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A. R. Felmy
D. Rai
R. W. Fulton

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Pacific Northwest Laboratory
Richland, Washington 99352

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The Solubility of $\text{Cr}(\text{OH})_3(\text{am})$ in Concentrated NaOH and NaOH-NaNO_3 Solutions

Andrew R. Felmy

Dhanpat Rai

Robert W. Fulton

Pacific Northwest Laboratory^(a)
Richland, WA 99352

Abstract

The solubility of $\text{Cr}(\text{OH})_3(\text{am})$ was measured in concentrated NaOH ranging in concentration from 0.1M to 6.0M and in NaOH-NaNO_3 solutions with fixed NaOH concentration and variable NaNO_3 concentration at room temperature (22-23°C). Equilibrium between solids and solutions was approached relatively slowly and required approximately 60-70 days before steady-state concentrations were reached. A thermodynamic model, based upon the Pitzer equations, was developed from the solubility data in NaOH , which includes only two aqueous Cr species ($\text{Cr}(\text{OH})_4^-$ and $\text{NaCr}(\text{OH})_4(\text{aq})$) and ion-interaction parameters for Na^+ with $\text{Cr}(\text{OH})_4^-$. This model was then tested in the mixed NaOH-NaNO_3 solutions and found to be reliable.

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Introduction

Chromium is a major component of the Hanford waste tank sludges, and the presence of Cr in the sludges is a significant concern in the disposal of these sludges because Cr can interfere with the formation of waste glasses. It is, therefore, of interest to develop methodologies for removing Cr from the tanks sludges before these sludges are solidified into glass. One of the current pretreatment strategies for removing constituents that can interfere with glass formation, such as P and Cr, is to wash/dissolve the sludges in basic NaOH solutions. It is, therefore, of interest to examine the solubility of likely Cr-containing precipitates in NaOH solutions. The NaOH wash solutions can also dissolve other constituents from the sludge, such as NaNO_3 , and since these constituents can reach high concentration, their effects, on the solubility of Cr compounds should also be examined. For these reasons the solubility of Cr precipitates was measured in both NaOH and NaOH- NaNO_3 solutions.

This study focused on the solubility of Cr(III) precipitates, rather than Cr(VI) phases, for three reasons. One, Cr(III) is stable over a wide range of pH and Eh conditions in aqueous solution (see Figure 1). Two, the presence of reduced nitrogen compounds, such as NO_2^- , can enhance the stability of Cr(III) species over Cr(VI) species, and three, most Cr(VI) solid phases are very soluble and are unlikely to limit the solubility of Cr in the tank sludges. In addition, to the best of our knowledge, there are no existing data in the literature on the solubility of Cr(III) precipitates in mixed NaOH- NaNO_3 solutions and only limited data in NaOH solutions.

Experimental Procedures

The experimental procedures utilized in this study followed as closely as possible the procedure of Rai et al. (1987) who examined the solubility of $\text{Cr}(\text{OH})_3(\text{am})$ in dilute sodium perchlorate solutions. All experiments were conducted in a controlled atmosphere chamber (99.99% N_2 with a few ppm O_2) at room temperature (22-23°C). A 1M Cr(III) stock solution was prepared from reagent grade $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in acidic 0.1M HNO_3 to remove any traces of carbonate from the solution. Approximately 4 ml of the Cr stock solution,

Figure 1. Eh-pH diagram representing stability fields for Cr(III) and Cr(VI) species at 25°C (WHC 1993). Boundaries are displayed for log activities of dissolved species = -6. Precipitated Cr(III) is represented as $\text{Cr(OH)}_3(c)$.

containing approximately 208 mg Cr, were added to separate polyethylene centrifuge tubes and diluted to 10 ml with deionized water that had been sparged with $N_2(g)$ to remove any trace of CO_2 . $Cr(OH)_3(am)$ was precipitated by adjusting the pH of the solution in each centrifuge tube to approximately 9.5 with CO_2 free NaOH. The precipitate was allowed to age overnight in the mother liquor. The next day the precipitate was washed three times with deionized water that had been adjusted to pH 9.5 to remove any residual NO_3^- . Following washing, the precipitates were suspended in 35 ml of the NaOH or NaOH+ $NaNO_3$ solution of the appropriate molarity and placed on a shaker and continuously agitated.

