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Solubility of Calcium Sulfate Dihydrate in Ca−Mg−K Chloride Salt Solution in the Range of (348.15 to 371.15) K

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Solubility data are given for calcium sulfate dihydrate in the system $CaCl_2-MgCl_2-KCl$ at the temperature range of (348.15 to 371.15) K and in ranges of concentrations up to 3.86 m $CaCl_2$, 1.17 m $MgCl_2$, 0.27 m KCl, and their admixture by using a dissolution method. The calcium ion exhibits the common ion effect on the solubility of calcium sulfate dihydrate. The magnesium ion augments the solubility of calcium sulfate dihydrate in the investigated concentrations by stable $MgSO_4^\circ$ ion pair formation. Potassium influences on the solubility of calcium sulfate dihydrate are found to be a salt effect by changing the activity coefficients of the calcium ion and sulfate ion. The temperature has a positive effect on the solubility both in magnesium chloride and potassium chloride solutions. There are two sharp falls. One is between (359.15 and 363.15) K in calcium chloride solution, and the other is at a potassium ion concentration of 0.108 $mol\cdot kg^{-1}$ in its solution. The common ion effect is the main factor on the solubility of calcium sulfate dihydrate in the mixed salts solution. The measured solubilities are also compared with available literature studies, and the relationship with ionic strength is discussed empirically.

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1. Introduction

The solubility and phase equilibrium of solid calcium sulfate in aqueous electrolyte solution are significant issues. These studies[1−10] touch on the fields of the manufacturing of phosphoric acid, the design and operation of cooling towers, the industrial process of reverse osmosis and electrodialysis for water desalination, wastewater treatment, and so on. It is also interesting to geologists and geochemists. Different solvent solutions included inorganic acids, organic acids, and salt solutions such as salts of sodium, magnesium, calcium, manganese, zinc, lithium, nitrate, and so on. Especially, the solubility of $CaSO_4$ and its hydrates in $NaCl-H_2O$ solutions at temperatures between (298.15 and 473.15) K have been investigated systematically for the purpose of preventing scale formation on heat exchanger surfaces during distillation processes for desalinating water.[11] There are some rules of calcium sulfate dissolution described by researchers. Some previous solubility studies in sulfuric acid solution[1] were summarized extensively. According to the comprehensive "map" presented by Wehde and Stichlmair,[2] solubility curves of calcium sulfate percent (% by weight) were not distinguishable and could not be reproduced in a wide sulfuric acid concentration range from (0 to 90) % (by weight) with a temperature range from (283.15 to 393.15) K. Ling and Demopoulos[1] indicated that the solubility of calcium sulfate in sulfuric acid solution was independent of the starting material, and the saturation time was only 5 min with the equilibrating phase of anhydrite. Barba et al.[3] pointed out that the solubility of calcium sulfate was influenced greatly by the total amount and proportion of different salts.

Popularly, salt solution is a suitable way for the conversion of flue-gas-desulfurized gypsum (FGD gypsum) into α-calcium sulfate hemihydrate (α-$CaSO_4\cdot 1/2H_2O$, α-HH) in salt solution at atmospheric pressure.[12−14] Accurate knowledge about the solubility of calcium sulfate is of great practical importance for the conversion. This paper presents the solubilities of $CaSO_4\cdot 2H_2O$ (DH) in alkali and alkali-earth salt solution at temperatures of (348.15 to 371.15) K as part of a broader project seeking to optimize process control for the conversion of FGD gypsum into α-HH in mixed salt solution at atmospheric pressure. It also compares them with literature data and interprets the results according to thermodynamics.

2. Experimental Section

Chemicals and Equipments. Generally, calcium sulfate phases are slightly soluble. According to Ostroff and Metler,[10] the condition of saturation of calcium sulfate could be reached from either under- or oversaturated conditions in a relative short time period. In this research, reagent-grade $CaSO_4\cdot 2H_2O$ and different salts $CaCl_2$, $MgCl_2$, and KCl were used as starting materials. The dissolution method[1,3,6] was utilized for the determination of the solubility of calcium sulfate dihydrate. The method was more reliable because it avoided complications arising from a reactive process such as precipitation. Pure water was used to prepare different salt solutions with various concentrations.

The experimental setup consisted of a three-necked round-bottom flask with 500 mL volume and a set of filtration. An oil-bath thermostat provided constant temperature regulated at ± 0.1 K adjusted by a precise mercury thermometer. Uniform agitation of (50 to 100) rpm for the slurry was supplied by an electromagnetic stirrer with an anchor agitator, 80 mm in length and 20 mm in width. The reactor was equipped with a spiral condenser for keeping water balanced in the experimental system. All equilibrium saturations were made at atmospheric pressure.

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Procedure and Reproducibility. The salt solution of around 500.00 mL was preheated to (348.15, 353.15, 358.15, 363.15, 368.15, and 371.15) K that was kept constant for half an hour. Then excess solid gypsum of 20.00 g was quickly introduced into the salt solution. In each experiment, samples in sequence were taken at (5, 10, 30, 60, 90, 120, 150, and 240) min. There were three replicate measurements that were averaged to get the final solubility value for each salt concentration. Liquid samples taken in sequence were first filtrated quickly through cellulosic filter papers with a porosity of 0.2 μm and then quantified by pipet (Gilson, P5000) for ICP analysis (IRIS Advantage Radial, ThemoElemental). The solubility was expressed as an equivalent calcium sulfate grams per 100 mL solvent ($CaSO_4$ g·100 mL^{-1}) based on the measured S abundance. Residual solid samples were washed quickly by hot water with the temperatures exceeding 363.15 K. Acetone of about 10 mL was used to fix the samples. Subsequently solid samples were dried at (318.15 to 333.15) K for 2 h and finally stored in a crucible for X-ray diffraction (XRD: X'Pert PRO MPD, Holland), scanning electron microscopy (SEM: Philips XL30 TMP, Holland), and differential scanning calorimetry/thermogravimetric analysis (DSC/TG: Netzsch STA 449 Luxx, Germany). XRD and DSC/TG thermal analyses were used to determine the phase of residual solid after 4 h dissolution equilibrium.

