Solubility and Density Isotherms for Potassium Aluminum Sulfate-Water-Alcohol Systems

J. W. Mullin* and M. Šipek†

Department of Chemical and Biochemical Engineering, University College London, London WC1E 7JE, United Kingdom

The solubilities of potassium aluminum sulfate (potash alum) in water and mixtures of water-methanol, water-ethanol, and water-2-propanol have been determined over the temperature range 13-35 °C. The densities of the resulting saturated solutions have also been measured. The solubility data may conveniently be expressed, with an accuracy of ±2.5%, by a relationship of the form $\log X = K_1m + K_2m^2$, where X = ratio of the solubilities, expressed as mole fractions, of alum in the ternary (aqueous alcohol) and binary (aqueous) systems, and m is the molality of the alcohol in the aqueous solution.

Introduction

The precipitation of soluble inorganic salts from aqueous solution by the addition of an alcohol, with the dual purpose of enhancing both yield and purity, has long been considered as a possible industrial separation process (*1-3*). One such substance capable of yielding to this treatment is the hydrated double salt potassium aluminum sulfate (potash alum), $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

The object of the present work was to provide accurate solubility and density data for solutions of potash alum in water and in several alcohol-water mixtures as an aid toward the assessment of the potential of alcohol precipitation as a separation technique.

The solvents used were analytical-grade (BDH Ltd) methanol, ethanol, and 2-propanol and twice-distilled water. The potash alum was prepared as follows. Commercial pure-grade potash alum was dissolved in hot water, filtered first through a bed of active charcoal and then through a No. 3 sintered-glass filter, and crystallized by cooling. The product crystals were filtered off and then recrystallized from water.

Experimental Section

The apparatus used for the solubility determinations (Figure 1) was a small glass vessel (~50 cm³) fitted with a four-blade glass stirrer with the vessel and stirrer shaft sealed with a glycerol seal. The cell was immersed in a thermostat water bath controlled to ±0.02 °C. The procedure was as follows.

Weighed quantities of potash alum and alcohol, together with predetermined amounts of water, were charged to the cell and agitated for ~1 h. At the end of this time, as predicted, only a small amount of crystalline material was left undissolved. Small quantities of water (maximum 1 mL) were then added to the mixture at hourly intervals until all traces of crystalline material (observed under a strong back-light) had disappeared. Toward the end point, water was added dropwise. This method, when carefully performed, could reproducibly determine the solubility to a precision of at least ±0.5%.

The solubilities of potash alum in water and in aqueous mixtures of methanol, ethanol, and 2-propanol were determined at three temperatures: 15, 25, and 35 °C. The densities of the various saturated solutions produced in the solubility cell were determined with a 10-mL bicapillary pycnometer of the type described by Lipkin et al. (*4*).

Table I. Solubilities and Densities of Potash Alum in Water and Aqueous Methanol at 15, 25, and 35 °C

alum (hydrate), g/(100 g of soln)	CH_3OH, g/(100 g of soln)	H_2O, g/(100 g of soln)	density, g/cm³	10^3x_a	m
15 °C: $x_0 = 1.8092 \times 10^{-3}$, $K_1 = -0.13624$, $K_2 = 3.8963 \times 10^{-3}$					
8.713		91.286	1.0452	1.8092	
5.861	3.874	90.265	1.0226	1.2022	1.3395
4.108	7.620	88.272	1.0071	0.8421	2.6943
2.651	11.982	85.367	0.9929	0.5462	4.3807
1.813	15.761	82.426	0.9831	0.3770	5.9682
1.135	21.230	77.635	0.9721	0.2405	8.5350
25 °C: $x_0 = 2.5962 \times 10^{-3}$, $K_1 = -0.12129$, $K_2 = 2.8087 \times 10^{-3}$					
12.056		87.944	1.0600	2.5962	
9.670	2.428	87.902	1.0423	2.0527	0.8621
7.521	5.012	87.467	1.0262	1.5792	1.7884
5.588	8.314	86.098	1.0104	1.1675	3.0141
3.425	13.631	82.944	0.9909	0.7172	5.1291
2.160	19.335	78.505	0.9758	0.4587	7.6870
0.929	29.010	70.061	0.9548	0.2042	12.9238
35 °C: $x_0 = 3.7388 \times 10^{-3}$, $K_1 = -0.10320$, $K_2 = 1.6883 \times 10^{-3}$					
16.503		83.497	1.0803	3.7388	
12.844	2.902	84.254	1.0542	2.8316	1.0750
9.888	6.192	83.920	1.0325	2.1436	2.3028
6.920	10.434	82.646	1.0097	1.4823	3.9403
4.192	16.790	79.018	0.9851	0.8990	6.6319
2.475	23.352	74.173	0.9658	0.5380	9.8261
1.466	29.052	69.482	0.9514	0.3242	13.0504

