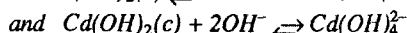
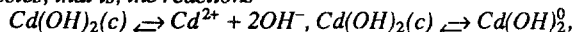


## Hydrolysis Constants and Ion-Interaction Parameters For Cd(II) in Zero to High Concentrations of NaOH-KOH, and the Solubility Product of Crystalline Cd(OH)<sub>2</sub>

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*The solubility of Cd(OH)<sub>2</sub>(c) was studied in 0.01M NaClO<sub>4</sub> solutions, from both the over- and the undersaturation directions, with OH<sup>-</sup> ion concentration ranging from 10<sup>-6</sup> to 1.0 mol·L<sup>-1</sup>, and the equilibration period ranging from 2 to 28 days. Equilibrium Cd concentrations were reached in less than 2 days. The Cd(OH)<sub>2</sub>(c) solubility showed an amphoteric behavior. In the entire range of OH<sup>-</sup>/H<sup>+</sup> investigated, the only dominant aqueous Cd(II) species required to explain the solubility of Cd(OH)<sub>2</sub>(c) are Cd<sup>2+</sup>, Cd(OH)<sub>2</sub><sup>0</sup>, and Cd(OH)<sub>4</sub><sup>2-</sup>. The logarithms of the thermodynamic equilibrium constants of the Cd(OH)<sub>2</sub>(c) solubility reactions involving these species, that is, the reactions*



*were found to be  $-14.14 \pm 0.21$ ,  $-7.04 \pm 0.21$ , and  $-5.62 \pm 0.32$ , respectively. The ion-interaction parameters reported in the literature, in conjunction with the values for Cd(OH)<sub>2</sub><sup>0</sup> - Na<sup>+</sup> ( $-0.20$ ), Cd(OH)<sub>4</sub><sup>2-</sup> - Na<sup>+</sup> ( $\beta^0 = 0.41$ ,  $\beta^1 = 0.7$ ), and Cd(OH)<sub>4</sub><sup>2-</sup> - K<sup>+</sup> ( $\beta^0 = 0.44$ ,  $\beta^1 = 1.44$ ) obtained in this study, show that our low-ionic strength solubility data are also consistent with Cd(OH)<sub>2</sub>(c) solubility data obtained in solutions as concentrated as 10M in NaOH or KOH and 7M in Na(OH,ClO<sub>4</sub>).*

**KEY WORDS:** Solubility; equilibrium constants; activity coefficient; hydrolysis;  $\beta$ -Cd(OH)<sub>2</sub>(c); ion-interaction parameters; cadmium.

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## 1. Introduction

Solid  $\text{Cd}(\text{OH})_2$  can exist in three crystalline forms:  $\alpha\text{-Cd}(\text{OH})_2$ ,  $\beta\text{-Cd}(\text{OH})_2$ , and  $\gamma\text{-Cd}(\text{OH})_2$ . Of these forms, only  $\beta\text{-Cd}(\text{OH})_2$  is stable in water suspensions.<sup>(1)</sup> The solubility of  $\beta\text{-Cd}(\text{OH})_2$  and the hydrolysis of  $\text{Cd}^{2+}$  have been studied by several researchers.<sup>(2-5)</sup> However, most of these studies have been conducted at relatively high ionic strengths. For example, Schindler<sup>(2)</sup> and Dyrssen and Lumme<sup>(3)</sup> conducted experiments in 3M  $\text{NaClO}_4$  and  $\text{Na}(\text{OH},\text{ClO}_4)$ , respectively. Gubeli and Taillon<sup>(4)</sup> conducted their experiments in 1M  $\text{NaClO}_4$ , and Ryan *et al.*<sup>(5)</sup> conducted theirs in 1 and 7M mixtures of  $\text{NaOH}$  and  $\text{NaClO}_4$ . In addition to the variability in reported solubility that might be expected as a result of differences in ionic strength and hydrogen ion concentration, Baes and Mesmer<sup>(1)</sup> concluded that considerable scatter occurs even within a single study. Furthermore, because of the differences in ionic media used in the different studies, cross-comparison of the study results is difficult, as is accurate extrapolation of these high-ionic-strength data to zero or low ionic strength. The difficulties arise in some cases because of the lack of appropriate analytical values for solution variables, such as  $\text{H}^+$ , or because of the unavailability of appropriate ion-interaction parameters, especially those relating to bulk electrolyte and the hydrolyzed  $\text{Cd}^{2+}$  species. Therefore, this study was conducted in relatively dilute electrolyte (0.01M  $\text{NaClO}_4$ ) so that thermodynamic equilibrium constants could be obtained. A thermodynamic model applicable to high-ionic-strength solutions was developed using these data and the data reported by previous researchers.

## 2. Methods and Materials

### 2.1. Stock Solutions and Reagents

The water was in all cases deaerated by boiling, followed by thorough sparging at 25°C with  $\text{N}_2$  (99.99%). A  $\text{NaOH}$  stock solution was prepared in an inert atmosphere, using deaerated water. The stock was treated with about 7% excess  $\text{BaCl}_2$  to lower the dissolved carbonate through  $\text{BaCO}_3$  precipitation, and the stock was kept in the  $\text{N}_2$  atmosphere until it was used. A double-distilled  $\text{HClO}_4$  was used when needed. A 0.01M  $\text{NaClO}_4$  stock solution was also prepared in an inert atmosphere, using deaerated water. A stock solution of  $\text{Cd}^{2+}$  was made from reagent-grade  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  in deaerated water adjusted to pH 2 with  $\text{HCl}$ .