Determination of Equilibration Time. There has been much research into the equilibration time of solubility measurements of solid gypsum. The equilibration time varied from several minutes to several days according to the dissolution rate of the solid phase and the applied system. Ling and Demopoulos[1] reported that the dihydrate or hemihydrate could saturate the sulfuric acid solution at 373.15 K in a very short period of time, around 5 min, and Sullivan et al.[15] also found that the "equilibration time" of the hemihydrate in phosphoric acid was established within 3 min. Li and Demopoulos[16] reported that the solubility equilibrium between solid gypsum and liquid was established very rapidly within 0.5 h, and a 5 h equilibration time for DH and AH and 1 h for HH was used to ensure achievement of the solubility equilibrium. Ostroff and Metler[10] also indicated that two days' stirring, the same equilibration time reported by Rock,[17] was a sufficient time for reaching saturation by dissolving finely divided calcium sulfate dihydrate with a precision of (6.60 ± 0.02) g in the system $NaCl-MgCl_2-H_2O$.

In this work, equilibration time experiments were carried out first to determine the necessary equilibration time for the formation of a saturated solution from solid gypsum, either in pure water or in salt solution. Equilibration time experiments for each sample lasted at least seven days for sufficient saturation in pure water and salt solution. The results of the experiments are shown in Figure 1, which shows that dissolution equilibrium between solid gypsum and solvent can be established within 2 h. An equilibration time of 4 h is selected to ensure solubility equilibrium of calcium sulfate. A longer equilibration time is not employed in the solubility equilibrium of dihydrate gypsum because dihydrated gypsum could be transformed directly into hemihydrated calcium sulfate in the temperature range from (358.15 to 371.15) K. In this work, the "equilibrium solubility" is referred to the final phase of solid gypsum during the calcium sulfate solubility determination. There are phase changes detected under the experimental conditions. The variation of the measured data is attributed to experimental errors such as volumetric sampling, dilution, and instrument analyses stability.

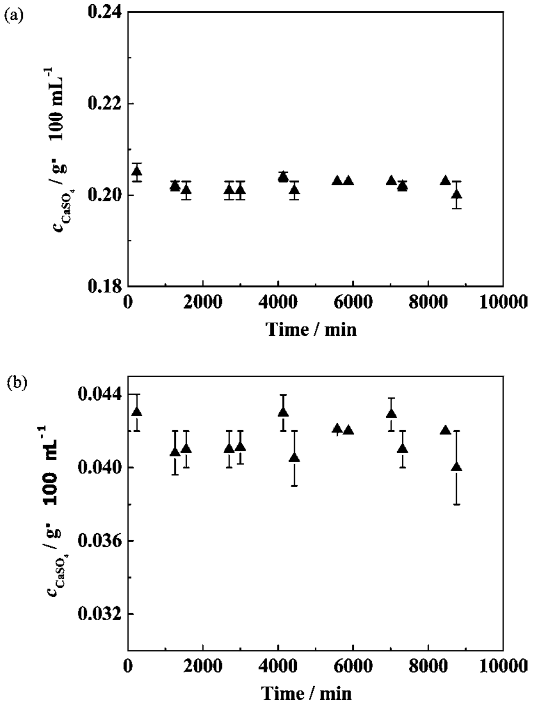

Figure 1. Equilibration test times of calcium sulfate solubility in pure water and in salt solution: (a) obtained with dihydrated gypsum in pure water at 298.15 K; average value = 0.203 g·100 mL^{-1}; standard deviation (s/g·100 mL^{-1}) = 0.00163 g·100 mL^{-1}; coefficient of variation (cv %) = 0.805 %. (b) obtained with dihydrated gypsum in salt solution (Ca, Mg, and K chloride, total concentration = 30 %) at 363.15 K; average value = 0.042 g·100 mL^{-1}; standard deviation (s/g·100 mL^{-1}) = 0.00109 g·100 mL^{-1}; coefficient of variation (cv %) = 2.59 %.

3. Results and Discussion

In this work, the solubilities of calcium sulfate are obtained in different salt solutions at temperatures of (348.15 to 371.15) K and in water at temperatures of (298.15 to 371.15) K. The data of the solubilites are grouped in each temperature according to identical salt concentrations shown in Table 1 to 4 with different units for comparison with literature data. However, there might be some deviations occurring during the salt solution preparation.

