An experimental study of salt expansion in sodium saline soils under transient conditions (Postprint)

Authors: WAN Xusheng, Zhemin You, WEN Haiyan William CROSSLEY

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Abstract

Salt expansion in sulfate saline soils that are wider distributed in northwestern China causes serious infrastructural damages under low-temperature conditions. However, the mechanism of salt expansion under low temperatures is not clear.

Full Text

Preamble

WAN Xusheng1*, **YOU Zhemin**2, **WEN Haiyan**3, **William CROSSLEY**4

1 School of Civil Engineering and Architecture, Southwest Petroleum University, Chengdu 610500, China
2 State Key Laboratory of Frozen Soil Engineering, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China
3 College of Pastoral Agriculture Science and Technology, State Key Laboratory of Grassland Agro-ecosystems, Lanzhou University, Lanzhou 730020, China
4 School of Foreign Languages, Southwest Petroleum University, Chengdu 610500, China

Abstract

Salt expansion in sulfate saline soils, which are widely distributed in northwestern China, causes serious infrastructural damage under low-temperature conditions, yet the underlying mechanism remains unclear. This study investigates this phenomenon through a series of cooling experiments combined with salt crystallization, employing an ionic model to calculate the supersaturation ratio of the solution. The experiments examined the magnitude and process of salt expansion under different cooling rates and various crystal morphologies, while also considering the relationship between temperature and supersaturation ratio under transient conditions. Results indicate that the initial supersaturation ratio of a sodium sulfate solution is closely related to environmental conditions, decreasing with slower cooling rates and stabilized crystal forms. Higher initial supersaturation ratios lead to an enlarged non-steady-state zone, resulting in reduced salt expansion. Conversely, chloride ion content exerts a distinct influence on the crystallization supersaturation ratio of sodium sulfate solution, with higher chloride ion content inhibiting salt expansion in sodium saline soils. These findings help explain salt expansion mechanisms in complex environments such as seasonally frozen soils and may contribute to improved methods for preventing salt expansion in sulfate saline soils.

Keywords: sulfate saline soil; supersaturation ratio; ionic model; cooling rate; salt expansion

Introduction

Saline soils are widely distributed across northwestern China, covering approximately 2% of the total land area (Luo, 1980). Salt expansion, governed by the chemical and physical properties of these soils, can seriously damage infrastructure including roads, canals, and airports. With increasing economic development in western China, such infrastructure is being densely constructed in saline soil regions, substantially elevating social and economic risks associated with salt expansion. Consequently, studying salt expansion in sulfate saline soils is essential for mitigating these risks.

Previous research on sodium sulfate soils in China has primarily focused on measuring expansion rates under varying salt contents, water contents, and other environmental conditions (Li et al., 1989; Yuan and Li, 1995; Xu et al., 1995, 2010; Wu et al., 2001). More recently, predictive models for salt expansion have been developed from experimental studies (Gao et al., 1996; Chen et al., 2006; Zhao, 2012), with calculations of salt expansion and crystal precipitation typically relying on steady-state solution phase diagrams. However, these predictive models cannot accurately estimate salt expansion in complex natural systems. Fundamentally, salt expansion originates from the thermodynamic conditions for salt crystallization: when the supersaturation ratio of a salt solution exceeds the initial supersaturation ratio, salt crystallization begins and soil heaving occurs (Mullin, 1993; Mersmann, 2001; Zhang, 2011). While the Pitzer model has been widely used to calculate supersaturation in porous media (Steiger, 2005; Espinosa et al., 2008), most related studies have examined salt crystallization and initial supersaturation ratios in construction materials such as brick, concrete, and rock rather than soils (Mersmann, 1995, 2001; Rocha and Martina, 2002; Espinosa et al., 2008; Derluyn, 2012). When soils have been examined, salt expansion has only been studied at room temperature (Mokni et al., 2010). Therefore, salt expansion at lower temperatures and under non-steady-state conditions remains uninvestigated, and infrastructure damage from salt expansion continues to pose challenges in cold regions.

Research on sulfate saline soils in cold regions must address several key questions: At what supersaturation ratio does salt crystallization occur in soils at low temperature? How does the initial supersaturation ratio of soil solutions vary under different environmental conditions? How does salt crystallization influence salt expansion? Given the large temperature variations on the Tibetan Plateau, this study aims to: (1) explore the crystallization behavior of sulfate under non-steady-state conditions; (2) identify the relationship between crystal morphology and salt expansion; and (3) analyze the influence of chloride ion content on the supersaturation ratio of sulfate saline soils. These results may prove useful for understanding saline soil properties and for studying land surface processes in cold regions with sulfate saline soils.