## 2.2. General Procedure

All experiments were conducted in a controlled-atmosphere chamber filled with  $N_2$  (99.99%). Cadmium hydroxide precipitates were prepared in an inert atmosphere by adjusting the pH of a portion of the  $Cd^{2+}$  stock solution to about 10.5 with carbonate-free NaOH. The precipitates were washed with deionized water until free of chlorides, as determined by lack of Cl precipitation in an aliquot of the wash containing  $AgNO_3$ . Approximately 1 g of each washed precipitate was suspended in 30 mL of the 0.01M  $NaClO_4$  in a polyaniline Oak Ridge-type centrifuge tube. The pH values of these samples were adjusted to between 8 and 12 using  $HClO_4$  or carbonate-free NaOH. To determine solubility values at pH higher than 12, the precipitates were suspended in standard NaOH solutions. These suspensions, which contained  $Cd(OH)_2$  precipitates, were analyzed after 3 days of continuous shaking. To approach solubility from the oversaturation direction, a different set of suspensions of precipitates was prepared and spiked with  $CdCl_2$  solution to raise the  $Cd^{2+}$  concentrations in suspensions by  $10^{-2.5}M$ . These suspensions were analyzed after 3 and 28 days of continuous shaking.

At the end of the equilibration periods, the pH of those suspensions (pH < 12) that were not in standard NaOH was measured with a combination glass electrode that was calibrated against pH buffers. The ionic strength of these suspensions is low; therefore, the measured pH values of these suspensions was taken to represent the  $H^+$  activity. The suspensions were centrifuged at about 2000 g for 7-10 min. Aliquots of the supernatants were withdrawn and filtered through Amicon Type F-25 Centriflo membrane cones with effective 25,000-molecular-weight cutoffs and approximately 0.0018- $\mu m$  pore sizes. The Centriflo membrane cones were selected based on the results of filtering  $CdCO_3$  suspensions of different pH values (Table I) through several different types of filters. Although the concentrations of Cd in solutions filtered through different filters were similar (Table I), the filters with the smallest pore size were selected to effectively eliminate colloidal  $Cd(OH)_2$  particles during filtration. The filters used in this study were pretreated as described by Rai,<sup>(6)</sup> according to the following steps: 1) the filters were washed and equilibrated with deionized waters adjusted to the pH values of the samples, to prevent precipitation of the solid phase because of a change in the pH during filtration; and 2) a small aliquot of the sample was passed through the filters to saturate any possible adsorption sites on the filters and filtration containers (this filtrate was discarded).

Filtrates were acidified with  $HClO_4$  and stored until they were analyzed for Cd using inductively coupled plasma (ICP) spectroscopy.

**Table I.** Evaluation of Filters for Separating Solutions from Equilibrating CdCO<sub>3</sub> - Water Suspensions

pH	log [Cd <sub>total</sub> ] <sup>a</sup> in Unfiltered and Filtered Solutions				
	Unfiltered <sup>a</sup>	0.22 μm	0.1 μm	0.0018 μm	
				Filter 1	Filter 2 <sup>b</sup>
4.10	-1.71	-1.70	-1.65	-1.65	-1.64
4.95	-2.48	-2.53	-2.55	-2.55	-2.54
5.72	-3.18	-3.48	-3.53	-3.53	-3.56
6.10	-4.30	-4.04	-4.12	-4.12	-4.19
7.10	-4.69	-5.42	-5.50	-5.50	-5.63

<sup>a</sup> Units; mol·L<sup>-1</sup>. <sup>b</sup> Centrifuged at about 2000 g for 7-10 min. <sup>c</sup> Second filtration of filtrate from Filter 1.

**Table II.** Summary of Results of X-Ray Diffraction Analyses

Sample pH	Crystalline Phases <sup>a</sup>		
	Major	Minor	Trace
3 Day Equilibration, Undersaturation			
8.71	β-Cd(OH) <sub>2</sub>	<sup>b</sup>	
9.50	β-Cd(OH) <sub>2</sub>	<sup>b</sup>	
11.45	β-Cd(OH) <sub>2</sub>	γ-Cd(OH) <sub>2</sub>	None
12.38	β-Cd(OH) <sub>2</sub>	γ-Cd(OH) <sub>2</sub>	None
12.60	β-Cd(OH) <sub>2</sub>	γ-Cd(OH) <sub>2</sub>	None
13.40	β-Cd(OH) <sub>2</sub>	γ-Cd(OH) <sub>2</sub>	None
28 Day Equilibration, Oversaturation			
8.54	β-Cd(OH) <sub>2</sub>	None	3CdCl <sub>2</sub> ·5Cd(OH) <sub>2</sub>
9.29	β-Cd(OH) <sub>2</sub>	None	γ-Cd(OH) <sub>2</sub>
12.06	β-Cd(OH) <sub>2</sub>	None	CdCO <sub>3</sub>
12.43	β-Cd(OH) <sub>2</sub>	None	None
13.20	β-Cd(OH) <sub>2</sub>	None	None
13.50	β-Cd(OH) <sub>2</sub>	None	CdCO <sub>3</sub>
13.70	β-Cd(OH) <sub>2</sub>	None	CdCO <sub>3</sub>
14.00	β-Cd(OH) <sub>2</sub>	None	None

<sup>a</sup> β-Cd(OH)<sub>2</sub>, JCPDS card file No. 31-228; γ-Cd(OH)<sub>2</sub>, JCPDS card file No. 20-179; 3CdCl<sub>2</sub>·5Cd(OH)<sub>2</sub>, JCPDS card file No. 3-0585; CdCO<sub>3</sub>, JCPDS card file No. 8-456.