Calcium Sulfate Solubility in Aqueous Solution. Solid calcium sulfate is a slightly soluble inorganic chemical. The dissolution of calcium sulfate and its hydrates could be expressed as follows:

$$CaSO_4 \cdot xH_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + xH_2O \qquad (1)$$

The solubility product can be expressed as follows:

$$a_i = \gamma_i m_i \qquad i = Ca^{2+} \text{ and } SO_4^{2-} \qquad (2)$$

$$K_{sp} = \gamma_{Ca^{2+}} m_{Ca^{2+}} \gamma_{SO_4^{2-}} m_{SO_4^{2-}} a_w^{\,x} \qquad (3)$$

In eq 3, $\gamma_{Ca^{2+}}$ and $\gamma_{SO_4^{2-}}$ are the activity coefficients of calcium and sulfate ions, respectively, $m_{Ca^{2+}}$ and $m_{SO_4^{2-}}$ are the calcium and sulfate ions molality concentrations, and a_w is the activity of water. $x = 2$ and 0.5. The average of two activity coefficients can be determined; the calcium concentration equals the sulfate concentration if there is no extra calcium ion or sulfate added to the aqueous solution, and then eq 3 can also be written for calcium sulfate dihydate as:

$$K_{sp} = \gamma_{\pm}^{2} m_{\pm}^{2} a_w^{2} \qquad (4)$$

The models of calcium sulfate solubility at either low ionic strength or high ionic strength were investigated on the basis

Table 1. Solubility of Calcium Sulfate (1) (Added as a Dihydrate) in $CaCl_2$ (2) + Water (3) (Equilibration Time: 4 h)

solution parameters				solubility as $CaSO_4$ in different units			solid phase after 4 h equilibration (by DSC/TG)
c_2[a] mol·L^{-1}	m_2 mol·kg^{-1}	100 w_2	ρ_s[b] g·cm^{-3}	C_1 g·100 mL^{-1}	m_2 mol·kg^{-1}	100 w_2	
				T = 348.15 K			
0.4658	0.4742	5.00	1.034	0.1590	0.0113	0.15	DH
0.9587	1.0011	10.00	1.064	0.1040	0.0072	0.10	DH
1.5178	1.5900	15.00	1.123	0.0746	0.0049	0.07	DH
2.0813	2.2525	20.00	1.155	0.0670	0.0043	0.06	DH
2.6580	3.0034	25.00	1.180	0.0504	0.0032	0.04	DH
3.4112	3.8615	30.00	1.262	0.0330	0.0019	0.03	DH
				T = 353.15 K			
0.4649	0.4742	5.00	1.032	0.1310	0.0093	0.13	DH
0.9560	1.0011	10.00	1.061	0.1060	0.0073	0.10	DH
1.5151	1.5900	15.00	1.121	0.0914	0.0060	0.08	DH
2.0759	2.2525	20.00	1.152	0.0924	0.0059	0.08	DH
2.6535	3.0034	25.00	1.178	0.0692	0.0043	0.06	DH
3.4058	3.8615	30.00	1.260	0.0601	0.0035	0.05	DH
				T = 358.15 K			
0.4640	0.4742	5.00	1.030	0.1840	0.0131	0.18	DH
0.9542	1.0011	10.00	1.059	0.1130	0.0078	0.11	DH
1.5124	1.5900	15.00	1.119	0.0864	0.0057	0.08	DH
2.0723	2.2525	20.00	1.150	0.0786	0.0050	0.07	DH
2.6490	3.0034	25.00	1.176	0.0427	0.0027	0.04	DH
3.4031	3.8615	30.00	1.259	0.0280	0.0016	0.02	DH
				T = 363.15 K			
0.4631	0.4742	5.00	1.028	0.0376	0.0027	0.04	DH
0.9524	1.0011	10.00	1.057	0.0342	0.0024	0.03	DH
1.5096	1.5900	15.00	1.117	0.0283	0.0019	0.03	DH
2.0669	2.2525	20.00	1.147	0.0266	0.0017	0.02	DH
2.6445	3.0034	25.00	1.174	0.0232	0.0015	0.02	DH
3.3977	3.8615	30.00	1.257	0.0149	0.0009	0.01	DH
				T = 371.15 K			
0.4613	0.4742	5.00	1.024	0.1090	0.0078	0.11	DH
0.9479	1.0011	10.00	1.052	0.1030	0.0072	0.10	DH
1.5042	1.5900	15.00	1.113	0.0937	0.0062	0.08	DH
2.0579	2.2525	20.00	1.142	0.0213	0.0014	0.02	DH
2.6377	3.0034	25.00	1.171	0.0138	0.0009	0.01	DH
3.3869	3.8615	30.00	1.253	0.0086	0.0005	0.01	DH

[a] Initial concentration of solutions prepared at room temperature without calcium sulfate. [b] Experimental density of initial solutions.

of molecular thermodynamics principles by many researchers.[3,18−21] The models were used to predict mineral solubilities in water and also more concentrated systems. A theoretical approach of activity coefficients was a virial expansion given as eq 5 which could represent the data accurately.[19]

$$\ln \gamma_i = \ln \gamma_{DH} + \sum_j B_{ij}(I)m_j + \sum_{jk} C_{ijk}(I)m_j m_k + ... \tag{5}$$

where B_{ij}(I) and C_{ijk}(I) are the second and third virial coefficients, respectively.

However, the higher order virial coefficient is uncertain, and its accuracy depends on the accurate description of the low order virial coefficient. The notable models for activity coefficient calculation are the Pitzer model[22] and the solvent model.[23,24] An adequate description of the solubility of calcium sulfate in salt solution should not only take into account total dissolved solid gypsum, but also the nature and the amount of each ion in mixed salt solution. In fact, Barba's solubility model[20] has indicated that a large quantity of chloride ion content would decrease the accuracy of the predicted model, particularly when the chloride ion concentration was more than one in molality. In general, the simplest and most widely used model is the extended Debye−Hükel model. In this model, the activity coefficient for ion i is given by the empirical equation as eq 6.

$$\ln \gamma_i = -\frac{A\sqrt{I}}{1 + Ba_i\sqrt{I}} + B_i I \tag{6}$$

Here, A and B are the Debye−Hükel constants, and a_i and B_i are parameters specific to particular ions. Equation 6 indicates that activity coefficients of dissolved calcium sulfate are mainly related to the total ionic strength of solution. Since the research into the solubility of calcium sulfate is mainly in concentrated salt solution, the concentrations of salts are usually higher than that of dissolved calcium sulfate by one to four orders of magnitude. There is little difference in the activity coefficients of Ca^{2+} and SO_4^{2-} at a certain salt concentration in the range of experimental temperatures. Consequently, the relationship of the solubility of calcium sulfate versus total ionic strength will show a true influence of the salts on the solubility of calcium sulfate.