Table II. Solubilities and Densities of Potash Alum in Water and Aqueous Ethanol at 15, 25, and 35 °C

alum (hydrate), g/(100 g of soln)	C_2H_5OH, g/(100 g of soln)	H_2O, g/(100 g of soln)	density, g/cm³	10^3x_a	m
15 °C: $x_0 = 1.8092 \times 10^{-3}$, $K_1 = -0.23136$, $K_2 = 6.7711 \times 10^{-3}$					
8.713		91.286	1.0452	1.8092	
5.490	3.811	90.699	1.0205	1.1295	0.9122
3.317	7.788	88.895	1.0030	0.6844	1.9018
2.082	11.731	86.187	0.9913	0.4353	2.9545
0.949	17.780	81.271	0.9780	0.2042	4.7485
25 °C: $x_0 = 2.5962 \times 10^{-3}$, $K_1 = -0.21946$, $K_2 = 7.0891 \times 10^{-3}$					
12.056		87.944	1.0600	2.5962	
10.450	1.169	88.381	1.0488	2.2284	0.2872
8.362	3.149	88.489	1.0335	1.7664	0.7725
5.012	7.493	87.495	1.0090	1.0513	1.8588
3.303	11.030	85.667	0.9952	0.6965	2.7947
1.867	16.459	81.674	0.9801	0.4021	4.3742
0.616	26.220	73.164	0.9597	0.1402	7.7787
0.573	26.302	73.125	0.9598	0.1305	7.8072
35 °C: $x_0 = 3.7388 \times 10^{-3}$, $K_1 = -0.19781$, $K_2 = 6.1938 \times 10^{-3}$					
16.503		83.497	1.0803	3.7388	
11.964	2.989	85.047	1.0442	2.6280	0.7628
8.971	5.788	85.241	1.0282	1.9428	1.4739
6.182	9.345	84.473	1.0071	1.3301	2.4013
3.730	14.602	81.668	0.9878	0.8099	3.8810
1.396	23.790	74.814	0.9614	0.3149	6.9023

† Present address: Department of Physical Chemistry, Institute of Chemical Technology, 166 28 Prague-6-Dejvice, Czechoslovakia.

0021-9568/81/1726-0164$01.25/0

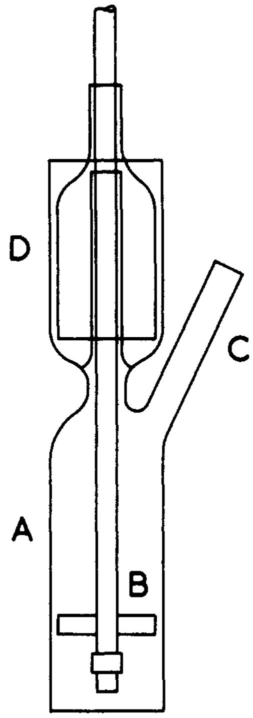

Figure 1. Solubility apparatus: (A) 50-cm³ glass cell; (B) four-bladed glass stirrer; (C) charging port; (D) glycerol seal for stirrer shaft.

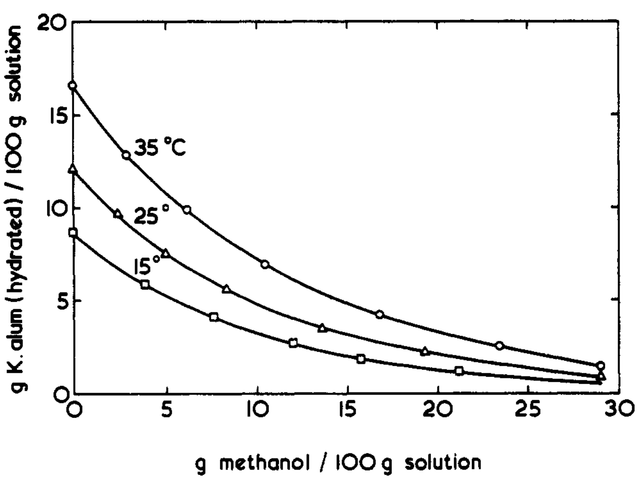

Figure 2. Solubility of potash alum in aqueous methanol at 15, 25, and 35 °C.