<sup>b</sup> An unidentified compound with interplanar distances of about 5.57, 5.00, 3.95, 3.09, 2.98, 2.88, 2.80, and more appeared to be present in large amounts; it is presumably some form of Cd(OH)<sub>2</sub>.

Samples of the solid phase were analyzed for crystallinity using X-ray diffraction. The solids that underwent X-ray diffraction analyses were removed from the suspensions, washed with ethanol, smear mounted, and air dried before powder patterns were obtained using  $\text{CuK}\alpha$  radiation. The X-ray diffraction analyses of the precipitates aged for 3 and 28 days (Table II) showed that, as expected,  $\beta\text{-Cd}(\text{OH})_2$  was the major crystalline phase in almost all cases. After 3 days of equilibration,  $\gamma\text{-Cd}(\text{OH})_2$  or unidentified  $\text{Cd}(\text{OH})_2$  was associated with the  $\beta\text{-Cd}(\text{OH})_2$ . After 28 days of equilibration, trace amounts of  $3\text{CdCl}_2 \cdot 5\text{Cd}(\text{OH})_2$ ,  $\gamma\text{-Cd}(\text{OH})_2$ , or  $\text{CdCO}_3$  were detected in different samples. Our previous studies have shown that, at high pH (greater than 13),  $\text{Cd}(\text{OH})_2$  is the stable phase in preference to  $\text{CdCO}_3$ , and  $\text{CdCO}_3$  in these studies was observed to convert to  $\text{Cd}(\text{OH})_2$ .<sup>(7)</sup> For this reason and because  $\text{CdCO}_3$  was not detected in all samples, it is hypothesized that  $\text{CdCO}_3$  was not present in the equilibrating suspensions but rather was produced during drying and analysis of the precipitates. Therefore,  $\beta\text{-Cd}(\text{OH})_2$  is expected to be the only solid phase in many equilibrating suspensions. Because 1) nearly pure  $\beta\text{-Cd}(\text{OH})_2$  is obtained with 28 days of aging; 2) steady-state solubilities were reached between 3 and 28 days; 3)  $\alpha\text{-Cd}(\text{OH})_2$ ,  $\gamma\text{-Cd}(\text{OH})_2$ , and  $\text{CdO}$  are converted in water to  $\beta\text{-Cd}(\text{OH})_2$ ;<sup>(1)</sup> and 4) solubilities observed in this study are similar to those reported in the literature for  $\beta\text{-Cd}(\text{OH})_2$ , the solubility data presented in this paper should be considered to be those for  $\beta\text{-Cd}(\text{OH})_2$ .

### 3. Results and Discussion

In solutions contacting  $\text{Cd}(\text{OH})_2(\text{c})$  for 2 days at pH values between 8 and 14 and in those in contact for 28 days at pH values greater than 13, the Cd concentrations are similar, indicating that steady-state concentrations are reached in less than 2 days. When solubility was approached from the oversaturation direction, by spiking the  $\text{Cd}(\text{OH})_2(\text{c})$  suspensions with Cd to raise the concentration of Cd by  $10^{-2.5}M$ , the Cd concentrations after 2 and 28 days of equilibration and over the entire experimental range of pH values were similar and had decreased, in many cases by several orders of magnitude, from  $10^{-2.5}M$  to levels that were similar to those found in the undersaturation experiments. These results collectively indicate that equilibrium is reached in less than 2 days.

In general, the Cd concentrations in different pH regions 1) decreased by about two orders of magnitude with each one-unit increase in pH in the region between about pH 8 and 10.5; 2) appeared to be independent of pH in the region between about pH 10.5 and 13; and 3) in-

**Table III.** Chemical Potentials of Different Species Used in Calculations

Species	$\mu^\circ/RT$	Ref.
$\text{Cd}^{2+}$	-31.311	11
$\text{OH}^-$	-63.435	12
$\text{H}_2\text{O}$	-95.664	12
$\text{Cd}(\text{OH})_2(\text{c})^a$	$-190.746 \pm 0.49$	<i>b</i>
$\text{Cd}(\text{OH})_2^0$	$-174.531 \pm 0.49$	<i>b</i>
$\text{Cd}(\text{OH})_4^{2-}$	$-304.681 \pm 0.73$	<i>b</i>

<sup>a</sup> Crystalline  $\text{Cd}(\text{OH})_2$ . <sup>b</sup> This study.

created by approximately two orders of magnitude with each one-unit increase in  $\text{OH}^-$  concentration beyond pH 13. These changes in the solubility of  $\text{Cd}(\text{OH})_2(\text{c})$  as a function of pH correspond respectively to the following three reactions



To evaluate the equilibrium constants for reactions (1 - 3) and for some of the other reactions [such as those involving aqueous species  $\text{CdOH}^+$  and  $\text{Cd}(\text{OH})_3^-$ ] that might be possible in this system, a coupled nonlinear least-squares and chemical equilibrium program (NONLIN<sup>(8)</sup>) was used. In this program, the actual quantity minimized was the standard deviation, defined as

$$\sigma = \left[ \frac{\sum_{i=1}^N [f(x)]^2}{N} \right]^{1/2} \quad (4)$$

where  $N$  is the total number of data points and  $f(x)$  is given by the phase equilibrium condition as  $f(x) = \mu_{\text{solid}} - \mu_{\text{sol}}$ . In the case of  $\text{Cd}(\text{OH})_2(\text{c})$  solubility, this condition gives

$$\begin{aligned} f(x) = & (\mu^\circ/RT)_{\text{Cd}(\text{OH})_2(\text{c})} - [(\mu^\circ/RT)_{\text{Cd}^{2+}} + (2\mu^\circ/RT)_{\text{OH}^-} \\ & + \ln[\text{Cd}^{2+}]\gamma_{\text{Cd}^{2+}} + 2\ln[\text{OH}^-]\gamma_{\text{OH}^-}] \end{aligned} \quad (5)$$

where  $\mu^\circ$  is the standard chemical potential, quantities in brackets are