2.1 Calculation of Supersaturation Ratio

The fundamental cause of salt expansion is crystallization, as salt heaving cannot occur without salt crystals. However, salt crystallization itself depends on supersaturation as the necessary thermodynamic condition. Supersaturation represents a metastable state during which crystal formation conditions shift from unsteady to steady. Crystallization occurs when the solution is supersaturated with respect to the crystallizing phase. For salts containing hydrated water, the water-salt interaction must be considered, and the supersaturation ratio of the solution can be expressed as:

$$U_a = \frac{a_w^{v_0}}{a_w^*} \times \frac{a_\pm^\nu}{a_\pm^{*\nu}}$$

where U_a is the supersaturation ratio of the salt solution; a_w is the water activity; a_w^* is the water activity at saturation; ν is the number of ions produced per solute molecule; v_0 is the number of hydrated water molecules per salt molecule; $a_\pm$ is the mean ion activity; and $a_\pm^*$ is the mean ion activity at saturation. The formulae for calculating these parameters are given in Appendix A.

In saline soils, ions are primarily present in moisture, thus the concentration of a salt in solution can be determined by the salt content and water content. Based on the saturation curve of a sodium sulfate solution (Xu et al., 1995), there is little salt crystallization below the initial freezing temperature of soil compared to that at room temperature. Therefore, we assume that solutes are excluded from ice crystals below freezing temperature, and the salt concentration in the remaining brine increases as water freezes. The unfrozen water content is mainly determined by the ice-water phase change and can be obtained by fitting experimental data (Wan et al., 2017).

2.2 Experimental Design

Sulfate soil is a predominant and representative type of sulfate saline soil found in western China (Wan et al., 2015), with sodium sulfate being most prevalent in large areas of the Beilu River region on the Qinghai-Tibet Plateau. Therefore, sodium sulfate soil was selected to study salt expansion mechanisms. The samples consist of silty clay soils collected approximately 1 km from the western side of the Beilu River highway overbridge (34°54.217 N, 92°56.362 E), near the abandoned Qinghai-Tibet Highway. Since factors affecting salt expansion include salt content, water content, and dry density (Xu et al., 1995; Mokni et al., 2010), we used the natural soil' s water content and dry density while studying the influence of salt content (salt concentration) on expansion under transient conditions.

2.2.1 Cooling Experiments Using Sodium Sulfate Soils

Sodium sulfate soils were prepared from natural samples at room temperature by adding sodium sulfate at percentages of 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1.0%, 1.1%, 1.2%, 1.4%, 1.5%, 2.1%, 2.6%, 3.2%, and 3.8%. The water content of each soil sample was 18%. Thermistors (accurate to ±0.01°C) encased in waterproof plastic sheets were inserted into the samples to monitor temperature variations. Test samples were placed into specially-made iron boxes (diameter 3.3 cm, height 3.8 cm) with a dry density of 1.84–1.86 g/cm³, consistent with in situ soil conditions. The samples were placed in a cooling bath at 25°C and maintained for 30 minutes. The cooling bath temperature was then decreased from 25°C to -20°C at a rate of 0.02°C/min, after which samples were maintained at -20°C for 2 hours. Data acquisition and logging were performed using a CR3000 micrologger (Campbell Scientific Headquarters, Logan, UT, USA) with a recording interval of 10 seconds. The initial salt crystallization temperature is identified by the abrupt rise in the cooling curve (resulting from heat released during salt crystallization). At negative temperatures, the initial salt crystallization temperature of soils with low salt content can be determined from the second phase-transition point on the cooling curve (Lai et al., 2016; Wan et al., 2017).

