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Measurement and modelling of solubility for calcium sulfate dihydrate and calcium hydroxide in NaOH/KOH solutions

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ABSTRACT

The solubility of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) in alkali solutions is essential to understand their desilication behavior from Bayer liquor. In this work, solubilities of calcium sulfate dihydrate and calcium hydroxide for the ternary systems of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – NaOH – H_2O , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – KOH – H_2O , and $\text{Ca}(\text{OH})_2$ – NaOH – H_2O were measured by using the classic isothermal dissolution method over the temperature range of 25–75 °C. The Pitzer model embedded in Aspen Plus platform was used to model the experimental solubility data for these systems. The experimental solubility data was employed to obtain the new binary interaction parameters for $\text{Ca}(\text{OH})^+ \text{--} \text{OH}^-$, $\text{Ca}(\text{OH})^+ \text{--} \text{Ca}^{2+}$ and $\text{Ca}(\text{OH})^+ \text{--} \text{K}^+$, suggesting that the species $\text{Ca}(\text{OH})^+$ is a dominant species in simulated solubility for alkali systems. Validation of the parameters was performed by predicting the solubility for the ternary systems of $\text{Ca}(\text{OH})_2$ – NaOH – H_2O , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – NaOH – H_2O and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – KOH – H_2O with the overall average relatively deviation (ARD) of 2.12%, 0.75% and 1.63%, respectively.

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1. Introduction

Bauxite, the major source of aluminium containing ore used in the production of alumina, includes several impurities, such as iron, titanium and silica components [1–3]. The presence of silica in bauxite can give rise to an appreciable loss of caustic soda and aluminum in forming desilication products (DSP), as well as cause scale build-up due to the re-precipitation of complex sodalite-type DSP on plant surfaces. Therefore, during the extraction of alumina from bauxite, the removal of silicate ions is necessary, especially when using diasporic bauxite containing high silica. The conventional method of removing silicates can be achieved by introducing chemicals, such as calcium oxide (CaO) and calcium hydroxide ($\text{Ca}(\text{OH})_2$) [4–6].

Previous experimental studies show that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ also has high desilication capacity, and significant amounts of sulfate in liquor can be included into the DSP which became more stable desilication product [7]. The solubilities of calcium sulfate dihydrate in acid solutions have been extensively studied. However, limited work has been done about the solubility of calcium sulfate dihydrate in alkali solutions. Furthermore, we found that calcium sulfate dihydrate in sodium hydroxide solutions was unstable and

quickly transformed to calcium hydroxide at NaOH concentration more than 0.10 mol L^{-1} . In order to fully understand the desilication behavior of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ in alkali solutions, it is necessary to investigate the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ in alkali solutions.

A suitable thermodynamic model is very important for calculating the thermodynamic properties of mixed electrolyte solutions, and for evaluating the results of solubility data. Most of the previous studies have focused on the solubility of calcium sulfate dihydrate in acid solutions. Tanji [8] developed a computer program around a chemical model based on the formation of the ion pairs of CaSO_4^0 , MgSO_4^0 , and NaSO_4^- . This model proved useful in dealing with the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in dilute acid systems. Li and Demopoulos [9] used the Bromley–Zemaitis activity coefficient model to calculate the solubility of calcium sulfate in multi-component aqueous chloride solutions. Azimi et al. [10] applied the mixed solvent electrolyte (MSE) activity coefficient model to accurately model the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and its scaling potential in sulfate systems. Barba et al. [11,12] successfully used their thermodynamic model based on the nonrandom two-liquid (NRTL) equation to investigate the behavior of calcium sulfate dihydrate solubility in aqueous solutions of Na_2SO_4 and MgCl_2 on the basis of experimental solubility values at 40 °C. Pitzer's equations were also used by Meijer and Rosmalen [13] who proposed a computer program to calculate the solubility and supersaturation of CaSO_4 in seawater. Harvie and Weare [14] using Pitzer's framework developed a chemical model

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for predicting solubility of gypsum in NaCl solutions. However, the chemistry of calcium sulfate dihydrate systems has been rarely modelled in multi-component alkali solutions due to scarce solubility data. Pitzer equation has been successfully used to calculate solubility of $\text{Ca}(\text{OH})_2$ in the NaOH solutions at 13, 20 and 40 °C [15], and the experimental solubility data can be well correlated by the model. Hence, the Pitzer model has shown the potential capability in predicting solubility data of salts for alkali systems. Furthermore, the Pitzer model has been rendered into AspenPlus™ commercial software and widely applied in industry. Consequently, we decided to choose the Pitzer model embedded in the AspenPlus platform to model the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ in alkali solutions in present study.

In this work, the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ for the ternary systems of CaSO_4 –NaOH– H_2O and CaSO_4 –KOH– H_2O were presented at the temperature range of 35–75 °C and the alkali concentration range of 0–0.09 mol L^{−1}. The solubility data of $\text{Ca}(\text{OH})_2$ for the ternary system $\text{Ca}(\text{OH})_2$ –NaOH– H_2O were also measured at the temperature range of 25–75 °C and the NaOH concentration range of 0–0.5 mol L^{−1}. The solubility data for above ternary systems were successfully modelled using the Pitzer model embedded in the AspenPlus platform. New interaction parameters for the associated hydroxyl calcium ion $\text{Ca}(\text{OH})^+$ with the other dominant species in alkali solutions were determined.

2. Experimental

2.1. Materials

All chemical reagents used in the experiments were analytical grade without further purification. The concentration of the solutions made with reagent grade NaOH and KOH was verified by titration with standardized H_2SO_4 . The water used in all experimental work was double distilled water (conductivity < 0.1 $\mu\text{S cm}^{-1}$).

2.2. Apparatus and procedure

The 200 mL of alkali solution of known composition was poured into a 250-mL polytetrafluoroethylene bottle, which were equipped with a magnetic stirrer and sealed with a polytetrafluoroethylene-lined cap. The bottles were then immersed in a temperature-controlled water bath, allowing the solution to stir continuously for about 0.5 h to establish the temperature equilibrium. The temperature was kept constant within 0.1 °C. Then, excess solid (4 g) was quickly added to the solutions in bottles, which were tightly sealed again. The standard equilibration time used was 6 h, and the determination of equilibration time is explained in the next section. After the solid–liquid equilibrium was attained, stirring was stopped to allow solids to settle by 6 h. The supernatant solution was then taken with a pipette and immediately filtered by using 0.22 μm Whatman Puradisc syringe filters. The clear filtrate was added into a 25-mL volumetric flask which was kept in the water bath and then heated to bath temperature for measuring the density of saturated solution. The solubility of solids was determined by titration of Ca with EDTA. The solid phase was filtered and washed three times with water. The washed solids were dried at 50 °C for 12 h and then analyzed by X-ray powder diffraction to determine the final solid phase.