Solubility of $CaSO_4 \cdot 2H_2O$ in Water. Figure 2 shows the solubility of calcium sulfate dihydrate in pure water determined in the present work as a function of temperature in the range of (298.15 to 371.15) K. The solubility increases slightly first and then decreases with increasing temperature. The maximum value is at 328.45 K. These results are coincident mostly with the theoretical solubility description, in which the maximum is at 315.15 K. Data in the present work are slightly different from the data by Ostroff and Metler.[10] Especially at high temperatures, the difference is marked. Equation 7 is used to describe the

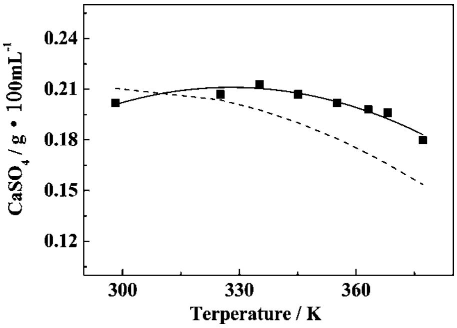

Figure 2. Solubility of calcium sulfate dihydrate in pure water: -■-, this work; ─, Ostroff and Metler.[10]

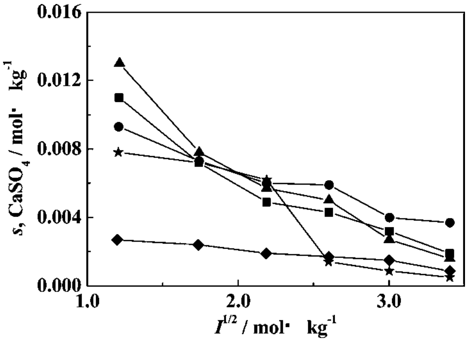

Figure 3. Solubility of calcium sulfate dihydrate in $CaCl_2$ solutions vs $I^{1/2}$, (348.15 to 371.15) K: ■, 348.15 K; ●, 353.15 K; ▲, 358.15 K; ◆, 363.15 K; ★, 371.15 K.

relationship between the solubility of calcium sulfate dihydrate and temperature from (298.15 to 371.15) K by using the least-squares method.

$$CaSO_4(g \cdot 100\ mL^{-1}) = -1.024 + 0.00754T - 1.149 \cdot 10^{-5}T^2 \qquad (7)$$

Solubility of $CaSO_4 \cdot 2H_2O$ in $CaCl_2$ Solutions. The solubility of calcium sulfate in calcium chloride solution was measured at (348.15, 353.15, 358.15, 363.15, and 371.15) K. The investigated concentration of calcium chloride was from (0.5 to 4) mol·kg^{-1} (about (5 to 30) % by weight). The data of the solubilities obtained in the experiments are shown in Table 1. Figure 3 describes the relationship between the ionic strength and the solubility of calcium sulfate dihydrate in aqueous calcium chloride solution. It is indicated that the solubility of calcium sulfate dihydrate decreases with ionic strength, that is, calcium chloride molality concentration. This phenomenon can be explained by the common ion effect according to eq 1. Compared with the solubility of calcium sulfate in pure water, 0.202 g·100 mL^{-1}, the solubility of calcium sulfate in calcium chloride solution decreases sharply when the molality of calcium chloride varies from (0.47 to 3.86) mol·kg^{-1}. There is a sharp fall between (358.15 and 363.15) K, and the solubility increases with temperature slightly. An interesting phenomenon is that the solubility of calcium sulfate dihydrate at higher ionic strength tends to be uniform in the investigated temperature range. There are a few data[16] in calcium chloride solution under the same equilibrium conditions to compare with the data obtained in this work shown in Figure 4. Some deviation exists between the two groups of data.

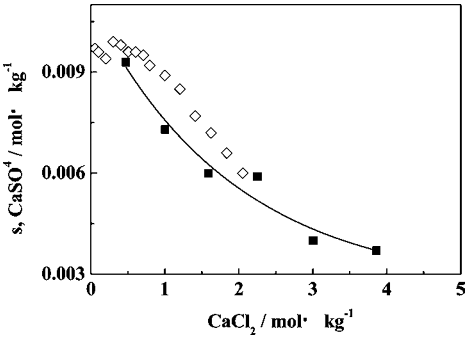

Figure 4. Solubility of calcium sulfate dihydrate in aqueous calcium chloride solution at 353.15 K: ■, this work; □, Li and Demopoulos.[16]

