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Modeling Actinide Solubilities in Alkaline to Hyperalkaline Solutions: Part One, Solubility of $Am(OH)_3(s)$ in KOH Solutions

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INTRODUCTION

Accurate knowledge of actinide speciation and solubilities in alkaline solutions is important to nuclear waste management. First, in the tank wastes such as those at Savanah River site and Hanford site, the solutions contain high concentrations of bases [1-2]. Second, the solutions in equilibrium with cements in geological repositories would also be highly alkaline with concentrations of OH^- in the order of hundreds of milli-molars [3]. Obviously, accurate predictions of actinide solubilities in these highly alkaline solutions require a thermodynamic model applicable to high ionic strengths with high base concentrations. The Nuclear Energy Agency (NEA) series on chemical thermodynamics of actinides (NEA-DB)[4] are based on the specific ion interaction theory (SIT) activity coefficient model for evaluation, which is valid to an ionic strength of ~3.5 m. The speciation scheme for Am(III) in the NEA series includes Am^{3+}, $Am(OH)^{2+}$, $Am(OH)_2^+$ and $Am(OH)_3(aq)$. This speciation scheme may not extend to the alkaline or hyperalkaline region, as the recent work has detected the possible presence of $Ho(OH)_4^-$ and $Tm(OH)_4^-$ around pH 10[5]. Therefore, it is not suitable for modeling actinide solubilities in highly alkaline solutions.

DESCRIPTION OF THE PRESENT WORK

In this work, a Pitzer model is tentatively developed for the $K^+(Na^+)$—$Am(OH)_4^-$—OH^- system based on $Am(OH)_3(s)$ solubility data in highly alkaline solutions. The database used for the modeling is summarized in [6]. The platform for the modeling is the computer program EQ3/6 Version 8.0a [7-8]. The purpose of this work is to stimulate, and to provide guidance for, the research investigating speciation and solubility of Am(III) in alkaline and hyperalkaline region, which would eventually lead to an improved model for accurate description of Am(III) solubility in this region in the near future.

It is observed that $Am(OH)_4^-$ is the dominant species in highly alkaline solutions [3]. Under highly alkaline conditions, solubility reaction of $Am(OH)_3(s)$ is expressed as,

$$Am(OH)_3(s) + OH^- = Am(OH)_4^- \qquad (1)$$

RESULTS AND DISCUSSIONS

In this work, solubilities of $Am(OH)_3(s)$ expressed as Reaction (1) are modeled as a function of KOH concentrations. In the modeling, the stability constant for $Am(OH)_4^-$ is evaluated from $Am(OH)_3(s)$ solubility data in KOH solutions to 10 M, which are taken from [3]. In the model preliminarily developed, the Pitzer interaction parameters related to $Al(OH)_4^-$ [9-10] are used as analogs for the interaction parameters involving $Am(OH)_4^-$ to obtain the stability constant for $Am(OH)_4^-$. The preliminary model developed in this study can reproduce the experimental data with good agreement. Notice that the model is subject to revision when additional data become available.

Table 1. Preliminary equilibrium constants at infinite dilution at 25°C and 1 bar for the K^+—$Am(OH)_4^-$—Cl^-—OH^- system

Reaction	log K^o	Reference and Remarks
$Am(OH)_4^- + 4H^+ = Am^{3+} + 4H_2O(l)$	39.83 ± 0.15 (2σ)	This study, based on solubility of $Am(OH)_3(cr)$ in KOH solutions from [3]

Table 2. Preliminary Pitzer interaction parameters at 25°C and 1 bar for the K^+—$Am(OH)_4^-$—Cl^-—OH^- system

Pitzer Binary Interaction Parameters					
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	Reference
K^+	$Am(OH)_4^-$	0.051	0.25	–0.00090	This study, using the parameters for $Na^+/Al(OH)_4^-$ from [9] as analogs
Pitzer Mixing Interaction Parameters (theta and psi parameters)					
Species *i*	Species *j*	Species *k*	θ_{ij}	Ψ_{ijk}	Reference
OH^-	$Am(OH)_4^-$	K^+	0.014	–0.0048	This study, using the parameters for $OH^-/Al(OH)_4^-$ and $OH^-/Al(OH)_4^-/Na^+$ from [9] as analogs
Cl^-	$Am(OH)_4^-$	K^+		–0.004857	This study, using the parameter for $Cl^-/Al(OH)_4^-/Na^+$ from [10] as an analog

Supporting Data

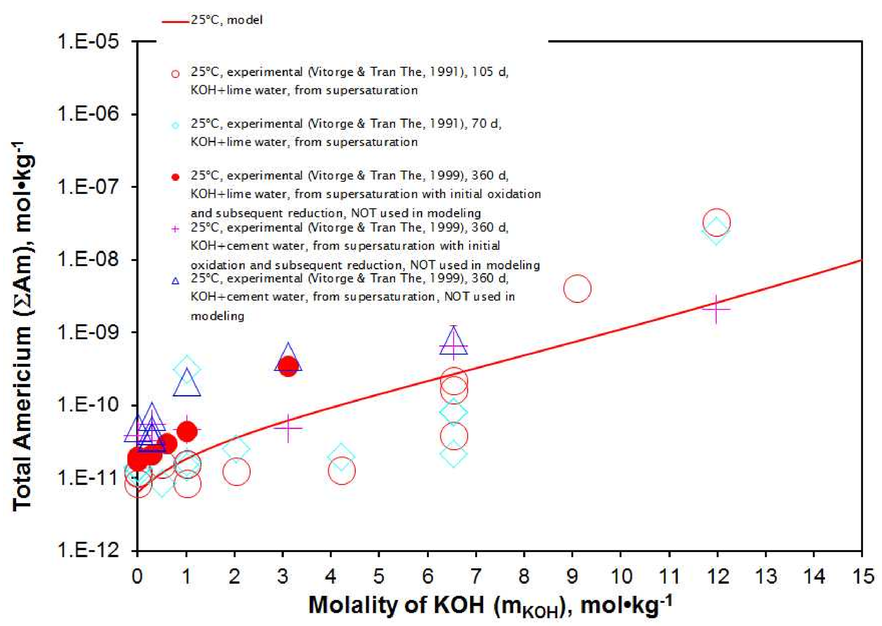

Figure 1. A plot showing solubilities of $Am(OH)_3(s)$ as a function of ionic strength in KOH solutions.

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