2.3. Determination of equilibration time

The equilibration time in solubility measurements normally varies from several hours to several days depending on the dissolution rate of the solid phase and the applied conditions [16]. Li and Demopoulos reported that the equilibration time of solid and liquid

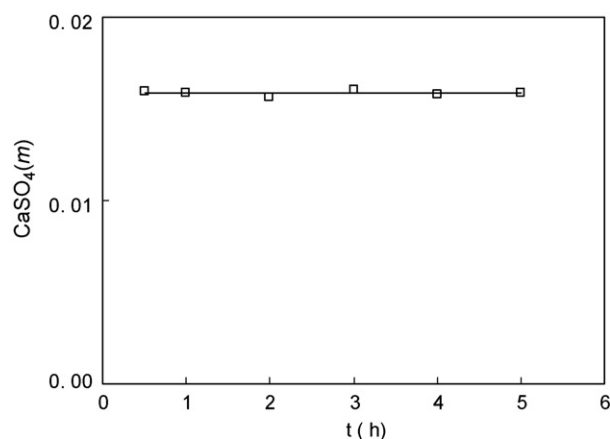


Fig. 1. Solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in NaOH solutions versus the equilibrium time.

can be reached within 0.5 h in determining the solubility of calcium sulfate dihydrate in HCl solution [17]. As can be seen from Fig. 1, after 30 min, the solubility of calcium sulfate dihydrate in sodium hydroxide solution stabilizes. In present work, a longer time of 6 h was selected to ensure solubility equilibrium.

2.4. Reproducibility

The solubility of calcium hydroxide in pure water has been investigated by Cameron and Robinson [18]. Similar experiments were carried out by the authors to verify the reproducibility and accuracy of the adopted procedure in this work. The solubility of calcium hydroxide in water at 25 °C was measured. The uncertainty of the determined solubility values was within $\pm 0.00009 \text{ mol kg H}_2\text{O}^{-1}$ with a relative deviation of 0.4%. The results showed that the experimental procedure for measuring solubility was considered to be reliable and feasible.

2.5. Solubility measurement

The XRD analysis of equilibrated solid phases showed calcium sulfate dihydrate in alkali solutions to be stable at the temperature range of 35–75 °C and the alkali concentration range of 0.01–0.09 mol L^{−1}. The results of equilibrated solids characterization by XRD are listed in Table 1. It can be clearly seen that calcium sulfate dihydrate in alkali solutions is stable at the alkali concentration range of 0.01–0.09 mol L^{−1} while it was partially transformed to calcium hydroxide at alkali concentration of 0.1 mol L^{−1}.

The solubility data of calcium sulfate dihydrate for the ternary systems of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ –NaOH– H_2O and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ –KOH– H_2O over the temperature range from 35 to 75 °C are measured by using

Table 1
XRD characterization of the equilibrated solids in the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ –NaOH–KOH– H_2O systems.

T (K)	c (mol L ^{−1})	t (h)	Equilibrated solid phase(s)
308.15	0.01–0.09 (NaOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
318.15	0.01–0.09 (NaOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
328.15	0.01–0.09 (NaOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
338.15	0.01–0.09 (NaOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
348.15	0.01–0.09 (NaOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
308.15–348.15	0.1 (NaOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
308.15	0.01–0.09 (KOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
318.15	0.01–0.09 (KOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
328.15	0.01–0.09 (KOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
338.15	0.01–0.09 (KOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
348.15	0.01–0.09 (KOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
308.15–348.15	0.1 (KOH)	6	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$

Table 2
Solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (1) in NaOH (2) + H_2O (3).

M_2 (mol L ⁻¹)	ρ_s (g mL ⁻¹)	C_1 (g L ⁻¹)	m_1^{exp} (mol kg ⁻¹)	m_1^{cal} (mol kg ⁻¹)	$(m_1^{\text{exp}} - m_1^{\text{cal}})/m_1^{\text{exp}}$ (%)
$T = 308.15 \text{ K}$					
0.00	0.9961	2.1044	0.01550	0.01541	0.60
0.01	0.9958	2.3281	0.01724	0.01720	0.24
0.03	0.9985	2.7347	0.02022	0.01979	2.12
0.05	1.0005	3.1097	0.02297	0.02303	-0.28
0.07	1.0004	2.7735	0.02050	0.02049	0.05
0.09	0.9984	2.5449	0.01886	0.01893	-0.40
$T = 318.15 \text{ K}$					
0.00	0.9923	2.0955	0.01539	0.01529	0.63
0.01	0.9912	2.3050	0.01715	0.01718	-0.20
0.03	0.9935	2.7111	0.02014	0.01991	1.14
0.05	0.9942	2.8216	0.02097	0.02118	-0.99
0.07	0.9957	2.6394	0.01960	0.01932	1.41
0.09	0.9964	2.4481	0.01817	0.01802	0.88
$T = 328.15 \text{ K}$					
0.00	0.9877	2.0535	0.01512	0.01503	0.57
0.01	0.9897	2.2612	0.01684	0.01704	-1.18
0.03	0.9903	2.6905	0.02006	0.02004	0.08
0.05	0.9899	2.6724	0.01995	0.02008	-0.68
0.07	0.9914	2.4432	0.01822	0.01820	0.12
0.09	0.9938	2.2964	0.01709	0.01715	-0.31
$T = 338.15 \text{ K}$					
0.00	0.9825	1.9860	0.01461	0.01457	0.26
0.01	0.9860	2.2103	0.01653	0.01672	-1.15
0.03	0.9863	2.6409	0.01977	0.02014	-1.87
0.05	0.9883	2.4620	0.01840	0.01858	-0.95
0.07	0.9875	2.2814	0.01708	0.01707	0.04
0.09	0.9908	2.1890	0.01634	0.01633	0.04
$T = 75^\circ \text{C}$					
0.00	0.9767	1.8995	0.01395	0.01385	0.69
0.01	0.9842	2.1133	0.01583	0.01606	-1.44
0.03	0.9847	2.6253	0.01968	0.01983	-0.74
0.05	0.9856	2.2792	0.01708	0.01693	0.89
0.07	0.9856	2.1400	0.01605	0.01592	0.79
0.09	0.9865	2.0524	0.01539	0.01555	-1.05
ARD (%) = 0.73					

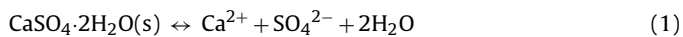
$$\text{ARD}(m) = \left(\sum_{i=1}^n |m^{\text{cal}} - m^{\text{exp}}| / m^{\text{exp}} \right) / n.$$

above procedure and tabulated in Tables 2 and 3. The solubility data of calcium hydroxide for ternary system $\text{Ca}(\text{OH})_2$ – NaOH – H_2O at the temperature range of 25–75 °C are also determined and listed in Table 4.

