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Ammonium Aluminum Sulfate (Ammonium Alum)–Water–Alcohol Systems. Composition, Density, and Viscosity of Saturated Solutions

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The solubilities of ammonium aluminum sulfate (ammonium alum) in water and mixtures of water–methanol, water–ethanol, and water–2-propanol have been determined over the temperature range 20–40 °C. The densities and the viscosities 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 object of the present work was to provide accurate solubility, density, and viscosity data for solutions of ammonium aluminum sulfate (ammonium alum, $(NH_4)_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$ mol wt = 906.63) in water and in several alcohol–water mixtures as an aid to the assessment of the potential of alcohol precipitation as a separation technique (*1*, *2*). This report is complementary to a similar study recently reported on the isomorphous potash alum (*3*).

Experimental Section

The materials used were analytical-grade (BDH Ltd.) ammonium alum, methanol, ethanol, and 2-propanol and twice-distilled water. The method used for solubility determination has been described previously (*3*). Briefly, weighed quantities of ammonium alum and alcohol, together with predetermined amounts of water, were charged to a 50-cm^3 glass cell and agitated for about 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 trace of crystalline material (observed under a strong backlight) had disappeared. Toward the end point, water was added dropwise at 20-min intervals. This method, when carefully performed, could reproducibly determine the solubility to a precision of at least ±0.5%. The solubilities of ammonium alum in water and in aqueous mixtures of methanol, ethanol, and 2-propanol were determined at three temperatures (20, 30, and 40 °C), and the solubilities in water compare well (maximum deviation, 1.9%) with values previously determined by conventional methods, approaching equilibrium from both the under- and oversaturated states (*4*).

The densities of the various saturated solutions produced in the solubility cell were determined, with a precision of ±0.2%, with a 10-mL bicapillary pycnometer of the type described by Lipkin et al. (*5*). The viscosities of the saturated solutions were measured, with a precision of ±0.2%, with an Ostwald-type viscometer by the method described by Findlay (*6*).

The solubility data are typified by the conventional curves shown in Figure 1 for aqueous methanol solutions at three different temperatures, but the most successful correlation method was found to be through a second-order function of the form

$$\log X = K_1m + K_2m^2 + C \qquad (1)$$

Table I. Solubilities, Densities (ρ) and Viscosities (η) of Ammonium Alum in Water and Aqueous Methanol at 20, 30, and 40 °C

alum (hydrate), g/100 g of soln	CH_3OH, g/100 g of soln	H_2O, g/100 g of soln	10^3x_a	m	ρ, g/cm^3	$10^3\eta$, Pa s
20 °C, $x_0 = 2.2012 \times 10^{-3}$, $K_1 = -0.108420$, $K_2 = 2.6387 \times 10^{-3}$						
9.993		90.007	2.2012		1.0464	1.3686
7.306	3.927	88.767	1.5931	1.3808	1.0255	1.3683
5.227	7.823	86.950	1.1357	2.8082	1.0090	1.4624
3.346	13.347	83.307	0.7316	5.0006	0.9913	1.6024
2.138	19.146	78.716	0.4744	7.5913	0.9773	1.6682
1.344	25.171	73.485	0.3047	10.6906	0.9644	1.8264
30 °C, $x_0 = 3.1713 \times 10^{-3}$, $K_1 = -0.093203$, $K_2 = 1.4858 \times 10^{-3}$						
13.801		86.199	3.1713		1.0613	1.2030
11.234	2.808	85.958	2.5435	1.0194	1.0432	1.1725
8.882	5.921	85.197	1.9896	2.1690	1.0259	1.1902
6.584	9.873	83.543	1.4662	3.6886	1.0082	1.2451
4.084	16.320	79.596	0.9132	6.3994	0.9860	1.2778
2.546	22.861	74.593	0.5781	9.5653	0.9687	1.3604
1.512	28.580	69.908	0.3493	12.7599	0.9546	1.3954
40 °C, $x_0 = 4.6028 \times 10^{-3}$, $K_1 = -0.085873$, $K_2 = 1.6372 \times 10^{-3}$						
18.878		81.122	4.6028		1.0822	1.0954
14.878	3.719	81.403	3.5282	1.4259	1.0549	1.0528
11.490	7.676	80.834	2.6740	2.9638	1.0305	1.0384
8.311	12.471	79.218	1.9115	4.9134	1.0070	1.0376
4.998	20.073	74.929	1.1505	8.3611	0.9788	1.0564
3.049	27.388	69.563	0.7126	12.2885	0.9575	1.0857
1.881	35.621	62.498	0.4528	17.7891	0.9376	1.0966

