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Saturation Composition and Density Data for the Sodium Sulfate + Sulfuric Acid + Methanol System

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The solubility of sodium sulfate in the concentrated sulfuric acid + methanol system was determined at temperatures of (273, 293, 303, 313, and 323) K. The saturation densities were also determined. The solubility increased with increasing temperature until about 323 K. When the result of this study was compared with an earlier study[7] of solubility for the sodium sulfate + water + aqueous methanol system, the solubility values of the present system were greater at all comparable temperatures. This may be due to the fact that "like dissolves like". In this case, the SO_4^{2-} anion is common to both sulfuric acid and sodium sulfate, whereas in the former study, it is not. Moreover, compounds containing the SO_4^{2-} anion are known to be less soluble in water.

Introduction

It has been shown by several authors[1−3] that high-purity crystals can be produced at ambient temperature by the addition of a low-molecular-weight organic substance (solvent) to an inorganic solution. The low-molecular-weight substance, usually called the "salting-out" substance, changes the solubility of the inorganic solute in the solution, thereby crystallizing it. A low-molecular-weight substance is often recommended to prevent the formation of a two- or more-phase system with its own complex separation requirement.

The 1990s saw the publication of two important studies—the continuous salting-out of sodium sulfate from spent acid by the addition of methanol[4] and the double reaction of seawater bittern with methanol[5]—that specifically applied this technique to the production of sodium sulfate. This procedure has been applied to a batch process for a study that has spanned several years by one of the authors. Batch crystallization has been described[6] as simple and flexible and often involves lower process development and operating costs.

In an earlier study,[7] accurate solubility and density data for sodium sulfate in water, aqueous methanol, and anhydrous methanol systems were measured. In an attempt to study the application of salting-out crystallization to the treatment of waste streams from the manufacture of paper by the kettle sulfate process, it was found that there are not enough published data for the sodium sulfate + concentrated sulfuric acid + methanol system in the open literature. The effluent stream from the kettle sulfate process is essentially sodium sulfate dissolved in concentrated sulfuric acid. This study reports data for the system sodium sulfate + 10.5 M sulfuric acid + methanol.

Experimental Section

The solubility of sodium sulfate + concentrated sulfuric acid + methanol was found by equilibrating anhydrous sodium sulfate (ACS grade granular, 95% purity) in a solution (a mixture of certified 9.95 to 10.5 M sulfuric acid and 99.3% ACS HPLC-grade methanol) contained in an agitated solubility cell. The cell was a 500 mL Erlenmeyer flask with a ground glass stopper (to prevent the loss of methanol by evaporation) cork and submersible magnetic stirrer. The flasks were immersed in a thermostatic bath (containing either ice chips for temperatures below room temperature or warm water for temperatures above room temperature) controlled to ±0.25 K. Various quantities of methanol were weighed and mixed with concentrated sulfuric acid to make solutions of different mass ratios (0.0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, and only methanol) of the methanol/sulfuric acid mixture. It should be noted that sulfuric acid was added to the methanol and not vice versa. The solutions (200 g each) were measured and placed in an Erlenmeyer flask. The flasks with submersible magnetic stirrers were placed in the controlled thermostatic bath at the desired temperature. Large quantities of anhydrous sodium sulfate were measured and placed in an empty beaker and placed in the bath to attain the desire temperature. After about 4 h, the salt had attained the temperature of the water bath. This step was necessary to minimize energy loss due to mixing at different temperatures. Large portions of the salt were measured into 11 flasks. The flasks and their contents, with the stirrer on, were allowed to sit in the bath for 12 h. There was still undissolved salt in some of the flasks at the end of this period. For cases where there was no undissolved salt present, more sodium sulfate was added, and the system was allowed to sit for another 12 h. At the end of the "sit-in" period and with the presence of undissolved salt, it is assumed that the solution has attained saturation at the desired temperature.

Table 1. Density of 99.3 Mass % ACS HPLC-Grade Methanol at Various Temperatures

T/K	ρ/g·cm^{-3}
273	0.800
298	0.787
303	0.786
313	0.779
323	0.768

The undissolved salt was removed from the cell by vacuum filtering with a Buchner funnel and a filter flask. Because the cells were not insulated, there was a temper-