2.2.2 Effects of Cooling Rate on Supersaturation Ratio and Salt Expansion

Mirabilite is the predominant crystal type in sodium sulfate soils at high humidity, and the variation of the initial supersaturation ratio with different salt contents can be studied under various cooling rates during mirabilite crystallization. We used sodium sulfate soils with sodium sulfate contents of 2.1%, 2.6%, 3.2%, and 3.8% and a water content of 18%. Samples were placed in plastic cups and compacted to a diameter of 6.3 cm and height of 7.5 cm. NS-WY02 displacement sensors with an accuracy of ±0.001 mm (Shanghai TM Automation Instruments Co., Ltd., Shanghai, China) were installed in the soil samples to monitor displacement variations. A programmable ultra-low temperature chamber (Dongguan Terchy Test Equipment Co. Ltd., China) was used to replicate the temperature regime of the Qinghai-Tibet Plateau. Thermistors were inserted into the samples to monitor temperature variations. Cooling rates were set at 0.02, 0.1, and 1°C/min, with temperature decreasing from 25°C to 0°C, followed by a 2-hour hold at 0°C.

2.2.3 Effect of Chloride Ion Content on Salt Expansion

This section outlines experiments studying the effect of chloride ion content on salt expansion in sodium sulfate soils. To ensure that sulfate crystals would not crystallize at 25°C, we prepared three sulfate soil samples at room temperature with different salt contents. Sodium sulfate content was fixed at 3.8%, while sodium chloride contents were 0%, 3.8%, and 5.8%. The water content of these preparations was 18% (corresponding to a sodium sulfate solution concentration of 1.5 mol/L and sodium chloride solution concentrations of 0, 3.6, and 5.5 mol/L, respectively). Dry bulk density was maintained above 1.65 g/cm^3. Test samples were placed into specially made organic glass containers (diameter 6.3 cm, height 10.0 cm) and then placed in a programmable ultra-low temperature chamber; displacement sensors were installed in the soil samples to monitor displacement variation. Temperature was decreased from 25°C to 0°C at intervals of 2°C or 1°C, with samples maintained at each temperature for 30 minutes. Soil displacement was measured using a dataTaker CR3000.

3.1.1 Initial Supersaturation Ratio

The initial supersaturation ratio can be calculated using Equation 1 for mirabilite crystal morphology. As shown in Figure 1 [Figure 1: see original paper], the freezing point marks the cutoff point for the rate change of the initial supersaturation ratio in sodium sulfate soils. Above the freezing point, the regression slope is -0.18, and the initial supersaturation ratio reaches up to 4.2. However, the initial supersaturation ratio increases sharply as temperature decreases below the freezing point of the sodium sulfate soils, with a regression line slope of -4.9 and values reaching 45 at -11.5°C. If the supersaturated state of the solution is defined as an unsteady state in which the supersaturation ratio changes from 1 to the value at which salt crystals begin to crystallize, then the unsteady zone of salt crystallization can be represented by the shaded zones in Figure 1.

3.1.2 Effect of Cooling Rate on Initial Supersaturation Ratio

Figure 2 [Figure 2: see original paper] shows that the initial supersaturation ratio increases with increasing cooling rate. Together with Figure 1, Figure 2 also demonstrates that the area of the unsteady-state zone of the solution increases with higher cooling rates. Additionally, the condensate depression of each solution at a given temperature increases with faster cooling rates, thereby making initial crystallization increasingly difficult. Figure 2 also reveals that the initial supersaturation ratio varies significantly with both cooling rate and salt concentration. In the sample with 3.8% salt content, this ratio increased from 0.037 to 0.131 as the cooling rate increased from 0.02 to 0.1°C/min and from 0.1 to 1°C/min, respectively. However, the ratio increased from 0.226 to 0.572 for soil with 2.1% salt content under the same cooling rate increases, illustrating that cooling rate significantly influences the initial supersaturation ratio in low-salt sodium sulfate soils.

3.1.3 Effect of Cooling Rate on Salt Expansion

For a given salt content, the salt expansion ratio decreases as cooling rate increases, and the difference in expansion ratio between different cooling rates becomes more pronounced as initial salt content increases (Fig. 3 [Figure 3: see original paper]). In the sample with 2.1% salt content, the expansion ratio increased by 0.021% and 0.292% as the cooling rate decreased from 1 to 0.1°C/min and from 0.1 to 0.02°C/min, respectively. However, for sodium sulfate saline soil with 3.8% salt content, the increase reached 0.818% and 1.268%, respectively, for the same cooling rate decreases. This demonstrates that soils with high salt content have smaller unsteady zones and that salt heaving is particularly enhanced when temperature drops quickly in these soils.

3.1.4 Salt Expansion Process

To highlight the effect of salt expansion, we analyzed sodium sulfate soils with a salt content of 3.8%. Mirabilite forms under cooling conditions (v =10, =3), and the supersaturation ratio is calculated by Equation 1. Changes in supersaturation ratio and salt expansion ratio with temperature are shown in Figure 4 [Figure 4: see original paper].

