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Effect of NaCl, $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$ on Solubility of $CaSO_4$ Phases in Aqueous HCl or HCl + $CaCl_2$ Solutions at 298 to 353 K

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The effect of various chloride salts (NaCl, $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$) on the solubility of three $CaSO_4$ modifications, namely, calcium sulfate dihydrate, hemihydrate, and anhydrite in aqueous HCl or HCl + $CaCl_2$ solutions up to 353 K was investigated. The concentration ranges (at ambient temperature) studied are up to 6 $mol\cdot dm^{-3}$ for HCl; 1.5 $mol\cdot dm^{-3}$ for $CaCl_2$; 3 $mol\cdot dm^{-3}$ for NaCl, $MgCl_2$, and $FeCl_2$; and 2 $mol\cdot dm^{-3}$ for $AlCl_3$ and $FeCl_3$. The solubility of $CaSO_4$ phases in all cases investigated was found to increase with temperature. In 0.5 $mol\cdot dm^{-3}$ HCl, the effect of metal chlorides on the solubility of dihydrate was a complex one with solubility increasing up to a certain metal chloride concentration and then decreasing in higher range of metal chloride concentration. On the other hand at higher HCl concentration (3 $mol\cdot dm^{-3}$), the solubility of dihydrate and anhydrite was found to consistently decrease with increasing metal chloride concentration. The only exception was NaCl, which was found not to influence to a significant degree the solubility of dihydrate in HCl solutions. The solubility of dihydrate in pure $AlCl_3$ solution smoothly passes through a maximum value in the (0 to 1.5) $mol\cdot dm^{-3}$ $AlCl_3$ concentration range. The presence of $CaCl_2$ causes the solubility of both dihydrate and hemihydrate to decrease due to common ion effect.

Introduction

Previously, we reported the solubility of three $CaSO_4$ modifications, namely, dihydrate (DH), hemihydrate (HH), and anhydrite (AH) in aqueous HCl + $CaCl_2$ solutions at the temperature range of (283 to 353) K.[1] These data are considered important both from the standpoint of developing chemical solution models[2] as well as from the standpoint of designing a process for HCl regeneration and production of valuable gypsum materials, like α-$CaSO_4$ hemihydrate.[3,4] In many industrial systems, however, there exist other metal chloride salts in addition to $CaCl_2$ in HCl media.[5−9] It is indeed the object of this research to evaluate the effect various metal chlorides, such as NaCl, $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$, have on the solubility of $CaSO_4$ phases in HCl or HCl + $CaCl_2$ solutions. There is currently limited work reported on the effect of metal chlorides on the solubility of $CaSO_4$ phases in particular in hot concentrated HCl solutions.

The solubility of calcium sulfate dihydrate at low temperature or anhydrite at elevated temperature in pure NaCl solutions was determined by many investigators. Raju and Atkinson[10] presented a comprehensive review of $CaSO_4$ solubility data in NaCl + H_2O system. Kruchenko[11] reported the solubility of gypsum (dihydrate) in aqueous solutions of $MgCl_2$ at (25, 40, and 50) °C. The results show that the solubility passes through a maximum at the concentration range of (0 to 35) % $MgCl_2$. Flint[12] investigated the effect of small additions of NaCl, $MgCl_2$, $AlCl_3$, and HCl on dihydrate solubility. According to Flint's work, the uptake (solubility) of calcium sulfate by seawater brines increases from 0.8 % to (3 or 6) % by $AlCl_3$ or HCl, respectively. Ostroff and Metler[13] measured the solubility of dihydrate in mixed NaCl + $MgCl_2$ solutions with concentration range of (0.01 to 0.325) $mol\cdot kg^{-1}$ $MgCl_2$ up to 70 °C. Finally, the solubility of gypsum in aqueous electrolyte systems (such as NaCl and $MgCl_2$) of limited ionic strength at 25 °C was reported by Tanji,[14] who also calculated these values with the aid of a computer program.

The above discussion suggests that there is still a requirement to systematically investigate the effects of various chloride salts on the solubility of calcium sulfate and its hydrates, especially in concentrated HCl- based solutions. This is done here for NaCl, $MgCl_2$, $FeCl_2$, $FeCl_3$, $AlCl_3$, $CaCl_2$, and their mixtures over the temperature range of (298 to 353) K.

Experimental Section

Chemicals. Analytically pure HCl, $CaCl_2\cdot 2H_2O$, NaCl, $MgCl_2\cdot 6H_2O$, $FeCl_2\cdot 4H_2O$, and $FeCl_3$ were supplied by Fisher with minimum purities of (36.5 to 38.0) %, 99.9 %, 99.9 %, 99.5 %, 99.9 %, and 99.9 %, respectively. $AlCl_3$ (98.5 %) was supplied by Aldrich. All solutions were prepared by carefully weighing the appropriate quantities of acid or salts and deionized water into 1 L flasks. Three solid substances were employed as the saturating solid phase; gypsum with 99 % purity that contained trace anhydrite ($CaSO_4$) was obtained from Alfa Aesar. Calcium sulfate hemihydrate (plaster of Paris, also called β-hemihydrate) was obtained from Fisher, while anhydrite with 99 % purity was obtained from Alfa Aesar. Deionized water with specific conductivity of 0.1 $\mu S\cdot cm^{-1}$ was used.

Procedure. The experimental technique used in the present work is the isothermal dissolution method that has been discussed in detail in an earlier report.[1] To summarize, the method involves saturating aqueous electrolyte solutions with known composition with $CaSO_4$ solids in glass flasks thermostated at selected temperature with constant magnetic stirring. The temperature was controlled to ± 0.2 K. Five hours of contact time was employed at 298 K to ensure the equilibration between calcium sulfate dihydrate or anhydrite and solution

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Table 1. Solubility of $CaSO_4$ (1) as Dihydrate in 0.5 mol·dm^{-3} HCl (2) + NaCl (3) + H_2O (4)

solution parameters				solubility as $CaSO_4$ in different units		
c_3	m_2	m_3	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
T = 323 K						
0.50	0.5089	0.5089	1.028	15.66	0.1150	0.1190
1.00	0.5137	1.0273	1.048	16.17	0.1187	0.1241
2.00	0.5236	2.0945	1.086	16.52	0.1213	0.1294
3.00	0.5369	3.2212	1.121	16.07	0.1180	0.1290
T = 353 K						
0.50	0.5083	0.5083	1.114	21.24	0.1560	0.1496
1.00	0.5132	1.0265	1.169	21.32	0.1566	0.1471
2.00	0.5232	2.0928	1.225	21.81	0.1602	0.1519
3.00	0.5364	3.2186	1.277	21.36	0.1569	0.1508