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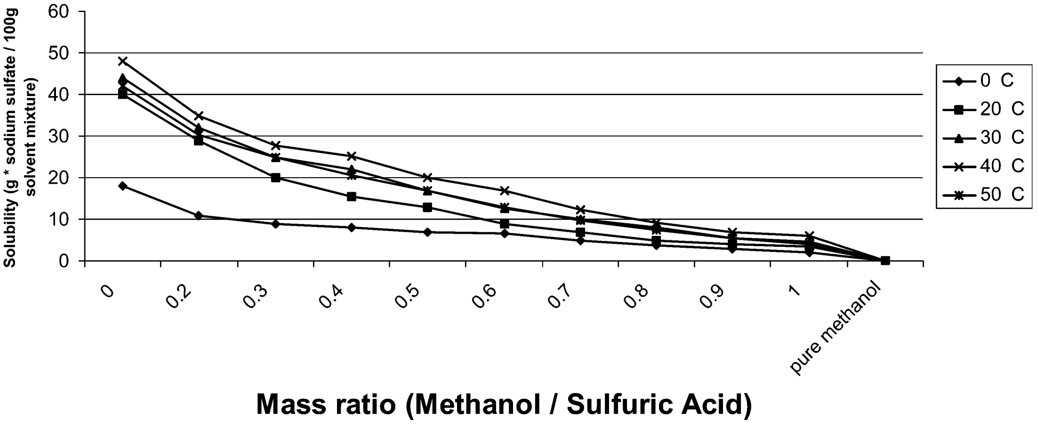

Figure 1. Solubility of sodium sulfate in methanol and 10.5 M sulfuric acid at various temperatures.

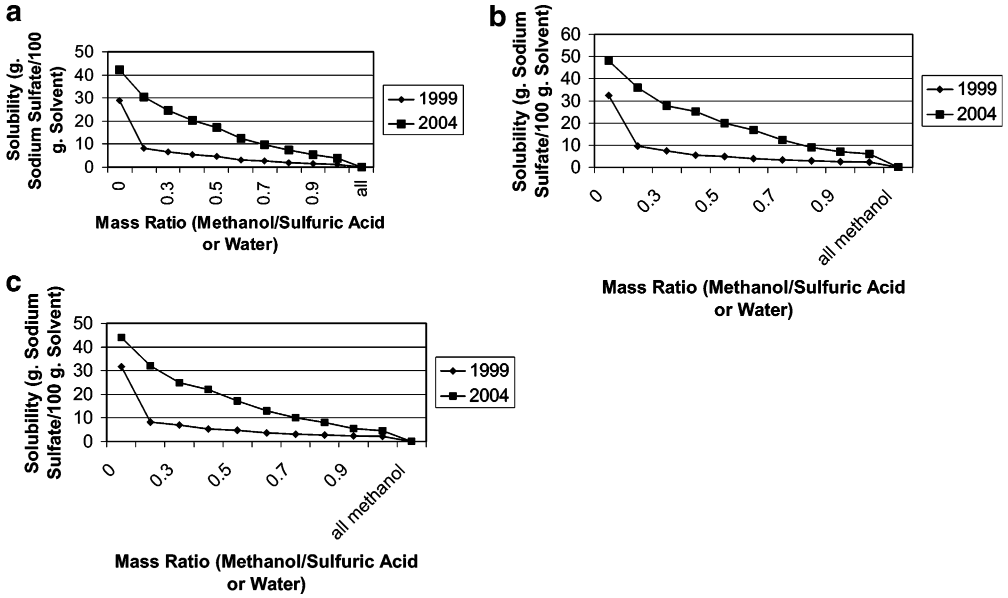

Figure 2. (a) Graphical comparison of solubility at 303 K. (b) Graphical comparison of solubility at 313 K. (c) Graphical comparison of solubility at 323 K.

Table 2. Solubility of Sodium Sulfate in Various Mass Ratios of Methanol to a 10.5 M Sulfuric Acid Mixture and Density of the Sodium Sulfate + 10.5 M Sulfuric Acid + Methanol System at Various Temperatures

mass ratio of solvent mixtures	solubility of sodium sulfate	density
CH_3OH/H_2SO_4	g of $NaSO_4$/100 g of solvent	ρ/g·cm^{-3}
	T = 273 K	
0.0	18	1.251
0.2	11	1.165
0.3	9.0	1.105
0.4	8.0	1.079
0.5	7.0	1.057
0.6	6.5	1.038
0.7	5.0	1.021
0.8	3.7	1.006
0.9	3.0	0.995
1.0	2.0	0.976
pure methanol	0.01	0.807
	T = 298 K	
0.0	40	1.451
0.2	29	1.321
0.3	20	1.278
0.4	15.5	1.231
0.5	13	1.182
0.6	9.0	1.095
0.7	7	1.067
0.8	5	1.015
0.9	4	1.001
1.0	3.5	0.986
pure methanol	0.017	0.810
	T = 303 K	
0.0	44	1.567
0.2	32	1.365
0.3	25	1.301
0.4	22	1.293
0.5	17	1.258
0.6	12.5	1.223
0.7	10	1.121
0.8	8	1.087
0.9	5.5	1.025
1.0	4.5	1.010
pure methanol	0.018	0.797
mass ratio of solvent mixtures	Solubility of sodium sulfate	density
CH_2OH/H_2SO	g of $NaSO_4$/100g of solvent	ρ/g·cm^{-3}
	T = 313 K	
0.0	48	1.673
0.2	35	1.464
0.3	27.8	1.333
0.4	25.2	1.306
0.5	20	1.287
0.6	16.9	1.253
0.7	12.3	1.220
0.8	9.2	1.106
0.9	7.0	1.068
1.0	6.0	1.028
pure methanol	0.02	0.781
	T = 323 K	
0.0	42	1.502
0.2	30.4	1.347
0.3	24.8	1.300
0.4	20.5	1.290
0.5	17	1.256
0.6	13	1.245
0.7	9.8	1.118
0.8	7.3	1.076
0.9	5.3	1.024
1.0	4	0.987
pure methanol	0.019	0.776

