Effect of chloride salts and bicarbonate on solubility of CaSO$_4$ in aqueous solutions at 37°C

Yuexia Zhang, Zhenhua Yang, Dan Guo, Hong Geng, Chuan Dong*

Research Center of Environmental Science and Engineering, Shanxi University, Wucheng Road 92#, Taiyuan 030006, China

Abstract

In the study, we present the results of thermodynamic simulation of CaSO$_4$ water-salt systems containing Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$ and HCO$_3^-$ at 37°C. The results showed that the solubility of CaSO$_4$ phase increased with increasing NaCl as well as KCl concentration in the range of 0.0 to 2.0 M and 0.0 to 1.0 M, respectively. Remarkably, enhanced effect of MgCl$_2$ on the solubility of CaSO$_4$ phase was much larger than that of KCl or NaCl. The only exception was CaCl$_2$, which was found to reduce solubility value of CaSO$_4$ in aqueous solution at 37 °C with the increase of CaCl$_2$ concentration. Also, the solubility of CaSO$_4$ phase in mixed salt solutions was investigated at 37 °C. The common ion effect was the main factor on the solubility of CaSO$_4$ in the mixed salts solution. Furthermore, CaSO$_4$ solubility was reduced by small amounts of NaHCO$_3$ in mixed solutions. These studies are of relevance in the estimating the changes of various salts in blood plasma and production of salt with low impurities of Ca$^{2+}$ and SO$_4^{2-}$ ions, as well as estimating oceanic-containing CaSO$_4$ uptake of CO$_2$.

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Keywords: calcium sulfate; mixed salt; bicarbonate; solubility; dynamics

1. Introduction

A substantial number of studies have shown a relationship between particulate air pollution and a variety of adverse health indicators [1-3]. The hazard caused by inhaled particles depends on their chemical composition and where they deposit. Classroom teaching with boards and chalks still dominates the world. Chalk for classroom use is generally made from calcium sulfate (CaSO$_4$). CaSO$_4$, as a major component of Chalk, can easily find their way into the respiratory tract of the teacher. And, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$ and Cl$^-$ are necessary in life.

* Corresponding author. Tel.:+86-0351-7011011; fax: +86-0351-7011011.
E-mail address:dc@sxu.edu.cn.

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Therefore, solubility of CaSO₄ is essential to estimating the changes of various salts in blood plasma phase. Furthermore, atmospheric CO₂ concentration could be over 800 parts per million by the end of the 21th century [4]. Also, Solubility of CaSO₄ is of great significance on the equilibrium of the ions in ocean containing CO₂. Also, the equilibrium constants of these ions could predict changes in the ionic concentrations in the blood as well as in other aqueous systems. Solubility values of CaSO₄ in various aqueous chloride solutions were available in some compilations [5-7]. However, most of the previous studies have been limited in reporting only the solubility of CaSO₄ phase in salt solutions at ambient temperature or very high temperature. And there has been limited information on the influence of mixed electrolytes and NaHCO₃ on the solubility of CaSO₄.

Here we present the results of thermodynamic simulation of CaSO₄ systems consisting of Ca²⁺, Mg²⁺, Na⁺, K⁺ and HCO₃⁻ at 37 °C. In particular, we investigated the solubility of the above system and estimated the effect of various salts on solubility of CaSO₄.

2. Experimental Section

2.1. Chemicals

All substances were directly used without further purification. All solutions used in this study were prepared by dissolving the chemicals in deionized water (18.2 MΩ). The dissolution method was utilized for the determination of the solubility of calcium sulfate. The method is more reliable because it avoided complications arising from a reactive process such as precipitation.

2.2. Procedure

A typical experimental procedure can be described as follows. The 150 mL of electrolyte aqueous solution was transferred into 250 mL Erlenmeyer flasks, which were equipped with a magnetic stirrer and capped with rubber stoppers. The flasks were then immersed in a temperature-controlled water bath, allowing the solution to stir continuously to establish the temperature equilibrium. The temperature was kept constant within ±0.2 °C. Then, excess solid (10 to 20 g of DH or AH) was quickly added to the solutions in flasks, which were tightly capped again by using rubber stoppers to avoid air pouring. After the solid-liquid equilibrium was attained, stirring was stopped to allow solids to settle. The supernatant solution was then withdrawn and immediately filtered by using syringe filters. The clear filtrate kept in water bath was taken by 10 mL glass pipet heated to bath temperature and diluted by deionized water in a 1000 mL volumetric flask. The SO₄²⁻ concentration was determined by turbidity method.

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. In the present study, the dissolution of calcium sulfate in aqueous solution at 37 °C was investigated as a function of time in order to select the appropriate equilibration time. However, in the experimental work, a longer time of 5 h for dihydrate and anhydrite was chosen to ensure achievement of solubility equilibrium.

