Solubility and Density Isotherms for Potash Alum-Water-Acetone

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Drowning-out precipitation provides a potentially attractive process for the production of inorganic salts. In this study the solubility of potash alum (potassium aluminum sulfate) in water and in aqueous acetone has been determined over the temperature range 15-35 °C, and the densities of the resulting saturated solutions have been measured. In all cases, the presence of acetone significantly reduces both the solubility and density of potash alum in aqueous solution. The solubility data may conveniently be expressed by a relationship of the form ln (w_{eq}) = $A + Bx + Cx^2$ with an accuracy ∓2%, where w_{eq} is the equilibrium saturation concentration of potash alum, expressed as kilograms of potash alum (hydrate) per kilogram of water, and x is the concentration of acetone expressed as kilograms of acetone per kilogram of water.

Introduction

Drowning-out precipitation of soluble inorganic salts from aqueous solution by the addition of an organic second solvent has a number of advantages over simple cooling. These generally lie in the possibility of carrying out the operation at ambient temperature and obtaining crystals of high purity. The technique is attracting the increasing attention of technologists in chemical and pharmaceutical industries (*1-8*).

Recent complementary investigations of the continuous drowning-out precipitation of potassium sulfate (*9*) and potash alum (*10*) have clearly shown that it is possible to retrieve a crystal product which is close to that obtained by cooling crystallization.

Various indirect methods of potash alum concentration measurements were investigated by Garside (*11*). The results of his work demonstrate that neither refractive index nor viscosity measurements could conveniently be made with sufficient accuracy but the measurements of electrical conductivity and solution density both appeared to be potentially promising; electrical conductivity, however, is very sensitive to changes in temperature.

The solubility of potash alum in aqueous alcohols (methanol, ethanol, and 2-propanol) was recently reported by Mullin and Šipek (*12*). The aim of the present work was to provide accurate solubility and density data for solutions of potash alum in water and aqueous acetone mixtures as an aid toward the assessment of the potential of drowning-out precipitation using organic substance as a separation technique.

Experimental Section

The solubility of potash alum in water-acetone was measured via its density measurements over the temperatures 15-35 °C. Under- and oversaturated solutions were prepared as follows. Volumetric quantities of twice-distilled water and acetone were charged to the glass flask closed by a ground glass stopper and fitted with a magnetic stirrer. Then an exactly known mass of analar grade potash alum was added to the water-acetone solution, and after dissolution of the solute, samples of clear solution were withdrawn and the sample density was measured.

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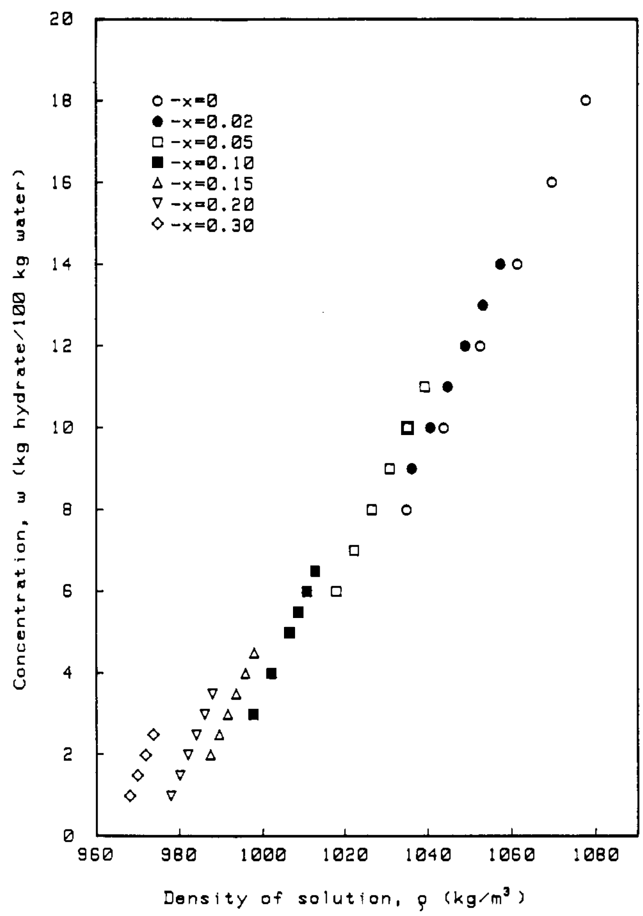

Figure 1. Density of potash alum-water and potash alum-aqueous acetone solution at 25 °C.

