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Solubilities of Magnesium Sulfite Hydrates

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Solubilities of $MgSO_3·6H_2O$ in water were determined in the temperature range from 43 to 94 °C where this hydrate is metastable. Solubilities of $MgSO_3·6H_2O$ and $MgSO_3·3H_2O$ in an aqueous solution containing 150 g of $MgSO_4$/L were determined from 30 to 95 °C.

Introduction

Hydrates of magnesium sulfite are encountered during desulfurization of flue gases by the magnezite method (*1*). Reaction of SO_2 from flue gases with an aqueous suspension of MgO results in formation of $MgSO_3·6H_2O$ or $MgSO_3·3H_2O$ according to the prevailing conditions. Since partial oxidation of sulfite takes place during this process, MgO is, in fact, suspended in an aqueous solution of magnesium sulfate containing approximately 150 g of $MgSO_4$/L.

$MgSO_3·6H_2O$ and $MgSO_3·3H_2O$ represent the stable phases in contact with aqueous solution below and above 42 °C, respectively (*2–4*). Both phases tend to convert into the stable phase at temperatures beyond their respective stability region (*5*). However, the conversion rate of the metastable phase is not fast enough to prevent establishing the metastable equilibrium between the solid and its aqueous solution for a limited period of time (*6*). Therefore, the solubility of the metastable phase is of practical interest.

Solubilities of magnesium sulfite hydrates reported in the literature do not cover the range of temperature sufficiently wide for practical purposes. Therefore, the solubilities of $MgSO_3·3H_2O$ and $MgSO_3·6H_2O$ in media encountered in practice, i.e. water and an aqueous solution of $MgSO_4$, were determined up to nearly 100 °C.

Experimental Section

A 100-mL sample of either distilled water or a solution containing 150 g of $MgSO_4$/L was placed in a jacketed glass vessel and agitated by a double-blade stirrer. A dilute aqueous glycerol was circulated through the vessel jacket from a constant-temperature bath operating with an accuracy of ±0.1 °C. When the liquid in the vessel reached a required temperature, an excess (30–50% over expected solubility) of solid $MgSO_3·6H_2O$ or $MgSO_3·3H_2O$, as appropriate, was quickly added. Samples of liquid were withdrawn at regular intervals from the vigorously stirred suspension and analyzed for the sulfite content by iodometric titration.

Preparation of $MgSO_3·6H_2O$. A solution of 756 g of Na_2SO_3 (Analar grade) in 5 L of distilled water was rapidly added to a solution of 1220 g of $MgCl_2·6H_2O$ (Analar grade) in 2 L of distilled water placed in a stirred vessel. This mixture was kept at 25 °C for approximately 1 h, and then the formed solid phase was separated, washed with 2-propanol, and dried at 60 °C. The resulting phase was pure crystalline $MgSO_3·6H_2O$ as confirmed by the appearance of crystals (uniform tetrahedrons about 100 μm in size) and X-ray diffraction analysis.

Table 1. Solubilities of $MgSO_3·6H_2O$ in Water

t, °C	g of $MgSO_3$/L	*t*, °C	g of $MgSO_3$/L
43.0	11.04	79.0	40.17
51.4	14.19	84.1	53.73
61.4	19.30	88.0	71.21
71.5	28.87	94.0	95.19

Table 2. Solubilities of $MgSO_3·6H_2O$ in Solution of 150 g of $MgSO_4$/L

t, °C	g of $MgSO_3$/L	*t*, °C	g of $MgSO_3$/L
31.8	12.84	75.5	62.90
44.4	19.86	80.6	78.83
53.5	27.85	85.6	100.56
61.6	36.00	89.2	113.95
69.9	50.71		

Table 3. Solubilities of $MgSO_3·3H_2O$ in Solution of 150 g of $MgSO_4$/L

t, °C	g of $MgSO_3$/L	*t*, °C	g of $MgSO_3$/L
33.4	15.88	76.8	15.70
42.1	15.24	85.5	15.88
53.6	14.73	96.2	17.39
64.2	14.73		

Preparation of $MgSO_3·3H_2O$. A 660-g sample of solid $MgSO_3·6H_2O$ was introduced into 2.4 L of distilled water at 75 °C and agitated for 3 h. The solid phase was filtered, washed with 2-propanol, and dried for 2 h at 60 °C. The solid phase was pure trihydrate as confirmed by the appearance of crystals (aggregates of hexagonal plates about 10 μm in size) and X-ray diffraction analysis.