The NaOH suspensions were sampled after 45 and 73 days of equilibration in the NaOH- $NaNO_3$ suspensions and were sampled after 24, 39, and 135 days of equilibration in the NaOH solutions. Sampling consisted of centrifugation followed by filtration through Amicon Type F-25 Centriflo Membrane Cones. Rai et al. (1987) describes the filtration procedure in detail and presents data demonstrating the effectiveness of these filters in separating solids from solutions in the case of dissolved Cr species. The resulting filtrate was then acidified to prevent the precipitation of $Cr(OH)_3(am)$ and the dissolved Cr concentration determined by inductively coupled plasma emission spectroscopy (ICP) or inductively coupled plasma mass spectrometry (ICP-MS).

X-Ray Diffraction (XRD) analysis was performed on selected Cr precipitates following the final sampling period. All precipitates were found to be amorphous to X-Ray. As a result, the solubility data reported in this study refer to the equilibrium solid phase as $Cr(OH)_3(am)$.

Results and Discussion

The solubility data for $Cr(OH)_3(am)$ in NaOH solutions in Figure 2a shows the same trend as the earlier results of Rai et al. (1987); Figure 2b, shows initially high solubilities that decrease with time. Equilibrium, or at least steady-state conditions, appear to be reached after approximately 60 days of equilibration. The solubilities in NaOH (Figure 2a) also show a consistent trend of increasing solubility with increasing NaOH concentration

Figure 2. Solubility data for $\text{Cr}(\text{OH})_3(\text{am})$ in NaOH solutions. (a) Data of Rai et al. 1987. (b) Data obtained in this study.

even to approximately 10 m NaOH. This result is important in that it indicates that significant amounts of Cr(III) can be solubilized at high NaOH concentration. The solubilities obtained in this study, at least below 2.0M NaOH, are also in good agreement with those of Rai et al. (1987), see Figure 3.

Rai et al. 1987 in their earlier work in dilute perchlorate media interpreted their results at pH values > 12 in terms of only one solubility reaction:

Because these data were in relatively dilute solution, the calculated standard state equilibrium constant for this reaction should be reasonable. However, it is not expected that their model would be valid at high NaOH concentration owing to the large variation in the activity coefficients for OH^- and Cr(OH)_4^- . At high concentration, activity coefficients are not universal functions of ionic strength and this fact is accounted for in the Pitzer formalism by the use of ion-interaction coefficients for binary (i.e., β^0 , β^1 , C^ϕ for $\text{Na}^+\text{-OH}^-$ and $\text{Na}^+\text{-Cr(OH)}_4^-$) and common-ion ternary interactions (i.e. Θ for $\text{OH}^-\text{-Cr(OH)}_4^-$). Although the necessary Pitzer ion-interaction parameters for $\text{Na}^+\text{-OH}^-$ are well known, the parameters involving the Cr(OH)_4^- ion are unknown and must be either calculated (fit) or estimated. As an example, if the equilibrium reaction (eqn 1) given by Rai et al. (1987) is combined with the Pitzer ion-interaction parameters for $\text{Na}^+\text{-OH}^-$ given by Pabalan and Pitzer (1987) and the values for the Al(OH)_4^- ion (Wesolowski 1992) are used as analogs for Cr(OH)_4^- , the predicted solubilities (see dashed line in Figure 3) give very good agreement with the experimental data at low NaOH (<2M) but are significantly below the experimental values at higher NaOH concentration. Several attempts to explain these deviations between model and experiment were tested. First, the values of β^0 , β^1 , C^ϕ for $\text{Na}^+\text{-Cr(OH)}_4^-$ were fit to the $\text{Cr(OH)}_3(\text{am})$ solubility data in NaOH. The resulting parameter values were all negative, a fact that can be indicative of ion association in the aqueous solution. However, when higher hydrolysis species such as Cr(OH)_5^{2-} , and Cr(OH)_6^{3-} were introduced into the model and their standard chemical potentials fit to the data in NaOH, the resulting model did not work well when tested on the $\text{Cr(OH)}_3(\text{am})$ solubility data in mixed NaOH- NaNO_3 solutions. In addition, there are no data in the JCPDS for Cr(III) solid phases of higher sodium content