3. Modelling approach

3.1. Thermodynamic equilibria of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (or $\text{Ca}(\text{OH})_2$)– NaOH – KOH – H_2O system

Eqs. (1)–(3) represent the common dissociation equilibria for all systems considered in this work.



The thermodynamic equilibrium constants for the dissociation reactions (1)–(3) are:

$$\begin{aligned} K_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})} &= (m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}})(m_{\text{SO}_4^{2-}} \gamma_{\text{SO}_4^{2-}})(\alpha_{\text{H}_2\text{O}})^2 \\ &= (m_{\text{Ca}^{2+}})(m_{\text{SO}_4^{2-}}) \gamma_{\pm \text{CaSO}_4}^2 (\alpha_{\text{H}_2\text{O}})^2 \end{aligned} \quad (4)$$

$$K_{\text{Ca}(\text{OH})_2(\text{s})} = (m_{\text{Ca}(\text{OH})^+} \gamma_{\text{Ca}(\text{OH})^+})(m_{\text{OH}^-} \gamma_{\text{OH}^-}) \quad (5)$$

$$K_{\text{Ca}(\text{OH})^+} = \frac{(m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}})(m_{\text{OH}^-} \gamma_{\text{OH}^-})}{(m_{\text{Ca}(\text{OH})^+} \gamma_{\text{Ca}(\text{OH})^+})} \quad (6)$$

By re-arranging Eqs. (4)–(6), the molalities of the free calcium ion Ca^{2+} for the ternary system $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ –alkali– H_2O , the free calcium ion Ca^{2+} for the ternary system $\text{Ca}(\text{OH})_2$ – NaOH – H_2O , and the hydroxyl calcium ion $\text{Ca}(\text{OH})^+$ are:

$$m_{\text{Ca}^{2+}} = \frac{K_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})}}{m_{\text{SO}_4^{2-}} \gamma_{\pm \text{CaSO}_4}^2 (\alpha_{\text{H}_2\text{O}})^2} \quad (7)$$

$$m_{\text{Ca}(\text{OH})^+} = \frac{K_{\text{Ca}(\text{OH})_2(\text{s})}}{\gamma_{\text{Ca}(\text{OH})^+}(m_{\text{OH}^-} \gamma_{\text{OH}^-})} \quad (8)$$

$$m_{\text{Ca}^{2+}} = \frac{K_{\text{Ca}(\text{OH})^+}(m_{\text{Ca}(\text{OH})^+} \gamma_{\text{Ca}(\text{OH})^+})}{\gamma_{\text{Ca}^{2+}}(m_{\text{OH}^-} \gamma_{\text{OH}^-})} \quad (9)$$

The solubility of calcium sulfate dihydrate and calcium hydroxide is equal to the sum of molalities of the calcium containing species as follows:

$$s_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} = m_{\text{Ca}^{2+}} + m_{\text{Ca}(\text{OH})^+} \quad (10)$$

$$s_{\text{Ca}(\text{OH})_2} = m_{\text{Ca}^{2+}} + m_{\text{Ca}(\text{OH})^+} \quad (11)$$

Table 3
Solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (1) in KOH (2) + H_2O (3).

M_2 (mol L ⁻¹)	ρ_s (g mL ⁻¹)	C_1 (g L ⁻¹)	m_1^{exp} (mol kg ⁻¹)	m_1^{cal} (mol kg ⁻¹)	$(m_1^{\text{exp}} - m_1^{\text{cal}})/m_1^{\text{exp}}$ (%)
$T = 308.15 \text{ K}$					
0.01	0.9954	2.3545	0.01744	0.01722	1.29
0.03	1.0016	2.8455	0.02098	0.01990	5.18
0.05	1.0021	3.2190	0.02376	0.02315	2.59
0.07	1.0026	2.7444	0.02026	0.02047	-1.05
0.09	1.0027	2.5557	0.01888	0.01891	-0.16
$T = 318.15 \text{ K}$					
0.01	0.9915	2.3420	0.01742	0.01720	1.24
0.03	0.9947	2.8147	0.02090	0.02000	4.30
0.05	0.9956	2.9109	0.02162	0.02124	1.79
0.07	0.9967	2.6164	0.01943	0.01932	0.55
0.09	0.9988	2.4556	0.01822	0.01799	1.22
$T = 328.15 \text{ K}$					
0.01	0.9910	2.2958	0.01708	0.01707	0.08
0.03	0.9898	2.7925	0.02084	0.02013	3.42
0.05	0.9949	2.6616	0.01978	0.02008	-1.54
0.07	0.9960	2.4354	0.01810	0.01820	-0.56
0.09	0.9977	2.3401	0.01737	0.01713	1.39
$T = 338.15 \text{ K}$					
0.01	0.9873	2.1929	0.01638	0.01674	-2.20
0.03	0.9875	2.7148	0.02031	0.02041	-0.53
0.05	0.9942	2.4420	0.01816	0.01861	-2.48
0.07	0.9953	2.2715	0.01689	0.01708	-1.16
0.09	0.9968	2.1787	0.01619	0.01631	-0.78
$T = 348.15 \text{ K}$					
0.01	0.9871	2.1765	0.01626	0.01609	1.04
0.03	0.9877	2.6395	0.01974	0.01976	-0.12
0.05	0.9896	2.3382	0.01746	0.01703	2.51
0.07	0.9919	2.1928	0.01636	0.01597	2.37
0.09	0.9942	2.1177	0.01578	0.01555	1.41
ARD (%) = 1.64					

In order to calculate the solubility of calcium sulfate dihydrate and calcium hydroxide in alkali solution, the solubility product $K_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})}$ and $K_{\text{Ca}(\text{OH})_2(\text{s})}$, and $K_{\text{Ca}(\text{OH})^+}$ as well as the activity coefficients of relevant species need to be determined.

3.2. Equilibrium constant

The equilibrium constant of a reaction can be evaluated from the Gibbs free energy relation:

$$K = \exp\left(-\frac{\Delta G_r^0}{RT}\right) = \exp\left(-\frac{\sum \nu_i \mu_i^0}{RT}\right) \quad (12)$$

Unfortunately, the equilibrium constant for the SLE calculation in Eq. (12) determined from the standard chemical potential μ^0 of individual species is not always available or accurate. Therefore, this equilibrium constant is regressed from experimental measurements in the form of a temperature function:

$$\ln K(T) = k_1 + \frac{k_2}{T} + k_3 \ln T + k_4 T \quad (13)$$

k_1 to k_4 are determined in extrapolation or regression procedures from various types of electrolyte data. In present work, these equilibrium constants existing in the databank of Aspen Plus were directly used.