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

while 1 h was used for hemihydrate saturation. At elevated temperatures, 2 h instead of 5 h was used since it was found to be adequate to ensure the attainment of equilibrium on one hand and on the other to minimize HCl and water vapor losses. After equilibration, the clear solution was sampled and filtered to determine the solution density at the temperature of the system. The measured densities were uncertain to ± 0.001 g·cm^{-3}. Next, the filtered $CaSO_4$ saturated solution was diluted, and its calcium or sulfur content was analyzed by ICP to determine the solubility. The triplicate determinations of dihydrate solubility in 1 mol·dm^{-3} HCl at ambient temperature were carried out. The uncertainty of the measured solubility values was within ± 0.111 g·dm^{-3} while the relative deviation was 0.77 %. The washed (with hot water and acetone) and dried solid phases were examined by XRD to determine whether the solid phase had been altered due to phase transformation during equilibration.

Results and Discussion

Solubility of $CaSO_4·2H_2O$ in HCl + NaCl Solutions. Calcium sulfate dihydrate solubilities in mixed HCl (0.5 mol·dm^{-3}) + NaCl solutions were measured at (323 and 353) K. The investigated concentration of NaCl is from (0.0 to 3) mol·dm^{-3} at ambient temperature. The results of experimentally determined solubilities are summarized in Table 1 and graphically in Figure 1. In Table 1, the concentration of HCl, NaCl, and calcium sulfate ($CaSO_4$) is expressed both in concentration (c/mol·dm^{-3}) and molality (m/mol·kg^{-1}) for convenient practical and thermodynamic reference. However, the concentration of NaCl marked with c_3 is the initial concentration of the solution prepared at ambient temperature (24 ± 1 °C) before introducing calcium sulfate dihydrate. The other quantities of acid and salts in different units express the concentration at the conditions of the system. Figure 1 demonstrates that the solubility of dihydrate slightly increases with increasing NaCl concentration at 323 K while NaCl has limited effect on solubility of dihydrate in 0.5 mol·dm^{-3} HCl solutions at 353 K. For comparison, the solubility of dihydrate in pure NaCl from Ostroff and Metler[12] is also included in Figure 1 (indicated with a dashed line). It can be clearly seen that HCl causes a sharp increase of $CaSO_4$ (as DH) solubility.

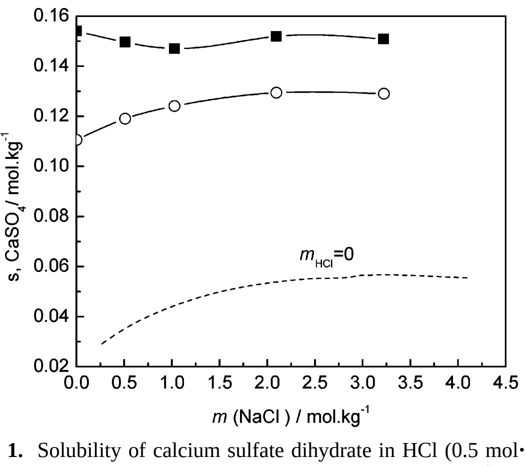

Figure 1. Solubility of calcium sulfate dihydrate in HCl (0.5 mol·dm^{-3}) + NaCl solutions: ○, 323 K; ■, 353 K; —, Ostroff and Metler[12] at 323 K.

Table 2. Solubility of $CaSO_4$ (1) as Dihydrate in 0.5 mol·dm^{-3} HCl (2) + $MgCl_2$ (3) + H_2O (4)

solution parameters				solubility as $CaSO_4$ in different units		
c_3	m_2	m_3	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
T = 298 K						
0.75	0.5128	0.7692	1.072	12.54	0.0921	0.0949
1.50	0.5222	1.5667	1.122	10.96	0.0805	0.0846
2.25	0.5340	2.4030	1.173	8.32	0.0611	0.0654
3.00	0.5459	3.2756	1.218	5.85	0.0430	0.0472
T = 323 K						
0.75	0.5123	0.7685	1.065	15.99	0.1175	0.1222
1.50	0.5217	1.5651	1.117	14.51	0.1065	0.1129
2.25	0.5335	2.4009	1.167	11.41	0.0838	0.0905
3.00	0.5455	3.2730	1.212	8.50	0.0624	0.0690
T = 353 K						
0.75	0.5115	0.7672	1.055	21.78	0.1600	0.1689
1.50	0.5209	1.5628	1.107	19.35	0.1421	0.1526
2.25	0.5327	2.3974	1.158	16.33	0.1199	0.1311
3.00	0.5449	3.2692	1.202	12.25	0.0900	0.1007

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

Table 3. Solubility of $CaSO_4$ (1) as Dihydrate in 3 mol·dm^{-3} HCl (2) + $MgCl_2$ (3) + H_2O (4)

solution parameters				solubility as $CaSO_4$ in different units		
c_3	m_2	m_3	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
T = 298 K						
0.25	3.2034	0.2670	1.077	18.37	0.1349	0.1456
0.50	3.2255	0.5376	1.093	16.27	0.1195	0.1296
1.00	3.2683	1.0894	1.127	13.50	0.0992	0.1089
1.25	3.3009	1.3754	1.142	12.45	0.0914	0.1013
1.50	3.3232	1.6616	1.158	11.36	0.0834	0.0930
2.00	3.3790	2.2527	1.190	8.98	0.0659	0.0746
2.50	3.4419	2.8683	1.203	7.83	0.0575	0.0673
3.00	3.4932	3.4932	1.252	6.34	0.0466	0.0545
T = 323 K						
0.25	3.1959	0.2663	1.074	26.23	0.1926	0.2099
0.50	3.2174	0.5362	1.090	24.79	0.1820	0.1996
1.00	3.2611	1.0870	1.123	20.83	0.1530	0.1697
1.25	3.2937	1.3724	1.136	19.65	0.1443	0.1616
1.50	3.3167	1.6584	1.154	17.76	0.1304	0.1468
2.00	3.3730	2.2487	1.186	14.83	0.1089	0.1243
2.50	3.4363	2.8636	1.213	13.18	0.0968	0.1128
3.00	3.4891	3.4891	1.243	10.01	0.0735	0.0870