Figure 3. Calculated and experimental solubility data for $\text{Cr}(\text{OH})_3(\text{am})$ in NaOH.

than $\text{NaCrO}_2(\text{c})$, indicating that structural units such as $\text{Cr}(\text{OH})_5^{2-}$ or $\text{Cr}(\text{OH})_6^{3-}$ are not important, at least in the solid phases. The only model that gave good overall agreement with the solubility data in NaOH (see solid line in Figure 3) and worked well when tested in the mixed NaOH-NaNO_3 system involved the introduction of a $\text{NaCr}(\text{OH})_4(\text{aq})$ species. The standard chemical potential of this species was determined (fit) from the data in NaOH with the same model parameters for the $\text{Cr}(\text{OH})_4^-$ as used to calculate the dashed line in Figure 3. The agreement between model and experiment for this model is quite good. In addition when this model is applied to the solubility data in the mixed NaOH-NaNO_3 system, the agreement between model and experiment is also quite good, with no model parameters adjusted (see Figure 4). This latter fact is especially important since it represents at least a partial validation of this thermodynamic model. The necessary model parameters for this thermodynamic model are summarized in Table 1.

In summary, the solubility of $\text{Cr}(\text{OH})_3(\text{am})$ was studied in NaOH and mixed NaOH-NaNO_3 solutions extending to high concentration. The results at lower NaOH (i.e., $<2.5\text{M}$ NaOH) were consistent with previous investigators. A relatively simple thermodynamic model was developed which includes only two aqueous Cr species and explains all of the solubility data for $\text{Cr}(\text{OH})_3(\text{am})$ in both NaOH and NaOH-NaNO_3 solutions extending to very high electrolyte concentration.

Table 1. Parameters for the aqueous thermodynamic model.

<u>Reaction</u>	<u>Log K^0</u>
$\text{Cr}(\text{OH})_3(\text{am}) + \text{OH}^- = \text{Cr}(\text{OH})_4^-$	-18.30
$\text{Na}^+ + \text{Cr}(\text{OH})_4^- = \text{NaCr}(\text{OH})_4(\text{aq})$	-0.052

Ion-Interaction Parameters(all $\text{Al}(\text{OH})_4^-$ analogs)

$B^0(\text{Na}^+-\text{Cr}(\text{OH})_4^-)$	= .045
$B^1(\text{Na}^+-\text{Cr}(\text{OH})_4^-)$	= .310
$C^0(\text{Na}^+-\text{Cr}(\text{OH})_4^-)$	= -.0003
$\theta(\text{OH}^--\text{Cr}(\text{OH})_4^-)$	= .014
$\psi(\text{Na}^+-\text{OH}^--\text{Cr}(\text{OH})_4^-)$	= -.0048

Figure 4. Solubility data for Cr(OH)₃(am) in mixed NaOH-NaNO₃ solutions.

References

Pabalan R.T. and K.S. Pitzer (1987). Thermodynamics of NaOH(aq) in hydrothermal solutions. Geochimica et Cosmochima Acta: 51;829-837.

Rai D., B.M. Sass, and D.A. Moore. (1987). Chromium (III) hydrolysis constants and solubility of chromium (III) hydroxide. Inorganic Chemistry: 26;345-349.

Wesolowski D.J. (1992). Aluminum speciation and equilibria in aqueous solution: I. The solubility of gibbsite in the system Na-K-Cl-OH-Al(OH)₃ from 0 to 100°C. Geochimica et Cosmochima Acta: 56;1065-1091.

WHC, (1993). Fate and Transport of Chromium in the Environment, WHC-SD-EN-ES-035, prepared by E. C. Thornton, Westinghouse Hanford Company, Richland, Washington.