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Table II. Solubilities, Densities (ρ) and Viscosities (η) of Ammonium Alum in Water and Aqueous Ethanol at 20, 30, and 40 °C

alum (hydrate), g/100 g of soln	C_2H_5OH, g/100 g of soln	H_2O, g/100 g of soln	10^3x_a	m	ρ, g/cm³	$10^3\eta$, Pa s
20 °C, $x_0 = 2.2012 \times 10^{-3}$, $K_1 = -0.19693$, $K_2 = 5.3311 \times 10^{-3}$						
9.993		90.007	2.2012		1.0464	1.3686
6.810	3.686	89.504	1.4857	0.8939	1.0235	1.4422
4.757	7.096	88.147	1.0385	1.7475	1.0082	1.6142
2.919	11.543	85.538	0.6437	2.9293	0.9929	1.8062
1.875	15.655	82.470	0.4204	4.1203	0.9829	1.9482
1.091	20.449	78.460	0.2507	5.6571	0.9726	2.2526
30 °C, $x_0 = 3.1713 \times 10^{-3}$, $K_1 = -0.18499$, $K_2 = 5.7556 \times 10^{-3}$						
13.801		86.199	3.1713		1.0613	1.2030
10.673	2.663	86.664	2.4123	0.6669	1.0407	1.2046
8.167	5.425	86.408	1.8297	1.3627	1.0236	1.2516
5.858	8.759	85.383	1.3090	2.2268	1.0071	1.3221
3.518	14.051	82.431	0.7945	3.7001	0.9882	1.4629
2.110	19.002	78.888	0.4855	5.2286	0.9744	1.5933
1.287	24.252	74.461	0.3046	7.0699	0.9628	1.7064
40 °C, $x_0 = 4.6028 \times 10^{-3}$, $K_1 = -0.16627$, $K_2 = 4.9440 \times 10^{-3}$						
18.878		81.122	4.6028		1.0822	1.0954
14.036	3.509	82.455	3.3160	0.9238	1.0508	1.0435
10.418	6.946	82.636	2.4193	1.8245	1.0269	1.0480
7.327	10.983	81.690	1.6903	2.9184	1.0056	1.0793
4.280	17.118	78.602	0.9959	4.7270	0.9815	1.1729
2.496	22.453	75.051	0.5913	6.4937	0.9647	1.2498
1.527	28.974	69.499	0.3751	9.0492	0.9488	1.3308

Table III. Solubilities, Densities (ρ) and Viscosities (η) of Ammonium Alum in Water and Aqueous 2-Propanol at 20, 30, and 40 °C