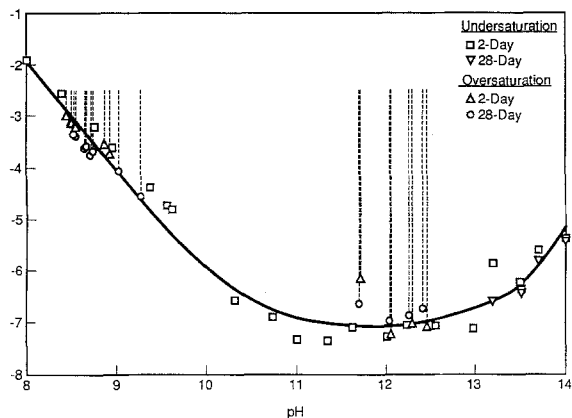
Table IV. Ion-Interaction Parameters Used in This Study

Species	Binary Interactions				Ref.
	$\beta^0$	$\beta^1$	$\beta^2$	$C^\phi$	
H <sup>+</sup> -ClO <sub>4</sub> <sup>-</sup>	0.1747	0.2931	0.00	0.00819	16
Cd <sup>2+</sup> -ClO <sub>4</sub> <sup>-</sup>	0.3899	1.9961	0.00	0.02075	17
Na <sup>+</sup> -ClO <sub>4</sub> <sup>-</sup>	0.0554	0.2755	0.00	-0.00118	16
Na <sup>+</sup> -OH <sup>-</sup>	0.0864	0.253	0.00	0.0044	16
Na <sup>+</sup> -Cd(OH) <sub>4</sub> <sup>2-</sup>	0.41	0.70	0.00	0.00	<sup>a</sup>
K <sup>+</sup> -Cd(OH) <sub>4</sub> <sup>2-</sup>	0.44	1.44	0.00	0.00	<sup>a</sup>
Ternary Interactions					
H <sup>+</sup> -Na <sup>+</sup>	0.036				12
Neutral Ion Interactions					
Cd(OH) <sub>2</sub> <sup>0</sup> -Na <sup>+</sup>	-0.20				<sup>a</sup>

<sup>a</sup>This study.

concentrations, and  $\gamma_i$  refers to the activity coefficient of the species *i*.

Except for  $(\mu^\circ/RT)_{\text{Cd(OH)}_2(\text{c})}$ , all of the variables in Eq. (5) are either known or calculated from the aqueous phase thermodynamic model. The values of  $\mu^\circ/RT$  used in these calculations are reported in Table III. The activity coefficients ( $\gamma_i$ ) were calculated by both the Davies equation<sup>(13)</sup> and the ion-interaction model developed by Pitzer,<sup>(14,15)</sup> with the ion-interaction values listed in Table IV. The values of  $(\mu^\circ/RT)_{\text{Cd(OH)}_2(\text{c})}$  and  $(\mu^\circ/RT)_{\text{Cd(OH)}_2^0}$  needed to calculate equilibrium constants for reactions (1, 2) were obtained by simultaneously fitting all of the experimental data in the region between pH 8 and 12.5. In these relatively dilute solutions, both the Davies equation and the ion-interaction model gave essentially the same results. The values for  $(\mu^\circ/RT)_{\text{Cd(OH)}_2(\text{c})}$  and  $(\mu^\circ/RT)_{\text{Cd(OH)}_2^0}$  calculated from the ion-interaction model were  $-190.746 \pm 0.49$  and  $-174.531 \pm 0.49$ , respectively, and those calculated from the Davies equation were  $-190.72 \pm 0.49$  and  $-174.50 \pm 0.49$ , respectively. Given the  $\mu^\circ/RT$  values obtained from the ion-interaction model and the  $\mu^\circ/RT$  values reported in Table III, the logarithms of the equilibrium constants equal  $-14.14 \pm 0.21$  and  $-7.04 \pm 0.21$  for reactions (1, 2), respectively. The measured solubility



**Fig. 1.** Concentration of Cd in 0.0018- $\mu\text{m}$  filtrates from  $\text{Cd}(\text{OH})_2(\text{c})$  suspensions equilibrated in 0.01M  $\text{NaClO}_4$  and for different periods, from both the oversaturation and the undersaturation directions. The pH values of greater than 13 are calculated from standard  $\text{NaOH}$  ( $14 + \log \text{OH}^-$ ) used in the suspensions. All other pH values were measured with a combination glass electrode. The top position of the vertical dashed lines indicates the Cd concentration added to the  $\text{Cd}(\text{OH})_2(\text{c})$  suspensions. The solid line is the predicted solubility from model parameters listed in Tables III and IV.

of  $\text{Cd}(\text{OH})_2(\text{c})$  and that calculated by the ion-interaction model (Fig. 1) agree closely, indicating that the solubility of  $\text{Cd}(\text{OH})_2(\text{c})$  in the less than 12.5-pH region can successfully be simulated by Eqs. (1, 2). In the high-pH region (greater than 12.5), the results are less clear. The solubilities increase but the slope of the  $\log \text{Cd}$  vs. pH curves is uncertain. A slope of +2, indicating the presence of  $\text{Cd}(\text{OH})_4^{2-}$ , appears to give the best overall fit to the data.