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

Solubility of $CaSO_4·2H_2O$ and $CaSO_4$ in HCl + $MgCl_2$ Solutions. The solubilities of calcium sulfate dihydrate and anhydrite in mixed HCl (0.5 and 3 mol·dm^{-3}) + $MgCl_2$ solutions are shown in Tables 2 to 4 and also presented graphically in Figures 2 to 4, respectively. The concentration of $MgCl_2$ investigated is in the range of (0 to 3) mol·dm^{-3} and

Table 4. Solubility of $CaSO_4$ (1) as Anhydrite in 3 mol·dm^{-3} HCl (2) + $MgCl_2$ (3) + H_2O (4)

solution parameters				solubility as $CaSO_4$ in different units		
c_3	m_2	m_3	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
			$T = 353$ K			
0.25	3.2203	0.2684	1.0586	24.81	0.1822	0.2015
0.50	3.2407	0.5401	1.0776	23.15	0.1700	0.1886
1.00	3.2812	1.0937	1.1059	18.77	0.1379	0.1552
1.25	3.3130	1.3804	1.1215	16.71	0.1228	0.1392
1.50	3.3344	1.6672	1.1377	14.89	0.1093	0.1247
2.00	3.3881	2.2588	1.1684	11.56	0.0849	0.0983
2.50	3.4503	2.8752	1.1980	9.41	0.0691	0.0814
3.00	3.5001	3.5001	1.2314	7.25	0.0533	0.0636

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

temperature range up to 353 K. As demonstrated in Figures 2 and 3, the solubility of dihydrate consistently increases with increasing temperature. It can be seen from Figure 2 that at low HCl concentration the solubility of dihydrate increases with increasing $MgCl_2$ concentration in the range of (0.0 to 0.5) mol·dm^{-3}. After passing a maximum, the solubility declines smoothly in the range of higher concentration of $MgCl_2$. However, addition of $MgCl_2$ in concentrated HCl solutions causes the solubility of dihydrate to decrease constantly as shown in Figure 3. These results show that the presence of $MgCl_2$ in HCl solutions markedly influences in a complex (unpredicted) fashion the dihydrate solubility. Similar trend is observed in the case of anhydrite solubility as illustrated in Figure 4.

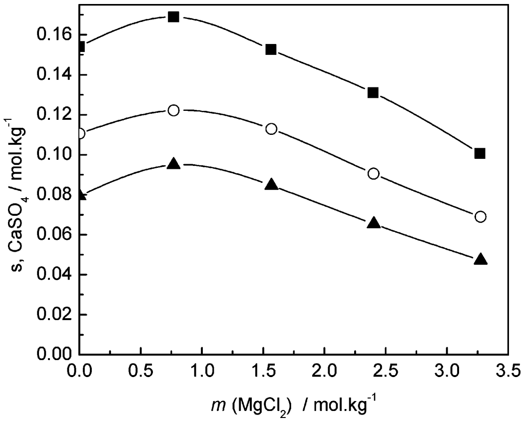

Figure 2. Solubility of calcium sulfate dihydrate in HCl (0.5 mol·dm^{-3}) + $MgCl_2$ solutions: ▲, 298 K; ○, 323 K; ■, 353 K.

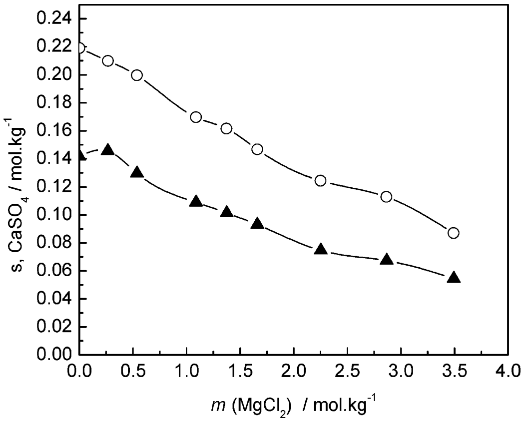

Figure 3. Solubility of calcium sulfate dihydrate in HCl (3 mol·dm^{-3}) + $MgCl_2$ solutions: ▲, 298 K; ○, 323 K.

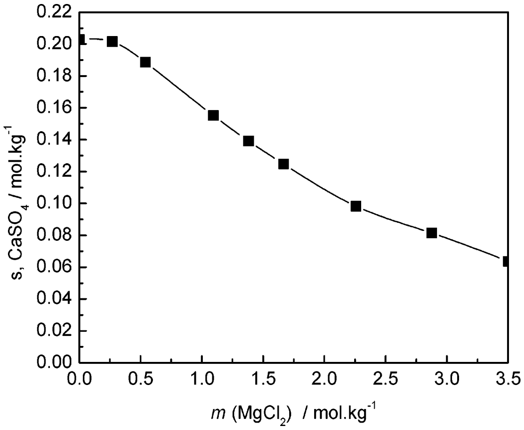

Figure 4. Solubility of calcium sulfate anhydrite in HCl (3 mol·dm^{-3}) + $MgCl_2$ solutions at 353 K.

Table 5. Solubility of $CaSO_4$ (1) as Dihydrate in $AlCl_3$(2) + H_2O(3)

solution parameters			solubility as $CaSO_4$ in different units		
c_2	m_2	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
			$T = 298$ K		
0.25	0.2517	1.033	9.47	0.0695	0.0702
0.50	0.5080	1.065	10.95	0.0805	0.0815
1.00	1.0386	1.117	11.12	0.0817	0.0841
1.25	1.3144	1.140	10.33	0.0759	0.0789
1.50	1.5985	1.170	8.49	0.0624	0.0651
			$T = 323$ K		
0.25	0.2516	1.027	10.79	0.0792	0.0805
0.50	0.5077	1.057	13.01	0.0956	0.0977
1.00	1.0378	1.110	13.59	0.0998	0.1035
1.25	1.3137	1.137	12.21	0.0897	0.0936
1.50	1.5975	1.164	10.69	0.0785	0.0825
			$T = 353$ K		
0.25	0.2514	1.013	13.13	0.0965	0.0997
0.50	0.5071	1.045	16.82	0.1235	0.1282
1.00	1.0363	1.101	18.70	0.1373	0.1444
1.25	1.3115	1.128	17.90	0.1314	0.1390
1.50	1.5948	1.155	16.41	0.1206	0.1284