3.3. The Pitzer activity coefficient model

The Pitzer model embedded in the Aspen Plus platform was employed for the studied systems. The model has been discussed in detail in many publications. Here, we give only the expression

for the excess Gibbs free energy [19]:

$$\frac{G^E}{RT} = n_w \left[f(I) + \sum_i \sum_j B_{ij} m_i m_j + \sum_i \sum_j \theta_{ij} m_i m_j + \frac{1}{2} \sum_i \sum_j \left(\sum_k m_k |z_k| \right) \times C_{ij} m_i m_j + \frac{1}{6} \sum_i \sum_j \sum_k \psi_{ijk} m_i m_j m_k \right] \quad (14)$$

The cation–anion parameters B_{ij} and C_{ij} are characteristic for an aqueous single-electrolyte system. B_{ij} is expressed as a function of β_{ij}^0 and β_{ij}^1 or β_{ij}^0 , β_{ij}^2 and β_{ij}^3 . θ_{ij} and ψ_{ijk} are for the difference of interaction of unlike ions of the same sign from the mean of like ions.

These parameters B_{ij} , C_{ij} , θ_{ij} and ψ_{ijk} follow the temperature dependency relation:

$$\text{parameter}(T) = a_1 + a_2(T - T^{\text{ref}}) + a_3 \left(\frac{1}{T} - \frac{1}{T^{\text{ref}}} \right) + a_4 \ln \left(\frac{T}{T^{\text{ref}}} \right) \quad (15)$$

The activity coefficient is a parameter which accounts for the nonideality of electrolyte solutions, and is defined by the excess Gibbs free energy of the solution:

$$\ln \gamma_i = \left(\frac{\partial(G^E/RT)}{\partial n_i} \right)_{T,P,n_{i \neq j}} \quad (16)$$

3.4. Compilation and reduction of experimental data

In order to use the Aspen regression property analysis, molality should be transformed to mole fraction. Therefore, the following

Table 4
Solubility of $\text{Ca}(\text{OH})_2$ (1) in NaOH (2) + H_2O (3).

M_2 (mol L ⁻¹)	ρ_s (g mL ⁻¹)	C_1 (g L ⁻¹)	m_1^{exp} (mol kg ⁻¹)	m_1^{cal} (mol kg ⁻¹)	$(m_1^{\text{exp}} - m_1^{\text{cal}})/m_1^{\text{exp}}$ (%)
<i>T</i> = 298.15 K					
0.00	0.9990	1.5566	0.02109	0.02180	-3.36
0.01	1.0000	1.3955	0.01889	0.01822	3.58
0.03	1.0013	0.9863	0.01334	0.01271	4.73
0.05	1.0023	0.7091	0.00959	0.00912	4.92
0.07	1.0030	0.5343	0.00722	0.00687	4.89
0.09	1.0037	0.4172	0.00564	0.00538	4.68
0.15	1.0066	0.2332	0.00315	0.00313	0.55
0.20	1.0095	0.1789	0.00241	0.00237	1.98
0.30	1.0122	0.1290	0.00174	0.00166	4.69
0.40	1.0157	0.0992	0.00134	0.00128	4.16
0.50	1.0204	0.0790	0.00107	0.00104	2.65
<i>T</i> = 308.15 K					
0.00	0.9958	1.4177	0.01927	0.02000	-3.78
0.01	0.9956	1.1989	0.01630	0.01643	-0.79
0.03	0.9963	0.7847	0.01066	0.01090	-2.19
0.05	0.9971	0.5352	0.00727	0.00747	-2.67
0.07	0.9976	0.3795	0.00516	0.00539	-4.60
0.09	0.9987	0.2790	0.00379	0.00408	-7.59
0.15	1.0012	0.1943	0.00264	0.00264	0.12
0.20	1.0032	0.1463	0.00199	0.00201	-1.31
0.30	1.0065	0.0997	0.00135	0.00137	-1.17
0.40	1.0125	0.0783	0.00106	0.00108	-1.41
0.50	1.0065	0.0647	0.00089	0.00090	-1.37
<i>T</i> = 313.15 K					
0.00	0.9939	1.3502	0.01838	0.01907	-3.73
0.01	0.9937	1.1470	0.01562	0.01553	0.56
0.03	0.9948	0.7469	0.01017	0.01019	-0.26
0.05	0.9955	0.4993	0.00679	0.00690	-1.58
0.07	0.9959	0.3478	0.00473	0.00494	-4.27
0.09	0.9971	0.2535	0.00345	0.00363	-5.22
0.15	0.9997	0.1835	0.00250	0.00247	0.96
0.20	1.0017	0.1375	0.00187	0.00188	-0.40
0.30	1.0041	0.0929	0.00127	0.00129	-1.97
0.40	1.0105	0.0739	0.00100	0.00101	-0.57
0.50	1.0146	0.0621	0.00084	0.00084	0.37
<i>T</i> = 318.15 K					
0.00	0.9918	1.2827	0.01750	0.01814	-3.66
0.01	0.9918	1.0760	0.01468	0.01463	0.37
0.03	0.9929	0.6965	0.00950	0.00945	0.50
0.05	0.9934	0.4775	0.00651	0.00644	1.04
0.07	0.9942	0.3444	0.00470	0.00468	0.33
0.09	0.9954	0.2464	0.00336	0.00350	-4.33
0.15	0.9974	0.1622	0.00221	0.00223	-1.01
0.20	0.9993	0.1221	0.00166	0.00169	-1.84
0.30	1.0018	0.0844	0.00115	0.00119	-2.95
0.40	1.0079	0.0667	0.00091	0.00092	-1.46
0.50	1.0127	0.0546	0.00074	0.00076	-2.69
<i>T</i> = 328.15 K					
0.00	0.9871	1.1546	0.01583	0.01630	-3.02
0.01	0.9878	0.9540	0.01307	0.01285	1.66
0.03	0.9888	0.5927	0.00811	0.00799	1.49
0.05	0.9895	0.3991	0.00546	0.00535	2.00
0.07	0.9902	0.2922	0.00400	0.00393	1.84
0.09	0.9919	0.2240	0.00306	0.00304	0.70
0.15	0.9935	0.1392	0.00190	0.00188	1.40
0.20	0.9952	0.1059	0.00145	0.00144	0.43
0.30	0.9975	0.0749	0.00103	0.00101	1.44
0.40	1.0030	0.0595	0.00081	0.00082	-0.59
0.50	1.0083	0.0505	0.00069	0.00068	1.83
<i>T</i> = 338.15 K					
0.00	0.9818	1.0355	0.01427	0.01454	-1.88
0.01	0.9844	0.8446	0.01161	0.01116	3.85
0.03	0.9858	0.5091	0.00699	0.00671	4.02
0.05	0.9864	0.3303	0.00454	0.00441	2.78
0.07	0.9870	0.2335	0.00321	0.00317	1.01
0.09	0.9887	0.1837	0.00252	0.00248	1.51
0.15	0.9906	0.1130	0.00155	0.00155	0.13
0.20	0.9923	0.0846	0.00116	0.00119	-2.24
0.30	0.9946	0.0614	0.00084	0.00085	-0.70
0.40	0.9986	0.0492	0.00068	0.00068	-0.67
0.50	1.0044	0.0444	0.00061	0.00060	2.08