When the supersaturation ratio of the sodium sulfate solution is less than 1, sodium sulfate soils remain in a stable state, though soil displacement decreases slightly due to soil contraction. As temperature decreases, the supersaturation ratio increases and exceeds 1, causing soils to enter an unsteady state. If the supersaturation ratio is higher than the initial ratio, salts crystallize. Salts crystallize first in soils with the lowest cooling rate, leading to salt expansion (Fig. 4). Increased cooling rate enlarges the unsteady zone and increases the supersaturation ratio of the solution, causing the initial crystallization temperature to decrease. A larger unsteady zone in the salt solution indicates higher salt solution concentration during cooling and relatively small amounts of salt crystal generation in these soils. Thus, larger salt expansion ratios correspond to smaller unsteady zones. Figure 4 also shows that unsteady zones of salt solutions continuously decrease as temperature drops following initial crystallization, with supersaturation ratios tending toward 1, suggesting that salt expansion occurs more readily when unsteady zones contract.

3.1.5 Effect of Sodium Sulfate Crystal Morphology on Supersaturation Ratio

The salt expansion ratio of sodium sulfate soils is directly influenced by salt crystal morphology. From Equation 1, we calculated initial supersaturation ratios of solutions for different sulfate crystal morphologies (Fig. 5 [Figure 5: see original paper]). Figure 5 shows that the initial supersaturation ratio decreases during transformation from anhydrous sodium sulfate to sodium sulfate heptahydrate and sodium sulfate decahydrate, with this reduction enhanced as temperature decreases. The initial supersaturation ratio for anhydrous sodium sulfate is 0.14 greater than that for sodium sulfate decahydrate at 17°C, while this difference increases to 0.54 at 0°C. Generally, for salt crystals to achieve stable morphology, the initial supersaturation ratio of the solution must decrease. Thus, cooling sodium sulfate soils causes crystals to continuously transition from unsteady to steady states.

3.1.6 Crystal Morphology Under Different Environmental Conditions

The morphology of sodium sulfate crystals changes with environmental humidity and material pore size, and crystal growth and size are also influenced by pore dimensions. Although mirabilite typically exhibits a needle-like structure (Fig. 6a [Figure 6: see original paper]), transformation from mirabilite to anhydrous sodium sulfate as temperature reaches 32.4°C still shows needle-like branches (Fig. 6b), whereas anhydrous sodium sulfate ultimately becomes powder-like after sodium sulfate soils experience wetting-drying cycles (Fig. 6c). Sodium sulfate heptahydrate has a pyramidal shape and is difficult to observe in soils due to its instability. Salt crystal shapes in soil differ from those in solution; typically, soil salt crystals are very small and require scanning electron microscopy (SEM) for observation. However, some salt crystals in sodium sulfate solutions can be observed with the naked eye, including some mirabilite forms that can be rather large (Fig. 6d) and some intermediate states between mirabilite and anhydrous sodium sulfate that exhibit grainy or layered structures (Figs. 6e and f).

3.2.1 Supersaturation Ratio in Na SO -NaCl Binary Solutions

Sodium chloride crystals cannot form due to their consistently high solubility in various sodium chloride solutions. Nevertheless, sodium chloride content significantly affects sodium sulfate solubility. The solubilities of sodium sulfate solutions under different sodium chloride contents and temperatures are given in Table 1 .

The saturation concentration of sodium sulfate solution gradually decreases with increasing sodium chloride concentration. When sodium chloride concentration exceeds 6 mol/L, the saturation concentration of sodium sulfate solution becomes very low; consequently, 6 mol/L was selected as the maximum sodium chloride concentration. The water activity and mean ion activity of the sodium sulfate solution in a Na SO -NaCl binary solution were then calculated from Equation 1, with related parameters listed in Appendix B. Assuming identical cooling rates, the calculated supersaturation ratios of the sodium sulfate solution are shown in Figure 7 [Figure 7: see original paper].

From Figures 7a and b, the supersaturation ratios of sodium sulfate solution decrease when sodium chloride solution concentration is less than 2.0 mol/L under 27°C and 21.5°C conditions, with inflection points observed at 5.0 mol/L sodium chloride concentration. Above this concentration, supersaturation ratios markedly increase with increasing sodium chloride solution concentration. However, when sodium sulfate solution concentration exceeds 2.0 mol/L, a critical point occurs at 3.0 mol/L sodium chloride solution. In other words, when sodium chloride solution concentration is lower or higher than 3.0 mol/L, supersaturation ratios decrease or increase correspondingly (Figs. 7a and b).

