J. Chem. Eng. Data **1999,** *44,* 488−490

Solubility and Density Isotherms for the Sodium Sulfate−Water−Methanol System

Ogbonnaya C. Okorafor

Department of Chemical Engineering, The Cooper Union, 51 Astor Place, New York, New York 10003

The solubility of sodium sulfate in water and aqueous methanol has been determined over the temperature range 10 °C to 50 °C. Also the saturated solution densities were measured. The presence of methanol was observed to reduce the solubility of the salt greatly. In fact, in pure methanol, sodium sulfate was essentially insoluble. The solubility data for the sodium sulfate−water solution were within ±1% of values in the literature. No attempt was made in the study to differentiate between the two stable salts of sodium sulfate (decahydrate and anhydrous) in the temperature range studied.

Introduction

The crystallization of soluble inorganic salts from aqueous solution by the addition of low molecular weight organic solvents (to prevent the creation of two-phase regions) is now commonly used in many chemical, pharmaceutical, and biochemical processes. This procedure has been variously called "salting-out" crystallization or "drowning-out" precipitation. It has been found that high-purity crystals are produced at ambient temperatures by this form of crystallization (Alfassi and Ata, 1983; Mydlarz et al., 1989; Mullin, 1972; Brenner et al., 1992; Korin and Soifer, 1997).

Two recent investigations, the continuous salting-out of sodium sulfate from spent acid by the addition of methanol by Mina-Mankarious and Pinder (1991) and the double reaction of bittern with methanol by Fernandez-Lozano (1996), have shown that it is possible to recover high-purity sodium sulfate crystals. This study aims to provide accurate solubility and density data for solutions of sodium sulfate in water and aqueous methanol mixtures, as an aid toward the determination of crystallization parameters for the sodium sulfate salting-out process.

Experimental Section

The solubility of sodium sulfate in water plus methanol was determined by equilibrating anhydrous sodium sulfate crystals and the solution in an agitated solubility cell. The cell was a 200-mL flat-bottom flask closed by a ground glass stopper and submersible magnetic stirrer. The flask was immersed in a thermostatic bath (containing either ice chips for temperature runs below room temperature or warm water) controlled to ±0.5 K.

Quantities of methanol were weighed and mixed with a fixed mass of water to create solutions of various mass ratio (0.0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, and pure methanol), respectively. The solutions were placed in 11 flasks, respectively. These flasks with submersible magnetic stirrers were placed in the controlled thermostatic bath at the desired temperature. A very large quantity of anhydrous sodium sulfate was measured into a beaker and placed in the bath. After about 4 h, the salt had attained

Table 1. Density of Methanol at Various Temperatures

t/°C	ρ/(g.cm)$^{-3}$	t/°C	ρ/(g.cm)$^{-3}$
10	0.798	40	0.774
20	0.794	50	0.773
30	0.783		

Table 2. Solubility of Sodium Sulfate and Density of the Sodium Sulfate, Water, and Methanol Solution Measured at 10, 20, 30, 40, and 50 °C

mass ratio solvent mixture g of MeOH/(g of water)	solubility of sodium sulfate g of Na_2SO_4/(100 g of soln)	density of soln ρ/(g·cm^{-3})	mass ratio solvent mixture g of MeOH/(g of water)	solubility of sodium sulfate g of Na_2SO_4/(100 g of soln)	density of soln ρ/(g·cm^{-3})
t = 10 °C					
0.0	8.28	1.07	0.7	1.31	0.941
0.2	4.69	1.01	0.8	0.92	0.938
0.3	3.68	0.994	0.9	0.71	0.928
0.4	2.85	0.973	1.0	0.46	0.903
0.5	2.11	0.962	pure MeOH	0.01	0.807
0.6	1.82	0.954			
t = 20 °C					
0.0	15.93	1.15	0.7	2.23	0.960
0.2	6.14	1.03	0.8	1.82	0.954
0.3	5.89	1.00	0.9	1.31	0.944
0.4	4.51	0.982	1.00	0.93	0.921
0.5	3.03	0.976	pure MeOH	0.017	0.810
0.6	2.93	0.967			
t = 30 °C					
0.0	28.89	1.28	0.7	2.8	0.964
0.2	8.34	1.07	0.8	2.0	0.958
0.3	6.81	1.03	0.9	1.4	0.950
0.4	5.32	0.991	1.0	1.01	0.931
0.5	4.65	0.986	pure MeOH	0.018	0.797
0.6	3.14	0.980			
t = 40 °C					
0.0	32.48	1.35	0.7	3.32	0.987
0.2	9.61	1.13	0.8	2.87	0.968
0.3	7.52	1.08	0.9	2.51	0.960
0.4	5.45	1.05	1.0	2.3	0.957
0.5	4.90	1.01	pure MeOH	0.02	0.781
0.6	3.84	0.991			
t = 50 °C					
0.0	31.65	1.29	0.7	3.2	0.974
0.2	8.25	1.11	0.8	2.72	0.974
0.3	6.91	1.06	0.9	2.45	0.959
0.4	5.3	1.03	1.0	2.21	0.945
0.5	4.8	1.00	pure MeOH	0.019	0.776
0.6	3.73	0.989			