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

Solubility of $CaSO_4·2H_2O$ in $AlCl_3$ Solutions. The solubility data of calcium sulfate dihydrate in aqueous $AlCl_3$ solutions at (298, 323, and 353) K is shown in Table 5 and Figure 5. Figure 5 shows that an increase in temperature from (298 to 353) K leads to an increase in the solubility of dihydrate, but the position

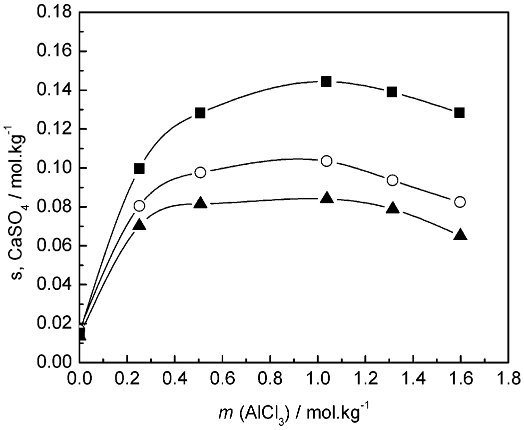

Figure 5. Solubility of calcium sulfate dihydrate in $AlCl_3$ solutions: ▲, 298 K; ○, 323 K; ■, 353 K.

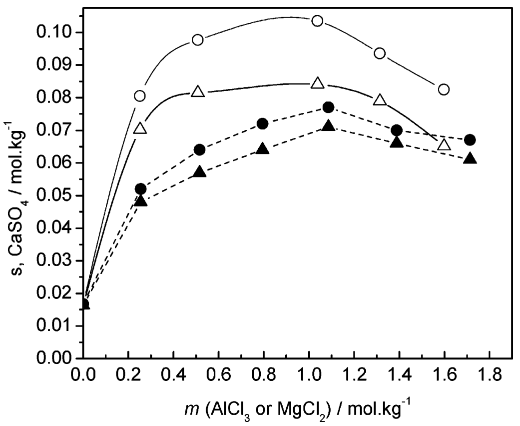

Figure 6. Comparison of dihydrate solubility in $MgCl_2$ and $AlCl_3$ solutions: ▲, $MgCl_2$ at 298 K;[11] ●, $MgCl_2$ at 323 K;[11] △, $AlCl_3$ at 298 K; ○, $AlCl_3$ at 323 K.

Table 6. Solubility of $CaSO_4$ (1) as Dihydrate in 0.5 mol·dm^{-3} HCl (2) + $AlCl_3$ (3) + H_2O (4)

solution parameters				solubility as $CaSO_4$ in different units		
c_3	m_2	m_3	ρ_s	γ_1	c_1	m_1
mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
T = 298 K						
0.50	0.5085	0.5085	1.075	14.16	0.1040	0.1065
1.00	0.5162	1.0325	1.127	11.96	0.0879	0.0911
1.50	0.5187	1.5561	1.180	8.67	0.0637	0.0667
2.00	0.5323	2.1292	1.227	6.37	0.0468	0.0499
T = 323 K						
0.50	0.5079	0.5079	1.069	18.81	0.1382	0.1428
1.00	0.5156	1.0312	1.124	16.43	0.1206	0.1259
1.50	0.5181	1.5543	1.172	12.69	0.0932	0.0986
2.00	0.5318	2.1271	1.221	9.72	0.0714	0.0768
T = 353 K						
0.50	0.5069	0.5069	1.061	25.70	0.1888	0.1980
1.00	0.5145	1.0290	1.113	23.60	0.1734	0.1838
1.50	0.5170	1.5511	1.167	19.97	0.1467	0.1566
2.00	0.5307	2.1229	1.212	16.43	0.1207	0.1314

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

of the maximum on the diagram remains unchanged. A similar behavior was observed by Kruchenko[11] in the case of dihydrate solubility in $MgCl_2$ solutions. The two sets of data are compared in Figure 6. It can be seen that the dihydrate solubility in $AlCl_3$ solutions represented by solid lines is larger than that in $MgCl_2$ solutions. This may be due to partial hydrolysis of $AlCl_3$ that generates HCl, hence the increase in solubility:

$$\mathrm{AlCl_3(aq) + H_2O \leftrightarrow AlOHCl_2(aq) + HCl} \tag{1}$$

Solubility of $CaSO_4·2H_2O$ in HCl + $AlCl_3$ Solutions. The solubility of calcium sulfate dihydrate in $AlCl_3$ + HCl solutions with two HCl concentration levels of (0.5 and 3) mol·dm^{-3} from (298 to 353) K was measured and listed in Tables 6 and 7 and Figures 7 and 8. Figure 7 shows that in 0.5 mol·dm^{-3} HCl the solubility of calcium sulfate dihydrate increases with increasing $AlCl_3$ concentration at first, passes through a maximum, and then decreases with further addition of $AlCl_3$. However, at the higher HCl concentration (i.e., 3.0 mol·dm^{-3}), the presence of $AlCl_3$ causes the solubility of dihydrate monotonically to decrease as depicted in Figure 8.

Table 7. Solubility of $CaSO_4$ (1) as Dihydrate in 3 mol·dm^{-3} HCl (2) + $AlCl_3$ (3) + H_2O (4)

solution parameters				solubility as $CaSO_4$ in different units		
c_3	m_2	m_3	ρ_s	γ_1	c_1	m_1
mol·dm$^{-3\,a}$	mol·kg^{-1}	mol·kg^{-1}	g·cm$^{-3\,b}$	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
T = 298 K						
0.50	3.2228	0.5371	1.113	14.83	0.1089	0.1179
1.00	3.2625	1.0875	1.166	10.48	0.0770	0.0842
1.50	3.3197	1.6599	1.215	7.51	0.0551	0.0613
T = 323 K						
0.50	3.2162	0.5360	1.109	21.68	0.1593	0.1741
1.00	3.2563	1.0854	1.161	16.96	0.1246	0.1376
1.50	3.3144	1.6572	1.208	12.86	0.0945	0.1060

