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"Poster for Actinide Brine Chemistry in Salt Repositories (ABC-Salt) Workshop"

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Experimental Determination of Solubilities of Sodium Tetraborate (Borax) in NaCl Solutions to High Ionic Strengths, and Thermodynamics of $NaB(OH)_4(aq)$

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ABSTRACT

Recent experimental studies have suggested that borate could potentially complex with Nd(III), an analog to Am(III) (Borkowski et al., 2010). Therefore, a comprehensive thermodynamic model involving interactions of borate with major ions in brines is needed to accurately describe the contributions of borate to the solubility of Am(III) in brines in salt formations, as they contain significant concentrations of borate. In WIPP brines, sodium concentrations are high. Therefore, the interactions of borate with sodium are important. In this study, solubility experiments on sodium tetraborate ($Na_2B_4O_7$•$10H_2O$, borax) are conducted in NaCl solutions up to 5.0 m at room temperature (22.5 ± 1.5ºC). In combination with solubility data for sodium tetraborate in Na_2SO_4 solutions from the literature, the solubility constant (log K) for sodium tetraborate regarding the following reaction,

$$Na_2B_4O_7•10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O\ (l)$$

is determined as –24.88 ± 0.10 ºC based on the Pitzer model. In addition, the lambda parameter ($\lambda_{NaB(OH)4(aq),\,Na}$) for the interaction between $NaB(OH)_4(aq)$ and Na^+ is evaluated as 0.09192. It is also discovered that it is necessary to revise $\theta_{B(OH)4,\,SO4}$ of the Felmy and Weare (1986) model and include $\Psi_{B4O5(OH)4,\,SO4,\,Na}$ in order to accurately model the solubility of sodium tetraborate in a Na_2SO_4 medium. The revised $\theta_{B(OH)4,\,SO4}$ is 0.1697 in comparison with the value of –0.012 in the Felmy and Weare (1986) model.

Experimental Methods

In our solubility experiments, about 5 grams of the solubility controlling material—sodium tetraborate from Fisher Scientific was weighed out and placed into 150 mL plastic bottles. Then, 100 mL of supporting solutions were added into those bottles. Once filled, the lids of the bottles were sealed with parafilm. The supporting electrolytes are a series of NaCl solutions. Undersaturation experiments are conducted at the laboratory room temperature (22.5 ± 1.5 ºC)

Boron and sodium concentrations of solutions were analyzed with a Perkin Elmer dual-view inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin Elmer DV 3300). Calibration blanks and standards were precisely matched with experimental matrices. The correlation coefficients of calibration curves in all measurements were better than 0.9995. The analytical precision is better than 1.00% in terms of the relative standard deviation (RSD) based on replicate analyses.

Acknowledgements

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Results and Discussions

The solubilities of sodium tetraborate shown as the total boron concentrations in NaCl and Na_2SO_4 media are presented in Figure 1. Solubility data in NaCl media are produced in this study. Solubility data in Na_2SO_4 media are from the literature (Sborgi et al., 1924). It is clear from Figure 1 that the revised model presented in this study performs very well in a wide range of ionic strength.

In Figure 2, solubilities of sodium tetraborate in mixtures of NaCl + Na_2SO_4 media predicted by the revised model and by the Felmy and Weare (1986) model (Table 1) are compared with independent experimental data from the literature up to ionic strengths of 8.0 m, which are not used in model development. The comparison demonstrates that there is a significant improvement associated with the current model (Table 2) in predicting the solubilities of sodium tetraborate. The validation test indicates that the differences between solubilities predicted by the current model and experimental solubilities are less than 0.05 m with an error less than 30%. In comparison, the differences between solubilities predicted by the Felmy and Weare model and experimental solubilities are generally higher than 0.05 m, and can be as high as 0.17 m with an error up to 150%.

