Solubility Measurements for Calcium Sulfate Dihydrate in Acid Solutions at 20, 50, and 70 °C

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Solubilities of calcium sulfate dihydrate were measured in mixtures of sulfuric and phosphoric acids at 20, 50, and 70 °C. The measurements were carried out according to a factorial design of experiments, where the H_3PO_4 content varied within the range 0–41.4 mass % and the H_2SO_4 content varied within the range 0–7.8 mass %.

Introduction

Calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), commonly called gypsum, is an important byproduct of phosphoric acid manufacture. Since it crystallizes in the so-called dihydrate process of phosphoric acid production, among others, the knowledge of its solubility in acid solutions is of major importance. Very few papers in the literature deal with the solubility of calcium sulfates in acid solutions (*1, 2*). Data presented by Taperova and Shulgina (*1*) concern the solubility of calcium sulfates (various hydrate forms) in phosphoric acid solutions. Kurteva and Brutskus (*2*) have obtained the solubility of calcium sulfate dihydrate in different acid solutions by "the crystallization method" as described by Nyvlt (*3*). In the operating field investigated by these latter researchers, calcium sulfate dihydrate mostly exists as a metastable phase whereas calcium sulfate hemihydrate ($CaSO_4 \cdot {}^1/_2H_2O$) and anhydrite ($CaSO_4$) are the unstable and the stable phases, respectively. In the operating conditions of the dihydrate process, these hydrates may undergo the following transformation:

$$CaSO_4 \cdot {}^1/_2H_2O \text{ (unstable)} \rightarrow CaSO_4 \cdot 2H_2O \text{ (metastable)} \rightarrow CaSO_4 \text{ (stable)}$$

So the crystallization technique may generate incorrect results since the nature of the formed compound is not well controlled.

The purpose of this paper is to present solubility data of calcium sulfate dihydrate over a wide range of the following parameters: phosphoric and sulfuric acid concentrations and temperature. The solubility determination was done by the classic dissolution method.

Experimental Section

Design of Experiments. The solubility measurements were done according to a factorial design of experiments (*4*), so that major and differential effects can be studied.

Measurements of the solubility of calcium sulfate dihydrate were made at 20, 50, and 70 °C in aqueous phosphoric acid solutions of 0.0, 13.8, 27.6, and 41.4 mass % and in sulfuric acid solutions of 0.0, 2.0, 3.9, 5.9, and 7.8 mass %. All concentrations are expressed as mass percentage given as mass of the constituent per mass of the liquid phase.

Each measurement was repeated three times. The pH values of the solutions were also measured.

Experimental Procedure. The experimental method used for the solubility determinations consists in maintaining, at a fixed temperature, a stirred solution containing some excess of the solid solute until equilibrium is reached, after which the concentration of the solution is measured.

A sample of 2.0 ± 0.1 g of calcium sulfate dihydrate supplied by Prolabo (purity >99%) was introduced in a 100-mL Erlenmeyer flask. The calcium sulfate dihydrate was dissolved in 50 ± 1 cm^3 of acid solution, prepared within the appropriate concentrations as established in the design of experiments. The solutions were prepared from analytical grade acids with an accuracy of ±0.7 mass % H_3PO_4 and of ±0.2 mass % H_2SO_4. The acids used for the preparation of the solutions are phosphoric acid supplied by Prolabo with a minimum claimed purity of 75 mass % H_3PO_4 and sulfuric acid supplied by Prolabo with a minimum claimed purity of 98 mass % H_2SO_4. The pH of the solutions was measured at 20 °C with a precision of ±0.01. The Erlenmeyer flasks containing the solute and the solution were introduced into the experimental shaking device which was maintained at the desired temperature with an accuracy of ±0.5 °C. About 8 h of intimate contact between solid and liquid phases was required to reach equilibrium. Preliminary tests showed that this period is sufficient to obtain equilibrium in the mixtures with no appreciable polymorphic transformations of the calcium sulfate dihydrate to other hydrate forms. The nature of the solid calcium sulfate in the mixture was verified by X-ray diffractometry. The equilibrium mixture was allowed to stand still for about 12 h to enable any finely dispersed solid to settle. Three samples of the clear supernatant liquid were carefully withdrawn and immediately weighed and diluted in bidistilled water to avoid any further precipitation. These solutions were then analyzed by atomic absorption in order to measure the calcium concentration. The accuracy of this determination is estimated to be ±0.006 mass % Ca.