alum (hydrate), g/100 g of soln	C_3H_7OH, g/100 g of soln	H_2O, g/100 g of soln	10^3x_a	m	ρ, g/cm³	$10^3\eta$, Pa s
20 °C, $x_0 = 2.2012 \times 10^{-3}$, $K_1 = -0.27853$, $K_2 = 12.0590 \times 10^{-3}$						
9.993		90.007	2.2012		1.0464	1.3686
6.699	3.569	89.732	1.4638	0.6616	1.0235	1.4742
4.624	6.922	88.454	1.0138	1.3019	1.0080	1.5582
2.828	11.208	85.964	0.6287	2.1691	0.9935	1.9041
1.738	15.273	82.989	0.3943	3.0618	0.9833	2.2539
0.914	21.170	77.916	0.2155	4.5200	0.9714	2.6956
30 °C, $x_0 = 3.1713 \times 10^{-3}$, $K_1 = -0.25544$, $K_2 = 11.5103 \times 10^{-3}$						
13.804		86.199	3.1713		1.0613	1.2030
10.505	2.624	86.871	2.3756	0.5026	1.0399	1.1874
7.951	5.352	86.697	1.7859	1.0270	1.0228	1.2647
5.738	8.603	85.659	1.2904	1.6708	1.0070	1.3659
3.414	13.619	82.967	0.7788	2.7309	0.9887	1.5679
2.022	18.597	79.381	0.4726	3.8976	0.9747	1.7834
1.248	23.712	75.040	0.3017	5.2571	0.9623	1.9611
40 °C, $x_0 = 4.6028 \times 10^{-3}$, $K_1 = -0.21739$, $K_2 = 6.7148 \times 10^{-3}$						
18.878		81.122	4.6028		1.0822	1.0954
13.757	3.441	82.802	3.2500	0.6913	1.0496	1.0708
10.217	6.809	82.974	2.3823	1.3652	1.0267	1.0755
7.086	10.621	82.293	1.6444	2.1470	1.0052	1.1399
4.149	16.573	79.278	0.9776	3.4780	0.9818	1.2615
2.451	22.062	75.487	0.5930	4.8624	0.9637	1.3996
1.429	27.092	71.479	0.3567	6.3053	0.9490	1.5217

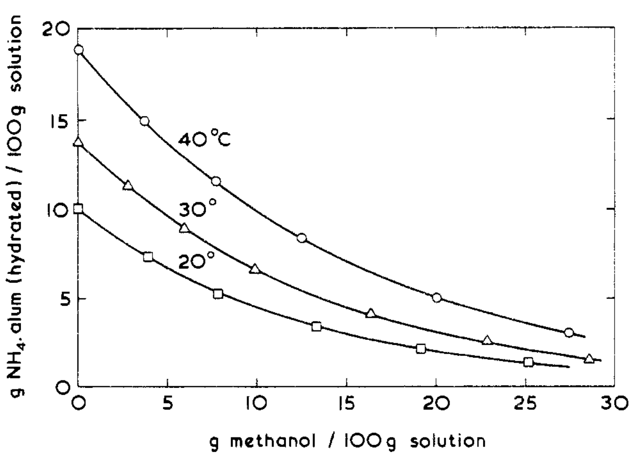

Figure 1. Solubility of ammonium alum in aqueous methanol at 20, 30, and 40 °C.

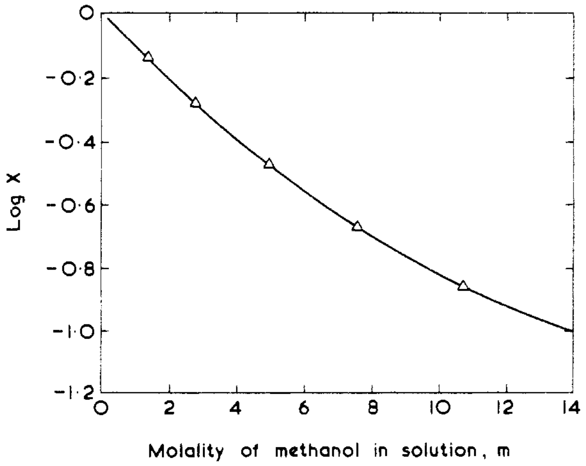

Figure 2. General correlation of ammonium alum solubilities in aqueous methanol at 20 °C (curve calculated according to eq 1).

where $X = x_a/x_0$, x_a = solubility (mole fraction) of ammonium alum (24 H_2O) in the ternary (aqueous alcohol) solution, x_0 = solubility (mole fraction) of ammonium alum (24 H_2O) in the binary (aqueous) solution, m = molality of alcohol in aqueous solution (mol of alcohol/kg of water), and K_1, K_2, C = constants. An example of one of the quadratic regression fits is shown in Figure 2 for alum-water-methanol at 20 °C. 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 an average 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.