Solubility of $CaSO_4 \cdot 2H_2O$ in $MgCl_2$ Solutions. The solubility of calcium sulfate in magnesium chloride solution was measured over the same temperature range as in calcium chloride solution. The investigated concentrations of magnesium chloride were from (0.1 to 1.0) mol·kg^{-1} (about (1 to 10) % by weight). The data of the solubility are shown in Table 2. Fortunately, there are a few data[10] under the same equilibrium conditions to compare with the data obtained in this work shown in Figure 5. Figure 6 describes the ionic strength influence on the solubility of calcium sulfate dihydrate in magnesium chloride solution. The data in Table 2 show that the solubility of calcium sulfate dihydrate is augmented with the magnesium cation at levels up to three to five times compared with the solubility in water. This result is consistent with prior research by Glater et al.[25] Of the early research about seawater desalination,[25−29] magnesium augmentation is on the basis of associating a portion of dissolved sulfate ion in the form of stable $MgSO_4°$ ion pairs. These associated sulfate ions result in much higher solubility levels of calcium sulfate. In the investigated Mg^{2+} concentration ranges, the augmentation increases with Mg^{2+} concentration and temperature. Moreover, it can be seen in Figure 5 that there is very good agreement of the solubility data in magnesium chloride solution at 363.15 K between the present work and literature data. In Figure 6 a significant feature also appears, that the relationship between the solubility of calcium sulfate dihydrate with $I^{1/2}$ varies from a concave curve to a convex curve at high ionic strength when the equilibrium temperature changes from (348.15 to 371.15) K. Accordingly, high temperature and high Mg^{2+} concentrations are beneficial to the stable aqueous solution in this investigated system.

Solubility of $CaSO_4 \cdot 2H_2O$ in KCl Solutions. The solubility of calcium sulfate in potassium chloride solutions was also measured at (348.15, 353.15, 358.15, 363.15, and 371.15) K. The investigated concentration of potassium chloride was only up to about 0.3 mol·kg^{-1}. The data on the solubility determined by using the same procedure as before are shown in Table 3. According to Barba,[30] potassium could be substituted by an equivalent amount of sodium, and there are also a few data under the same equilibrium conditions to compare with the data obtained in this work shown in Figure 7. Figure 7 shows that the solubility of calcium sulfate dihydrate can be augmented in both potassium chloride solution and sodium chloride solution, and potassium cannot be substituted absolutely by the equivalent amount of sodium. The influence of potassium chloride on the solubility of calcium sulfate dihydrate is much stronger than that of sodium chloride. Figure 8 only plots the curves of the solubility of calcium sulfate dihydrate versus ionic strength at (353.15, 358.15, and 371.15) K to describe the relationships more distinctly. Figure 8 indicates that there is a sharp fall in the solubility versus $I^{1/2}$ at an initial potassium chloride molality concentration of 0.108 mol·kg^{-1} (about 0.8 % by weight), and the solubility increases with temperature over the whole investigated temperature range. The results may explain indirectly that why a potassium chloride concentration exceeding

Table 2. Solubility of Calcium Sulfate (1) (Added as a Dihydrate) in $MgCl_2$ (2) + Water (3) (Equilibration Time: 4 h)

solution parameters				solubility as $CaSO_4$ in different units			solid phase after 4 h equilibration (by DSC/TG)
c_2[a] / mol·L^{-1}	m_2 / mol·kg^{-1}	100 w_2	ρ_s[b] / g·cm^{-3}	C_1 / g·100 mL^{-1}	m_2 / mol·kg^{-1}	100 w_2	
				T = 348.15 K			
0.1048	0.1061	1.00	0.998	0.3970	0.0292	0.40	DH
0.2117	0.2143	2.00	1.008	0.5700	0.0415	0.56	DH
0.3204	0.3248	3.00	1.017	0.6840	0.0494	0.67	DH
0.4307	0.4376	4.00	1.025	0.7850	0.0563	0.76	DH
0.5425	0.5528	5.00	1.033	0.8550	0.0608	0.82	DH
0.6548	0.6704	6.00	1.039	0.8880	0.0628	0.85	DH
0.8999	0.9133	8.00	1.071	0.9280	0.0636	0.86	DH
1.1427	1.1670	10.0	1.088	1.0070	0.0680	0.92	DH
				T = 353.15 K			
0.1047	0.1061	1.00	0.997	0.4250	0.0313	0.43	DH
0.2113	0.2143	2.00	1.006	0.5730	0.0418	0.57	DH
0.3198	0.3248	3.00	1.015	0.6830	0.0494	0.67	DH
0.4298	0.4376	4.00	1.023	0.8080	0.0580	0.78	DH
0.5414	0.5528	5.00	1.031	0.8710	0.0621	0.84	DH
0.6535	0.6368	6.00	1.037	0.9070	0.0642	0.87	DH
0.8982	0.9133	8.00	1.069	0.9480	0.0651	0.88	DH
1.1406	1.1670	10.00	1.086	1.2600	0.0852	1.15	DH
				T = 358.15 K			
0.1045	0.1061	1.00	0.995	0.4010	0.0296	0.40	DH
0.2109	0.2143	2.00	1.004	0.5760	0.0421	0.57	DH
0.3192	0.3248	3.00	1.013	0.6890	0.0500	0.68	DH + HH
0.4289	0.4376	4.00	1.021	0.9130	0.0657	0.89	DH + HH
0.5403	0.5528	5.00	1.029	0.8140	0.0581	0.79	DH + HH
0.6522	0.6704	6.00	1.035	0.9790	0.0695	0.94	DH + HH
0.8965	0.9133	8.00	1.067	0.9660	0.0665	0.90	DH + HH
1.1396	1.1670	10.00	1.085	1.2980	0.0879	1.18	DH + HH
				T = 363.15 K			
0.1043	0.1061	1.00	0.993	0.4040	0.0299	0.41	DH
0.2105	0.2143	2.00	1.002	0.5870	0.0430	0.58	DH
0.3186	0.3248	3.00	1.011	0.7110	0.0517	0.70	HH
0.4281	0.4376	4.00	1.019	0.8450	0.0609	0.82	HH
0.5388	0.5527	5.00	1.026	0.8050	0.0576	0.78	HH
0.6510	0.6704	6.00	1.033	1.1520	0.0819	1.10	HH
0.8949	0.9133	8.00	1.065	1.160	0.0800	1.08	HH
1.1374	1.1670	10.00	1.083	1.2640	0.0857	1.15	HH
				T = 371.15 K			
0.1038	0.1061	1.00	0.989	0.4820	0.0358	0.49	DH
0.2096	0.2143	2.00	0.998	0.5870	0.0432	0.59	HH
0.3173	0.3248	3.00	1.007	0.9320	0.0679	0.92	HH
0.4264	0.4376	4.00	1.015	1.0660	0.0771	1.04	HH
0.5372	0.5528	5.00	1.023	1.0340	0.0742	1.00	HH
0.6484	0.6704	6.00	1.029	1.0900	0.0778	1.05	HH
0.8923	0.9133	8.00	1.062	1.2200	0.0844	1.14	HH
1.1343	1.1670	10.00	1.080	1.2760	0.0868	1.17	HH

