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Solubility of Calcium Sulfate Hydrates in (0 to 3.5) mol·kg^{-1} Sulfuric Acid Solutions at 100 °C

Yuanbing Ling and George P. Demopoulos*

Department of Metals and Materials Engineering, McGill University, 3610 University Street, Montreal, Quebec, Canada H3A2B2

Solubilities of calcium sulfate hemihydrate in the low-concentration range from (0 to 3.5) mol·kg^{-1} (equivalent to mol·kg^{-1} H_2O) of sulfuric acid solutions at 100 °C (373 K) were measured. The measured solubilities were compared with available literature studies and simulated with empirical equations.

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1. Introduction

For the past half-century, the solubilities of various calcium sulfate phases, including dihydrate (DH), hemihydrate (HH), and anhydrite (AH) in sulfuric acid, have been extensively studied. The solvent solution is either aqueous sulfuric acid or a mixture of sulfuric acid with nitric acid, phosphoric acid, hydrochloric acid, fluosilicic acid, or salts such as sodium sulfate, calcium chloride, zinc sulfate, and so forth; the concentration ranges from (0 to 100) mass % (mass % of H_2SO_4 is defined as $\{(100\cdot \text{mass}_{H_2SO_4}/\text{mass}_{H_2SO_4} + \text{mass}_{H_2O})\}$, and the temperature spans from (0 to 350) °C. Surprisingly, there is no data reported for the solubilities of calcium sulfate phases in the low-concentration range of (0 to about 3.5) mol·kg^{-1} or (0 to 25.5) mass % of H_2SO_4 and at 100 °C, which is of particular interest in the present study as part of a broader project seeking to develop a novel, cost-effective process for the production of a high-value building/dental material, alpha-calcium sulfate hemihydrate directly out of sulfuric acid media under atmospheric pressure conditions at around 100 °C.

A summary of previously published solubility studies is presented in Table 1. Wehde and Stichlmair presented a comprehensive “map” of the solubility of calcium sulfate in a wide H_2SO_4 concentration range from (0 to around 90) mass % at various temperatures from 10 °C up to 120 °C. Here some of their data is reproduced and presented in Figure 1.[1] Most of their solubility curves {in terms of mass % of $CaSO_4$ as defined by $(100\cdot\text{mass}_{CaSO_4}/(\text{mass}_{H_2SO_4} + \text{mass}_{H_2O} + \text{mass}_{CaSO_4})\}$ are not distinguishable and hence cannot be reproduced.

Theoretically, the solubility of calcium sulfates is governed by the equilibrium

$$CaSO_4\cdot nH_2O(s) \xrightleftharpoons{K_{sp}} Ca^{2+} + SO_4{}^{2-} + nH_2O \qquad (1)$$

where K_{sp} is the thermodynamic solubility product, which is given by

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

$m_{Ca}{}^{2+}$ and $m_{SO_4}{}^{2-}$ are the concentrations of Ca^{2+} and $SO_4{}^{2-}$, $\gamma_{Ca}{}^{2+}$ and $\gamma_{SO_4}{}^{2-}$ are the activity coefficients of the respective ions, and a_{H_2O} is the activity of H_2O; $n = 2$, 0.5, and 0 correspond, respectively, to the dihydrate, hemihydrate, and the anhydrite.

In sulfuric acid media, equilibrium 1 is further influenced by the dissociation of H_2SO_4 solution:

$$H_2SO_4 \xrightleftharpoons{K_1} HSO_4{}^- + H^+ \qquad (3)$$

$$HSO_4{}^- \xrightleftharpoons{K_2} SO_4{}^{2-} + H^+ \qquad (4)$$

where K_1 and K_2 are the first and second thermodynamic dissociation constants of H_2SO_4, respectively.