From Figures 7c–e, variations in supersaturation ratios are similar: they increase as sodium chloride solution concentration is lower than 3.0 mol/L, then decrease until concentration reaches 5.5 mol/L. Furthermore, an abrupt increase occurs when concentration exceeds 5.5 mol/L. On the other hand, supersaturation ratios increase as sodium sulfate solution concentration is less than 1.5 mol/L. As shown in Figures 7a–e, the maximum supersaturation ratio at 5°C is about 40 times higher than that at 27°C, suggesting that supersaturation ratios will continuously increase at a given concentration with decreasing temperature for binary system solutions.

3.2.2 Effect of Sodium Chloride Content on Salt Expansion

The salt expansion ratio of sulfate saline soils increases concurrently with sodium chloride content (Fig. 8 [Figure 8: see original paper]). Salt expansion at temperatures above 20°C occurs only in the sample containing 3.8% sodium chloride, consistent with the supersaturation ratio rule for sodium sulfate solution in Na SO -NaCl binary solution. The supersaturation ratio of sodium sulfate solution increases as chloride concentration increases. When this ratio exceeds the initial supersaturation ratio, mirabilite precipitates and causes salt expansion. However, in sulfate saline soil containing 5.8% sodium chloride, the sodium sulfate solution is saturated. In this case, sodium sulfate exists as powder in soils above 20°C (as in Fig. 6c) and soil displacement remains constant. With declining temperature, more powdered sodium sulfate dissolves to form mirabilite, and due to greater mirabilite precipitation, the salt expansion ratio increases sharply and exceeds that of sulfate saline soil containing 3.8% sodium chloride.

Discussion

The behavior of salt solutions in soils is typically affected by temperature, pressure, and concentration. While soil pore pressure changes with salt crystallization, this has little effect on liquid-solid equilibria; therefore, pressure effects on crystallization need not be considered. The results presented above suggest that the supersaturation ratio of sodium sulfate solution is strongly associated with crystal morphology, cooling rate, and chloride ion concentration. Small supersaturation ratios generally lead to stable crystal shapes, while large unsteady-state zones are associated with unstable crystal formation, such as sodium sulfate heptahydrate. The cooling rate not only affects the supersaturation ratio but also influences the extent of the non-steady-state zone. Increased cooling rate likely results in unstable crystal formation and may reduce salt expansion.

The temperature of precipitated salt crystals in soils is generally lower than that in pure solution (Wan and Lai, 2013), and the adsorptive action of free energy on soil particle surfaces leads to increased supersaturation ratios for salt solutions in soils, resulting in enlarged non-steady-state zones. This demonstrates that salt crystallization is more complex in soils than in pure solutions. Crystallization theory states that salt crystals first generate in larger pores of porous materials, with crystallization becoming more difficult as pore size decreases (Steiger, 2005). During salt expansion, crystals continue filling pores and decreasing pore volume, so the salt expansion ratio increases slowly with time (Fig. 4). When temperature falls below the freezing point of saline soils, water begins to freeze and ice crystal growth decreases pore size while increasing the concentration of the remaining salt solution. These combined effects result in a high initial supersaturation ratio (Fig. 1) and consequently weak salt expansion.

The condensate depression of the solution decreases with decreasing cooling rate, which can promote salt crystal precipitation. Crystal mass increases more quickly in slowly cooled soils than in rapidly cooled soils. Additionally, because the volume of one mole of sodium sulfate decahydrate is 3.1 times greater than that of anhydrous sodium sulfate (Chen et al., 2006), transformation of anhydrous sodium sulfate into mirabilite enhances the salt expansion process. The greatest variation in salt expansion occurs as salt crystal precipitation begins and the salt solution concentration approaches the saturation concentration for crystallization. Therefore, saline soil deformation in saturated soil during cooling can be estimated based on the actual solubility curve by subtracting water loss volume from salt crystal volume increase. However, calculating salt heaving in unsaturated soil remains very difficult.