Table 4 (Continued)

M_2 (mol L ⁻¹)	ρ_s (g mL ⁻¹)	C_1 (g L ⁻¹)	m_1^{exp} (mol kg ⁻¹)	m_1^{cal} (mol kg ⁻¹)	$(m_1^{\text{exp}} - m_1^{\text{cal}})/m_1^{\text{exp}}$ (%)
T=348.15 K					
0.00	0.9760	0.9261	0.01283	0.01287	-0.30
0.01	0.9817	0.7254	0.01000	0.00957	4.30
0.03	0.9826	0.3960	0.00546	0.00538	1.43
0.05	0.9834	0.2523	0.00347	0.00344	0.91
0.07	0.9846	0.1779	0.00245	0.00248	-1.36
0.09	0.9860	0.1358	0.00187	0.00195	-4.12
0.15	0.9880	0.0921	0.00127	0.00127	-0.36
0.20	0.9901	0.0730	0.00101	0.00100	0.71
0.30	0.9920	0.0544	0.00075	0.00072	3.65
0.40	0.9958	0.0439	0.00060	0.00059	1.78
0.50	1.0006	0.0375	0.00051	0.00052	2.08
ARD (%) = 2.15					

relation for aqueous multi-component solutions was used for the conversion:

$$x_i = \frac{m_i}{\sum_j v_j m_j + 55.508} \quad (17)$$

Based on the maximum-likelihood principle [20], the following general objective function was used to optimize the solubility data:

$$\text{OBF} = \text{Min} \sum_i \left[w_1 \left(\frac{T_i^{\text{exp}} - T_i^{\text{cal}}}{\sigma_T} \right)^2 + w_2 \left(\frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{\sigma_P} \right)^2 + w_3 \left(\frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{\sigma_x} \right)^2 \right] \quad (18)$$

4. Results and discussion

4.1. Solubility results

Fig. 2 shows the solubility of calcium sulfate dihydrate as a function of NaOH concentration at various temperatures. It can be observed that the solubility of calcium sulfate dihydrate increases with increasing NaOH concentration. After passing a maximum, the solubility decreases at higher NaOH concentrations. The increase in the solubility can be explained by the association of Ca^{2+} and OH^- ions and formation of Ca(OH)^+ ion. However, the solubility decreases in concentrated NaOH solutions may be related to changes in the activity coefficient of the calcium, hydroxide and

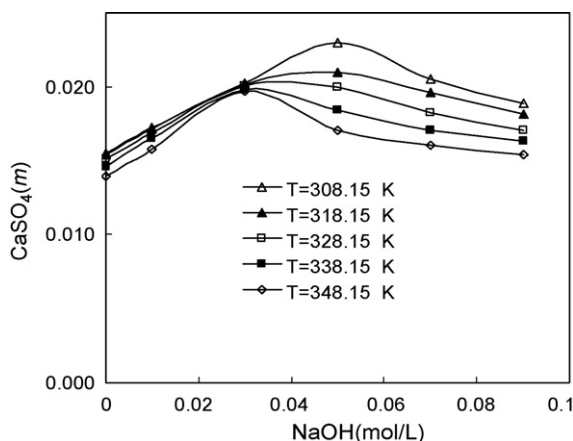


Fig. 2. The experimental solubility data of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as a function of NaOH concentration at different temperatures.

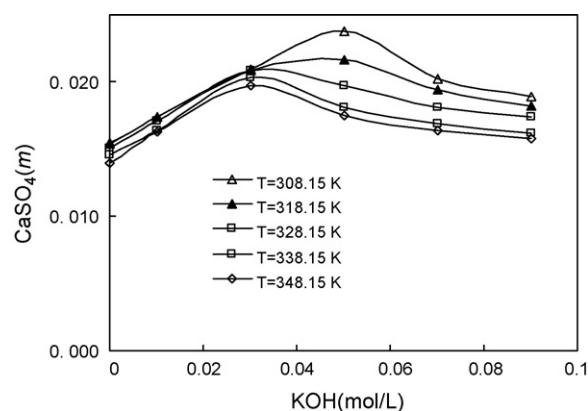


Fig. 3. The experimental solubility data of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as a function of KOH concentration at different temperatures.

hydroxyl calcium ions as well as the activity of water. At the NaOH concentration range of 0–0.03 mol L⁻¹, the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ slightly varies with the increasing temperature. Similar trends are observed for the solubility of calcium sulfate dihydrate in KOH solutions, although the solubilities are higher than those of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at a given NaOH concentration. The m – T diagram for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ –KOH– H_2O system is illustrated in Fig. 3.

Fig. 4 shows the experimental solubility data of calcium hydroxide in NaOH solutions at different temperatures. It can be seen from the figure that the solubility of Ca(OH)_2 decreases with increasing temperatures, and sharply decreases with the increment of alkali concentration due to the common ion effect of OH^- .

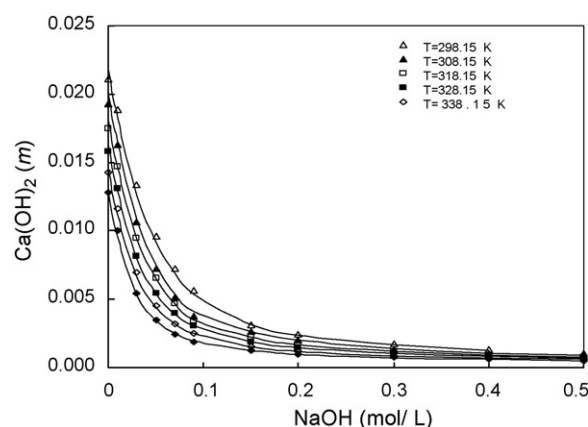


Fig. 4. The experimental solubility of Ca(OH)_2 as a function of NaOH concentration at different temperatures.

Table 5

Pitzer model interaction parameters obtained by regressing solubility data for the binary $\text{Ca}(\text{OH})_2\text{--H}_2\text{O}$ system.