At low temperatures (25 °C to around 60 °C), according to Marshall et al.[2] and Zhang et al.,[3] H_2SO_4 has a positive effect on the solubility of calcium sulfate in the low-concentration range from (0 to about 15) mass %. This increase in solubility is attributed to the influence of the second dissociation constant of H_2SO_4 as well as to an increase in ionic strength that results in a decrease in the respective activity coefficients (eq 2).[2] With further increases in H_2SO_4 concentration (about 15 mass % to about 50 mass %), the solubility decreases because of a combination of effects such as changes in activity coefficient and common-ion salting-out; and when the concentration of H_2SO_4 goes to very high values (about 50 mass % or higher), the solubility increases again because of the formation of $CaSO_4\cdot nH_2SO_4$ complexes.[4−6]

Finally, upon temperature elevation, the solubility curves basically follow the same trend with the solubility increasing with temperature.[26]

2. Experimental Section

Generally, there are two ways to determine the solubility: one is the precipitation method and the other is the dissolution method. The dissolution method is thought to be more reliable because it avoids the complications arising from a reactive process such as precipitation. In this work, the dissolution method was used.

The experiment setup consisted of (i) a 2-L Applikon autoclaveable glass reactor and (ii) a filtration unit. The glass reactor was equipped with a reflux condenser for recollecting the water vapor. Heating was provided with circulating oil, which was maintained hot with a Cole-

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

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Table 1. Review of Literature on the Solubilities of Calcium Sulfates in Aqueous Solution + H_2SO_4[a]

reference	calcium sulfate(s)	experimental conditions
Kleinert and Wurm[7]		aqueous system H_2SO_4 + Na_2SO_4 + $CaSO_4$ at (45, 60, and 80) °C
Marshall and Jones[2]	DH, AH, HH	DH: (0 to 1.0) *m* H_2SO_4 at (25, 30, 40, 45, 50, 60) °C HH: (0 to 1.0) *m* H_2SO_4 at 125 °C AH: (0 to 1.2) *m* H_2SO_4 at (150, 200, 250, 300, 350) °C
Augustyn and Fligier [8]	AH	aqueous system H_2SO_4 + H_2SiF_6 + $CaSO_4$ at (0, 20, 50, and 70) °C
Zdnaovskii et al. [9−13]	DH, AH, HH	(0 to 40) mass % H_2SO_4 at (25, 50,75,95) °C for DH, AH, and HH
Ostrovskii et al.[4]		(100, 98 and 94) mass % H_2SO_4 at (40 to 80) °C
Schaefre and Hunger [14]	AH	(0 to 10) mass % H_2SO_4 containing (0 to 40) g $NaSO_4$ or $MgSO_4$ at 25 °C
Beremzhanov and Kruchenko [15 − 17]	DH, HH	(0 to 10) mass % H_2SO_4 and (0 to 55) mass % HNO_3 at (25, 40, 50, and 60) °C
Zemelman [18]		aqueous system H_2SO_4 + H_3PO_4 + $CaSO_4$ at different system
Tsikaeva [5]	AH	(65 to 95) mass % H_2SO_4 at (40, 80, and100) °C
Dvegubskii and Shchiponiova[19]		concentrated H_2SO_4 at (120 to 180) °C
Wehde and Stichlmair [1]		(0 to 90) mass % H_2SO_4 at (10 to 80) °C; above 40 mass % H_2SO_4 at (90, 100, 110, 120) °C; and $CaSO_4$ + $FeSO_4$ + H_2SO_4 + H_2O system
Khavskii et al.[20]	DH	(0 to 0.255) mol·L^{-1} H_2SO_4 at (25 to 90) °C
Zhang and Muhammed[3]	DH	aqueous HNO_3 containing $Ca(NO_3)_2$, H_3PO_4, H_2SO_4 at 25 °C
Huang and Luo[6]	AH	96 mass % H_2SO_4 at (10 to 200) °C
Mutalala et al.[21]	DH	H_2SO_4 and/or $ZnSO_4$ at (25 to 60) °C
Kojima et al.[22]	HH	HNO_3 with or without (0 to 1) mol·L^{-1} H_2SO_4 at 100 °C
Calmanovici et al.[23]	DH	mixture of (0 to 41.4) mass % H_3PO_4 and (0 to 7.8) mass % H_2SO_4 at (20, 50, and 70) °C
Martynowicz et al.[24]	DH, HH	mixture of H_3PO_4 and H_2SO_4 at (75 and 90) °C
Dutrizac[25]	DH	(0 to 0.6) mol·L^{-1} H_2SO_4 at (25 to 95) °C (0.8, 1.2, 1.6, 1.8) mol·L^{-1} H_2SO_4 at (25 to 90) °C, 0.8 mol·L^{-1} to 90 °C mixture of H_2SO_4 with $ZnSO_4$, or $MnSO_4$ or $MgSO_4$