The presence of sodium chloride influences both water and ionic activities of the sodium sulfate solution. With increasing sodium chloride solution concentration, the maximum temperature for mirabilite precipitation first decreases from 32.4°C to 17.9°C, then increases for supersaturated concentrations. In high-salt-content solutions (sodium sulfate concentration exceeding 2.0 mol/L), increased chloride ion content can effectively reduce the supersaturation ratio of sodium sulfate solution at temperatures above 17.9°C, thereby inhibiting salt expansion. However, below 17.9°C, mirabilite exists in a stable state and sulfate saline soils readily undergo salt expansion.

In seasonally frozen regions where temperatures are sometimes below zero, increased chloride ion content may lead to crystallization of sodium chloride dihydrate and cause salt expansion. Consequently, it is crucial to use chloride ion content appropriately, considering the intended environment' s temperature range, to control salt expansion and frost heaving in sulfate saline soils. Additionally, increasing subgrade fill dry density and decreasing median pore size are effective methods for weakening salt expansion.

Conclusions

Based on cooling experiments and theoretical analyses of sulfate saline soils, we found that the initial supersaturation ratio of brine in sulfate soils increases linearly as temperature decreases, with this increase being more rapid below the soil' s freezing temperature. The non-steady-state zone of sulfate saline soils is determined by cooling rate; higher cooling rates produce larger initial supersaturation ratios in sodium sulfate solution. The supersaturation ratio is closely related to the crystal morphology of precipitating mineral phases, with the initial supersaturation ratio decreasing as crystal shape stability increases. When salt crystals precipitate as mirabilite, the salt expansion ratio reaches its maximum and the salt expansion effect becomes significant. Chloride ion concentration distinctly influences the crystallization supersaturation ratio of sodium sulfate solution; below 17.9°C, increased chloride ion content induces soil heaving in sulfate saline soils.

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Appendix A

The detailed definition of water activity in solution can be found in Prausnitz et al. (1999). It is related to the osmotic coefficient (Steiger, 2005) and can be calculated by Equation A1:

$$\ln a_w = -\frac{M_w}{1000} \sum_i m_i \phi$$

where M_w is the molar mass of water, and m_i is the molar mass fraction of the ith ion. In the Pitzer approach, the osmotic coefficient for a single electrolyte is given by:

$$\phi - 1 = -\frac{A^{\phi} I^{1/2}}{1 + bI^{1/2}} + m\frac{2\nu_{+}\nu_{-}}{\nu} B_{MX}^{\phi} + m^{2}\frac{2(\nu_{+}\nu_{-})^{3/2}}{\nu} C_{MX}^{\phi}$$

where I is the ionic strength; $z_{+}z_{-}$ is the charge number of electrolyte ions; m is the molar mass fraction of the solute; ν is the total number of ions released upon complete dissociation of the salt; $\nu_{+}\nu_{-}$ is the number of positive and negative ions; b is a constant ($b = 1.2$ kg¹/²mol ¹/²); and α_1 and α_2 are regression coefficients with different values for different ionic types. The interaction parameters $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX}^{ϕ} are specific to a salt MX and are functions of temperature. The relationship between interaction parameters and temperature is expressed by:

$$\beta_{MX}^{(i)} = a_1 + a_2\left(\frac{1}{T} - \frac{1}{T_R}\right) + a_3 \ln\left(\frac{T}{T_R}\right) + a_4(T - T_R) + a_5(T^2 - T_R^2) + a_6\left(\frac{1}{T^2} - \frac{1}{T_R^2}\right)$$

where a_1-a_6 are regression parameters (Steiger et al., 2008) with values varying for different solutes, and $T_R = 298.15$ K.

The mean ion activity is defined as:

$$a_{\pm} = m_{\pm}\gamma_{\pm}$$

where $m_{\pm}$ is the mean mass molarity, and $\gamma_{\pm}$ is the mean ionic activity coefficient.

For 2-1 salt types such as Na SO , $m_{\pm}$ can be approximated as (Prausnitz et al., 1999):

$$m_{\pm} = m^{1/3}(M_X)^{1/3}$$

where MX is the corresponding salt.