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

Solubility of $CaSO_4·2H_2O$ in HCl + $FeCl_2$ or $FeCl_3$ Solutions. The experimental data of solubility of dihydrate in aqueous solutions containing HCl (0.5 mol·dm^{-3}) + $FeCl_2$ at (323 and 353) K were determined and shown in Table 8 and Figure 9. Figure 9 shows the dihydrate solubility to increase with increasing concentration of $FeCl_2$ up to certain level and then to decrease with further increase in $FeCl_2$ concentration. In addition, the influence of $FeCl_3$ in HCl solutions from (0.5 or 3) mol·dm^{-3} on the solubility of dihydrate was investigated, and the results are given in Tables 9 and 10 and Figures 10 and 11. Once more, upon an increase in $FeCl_3$ concentration the solubility of dihydrate in 0.5 mol·dm^{-3} HCl solutions increases

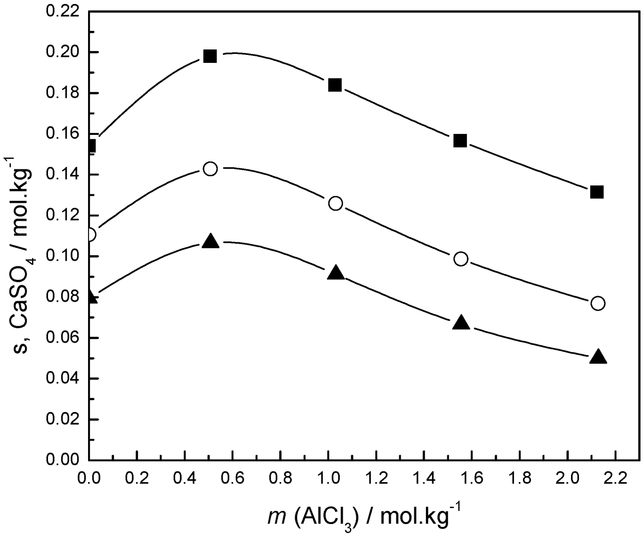

Figure 7. Solubility of calcium sulfate dihydrate in HCl (0.5 mol·dm^{-3}) + $AlCl_3$ solutions: ▲, 298 K; ○, 323 K; ■, 353 K.

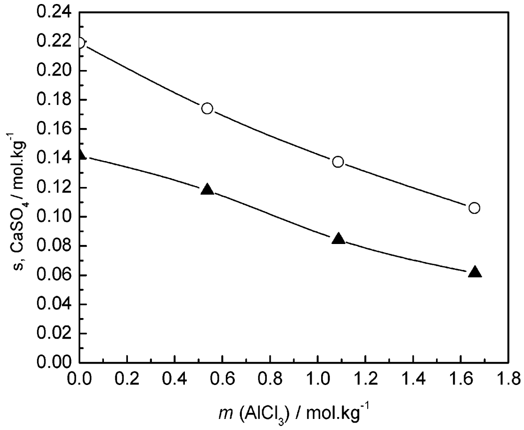

Figure 8. Solubility of calcium sulfate dihydrate in HCl (3 mol·dm^{-3}) + $AlCl_3$ solutions: ▲, 298 K; ○, 323 K.

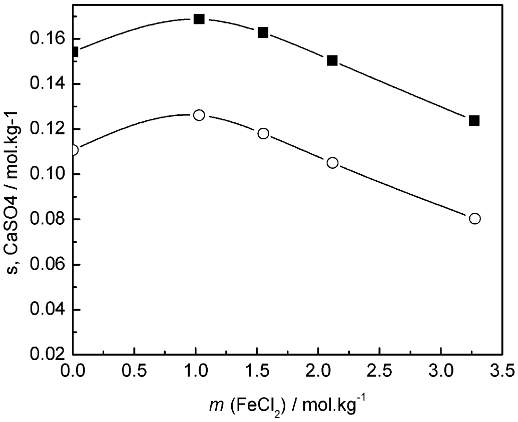

Figure 9. Solubility of calcium sulfate dihydrate in HCl (0.5 mol·dm^{-3}) + $FeCl_2$ solutions: ○, 323 K; ■, 353 K.

Table 8. Solubility of $CaSO_4$ (1) as Dihydrate in 0.5 mol·dm^{-3} HCl (2) + $FeCl_2$ (3) + H_2O (4)

solution parameters				solubility as $CaSO_4$ in different units		
c_3	m_2	m_3	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
			T = 323 K			
1.00	0.5148	1.0297	1.117	16.46	0.1209	0.1261
1.50	0.5175	1.5525	1.166	15.21	0.1117	0.1180
2.00	0.5292	2.1166	1.212	13.31	0.0978	0.1050
3.00	0.5460	3.2760	1.306	9.88	0.0725	0.0803
			T = 353 K			
1.00	0.5140	1.0281	1.103	21.62	0.1588	0.1686
1.50	0.5167	1.5500	1.154	20.67	0.1518	0.1627
2.00	0.5283	2.1132	1.203	18.84	0.1384	0.1503
3.00	0.5451	3.2708	1.295	15.03	0.1104	0.1237

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

Table 9. Solubility of $CaSO_4$ (1) as Dihydrate in 0.5 mol·dm^{-3} HCl (2) + $FeCl_3$ (3) + H_2O (4)

solution parameters				solubility as $CaSO_4$ in different units		
c_3	m_2	m_3	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
			T = 323 K			
0.50	0.5125	0.5125	1.079	22.25	0.1635	0.1703
1.00	0.5222	1.0444	1.136	21.82	0.1602	0.1708
1.50	0.5368	1.6105	1.190	18.50	0.1359	0.1485
2.00	0.5455	2.1820	1.253	14.64	0.1075	0.1192
			T = 353 K			
0.50	0.5114	0.5114	1.068	29.29	0.2151	0.2282
1.00	0.5211	1.0422	1.125	28.77	0.2113	0.2289
1.50	0.5356	1.6067	1.180	26.18	0.1923	0.2133
2.00	0.5443	2.1772	1.239	21.69	0.1593	0.1796

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

up to a certain level and thereafter decreases while the solubility of dihydrate in 3 mol·dm^{-3} HCl constantly decreases with increasing $FeCl_3$ concentration.

Comparison of Solubility Data. The effect of the various chloride salts at 323 K on the solubility of dihydrate in (0.5 and 3) mol·dm^{-3} HCl solutions is compared in Figures 12 to 15. Figure 12 depicts the influence of NaCl, $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$ in 0.5 mol·dm^{-3} HCl solutions on dihydrate solubility as a function of chloride concentration. It is interesting to note that with the exception of largely $FeCl_3$ the effect of the other metal chlorides is proportional to their chloride content. In the case of $FeCl_3$, the solubility of dihydrate increases substantially greater than with the other salts, although still it follows the shoulder-type dependency. Figure 13 provides a comparison of the same solubility data (as in Figure 12) but this time in terms of ionic strength. This time the effect is somewhat magnified with $AlCl_3$ clearly separated from the divalent chloride salts. Similarly, Figures 14 and 15 show the respective data for dihydrate solubility in 3 mol·dm^{-3} HCl as a function of total chloride concentration and ionic strength, respectively.