Component <i>i</i>	Component <i>j</i>	Parameters		Value
$\text{Ca}(\text{OH})^+$	OH^-	β_{ij}^0	a_1	0.13618
			a_2	0.03584
		β_{ij}^1	a_1	−0.36923
			a_2	−0.06441
		C_{ij}	a_1	−0.04982
			a_2	−0.05177
$\text{Ca}(\text{OH})^+$	Ca^{2+}	θ_{ij}	a_1	−10.0032
			a_2	0.00014

4.2. Solubility evaluation with existing model parameters

In order to test the capability of predicting the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Ca}(\text{OH})_2$ in alkali solution, the solubility of $\text{Ca}(\text{OH})_2$ in water over the temperature range from 25 to 75 °C was calculated by using the Pitzer model with the Aspen Plus default database (version 2006) and compared with experimental data listed in Table 4. The overall average relative deviation (ARD) is 5.31% and the maximum relative deviation is 6.58%, indicating that the solubility of $\text{Ca}(\text{OH})_2$ in water cannot be calculated accurately with the Aspen Plus default database. Koenigsberger et al. [21] reported that when they use thermodynamic quantities for calcium hydroxide from CODATA [22] they need to include an associated $\text{Ca}(\text{OH})^+$ species in addition to the $\text{Ca}^{2+}\text{--OH}^-$ interaction parameters to accurately calculate pure water calcium hydroxide solubility at 25 °C. Consequently, new interaction parameters for the associated hydroxyl calcium ion $\text{Ca}(\text{OH})^+$ with the other dominant species in alkali solutions should be regressed.

Similarly, in order to evaluate the interaction parameters between Ca^{2+} and SO_4^{2-} ions in the Aspen Plus default database, the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in water listed in Table 2 was predicted using the Pitzer model with the maximum relatively deviation of 45.68%. The results show that Aspen Plus predictions are in poor agreement with the experimental data. Therefore, it is decided to perform an estimation of the parameters for $\text{Ca}^{2+}\text{--SO}_4^{2-}$ using the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in water over the temperature range from 35 to 75 °C through the Aspen Plus built-in regression feature.

4.3. Model parameterization

4.3.1. $\text{Ca}(\text{OH})_2\text{--H}_2\text{O}$ system

In order to improve Aspen Plus's prediction capacity, the new interaction parameters for $\text{Ca}(\text{OH})^+\text{--OH}^-$ and $\text{Ca}(\text{OH})^+\text{--Ca}^{2+}$ were obtained by regressing the solubility data of calcium hydroxide in water over temperature range from 25 to 75 °C, and listed in Table 5. Fig. 5 shows the comparison of the regressed and experimental solubility for $\text{Ca}(\text{OH})_2\text{--H}_2\text{O}$ system at different temperatures. As shown in Fig. 5, the calculated solubility data agree well with the experimental values with the ARD of 2.78% and the maximum relatively deviation is −3.78%.

4.3.2. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\text{--NaOH}\text{--KOH}\text{--H}_2\text{O}$ system

As was seen from the above, the current Pitzer model embedded in Aspen Plus cannot predict well the solubility data of calcium sulfate dihydrate in water. Therefore, we opted to determine the binary interaction parameter for $\text{Ca}^{2+}\text{--SO}_4^{2-}$ via regression of solubility data of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in water over the temperature range from 35 to 75 °C. The obtained model parameters are presented in Table 6. The correlated results can accurately mimic

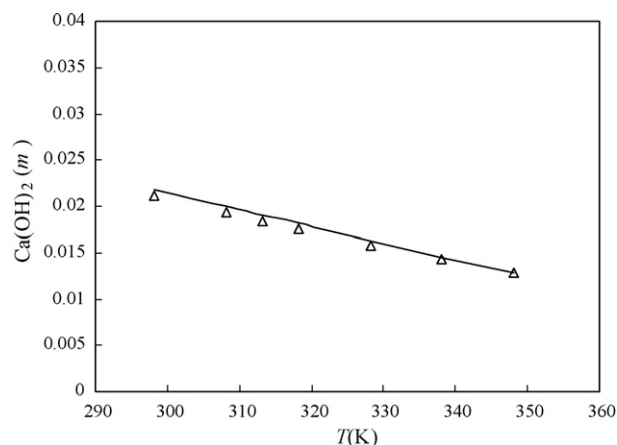


Fig. 5. Experimental and regressed solubility of $\text{Ca}(\text{OH})_2$ in H_2O . Legend: Δ , experimental data from this work; $-$, regressed values.

Table 6

Pitzer model interaction parameters obtained by regressing solubility data for the binary system $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\text{--H}_2\text{O}$ and the ternary system $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\text{--NaOH}\text{--H}_2\text{O}$.

Component <i>i</i>	Component <i>j</i>	Parameters		Value
Ca^{2+}	SO_4^{2-}	β_{ij}^0	a_1	13.1654
			a_2	−0.13683
		β_{ij}^2	a_1	−164.540
			a_2	−2.13694
		β_{ij}^3	a_1	−28.6004
			a_2	0.09130
		C_{ij}	a_1	−192.276
			a_2	2.13099
OH^-	SO_4^{2-}	θ_{ij}	a_1	3.75756
			a_2	−0.03263

the experimental data with the maximum relatively deviation of 0.68%.

The experimental solubility data of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ for the ternary $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\text{--NaOH}\text{--H}_2\text{O}$ system at 35 °C were used to regress the mixing parameter $\text{OH}^-\text{--SO}_4^{2-}$ in order to allow a more precise estimation of the chemistry of this system. Fig. 6 shows the calculated and experimental solubility data of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the ternary system as a function of the NaOH concentration. It is seen that the influence of temperature and NaOH concentration on the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ can be well depicted by the model. For the ternary $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\text{--KOH}\text{--H}_2\text{O}$ system, the mixing parameters,

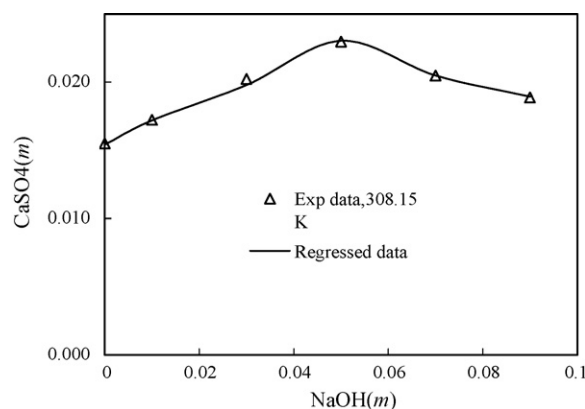


Fig. 6. Experimental and regressed solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in NaOH solutions at 308.15 K.

Table 7
Pitzer model interaction parameters obtained by regressing solubility data for the ternary system $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – KOH – H_2O at 35 °C.

Component <i>i</i>	Component <i>j</i>	Parameters	Value
$\text{Ca}(\text{OH})^+$	K^+	θ_{ij}	a_1 0.44779
			a_2 0.00000
Ca^{2+}	K^+	θ_{ij}	a_1 0.21223
			a_2 0.00066

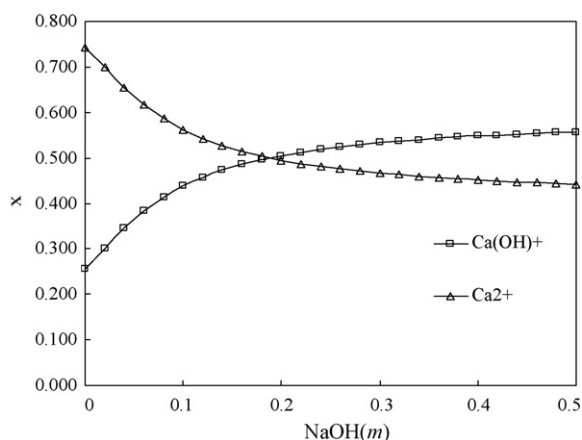


Fig. 7. The distribution of Ca-bearing species for the ternary system $\text{Ca}(\text{OH})_2$ – NaOH – H_2O at 313.15 K versus the NaOH concentration.