10.1021/je980243v CCC: $18.00

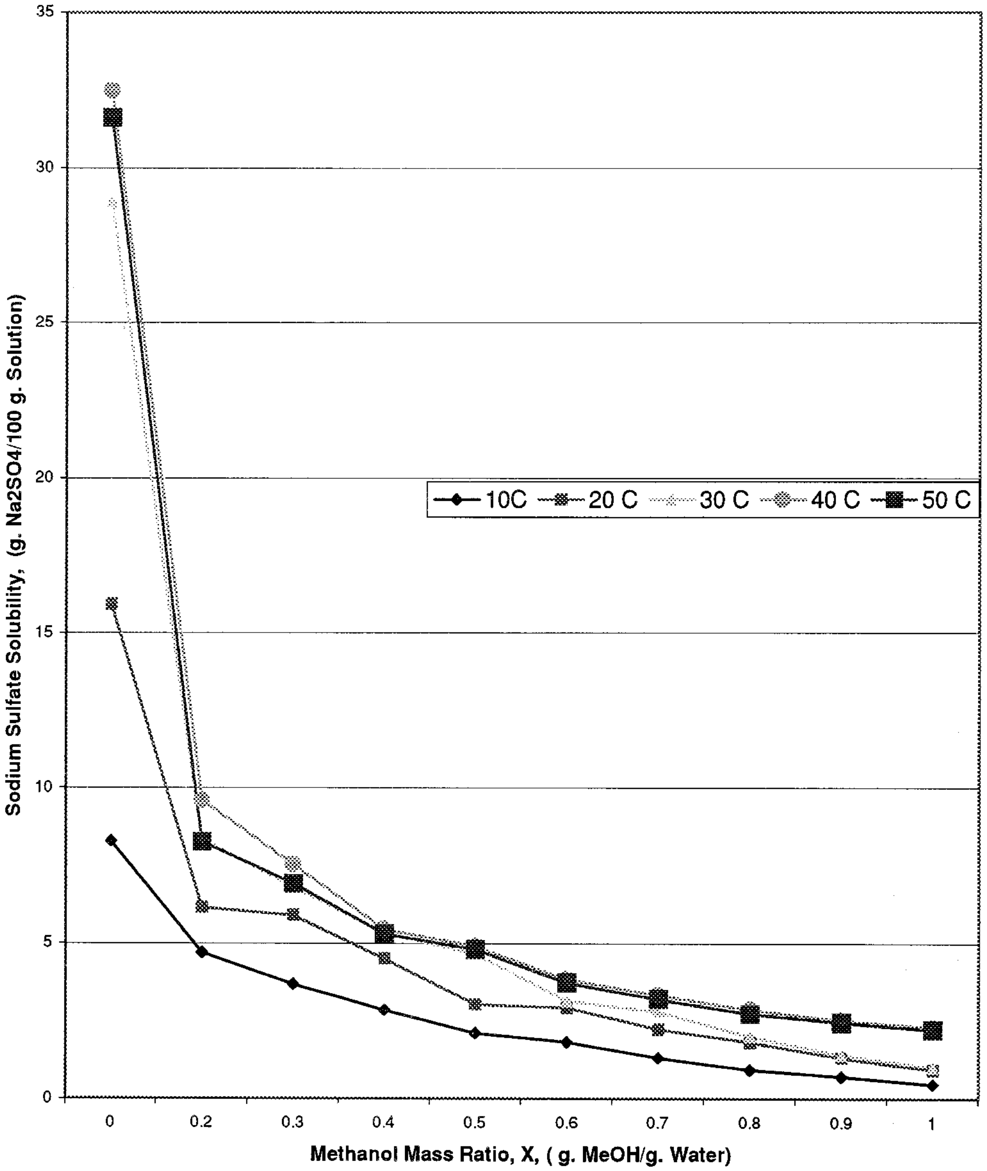

Figure 1. Solubility of sodium sulfate in aqueous methanol at 10, 20, 30, 40, and 50 °C.

Table 3. Comparison of Sodium Sulfate Solubility and Solution Density

t/°C	Broul et al. (1981)	Stephen and Stephen (1963)	Brenner et al. (1992)	von Plessen (1993)	this study
Solubility (g of Na_2SO_4/(100 g of soln))					
10		8.3		8.3	8.28
20		16.3	16	16	15.93
30	29.10	29.0		29.2	28.89
40		32.8		32.5	32.48
50		31.8		31.7	31.65
Density (ρ/(g.cm^{-3}))					
10					1.07
10.25		1.08			
15.65		1.115			
20					1.15
20.35		1.154			
30	1.2834				1.28
30.2		1.289			
35	1.3278				
40					1.35
50					1.29

the bath temperature. The salt was brought to the bath temperature in order to minimize the initial temperature drop when it was added to the solvent mixture. Large portions of the salt were measured into the 11 flasks. The flasks and their contents, with stirrer on, were allowed to sit in the bath for 24 h. At the end of this period, there was still undissolved salt in each of the flasks. Thus, it was assumed that no net salt dissolution will occur at that temperature again. A no. 3 sintered glass filter maintained at the desired temperature was used to filter the flask content. During the filtration, there was an increase in temperature of about 1 K for temperature runs below room temperature, while for runs above room temperature there was a 1 K drop. Due to this, the filtrates were allowed to sit in the bath until they regained the bath temperature. Often, this period was about an hour. At the end of the hour, samples of clear solution were withdrawn and the solubility of sodium sulfate was determined by the wet-residue method. The density of the solution was measured using a digital density meter (PAAR DMA 38), which gives a claimed precision of $\pm 10^{-3}$ g·cm^{-3}. A second thermostatic bath was used to duplicate the runs. The solubility and density data from both setups were compared. When there was more than 1% difference in either the solubility or density for each pair, the run was repeated.