[a] The units in the original sources are preserved.

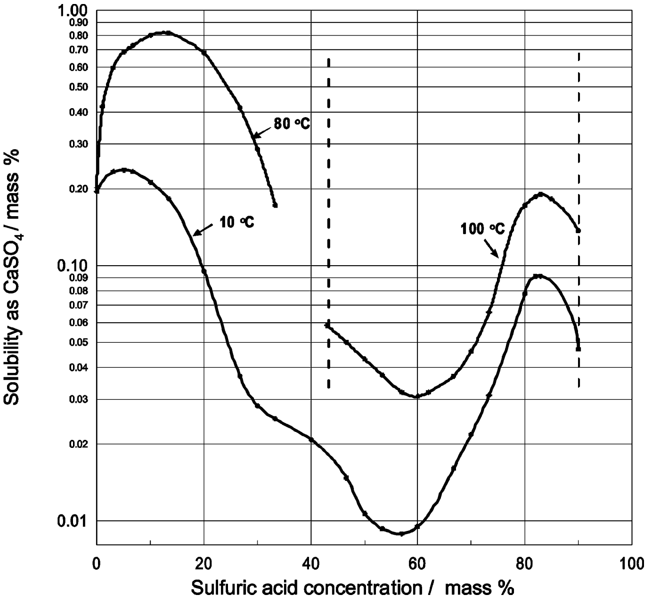


Figure 1. Solubility curves of calcium sulfate(s) in H_2O (1) + H_2SO_4 (2) solutions as a function of H_2SO_4 concentrations at various temperatures (after Wehde and Stichlmair).[1]

Parmer bath and circulator. The temperature control stability is ±0.03 °C. Around 20 g of calcium sulfate dihydrate or hemihydrate was introduced into 500 mL of H_2SO_4 solution (measured at 20 °C) that was preheated to (25, 70, or 100) °C accordingly. At different temperatures (25 and 100 °C), the effect of retention time to allow equilibration was first investigated in 1.5 mol·L^{-1} (1.59 mol·kg^{-1} or 13.49 mass %) H_2SO_4 solution by sampling at different time intervals. When optimum retention time was determined, other concentrations such as (0, 0.1, 0.25, 0.4, 0.5, 0.6, 0.8, 1.0, 1.1, 1.2, 1.3, 1.4, 1.6, 1.8, 2.4, 3.0, and 6.0) mol·L^{-1} were studied. The solids were filtered with cellulosic filter papers from OSMONICS Inc. with a porosity of 0.10 μm (cat. no. E01WP02500). For tests above room temperature, the filtration unit including the filtrate was heated with heating tape. When necessary, solid samples were collected and subjected to XRD for phase characterization.

The final analysis of Ca and S was done with ICP-AES. The solubility was expressed as an equivalent amount of $CaSO_4$ based on the measured Ca abundance. The density values used to convert among different units such as g·L^{-1}, mol·L^{-1}, mass %, and mol·kg^{-1} were calculated with OLI StreamAnalyzer[27] and verified with a few experimental data points obtained by measuring the weights of sulfuric acid solutions, which were saturated with calcium sulfate in 2-L volumetric flasks at (20 and 100) °C, followed by filtration removal of undissolved solids. The uncertainty of the measured density values was within ±0.0015 g·cm^{-3}. The density of the saturated solution at 100 °C, ρ_s (100 °C), can be correlated to the H_2SO_4 concentration from c = (0 to 6.0) mol·L^{-1} with the following empirical equation:

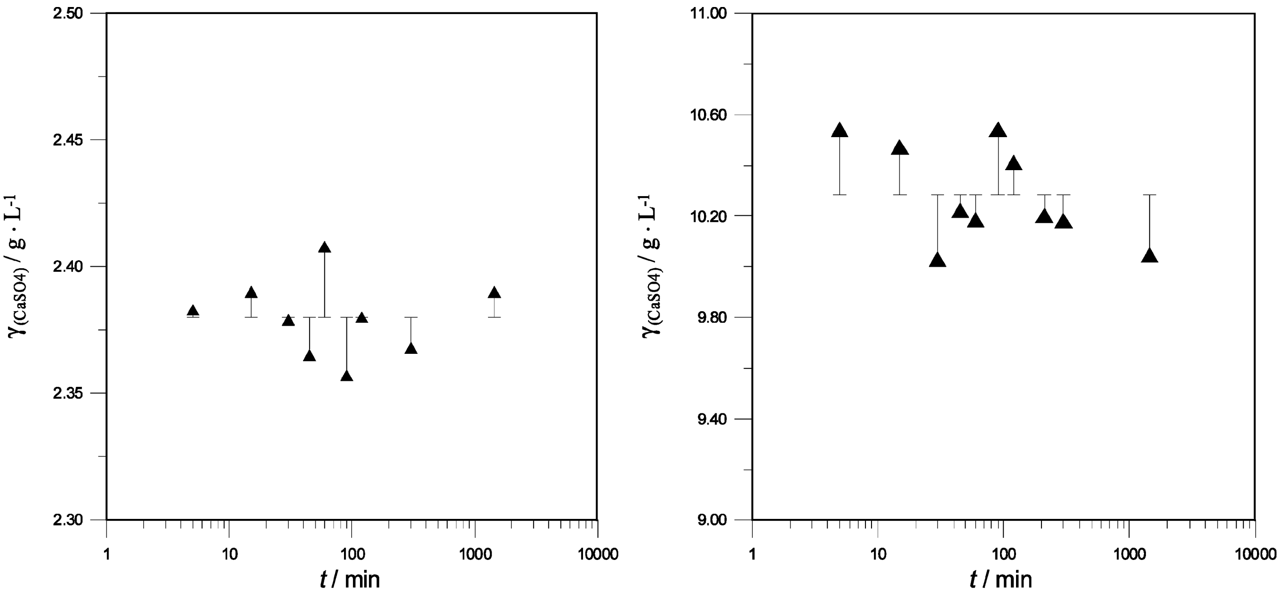
$$\rho_s(100\ °\text{C}) = 0.9610 + 0.0565c - 0.0008c^2 \qquad (5)$$

with a standard deviation of 0.0013 g·cm^{-3}.