Table 1. Felmy and Weare (1986) model for the Na–$B(OH)_3$–Cl–SO_4 system

Pitzer Binary Interaction Cofficients				
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ
Na^+	$B(OH)_4^-$	–0.0427	0.089	0.0114
Na^+	$B_3O_3(OH)_4^-$	–0.056	–0.910	
Na^+	$B_4O_5(OH)_4^{2-}$	–0.11	–0.40	
Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Species				
Species, *i*	Species, *j*	Species, *k*	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}
$B(OH)_4^-$	Cl^-	Na^+	–0.065	–0.0073
$B(OH)_4^-$	SO_4^{-2}		–0.012	
$B_3O_3(OH)_4^-$	Cl^-	Na^+	0.12	–0.024
$B_3O_3(OH)_4^-$	SO_4^{-2}		0.10	
$B_4O_5(OH)_4^{-2}$	Cl^-	Na^+	0.074	0.026
$B_4O_5(OH)_4^{-2}$	SO_4^{-2}		0.12	
$B(OH)_3(aq)$	Cl^-		0.091	
$B(OH)_3(aq)$	SO_4^{-2}	Na^+	0.018	0.046
$B(OH)_3(aq)$	$B_3O_3(OH)_4^-$		–0.20	
$B(OH)_3(aq)$	Na^+		–0.097	
Equilibrium Constant for Solubility Reaction				
Reaction			log K	
$Na_2B_4O_7•10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$			–24.49	

Table 2. The revised thermodynamic model for the Na–$B(OH)_3$–Cl–SO_4 system developed in this study. Unless otherwise noted, other parameters, which are not listed, are the same as those in Felmy and Weare (1986) model.

Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Species				
Species, *i*	Species, *j*	Species, *k*	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}
$B(OH)_4^-$	SO_4^{-2}		0.1697	
$NaB(OH)_4(aq)$	Na^+		0.09192	
$B_4O_5(OH)_4^{-2}$	SO_4^{-2}	Na^+		0.096
Equilibrium Constants for Solubility and Complex Formation Reactions				
Reaction			log K	
$Na_2B_4O_7•10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$			–24.88 ± 0.10 (2σ) (This Study)	
$Na^+ + B(OH)_4^- = NaB(OH)_4(aq)$			0.25 (Akinfiev et al., 2006)	

Supporting Data

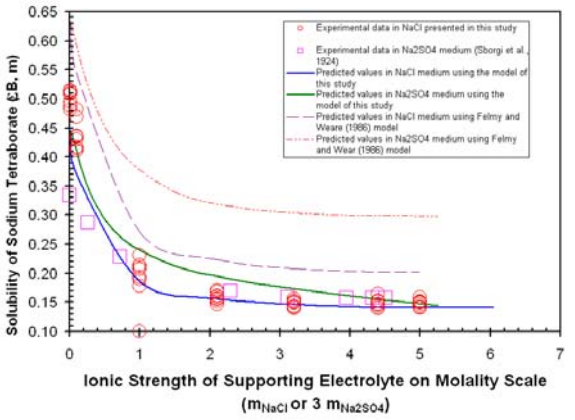

Figure 1. Solubility of sodium tetraborate as a function of ionic strength in NaCl and Na_2SO_4 media.

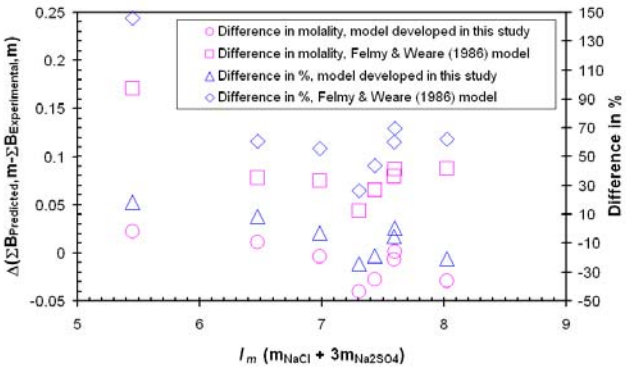

Figure 2. Comparison of model predicted solubilities of sodium tetraborate in mixtures of NaCl + Na_2SO_4 with experimental data from the literature in the same mixtures. Experimental data, which are complied by Silcock (1979), are independent from model development.