3. Results and discussion

The solubility of CaSO₄·2H₂O and anhydrite CaSO₄ in water has been extensive investigated. In present work, the solubility of CaSO₄·2H₂O in water at 25-60 °C was measured in order to verify the
experimental procedure. The newly solubility date are shown in Fig. 1. As the temperature is increased, the relative solubility of CaSO₄·2H₂O decreases slightly. As is clear, these data is in good agreement with the other measurements [8].

3.1. Effect of NaCl concentration and temperature on solubility of CaSO₄

The solubility of anhydrous CaSO₄ in NaCl aqueous solution was measured from 25 to 60 °C under atmospheric pressure. The investigated concentration of NaCl solution is 0.0 - 5.0 M. The results of experimentally determined solubility are given in Fig. 2.

In reference to temperature, the solubility of anhydrous CaSO₄ increases systematically as the temperature ranges from 25 to 60 °C. Fig. 2(b) demonstrates the solubility of anhydrous CaSO₄ phase in aqueous NaCl at 37 °C. For comparison, the solubility of CaSO₄·2H₂O in NaCl from Arvind Kumar [9] is also included in Fig. 2(b). The solubilities of CaSO₄ and CaSO₄·2H₂O increase with increasing NaCl concentration in the range of 0.0 to 2.0 M. After passing a maximum, the solubility declines smoothly in the range of higher concentration of NaCl.

3.2. Effect of KCl concentration and temperature on solubility of CaSO₄

Solubility values of CaSO₄ and CaSO₄·2H₂O in KCl solution with concentrations up to 5 M from 25-
60 °C were determined by using the same procedure. The obtained experimental results are shown in Fig. 3. The solubility values of CaSO₄ phase increase slightly as the temperature increases from 25 to 60 °C. Fig. 3(c) illustrates that the solubility of CaSO₄ dihydrate increases with the concentration of KCl in the range of 0.0-1.0 M. Anhydrite CaSO₄ possesses two features. The solubility of anhydrite increases with the increase of KCl concentration in the range of 0.0-1.5 M. After passing a maximum, the solubility declines smoothly in the range of higher concentration of KCl.

Yang Liuchun [5] found that the relative magnitudes of the variance of solubility for CaSO₄ were larger than that for CaSO₄·2H₂O at 85-100°C in 0.0-18.0 wt % KCl solutions. This is considered to be correlated to the combined effects of the temperature and concentration of KCl solution on the activity coefficients and water activity.

Fig. 3. Solubility of CaSO₄ (a) and CaSO₄·2H₂O (b) in KCl with temperature; CaSO₄ and CaSO₄·2H₂O solubility as a function of KCl (c).

3.3. Effect of CaCl₂ concentration and temperature on solubility of CaSO₄

Solubilities of CaSO₄·2H₂O and CaSO₄ in CaCl₂ solutions were also investigated. The generated solubility data are plotted in Fig. 4. Little influence of temperature on CaSO₄ phase was found. The dependence of CaSO₄ solubility on CaCl₂ concentration was similar to that for CaSO₄·2H₂O. The
solubility of CaSO₄·2H₂O decreases with the increase of CaCl₂ concentration. Initially, the solubility drops sharply and then continues to be constant with the increasing concentration of CaCl₂. Common ion effect is responsible for this behavior.

![Fig. 4. Solubility of CaSO₄ (a) and CaSO₄·2H₂O (b) in CaCl₂ with temperature; CaSO₄ and CaSO₄·2H₂O solubility as a function of CaCl₂ at 37 °C (c).](image)

3.4. Effect of MgCl₂ concentration and temperature on solubility of CaSO₄

The role of Mg²⁺ in the coagulation cascade is more ambiguous [10]. Mg²⁺ is present in plasma at a concentration of 0.9 mM, considering less than that of Ca²⁺ (2.4 mM). The solubility of calcium sulfate phase in mixed solutions was measured from 25 to 60 °C. The investigated concentration of MgCl₂ is from 0.0 to 1.0 M at ambient temperature. The results of experimentally determined solubility are given in Fig. 5. It is evident that the solubility of CaSO₄ increases with increasing MgCl₂ concentration at 37 °C. It can be seen that the CaSO₄ solubility in MgCl₂ solutions is much larger than that in NaCl or KCl solution (see Figs. 2–3).

