J. Chem. Eng. Data **2005,** *50,* 1971−1982

Solubility of $CaSO_4$ Phases in Aqueous HCl + $CaCl_2$ Solutions from 283 K to 353 K

Zhibao Li and George P. Demopoulos*

Department of Mining, Metals and Materials Engineering, McGill University, M. H. Wong Building, 3610
University Street, Montreal, Quebec H3A 2B2, Canada

Solubilities of calcium sulfate dihydrate, hemihydrate, and anhydrite in concentrated HCl, $CaCl_2$, and their mixed aqueous solutions were measured by using the classic isothermal dissolution method at the temperature range from (283 to 353) K. The concentration investigated for HCl is up to 12 $mol \cdot dm^{-3}$ and for $CaCl_2$ is up to 3.5 $mol \cdot dm^{-3}$ at room temperature. The solubility of $CaSO_4$ phases in all cases investigated was found to increase with the temperature increment with the exception of anhydrite in $CaCl_2$ solutions. In pure HCl media, increasing the acid concentration in the range of (0.0 to 3) $mol \cdot dm^{-3}$ HCl causes the solubility of $CaSO_4 \cdot 2H_2O$ or $CaSO_4$ to increase reaching a maximum value and then decrease gradually with further increasing HCl concentration. In the concentrated range of (8 to 12) $mol \cdot dm^{-3}$ HCl, the solubility of $CaSO_4 \cdot {}^1/_2H_2O$ decreases with acid concentration. In HCl + $CaCl_2$ mixed media, the addition of $CaCl_2$ causes the solubility of all three phases to decrease due apparently to common ion effect.

Introduction

The solubility and phase equilibria of salts in electrolyte aqueous solutions play a significant role in the development, design, optimization, and operation of precipitation processes.[1−3] Precipitation is important in inorganic processing of materials but also in environmental protection, such as, wastewater treatment.

Solubility is essential to determine phase relationships in a system that includes unstable or metastable solid phases. In these cases, solubility determination becomes possible when equilibrium of unstable and metastable solids in solutions is reached before phase transformation occurs. One example is the solubility of calcium sulfate[4] that can be precipitated as dihydrate ($CaSO_4 \cdot 2H_2O$, DH) at low temperature and hemihydrate ($CaSO_4 \cdot {}^1/_2H_2O$, HH) or anhydrite ($CaSO_4$, AH) at elevated temperature in chloride media, such as the solutions containing HCl, $CaCl_2$, NaCl, $MgCl_2$, $AlCl_3$, or other chloride salts. These data are of considerable practical importance and theoretical significance in developing a new atmospheric process for the production of either dihydrate or the high value α-hemihydrate with simultaneous regeneration of hydrochloric acid from spent calcium chloride solutions by reaction with sulfuric acid.[5,6]

Solubility values of calcium sulfate in various aqueous chloride solutions are available in some compilations.[7,8] However, as we discussed in an earlier paper,[9] most of the previous studies have been limited in reporting only the solubility of dihydrate in single acid or salt solutions at ambient temperature. There has been limited information on the influence of mixed electrolytes and no information on $CaSO_4$ solubility in concentrated chloride electrolytes at elevated temperatures.

Commercial software such as OLI Systems' StreamAnalyzer (OLI),[10] based on the thermodynamic model developed by Bromley and Zemaitis,[11] can be employed to calculate the solubility of calcium sulfate dihydrate and anhydrite and even further to obtain the stability diagram. However, the accuracy of such software predictions strongly depends on the parameters stored in the databank, normally correlated from experimental data. Therefore, the applicability of the software is limited as their accuracy usually decreases with increasing component, concentration, and temperature.[9]

The above discussion indicates that there is still a need to systematically investigate the solubility of calcium sulfate and its hydrates in concentrated chloride electrolyte solutions, and this is done here for the system HCl + $CaCl_2$ + H_2O over the temperature range of (283 to 353) K. Additionally, the densities of the corresponding saturated solutions are reported. In a subsequent paper, a thermodynamic model for the system investigated in this work will be described.

Experimental Section

A number of approaches[12,13] in the literature have been proposed to determine the solubility of salts in solutions, which can be categorized as either dissolution method or precipitation method. The dissolution method is considered to be more reliable and feasible since it avoids the complication of formation of intermediate phases that is commonly encountered in precipitation. In this work, the dissolution method was employed.

Chemicals. All substances, reagent grade, were directly used without further purification. All solutions used in this study were prepared by dissolving the following chemicals in deionized water (conductivity < 0.1 $\mu S \cdot cm^{-1}$): hydrochloric acid (mass fraction: (36.5 to 38.0) %) and calcium chloride dihydrate with high purity both from Fisher. Four solid substances were employed as the saturating solid phase: gypsum from Alfa Aesar with 99 % purity, which contained trace anhydrite ($CaSO_4$); calcium sulfate hemihydrate (plaster of paris, also called β-hemihydrate) from Fisher; a commercial α-hemihydrate from Eastroc-BPB,[14] which contained trace quantities of unknown additives; and anhydrite from Alfa Aesar with 99 % purity.

---

* Corresponding author. E-mail: george.demopoulos@mcgill.ca. Fax: (514)398-4492.

10.1021/je050217e CCC: $30.25

Procedure. A typical experimental procedure can be described as follows. The 150 mL of electrolyte aqueous solution of known composition was introduced to Erlenmeyer flasks, 250 mL volume, 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 for about 0.5 h to establish the temperature equilibrium. The temperature was kept constant within ± 0.2 K. Then, excess solid (10 to 20 g of DH, HH, or AH) was quickly added to the solutions in flasks, which were tightly capped again by using rubber stoppers to avoid loss of HCl vapor. The standard equilibration time used was 5 h although other equilibration times were investigated as well as explained in the next section. 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 0.22 μm Whatman Puradisc 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 content of Ca or S was determined by inductively coupled plasma (ICP) analysis. The solubility (s) of calcium sulfate, expressed as g of $CaSO_4$/L, was obtained from the Ca and S analysis. The saturated filtrate was also used to determine the density of saturated solutions at the experimental temperature by using a 50 mL volumetric flask. The solid phase was filtered and washed each with water and acetone for 3 times. The washed solids were dried at 333 K for 24 h and then subjected to XRD analysis by a Philips PW1710 diffractometer to determine whether the solid phase had been altered by phase transformation. Girgin and Demopoulos[5] have previously demonstrated that drying of DH or HH materials at 60 °C for 24 h causes in itself no phase changes. Additionally, scanning electron microscopy (SEM) image techniques were used for examination of the solid phases.

Determination of Equilibration Time. The equilibration time in solubility measurements normally varies from several hours to several days depending on the dissolution rate[15] of the solid phase and the applied conditions. Power et al.[16,17] reported that the equilibrium of gypsum dissolution in pure water is reached within 1 min, but the rate of phase transformation of gypsum to anhydrite above their transition temperature was reported to be extremely low. The analysis of the solid phase consistently indicated the presence of the dihydrate at all contact times studied for up to 222 h. For the solubility determination of calcium sulfate dihydrate, Gupta[18] used 24 h to attain the equilibrium between gypsum and hydrochloric acid solutions of less than 1 mol·kg^{-1} while 5 h was used by Kruchenko and Beremzhanov.[19] Rock[20] reported that the slurries were agitated for at least 48 h during the measurement of gypsum and anhydrite solubilities in sodium chloride solution up to 323 K. The same interval was employed by Ostroff and Metler,[21] who investigated the dihydrate solubility in mixed NaCl + $MgCl_2$ solutions from (301 to 343) K.

For the determination of the solubility of calcium sulfate hemihydrate, in general much shorter equilibration times have been employed since hemihydrate is a metastable phase that experiences relatively fast transformation to gypsum at low temperature or anhydrite at elevated temperature. For example, β-hemihydrate, which is unstable in pure water, rapidly converts to gypsum at low temperature.[7] In 1 mol·kg^{-1} sodium chloride, the same phenomenon occurs. Actually, it is very difficult to determine the solubility of hemihydrate at low temperature[17] within such a short time. However, hemihydrate at high temperature and high electrolyte concentration becomes less unstable so that there is enough time to attain solubility equilibrium. Kruchenko and Beremzhanov[19] determined the solubility of α-hemihydrate in concentrated HCl solutions at room temperature by equilibrating the solids for 5 h. Sullivan et al.[22] found that the equilibrium between α-hemihydrate and phosphoric acid solutions at 353 K is established quite rapidly within about 3 min and there that is no decrease in solubility over time intervals up to 70 h, but 1 to 3 h was used in their investigation. Similar procedure and time (1 h) was used by Martynowicz et al.[23]

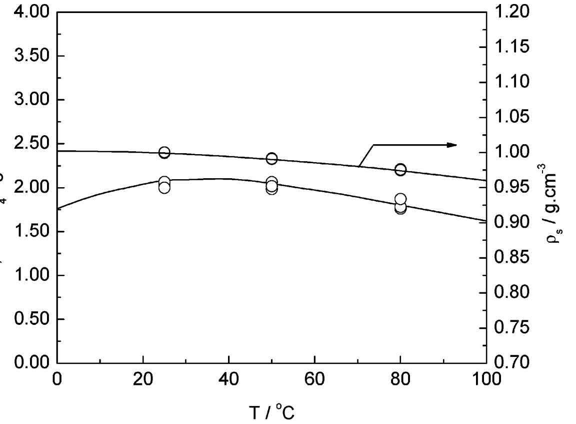

Figure 1. Solubility of calcium sulfate dihydrate in water and the density of the saturated solutions: −, Hulett and Allen;[7] ○, this work.

In the present study, the dissolution of calcium sulfate dihydrate in 1 mol·dm^{-3} HCl solution at room temperature was investigated as a function of time in order to select the appropriate equilibration time. The results of these kinetic experiments show that the solubility equilibrium between solid and liquid was established very rapidly within 0.5 h. However, in the experimental work, a longer time of 5 h for dihydrate and anhydrite and 1 h for hemihydrate, respectively, was chosen to ensure achievement of solubility equilibrium. Longer times were not employed because of the possibility of conversion of the starting phases to other calcium sulfate hydrates.

Reproducibility. The solubility of calcium sulfate dihydrate in pure water has been investigated by many authors.[7,8] Similar experiments were carried out by the authors to verify the reproducibility and accuracy of the adopted procedure in this work. The solubility comparison between experimental and literature values[7] is demonstrated in Figure 1. The uncertainty of the measured solubility values was within ± 0.031 g·dm^{-3}, and relative deviation is 1.62 %. Three replicate measurements of dihydrate solubility in 1 mol·dm^{-3} HCl at ambient temperature were also carried out. The average deviation was ± 0.111 g·dm^{-3} with relative deviation of 0.77 %. Equally good accuracy was associated with the determined densities of calcium sulfate dihydrate saturated solutions as it can be deduced from the data in Figure 1. The measured densities were uncertain to ± 0.001 g·cm^{-3}.

