repeat;
   $i = 1\ (1)\ 4$; $W = ie_1 + 4ie_2 - iie_2$; print $(W)$ 1,3;
   $b_i = \psi\exp(HW)$; repeat; $b_5 = \psi\exp\ (He_3)$
5) $U = \psi\ \exp\ (-HU_K)$
7) $W = b_4UUUU + b_3UUU + b_2UU + b_1U + 1$; $V = b_5UU/W$
10) $G_o = 1$; $W = \psi\ \log\ (V)$; $Z_o = W/H$; $Z_K = F_K$; jump 11; $\psi$ exp; $\psi$ log;
   close; →
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Then followed the 26 data as $F_K = \log q$; $U_K = -\log [\mathrm{OH^-}]$; $Z_K = 0$ and the DS part as 3; $e_1 = a = 3.00$; $e_2 = b = 0.45$; $e_3 = \log \beta_2\lambda_2 = 10.30$; $E = 0.0001$. The values of h_1 and h_2 were taken as 0.05 and h_3 as 0.10.

The computer found the error-pit easily and printed the following values and standard deviations:

$$a = 3.012 \pm 0.043$$
$$b = 0.429 \pm 0.047$$
$$\log \beta_2\lambda_2 = 10.345 \pm 0.082$$

The error sum, $U = \sum_{1}^{26} (\log q_{\mathrm{calc}} - \log q_{\mathrm{exp}})^2$, was 1.911 and $\sigma = \sqrt{U/23} = 0.288$.

In Fig. 3 a and b the iso-error lines for combinations of the parameters are shown with a rectangle which encloses the error-level $U + \sigma^2$ (the D-boundary). Other levels with $U + 2\,\sigma^2$, $3\,\sigma^2$ and $4\,\sigma^2$ are also shown. These

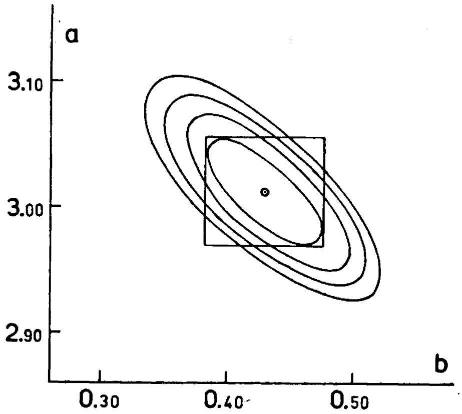

Fig. 3. Error-square sum ellipses for $U + \sigma^2$, $2\ \sigma^2$, $3\ \sigma^2$ and $4\ \sigma^2$ which show the way the parameters a and b influence each other. The rectangle encloses the D-boundary obtained by the LETAGROP computer program [13] and the point is the values of a and b which together with $\log \beta_2\lambda_2 = 10.345$ give the minimum error-square sum.

ellipses (or ellipsoids if the error in $\log \beta_2\lambda_2$ is included) have been calculated by the aid of a simple program. We may see from Fig. 3 that the constants a and b are not independent.

From the values of the three parameters the following approximate values of the stepwise formation constants may be calculated:

$$\log K_1 = 4.30 \pm 0.18$$
$$\log K_2 = 3.44 \pm 0.09$$
$$\log K_3 = 2.58 \pm 0.09$$
$$\log K_4 = 1.72 \pm 0.18$$
$$\log \lambda_2(20\ \%\ \text{LA-1}) = 2.60 \pm 0.36$$

Biedermann and Ciavatta [2] found $14.22-10.2 \pm 0.2 = 4.0 \pm 0.2$ for $\log K_1$ in good agreement with our value. The value given by Marcus [14] seems too high.