Table 10. Solubility of $CaSO_4$ (1) as Dihydrate in 3 mol·dm^{-3} HCl (2) + $FeCl_3$ (3) + H_2O (4)

solution parameters				solubility as $CaSO_4$ in different units		
c_3	m_2	m_3	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
			T = 298 K			
0.50	3.2541	0.5424	1.118	15.86	0.1165	0.1275
1.00	3.3377	1.1126	1.175	12.50	0.0918	0.1028
1.50	3.4253	1.7126	1.233	9.70	0.0713	0.0817
2.00	3.5130	2.3420	1.290	7.74	0.0569	0.0669
			T = 323 K			
0.50	3.2468	0.5411	1.114	23.37	0.1717	0.1899
1.00	3.3307	1.1102	1.169	19.37	0.1423	0.1610
1.50	3.4191	1.7096	1.225	15.46	0.1135	0.1315
2.00	3.5075	2.3383	1.277	12.57	0.0923	0.1100

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

Solubility of $CaSO_4$·$2H_2O$ in HCl + Chloride Salts + $CaCl_2$ Solutions. In this section, the effect of $CaCl_2$ on the solubility

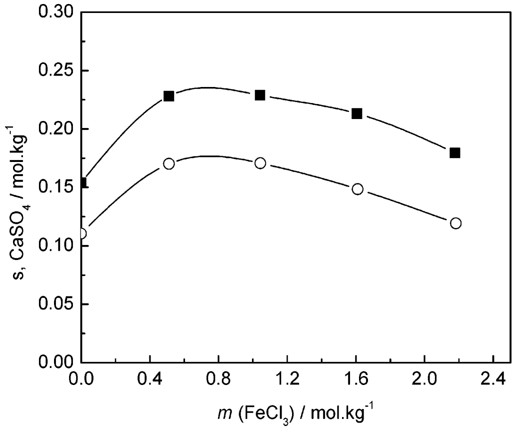

Figure 10. Solubility of calcium sulfate dihydrate in HCl (0.5 mol·dm^{-3}) + $FeCl_3$ solutions: ○, 323 K; ■, 353 K.

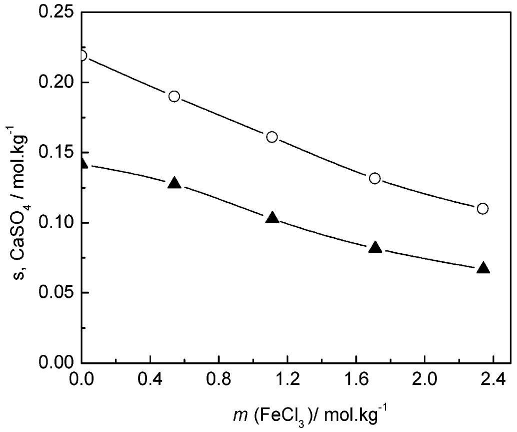

Figure 11. Solubility of calcium sulfate dihydrate in HCl (3 mol·dm^{-3}) + $FeCl_3$ solutions: ▲, 298 K; ○, 323 K.

Table 11. Solubility of $CaSO_4$ (1) as Dihydrate in 0.5 mol·dm^{-3} HCl (2) + 1 mol·dm^{-3} $MgCl_2$ (3) + $CaCl_2$ (4) + H_2O (5) at 323 K

solution parameters					solubility as $CaSO_4$ in different units		
c_4	m_2	m_3	m_4	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
0.25	0.5203	1.0406	0.2601	1.094	6.78	0.0498	0.0525
0.50	0.5210	1.0419	0.5210	1.115	3.54	0.0260	0.0275
1.00	0.5325	1.0649	1.0649	1.153	1.56	0.0115	0.0124
1.50	0.5440	1.0879	1.6319	1.190	0.86	0.0063	0.0069

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

Table 12. Solubility of $CaSO_4$ (1) as Dihydrate in 0.5 mol·dm^{-3} HCl (2) + 0.5 mol·dm^{-3} Chloride Salts (3) + $CaCl_2$ (4) + H_2O (5) at 323 K

solution parameters					solubility as $CaSO_4$ in different units		
c_4	m_2	m_3	m_4	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1} [c]	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
0.25	0.5467	0.5467	0.2734	1.237	3.62	0.0266	0.0294
0.50	0.5499	0.5499	0.5499	1.251	1.75	0.0128	0.0144
1.00	0.5653	0.5653	1.1306	1.288	0.70	0.0052	0.0059
1.50	0.5779	0.5779	1.7336	1.326	0.39	0.0029	0.0033

[a] Initial concentration of solutions prepared at room temperature without calcium sulfate. [b] Experimental density of saturated solutions. [c] The concentration of individual salt (NaCl, $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$).

Table 13. Solubility of $CaSO_4$ (1) as Hemihydrate in 6 mol·dm^{-3} HCl (2) + 1 mol·dm^{-3} $MgCl_2$ (3) + $CaCl_2$ (4) + H_2O (5) at 333 K

solution parameters					solubility as $CaSO_4$ in different units		
c_4	m_2	m_3	m_4	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
0.25	7.1519	1.1920	0.2980	1.165	6.22	0.0457	0.0554
0.50	7.2324	1.2054	0.6027	1.181	3.04	0.0223	0.0274
1.00	7.3901	1.2317	1.2317	1.218	1.27	0.0093	0.0116
1.50	7.5826	1.2638	1.8956	1.253	0.72	0.0053	0.0068

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

Table 14. Solubility of $CaSO_4$ (1) as Hemihydrate in 6 mol·dm^{-3} HCl (2) + 0.2 mol·dm^{-3} $FeCl_2$ (3) + $CaCl_2$ (4) + H_2O (5) at 333 K

solution parameters					solubility as $CaSO_4$ in different units		
c_4	m_2	m_3	m_4	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
0.25	6.9457	0.2315	0.2894	1.1254	11.38	0.0836	0.0987
0.50	6.9637	0.2321	0.5803	1.1380	6.12	0.0449	0.0535
1.00	7.1520	0.2384	1.1920	1.1763	2.33	0.0171	0.0207
1.50	7.3149	0.2438	1.8287	1.2097	1.23	0.0091	0.0112