It is also of interest to determine whether this thermodynamic model is consistent with the solubility data obtained in concentrated solutions. Gubeli and Taillon<sup>(4)</sup> studied the solubility of  $\text{Cd}(\text{OH})_2(\text{c})$  in the presence of 1M  $\text{NaClO}_4$ ; the equilibrium Cd concentrations they observed are plotted in Fig. 2 as a function of the observed pH, which is not the same as either the true  $\text{H}^+$  activity or the concentration. To compare the results obtained by Gubeli and Taillon<sup>(4)</sup> with those predicted using the model developed in this study (Fig. 2), we assumed that  $\text{pc}_{\text{H}^+} = \text{pH}_{\text{obs}} + 0.37$ , where  $\text{pc}_{\text{H}^+}$  is the negative logarithm of  $\text{H}^+$  concentration. The constant 0.37 corrects for the  $\gamma_{\text{H}^+}$  and the liquid junction potential, and its value is based on our experimental data for a  $\text{NaClO}_4$  system obtained in a similar fashion, as discussed in our earlier paper.<sup>(18)</sup> The results indicate that our predicted Cd concentrations in equilibrium with



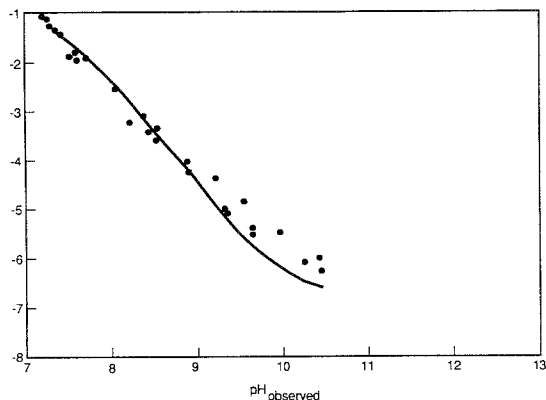
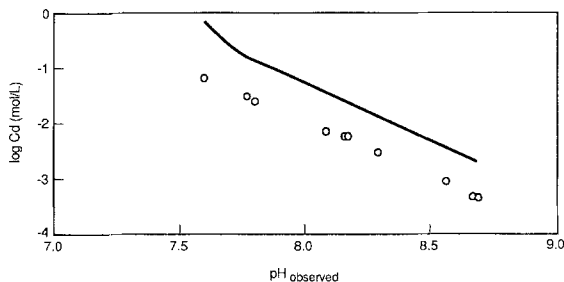


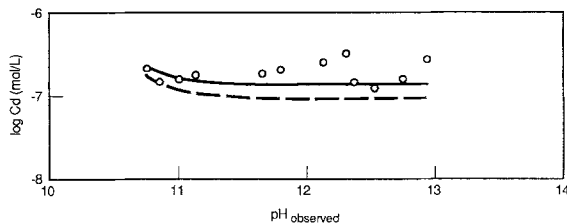
Fig. 2. Aqueous Cd concentrations in equilibrium with  $\text{Cd}(\text{OH})_2(\text{c})$  in the presence of  $1M$   $\text{NaClO}_4$ , as a function of  $\text{pH}_{\text{obs}}$  (data from Ref. 4). The solid line indicates the predicted Cd concentrations from the model parameters reported in Tables III and IV and with the assumption that  $\text{pc}_{\text{H}^+} = \text{pH}_{\text{obs}} + 0.37$  (see text for details).

$\text{Cd}(\text{OH})_2(\text{c})$  are in excellent agreement with the concentrations observed by Gubeli and Taillon.<sup>(4)</sup> The solubility of  $\text{Cd}(\text{OH})_2(\text{c})$  in higher-ionic-strength solutions ( $3M$   $\text{NaClO}_4$ ) as a function of  $\text{H}^+$  concentration has also been reported in the literature.<sup>(2)</sup> At these high ionic strengths, ternary ion interactions (such as  $\Theta_{\text{H}^+ \cdot \text{Na}^+}$ ,  $\Theta_{\text{Cd}^{2+} \cdot \text{Na}^+}$ ,  $\Theta_{\text{ClO}_4^- \cdot \text{OH}^-}$ ,  $\Psi_{\text{Cd}^{2+} \cdot \text{Na}^+ \cdot \text{ClO}_4^-}$ , and  $\Psi_{\text{Na}^+ \cdot \text{ClO}_4^- \cdot \text{OH}^-}$ ) are very important. With the exception of  $\Theta_{\text{H}^+ \cdot \text{Na}^+}$ , the values for these parameters are not available. It is therefore impossible to accurately interpret these high-ionic-strength data. In the predictions made without the inclusion of these parameters, the predicted concentrations are systematically correlated with the observed concentrations as a function of pH but approximately 0.6 log units higher (Fig. 3). Considering the facts that 1) the predicted values are only 0.6 log units different in the absence of the important ion-interaction parameters and 2) concentrations are systematically correlated with the pH, predictions would be expected to improve if values for these parameters were available. Given the assumptions involved, these results show that the model developed in this study for the less than 10 pH region is consistent with the  $\text{Cd}(\text{OH})_2(\text{c})$  solubility data in both the low- and the high-ionic-strength solutions.