Results and Discussion

Solubility of $CaSO_4 \cdot 2H_2O$ in HCl Solutions. Calcium sulfate dihydrate solubilities in hydrochloric acid solution were measured at 283, 295, 313, 333, and 353 K. The

Table 1. Solubility of $CaSO_4$ (1) as Dihydrate in HCl (2) + H_2O (3) (Equilibration Time: 5 h)

solution parameters						solubility as $CaSO_4$ in different units					
M_2	m_2	ρ_s	M_2	m_2	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
$mol \cdot dm^{-3}$ [a]	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$ [b]	$mol \cdot dm^{-3}$ [a]	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$ [b]	$g \cdot dm^{-3}$	$mol \cdot dm^{-3}$	$mol \cdot kg^{-1}$	$g \cdot dm^{-3}$	$mol \cdot dm^{-3}$	$mol \cdot kg^{-1}$
$T = 283$ K											
0.000	0.0000	1.002	1.500	1.5431	1.037	1.928	0.0142	0.0142	13.062	0.0959	0.0990
0.200	0.2011	1.005	2.000	2.0779	1.047	5.182	0.0381	0.0383	13.964	0.1026	0.1067
0.400	0.4034	1.013	3.000	3.1828	1.064	7.218	0.0530	0.0535	13.926	0.1023	0.1087
0.600	0.6072	1.016	4.000	4.3396	1.079	8.994	0.0661	0.0670	12.330	0.0906	0.0983
0.800	0.8123	1.019	5.000	5.5524	1.094	10.492	0.0771	0.0786	10.726	0.0788	0.0874
1.000	1.0191	1.028				11.403	0.0838	0.0854			
$T = 295$ K											
0.000	0.0000	2.200	2.2919			2.080	0.0153	0.0153	18.901	0.1388	0.1458
0.200	0.2010	2.400	2.5104			6.755	0.0496	0.0500	19.189	0.1409	0.1487
0.400	0.4032	2.600	2.7311			9.676	0.0711	0.0719	19.135	0.1405	0.1489
0.600	0.6067	2.800	2.9535			11.854	0.0871	0.0885	19.091	0.1402	0.1492
0.800	0.8116	3.000	3.1782	1.066		13.520	0.0993	0.1013	18.975	0.1394	0.1489
1.000	1.0182	3.200	3.4048			14.573	0.1070	0.1096	18.833	0.1383	0.1484
1.200	1.2260	3.600	3.8651			16.350	0.1201	0.1235	17.752	0.1304	0.1411
1.400	1.4360	4.000	4.3337	1.078		16.574	0.1217	0.1257	16.958	0.1246	0.1360
1.600	1.6473	4.300	4.6908			17.491	0.1285	0.1333	16.496	0.1212	0.1332
1.800	1.8601	4.600	5.0538			18.391	0.1351	0.1407	15.636	0.1148	0.1271
2.000	2.0751	5.000	5.5456	1.092		18.751	0.1377	0.1441	14.770	0.1085	0.1211
$T = 313$ K											
0.000	0.0000		2.200	2.2881		2.097	0.0154	0.0155	23.986	0.1762	0.1856
0.200	0.2009		2.400	2.5062		7.811	0.0574	0.0581	24.675	0.1812	0.1917
0.400	0.4030		2.600	2.7263		11.514	0.0846	0.0860	24.923	0.1831	0.1945
0.600	0.6062		2.800	2.9484		14.425	0.1060	0.1083	25.124	0.1845	0.1969
0.800	0.8109		3.000	3.1725		16.665	0.1224	0.1256	25.036	0.1839	0.1971
1.000	1.0170		3.600	3.8580		18.687	0.1373	0.1415	25.087	0.1843	0.1983
1.200	1.2245		4.000	4.3258		20.664	0.1518	0.1571	23.932	0.1758	0.1917
1.400	1.4338		4.300	4.6824		21.846	0.1605	0.1668	23.059	0.1694	0.1864
1.600	1.6449		4.600	5.0448		22.580	0.1658	0.1732	22.454	0.1649	0.1827
1.800	1.8574		5.000	5.5362		23.446	0.1722	0.1806	21.496	0.1579	0.1761
2.000	2.0720								20.283	0.1490	0.1677
$T = 333$ K											
0.000	0.0000		2.800	2.9411		1.971	0.0145	0.0147	33.324	0.2448	0.2653
0.200	0.2009		3.000	3.1647		9.360	0.0688	0.0703	33.229	0.2441	0.2658
0.600	0.6055		3.200	3.3897		18.541	0.1362	0.1405	33.671	0.2473	0.2705
1.000	1.0154		3.600	3.8477		24.217	0.1779	0.1852	32.665	0.2399	0.2648
1.400	1.4312		4.000	4.3142		28.096	0.2064	0.2168	31.779	0.2334	0.2600
2.000	2.0673		4.300	4.6693		31.653	0.2325	0.2475	31.503	0.2314	0.2595
2.400	2.5004		4.600	5.0310		32.692	0.2401	0.2580	30.335	0.2228	0.2516
2.600	2.7199		5.000	5.5210		33.012	0.2425	0.2616	29.126	0.2139	0.2439
$T = 353$ K											
0.000	0.0000		2.000	2.0618	1.041	1.801	0.0132	0.0136	40.607	0.2983	0.3206
0.200	0.2008		2.200	2.2761		11.037	0.0811	0.0838	42.190	0.3099	0.3359
0.400	0.4023		2.600	2.7112		16.898	0.1241	0.1290	43.583	0.3201	0.3502
0.800	0.8085		2.800	2.9312		27.019	0.1985	0.2083	44.364	0.3258	0.3582
1.000	1.0134	1.016	3.000[c]	3.1541	1.054	30.756	0.2259	0.2377	44.126	0.3241	0.3578
1.200	1.2204		4.000[c]	4.3008	1.071	32.302	0.2373	0.2513	41.898	0.3077	0.3456
1.600	1.6378		5.000[c]	5.5060	1.084	37.129	0.2727	0.2915	37.788	0.2775	0.3184

[a] Initial concentration of solutions prepared at room temperature without calcium sulfate. [b] Experimental density of saturated solutions. [c] Equilibration time is 1 h.

investigated concentration of acid is from (0.0 to 5) $mol \cdot dm^{-3}$ at room temperature. The results of experimentally determined solubilities are summarized in Table 1 and graphically in Figure 2. In Table 1, the concentration of hydrochloric acid and calcium sulfate is expressed both in molarity ($M/mol \cdot dm^{-3}$) and molality ($m/mol \cdot kg^{-1}$) for convenient practical and thermodynamic reference. However, the concentration of HCl in molarity marked with M_2 is the initial concentration of the solution prepared at ambient temperature before introducing calcium sulfate dihydrate. The other quantities of acid and salts in different units express the solubility at the conditions of the system. In addition, the measured densities (required to convert solubility units from molarity to molality) for several saturated solution compositions are given in Table 1. OLI's StreamAnalyzer1.1 was used to convert the solubility units from molarity to molality when the experimental density of saturated solution was not available. Justification for the use of OLI in this context is given later in this paper (refer to Figure 7).

Figure 2 demonstrates that at constant temperature the solubility of calcium sulfate dihydrate in aqueous HCl solutions possesses two features. The solubility of dihydrate increases with increasing HCl concentration in the range of (0.0 to 3.0) $mol \cdot dm^{-3}$. After passing a maximum, the solubility declines smoothly in the range of higher concentration of acid. In reference to temperature, the solubility increases systematically as the temperature increases from (283 to 353) K. Some of the data generated in this work is compared to the data available in the literature[18,19] in Figure 3. There is good agreement of present data and earlier measurements.

The XRD analysis of equilibrated solid phases showed the calcium sulfate dihydrate to be stable in HCl solutions

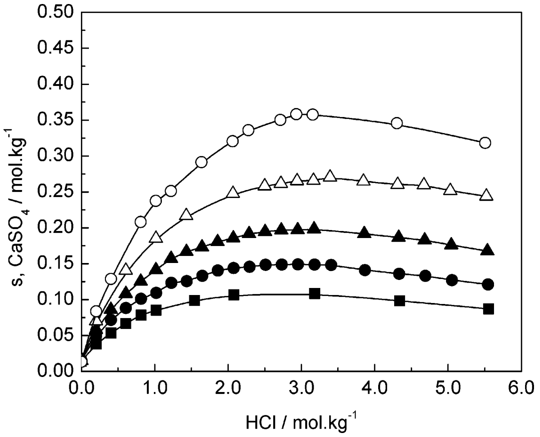

Figure 2. Solubility of calcium sulfate dihydrate in hydrochloric acid solutions: ■, 283 K; ●, 295 K; ▲, 313 K; △, 333 K; ○, 353 K.

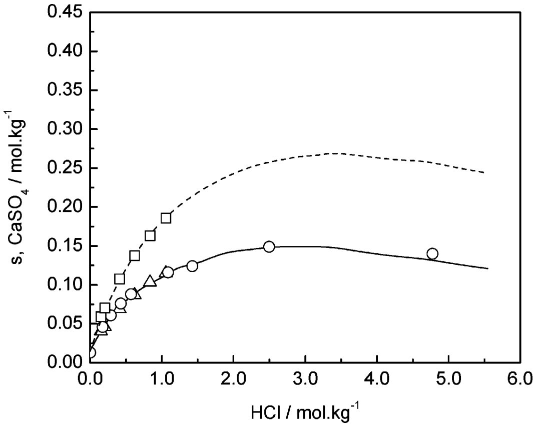

Figure 3. Comparison of the solubility of calcium sulfate as dihydrate in HCl solutions from different sources (lines, this work): △, Gupta[18] at 293 K; ○, Kruchenko et al.[19] at 298 K; □, Gupta[18] at 333 K.

with the concentration of (0.0 to 5.0) mol·dm^{-3} at temperatures below 333 K within 5 h. However, at elevated temperature, such as at 353 K, and higher HCl concentration (more than 1 mol·dm^{-3}), the transformation from dihydrate to anhydrite is observed. For example, dihydrate in 5 mol·dm^{-3} HCl solutions at 353 K was completely converted to anhydrite within the time of 5 h while in 1 mol·dm^{-3} HCl solution at 353 K no anhydrite was detected in equilibrated solids. The results of solids characterization by XRD are tabulated in Table 2. The equilibrated solids were examined by SEM. Typical SEM images are presented in Figure 4. It can be clearly seen that original crystals underwent ripening (compare Figure 4, panels a and b) with the small "dust" particles on the surface of the original gypsum crystals to have dissolved and crystallographic characteristics to have been "sharpened". This is the case when the equilibrated solids are dihydrate (1 mol·dm^{-3} HCl, 353 K, and 5 h). However, the gypsum crystals were transformed to needle-shape anhydrite when the HCl concentration was 4 mol·dm^{-3} (see Figure 4c). The solubility data presented in Table 1 and Figure 2 though is for DH in equilibration only (i.e., the data associated with conversion of DH to AH is excluded).