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

Table 15. Solubility of $CaSO_4$ (1) as Hemihydrate in 6 mol·dm^{-3} HCl (2) + 0.1 mol·dm^{-3} Chloride Salts (3) + $CaCl_2$ (4) + H_2O (5) at 333 K

solution parameters					solubility as $CaSO_4$ in different units		
c_4	m_2	m_3	m_4	ρ_s	γ_1	c_1	m_1
mol·dm^{-3} [a]	mol·kg^{-1}	mol·kg^{-1} [c]	mol·kg^{-1}	g·cm^{-3} [b]	g·dm^{-3}	mol·dm^{-3}	mol·kg^{-1}
0.25	7.0134	0.1169	0.2922	1.138	9.51	0.0699	0.0835
0.50	7.0329	0.1172	0.5861	1.149	5.01	0.0368	0.0445
1.00	7.2282	0.1205	1.2047	1.192	1.89	0.0139	0.0170
1.50	7.3788	0.1230	1.8447	1.225	1.01	0.0074	0.0094

[a] Initial concentration of solutions prepared at room temperature without calcium sulfate. [b] Experimental density of saturated solutions. [c] The concentration of individual salt ($MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$).

of dihydrate in aqueous HCl (0.5 mol·dm^{-3}) + various chloride salt solutions was investigated at 323 K. The solubility of dihydrate in HCl (0.5 mol·dm^{-3}) + $MgCl_2$ (1 mol·dm^{-3}) + $CaCl_2$ at 323 K is listed in Table 11 and presented graphically in Figure 16. Figure 16 shows that the solubility of dihydrate consistently decreases with increasing concentration of $CaCl_2$ due to the common ion effect. In addition, the solubility of $CaSO_4$ as dihydrate in 0.5 mol·dm^{-3} HCl + chloride salts (NaCl, $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$ with 0.5 mol·dm^{-3} concentration for each salt) + $CaCl_2$ solutions at 323 K was determined and given in Table 12. Similar trend with that of Figure 16 was observed (i.e., systematic decrease of solubility with increasing $CaCl_2$ concentration).

Solubility of $CaSO_4 \cdot 0.5H_2O$ in HCl + Chloride Salts + $CaCl_2$ Solutions. In this section, the effect of $CaCl_2$ on the solubility of hemihydrate in aqueous HCl (6 mol·dm^{-3}) + various chloride salt solutions was determined at 333 K. The solubility of hemihydrate in HCl (6 mol·dm^{-3}) + $MgCl_2$ (1 mol·dm^{-3}) + $CaCl_2$ at 333 K is recorded in Table 13 and graphically illustrated in Figure 17. It can be seen from this

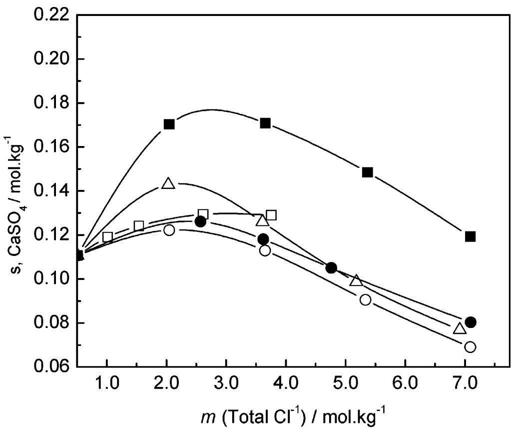

Figure 12. Comparison of dihydrate solubility in HCl (0.5 mol·dm^{-3}) + various chloride salts solutions vs total concentration of chloride at 323 K: □, NaCl; ○, $MgCl_2$; △, $AlCl_3$; ●, $FeCl_2$; ■, $FeCl_3$.

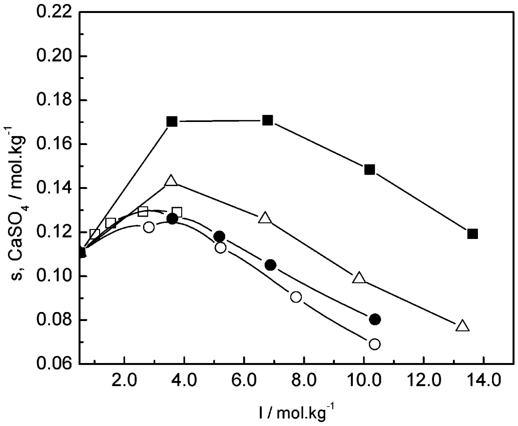

Figure 13. Comparison of dihydrate solubility in HCl (0.5 mol·dm^{-3}) + various chloride salts solutions vs ionic strength at 323 K: □, NaCl; ○, $MgCl_2$; △, $AlCl_3$; ●, $FeCl_2$; ■, $FeCl_3$.

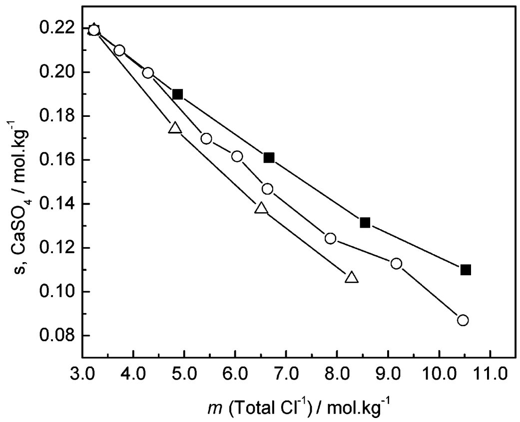

Figure 14. Comparison of dihydrate solubility in HCl (3 mol·dm^{-3}) + various chloride salts solutions vs total concentration of chloride at 323 K: ○, $MgCl_2$; △, $AlCl_3$; ■, $FeCl_3$.

figure that the solubility of hemihydrate consistently decreases with increasing concentration of $CaCl_2$ due to the common ion effect. Similar results were obtained in the case of solubility of hemihydrate in HCl (6 mol·dm^{-3}) + $FeCl_2$ (0.2 mol·dm^{-3}) + $CaCl_2$ at 333 K (data recorded in Table 14) and in 6 mol·dm^{-3} HCl + chloride salts ($MgCl_2$, $FeCl_3$, $FeCl_2$ and $AlCl_3$ with 0.2 mol·dm^{-3} concentration for each salt) + $CaCl_2$ solutions at 333 K (data recorded in Table 15).