Results

The concentration of dissolved magnesium sulfite in a solution increased rapidly at the beginning of the experiment, and soon reached a constant value if the dissolving solid was the stable phase. However, if the solid was metastable, the solution concentration started to decrease after reaching a maximum due to conversion of the metastable to the stable, less soluble phase. The maximum concentration of solution attained was taken as the solubility of the respective solid phase at a given temperature.

The solubilities at each temperature were determined by three independent experiments. Agreement among these results was always better than 2%. Values reported in Tables 1–3 represent the arithmetic mean of three results obtained for each temperature.

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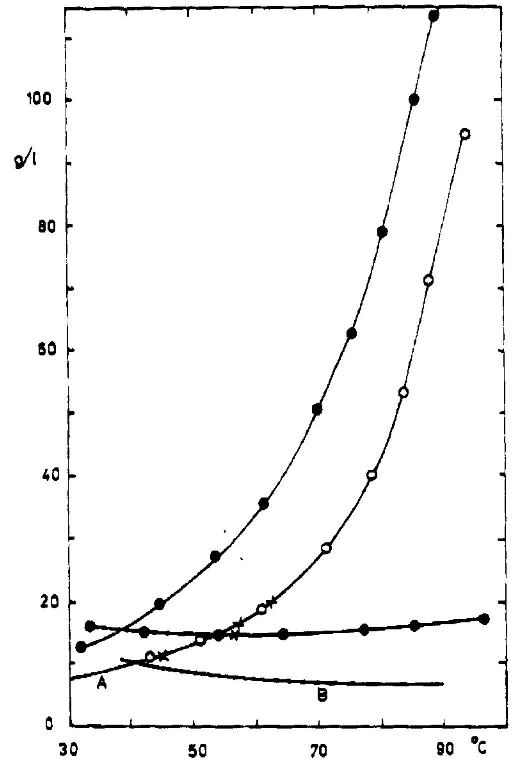

Figure 1. Solubilities of $MgSO_3 \cdot 6H_2O$ and $MgSO_3 \cdot 3H_2O$ in water and a solution of magnesium sulfate containing 150 g of $MgSO_4$/L. $MgSO_3 \cdot 6H_2O$ in water: our data (○), Higasawa (×), Broul et al. (A). $MgSO_3 \cdot 6H_2O$ in $MgSO_4$ solution: our data (●). $MgSO_3 \cdot 3H_2O$ in water: Broul et al. (B). $MgSO_3 \cdot 3H_2O$ in $MgSO_4$ solution: our data (⊗).

Values quoted in Table 1 represent the solubilities of $MgSO_3 \cdot 6H_2O$ in the temperature range where this hydrate is the metastable phase. Our values agree with the data reported in ref 2, as shown in Figure 1. Curves A and B in Figure 1, showing the solubilities of $MgSO_3 \cdot 6H_2O$ and $MgSO_3 \cdot 3H_2O$, respectively, in water within their stability regions, were taken from ref 4. These data expressed originally in mass % were converted to grams per liter using the density of an aqueous $MgSO_4$ solution with a concentration identical to the $MgSO_3$ solution concentration (7).

As shown in Figure 1, solubilities of both hydrates in water are enhanced by the presence of $MgSO_4$. Also, the addition of $MgSO_4$ in water to form a 150 g of $MgSO_4$/L solution lowers the trihydrate–hexahydrate transition temperature from 42 to 38 °C.

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