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Thermodynamic Properties of Binary Mixtures Involving Sulfolane. 1. Excess Volumes on Mixing Sulfolane and Propionitrile, Butyronitrile, and Valeronitrile

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Excess volumes on mixing sulfolane and propionitrile, butyronitrile, and valeronitrile were measured over the entire composition range $0 \leq x \leq 1$, at four temperatures between 293.1 and 323.1 K. All mixtures exhibit negative excess volumes with a minimum which occurs approximately at $x = 0.5$ in the case of the butyronitrile-sulfolane and valeronitrile-sulfolane systems; it is shifted toward the propionitrile-rich region in the case of the propionitrile-sulfolane system. The magnitude of the minimum steadily increases with temperature and decreasing nitrile chain length. Data are interpreted in terms of moderate interactions of all kinds decreasing in importance with increasing nitrile carbon chain length and an increase of the nitrile self-association with respect to the interactions with sulfolane as the temperature increases.

Introduction

Our previous measurements (*1-9*) of excess properties of liquid mixtures involving sulfolane and a large number of selected apolar and polar substances (water, normal and branched alcohols, benzene, nitrobenzene, carbon tetrachloride, dioxane, nitriles) are indicative of only weak interactions between unlike molecules. Furthermore, our recent investigations (*10*) on the nitrobenzene-sulfolane solid-liquid phase diagram strongly support the supposition of an ideal behavior; excess enthalpies on mixing benzene and sulfolane have been found by Carvo (*11*) to be so small that this system can be treated as athermal, and this is in good agreement with our previous interpretation of viscosity, density, dielectric-constant data and solid-liquid equilibrium temperatures (*3*).

In other words, sulfolane, in these binary systems, is suspected to behave as an almost inert diluent, in spite of its fairly high polarity (μ = 4.8 D), presumably because of the steric hindrance of its globular molecules.

These statements prompted us to collect further data on sulfolane solutions for a more complete review. We present herewith excess volumes on mixing of some binary systems involving sulfolane and propionitrile, butyronitrile, and valeronitrile. Data on the acetonitrile-sulfolane system have been published previously (*8*).

Our choice of nitrile series has been guided by a regular varying molecular size of selected nitriles without inordinate alteration in molecular structure and the effective polarity of the nitrile (μ = 3.57 D). Hence, moderate interactions, if any, between like and unlike molecules, mainly dipole-dipole interactions, are expected to occur in these systems, dominated by steric factors univocally.

Experimental Section

Materials. Sulfolane kindly supplied by Shell Italia was purified and dried carefully, as already reported (*12*); the melting point of the final product was 301.61 K, in close agreement with our own previous data and the most reliable literature data (*13*); BDH nitriles (propionitrile, butyronitrile, and valeronitrile) were dried and distilled from anhydrous P_2O_5 by using a 1-m, glass-packed fractionating column as recommended in the literature (*14*). Immediately before use, all materials were degassed by repeated freeze-thaw cycles. Solutions were made by weight (reduced to mass) and then stored in dark containers and protected from moisture as far as possible.

The apparatus (an Anton Paar DMA 60 digital densimeter) and the procedure in measuring densities were described elsewhere (*8*). The maximum error in the densities was estimated to be 3×10^{-5} g cm^{-3}.

Densities of solutions were measured over the entire composition range, at different temperatures. Working temperatures were 293.12, 303.07, 313.10, and 323.10 K in the case of the propionitrile-sulfolane and butyronitrile-sulfolane systems (data at 323.10 K were not taken in the case of butyronitrile). The temperatures were 303.16, 313.16, 323.16, and 333.16 K in the case of the valeronitrile-sulfolane system.

For the sake of uniformity with previous work, the sulfolane was identified as component (2) and the other substance as component (1); compositions were stated as mole fractions, x_2.

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