BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(10), 2603—2604 (1974)

A Study on the Hydrolysis of Cadmium Ion in Aqueous 3M (Li)ClO_4 Solution

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(Received April 25, 1974)

Synopsis. The equilibrium constants of hydrolytic reactions of cadmium ion have been determined in a 3M (Li)ClO_4 aqueous medium at 25 °C as follows: log $*\beta_{1,1}=-10.3\pm0.1$ and log $*\beta_{1,2}=-9.13\pm0.01$.

Concerning the hydrolytic reactions of cadmium ion many authors reported the formation of mononuclear complexes.[1–6] The work by Biedermann and Ciavatta[7] was the only case in which polynuclear complexes were found. They prepared the solution by the addition of CdO powder to a slightly acidic 3M (Li)ClO_4 solution containing a suitable amount of $Cd(ClO_4)_2$, stirring the resulting mixture for about half a day. The supernatant was then subjected to titration. Schindler,[5] however, stated that a much longer time is required in order to establish an equilibrium between solid CdO (or $Cd(OH)_2$) and the aqueous phase which is saturated with hydroxo complexes of cadmium ions. Experiments we carried out for the preparation of test solutions containing hydrolyzed cadmium ions showed that a white precipitate is gradually formed after the CdO powder, turned white due to the formation of $Cd(OH)_2$ on the surface, has been removed from the solution which should be left to stand for at least ten days under agitation.

From these observations the question arose as to whether some polynuclear complexes really can be present as equilibrium species of hydrolyzed cadmium ions in solution. We have reexamined the procedure of Biedermann and Ciavatta[7] in order to confirm the formation of polynuclear complexes of hydrolyzed species of cadmium ions.

Experimental

Reagents and Apparatus. Cadmium perchlorate was prepared by dissolving CdO (99.99%, Mitsuwa Pure Chemicals Co., Osaka) in 1 : 1 $HClO_4$ (reagent grade). The purity of the cadmium oxide was checked by emission spectroscopy. The cadmium perchlorate was recrystallized twice from water.

Lithium perchlorate was prepared according to the method of Biedermann and Ciavatta.[7]

An Orion Digital pH Meter Model 801 was used in combination with a Beckman Glass Electrode No. 40498 and a Silver-Silver Chloride electrode.

A Metrohm E 211 A Type coulometer was employed as a current source for generation of hydrogen ions in a solution during the course of titration.

Preparation of Test Solutions. A small amount of CdO powder was added to 50 ml of a lithium perchlorate solution containing a suitable amount of $Cd(ClO_4)_2$, the total concentration of perchlorate ion being kept at 3M, and that of cadmium ion in the range 0.2261—1.401 M. The mixture was allowed to stand 3—7 days under agitation in nitrogen atmosphere and white precipitates formed were removed with a set of G-3 and G-4 glass filters. The filtrate was left to stand 7—20 days. When a precipitate was recognized in the solution, the solution was filtered again with the G-3 and G-4 glass filters. A twenty-five milliliter portion of the clear solution was used for emf measurements.

The method of measurement was essentially the same as those described previously.[8–10] All the measurements were carried out at 25.00 °C±0.01 °C. 3M (Li)ClO_4 was used as an ionic medium.

Results and Discussion

The results are given in Fig. 1 as the plot, Z *vs.* $-\log h$, where Z denotes the average number of hydrogen ions set free per cadmium atom and h the concentration of hydrogen ion at equilibrium. Since the Z values are low, the concentration of free cadmium ion (b) can approximately be made equal to the concentration of total cadmium (B) in preliminary calculations. Thus,

$$BZ = \sum_p \sum_q p[Cd_q(OH)_p{}^{(2q-p)+}] = \sum_p \sum_q p{*\beta_{p,q}}B^q h^{-p}$$

where

$$*\beta_{p,q} = [Cd_q(OH)_p{}^{(2q-p)+}][H^+]^p/[Cd^{2+}]^q.$$

Plots of Zh *vs.* h^{-1} gave a set of horizontal lines with intercepts dependent on B. A family of curves drawn according to a normalized function $y=x=f(\log x)$ fitted the Z *vs.*$-\log h$ plots. We thus conclude that the species formed are only the $CdOH^+$ and Cd_2OH^{3+}

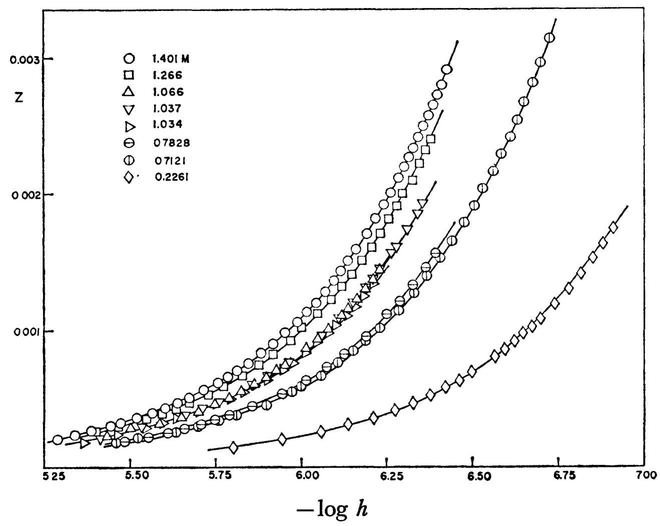

Fig. 1. The average number of hydrogen ion set free per cadmium atom Z plotted against $-\log h$. The solid lines show calculated curves using values finally obtained. The experimental data are available by request.

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complexes and the $Cd_4(OH)_4^{4+}$ complex proposed by Biedermann and Ciavatta was not formed.

The formation constants of the $CdOH^+$ and Cd_2OH^{3+} complexes were finally determined by means of a generalized least-squares method with the help of an electronic computer HITAC 8700. The values obtained were as follows:

$$\log {}^*\beta_{1,1} = -10.3 \pm 0.1$$
$$\log {}^*\beta_{1,2} = -9.13 \pm 0.01$$

These values agree with those reported by Biederamnn and Ciavatta ($\log {}^*\beta_{1,1} = -10.2 \pm 0.1$ and $\log {}^*\beta_{1,2} = -9.10 \pm 0.05$).

The maximum values of Z we obtained ($Z_{max} \approx 0.003$) were much lower than theirs ($Z_{max} = 0.01 \sim 0.02$). This suggests that the $Cd_4(OH)_4^{4+}$ complex and any other highly polymerized complexes, if formed at all, were unstable and precipitated and could not be present as equilibrium species of hydrolyzed cadmium ions in the solution.

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