3. Results and Discussion

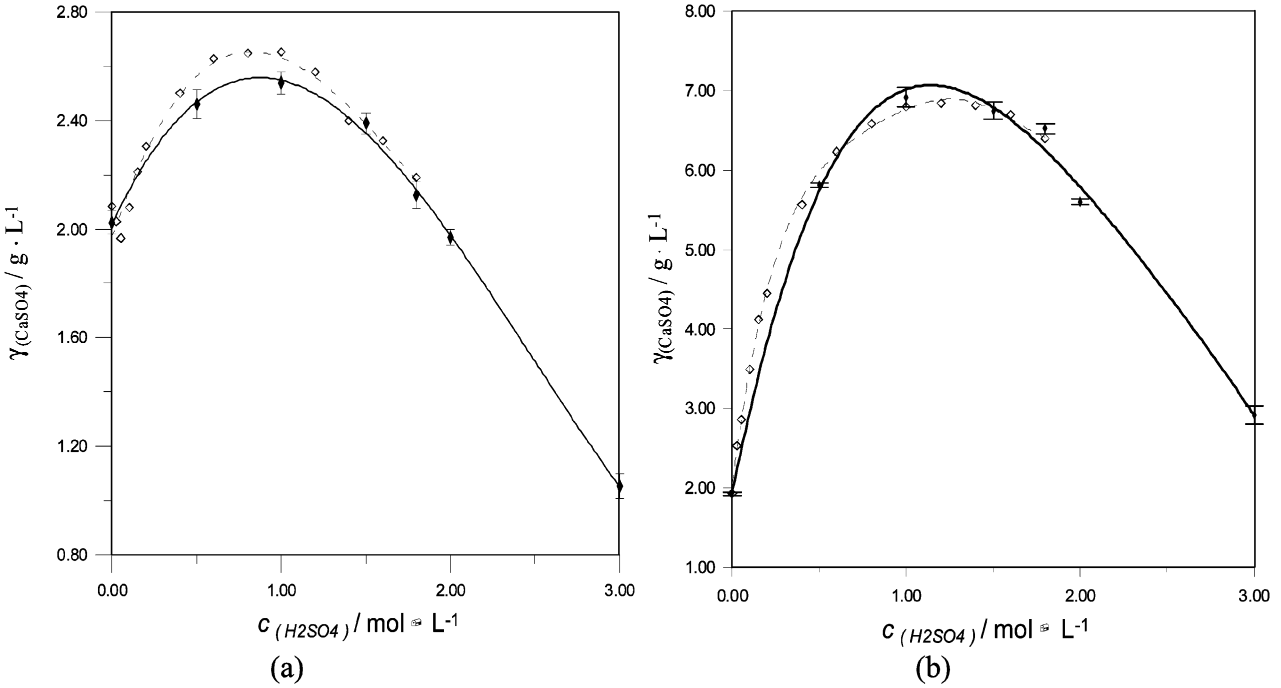
As shown in Figure 2, either starting material, dihydrate or hemihydrate, can saturate the sulfuric acid solution in a very short period of time, around 5 min. This conclusion was also indirectly supported by the work of Sullivan et al.,[28] in which they found that the "equilibrium" of hemihydrate in phosphoric acid was established within 3 min. In this work, avoided using the term "equilibrium" because hemihydrate is a metastable phase and the only final stable phase at the equilibrium point is anhydrite under such conditions.[29,30] No phase change was detected under the tested conditions. The variation of the measured data is attributed to experimental errors such as volumetric sampling, dilution, and ICP stability.

On the basis of the results of the equilibration time tests, the retention time for the following tests was set at 2 h with samples taken at (60, 90, and 120) min. There were



(a) (b)

Figure 2. Effect of equilibration time on $CaSO_4$ solubility at (25 and 100) °C: (a) obtained with dihydrate in 1.5 mol·L^{-1} H_2SO_4 at 25 °C; average value = 2.380 g·L^{-1}; standard deviation (σ/g·L^{-1}) = 0.0154; coefficient of variation = 0.646%; (b) obtained with hemihydrate in 1.5 mol·L^{-1} H_2SO_4 at 100 °C; average value = 10.284 g·L^{-1}; standard deviation (σ/g·L^{-1}) = 0.184; coefficient of variation = 1.787%.



(a) (b)

Figure 3. Dihydrate solubility data in H_2SO_4 solutions measured at (25 and 70) °C: (a) 25 °C, ◆, this study; ◇, Dutrizac;[25] (b) 70 °C, ◆, this study; ◇, Dutrizac.[25]

three replicate measurements that were averaged to get the final solubility value for each H_2SO_4 concentration.

Measurements at 25 °C and 70 °C were made for the purpose of confirmation. As can be seen in Figure 3, the data collected in this work exhibit good reproducibility behavior and compare reasonably well with published data.

XRD analysis found dihydrate to be the only phase at the end of each test independent of temperature (25 °C and 70 °C) and H_2SO_4 concentration (tested from 0 to 1.5 mol·L^{-1}). However, at 100 °C, dihydrate was metastable only at zero acidity. All other acid concentrations resulted in the conversion of the dihydrate to the hemihydrate or anhydrite (Table 2).[29,30] However, hemihydrate remained metastable (within the 2-h testing time) in the concentration range (0 to 1.8 mol·L^{-1}) at 100 °C (Table 3). The solubility was found to be almost the same for both starting materials (Figure 4).

