

SOLUBILITIES OF MAGNESIUM SULFITE

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Abstract

Literature data of solubility of MgSO_3 in water and in aqueous solutions of MgSO_4 have been correlated. Magnesium sulfite forms hexahydrate (stable below 40°C) and trihydrate (above 40°C), nevertheless, metastable hexahydrate can precipitate at temperatures significantly higher than this transition temperature. Magnesium sulfate increases the solubility of the sulfite.

Keywords: magnesium sulfate, magnesium sulfite, metastable solid, solubility

Introduction

Among several methods, developed for desulfurization of fuel gases from power-stations or metallurgical works, the magnesite method has to be mentioned [1–7]. Sulfur dioxide is absorbed in a suspension containing [8] about 2% MgSO_3 and 10–15% MgSO_4 ; the concentration of $\text{Mg}(\text{HSO}_3)_2$ then rises up to 2.5%, the suspension is neutralised by magnesite and after crystallization of a part of MgSO_3 recycled again to the absorption tower. Because of the possible metastability of the magnesium sulfite [8, 9], making this process difficult, reliable solubility data are of the highest importance.

The aim of this paper is to process available literature data on the magnesium sulfite solubility in water and in aqueous solutions of the magnesium sulfate by using an equation based on thermodynamics for temperature dependence of data and a semiempirical equation for the effect of an admixture in order to allow their interpolation and possibly slight extrapolation.

Solubilities in the system $\text{MgSO}_3\text{--H}_2\text{O}$

Literature data of this system [7–12] show that the magnesium sulfite crystallizes in two forms: below $40\text{--}42.5^\circ\text{C}$ the hexahydrate $\text{MgSO}_3\cdot 6\text{H}_2\text{O}$ is the stable equilibrium solid phase whereas above this temperature the stable phase is the trihydrate, $\text{MgSO}_3\cdot 3\text{H}_2\text{O}$. However, the metastable hexahydrate crystallizes [9, 13, 14] often even at temperatures higher than 50°C .

Solubility data given in the literature are correlated by using an equation

$$\log x_1 = A + B/T + C \log T \quad (1)$$

with x_1 representing the mole fraction of the solute, T absolute temperature (K) and A , B and C adjustable constants, given in Table 1. Correlated data are plotted in Fig. 1. It is obvious that even with very different values of constants evaluated for individual data sets the corresponding constants result in very close plots.

Table 1 Coefficients of Eq. (1) for literature data

A	B	C	Reference
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$			
-82.918	2668.11	28.698	[6]
-84.269	2720.25	29.175	[10]
-73.251	2265.85	25.336	[12]
-404.226	17057.94	139.008	[8]
$\text{MgSO}_3 \cdot 3\text{H}_2\text{O}$			
-79.595	4179.381	25.435	[6]
-79.271	4167.06	25.323	[10]

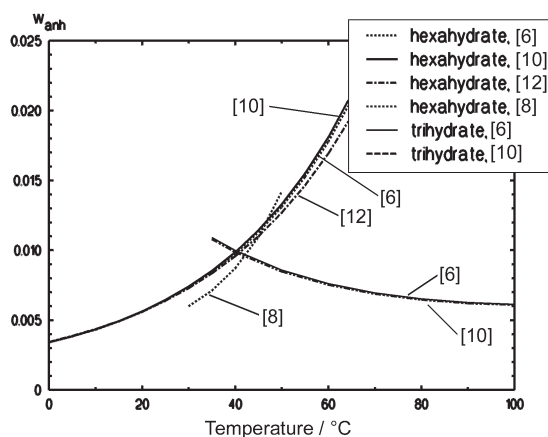


Fig. 1 Solubility of MgSO_3 in water (w_{anh} , kg of anhydrous substance/kg H_2O)

Solubilities in the system $\text{MgSO}_3\text{--MgSO}_4\text{--H}_2\text{O}$

Solubility data published in literature [6, 7, 12] are given for the temperature 40, 50 and 60°C. Comparison of these data as well as data published in literature [8] lead to the conclusion that the precipitating solid phase was the metastable hexahydrate even in this temperature range. For the correlation of data a modified method has been used [15].

$$w_{1eq}/w_{10} = 1 + k_1 w_2 + k_2 w_2^2 \tag{2}$$

where w_{1eq} is the solubility of $MgSO_3$ in the ternary system (kg of anhydrous substance/kg H_2O), w_{10} is the solubility of $MgSO_3$ in pure water at the same temperature and w_2 is the concentration of $MgSO_4$ (kg of anhydrous substance/kg H_2O). Adjustable constants k_1 and k_2 are given in Table 2. Corresponding solubility curves are plotted in Fig. 2.