Solubility of $CaSO_4 \cdot 2H_2O$ in $CaCl_2$ Solutions. Solubilities of calcium sulfate dihydrate (and saturated solution densities) at (295, 313, 333, and 353) K in calcium chloride solutions with concentrations up to 2 mol·dm^{-3} were determined by using the same procedure. The obtained experimental results are shown in Table 3 and Figure 5.

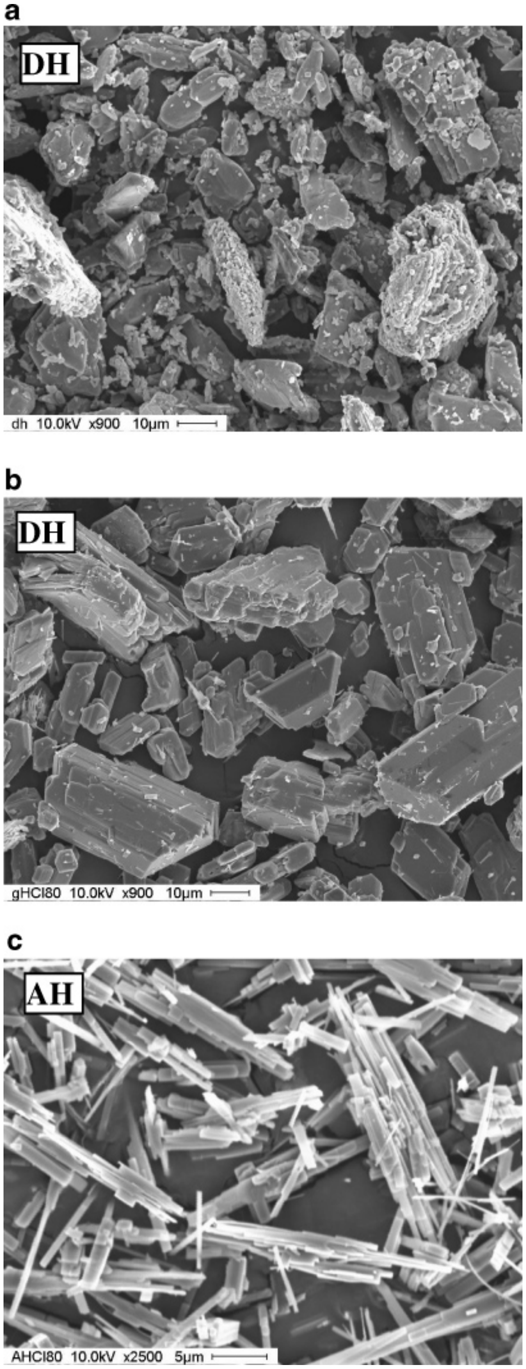

Figure 4. SEM images of original gypsum and equilibrated solids: (a) original gypsum from Alfa; (b) solids in 1 mol·dm^{-3} HCl at 353 K after 5 h; (c) solids in 4 mol·dm^{-3} HCl at 353 K after 5 h.

Figure 5 illustrates that the solubility of calcium sulfate dihydrate decreases with the concentration of $CaCl_2$. Initially, the solubility drops sharply and then continues to fall almost linearly with increasing concentration of $CaCl_2$. Common ion effect is responsible for this behavior. As also seen in Figure 5, the solubility slightly increases with increasing temperature. The XRD study in Table 2 shows that a trace of calcium sulfate hemihydrate was detected at 353 K, but otherwise the equilibrated solid-phase remains gypsum.

Solubility of $CaSO_4 \cdot 2H_2O$ in Mixed HCl + $CaCl_2$ Solutions. The same approach was used to obtain the solubility of calcium sulfate dihydrate in HCl (1, 3, and 5 mol·dm^{-3}) + $CaCl_2$ mixed electrolyte solutions at (295, 313,

Table 2. XRD Characterization of the Equilibrated Solids (Starting Material Is Dihydrate)

T	M	equilibration t	equilibrated
K	$mol \cdot dm^{-3}$	h	solid phase(s)[a]
333	4 (HCl)	1	DH
		2	DH
		3	DH + trace AH
		4−5	DH + minor AH
353	1 (HCl)	1−5	DH
353	3 (HCl)	5	DH + minor AH
353	4 (HCl)	1	DH + minor AH
		2	DH + major AH
		3−5	AH
353	2 ($CaCl_2$)	5	DH + trace HH
353	1 (HCl) + 2 ($CaCl_2$)	5	DH + minor AH
353	3 (HCl) + <2 ($CaCl_2$)	5	DH + AH
353	3 (HCl) + 2 ($CaCl_2$)	5	AH + HH
333	5 (HCl) + 0.5 ($CaCl_2$)	5	DH
333	5 (HCl) + 2 ($CaCl_2$)	5	AH + HH

[a] DH, $CaSO_4 \cdot 2H_2O$; HH, $CaSO_4 \cdot {}^1/_2H_2O$; AH, $CaSO_4$.

333, or 353) K. The results determined in this study are given in Tables 4 to 6 and graphically in Figure 6 for 1 $mol \cdot dm^{-3}$ HCl as an example.

The general behavior observed with all three acidic levels investigated is consistent showing an increase in solubility of $CaSO_4 \cdot 2H_2O$ with increasing temperature. The presence of $CaCl_2$ in the solutions makes the solubility fall sharply at the lower concentration of calcium chloride and then drop smoothly with increasing concentration. Once again the depressing effect of $CaCl_2$ on $CaSO_4$ solubility is attributed to the common ion effect. XRD analysis (see results in Table 2) showed the equilibrated solids in 1 $mol \cdot dm^{-3}$ HCl + $CaCl_2$ solutions at all temperatures after 5 h to be predominantly dihydrate, but in higher HCl concentration (3 $mol \cdot dm^{-3}$) solutions with $CaCl_2$ present

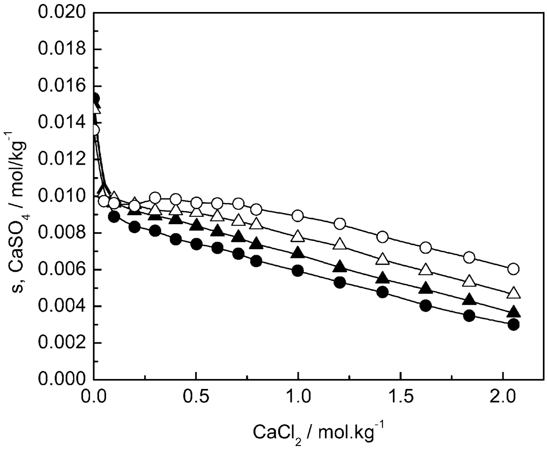

Figure 5. Solubility of calcium sulfate dihydrate in aqueous calcium chloride solutions: ●, 295 K; ▲, 313 K; △, 333 K; ○, 353 K.

Table 3. Solubility of $CaSO_4$ (1) as Dihydrate in $CaCl_2$ (2) + H_2O (3) (Equilibration Time: 5 h)

solution parameters						solubility as $CaSO_4$ in different units					
M_2	m_2	ρ_s	M_2	m_2	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
$mol \cdot dm^{-3}$ [a]	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$ [b]	$mol \cdot dm^{-3}$ [a]	$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$ [b]	$g \cdot dm^{-3}$	$mol \cdot dm^{-3}$	$mol \cdot kg^{-1}$	$g \cdot dm^{-3}$	$mol \cdot dm^{-3}$	$mol \cdot kg^{-1}$
$T = 295$ K											
0.049	0.0498	1.002	0.778	0.7943	1.066	1.353	0.0099	0.0099	0.863	0.0063	0.0064
0.099	0.0997	1.007	0.972	0.9980	1.083	1.204	0.0088	0.0088	0.788	0.0057	0.0059
0.198	0.1998	1.016	1.167	1.2038	1.099	1.127	0.0082	0.0083	0.700	0.0051	0.0053
0.297	0.3004	1.024	1.361	1.4121	1.115	1.096	0.0080	0.0081	0.628	0.0046	0.0047
0.396	0.4013	1.033	1.556	1.6231	1.131	1.031	0.0075	0.0076	0.527	0.0038	0.0040
0.496	0.5029	1.042	1.750	1.8367	1.147	0.992	0.0072	0.0073	0.452	0.0033	0.0034
0.595	0.6048	1.050	1.945	2.0532	1.163	0.963	0.0070	0.0071	0.388	0.0028	0.0030
0.694	0.7073	1.059				0.918	0.0067	0.0068			
$T = 313$ K											
0.049	0.0498	0.997	0.778	0.7943	1.061	1.399	0.0102	0.0103	0.977	0.0071	0.0073
0.099	0.0997	1.002	0.972	0.9979	1.077	1.296	0.0095	0.0096	0.905	0.0066	0.0068
0.198	0.1998	1.011	1.167	1.2038	1.093	1.235	0.0090	0.0091	0.801	0.0058	0.0061
0.297	0.3004	1.019	1.361	1.4121	1.109	1.197	0.0088	0.0089	0.715	0.0052	0.0054
0.396	0.4013	1.028	1.556	1.6230	1.125	1.167	0.0085	0.0087	0.640	0.0047	0.0049
0.496	0.5029	1.037	1.750	1.8366	1.141	1.118	0.0082	0.0083	0.554	0.0040	0.0043
0.595	0.6048	1.045	1.945	2.0532	1.157	1.073	0.0078	0.0080	0.465	0.0034	0.0036
0.694	0.7073	1.054				1.030	0.0075	0.0077			
$T = 333$ K											
0.049	0.0498	0.989	0.778	0.7943	1.052	1.360	0.0099	0.0101	1.107	0.0081	0.0084
0.099	0.0997	0.993	0.972	0.9979	1.069	1.317	0.0096	0.0098	1.014	0.0074	0.0077
0.198	0.1998	1.002	1.167	1.2037	1.086	1.271	0.0093	0.0095	0.953	0.0070	0.0073
0.297	0.3004	1.011	1.361	1.4120	1.102	1.223	0.0089	0.0092	0.843	0.0061	0.0065
0.396	0.4013	1.019	1.556	1.6230	1.118	1.219	0.0089	0.0091	0.765	0.0056	0.0059
0.496	0.5029	1.028	1.750	1.8365	1.134	1.207	0.0088	0.0091	0.679	0.0049	0.0053
0.595	0.6047	1.036	1.945	2.0531	1.150	1.171	0.0086	0.0088	0.594	0.0043	0.0046
0.694	0.7073	1.045				1.138	0.0083	0.0086			
$T = 353$ K											
0.049	0.0498	0.977	0.778	0.7943	1.041	1.286	0.0094	0.0097	1.208	0.0088	0.0092
0.099	0.0997	0.982	0.972	0.9978	1.058	1.270	0.0093	0.0096	1.156	0.0084	0.0089
0.198	0.1998	0.991	1.167	1.2037	1.074	1.247	0.0091	0.0094	1.096	0.0080	0.0085
0.297	0.3004	0.999	1.361	1.4120	1.091	1.305	0.0095	0.0099	0.998	0.0073	0.0077
0.396	0.4013	1.008	1.556	1.6229	1.107	1.291	0.0094	0.0098	0.918	0.0067	0.0072
0.496	0.5029	1.017	1.750	1.8365	1.123	1.262	0.0092	0.0096	0.845	0.0062	0.0066
0.595	0.6047	1.025	1.945	2.0530	1.139	1.256	0.0092	0.0096	0.762	0.0056	0.0060
0.694	0.7073	1.034				1.250	0.0091	0.0095			