In the pH region from about 10.7 to 13, the solubility reaction [reaction (2)] involving  $\text{Cd}(\text{OH})_2^0$  is independent of hydrogen ion concentration, and highly accurate values of  $\text{H}^+$  are not needed. Therefore, we have examined the solubility of  $\text{Cd}(\text{OH})_2(\text{c})$  in  $1M$   $\text{NaClO}_4$  at the pH



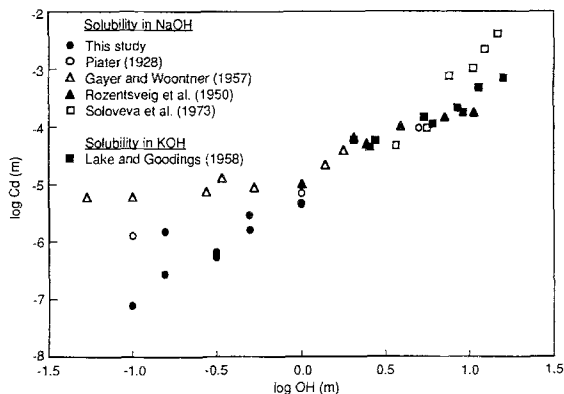
**Fig. 3.** Aqueous Cd concentrations, in equilibrium with  $\text{Cd}(\text{OH})_2(\text{c})$  in the presence of  $3M$   $\text{NaClO}_4$ , as a function of  $\text{pH}_{\text{obs}}$  (data from Ref. 2). The solid line indicates the predicted Cd concentrations from the model parameters reported in Tables III and IV.



**Fig. 4.** Aqueous Cd concentrations in equilibrium with  $\text{Cd}(\text{OH})_2(\text{c})$  in the presence of  $1M$   $\text{NaClO}_4$  (data from Ref. 4). The lines indicate the predicted Cd concentrations; dashed line, predicted without the inclusion of  $\text{Cd}(\text{OH})_2^0\text{-Na}^+$  interactions; solid line, with the inclusion of  $\text{Cd}(\text{OH})_2^0\text{-Na}^+$  interactions.

values reported by Gubeli and Taillon.<sup>(4)</sup> The most important ion-interaction parameters for this system are expected to involve neutral  $\text{Cd}(\text{OH})_2^0$  with either of the bulk electrolyte species of  $\text{Na}^+$  or  $\text{ClO}_4^-$  (*i.e.*,  $\lambda_{\text{Na}^+\text{-Cd}(\text{OH})_2^0}$  or  $\lambda_{\text{Cd}(\text{OH})_2^0\text{-ClO}_4^-}$ ). Unfortunately, such information is not available. However, even in the absence of such data, the solubilities calculated using only the available parameters for the bulk electrolyte ions gives a reasonably good prediction (about 0.3 log units low) of the observed solubilities (Fig. 4). Using NONLIN, we adjusted the ion-interaction parameter for  $\text{Cd}(\text{OH})_2^0\text{-Na}^+$  to fit the experimental data of Gubeli and Taillon<sup>(4)</sup> (Fig. 4). Our calculated value of  $-0.20$  for  $\lambda_{\text{Cd}(\text{OH})_2^0\text{-Na}^+}$  is consistent with the values for such other neutral species interactions as  $\text{B}(\text{OH})_3(\text{aq})$ .<sup>(16)</sup> We have therefore included  $\lambda_{\text{Cd}(\text{OH})_2^0\text{-Na}^+} = -0.20$  in our final thermodynamic model.

The available solubility data on  $\text{Cd}(\text{OH})_2(\text{c})$  in  $\text{NaOH}$  and  $\text{KOH}$  have been summarized and reviewed by Dirkse.<sup>(20)</sup> In comparing these data with our solubility data in the high-pH region (Fig. 5), it is apparent



**Fig. 5.** Experimental  $\text{Cd}(\text{OH})_2(\text{c})$  solubilities as a function of molality of NaOH and KOH. Data in NaOH taken from the summary of Ref. 20 and that obtained in this study. [Additional reference: V. D. Soloveva, E. G. Svirchevskaya, V. V. Bobrova, and N. M. Eltsov, *Tr. Inst. Metal. Obogashch. An Kazssr.* **49**, 37 (1973).]

that our high-pH data are consistent with those of previous investigators, who primarily worked at higher  $\text{OH}^-$  concentrations than were used in this study. With the exception of  $\text{Cd}(\text{OH})_2(\text{c})$  solubility in low  $\text{OH}^-$  (less than  $0.18M$ ) where both the Cd concentrations observed by Gayer and Woontner<sup>(21)</sup> and a data point obtained by Piater<sup>(22)</sup> are higher than those obtained in this study, all of the solubility data over a wide range of  $\text{OH}^-$  concentrations ( $0.18$  to  $10M$ ) maintained with NaOH or KOH are remarkably consistent with our data, in that the solubility of  $\text{Cd}(\text{OH})_2(\text{c})$  continuously increases with the increase in  $\text{OH}^-$  concentrations.