No attempt was made to determine the form of sodium sulfate in each of the runs but from literature (von Plessen, 1993), only the decahydrate is stable below 32.4 °C, while the anhydrous form is stable above this temperature. This study assumed this to be true here.

The alcohol used was methanol "optima" of an assay of 99.9%, produced by Fisher Chemical. The anhydrous sodium sulfate (granular 10−60 mesh), also from Fisher, was of an assay of more than 99%. These chemicals were used without further treatment. The other solvent used was laboratory-distilled water.

Solubilities of sodium sulfate in water, aqueous methanol, and anhydrous methanol with solution densities were determined at five temperatures, viz., 10, 20, 30, 40, and 50 °C. The density of methanol at these temperatures is shown in Table 1. Sodium sulfate solubility data in water, methanol, and aqueous methanol are presented in Figure 1 and Table 2. Figure 1 has solubility data of sodium sulfate in water and aqueous methanol only. The solution densities are shown in column 3 of Table 2.

A comparison has been made of the solubility of sodium sulfate in water and solution densities from this study with others in the literature (Broul et al., 1981; Stephen and Stephen, 1963; Brenner et al., 1992; von Plessen, 1993), Table 3. For the temperature range studied, the solubility data for the sodium sulfate solution is within −0.3% of data reported by von Plessen, who provided more extensive data than other references.

Acknowledgment

I thank the following summer 'Interns' for their assistance in this study: S. Bhaerman, K. Bhatt, A. Chan, J. Eng, D. Golab, A. Jayarantnam, A. Kalitenko, J. Oliva, and S. Tam.

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Received for review October 5, 1998. Accepted January 4, 1999.

JE980243V