The solubility data (as equivalent $CaSO_4$) of calcium sulfate in sulfuric acid solutions at 100 °C is given in Tables 2 and 3, where solubilities are expressed in, respectively, g·L^{-1}, mass %, and mol·kg^{-1}; here mass % of $CaSO_4$ is defined as $100w_1 = 100 \cdot \text{mass}_{CaSO_4}/(\text{mass}_{H_2SO_4} + \text{mass}_{H_2O} + \text{mass}_{CaSO_4})$. It was decided to present solubility data in such way that they are both practical (when expressed in g·L^{-1}) and consistent with thermodynamics (when expressed in molality or mass fraction units). Such multiple unit rep-

Table 2. Solubility of Calcium Sulfate (1) (Added as a Dihydrate) in Water (3) + H_2SO_4 (2) and Density of Saturated Solution at 100 °C, ρ_s(100 °C)

solution parameters				solubility as $CaSO_4$ in different units[c]			solid phase after 2 h equilibration (by XRD)
c_2/mol·L^{-1} [a]	m_2/mol·kg^{-1}	$100w_2$	ρ_s (100°C)/g·cm^{-3} [b]	γ_1/g·L^{-1}	$100w_1$	m_1/mol·kg^{-1}	
0.00	0.00	0.00	0.9593	2.012 ± 0.082	0.210	0.0154	DH
0.10	0.10	0.97	0.9665	4.210 ± 0.173	0.436	0.0323	DH + HH
0.25	0.25	2.42	0.9733	5.934 ± 0.279	0.610	0.0459	DH + HH
0.40	0.41	3.83	0.9848	7.485 ± 0.165	0.760	0.0581	DH + HH
0.50	0.51	4.76	0.9900	9.131 ± 0.139	0.922	0.0712	HH
0.60	0.61	5.68	0.9930	10.917 ± 0.139	1.099	0.0857	HH
0.80	0.83	7.49	1.0073	11.100 ± 0.125	1.102	0.0876	HH
1.00	1.04	9.25	1.0180	11.510 ± 0.098	1.131	0.0916	HH
1.10	1.15	10.12	1.0235	11.400 ± 0.191	1.114	0.0911	HH
1.20	1.26	10.97	1.0272	11.434 ± 0.182	1.113	0.0919	HH
1.30	1.37	11.82	1.0342	11.000 ± 0.180	1.064	0.0887	HH
1.40	1.48	12.66	1.0395	10.850 ± 0.157	1.044	0.0879	HH
1.50	1.59	13.49	1.0434	10.340 ± 0.156	0.991	0.0842	HH
1.60	1.70	14.30	1.0503	9.910 ± 0.408	0.944	0.0810	HH
1.80	1.93	15.91	1.0582	8.995 ± 0.116	0.850	0.0743	HH
2.40	2.64	20.54	1.0902	6.343 ± 0.199	0.582	0.0538	AH
3.00	3.38	24.87	1.1221	3.643 ± 0.274	0.325	0.0318	AH
6.00	7.90	43.64	1.2700	0.730 ± 0.018	0.057	0.0075	AH

[a] Refer to 20 °C. [b] Density of saturated solution at 100 °C, ρ_s (100 °C), is estimated with the aid of OLI. [c] Solubility values are averaged values of the samples at (60, 90, and 120) min.