[a] Initial concentration of solutions prepared at room temperature without calcium sulfate. [b] Experimental density of initial solutions.

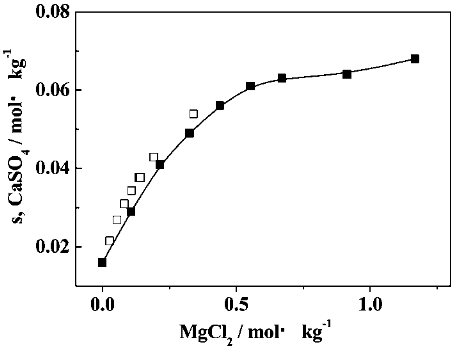

Figure 5. Solubility of calcium sulfate dihydrate in aqueous magnesium chloride solution at 363.15 K: ■, this work; □, Ostroff and Metler.[10]

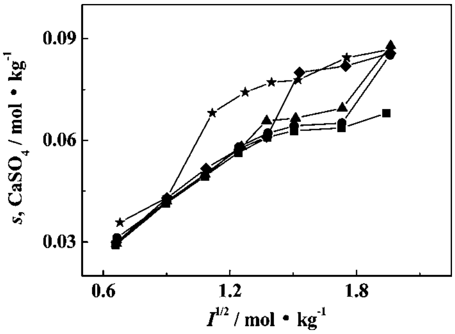

Figure 6. Solubility of calcium sulfate dihydrate in $MgCl_2$ solutions vs $I^{1/2}$, (348.15 to 371.15) K: ■, 348.15 K; ●, 353.15 K; ▲, 358.15 K; ◆, 363.15 K; ★, 371.15 K.

1 % is sufficient to convert FGD gypsum into α-HH.[31] 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 dihydrate by a salt effect. Potassium chloride is a strong electrolyte, and the activity of its solution changes from 0.97 to 0.65 when its molarity varies from (0.001 to 0.5) mol·L^{-1} at 298.15 K.[32] According to the Debye−Hückel ion-attraction theory, K^+ and

Table 3. Solubility of Calcium Sulfate (1) (Added as a Dihydrate) in KCl (2) + Water (3) (Equilibration Time: 4 h)

solution parameters				solubility as $CaSO_4$ in different units			
c_2[a]	m_2		ρ_s[b]	C_1	m_2		solid phase after 4 h equilibration (by DSC/TG)
$mol \cdot L^{-1}$	$mol \cdot kg^{-1}$	$100\ w_2$	$g \cdot cm^{-3}$	$g \cdot 100\ mL^{-1}$	$mol \cdot kg^{-1}$	$100\ w_2$	
				$T = 348.15$ K			
0.0266	0.0269	0.20	0.991	0.2950	0.0219	0.30	DH
0.0532	0.0539	0.40	0.993	0.3310	0.0245	0.33	DH
0.0800	0.0810	0.60	0.994	0.2700	0.0200	0.27	DH
0.1069	0.1082	0.80	0.996	0.2940	0.0217	0.29	DH
0.1338	0.1355	1.00	0.998	0.2810	0.0207	0.28	DH
0.2016	0.2043	1.50	1.002	0.3310	0.0243	0.33	DH
0.2701	0.2701	2.00	1.007	0.3880	0.0283	0.38	DH
				$T = 353.15$ K			
0.0265	0.0269	0.20	0.989	0.2770	0.021	0.28	DH
0.0532	0.0539	0.40	0.991	0.3290	0.024	0.33	DH
0.0799	0.0810	0.60	0.993	0.3570	0.026	0.36	DH
0.1067	0.1082	0.80	0.994	0.2780	0.020	0.28	DH
0.1336	0.1355	1.00	0.996	0.2950	0.022	0.29	DH
0.2012	0.2043	1.50	1.000	0.3440	0.025	0.34	DH
0.2696	0.2737	2.00	1.005	0.3840	0.028	0.38	DH
				$T = 358.15$ K			
0.0265	0.0269	0.20	0.987	0.3510	0.0261	0.35	DH
0.0531	0.0539	0.40	0.989	0.3810	0.0283	0.38	DH
0.0797	0.0810	0.60	0.990	0.3890	0.0289	0.39	DH
0.1065	0.1082	0.80	0.992	0.3030	0.0224	0.30	DH
0.1333	0.1355	1.00	0.994	0.3210	0.0237	0.32	DH
0.2008	0.2043	1.50	0.998	0.3390	0.0249	0.34	DH
0.2691	0.2737	2.00	1.003	0.3990	0.0292	0.40	DH + HH
				$T = 363.15$ K			
0.0264	0.0269	0.20	0.985	0.4840	0.0361	0.49	DH
0.0529	0.0539	0.40	0.986	0.4760	0.0355	0.48	DH
0.0795	0.0810	0.60	0.988	0.3650	0.0271	0.37	DH
0.1062	0.1082	0.80	0.990	0.4190	0.0311	0.42	DH
0.1331	0.1355	1.00	0.992	0.3870	0.0287	0.39	DH
0.2004	0.2043	1.50	0.996	0.3390	0.0250	0.34	DH + HH
0.2683	0.2737	2.00	1.000	0.4090	0.0300	0.41	DH + HH
				$T = 371.15$ K			
0.0263	0.0269	0.20	0.981	0.3950	0.0296	0.40	HH
0.0527	0.0539	0.40	0.983	0.4480	0.0335	0.45	HH
0.0792	0.0810	0.60	0.984	0.5250	0.0392	0.53	HH
0.1058	0.1082	0.80	0.986	0.4050	0.0302	0.41	HH
0.1325	0.1355	1.00	0.988	0.4770	0.0355	0.48	HH
0.1996	0.2043	1.50	0.992	0.4200	0.0311	0.42	HH
0.2675	0.2737	2.00	0.997	0.4860	0.0358	0.49	HH