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

Table 4. Solubility of $CaSO_4$ (1) as Dihydrate in 1 mol·dm^{-3} HCl (2) + $CaCl_2$ (3) + H_2O (4) (Equilibration Time: 5 h)

solution parameters								solubility as $CaSO_4$ in different units					
M_3	m_2	m_3	ρ_s	M_3	m_2	m_3	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
T = 295 K													
0.010	1.0186	0.0102	1.027	0.500	1.0338	0.5169	1.061	13.955	0.1025	0.1050	3.629	0.0267	0.0276
0.020	1.0190	0.0204	1.027	0.750	1.0411	0.7808	1.081	13.377	0.0983	0.1006	2.516	0.0185	0.0192
0.050	1.0201	0.0510	1.029	1.000	1.0487	1.0487	1.102	12.100	0.0889	0.0911	1.821	0.0134	0.0140
0.100	1.0218	0.1022	1.032	1.500	1.0648	1.5971	1.142	10.186	0.0748	0.0767	1.054	0.0077	0.0082
0.250	1.0266	0.2566	1.041	2.000	1.0825	2.1651	1.182	6.335	0.0465	0.0479	0.589	0.0043	0.0046
T = 313 K													
0.010	1.0176	0.0102	1.024	0.500	1.0333	0.5167	1.056	17.678	0.1298	0.1338	5.489	0.0403	0.0419
0.020	1.0180	0.0204	1.025	0.750	1.0407	0.7805	1.076	17.066	0.1253	0.1292	3.877	0.0285	0.0298
0.050	1.0191	0.0510	1.026	1.000	1.0484	1.0484	1.096	15.568	0.1143	0.1179	2.802	0.0206	0.0217
0.100	1.0206	0.1021	1.029	1.500	1.0646	1.5969	1.136	14.177	0.1041	0.1075	1.680	0.0123	0.0132
0.250	1.0257	0.2564	1.038	2.000	1.0824	2.1648	1.175	9.411	0.0691	0.0715	0.994	0.0073	0.0079
T = 333 K													
0.010	1.0158	0.0102	1.020	0.500	1.0323	0.5161	1.050	23.648	0.1737	0.1808	9.069	0.0666	0.0700
0.020	1.0162	0.0203	1.021	0.750	1.0400	0.7800	1.070	23.197	0.1704	0.1774	6.398	0.0470	0.0496
0.050	1.0174	0.0509	1.022	1.000	1.0478	1.0478	1.089	21.439	0.1575	0.1641	4.822	0.0354	0.0376
0.100	1.0191	0.1019	1.024	1.500	1.0642	1.5963	1.130	19.329	0.1420	0.1480	2.938	0.0216	0.0232
0.250	1.0243	0.2561	1.033	2.000	1.0822	2.1643	1.165	14.160	0.1040	0.1087	1.759	0.0129	0.0142
T = 353 K													
0.010	1.0139	0.0101	1.014	0.500	1.0309	0.5154	1.042	30.302	0.2226	0.2347	13.658	0.1003	0.1067
0.020	1.0146	0.0203	1.014	0.750	1.0388	0.7791	1.061	28.566	0.2098	0.2212	10.169	0.0747	0.0798
0.050	1.0157	0.0508	1.015	1.000	1.0469	1.0469	1.080	27.366	0.2010	0.2121	7.807	0.0573	0.0617
0.100	1.0173	0.1017	1.018	1.500	1.0635	1.5953	1.120	25.396	0.1865	0.1970	4.978	0.0366	0.0398
0.250	1.0226	0.2557	1.026	2.000	1.0817	2.1634	1.159	19.776	0.1453	0.1537	3.155	0.0232	0.0256

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

Table 5. Solubility of $CaSO_4$ (1) as Dihydrate in 3 mol·dm^{-3} HCl (2) + $CaCl_2$ (3) + H_2O (4) (Equilibration Time: 5 h)

solution parameters								solubility as $CaSO_4$ in different units					
M_3	m_2	m_3	ρ_s	M_3	m_2	m_3	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
T = 295 K													
0.010	3.1807	0.0106	1.062	0.500	3.2389	0.5398	1.092	17.576	0.1291	0.1380	3.971	0.0292	0.0315
0.020	3.1822	0.0212	1.062	0.750	3.2655	0.8164	1.110	16.780	0.1233	0.1317	2.467	0.0181	0.0197
0.050	3.1870	0.0531	1.063	1.000	3.2929	1.0976	1.129	14.517	0.1066	0.1140	1.699	0.0125	0.0137
0.100	3.1935	0.1064	1.067	1.500	3.3514	1.6757	1.170	12.458	0.0915	0.0979	0.951	0.0070	0.0078
0.250	3.2112	0.2676	1.074	2.000	3.4155	2.2770	1.208	7.884	0.0579	0.0622	0.538	0.0040	0.0045
T = 313 K													
0.010	3.1757	0.0106	1.060	0.500	3.2362	0.5394	1.087	22.958	0.1686	0.1814	6.736	0.0495	0.0539
0.020	3.1768	0.0212	1.061	0.750	3.2639	0.8160	1.107	22.520	0.1654	0.1780	4.116	0.0302	0.0331
0.050	3.1812	0.0530	1.061	1.000	3.2916	1.0972	1.124	20.805	0.1528	0.1647	3.041	0.0223	0.0247
0.100	3.1879	0.1063	1.064	1.500	3.3507	1.6753	1.162	18.423	0.1353	0.1459	1.678	0.0123	0.0139
0.250	3.2073	0.2673	1.071	2.000	3.4151	2.2767	1.200	11.968	0.0879	0.0951	0.949	0.0070	0.0080
T = 333 K													
0.010	3.1676	0.0106	1.059	0.500	3.2317	0.5386	1.082	31.622	0.2323	0.2523	11.512	0.0846	0.0929
0.020	3.1684	0.0211	1.060	0.750	3.2603	0.8151	1.101	31.460	0.2311	0.2511	7.797	0.0573	0.0633
0.050	3.1735	0.0529	1.058	1.000	3.2889	1.0963	1.116	28.870	0.2120	0.2310	5.733	0.0421	0.0470
0.100	3.1808	0.1060	1.061	1.500	3.3492	1.6746	1.154	25.997	0.1909	0.2079	3.143	0.0231	0.0262
0.250	3.2004	0.2667	1.069	2.000	3.4140	2.2760	1.192	19.334	0.1420	0.1550	2.032	0.0149	0.0172

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

(at 353 K) the equilibrated solids were a mixture of $CaSO_4$ dihydrate and hemihydrate after 5 h of equilibration. When the acid concentration was 5 mol·dm^{-3} (in mixed HCl + 2 mol·dm^{-3} $CaCl_2$ solution), the dihydrate was transformed completely to anhydrite and hemihydrate after 5 h at 333 K. Once more the solubility data listed in Tables 4 to 6 refer to DH equilibrated solids (i.e., tests associated with the complete conversion of DH to AH and/or HH within the prescribed 5 h period were repeated at shorter equilibration time to ensure the integrity of DH).

Density Comparison with OLI Software. The density of the saturated solutions is required to allow for unit conversion of solubility data from molarity to molality scale. For the $CaSO_4·2H_2O$ + HCl + H_2O system (refer to Table 1), saturated solution densities were estimated using the StreamAnalyzer program of OLI only when experimental densities were not measured. This was done only after OLI proved reliable in estimating density data in this work. However, for the other systems all densities reported in Tables 3 to 8 and Tables 10 to 13 are measured values. A measure of the accuracy of the OLI estimated density data can be obtained by referring to Figure 7 where a comparison is made with our experimentally determined density data. As it can be seen there is very good agreement between OLI predictions and experimental measurements for both single and mixed electrolytes (average relative deviation < 0.5 %).

Solubility of $CaSO_4·{}^1/_2H_2O$. The measured results of the hemihydrate solubility in pure HCl solutions are given in Table 7 and presented in Figure 8. The solubility of hemihydrate decreases with increasing acid concentration (in the investigated range of 8.5 to 16 mol·kg^{-1}) and

Table 6. Solubility of $CaSO_4$ (1) as Dihydrate in 5 mol·dm^{-3} HCl (2) + $CaCl_2$ (3) + H_2O (4) (Equilibration Time: 5 h)

solution parameters								solubility as $CaSO_4$ in different units					
M_3	m_2	m_3	ρ_s	M_3	m_2	m_3	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
						$T = 295$ K							
0.010	5.5513	0.0111	1.091	0.500	5.6625	0.5662	1.120	13.138	0.0965	0.1077	2.289	0.0168	0.0191
0.020	5.5541	0.0222	1.092	0.750	5.7148	0.8572	1.139	12.607	0.0926	0.1033	1.411	0.0104	0.0118
0.050	5.5621	0.0556	1.091	1.000	5.7693	1.1539	1.158	10.841	0.0796	0.0890	0.971	0.0071	0.0082
0.100	5.5746	0.1115	1.092	1.500	5.8869	1.7661	1.194	8.739	0.0642	0.0719	0.557	0.0041	0.0048
0.250	5.6095	0.2805	1.101	2.000	6.0169	2.4068	1.233	4.893	0.0359	0.0405	0.340	0.0025	0.0030
						$T = 313$ K							
0.010	5.5447	0.0111	1.087	0.500	5.6590	0.5659	1.114	17.040	0.1252	0.1407	4.321	0.0317	0.0362
0.020	5.5476	0.0222	1.087	0.750	5.7126	0.8569	1.132	16.453	0.1208	0.1359	2.622	0.0193	0.0222
0.050	5.5549	0.0555	1.089	1.000	5.7678	1.1536	1.151	15.164	0.1114	0.1253	1.800	0.0132	0.0153
0.100	5.5678	0.1114	1.089	1.500	5.8859	1.7658	1.188	12.751	0.0937	0.1057	1.064	0.0078	0.0092
0.250	5.6046	0.2802	1.097	2.000	6.0163	2.4065	1.225	7.744	0.0569	0.0645	0.678	0.0050	0.0060
						$T = 333$ K							
0.010	5.5298	0.0111	1.084	0.500	5.6515	0.5652	1.106	25.751	0.1891	0.2149	8.554	0.0628	0.0725
0.020	5.5319	0.0221	1.085	0.750	5.7071	0.8561	1.124	25.626	0.1882	0.2139	5.746	0.0422	0.0491
0.050	5.5409	0.0554	1.086	1.000	5.7638	1.1528	1.137	23.316	0.1713	0.1946	4.007	0.0294	0.0347
0.100	5.5533	0.1111	1.086	1.500	5.8834	1.7650	1.177	21.223	0.1559	0.1778	2.398	0.0176	0.0211
0.250	5.5919	0.2796	1.094	2.000	6.0153	2.4061	1.212	15.127	0.1111	0.1271	1.150	0.0084	0.0103

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

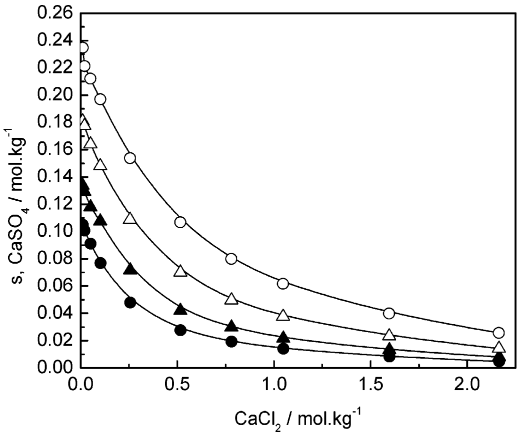

Figure 6. Solubility of calcium sulfate dihydrate in HCl (1 mol·dm^{-3}) + $CaCl_2$ solutions: ●, 295 K; ▲, 313 K; △, 333 K; ○, 353 K.