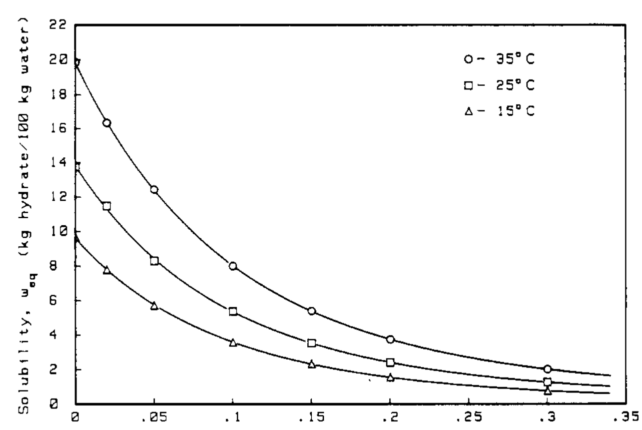

Figure 2. Solubility of potash alum in aqueous acetone at 15, 25, and 35 °C.

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Table I. Density of Under- and Supersaturated Potash Alum-Water and Potash Alum-Water-Acetone Solutions at 15, 25, and 35 °C (kg m^{-3})

θ = 15 °C

acetone concn, kg of acetone/kg of H_2O	solute concn, kg of hydrate/100 kg of H_2O											
	1	2	3	4	5	6	7	8	9	10	12	14
0				1019.298		1028.889		1038.197		1047.201	1055.937	1064.544
0.02				1016.146		1025.569	1030.116	1034.639	1039.101	1043.481		
0.05			1007.298	1011.932	1016.538	1021.030	1025.342	1029.779				
0.10	992.191	996.774	1001.243	1005.662								
0.15	987.196	991.535	995.779									
0.20	982.695	986.689	990.726									
0.30	973.956	977.741	981.099									

θ = 25 °C

acetone concn, kg of acetone/kg of H_2O	solute concn, kg of hydrate/100 kg of H_2O											
	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5
0.05											1017.968	
0.10					997.775		1002.143		1006.423	1008.580	1010.658	1012.719
0.15			987.485	989.636	991.692		995.906	997.955				
0.20	978.117	980.194	981.111	984.143	986.107	988.064						
0.30	968.299	970.153	971.995	973.857								

acetone concn, kg of acetone/kg of H_2O	solute concn, kg of hydrate/100 kg of H_2O									
	7	8	9	10	11	12	13	14	16	18
0		1035.029		1043.916		1052.624		1061.572	1069.831	1077.853
0.02			1036.202	1040.637	1044.909	1049.118	1053.317	1057.545		
0.05	1017.968	1026.700	1031.052	1035.286	1039.413					

θ = 35 °C

acetone concn, kg of acetone/kg of H_2O	solute concn, kg of hydrate/100 kg of H_2O											
	1	2	3	4	6	8	10	12	14	16	18	20
0							1040.863	1049.483	1057.730	1065.935	1073.916	1081.729
0.02						1028.252	1036.858	1045.227	1053.619	1061.597		
0.05					1014.221	1022.921	1031.473	1039.346	1047.304			
0.10				998.046	1006.470	1014.503	1022.657					
0.15	978.760	982.918		991.089	999.120							
0.20	972.908	976.876	980.985	984.809								
0.30	962.486	966.088	969.654									

Table II. Solubility and Density of Potash Alum-Aqueous Acetone Measured at 15, 25, and 35 °C

concn of acetone, kg of acetone/kg of H_2O	solubility of potash alum, kg of hydrate/100 kg of H_2O	density of satd soln, kg/m^3
	15 °C	
0	9.66	1045.669
0.02	7.78	1033.637
0.05	5.70	1019.667
0.10	3.55	1003.681
0.15	2.31	992.822
0.20	1.54	984.865
0.30	0.76	973.153
	25 °C	
0	13.72	1060.712
0.02	11.45	1045.616
0.05	8.29	1028.045
0.10	5.35	1007.556
0.15	3.51	993.849
0.20	2.39	983.712
0.30	1.25	969.223
	35 °C	
0	19.83	1081.075
0.02	16.31	1062.832
0.05	12.41	1041.055
0.10	7.99	1014.522
0.15	5.38	997.026
0.20	3.72	983.734
0.30	2.00	966.079