Table 3. Solubility of Calcium Sulfate (1) (Added as a Hemihydrate) in Water (3) + H_2SO_4 (2) and Density of Saturated Solution at 100 °C, ρ_s(100 °C)

solution parameters				solubility as $CaSO_4$ in different units[c]			solid phase after 2 h equilibration (by XRD)
c_2/mol·L^{-1} [a]	m_2/mol·kg^{-1}	$100w_2$	ρ_s (100°C)/g·cm^{-3} [b]	γ_1/g·L^{-1}	$100w_1$	m_1/mol·kg^{-1}	
0.00	0.00	0.00	0.9593	2.012 ± 0.082	0.210	0.0154	HH
0.10	0.10	0.97	0.9665	4.200 ± 0.142	0.435	0.0323	HH
0.25	0.25	2.42	0.9733	6.006 ± 0.027	0.617	0.0465	HH
0.40	0.41	3.83	0.9848	7.500 ± 0.119	0.762	0.0582	HH
0.50	0.51	4.76	0.9900	9.431 ± 0.136	0.953	0.0735	HH
0.60	0.61	5.68	0.9930	10.117 ± 0.199	1.019	0.0794	HH
0.80	0.83	7.49	1.0073	11.100 ± 0.119	1.102	0.0876	HH
1.00	1.04	9.25	1.0180	11.410 ± 0.274	1.121	0.0908	HH
1.10	1.15	10.12	1.0235	11.400 ± 0.241	1.114	0.0911	HH
1.20	1.26	10.97	1.0272	11.405 ± 0.225	1.110	0.0917	HH
1.30	1.37	11.82	1.0342	11.220 ± 0.296	1.085	0.0905	HH
1.40	1.48	12.66	1.0395	11.020 ± 0.188	1.060	0.0892	HH
1.50	1.59	13.49	1.0434	10.840 ± 0.268	1.039	0.0883	HH
1.60	1.70	14.30	1.0503	10.740 ± 0.215	1.023	0.0877	HH
1.80	1.93	15.91	1.0582	10.590 ± 0.233	1.001	0.0875	HH
2.40	2.64	20.54	1.0902	6.243 ± 0.106	0.573	0.0530	AH
3.00	3.38	24.87	1.1221	3.543 ± 0.116	0.316	0.0309	AH
6.00	7.90	43.64	1.2700	0.740 ± 0.034	0.058	0.0076	AH

[a] Refer to the temperature of 20 °C. [b] Density of saturated solution at 100 °C, ρ_s (100 °C), is estimated with the aid of OLI. [c] Solubility values are averaged values of the samples at (60, 90 and 120) min.

resentation makes comparison with literature data easier. Graphical plots are shown as well in Figure 5. It was found that, in the lower range of H_2SO_4 concentration from c = (0 to 3.0) mol·L^{-1}, the solubility data could be empirically fit with a third-degree polynomial:

$$\gamma_{CaSO_4}/\mathrm{g{\cdot}L^{-1}} = 1.596c^3 - 10.817c^2 + 18.533c + 2.193 \quad (6)$$

with a standard deviation of (σ/g·L^{-1}) = 0.336. If in terms of m = (0 to 3.5) mol·kg^{-1} the solubility can be expressed as

$$m_{CaSO_4}/\mathrm{mol{\cdot}kg^{-1}} = 0.0098m^3 - 0.0722m^2 + 0.1356m + 0.0176 \quad (7)$$

with a standard deviation of (σ/mol·kg^{-1}) = 0.0029.

Unfortunately, there is no literature data for 100 °C to compare with the data obtained in this work. Wehde and Stichlmair did not provide numerical results in their paper;[1] it is almost impossible to extract with accuracy data from their plotted solubility curves (refer to Figure 1). Dutrizac listed a series of fitting equations[25] that permitted us to calculate the solubility of calcium sulfate in g·L^{-3} $CaSO_4$ at 90 °C. His data are plotted in Figure 5. Zdanovskii et al.[10] reported data in terms of mass % for both hemihydrate and dihydrate at 95 °C. However, Marshall and Jones reported their data in terms of mol·kg^{-1} of $CaSO_4$ for hemihydrate at 125 °C. [2] It is rather surprising to see that their data at 125 °C are “in very good agreement” with our result at 100 °C. The reason for this agreement could be found in the later work of Marshall and Jones,[31] where it was reported that there is only small change in solubility over the temperature range of (125 to 350) °C; this