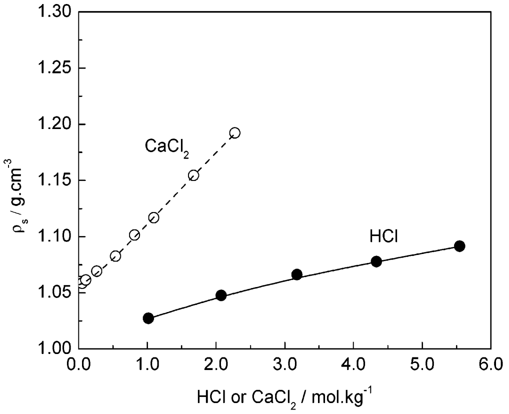

Figure 7. Density of $CaSO_4$-saturated HCl + $CaCl_2$ mixed electrolyte solutions (lines, OLI): ●, this work in HCl solutions at 295 K; ○, this work in HCl (3 mol·dm^{-3}) + $CaCl_2$.

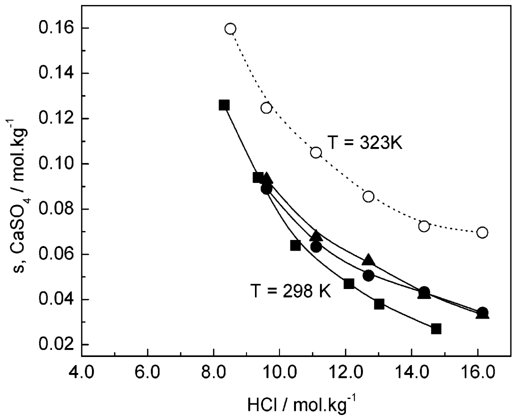

Figure 8. Comparison of the solubility of $CaSO_4\cdot{}^1/_2H_2O$ modifications in concentrated HCl solutions: ●, α-HH at 298 K; ▲, β-HH at 298 K; ○, β-HH at 323 K; ■, Kruchenko et al.[19] at 298 K (α-HH).

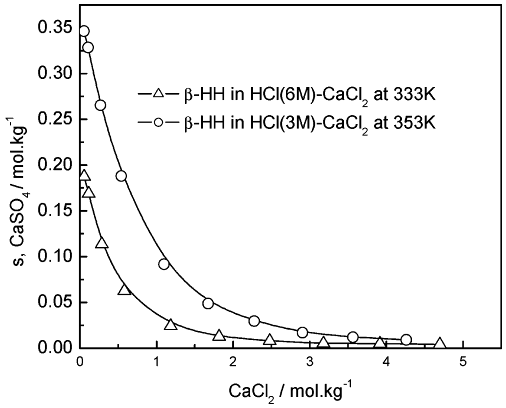

Figure 9. Solubility of β-hemihydrate in HCl + $CaCl_2$ mixed electrolyte solutions:, 6 mol·dm^{-3} HCl + $CaCl_2$ at 333 K; ○, 3 mol·dm^{-3} HCl + $CaCl_2$ at 353 K.

increases with increasing temperature. The results in Figure 8 further show that there is no significant difference in solubility between α-hemihydrate and β-hemihydrate while our α-hemihydrate solubility is slightly higher than that reported in the literature.[19] β-Hemihydrate is known (at least in H_2SO_4 solutions[29]) to be more soluble than α-hemihydrate. It is possible, therefore, in the context of the present work that the proximity in solubility between α-hemihydrate and β-hemihydrate is due to the origin of the α-hemihydrate used here, which was of industrial commercial grade. Impurities in the α-hemihydrate commercial product may be responsible for its somewhat elevated solubility. Table 8 and Figure 9 present the solubility of β-hemihydrate in HCl + $CaCl_2$ mixed solutions

Table 7. Solubility of $CaSO_4$ (1) as Hemihydrate in HCl (2) + H_2O (3) (Equilibration Time: 1 h)

solution parameters						solubility as $CaSO_4$ in different units					
M_2	m_2	ρ_s	M_2	m_2	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	g·cm^{-3} [b]	mol·dm^{-3} [a]	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
T = 298 K, Solid: α-Hemihydrate											
8.000	9.6032	1.132	11.000	14.3767	1.168	10.066	0.0739	0.0890	4.496	0.0330	0.0433
9.000	11.1046	1.140	12.000	16.1449	1.180	6.970	0.0512	0.0634	3.449	0.0253	0.0342
10.000	12.6938	1.161				5.446	0.0400	0.0506			
T = 298 K, Solid: β-Hemihydrate											
8.000	9.6029	1.126	11.000	14.3768	1.167	10.474	0.0769	0.0931	4.385	0.0322	0.0422
9.000	11.1042	1.141	12.000	16.1450	1.182	7.430	0.0546	0.0676	3.360	0.0247	0.0333
10.000	12.6933	1.156				6.099	0.0448	0.0570			
T = 323 K, Solid: β-Hemihydrate											
7.000	8.5098	1.113	10.000	12.6908	1.146	18.174	0.1335	0.1597	9.066	0.0666	0.0856
8.000	9.6008	1.118	11.000	14.3739	1.155	13.879	0.1019	0.1247	7.427	0.0546	0.0724
9.000	11.1013	1.131	12.000	16.1412	1.165	11.404	0.0838	0.1050	6.909	0.0507	0.0696

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

Table 8. Solubility of $CaSO_4$ (1) as Hemihydrate in HCl (2) + $CaCl_2$ (3) + H_2O (4) (Equilibration Time: 1 h)

solution parameters								solubility as $CaSO_4$ in different units					
M_3	m_2	m_3	ρ_s	M_3	m_2	m_3	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
T = 333 K, HCl = 6 M,[a] Solid: β-Hemihydrate													
0.050	6.8483	0.0571	1.099	1.500	7.2666	1.8167	1.193	21.833	0.1607	0.1874	1.392	0.0102	0.0126
0.100	6.8608	0.1143	1.105	2.000	7.4390	2.4797	1.231	19.700	0.1450	0.1687	0.861	0.0063	0.0079
0.250	6.9018	0.2876	1.110	2.500	7.6293	3.1789	1.264	13.191	0.0971	0.1136	0.546	0.0040	0.0051
0.500	6.9688	0.5807	1.126	3.000	7.8356	3.9178	1.292	7.196	0.0530	0.0624	0.494	0.0036	0.0048
1.000	7.1108	1.1851	1.157	3.500	8.0534	4.6978	1.334	2.719	0.0200	0.0241	0.407	0.0030	0.0040
T = 353 K, HCl = 3 M,[a] Solid: β-Hemihydrate													
0.050	3.1902	0.0532	1.064	1.500	3.3509	1.6754	1.153	42.85	0.3154	0.3463	5.82	0.0428	0.0488
0.100	3.1953	0.1065	1.065	2.000	3.4152	2.2768	1.183	40.54	0.2984	0.3286	3.44	0.0254	0.0295
0.250	3.2107	0.2676	1.074	2.500	3.4866	2.9055	1.221	32.71	0.2408	0.2651	1.96	0.0144	0.0171
0.500	3.2370	0.5395	1.082	3.000	3.5651	3.5651	1.253	22.97	0.1691	0.1880	1.34	0.0099	0.0120
1.000	3.2918	1.0973	1.117	3.500	3.6524	4.2612	1.295	11.10	0.0817	0.0917	1.01	0.0074	0.0092

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

Table 9. XRD Characterization of the Equilibrated Solids (Starting Material is Hemihydrate)

T	M	equilibration t	equilibrated solid phase(s)[a]
K	mol·dm^{-3}	h	
298	8−12 (HCl)	1	HH
323	7−12 (HCl)	1	HH
353	1−7 (HCl)	1	AH
333	0.0−3 ($CaCl_2$)	1	HH + DH
	3.5 ($CaCl_2$)	1	HH
353	0.0−2 ($CaCl_2$)	1	HH + DH
	2.5−3.5 ($CaCl_2$)	1	HH
333	3 (HCl) + 0.0−2 ($CaCl_2$)	1	HH + DH
	3 (HCl) + 2−3.5 ($CaCl_2$)	1	HH
353	3 (HCl) + 0.05−0.1 ($CaCl_2$)	1	HH + trace DH
	3 (HCl) + 0.25−3.5 ($CaCl_2$)	1	HH
333	6 (HCl) + 0.0−3.5 ($CaCl_2$)	1	HH

[a] DH, $CaSO_4 \cdot 2H_2O$; HH, $CaSO_4 \cdot {}^1/_2H_2O$; AH, $CaSO_4$.