[a] Initial concentration of solutions prepared at room temperature without calcium sulfate. [b] Experimental density of initial solutions.

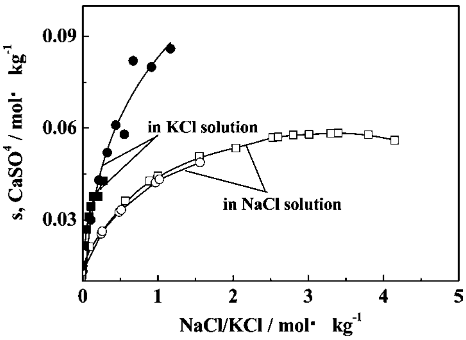

Figure 7. Solubility of calcium sulfate dihydrate in aqueous sodium/potassium chloride solution: ■, this work in aqueous potassium chloride solution at 348.15 K; □, Ostroff and Metler[10] in aqueous sodium chloride solution at 343.15 K; ●, this work in aqueous potassium chloride solution at 348.15 K; ○, Ostroff and Metler[10] in aqueous sodium chloride solution at 343.15 K.

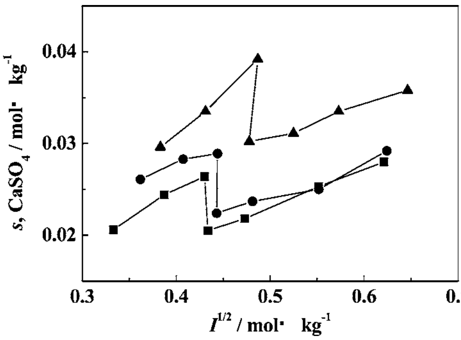

Figure 8. Solubility of calcium sulfate dihydrate in KCl solutions vs $I^{1/2}$, (348.15 to 371.15) K: ■, 353.15 K; ●, 358.15 K; ▲, 371.15 K.

Cl^- can surround SO_4^{2-} and Ca^{2+} by electrostatic forces to form an ionic atmosphere which restrains the activities of SO_4^{2-} and Ca^{2+}. Theoretically, the solubility product of calcium sulfate keeps constant at a specific temperature on the basis of thermodynamics which results in constant activities of SO_4^{2-} and Ca^{2+}, as defined by eq 2. To keep a uniform thermodynamic dissociation equilibrium of calcium sulfate dihydrate, the measured concentrations of SO_4^{2-} and Ca^{2+} as solubility are higher in potassium chloride solution than in pure water. So it appears that the solubility of calcium sulfate dihydrate is augmented by potassium chloride. However, the augmentation of potassium chloride is limited compared to the common ion effect by calcium chloride and the association effect by magnesium chloride.

Table 4. Solubility of Calcium Sulfate (1) (Added as a Dihydrate) in $CaCl_2$ + $MgCl_2$ + KCl (2) + Water (3) (Equilibration Time: 4 h)