We began thermodynamic analysis of these data by first examining our data for lower concentrations of  $\text{OH}^-$  ( $0.1$  -  $1.0M$ ) where specific ion interactions between the bulk electrolyte ions ( $\text{Na}^+$ ) and  $\text{Cd}^{2+}$  hydrolysis species [e.g.,  $\text{Cd}(\text{OH})_3^- \text{Na}^+$  or  $\text{Cd}(\text{OH})_4^{2-} \text{Na}^+$ ] would be minimal and where accurate standard chemical potentials for the hydrolysis species could be obtained. As a first attempt, it was assumed that the dominant aqueous species is  $\text{Cd}(\text{OH})_3^-$ . The values of the Pitzer ion-interaction parameters  $\beta^0$  and  $\beta^1$  for  $\text{Cd}(\text{OH})_3^- \text{Na}^+$  were adjusted to obtain the best fit. The fact that the calculated values of  $\beta^0$  and  $\beta^1$  were considerably out of the range of values reported for 1:1 electrolytes<sup>(13)</sup> and were negative suggested the absence of  $\text{Cd}(\text{OH})_3^-$  and supported our

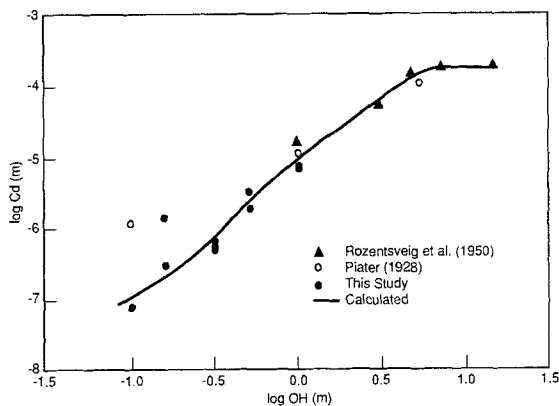


Fig. 6. Experimental and calculated  $\text{Cd}(\text{OH})_2(\text{c})$  solubilities in NaOH. Only most consistent experimental data included in model comparison.

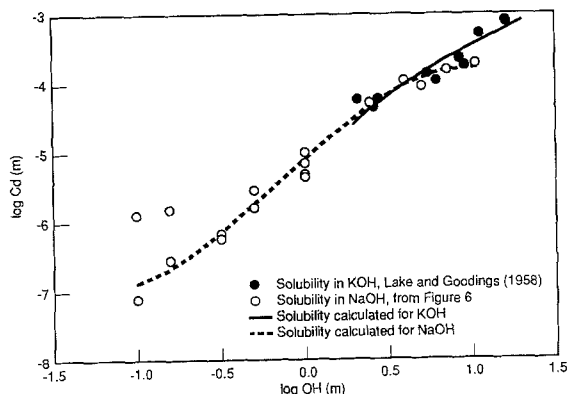


Fig. 7. Experimental (points) and calculated (lines)  $\text{Cd}(\text{OH})_2(\text{c})$  solubilities as a function of molality of NaOH and KOH.

earlier result in 0.01M  $\text{NaClO}_4$  regarding the formation of higher-order complexes of Cd and  $\text{OH}^-$ , such as  $\text{Cd}(\text{OH})_4^{2-}$ . Therefore, the value of  $(\mu^\circ/RT)_{\text{Cd}(\text{OH})_4^{2-}}$  was calculated from our  $\text{Cd}(\text{OH})_2(\text{c})$  solubility in 0.1 to 1M NaOH. The calculated value for  $\mu^\circ/RT$  of  $-304.681 \pm 0.73$  for  $\text{Cd}(\text{OH})_4^{2-}$ , in conjunction with the value of  $\mu^\circ/RT$  for  $\text{Cd}(\text{OH})_2(\text{c})$ , was used to calculate the logarithm of the equilibrium constant for Eq. (3), and it was found to be  $-5.62 \pm 0.32$ .

With the standard chemical potential for  $\text{Cd}(\text{OH})_4^{2-}$  fixed, we next evaluated what values for the important Pitzer ion-interaction parameters ( $\beta^0$  and  $\beta^1$ ) for  $\text{Na}^+$  or  $\text{K}^+$  with  $\text{Cd}(\text{OH})_4^{2-}$  would be most ap-

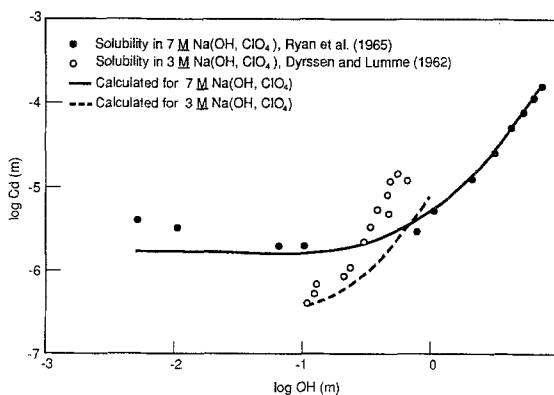


Fig. 8. Experimental (points) and calculated (lines)  $\text{Cd}(\text{OH})_2(\text{c})$  solubilities in  $\text{NaOH-NaClO}_4$  solutions. Data taken from the summary of Ref. 20.

appropriate for extending this model to the concentrated-solution region (*i.e.*, 10M) yet still consistent with our low-ionic-strength data. The calculated Pitzer ion-interaction parameters for  $\text{Na}^+-\text{Cd}(\text{OH})_4^{2-}$  were  $\beta^0 = 0.41$  and  $\beta^1 = 0.70$ , and those for  $\text{K}^+-\text{Cd}(\text{OH})_4^{2-}$  were  $\beta^0 = 0.44$  and  $\beta^1 = 1.44$ . The agreement between model calculations and the most consistent experimental data sets is shown in Fig. 6 for the solubility of  $\text{Cd}(\text{OH})_2(\text{c})$  in  $\text{NaOH}$ . Agreement between the model calculations and the experimental data is excellent. These results (Fig. 6), when compared with the experimental and calculated solubilities of  $\text{Cd}(\text{OH})_2(\text{c})$  in  $\text{KOH}$  (Fig. 7), clearly show that, for both the  $\text{KOH}$  and  $\text{NaOH}$  systems, the agreement between the model calculations and the experimental data is excellent. The patterns for the two systems are also similar and consistent with each other.