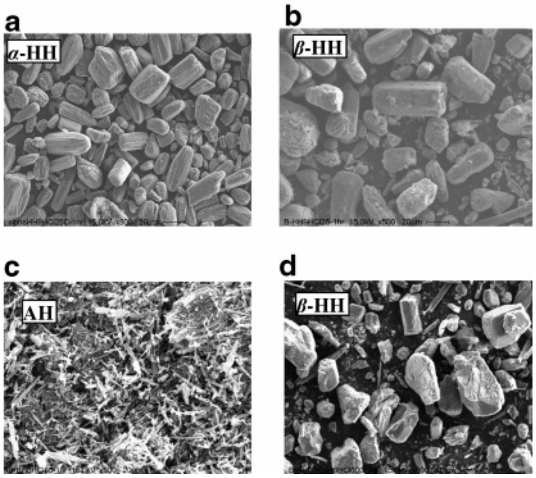

Figure 10. SEM images of equilibrated solids (the starting material is α- or β-hemihydrate): (a) solids (α-hemihydrate) in 9 mol·dm^{-3} HCl at 298 K after 1 h; (b) solids (β-hemihydrate) in 9 mol·dm^{-3} HCl at 298 K after 1 h; (c) solids in 6 mol·dm^{-3} HCl at 353 K after 1 h; (d) solids in 0.1 mol·dm^{-3} $CaCl_2$−6 mol·dm^{-3} HCl solution at 333 K after 1 h.

at 333 K and 353 K. Once again the apparent common ion effect causes the solubility to decline sharply with increasing concentration of $CaCl_2$. The XRD analysis of the equilibrated solids for this system is summarized in Table 9. It can be observed that the presence of $CaCl_2$ in HCl suppressed the transformation of hemihydrate to anhydrite, hence making possible the determination of its solubility by this isothermal dissolution method. The solubility data reported in Tables 7 and 8 refer to HH as equilibrated phase only. The SEM micrographs of Figure 10, panels a and b, indicate that the α- and β-calcium sulfate hemihydrate remained unaltered in concentrated 9 mol·dm^{-3} HCl solutions at 298 K (for 1 h) while hemihydrate in 6 mol·dm^{-3} HCl at 353 K was converted to anhydrite (within the 1 h equilibration time once more). As it can be deduced from Figure 10c, however, when $CaCl_2$ is present in 6 mol·dm^{-3} HCl solution that hemihydrate remains unaltered (within the 1 h period) (compare Figure 10, panels a and b). The stability effect of $CaCl_2$ on HH is explored elsewhere for the elaboration of a method to produce the high value material α-hemihydrate.[5]

Table 10. Solubility of $CaSO_4$ (1) as Anhydrite in HCl (2) + H_2O (3) (Equilibration Time: 5 h)

solution parameters						solubility as $CaSO_4$ in different units					
M_2	m_2	ρ_s	M_2	m_2	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
$mol \cdot dm^{-3\,a}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3\,b}$	$mol \cdot dm^{-3\,a}$	$mol \cdot kg^{-1}$	$g \cdot cm^{-3\,b}$	$g \cdot dm^{-3}$	$mol \cdot dm^{-3}$	$mol \cdot kg^{-1}$	$g \cdot dm^{-3}$	$mol \cdot dm^{-3}$	$mol \cdot kg^{-1}$
$T = 298$ K											
0.200	0.2014	1.008	3.000	3.1956	1.064	8.723	0.0641	0.0646	19.740	0.1450	0.1550
0.500	0.5063	1.018	3.500	3.7693	1.072	13.663	0.1003	0.1018	18.578	0.1365	0.1474
0.800	0.8147	1.025	4.000	4.3559	1.077	16.647	0.1223	0.1247	16.791	0.1233	0.1347
1.000	1.0223	1.031	4.500	4.9562	1.083	18.534	0.1361	0.1395	15.198	0.1116	0.1233
1.200	1.2315	1.034	5.000	5.5710	1.090	19.685	0.1446	0.1488	12.987	0.0954	0.1066
1.500	1.5487	1.041	5.500	6.2017	1.095	20.406	0.1499	0.1552	11.563	0.0849	0.0961
2.000	2.0859	1.049	6.000	6.8478	1.103	20.997	0.1542	0.1614	9.953	0.0731	0.0836
2.500	2.6348	1.057				20.844	0.1531	0.1620			
$T = 313$ K											
0.200	0.2014	1.003	3.000	3.1956	1.060	7.623	0.0560	0.0566	20.956	0.1539	0.1654
0.500	0.5063	1.012	3.500	3.7693	1.067	12.942	0.0951	0.0969	19.944	0.1465	0.1591
0.800	0.8147	1.021	4.000	4.3559	1.073	16.326	0.1199	0.1229	18.184	0.1336	0.1467
1.000	1.0223	1.025	4.500	4.9562	1.078	18.914	0.1389	0.1431	16.608	0.1220	0.1356
1.200	1.2315	1.030	5.000	5.5710	1.084	19.638	0.1442	0.1492	14.712	0.1081	0.1215
1.500	1.5487	1.036	5.500	6.2017	1.091	20.834	0.1530	0.1592	12.810	0.0941	0.1070
2.000	2.0859	1.045	6.000	6.8478	1.098	21.645	0.1590	0.1671	11.217	0.0824	0.0948
2.500	2.6348	1.053				21.546	0.1583	0.1681			
$T = 333$ K											
0.200	0.2014	0.994	3.000	3.1956	1.054	7.594	0.0558	0.0569	23.245	0.1707	0.1849
0.500	0.5063	1.003	3.500	3.7693	1.059	13.085	0.0961	0.0988	22.039	0.1619	0.1775
0.800	0.8147	1.013	4.000	4.3559	1.065	16.869	0.1239	0.1280	20.314	0.1492	0.1655
1.000	1.0223	1.019	4.500	4.9562	1.072	18.860	0.1385	0.1437	18.333	0.1347	0.1508
1.200	1.2315	1.022	5.000	5.5710	1.077	20.096	0.1476	0.1539	17.043	0.1252	0.1420
1.500	1.5487	1.028	5.500	6.2017	1.084	21.574	0.1585	0.1663	14.994	0.1101	0.1263
2.000	2.0859	1.038	6.000	6.8478	1.089	23.164	0.1701	0.1804	13.584	0.0998	0.1159
2.500	2.6348	1.046				23.739	0.1744	0.1869			
$T = 353$ K											
0.200	0.2014	0.985	3.000	3.1956	1.045	7.319	0.0538	0.0554	25.120	0.1845	0.2019
0.500	0.5063	0.994	3.500	3.7693	1.051	13.392	0.0984	0.1021	23.959	0.1760	0.1949
0.800	0.8147	1.003	4.000	4.3559	1.057	17.280	0.1269	0.1325	22.692	0.1667	0.1867
1.000	1.0223	1.008	4.500	4.9562	1.064	19.458	0.1429	0.1500	20.935	0.1538	0.1740
1.200	1.2315	1.013	5.000	5.5710	1.071	20.972	0.1540	0.1621	19.169	0.1408	0.1610
1.500	1.5487	1.018	5.500	6.2017	1.075	22.636	0.1663	0.1764	17.848	0.1311	0.1520
2.000	2.0859	1.028	6.000	6.8478	1.081	24.529	0.1802	0.1931	15.636	0.1148	0.1347
2.500	2.6348	1.037				25.389	0.1865	0.2019			

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

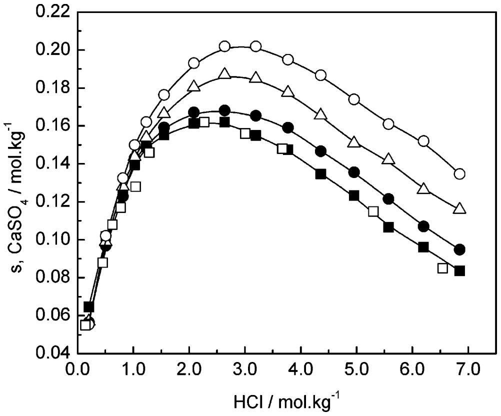

Figure 11. Solubility of calcium sulfate anhydrite in hydrochloric acid solutions: ■, 298 K; ●, 313 K; △, 333 K; ○, 353 K; □, Kruchenko et al.[19] at 298 K.

Solubility of $CaSO_4$ in HCl Solutions. Solubilities of calcium sulfate anhydrite in pure hydrochloric acid solutions were determined at (298, 313, 333, and 353) K. The investigated concentration of acid is from (0.0 to 6) $mol \cdot dm^{-3}$ at room temperature. The experimental results are presented in Table 10 and graphically in Figure 11.

It can be deduced by comparing Figure 11 to Figure 2 that the solubility of anhydrite in HCl aqueous solutions possesses similar features as dihydrate. The solubility of anhydrite increases with increasing the HCl concentration in the range of (0.0 to 3.0) $mol \cdot kg^{-3}$. After passing a maximum, the solubility decreases sharply with further increasing HCl concentration. In reference to temperature, the solubility increases systematically as the temperature increases from (298 to 353) K. The solubility of anhydrite in HCl solutions at 25 °C was compared with experimental data from ref 19 as shown in Figure 11. The present experimental data is in good agreement with early measurements.

Solubility of $CaSO_4$ in $CaCl_2$ Solutions. The generated solubility data are tabulated in Table 11 and plotted in Figure 12.

The solubility curves in Figure 12 illustrate that the solubility of calcium sulfate anhydrite sharply decreases with the addition of $CaCl_2$ due to common ion effect. In contrast to the behavior of calcium sulfate dihydrate, the solubility of anhydrite in calcium chloride decreases with increasing temperature investigated. Interestingly, the anhydrite solubilities at the three temperatures approach a constant value at high $CaCl_2$ concentration.

Solubility of $CaSO_4$ in Mixed HCl + $CaCl_2$ Solutions. The solubility of calcium sulfate anhydrite in mixed HCl (3 and 6) $mol \cdot dm^{-3}$ + $CaCl_2$ solutions was obtained over the temperature range from (298 to 353) K. The determined experimental data are presented in Tables 12 and 13. The same data is shown also graphically in Figure 13.