Results and Discussion

Calcium concentration in the equilibrium solution is a measure of the solubility of calcium sulfate. The sulfate concentration in solution was calculated supposing congruent dissolution of calcium sulfate. With the total calcium and sulfate content in solution at equilibrium, we may calculate an apparent solubility constant (K) as follows:

$$K = [Ca]_t[SO_4]_t$$

where $[Ca]_t$ is the total concentration of calcium species in solution (mass %) and $[SO_4]_t$ is the total concentration of sulfate species in solution (mass %). That is why their charges are left out. The apparent solubility constant (K) is a convenient representation of solubility data of inorganic compounds. It is defined by analogy with the solubility

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Table I. Solubility of Calcium Sulfate Dihydrate in Acid Solutions at 20, 50, and 70 °C

H_3PO_4 content (mass %)	pH[a]	20 °C			50 °C			70 °C		
		−log(*K*)	$[SO_4]_t$ (mass %)	$[Ca]_t$ (mass %)	−log(*K*)	$[SO_4]_t$ (mass %)	$[Ca]_t$ (mass %)	−log(*K*)	$[SO_4]_t$ (mass %)	$[Ca]_t$ (mass %)
0.0	5.46	2.073	0.142	0.059	2.056	0.145	0.061	2.119	0.135	0.056
	0.60	0.914	2.137	0.057	0.627	2.252	0.105	0.488	2.334	0.139
	0.38	0.599	4.146	0.061	0.285	4.290	0.121	0.127	4.407	0.169
	0.22	0.416	6.150	0.062	0.089	6.310	0.129	−0.067	6.435	0.181
	0.14	0.285	8.153	0.064	−0.038	8.315	0.131	−0.210	8.460	0.192
13.8	0.52	1.172	0.402	0.167	0.779	0.632	0.263	0.667	0.719	0.300
	0.27	0.845	2.159	0.066	0.532	2.306	0.127	0.345	2.444	0.185
	0.14	0.689	4.119	0.050	0.331	4.263	0.109	0.140	4.395	0.165
	−0.01	0.572	6.105	0.044	0.189	6.249	0.104	0.000	6.376	0.157
	−0.10	0.505	8.093	0.039	0.101	8.231	0.096	−0.097	8.359	0.150
27.6	0.20	1.096	0.439	0.183	0.674	0.713	0.297	0.584	0.790	0.329
	0.02	0.954	2.126	0.052	0.534	2.305	0.127	0.328	2.459	0.191
	−0.17	0.849	4.083	0.035	0.457	4.199	0.083	0.234	4.324	0.135
	−0.25	0.805	6.062	0.026	0.365	6.168	0.070	0.133	6.282	0.117
	−0.34	0.773	8.050	0.021	0.316	8.143	0.059	0.086	8.239	0.100
41.4	−0.17	1.269	0.359	0.150	0.796	0.620	0.258	0.726	0.672	0.280
	−0.34	1.189	2.075	0.031	0.714	2.210	0.087	0.440	2.368	0.153
	−0.45	1.265	4.032	0.013	0.647	4.131	0.055	0.440	4.206	0.086
	−0.65	1.131	6.029	0.012	0.602	6.098	0.041	0.452	6.138	0.057
	−0.70	1.063	8.026	0.011	0.674	8.063	0.026	0.499	8.094	0.039

[a] The first row refers to pure bidistilled water, and the following ones correspond to aqueous acid solutions.

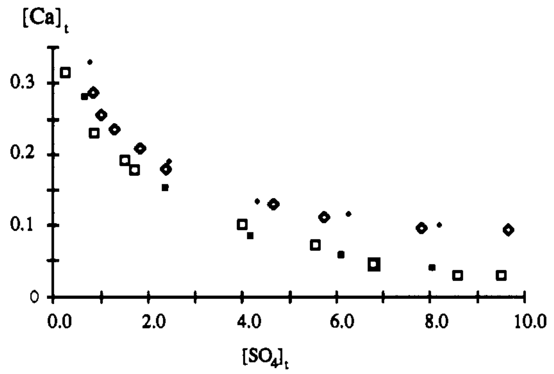

Figure 1. Solubility of calcium sulfate dihydrate at 70 °C: (■) 41.4 mass % H_3PO_4 (this work), (◆) 27.6 mass % H_3PO_4 (this work), (□) 41.4 mass % H_3PO_4 (2), (◇) 27.6 mass % H_3PO_4 (2).