As a final test of our thermodynamic model, we examined the  $\text{Cd}(\text{OH})_2(\text{c})$  solubility data in mixed  $\text{NaOH-NaClO}_4$  systems. For this system, no Pitzer ion-interaction parameters are available for  $\text{OH}^--\text{ClO}_4^-$  and  $\text{Na}^+-\text{OH}^--\text{ClO}_4^-$  interactions, although these are important parameters for this mixed system at high concentration. Therefore, a detailed and rigorous comparison cannot be performed, but it is still of interest to test our model on this complex mixed system. Figure 8 shows a comparison of our model calculations with the experimental  $\text{Cd}(\text{OH})_2$  solubility data summarized by Dirkse<sup>(20)</sup> in the high-concentration  $\text{Na-OH - ClO}_4\text{-H}_2\text{O}$  system. The model gives remarkably good predictions of the solubility data in the 7M  $\text{Na}(\text{OH},\text{ClO}_4)$  system and a reasonable approximation of the  $\text{Cd}(\text{OH})_2(\text{c})$  solubility data in 3M  $\text{Na}(\text{OH},\text{ClO}_4)$ . Of course, these comparisons should be interpreted only

Table V. Equilibrium Constants Involving Hydrolysis of Cd

Species <sup>a</sup>	logK <sup>b</sup>	Ionic Strength	Ref.
Cd(OH) <sub>2</sub> (c)	-14.14 <sup>c</sup>	0	c
	-14.41	3.0	2
	-14.35	0	1,2
	-14.28	0	11
	-12.77 to -14.58	0	23
CdOH <sup>+</sup>	d		
	4.60	0	11
	3.92	0	1
Cd(OH) <sub>2</sub> <sup>0</sup>	7.13 <sup>c</sup>	0	c
	8.85	0	11
	7.65	0	1
Cd(OH) <sub>3</sub> <sup>-</sup>	d		
	9.00		11
	< 8.70		1
Cd(OH) <sub>4</sub> <sup>2-</sup>	8.52 <sup>c</sup>	0	c
	9.08	0	11
	8.65	0	1

<sup>a</sup> The equilibrium constant for Cd(OH)<sub>2</sub>(c) pertains to Cd(OH)<sub>2</sub>(c)  $\rightleftharpoons$  Cd<sup>2+</sup> + 2OH<sup>-</sup>; for the other species the constants are for the reaction Cd<sup>2+</sup> + nOH<sup>-</sup>  $\rightleftharpoons$  Cd(OH)<sub>n</sub><sup>2-n</sup>. <sup>b</sup> The logK value of -14.00 for H<sub>2</sub>O  $\rightleftharpoons$  H<sup>+</sup> + OH<sup>-</sup> was used to convert values reported by Ref. 1 in terms of Cd<sup>2+</sup> + nH<sub>2</sub>O  $\rightleftharpoons$  Cd(OH)<sub>n</sub> + nH<sup>+</sup>. <sup>c</sup> This study. <sup>d</sup> Not important, this study.

as indications that the model for Cd(OH)<sub>2</sub>(c) solubility in NaOH and KOH is reasonable. No precise model for the solubility of Cd(OH)<sub>2</sub>(c) in NaOH-NaClO<sub>4</sub> systems at high concentrations can be developed until accurate experimental data become available with which the OH<sup>-</sup>-ClO<sub>4</sub><sup>-</sup> and Na<sup>+</sup>-OH<sup>-</sup>-ClO<sub>4</sub><sup>-</sup> ion-interaction parameters  $\Theta$  and  $\psi$  can be determined.

In Table V, the thermochemical data for hydrolysis of Cd obtained in this study are compared with those reported in widely accepted compilations of thermochemical data.<sup>(1,11)</sup> These comparisons show that the values of the solubility product obtained in this study are similar to those extrapolated from high ionic strengths and reported in the literature. However, there are significant differences in 1) values of the equi-

librium constants for other Cd hydrolysis species and 2) numbers of hydrolysis species needed to completely describe the system. Our data show that  $\text{CdOH}^+$  and  $\text{Cd}(\text{OH})_3^-$  are not necessary to describe the solubility of  $\text{Cd}(\text{OH})_2(\text{c})$ .

In summary, this final model, which includes all of the parameters listed in Tables III and IV, has been used to predict the Cd concentrations in equilibrium with the  $\text{Cd}(\text{OH})_2(\text{c})$  in the presence of 1) 0.01M  $\text{NaClO}_4$  obtained in this study; 2) 1.0M  $\text{NaClO}_4$  reported by Gubeli and Taillon;<sup>(4)</sup> 3) low concentration to 10M NaOH or KOH reported by Rozentsveig *et al.*,<sup>(24)</sup> Piater,<sup>(22)</sup> and Lake and Goodings;<sup>(25)</sup> and 4) 3.0 or 7.0M  $\text{Na}(\text{OH}, \text{ClO}_4)$  reported by Dyrssen and Lumme<sup>(3)</sup> and Ryan *et al.*<sup>(5)</sup> In all of these cases, the close agreement between the predicted and the observed solubilities shows that the model is consistent with the solubility data in both the low- and the high-ionic-strength solutions.

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