Table 11. Solubility of $CaSO_4$ (1) as Anhydrite in $CaCl_2$ (2) + H_2O (3) (Equilibration Time: 5 h)

solution parameters						solubility as $CaSO_4$ in different units					
M_2	m_2	ρ_s	M_2	m_2	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
$mol\cdot dm^{-3}$ [a]	$mol\cdot kg^{-1}$	$g\cdot cm^{-3}$ [b]	$mol\cdot dm^{-3}$ [a]	$mol\cdot kg^{-1}$	$g\cdot cm^{-3}$ [b]	$g\cdot dm^{-3}$	$mol\cdot dm^{-3}$	$mol\cdot kg^{-1}$	$g\cdot dm^{-3}$	$mol\cdot dm^{-3}$	$mol\cdot kg^{-1}$
$T = 298$ K											
0.050	0.0502	1.004	1.500	1.5620	1.126	2.149	0.0158	0.0158	0.892	0.0066	0.0068
0.100	0.1005	1.008	2.000	2.1148	1.165	2.033	0.0149	0.0150	0.574	0.0042	0.0045
0.250	0.2521	1.022	2.500	2.6879	1.205	1.858	0.0136	0.0137	0.338	0.0025	0.0027
0.500	0.5070	1.043	3.000	3.2841	1.243	1.663	0.0122	0.0124	0.188	0.0014	0.0015
1.000	1.0269	1.085	3.500	3.9067	1.281	1.298	0.0095	0.0098	0.110	0.0008	0.0009
$T = 323$ K											
0.050	0.0502	0.993	1.500	1.5620	1.116	1.469	0.0108	0.0109	0.712	0.0052	0.0055
0.100	0.1005	0.998	2.000	2.1148	1.154	1.391	0.0102	0.0104	0.479	0.0035	0.0038
0.250	0.2521	1.012	2.500	2.6879	1.193	1.301	0.0096	0.0097	0.303	0.0022	0.0024
0.500	0.5070	1.033	3.000	3.2841	1.232	1.224	0.0090	0.0092	0.184	0.0013	0.0015
1.000	1.0269	1.074	3.500	3.9067	1.271	0.979	0.0072	0.0075	0.104	0.0008	0.0009
$T = 353$ K											
0.050	0.0502	0.977	1.500	1.5620	1.099	0.755	0.0055	0.0057	0.507	0.0037	0.0040
0.100	0.1005	0.982	2.000	2.1148	1.139	0.756	0.0056	0.0057	0.369	0.0027	0.0029
0.250	0.2521	0.995	2.500	2.6879	1.177	0.754	0.0055	0.0057	0.248	0.0018	0.0020
0.500	0.5070	1.017	3.000	3.2841	1.216	0.761	0.0056	0.0058	0.173	0.0013	0.0014
1.000	1.0269	1.060	3.500	3.9067	1.254	0.665	0.0049	0.0051	0.107	0.0008	0.0009

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

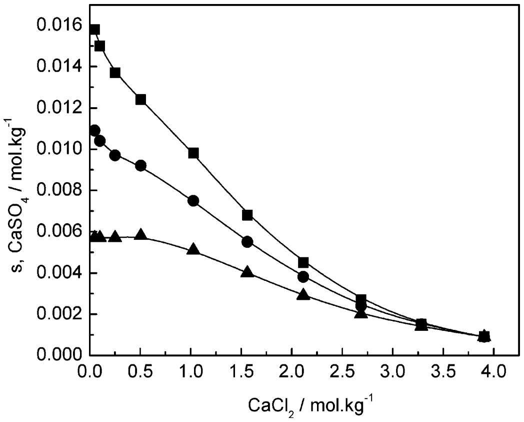

Figure 12. Solubility of calcium sulfate anhydrite in aqueous calcium chloride solutions: ■, 298 K; ●, 323 K; ▲, 353 K.

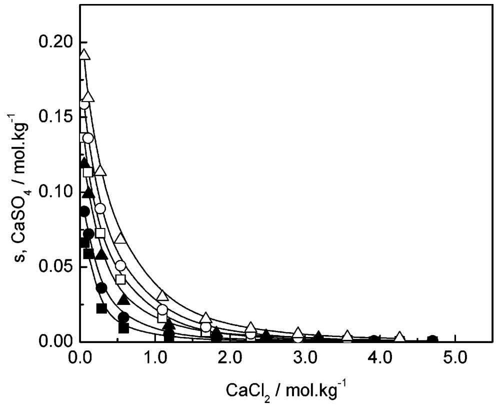

Figure 13. Solubility of calcium sulfate anhydrite in HCl + $CaCl_2$ mixed electrolyte solutions (solid points, 6 mol·dm^{-3}; empty points, 3 mol·dm^{-3}): ■, □, 298 K; ●, ○, 323 K; ▲, △, 353 K.

It can be seen in Figure 13 that the solubility of anhydrite in both acidic concentrations slightly increases with increasing temperature. The addition of calcium chloride in saturated solution leads the solubility to decrease more sharply in 6 mol·dm^{-3} HCl concentration than in 3 mol·dm^{-3} HCl, suggesting that HCl lowers water activity and results in decreasing solubility. The XRD analysis of equilibrated solids showed that there was no phase transformation of anhydrite in the course of 5 h equilibration at the three temperatures investigated.

Thermodynamic Interpretation

The observed behavior of $CaSO_4$ solubility in the current study may be explained by considering the various equilibria, such as solid−liquid and chemical solution (speciation), involved in the system. The solubility equilibrium for $CaSO_4$ solids in electrolyte aqueous solutions is expressed as follows:[24]

$$CaSO_4{\cdot}nH_2O \leftrightarrow Ca^{2+} + SO_4^{\;2-} + nH_2O \tag{1}$$

where n is 2, 0.5, or 0 corresponding to DH, HH, and AH, respectively. The thermodynamic solubility product for gypsum is given by

$$K_{sp} = a_{Ca^{2+}}a_{SO_4^{2-}}a_{H_2O}^2 = (m_{Ca^{2+}}\gamma_{Ca^{2+}})(m_{SO_4^{2-}}\gamma_{SO_4^{2-}})a_{H_2O}^2 \tag{2}$$

where $m_{Ca^{2+}}$ and $m_{SO_4^{2-}}$ are the molal concentrations of cation Ca^{2+} and anion SO_4^{2-} in solution. $\gamma_{Ca^{2+}}$ and $\gamma_{SO_4^{2-}}$ are the ion activity coefficients, and a_{H_2O} is the activity of water in solution. In contrast to the solubility in pure water, the solubility of gypsum in acidic HCl solution is complicated because of the bisulfate (HSO_4^-) ion formation. The dissociation equilibrium is expressed as

$$HSO_4^{\;-} \leftrightarrow H^+ + SO_4^{\;2-} \tag{3}$$

The thermodynamic equilibrium constant of reaction 3 is described as

$$K_2 = \frac{(m_{H^+}\gamma_{H^+})(m_{SO_4^{2-}}\gamma_{SO_4^{2-}})}{m_{HSO_4^-}\gamma_{HSO_4^-}} \tag{4}$$

where K_2, the second dissociation constant of H_2SO_4, has been investigated by numerous authors,[25−27] and $m_{HSO_4^-}$ and $\gamma_{HSO_4^-}$ are the molal concentration and activity coefficient of the HSO_4^- ion.

In the system $CaSO_4{\cdot}2H_2O$(s) + HCl + H_2O, the solubility of gypsum (s) is expressed by the molal concentration of Ca^{2+} ion or the summation of all the sulfur-bearing species:

$$s = m_{Ca^{2+}} = m_{SO_4^{2-}} + m_{HSO_4^-} \tag{5}$$

Table 12. Solubility of $CaSO_4$ (1) as Anhydrite in 3 mol·dm^{-3} HCl (2) + $CaCl_2$ (3) + H_2O (4) (Equilibration Time: 5 h)

solution parameters								solubility as $CaSO_4$ in different units					
M_3	m_2	m_3	ρ_s	M_3	m_2	m_3	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
							T = 298 K						
0.050	3.2002	0.0533	1.066	1.500	3.3523	1.6762	1.169	17.357	0.1275	0.1364	0.811	0.0060	0.0067
0.100	3.2048	0.1068	1.067	2.000	3.4161	2.2774	1.209	14.398	0.1058	0.1133	0.429	0.0031	0.0036
0.250	3.2184	0.2682	1.076	2.500	3.4872	2.9060	1.247	9.188	0.0675	0.0726	0.206	0.0015	0.0018
0.500	3.2425	0.5404	1.093	3.000	3.5655	3.5655	1.286	5.244	0.0385	0.0417	0.120	0.0009	0.0010
1.000	3.2945	1.0982	1.131	3.500	3.6527	4.2615	1.319	1.996	0.0147	0.0161	0.067	0.0005	0.0006
							T = 323 K						
0.050	3.2002	0.0533	1.057	1.500	3.3523	1.6762	1.157	19.973	0.1467	0.1588	1.221	0.0090	0.0102
0.100	3.2048	0.1068	1.060	2.000	3.4161	2.2774	1.196	17.124	0.1258	0.1361	0.648	0.0048	0.0055
0.250	3.2184	0.2682	1.067	2.500	3.4872	2.9060	1.234	11.175	0.0821	0.0891	0.323	0.0024	0.0028
0.500	3.2425	0.5404	1.083	3.000	3.5655	3.5655	1.271	6.348	0.0466	0.0510	0.196	0.0014	0.0017
1.000	3.2945	1.0982	1.120	3.500	3.6527	4.2615	1.305	2.646	0.0194	0.0216	0.118	0.0009	0.0011
							T = 353 K						
0.050	3.2002	0.0533	1.046	1.500	3.3523	1.6762	1.143	23.663	0.1738	0.1908	1.819	0.0134	0.0153
0.100	3.2048	0.1068	1.047	2.000	3.4161	2.2774	1.179	20.168	0.1481	0.1628	1.037	0.0076	0.0089
0.250	3.2184	0.2682	1.055	2.500	3.4872	2.9060	1.216	14.020	0.1030	0.1134	0.594	0.0044	0.0052
0.500	3.2425	0.5404	1.071	3.000	3.5655	3.5655	1.253	8.381	0.0616	0.0683	0.361	0.0027	0.0032
1.000	3.2945	1.0982	1.105	3.500	3.6527	4.2615	1.287	3.621	0.0266	0.0300	0.266	0.0020	0.0024

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

Table 13. Solubility of $CaSO_4$ (1) as Anhydrite in 6 mol·dm^{-3} HCl (2) + $CaCl_2$ (3) + H_2O (4) (Equilibration Time: 5 h)

solution parameters								solubility as $CaSO_4$ in different units					
M_3	m_2	m_3	ρ_s	M_3	m_2	m_3	ρ_s	C_1	M_1	m_1	C_1	M_1	m_1
mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
							T = 298 K						
0.050	6.8599	0.0572	1.103	1.500	7.2674	1.8169	1.212	7.863	0.0578	0.0663	0.154	0.0011	0.0014
0.100	6.8713	0.1145	1.106	2.000	7.4396	2.4799	1.249	6.966	0.0512	0.0588	0.086	0.0006	0.0008
0.250	6.9089	0.2879	1.116	2.500	7.6297	3.1790	1.286	2.635	0.0194	0.0223	0.050	0.0004	0.0005
0.500	6.9727	0.5811	1.133	3.000	7.8360	3.9180	1.318	1.092	0.0080	0.0093	0.035	0.0003	0.0003
1.000	7.1124	1.1854	1.174	3.500	8.0537	4.6980	1.353	0.372	0.0027	0.0032	0.029	0.0002	0.0003
							T = 323 K						
0.050	6.8599	0.0572	1.094	1.500	7.2674	1.8169	1.197	10.228	0.0751	0.0871	0.281	0.0021	0.0025
0.100	6.8713	0.1145	1.097	2.000	7.4396	2.4799	1.236	8.460	0.0621	0.0721	0.165	0.0012	0.0015
0.250	6.9089	0.2879	1.105	2.500	7.6297	3.1790	1.271	4.214	0.0310	0.0361	0.114	0.0008	0.0011
0.500	6.9727	0.5811	1.125	3.000	7.8360	3.9180	1.302	1.900	0.0140	0.0164	0.085	0.0006	0.0008
1.000	7.1124	1.1854	1.164	3.500	8.0537	4.6980	1.336	0.601	0.0044	0.0053	0.076	0.0006	0.0008
							T = 353 K						
0.050	6.8599	0.0572	1.081	1.000	7.1124	1.1854	1.147	13.710	0.1007	0.1185	1.245	0.0091	0.0111
0.100	6.8713	0.1145	1.084	1.500	7.2674	1.8169	1.181	11.426	0.0839	0.0988	0.638	0.0047	0.0058
0.250	6.9089	0.2879	1.090	2.000	7.4396	2.4799	1.216	6.636	0.0487	0.0577	0.415	0.0031	0.0039
0.500	6.9727	0.5811	1.107	2.500	7.6297	3.1790	1.251	3.125	0.0230	0.0274	0.282	0.0021	0.0027

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

Substituting eqs 2 and 4 into eq 5 yields the following relationship:

$$s = \frac{1}{a_{H_2O}}\left(\frac{K_{sp}}{\gamma_{Ca^{2+}}}\right)^{1/2}\left(\frac{1}{\gamma_{SO_4^{2-}}} + \frac{1}{K_2}\frac{\gamma_{H^+}}{\gamma_{HSO_4^-}}m_{H^+}\right)^{1/2} \tag{6}$$

Equation 6 indicates qualitatively that the solubility of gypsum increases with increasing acid concentration at the range of less than 3 M HCl as shown in Figure 2. At this range the formation of bisulfate apparently contributes to the solubility increase. In the concentrated acid (> 3 mol·dm^{-3}) solutions, however, the opposite effect on the solubility of gypsum has been observed since apparently the activity of water and ion activity coefficients become to have more influence on the solubility.