Magnesium augmentation is on the basis of associating a portion of dissolved sulfate ion in the form of stable MgSO₄ ion pairs. These associated sulfate ions result in much higher solubility levels of calcium sulfate. Being different from either the common ion effect by calcium chloride or the association effect by magnesium chloride, potassium chloride influences the solubility of calcium sulfate dehydrate by a salt effect. The influence of potassium chloride on the solubility of calcium sulfate anhydrate was no more than that of sodium chloride [11].
3.5. NaCl-KCl-CaCl₂-MgCl₂-NaHCO₃ system

The solubility of CaSO₄ in mixed salt solutions was investigated at 37 °C. The data on the solubility are shown in Fig. 6.

CaSO₄ solubility decreases with the additions of KCl in aqueous NaCl solution without altering the
basic pattern of the solubility curve (see Fig. 6a). A similar behavior was observed by Barba [11].

Addition of CaCl$_2$ into aqueous NaCl system also reduced the solubility of CaSO$_4$·2H$_2$O quite dramatically while maintaining the basic pattern of the solubility curve. Our results show that the common ion effect is the main factor in the mixed chloride salts solution. When CaCl$_2$ concentration is more than 0.061 M, solubility of CaSO$_4$ is decreased with the increase of NaHCO$_3$ concentration. Instead, effect of NaHCO$_3$ is negligible at lower CaCl$_2$ concentration. The presence of small amounts of NaHCO$_3$ in mixed solutions markedly influences CaSO$_4$ solubility.

3.6. Dynamics

Solid calcium sulfate is slightly soluble inorganic chemical. The observed behavior of CaSO$_4$ solubility may be explained by considering the various equilibria, involved in the system. For the CaSO$_4$ in mixed salt system, the following independent reactions should be considered,

\[
\begin{align*}
\text{HCO}_3^- & \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \\
\text{CaSO}_4 \cdot \text{nH}_2\text{O} & \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{nH}_2\text{O} \\
\text{CO}_3^{2-} + \text{Ca}^{2+} & \rightleftharpoons \text{CaCO}_3 \\
\text{CO}_3^{2-} + \text{Mg}^{2+} & \rightleftharpoons \text{MgCO}_3
\end{align*}
\]

In the system, the solubility is expressed by the molar concentration of Ca$^{2+}$ or SO$_4^{2-}$,

\[
S = m(\text{Ca}^{2+}) = m(\text{SO}_4^{2-})
\]

The solubility product can be expressed as follows:

\[
K_{sp} = \gamma(\text{Ca}^{2+})m(\text{Ca}^{2+})\gamma(\text{SO}_4^{2-})m(\text{SO}_4^{2-})\alpha_{w}^{n}
\]

\[
\ln \gamma_i = -\frac{A_i I^{1/2}}{1 + B_i I} + B_i I
\]

Here, A and B are the Debye-Hükel constants, and $A_i$ and $B_i$ are parameters specific to particular ions. Equation 8 indicates that activity coefficients of dissolved calcium sulfate are mainly related to the total ionic strength of solution.

Solutions containing several dissolved components at high concentrations similar to those described here did not conform strictly to thermodynamic theories or theories of electrolyte solutions which pertain to the solubility of a dissolved component, but deviate from these theories. At higher values (more than 0.8) of $I^{1/2}$ or in solutions containing both magnesium chloride and sodium chloride, pronounced deviations from theory occurred, and even the addition of the empirical extended terms would not compensate satisfactorily for the deviation [12].

4. Conclusions

Dusting-chalk could produce PM$_{2.5}$ size particles, beside coarse particles. In a large cohort study of 552,000 subjects with a follow-up period of 16 years (American Cancer Society Study), each additional 10 μg/m$^3$ PM$_{2.5}$ led to an increase of cardiovascular mortality by 8–18%. In the study, we present the
results of thermodynamic simulation of CaSO₄ systems consisting of Ca²⁺, Mg²⁺, Na⁺, K⁺ and HCO₃⁻ at 37 °C.

The solubility of CaSO₄ phase increased with increasing NaCl, KCl and MgCl₂ concentration up to 1M. And, the dependence of CaSO₄ solubility on concentration of CaCl₂ solution was similar to that for CaSO₄·2H₂O. The solubility of CaSO₄·2H₂O decreased with the concentration of CaCl₂, compared with the solubility of CaSO₄ in pure water. Initially, the solubility dropped sharply and then continued to be constant with increasing concentration of CaCl₂. The experimental results showed that the presence of small amounts of NaHCO₃ in mixed solutions markedly influences CaSO₄ solubility.

The influence of potassium chloride was attributed to the activity coefficients and water activity. Being different from effect of K⁺, the common ion effect by calcium chloride was responsible for the solubility of CaSO₄. However, Magnesium augmentation is on the basis of associating a portion of dissolved sulfate ion in the form of stable MgSO₄ ion pairs. These associated sulfate ions resulted in much higher solubility levels of CaSO₄. The common ion effect was the main factor on the solubility of CaSO₄ in the mixed salts solution.

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