$\text{Ca}(\text{OH})^+ - \text{K}^+$ and $\text{Ca}^{2+} - \text{K}^+$ in solution were regressed using the solubility of calcium sulfate dihydrate in KOH solutions at 35 °C. The overall ARD is 2.05% and the resulting interaction parameters are listed in Table 7.

4.4. Model validation

4.4.1. $\text{Ca}(\text{OH})_2$ – NaOH – H_2O system

In order to test whether the model parameters obtained from simple system perform equally well in multi-component solutions, the solubility data of calcium hydroxide in NaOH solutions at elevated temperatures were predicted without introducing any new parameters. Fig. 7 shows the distribution of Ca-bearing species in solutions versus the NaOH concentrations. It is apparent that the $\text{Ca}(\text{OH})^+$ always increases with the increase in NaOH concentrations. Fig. 8 shows the comparison of the

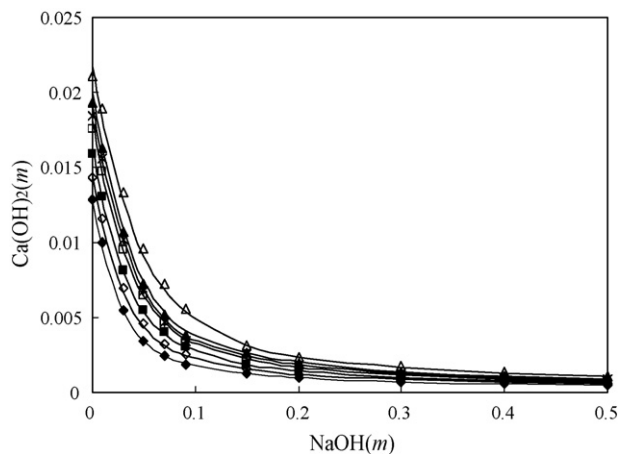


Fig. 8. Experimental and predicted solubility of $\text{Ca}(\text{OH})_2$ in NaOH solutions at different temperatures. Legend: Δ , 298.15 K; \blacktriangle , 308.15 K; \times , 313.15 K; \square , 318.15 K; \blacksquare , 328.15 K; \diamond , 338.15 K; \blacklozenge , 348.15 K; —, predicted results.

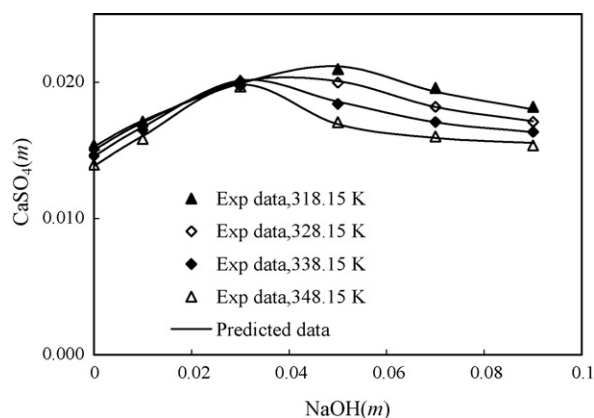


Fig. 9. Experimental and predicted solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in NaOH solutions at different temperatures.

predicted and experimental solubility data for $\text{Ca}(\text{OH})_2$ in the $\text{Ca}(\text{OH})_2$ – NaOH – H_2O system. As shown in Fig. 8, the experimental solubility data can be well predicted by the model with the overall ARD of 2.15%.

4.4.2. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – NaOH – KOH – H_2O system

The solubility data of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in NaOH solutions over the temperature range from 45 to 75 °C are predicted with the new interaction parameters, $\text{Ca}^{2+} - \text{SO}_4^{2-}$, $\text{Ca}(\text{OH})^+ - \text{Ca}^{2+}$ and $\text{OH}^- - \text{SO}_4^{2-}$. The predicted results obtained for the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ versus NaOH concentrations are shown in Fig. 9 along with the experimental data. The model parameters closely reflect the experimental data with the overall ARD of 0.75% and the maximum relatively deviation of 2.12%.

Similarly, the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in KOH solutions over the temperature range from 45 to 75 °C is predicted using the available interaction parameters, $\text{Ca}^{2+} - \text{SO}_4^{2-}$, $\text{Ca}(\text{OH})^+ - \text{Ca}^{2+}$, $\text{OH}^- - \text{SO}_4^{2-}$, $\text{Ca}(\text{OH})^+ - \text{K}^+$ and $\text{Ca}^{2+} - \text{K}^+$. To show the overall performance of the present model, the predicted and the experimental solubilities are compared and plotted in Fig. 10. The results indicate that the deviation is basically evenly occurred and no data points show a biased deviation from the diagonal. Although, the predicted results obtained for the solubility of CaSO_4 in KOH solutions are relatively accurate compared to the experimental data with the overall ARD of 1.53% and the maximum relatively deviation of 4.30%, the solubility prediction accuracy decreases with the increase of temperature.

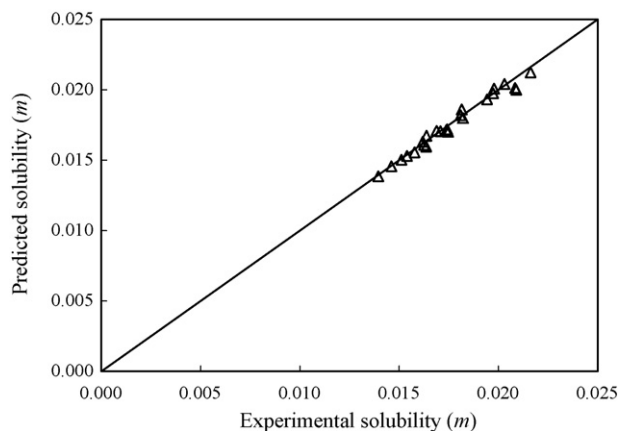


Fig. 10. Experimental and predicted solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in KOH solutions at different temperatures.

5. Conclusions

In this work, new experimental data for the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were presented for the ternary systems of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – NaOH – H_2O , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – KOH – H_2O , and $\text{Ca}(\text{OH})_2$ – NaOH – H_2O over the temperature range from 25 to 75 °C.