The mean ionic activity coefficient can be calculated using the following equations (Marliacy, 2000):

$$\ln\gamma_{\pm} = \frac{1}{\nu}(\nu_{+}\ln\gamma_{+} + \nu_{-}\ln\gamma_{-})$$

where

$$\ln\gamma_{MX} = \frac{z_{+}z_{-}A^{\phi} I^{1/2}}{1 + bI^{1/2}} + m\frac{2\nu_{+}\nu_{-}}{\nu} B_{MX} + m^{2}\frac{2(\nu_{+}\nu_{-})^{3/2}}{\nu} C_{MX}$$

The Pitzer model is used to calculate the supersaturation ratio at positive temperatures (Pitzer, 1975; Steiger et al., 2008), while the FREZCHEM or SMW model is used below the freezing point of pure water (Spencer et al., 1990; Marion and Grant, 1994; Marion and Farren, 1999). A^{ϕ} is the Debye-Hückel parameter for the osmotic coefficient, representing a nonlinear relationship with temperature T (Clegg and Whitfield, 1991):

$$A^{\phi} = -0.04944 - 0.381 \ln T + \frac{205.38}{T} + \frac{1.963 \times 10^{7}}{T^{2}}$$

Ionic strength I is defined as:

$$I = \frac{1}{2} \sum_{i} m_i z_i^2$$

where z_i is the charge number of electrolyte ion i.

Appendix B

For a Na SO -NaCl binary solution system, the osmotic coefficient   can be calculated using the formula defined by Marliacy et al. (2000). The mean molarity ($m_{\pm}$) and mean ion activity coefficient ($\gamma_{\pm}$) are respectively defined as:

$$m_{\pm} = (m_{+}^{\nu_{+}} m_{-}^{\nu_{-}})^{1/\nu}$$

$$\gamma_{\pm} = (\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}})^{1/\nu}$$

where m_{+} and m_{-} refer to the molar mass of positive and negative ions, respectively, and γ_{+} and γ_{-} refer to the ion activity coefficients of positive and negative ions, respectively. Remaining parameters are defined above.

The ion activity coefficients of sodium and sulfate ions can be calculated by Equations B2 and B3, respectively:

$$\ln \gamma_{Na^{+}} = \frac{z_{Na^{+}}^{2} F}{2} + m_{Cl^{-}}(2B_{NaCl} + ZC_{NaCl}) + m_{SO_4^{2-}}(2B_{Na_2SO_4} + ZC_{Na_2SO_4}) + m_{Na^{+}} m_{Cl^{-}} \left(\frac{\partial B_{NaCl}}{\partial I} + C_{NaCl} \right) +$$

$$\ln \gamma_{SO_4^{2-}} = \frac{z_{SO_4^{2-}}^{2} F}{2} + m_{Na^{+}}(2B_{Na_2SO_4} + ZC_{Na_2SO_4}) + m_{Cl^{-}}(2\Phi_{ClSO_4} + m_{Na^{+}} \Psi_{NaClSO_4}) + m_{Na^{+}} m_{SO_4^{2-}} \left(\frac{\partial B_{Na_2SO}}{\partial I} \right.$$

where B_{MX} is the second virial coefficient, C_{MX} is the third virial coefficient, and $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX}^{ϕ} are fitting parameters for the binary solution of sodium sulfate and sodium chloride. B_{MX} and C_{MX} are calculated by Equations B4 and B5, respectively (Marliacy et al., 2000; Steiger et al., 2008):

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} g(\alpha_2 I^{1/2})$$

$$C_{MX} = \frac{C_{MX}^{\phi}}{2|z_+ z_-|^{1/2}}$$

The parameter Φ_{ClSO_4} can be calculated as:

$$\Phi_{ClSO_4} = \theta_{ClSO_4} + {}^{E}\theta_{ClSO_4}(I) + I\,{}^{E}\theta'_{ClSO_4}(I)$$

where θ_{ClSO_4} is the term accounting for asymmetrical mixing (Pitzer, 1975), and ${}^{E}\theta'_{ClSO_4}$ is the derivative of ${}^{E}\theta_{ClSO_4}$.

The function F in Equations B2 and B3 is defined as:

$$F = -A^{\phi}\left[\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b}\ln(1+bI^{1/2})\right] + m_{Na^+} m_{Cl^-} B'_{NaCl} + m_{Na^+} m_{SO_4^{2-}} B'_{Na_2SO_4} + m_{Cl^-} m_{SO_4^{2-}} \Phi'_{ClSO_4}$$

where g' is the derivative of g.

The function g in Equation B4 is defined as:

$$g(x) = \frac{2}{x^2}[1 - (1+x)e^{-x}]$$

with $x = \alpha_1 I^{1/2}$ or $\alpha_2 I^{1/2}$. Remaining parameters in Equations B2 and B3 are defined as above.