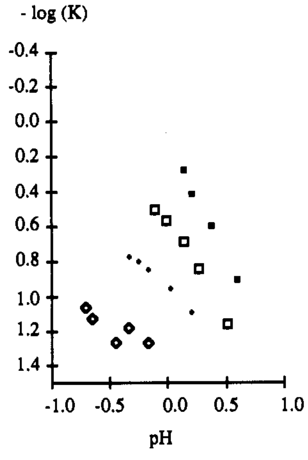

Figure 2. Solubility of calcium sulfate dihydrate as a function of pH and H_3PO_4 content at 20 °C: (■) 0.0 mass % H_3PO_4, (◆) 27.6 mass % H_3PO_4, (□) 13.8 mass % H_3PO_4, (◇) 41.4 mass % H_3PO_4.

product, but it considers the total concentration of calcium- and sulfate-containing species, ion complexes included, instead of activities.

The experimental results concerning calcium sulfate dihydrate solubility are shown in Table I.

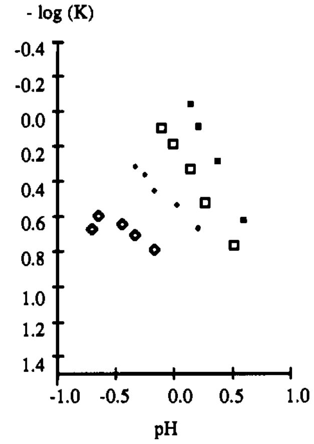

Figure 3. Solubility of calcium sulfate dihydrate as a function of pH and H_3PO_4 content at 50 °C: (■) 0.0 mass % H_3PO_4, (◆) 27.6 mass % H_3PO_4, (□) 13.8 mass % H_3PO_4, (◇) 41.4 mass % H_3PO_4.

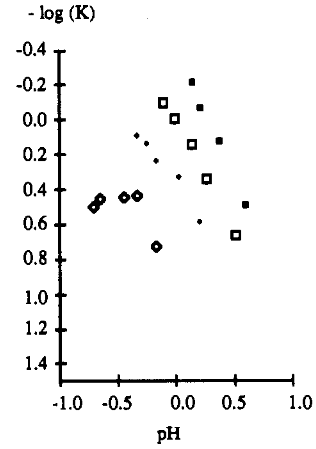

Figure 4. Solubility of calcium sulfate dihydrate as a function of pH and H_3PO_4 content at 70 °C: (■) 0.0 mass % H_3PO_4, (◆) 27.6 mass % H_3PO_4, (□) 13.8 mass % H_3PO_4, (◇) 41.4 mass % H_3PO_4.

Some of our results are compared with those presented by Kurteva and Brutskus (2) in Figure 1. This figure concerns the solubility of calcium sulfate dihydrate at 70 °C. Since there is good agreement between these data, the solubility of calcium sulfate dihydrate may be determined either by crystallization or by dissolution. Nevertheless, the dissolution method seems to be better since it is more reliable over a wide range of the independent variables. The variation of *K* in a function of pH may be seen in Figures 2–4 at 20, 50, and 70 °C, respectively. In these figures, it can be observed that the solubility of dihydrate increases with decreasing values of P_2O_5 content. Moreover, the solubility increases slightly when the temperature rises.

The influence of the independent variables on the solubility of calcium sulfate dihydrate was determined with the analysis of variance method. Phosphoric and sulfuric acid concentrations and temperature have a significant effect on the solubility as well as their two-factor interactions, within a significance level of 98%. The effect of the sulfuric acid concentration is predominant although it is ambiguous. The presence of sulfuric acid in the solution reduces the solubility of calcium sulfate dihydrate crystals because of the common ion (SO_4^{2-}) effect. On the other hand, increasing amounts of this acid decrease the pH of the solution which may increase the calcium sulfate solubility. This is why the pH is an important parameter to be taken into account when determining the solubility of calcium sulfate dihydrate in acid solutions.

Literature Cited

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