ature rise or fall of about 1.5 K for conditions above or below room temperature, respectively, during the filtration operation. The filtrate was then allowed to sit in the bath until it attained the desired temperature. This is usually achieved within 2 h. There was no crystal precipitation observed during the filtration operation. This was a necessary and required step for better accuracy and improved confidence in the result.

After 2 h, samples were withdrawn, and the solubility of sodium sulfate was determined by the wet residue method. This method involved evaporating a weighed sample of the solution to dryness, followed by weighing the residue, which happened to be the salt.

The density of the solution was also measured using a digital density meter (Paar DMA 38), which gives a claimed precision of $\pm 10^{-3}\,\mathrm{g \cdot cm^{-3}}$. All density measurements have an expanded uncertainty (ku_j) of 0.0236, whereas the composition uncertainty is 0.05. A second thermostatic bath was used as a duplicate for the above test run. The solubility and density data from both experiments were compared. When there was more than a 1% difference in the solubility for each pair, the run was repeated. For differences of less than 1%, the arithmetic mean of the pair was taken to represent the solubility.

The solubility and density of sodium sulfate in a mixture of methanol and 9.5 to 10.5 M sulfuric acid were determined at five temperatures (273, 298, 303, 313, and 323 K). These data are presented in Table 2, and the solubility data are also shown graphically in Figure 1. The density of the pure methanol used in this study is shown in Table 1. As can be observed from this Table, increasing temperature results in decreasing density. In most common substances, this is true because the volume of the species increases with temperature because of volume expansion, whereas the mass (quantity of matter contained in the substance) remains constant. The solubility and density of the system (Table 2) increases with temperature until about 313 K, when it starts decreasing. A possible explanation for this trend is that the mixed solvent volume may have increased because of thermal expansion. Thus, a sodium sulfate molecule can interstitially and/or substitutionally attach itself easily to the solvent structure. Above 313 K, the solvent mixture temperature is closer to the boiling point of methanol, and thus sodium sulfate becomes less soluble. Figure 2 shows graphical comparisons of the solubility data obtained in this study with that from an earlier study[7] at comparable temperatures.

Literature Cited

(1) Alfassi, Z. B.; Ata, I. Separation of the system NaCl − NaBr − NaI by 'solventing-out' from aqueous solution. *Sep. Sci. Technol.* **1983**, *18*, 598−601.

(2) Brenner, D. K.; Anderson, E. W.; Lynn, S.; Prausnitz, J. M. Liquid−Liquid Equilibrium for 1-Propanol, 2-Propanol, or 2-Methylpropan-2-ol *J. Chem. Eng. Data* **1992**, *27*, 419−422.

(3) Taboada, M. C.; Palma, P. A.; Graber, T. A. Crystallization of K_2SO_4 by cooling and salting-out using 1 -propanol in a calometric reactor. *Cryst. Res. Technol.* **2003**, *38*, 1, 21−29.

(4) Mina-Mankarious, G.; Pinder, K. L. Salting-out crystallization of sodium sulfate. *Can. J. Chem. Eng.* **1991**, *69*, 308−324.

(5) Fernandez-Lozano, J. A. Sodium sulfate from bittern by methanol *Chem. Eng. Commun.* **1996**, *154*, 87−89.

(6) Mohammed, H. A.; Abdel-Jabber, N.; Takrouri, K.; Nar, A. Model-based optimal cooling strategy for batch crystallization process *Trans. IchemE.* **May 2003**, *81A*, 578−584.

(7) Okorafor, O. C. Solubility and Density Isotherms for the Sodium Sulfate−Water−Methanol System *J. Chem. Eng. Data* **1999**, *44*, 489−490.

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