The data are typified by the conventional solubility curves shown in Figure 2, for aqueous methanol solutions, but the most successful correlation method was found to be through a second-order function of the form

$$\log X = K_1 m + K_2 m^2 + C \qquad (1)$$

where $X = x_a/x_0$, x_a = solubility (mole fraction) of alum in the ternary (aqueous alcohol) solution, x_0 = solubility (mole fraction) of alum in the binary (aqueous) solution, m = molality of alcohol in aqueous solution (mol of alcohol/kg of water), and K_1, K_2, and C are constants. An example of one of the quadratic regression fits is shown in Figure 3 (alum–water–methanol at 15 °C).

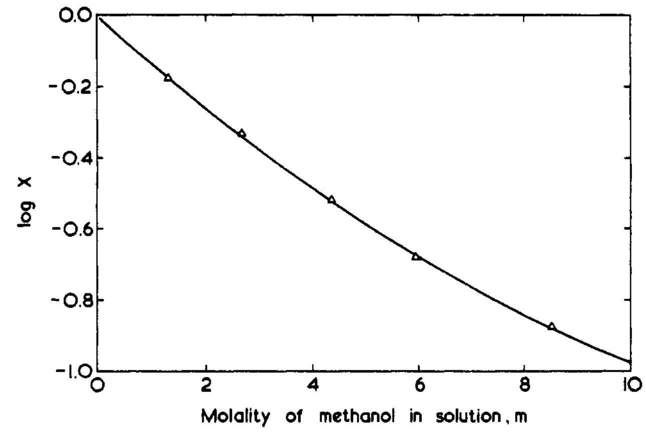

Figure 3. General correlation of potash alum solubilities in aqueous methanol at 15 °C (curve calculated according to eq 1).

Table III. Solubilities and Densities of Potash Alum in Water and Aqueous 2-Propanol at 15, 25, and 35 °C

alum (hydrate), g/(100 g of soln)	C_3H_7OH, g/(100 g of soln)	H_2O, g/(100 g of soln)	density, g/cm³	$10^3 x_a$	m
15 °C: $x_0 = 1.8092 \times 10^{-3}$, $K_1 = -0.31230$, $K_2 = 1.0310 \times 10^{-2}$					
8.713		91.286	1.0452	1.8092	
5.459	3.622	90.919	1.0209	1.1252	0.6627
3.298	7.439	89.263	1.0036	0.6839	1.3864
2.043	11.371	86.586	0.9921	0.4308	2.1847
0.919	16.981	82.100	0.9797	0.2001	3.4408
25 °C: $x_0 = 2.5962 \times 10^{-3}$, $K_1 = -0.30732$, $K_2 = 1.6656 \times 10^{-2}$					
12.056		87.944	1.0600	2.5962	
9.115	2.275	88.610	1.0396	1.9345	0.4272
6.937	4.612	88.451	1.0239	1.4641	0.8675
4.960	7.432	87.608	1.0092	1.0473	1.4113
2.953	11.711	85.336	0.9928	0.6307	2.2831
1.787	15.970	82.243	0.9810	0.3897	3.2304
0.771	24.140	75.089	0.9630	0.1778	5.3484
35 °C: $x_0 = 3.7388 \times 10^{-3}$, $K_1 = -0.26947$, $K_2 = 1.0970 \times 10^{-2}$					
16.503		83.497	1.0803	3.7388	
13.578	1.490	84.932	1.0610	3.0106	0.2919
11.044	3.628	85.328	1.0434	2.4209	0.7074
8.019	6.644	85.337	1.0224	1.7405	1.2951
5.400	10.182	84.418	1.0030	1.1708	2.0066
2.860	16.194	80.946	0.9807	0.6326	3.3281
1.240	23.652	75.108	0.9595	0.2864	5.2388

In all cases, the constant C in eq 1 was found to be insignificant, and it is thus possible to estimate the solubilities (mole fraction x_a) of alum in the aqueous alcohol systems, with a precision of ±2.5%, from the simpler relationship:

$$\log X = K_1 m + K_2 m^2 \qquad (2)$$

Values of K_1 and K_2 are listed in Tables I–III.

Literature Cited

(1) Thompson, A. R.; Molstad, M. C. *Ind. Eng. Chem.* **1945**, *37*, 1244.
(2) Thompson, A. R.; Blecharczyk, S. S. Kingston, RI, 1959, University of Rhode Island Engineering Research and Development Report No. 2.
(3) Hoppe, R. *Chem. Process Eng.* (*London*) **1968**, *49*, 61.
(4) Lipkin, H. R.; Davidson, J. A.; Harvey, W. T.; Kurtz, S. S. *Ind. Eng. Chem., Anal. Ed.* **1944**, *16*, 55.

Received for review October 14, 1980. Accepted January 12, 1981. We are indebted to the Science Research Council for financial support.