Table III. Coefficients of the Model Equation (1)

θ, °C	coeff of model eq 1		
	A	B	C
15	2.2609	−10.5980	7.1408
25	2.6243	−10.2610	7.5144
35	2.9868	−9.7789	7.1105

Saturated solutions of potash alum aqueous and aqueous acetone solutions were made by approaching equilibrium from undersaturated states (*12*). The apparatus used is described in detail elsewhere (*12*). Briefly, it consists of a 150-mL glass vessel closed by a ground glass stopper and is fitted with a magnetic stirrer. The cell is immersed in a thermostatic water bath controlled to ±0.05 °C. The procedure is as follows. Volumetric quantities of twice-distilled water and analar grade acetone are charged to the solubility cell. Then the mass (in excess of saturation) of analar grade potash alum is added to the solubility cell and agitated for a minimum of 1 h at a temperature at least 2 °C lower than the saturation temperature. The contents of the solubility cell are then agitated for at least 10 h at constant temperature. At the end of this time, the agitator is switched off, and 1 h later samples of clear solution are withdrawn and their density is measured.

The solvents used were analytical grade (BDH Chemical Ltd.) acetone with a minimum assay of 99.5% and twice-distilled water. The solute used was analar grade aluminum potassium sulfate (potash alum; BDH Chemical Ltd.).

Table IV. Solubility and Density of Potash Alum Aqueous Solution at 15, 25, and 35 °C

	solubility, kg of hydrate/100 kg of water						density, kg/m³				
θ, °C	this study	ref *12*	ref *11*	ref *14*	ref *15*	ref *18*	this study	ref *12*	ref *11*	ref *15*	ref *18*
15	9.66	9.545	9.62	9.51		9.101	1045.669	1045.2	1047.0		1045.8
25	13.72	13.709	13.76	13.43	13.64	13.113	1060.712	1060.0	1062.0	1058.6	1061.5
35	19.83	19.765		19.44	19.19		1081.075	1080.3		1080.8	

The densities of the various solutions were subsequently determined by using a digital density meter (PAAR DMA 60) which gives a claimed precision up to 10^{-7} g cm^{-3}. The densities of potash alum–water solutions and potash alum–water–acetone mixtures at 15, 25, and 35 °C are shown in Table I. The densities at 25 °C are also presented in Figure 1. It is apparent from Figure 1 and Table I that densities of potash alum–water and potash alum–water–acetone solutions are practically proportional to the concentration of solute. At each concentration of acetone in solution the density data of under- and oversaturated solutions were correlated with concentration by an polynomial equation (not shown) and the solubility calculated.

Potash alum solubility data in water and in aqueous acetone mixtures are presented in Table II and in Figure 2. In all cases, the solubility of potash alum is significantly reduced by the presence of acetone. The experimental solubility data are well correlated by an expression of the form

$$\ln (w_{eq}) = A + Bx + Cx^2 \quad (1)$$

where w_{eq} is the equilibrium concentration of potash alum (kg of hydrate/100 kg of water), x is the prevailing concentration of acetone in solution (kg of acetone/kg of water), and A, B, and C are coefficients. Values of A, B, and C determined are also presented in Table III.

For the purpose of comparison, both the solubility and density data of potash alum in pure aqueous solutions obtained in this work are presented in Table IV together with those data available in literature (*11*, *12*, *14–18*). The solubility data of potash alum in pure aqueous solutions obtained in the present study are intermediate between those of Mullin and Šipek (*12*) and of Garside (*11*), with higher values than those reported by Broul et al. (*14*), Schlein et al. (*15*), Berkeley (*16*), *International Critical Tables* (*17*), and *Solubility of Inorganic and Organic Compounds* (*18*). A more significant difference is observed in the case of density. The latter is likely to be due to using a more accurate instrument here than in previous work.

Glossary

- A, B, C — coefficients (eq 1)
- w — potash alum concentration, kg of hydrate/kg of free water
- w_{eq} — solubility, kg of hydrate/100 kg of free water
- x — acetone concentration, kg of acetone/100 kg of water
- ρ — density of solution, kg/m^3
- θ — temperature, °C

Registry No. Potassium aluminum sulfate, 10043-67-1; acetone, 67-64-1.

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