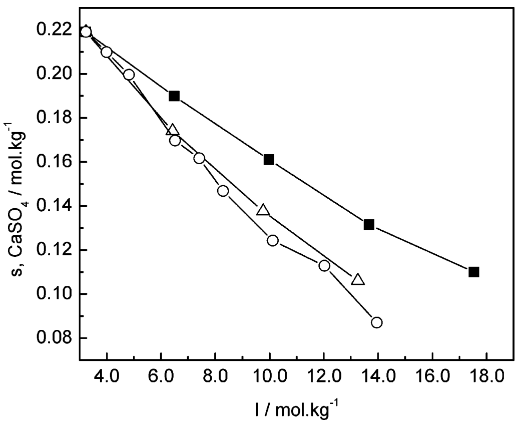

Figure 15. Comparison of dihydrate solubility in HCl (3 mol·dm^{-3}) + various chloride salts solutions vs ionic strength at 323 K: ○, $MgCl_2$; △, $AlCl_3$; ■, $FeCl_3$.

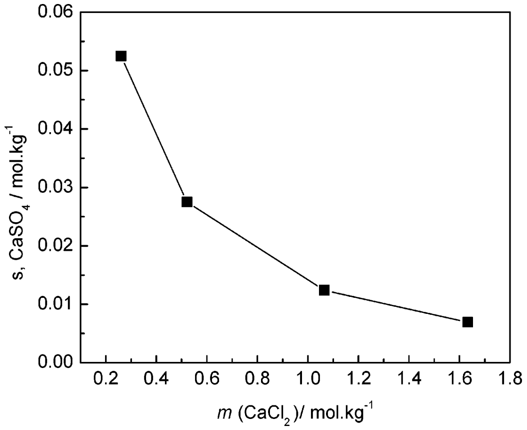

Figure 16. Solubility of calcium sulfate dihydrate in HCl (0.5 mol·dm^{-3}) + $MgCl_2$ (1 mol·dm^{-3}) + $CaCl_2$ solutions at 323 K.

Table 16. XRD Characterization of the Equilibrated Solids with Equilibrium Time

T/K	*c*/mol·dm^{-3}	*t*/h	equilibrated solid phase(s)[a]	Table
	Starting Material Is Calcium Sulfate Dihydrate			
298	0.5(HCl) + 3($MgCl_2$)	5	DH	2
323	3(HCl) + 2($MgCl_2$)	5	DH	3
323	3(HCl) + 3($MgCl_2$)	5	HH	
323	3(HCl) + 3($MgCl_2$)	2	DH	3
353	1.5($AlCl_3$)	5	DH	5
323	3(HCl) + 1.5($AlCl_3$)	5	DH	7
353	0.5(HCl) + 2($AlCl_3$)	2	DH	6
353	0.5(HCl) + 2($FeCl_3$)	2	DH	9
323	3(HCl) + 2($FeCl_3$)	5	DH	10
353	0.5(HCl) + 3($FeCl_2$)	2	DH	8
323	0.5(HCl) + 0.5 (NaCl, $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$) + 1.5($CaCl_2$)	5	DH	12
	Starting Material Is β-Calcium Sulfate Hemihydrate			
333	6(HCl) + 1($MgCl_2$) + 0.25($CaCl_2$)	1	HH	13
333	6(HCl) + 1($MgCl_2$) + 0.5($CaCl_2$)	1	HH	13
333	6(HCl) + 1($MgCl_2$) + 1($CaCl_2$)	1	HH	13
333	6(HCl) + 1($MgCl_2$) + 1.5($CaCl_2$)	1	HH	13

[a] DH, $CaSO_4·2H_2O$; HH, $CaSO_4·0.5H_2O$.

Identification of Equilibrated Solids. Partial results of solids characterization by XRD following the completion of the various solubility tests are tabulated in Table 16. The dihydrate in 3 mol·dm^{-3} HCl + 3 mol·dm^{-3} $MgCl_2$ solution at 323 K was converted to hemihydrate within the time of 5 h while in 3 mol·dm^{-3} HCl + 2 mol·dm^{-3} $MgCl_2$ solution at 323 K no hemihydrate and anhydrite were detected in equilibrated solids. The solubility data presented in Tables 1 to 12, though, are for DH only (i.e., the data associated with conversion of DH to

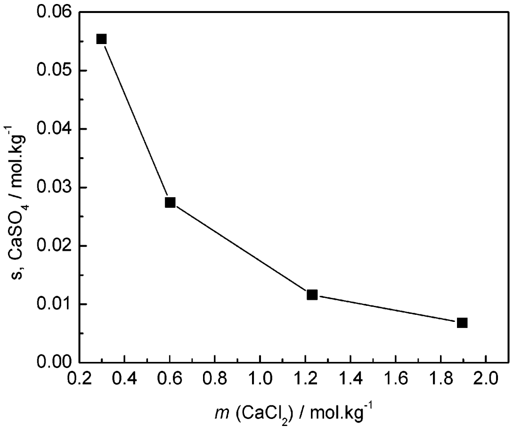

Figure 17. Solubility of calcium sulfate hemihydrate in HCl (6 mol·dm^{-3}) + $MgCl_2$ (1 mol·dm^{-3}) + $CaCl_2$ solutions at 333 K.

HH are excluded). It can be observed from Table 16 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 13 to 15 refer to HH as the only equilibrated phase.

Conclusions

The effect of various chloride salts, such as NaCl, $CaCl_2$, $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$ on the solubility of three $CaSO_4$ modifications (namely, dihydrate, hemihydrate, and anhydrite) in HCl solutions has been investigated. The solubility of dihydrate increases with increasing concentration of $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$ up to a certain level thereafter decreasing with further increase of metal chloride concentration when the HCl concentration is 0.5 mol·dm^{-3}. However, in the case of 3 mol·dm^{-3} HCl concentration, the solubility of dihydrate consistently decreases with increasing metal chloride concentration. Comparing with divalent chloride salts ($MgCl_2$ and $FeCl_2$), the trivalent chloride salts $AlCl_3$ and $FeCl_3$ were found to have a larger influence on the solubility of dihydrate for same ionic strength. $CaCl_2$, owing to the common ion effect, causes the solubility of dihydrate and hemihydrate in the system HCl + various chloride salts + H_2O to decrease.

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