Table 2 Constants of Eq. (2) for individual literature data.

	k_1	k_2	Reference
	7.60	-24.84	[7]
	8.75	-29.08	[12]
	9.29	-32.84	[6]
Average	8.54	-28.92	

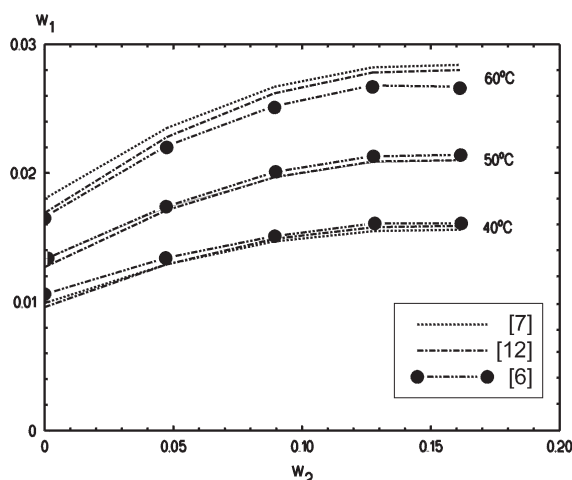


Fig. 2 Solubility of $MgSO_3 \cdot 6H_2O$ (w_1 , kg of anhydrous substance/kg H_2O) in aqueous solutions of $MgSO_4$ (w_2 , kg of anhydrous substance/kg H_2O)

Conclusions

1. Solubility data of the system $MgSO_3-H_2O$ can be satisfactorily correlated by using Eq. (1). They show two different phases – hexahydrate and trihydrate with the transition point slightly above $40^\circ C$. Metastable hexahydrate can precipitate even at much higher temperatures.
2. Solubility of $MgSO_3$ is risen by addition of $MgSO_4$. The data can be satisfactorily correlated by Eq. (2). The coefficients of the equation are just slightly dependent on

temperature in the given temperature range. Literature data show that in the ternary system the metastable hexahydrate precipitates at temperatures even well above 40°C.

References

- 1 Sulphur, 105 (1973) 45.
- 2 G. G. Bratchikov, M. D. Babushkina and Zh. A. Koval, USSR patent 449014 (1974).
- 3 I. S. Shah, US patent 3655338 (1972).
- 4 Batelle Memorial Inst., NTIS Bull. PB-176-843 (6/1966).
- 5 York Res. Corp. Stamford, Conn., Res. Report Y-8513 (1975).
- 6 P. S. Lowell and F. B. Meserole, EPA Report 600/7-77-109 (9/1977).
- 7 V. A. Pinaev, Zhur. Prikl. Khim., 36 (1963) 2116; *ibid.* 37 (1964) 1361; *ibid.* 43 (1970) 871.
- 8 J. Nývlt, R. Rychlý and J. Kříčková, Chem. průmysl (Prague), 27 (1977) 552.
- 9 O. Söhnel and A. Rieger, Crystal Res. Technol., 28 (1993) 487.
- 10 M. Broul, J. Nývlt and O. Söhnel, Solubility in Inorganic Two-Component Systems. Elsevier Amsterdam and Academia Prague, 1981.
- 11 O. Söhnel and A. Rieger, J. Chem. Eng. Data, 39 (1994) 161.
- 12 H. Hagiwara, Sci. Repts. Tohoku Univ., 2 (1934) 132.
- 13 G. G. Glamery, Report TVA EPA-R2-73-244 (1973).
- 14 J. Nývlt, Crystal Res. Technol., 32 (1997) 695.
- 15 J. Nývlt, Chem. průmysl (Prague), 29 (1979) 238.