Studies on the Hydrolysis of Metal Ions

20. The Hydrolysis of the Cd Ion, Cd^{2+}

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Potentiometric (glass electrode) titrations of Cd^{2+} with NaOH in 3 M (Na^+) ClO_4^- ionic medium at 25° C were made. At first a slight hydrolysis was observed (not much more than 1 %), according to $\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{H}^+$, $\log K_{a1} = -9.0 \pm 0.2$, and subsequently precipitation of $\text{Cd}(\text{OH})_2$ was found with $\text{pL} \geq 15.6$. There was no evidence for polynuclear species.

The method of study employed was the one in general use in this laboratory. Cadmium solutions were titrated with NaOH at $25.0 \pm 0.1^\circ \text{C}$, at constant Cd concentrations ($= B$), and in an ionic medium of 3 000 mM (Na^+) ClO_4^- . The cell used was: Ag, AgCl / 10 mM Ag^+ , 2 990 mM Na^+ , 3 000 mM ClO_4^- / 3 000 mM NaClO_4 / B mM Cd^{2+} , H mM H^+ , 3 000— $2B$ — H mM Na^+ , 3 000 mM ClO_4^- / glass electrode. In the range of pH under consideration the liquid junction potential could be neglected, and the electromotive force E in mV followed the expression

$$E = E_0 - 59.16 \log h = E_0 + 59.16 \text{ pH} \quad (1)$$

where h is the concentration of free hydrogen ions. The solutions were swept with purified nitrogen during titrations to guard against CO_2 . The titrations proved to be completely reversible and reproducible. Above pH 6 considerable time was needed for attainment of equilibrium, and at a definite higher pH precipitation could be observed.

H_0 , the excess acid present in the solutions, and E_0 were calculated by successive approximations from the portion of the titration data where no hydrolysis occurred (pH below 4). The average number of hydroxyl ions bound per metal ion, Z , was calculated from

$$Z = (h - H_0 - H) B^{-1} \quad (2)$$

where H was the analytical excess acid (acid added — base added / total volume), and h was obtained from the measured electromotive force by (1).

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Fig. 1. The average number of hydroxyl ions bound per metal ion, Z' , as function of the free hydrogen ion concentration $-\log h$. The symbols refer to the Cd concentrations B : $\times$ 10.7 mM, $\circ$ 26.8 mM, $\square$ 53.6 mM, $\bullet$ 107.1 mM, $\triangle$ 910 mM. The curves — were calculated with the limiting values of $\log K_{a1} = -8.8$ and -9.2 , while - - - - was calculated with the constant for reaction (4), $\log K_{a2} = -14.6$. Selection of a different value for K_{a2} will only shift the curve horizontally to left or right, but it will not fit the data.

Titration were made for five B values between 10 and 900 mM, and the data $Z(-\log h)_B$ calculated. The scattering was very considerable, because Z was usually much smaller than 0.01. Some acid impurity was found to be titrated together with the Cd, and its contribution, about 0.001 units, was subtracted from the Z values to give Z' . A plot of Z' against $-\log h$ is shown in Fig. 1.

Fig. 1 shows that B has no significant effect, as all points seem to fall on the same curve. A plot of $\log Z'$ against $-\log h$ gave a straight line $\log Z' = (-8.09 \pm 0.17) - (0.86 \pm 0.03) \log h$ as was found by a least squares treatment.

The following mechanisms were considered:

Mechanism (3) requires the data to show an effect due to B , and is ruled out. Mechanism (4) requires a slope of $+2$ in a $\log Z$ against $-\log h$ plot, and does not agree with the data (see also Fig. 1). Mechanism (5) is therefore the most likely. The equilibrium constant K_{a1} is given by

$$K_{a1} = [\text{CdOH}^+] h [\text{Cd}^{2+}]^{-1} \approx Z h \quad (6)$$

Table 1. The p_h of beginning precipitation and the solubility product of $\text{Cd}(\text{OH})_2$.

pB	1.970	1.572	1.271	0.970	0.041
p h	7.43	7.29	6.91	6.85	6.50
pL	15.5	15.4	15.8	15.7	15.5

because $Z = [\text{CdOH}^+] B^{-1}$ and as Z was very small, $B \approx [\text{Cd}^{2+}]$. From (6) follows $\log Z = \log K_{a1} - \log h$, and a plot of $\log Z$ against $-\log h$ should have unit slope. The observed slope of 0.86 is fairly near to unity, and the best straight line with unit slope through the points has $\log K_{a1} = -(9.0 \pm 0.2)$.

Chaberek, Courtney and Martell¹ found with a glass electrode $p_k = \log [\text{CdOH}^+] [\text{H}^+] [\text{Cd}^{2+}]^{-1} = -11.6$ at 30° and 0.1 M KCl ionic medium. These authors state, however, that "at best the value of k listed is reliable to only one significant figure". Earlier, the value $\log K_w - \log K_{a1} = -5.52$ was calculated by Jellinek² from distribution data of Löfman³, while Kullgren⁴ found by a kinetic method $\log K_{a1} = -9.49$ at 100° . The last two constants are of the same magnitude as the value found here. Hayek⁵ found negligible solubility of CdO in $\text{Cd}(\text{ClO}_4)_2$ solutions, which shows negligible formation of polynuclear hydrolysis products.

The approximate p_h of beginning precipitation enables one to calculate a lower limit of the solubility product L

$$pL \geq 2 pK_w - 2 p_h + pB \quad (7)$$

Assuming pK_w , the dissociation constant of water, to be 14.22, the data in Table 1 give the average $pL \geq 15.6$.

The following values of pL were previously reported in literature: Akselrud⁶ 14.58, Kertman⁷ 13.65, Bodländer⁸ 13.65, Tananaev⁹ 12.62, all at 18°C , Kovalenko¹⁰ 15.81 at 22°C and Piater¹¹ 14.22 at 25°C , all for infinite dilution.

Note added in proof: Since the completion of this work Gayer and Woontner¹² have published results of their solubility measurements at 25°C : $\log K_{a1} = -9.3$ and $pL = 14.31$, besides values for species formed in alkaline solutions.

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