The thermodynamic equilibrium for the above ternary systems was modelled through the Pitzer model embedded in the Aspen Plus platform. The modelling involved the regression of binary solubility data and ternary solubility data. New interaction parameters for the associated hydroxyl calcium ion $\text{Ca}(\text{OH})^+$ with the other dominant species in alkali solutions were determined. It was shown that the speciation employed in binary systems, as well as the interaction parameters obtained by regressing solubilities is sufficient to represent the solubilities in ternary systems (not used in the regression state) very well. The developed Pitzer model proved to be an accurate model for describing the phase equilibria of calcium sulfate dihydrate and calcium hydroxide in alkali solutions.

List of symbols

n	number of data points
m	the molality of species ($\text{mol kg H}_2\text{O}^{-1}$)
m^{exp}	the experimental solubility ($\text{mol kg H}_2\text{O}^{-1}$)
m^{cal}	the calculated solubility ($\text{mol kg H}_2\text{O}^{-1}$)
T	temperature (K)
T^{ref}	298.15 K
K	the equilibrium constant
$K_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})}$	the solubility product constant of calcium sulfate dihydrate
$K_{\text{Ca}(\text{OH})^+}$	the dissociation constant of hydroxyl calcium ion
ΔG_r^0	the standard Gibbs free energy of the reaction
ν_i	the stoichiometric coefficient of species i
B_{ij}, C_{ij}	the interaction parameters
i, j and k	cations and anions of the solution
w	the weight factor
P	the pressure of system (kPa)
x	the solubility of electrolytes in terms of mole fractions
n_i	the number of moles of the solution constituents
$f(I)$	an electrostatic term as a function of ionic strength

Greek letters

γ	the activity coefficient of component
μ^0	the standard chemical potential of individual species
θ_{ij}, ψ_{ijk}	the mixing parameters
σ	the standard deviations
$\gamma_{\pm\text{CaSO}_4}$	the mean activity coefficient of calcium sulfate
$\alpha_{\text{H}_2\text{O}}$	the activity of water

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References

- [1] J.J. Kotte, Bayer digestion and predigestion desilication reactor design, in: P.G. Campbell (Ed.), *Light Metals*, TMS, Warrendale, 1981, pp. 46–81.
- [2] G. Wargalla, W. Brandt, Processing of diaspore bauxites, in: G.M. Bell (Ed.), *Light Metals*, TMS, Warrendale, 1981, pp. 83–100.
- [3] P.G. McCormick, T. Picaro, P.A.I. Smith, Mechanochemical treatment of high silica bauxite with lime, *Miner. Eng.* 15 (2002) 211–214.
- [4] H. Zhao, et al., Digestion of diaspore bauxite with mass ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ no greater than 7 by Bayer process with an excessive addition of lime, in: *Proceedings of TMS Light Metals*, Seattle, WA, 2002, pp. 101–104.
- [5] S. Gu, Z. Yin, L. Qi, Intensifying method of Bayer digestion process of diaspore bauxite in China, in: *Proceedings of TMS Light Metals*, Seattle, WA, USA, 2002, pp. 83–88.
- [6] V.M. Sizyakov, N.A. Kaluzhsky, K.A. Badaiaants, Process for desilication of aluminate solution, US patent No. 4,455,284.
- [7] B.I. Whittington, B.L. Fletcher, C.T. Talbot, The effect of reaction conditions on the composition of desilication product (DSP) formed under simulated Bayer conditions, *Hydrometallurgy* 49 (1998) 1–22.
- [8] K.K. Tanji, Solubility of gypsum in aqueous electrolytes as affected by ion association and ionic strengths up to 0.15 M and at 25 °C, *Environ. Sci. Technol.* 3 (1969) 656–661.
- [9] Z. Li, G.P. Demopoulos, Development of an improved chemical solution model for the estimation of CaSO_4 solubilities in the CaCl_2 – HCl systems, *Ind. Eng. Chem. Res.* 45 (9) (2006) 2914–2922.
- [10] G. Azimi, V.G. Papangelakis, J.E. Dutrizac, Development of an MSE-based chemical model for the solubility of calcium sulphate in mixed chloride–sulphate solutions, *Fluid Phase Equilib.* 266 (2008) 172–186.
- [11] D. Barba, V. Brandani, G.D.A. Giacomo, Thermodynamic model of CaSO_4 solubility in multicomponent aqueous solutions, *Chem. Eng. J.* 24 (1982) 191–200.
- [12] D. Barba, V. Brandani, G.D.A. Giacomo, Solubility of calcium sulfate dihydrate in the system Na_2SO_4 – MgCl_2 – H_2O , *J. Chem. Eng. Data* 29 (1984) 42.
- [13] J.A.M. Meijer, G.M. Rosmalen, Solubilities and supersaturations of calcium sulfate and its hydrates in seawater, *Desalination* 51 (1984) 255.
- [14] C.E. Harvie, J.H. Weare, The prediction of mineral solubilities in natural waters: the Na – K – Mg – Ca – Cl – SO_4 – H_2O system from zero to high concentration at 25 °C, *Geochim. Cosmochim. Acta* 44 (1980) 981.
- [15] C. Christov, N. Moller, A chemical equilibrium model of solution behavior and solubility in the H – Na – K – Ca – OH – Cl – HSO_4 – SO_4 – H_2O system to high concentration and temperature, *Geochim. Cosmochim. Acta* 68 (2004) 3717–3739.
- [16] A. Lucas, L. Rodriguez, P. Sancher, M. Carmona, P. Romero, J. Lobato, Comparative study of the solubility of the crystalline layered silicates α - $\text{Na}_2\text{Si}_2\text{O}_5$ and δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and the amorphous silicate $\text{Na}_2\text{Si}_2\text{O}_5$, *Ind. Eng. Chem. Res.* 43 (2004) 1472–1477.
- [17] Z. Li, G.P. Demopoulos, Solubility of CaSO_4 phases in aqueous HCl + CaCl_2 solutions from 283 K to 353 K, *J. Chem. Eng. Data* 50 (2005) 1971–1982.
- [18] F.K. Cameron, W.O. Robinson, The system, lime, nitric acid and water, *J. Phys. Chem.* 11 (1907) 273–278.
- [19] K.S. Pitzer, Thermodynamics of electrolytes. I. Theoretical basis and general equations, *J. Phys. Chem.* 77 (1973) 268–277.
- [20] AspenTech, Aspen Property System: Physical Property Methods and Models 11.1, AspenTech, 2001, pp. 405–435 www.aspentech.com.
- [21] E. Koenigsberger, L.-C. Koenigsberger, H. Gamsjaeger, Low-temperature thermodynamic model for the system Na_2CO_3 – MgCO_3 – CaCO_3 – H_2O , *Geochim. Cosmochim. Acta* 63 (1999) 3105–3119.
- [22] D. Garvin, V.B. Parker, H.J. White, CODATA Thermodynamic Tables, Springer-Verlag, 1987.