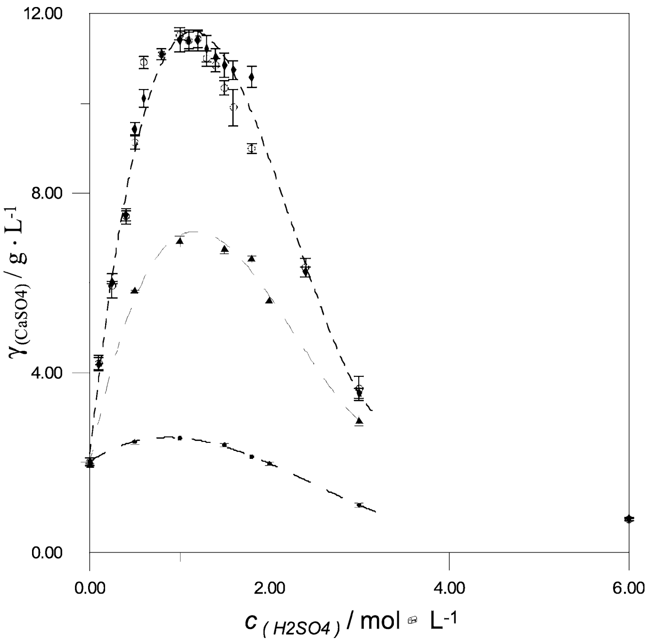


Figure 4. $CaSO_4$ mass per unit volume solubility in (0 to 6.0) mol·L^{-1} H_2SO_4 as a function of temperature: ◆, 100 °C with hemihydrate; ○, 100 °C with dihydrate; ▲, 70 °C with dihydrate; ●, 25 °C with dihydrate.

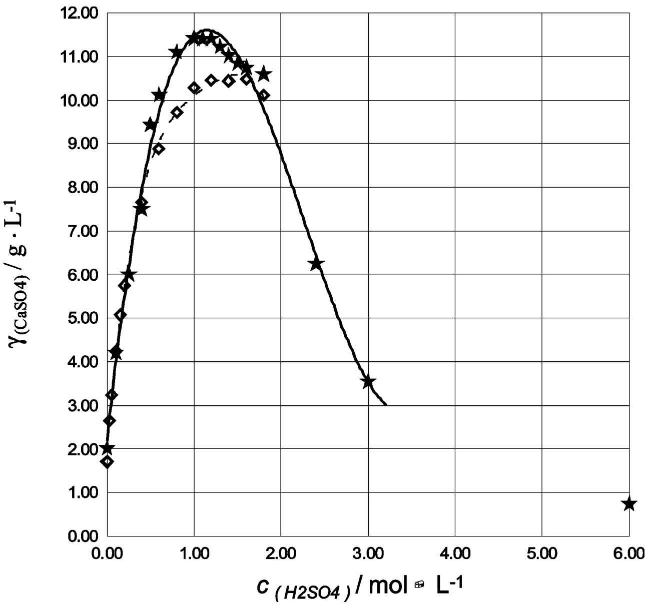


Figure 5. $CaSO_4$ solubility at 100 °C in (0 to 6.0) mol·L^{-1} H_2SO_4: ★, this study, with hemihydrate at 100 °C; ◇, Dutrizac, with dihydrate at 90 °C. [25]

temperature range can be extended to (100 to 350) °C if the results of this work are included. The effect of temperature in the range of (25 to 100) °C is better illustrated with the plots of Figure 4.

4. Conclusions

Independent of the starting material used (i.e., dihydrate or hemihydrate), the sulfuric acid solution was saturated in a very short period of time, around 5 min.

The solubility of calcium sulfate (more specifically, calcium sulfate hemihydrate) in H_2SO_4 solutions having a concentration range of (0 to 3.0) mol·L^{-1} or (0 to 3.5) mol·kg^{-1}at 100 °C was determined for the first time. It should be noted that if the starting material is in the form of dihydrate or hemihydrate the equilibrating phase is anhydrite at the 2-h testing interval in the H_2SO_4 solutions with concentrations of $\gtrsim$2.0 mol·L^{-1}.

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