Comparison with other d^{10} ions

In order to see how reasonable the constants obtained above are, we may compare the formation constants of Ag^+, Cd^{2+} and Hg^{2+} with the ligands OH^- and NH_3:

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	Ref. No.
OH^- — 3 M $NaClO_4$					
Ag^+	1.5	2.0	< 0.3	—	5(K_1K_2), 15(K_2)
Cd^{2+}	4.3	3.4	2.6	1.7	this work
Hg^{2+}	10.7	11.6	< 0	—	16
NH_3 — 2 M NH_4NO_3					
Ag^+	3.20	3.83	—	—	8
Cd^{2+}	2.65	2.10	1.44	0.93	8
Hg^{2+}	8.8	8.7	1.0	0.8	8

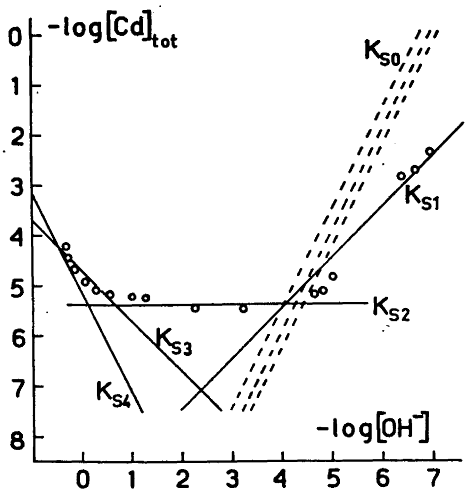

Fig. 4. Solubility data of Gayer and Woontner [7] plotted as log $[Cd]_{tot}$ against – log $[OH^-]$. The fulldrawn lines are based on their values of K_{s1} , K_{s2}, K_{s3} and K_{s4} (for equations see definition of equilibrium constants). The dashed lines represent different values of the solubility product (see text).

It may be seen that Ag^+ and Hg^{2+} form complexes with two OH^- and NH_3 readily, but additional ligands are only added with difficulty. The two ligands are coordinated linearly. The first constant is small as compared with the second one. Cd^{2+} on the other hand forms four complexes with NH_3 and the stepwise formation constants decrease regularly in nearly equal steps. Orgel [17] has explained this difference by the small d—s separation of Ag^+ and Hg^{2+} (5 eV against 10 for Cd^{2+}).

The formation constants of the OH^- complexes are larger than for NH_3 in the case of the divalent ions Cd^{2+} and Hg^{2+}, but smaller in the case of Ag^+. This may be a charge effect.

The comparison with other data which is made here gives some confidence in the data we have obtained for the complex formation between Cd^{2+} and OH^-.

THE SOLUBILITY MEASUREMENTS

As mentioned in the introduction Gayer and Woontner [7] have measured the solubility of $Cd(OH)_2$ at different pH. We have plotted their data as log $[Cd]_{tot}$ against —log $[OH^-]$ in Fig. 4 together with four straight lines (fulldrawn) which are determined by the values of log K_{s1}, log K_{s2}, log K_{s3} and log K_{s4} (tentative lower limit) given by Gayer and Woontner [7]. The most serious objection against the data is that they do not fit with reported values of the solubility product, K_{s0}; the lines (dashed), which are determined by log K_{s0} values of Moeller and Rhymer [8] (—13.49), Ishikawa and Shibata [8] (—13.93) and Feitknecht and Reinmann [8] (—14.20), are also shown in Fig. 4.

It should be mentioned that the straight lines in Fig. 4 are only asymptotes to the solubility curve. Their real positions relative to the curve are shown in Fig. 2.

Our solubility work was carried out in 3 M Na(OH, ClO_4) with a solubility column. The data differ from Gayer's and Woontner's [7] in two ways: The solubility minimum is about 20 times lower in our case; this may be a salt effect. The increase in solubility in the strongly alkaline region is more marked in our case.

However, our data also do not fit the values of K_{s0}. The value by Schindler [4] in 3 M $NaClO_4$ (−14.41, *cf.* also Ref.[2]) was used to fix the straight line with slope + 2 in Fig. 2. This line may be used to fit the curve obtained in the distribution experiments (Fig. 1) to the axes. As we do this we assume that we have only mononuclear complexes in the aqueous solution. Obviously, the solubility data are too low to fit the curve. One reason might be that in spite of our precautions the surface of the $Cd(OH)_2$ in the column might have been covered with $CdCO_3$ which is less soluble. By using another procedure to prepare $Cd(OH)_2$ it might be possible to solve this problem in the future.

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