solution parameters				solubility as $CaSO_4$ in different units			
c_2[a] mol·L^{-1}	m_2 mol·kg^{-1}	100 w_2	ρ_s[b] g·cm^{-3}	C_1 g·100 mL^{-1}	m_2 mol·kg^{-1}	100 w_2	solid phase after 4 h equilibration (by DSC/TG)
				T = 348.15 K			
0.4735	0.4819	4.88	1.033	0.151	0.011	0.15	DH
0.9681	0.9860	9.50	1.085	0.155	0.010	0.14	DH
1.4704	1.5215	13.94	1.123	0.104	0.0068	0.09	DH
1.9582	2.0843	18.16	1.148	0.078	0.0050	0.07	DH
2.4183	2.6185	21.80	1.181	0.055	0.0034	0.05	DH
2.9901	3.3088	26.05	1.222	0.037	0.0022	0.03	DH
3.5449	4.0256	30.00	1.258	0.035	0.0020	0.03	DH
4.2935	5.0578	35.00	1.306	0.024	0.0013	0.02	DH
				T = 353.15 K			
0.4726	0.4819	4.88	1.031	0.203	0.014	0.20	DH
0.9664	0.9860	9.50	1.083	0.127	0.0086	0.12	DH
1.4678	1.5215	13.94	1.121	0.106	0.0069	0.09	DH
1.9548	2.0843	18.16	1.146	0.079	0.0051	0.07	DH
2.4142	2.6185	21.80	1.179	0.071	0.0044	0.06	DH
2.9852	3.3088	26.05	1.220	0.044	0.0026	0.04	DH
3.5421	4.0256	30.00	1.257	0.038	0.0022	0.03	DH
4.2902	5.0578	35.00	1.305	0.024	0.0013	0.02	DH
				T = 358.15 K			
0.4717	0.4819	4.88	1.029	0.215	0.015	0.21	DH
0.9646	0.9860	9.50	1.081	0.175	0.012	0.16	DH
1.4652	1.5215	13.94	1.119	0.105	0.0069	0.09	DH
1.9514	2.0843	18.16	1.144	0.083	0.0053	0.07	DH
2.4122	2.6185	21.80	1.178	0.067	0.0042	0.06	DH
2.9803	3.3088	26.05	1.218	0.040	0.0024	0.03	DH
3.5365	4.0256	30.00	1.255	0.035	0.0020	0.03	DH
4.2837	5.0578	35.00	1.303	0.024	0.0013	0.02	DH
				T = 363.15 K			
0.4708	0.4819	4.88	1.027	0.190	0.014	0.19	DH
0.9638	0.9860	9.50	1.079	0.140	0.0095	0.13	DH
1.4626	1.5215	13.94	1.117	0.108	0.0071	0.10	DH
1.9480	2.0843	18.16	1.142	0.095	0.0061	0.08	DH
2.4081	2.6185	21.80	1.176	0.068	0.0042	0.06	DH + HH
2.9754	3.3088	26.05	1.216	0.052	0.0031	0.04	DH + HH
3.5308	4.0256	30.00	1.253	0.042	0.0025	0.03	DH + HH
4.2804	5.0578	35.00	1.302	0.027	0.0015	0.02	DH + HH
				T = 371.15 K			
0.4689	0.4819	4.88	1.023	0.186	0.013	0.18	DH
0.9602	0.9860	9.50	1.076	0.182	0.012	0.17	DH
1.4587	1.5215	13.94	1.114	0.142	0.0092	0.12	DH
1.9429	2.0843	18.16	1.139	0.118	0.0078	0.11	DH
2.3999	2.6185	21.80	1.172	0.065	0.0041	0.06	HH
2.9681	3.3088	26.05	1.213	0.048	0.0029	0.04	HH
3.5224	4.0256	30.00	1.250	0.042	0.0025	0.03	HH
4.2705	5.0578	35.00	1.299	0.021	0.0012	0.02	HH

[a] Initial concentration of solutions prepared at room temperature without calcium sulfate. [b] Experimental density of initial solutions.

Solubility of $CaSO_4\cdot 2H_2O$ in Ca−Mg−K−Cl Mixed Solutions. The solubility of calcium sulfate in mixed salt solutions was investigated over the same temperature range as before. The investigated concentration of total salt concentration was from about (0.5 to 5) mol·kg^{-1} (about (5 to 35) % by weight). The data on the solubility are shown in Table 4 and Figure 9, which exhibits good reproducibility behavior and compares reasonably well with the data in the single salt solutions. Analyses of the comprehensive thermal analysis and XRD indicated that DH and α-HH can be both obtained which is dependent on temperature and salt solution concentration. DH is the stable phase below 363.15 K in 4 h dissolution equilibrium, while DH is converted into α-HH when the temperature exceeds 363.15 K and total salt concentration exceeds 20 %.

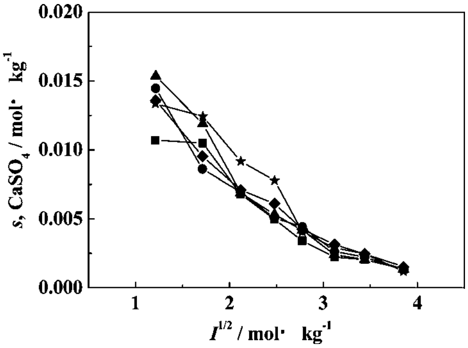

Figure 9. Solubility of calcium sulfate dihydrate in Ca−Mg−K−Cl solutions vs $I^{1/2}$, (348.15 to 371.15) K: ■, 348.15 K; ●, 353.15 K; ▲, 358.15 K; ◆, 363.15 K; ★, 371.15 K.

4. Conclusions

This work studied the solubility of calcium sulfate dihydrate in Ca−Mg−K chloride salt solutions with an experimental temperature range from (348.15 to 371.15) K. Of the investigated salts, experimental results show that there is a common ion effect with calcium chloride, an association effect with magnesium chloride, and a salt effect with potassium chloride. The influence of these three effects arranged in a decreasing order is the common ion effect, the association effect, and the salt effect. There are two mechanisms associated with the action of the effects. The two former effects change the dissociation equilibrium of calcium sulfate dihydrate in salt solution which results in variations in the magnitude of the solubility. The last one only changes the activity coefficients of Ca^{2+} and SO_4^{2-} minimally, and its influence is limited. Since calcium chloride has the highest proportion in the mixed salt solution, the common ion effect is the main factor. However, the solubility of calcium sulfate dihydrate in mixed salt solutions is not as low as in the calcium chloride solution because of the coexistence of both magnesium chloride and potassium chloride.

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