Similarly, the effect of calcium chloride in the system $CaSO_4·2H_2O(s) + HCl + CaCl_2 + H_2O$ may be qualitatively explained by referring to eq 7:

$$s = \frac{K_{sp}}{\gamma_{Ca^{2+}}a_{H_2O}^2}\left(\frac{1}{\gamma_{SO_4^{2-}}} + \frac{1}{K_2}\frac{m_{H^+}\gamma_{H^+}}{\gamma_{HSO_4^-}}\right)\frac{1}{m_{Ca^{2+}}} \tag{7}$$

It can be seen in eq 7 that at fixed HCl concentration the solubility of gypsum decreases consistently with the concentration of calcium chloride, such as shown in Figure 5. A comprehensive thermodynamic model developed and described elsewhere[28] provides quantitative explanation for the obtained solubility behavior.

Conclusions

The solubility of calcium sulfate dihydrate, hemihydrate, and anhydrite in HCl and $CaCl_2$ or their mixed electrolyte solutions has been measured for a wide range of conditions up to 12 mol·dm^{-3} HCl, 3 mol·dm^{-3} $CaCl_2$, and (283 to 353) K. The solubility of all calcium sulfate modifications in chloride solutions increases monotonically with increasing systems temperature except for AH in $CaCl_2$ solutions. The solubility of dihydrate or anhydrite in HCl solution increases with the acid concentration up to around (2.5 to 3.0) mol·dm^{-3} HCl. It decreases gradually above this value. The solubility of calcium sulfate hemihydrate in HCl solution with more than 8 mol·dm^{-3} concentration decreases with increasing acid concentration, and both α- or β-hemihydrate forms have close solubility values. The addition of $CaCl_2$ in acid solution makes the solubility of all $CaSO_4$ modifications to decrease sharply due to the common ion effect. The behavior of solubility of calcium sulfate was partially explained by thermodynamic interpretation considering the various equilibria in solutions. The formation of the HSO_4^- ion in acidic solution was thought to be responsible for the solubility increase. XRD results and SEM micrographs indicate that the gypsum and hemihydrate crystals are unstable at elevated temperatures and high HCl concentration converting to anhydrite within a short period of time (< 5 h). The presence of $CaCl_2$ was found to suppress this transformation of hemihydrate to anhydrite.

Literature Cited

(1) Sohnel, O.; Garside, J. *Precipitation: Basic Principles and Industrial Application*; Butterworth Heinemann: Oxford, 1995.

(2) Mullin, J. W. *Crystallization*; Butterworth-Heinemann: Oxford, 2001.

(3) Myerson, A. S. *Handbook of Industrial Crystallization*; Butterworth-Heinemann: Oxford, 2002.

(4) Dutrizac, J. E. Calcium sulfate solubilities in simulated zinc processing solutions. *Hydrometallurgy* **2002**, 65, 109−135.

(5) Girgin, S.; Demopoulos, G. P. Production of the high value material, alpha-$CaSO_4$ hemihydrate out of spent $CaCl_2$ solutions by reaction with H_2SO_4. In *EPD Congress 2004*; Schlesinger, M. E., Ed.; TMS: Warendale, PA, 2004; pp 627−639.

(6) Al-Othman, A.; Cheng, T. C.; Demopoulos, G. P. Regeneration of HCl and production of saleable gypsum by reaction of spent $CaCl_2$ leach solutions with H_2SO_4. In *Proceedings of Fifth International Symposium on Waste Processing and Recycling in Mineral and Metallurgical Industries*; Rao, S. R., et al., Eds.; CIM: Montreal, Canada, 2004; pp 453−467.

(7) Linke, W. F.; Seidell, A. *Solubilities of Inorganic and Metal-Organic Compounds*; American Chemical Society: Washington, DC, 1965.

(8) Silcock, H. L. *Solubilities of Inorganic and Organic Compounds*, *Vol. 3*: *Multicomponent Systems of Inorganic Substances*; Pergamon Press: Toronto, 1979.

(9) Li, Z.; Demopoulos, G. P. $CaSO_4$ solubilities in concentrated aqueous chloride solutions. In *Chloride Metallurgy 2002: International Conference on Practice and Theory of Chloride/Metal Interaction, 32nd Annual Hydrometallurgy Meeting*; Peek, E., Van Weert, G., Eds.; CIM: Montreal, 2002; pp 561−574.

(10) *Aqueous System Modeling Course and Workshop*, OLI's manual; OLI System Inc.: Morris Plains, NJ, 2002.

(11) Zemaitis, J. F.; Clark, D. M.; Rafal, M.; Scrivner, N. C. *Handbook of Aqueous Electrolyte Thermodynamics: Theory & Application*; AIChE: New York, 1986.

(12) Nyvlt, J. *Solid−Liquid-Phase Equilibrium*; Publishing House of the Czechoslovak: Praha, 1977.

(13) Zhang, L.; Gui, Q.; Lu, X.; Wang, Y.; Shi, J. Lu, B. C. Y. Measurement of solid−liquid equilibria by a flow-cloud-point method. *J. Chem. Eng. Data* **1998**, *43*, 32−37.

(14) Ling, Y.; Demopoulos, G. P.; Giove, A.; Filippou, D. Technical evaluation and characterization of alpha calcium sulfate materials. In *Gypsum and Fly Ash 2002, 7th International Science and Technology Conference and Short Course*; Toronto, 2002; pp 1−14.

(15) Lucas, A.; Rodriguez, L.; Sanchez, P.; Carmona, M.; Romero, P. Lobato, J. Comparative study of the solubility of the crystalline layered silicates α-$Na_2Si_2O_5$ and δ-$Na_2Si_2O_5$ and the amorphous silicate $Na_2Si_2O_5$. *Ind. Eng. Chem. Res.* **2004**, *43*, 1472−1477.

(16) Power, W. H.; Fabuss B. M.; Satterfield, C. N. Transient solubilities in the calcium sulfate−water system. *J. Chem. Eng. Data* **1964**, *9*, 437−442.

(17) Power, W. H.; Fabuss B. M.; Satterfield, C. N. Transient solute concentrations and phase changes of calcium sulfate in aqueous sodium chloride. *J. Chem. Eng. Data* **1966**, *11*, 149−154.

(18) Gupta, R. K. Solubility of calcium sulphate dihydrate in hydrochloric acid solutions. *J. Appl. Chem.* **1968**, *18*, 49−51.

(19) Kruchenko, V. P.; Beremzhanov, V. A. The solubilities of the salts in the calcium sulphate−hydrochloric acid−water system at 25 °C. *Russ. J. Inorg. Chem.* **1976**, *21*, 281−282.

(20) Rock, E. On the solubility of anhydrous calcium sulphate and gypsum in concentrated solutions of sodium chloride. *Can. J. Chem.* **1961**, *39*, 1746−1751.

(21) Ostroff, A. G.; Metler, A. V. Solubility of calcium sulfate dihydrate in the system $NaCl-MgCl_2-H_2O$ from 28 ° to 70 °C. *J. Chem. Eng. Data* **1966**, *11*, 346−350.

(22) Sullivan, J. M.; Kohler, J. J.; Grinstead, J. H., Jr. Solubility of α-calcium sulfate hemihydrate in 40, 45, 50, and 55% P_2O_5 phosphoric acid solutions at 80, 90, 100, and 110 °C. *J. Chem. Eng. Data* **1988**, *33*, 367−370

(23) Martynowicz, E. T. M. J.; Witkamp, G. J.; Rosmalen, G. M. The effect of aluminium fluoride on the formation of calcium sulfate hydrates. *Hydrometallurgy* **1996**, *41*, 171−186.

(24) Marshall, W. L.; Slusher, R. Thermodynamics of calcium sulfate dihydrate in aqueous sodium chloride solutions, 0−110 °C. *J. Phys. Chem.* **1966**, *70*, 4015−4027.

(25) Marshall, W. L.; Jones, E. V. Second dissociation constant of sulfuric acid from 25 to 350 °C evaluated from solubilities of calcium sulfate in sulfuric acid solutions. *J. Phys. Chem.* **1966**, *70*, 4028−4044.

(26) Filippou, D.; Demopoulos, G. P.; Papangelakis, V. G. Hydrogen ion activities and species distribution in mixed metal sulfate aqueous systems. *AIChE J.* **1995**, *41*, 171−184.

(27) Dickson, A. G.; Wesolowski, D. J.; Palmer, D. A.; Mesmer, R. E. Dissociation constant of bisulfate ion in aqueous sodium chloride solutions to 250 °C. *J. Phys. Chem.* **1990**, *94*, 7978−7985.

(28) Li, Z.; Demopoulos, G. P. Modelling of phase transformations and equilibria of calcium sulfate hydrates in concentrated aqueous chloride solutions using the OLI Software. In *COM 2005*: *International Conference on Computational Analysis in Hydrometallurgy*, *35th Annual Hydrometallurgy Meeting*; CIM: Montreal, 2005; pp 387−404.

(29) Zdanovskii, A. B.; Vlasov, G. A. Solubility of the various modifications of calcium sulphate in H_2SO_4 solutions at 25 °C. *Russ. J. Inorg. Chem.* **1968**, *13*, 1415−1418.

Received for review June 2, 2005. Accepted September 13, 2005. The support of Hatch, Noranda, Process Research Ortech, and NSERC (Natural Sciences and Engineering Research Council of Canada) is gratefully acknowledged.

JE050217E