(4) Fernández, J.; Velasco, I.; Otin, S. *J. Chem. Thermodyn.* **1989**, *21*, 419.
(5) Velasco, I.; Otin, S.; Gutiérrez Losa, C. *Int. DATA Ser., Sel. DATA Mixtures, Ser. A* **1981**, *1*, 63.
(6) Letcher, T. M.; Bayles, J. W. *J. Chem. Eng. Data* **1971**, *16*, 266.
(7) Gutiérrez Losa, C.; Gracia, M. *Rev. Acad. Cienc. Exactas, Fis., Quim. Nat. Zaragoza* **1971**, *26*, 101.
(8) Polo, C.; Otin, S.; Gutiérrez Losa, C. *Int. DATA Ser., Sel. DATA Mixtures, Ser. A* **1976**, *2*, 139.
(9) Ewing, M. B.; Marsh, K. N.; Stokes, R. H.; Tuxford, C. W. *J. Chem. Thermodyn.* **1970**, *2*, 751. Marsh, K. N. *Int. DATA Ser., Sel. DATA Mixtures, Ser. A* **1973**, 22.

Received for review July 13, 1989. Accepted December 10, 1989. We are grateful for the financial assistance of the Dirección General de Investigación Cientifica y Técnica of Spain, Proyecto PB86-0184.

Potassium Sulfate Water–Alcohols Systems: Composition and Density of Saturated Solutions

Jerzy Mydlarz[†] **and Alan G. Jones***

Department of Chemical and Biochemical Engineering, University College London, Torrington Place, London WC1 7JE, England

New data are presented for assessment of the crystallization of potassium sulfate by drowning-out precipitation. The solubility of potassium sulfate in water, in aqueous alcohols, 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 either alcohol or acetone significantly reduces both the solubility of potassium sulfate in aqueous solution and the density of its saturated solution. The solubility data may conveniently be expressed by a relationship of the form $\ln(w_{eq}) = A + Bx + Cx^2$ with an accuracy $\mp 2\%$ where w_{eq} is the equilibrium saturation concentration of potassium sulfate, expressed as kilograms of potassium sulfate per kilogram of water, and x is the concentration of precipitant expressed as kilograms of organic cosolvent per kilogram water.

Introduction

Addition of an organic second solvent, or cosolvent, to induce drowning-out precipitation of soluble inorganic salts from aqueous solution has a number of potential advantages over alternative crystallization techniques since it creates the possibility of carrying out the operation at ambient temperature, yielding crystals of high purity.

Although the precipitation technique has been used for many years for production of fine crystals in the chemical and pharmaceutical industries, relatively few commercial and laboratory investigations have been reported in the literature (*1–9*).

Recently, complementary investigations of the continuous drowning-out precipitation of potassium sulfate (*10*) and potash alum (*11*) have clearly shown that it is possible to retrieve a crystal product that is close in filterability to that obtained by cooling crystallization.

The solubility of potassium sulfate in aqueous 2-propanol has been reported by Mydlarz et al. (*12*). The aim of this present work was to provide accurate solubility and density data for solutions of potassium sulfate in water, aqueous alcohols (methanol, ethanol), and aqueous acetone mixtures as an aid toward the assessment of the potential of drowning-out with alternative precipitants.

Experimental Section

The solubility of potassium sulfate in water–acetone and water–alcohol mixtures was determined by equilibrating crystals and solution in an agitated solubility cell (*12*, *13*). The experimental procedure is described in detail elsewhere (*12*). Briefly, the apparatus used for the solubility measurements was a 150-mL glass flask closed by a ground glass stopper and fitted with a magnetic stirrer. The cell was immersed in a thermostatic water bath controlled to ∓ 0.05 °C. The procedure is as follows. Volumetric quantities of twice-distilled water and analytical-grade cosolvent (BDH Chemical Ltd.; acetone, methanol, or ethanol with a minimum assay of 99.5%) are charged to the solubility cell. Then, the mass (in excess of saturation) of analytical-grade potassium sulfate crystals (BDH) is added to the solubility cell and agitated for a minumum 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 measured.

Solution concentration measurements were made by evaporating a sample to dryness, giving an estimated accuracy of $\mp 10^{-7}$ kg of K_2SO_4/kg of solution.

The densities of the various solutions were subsequently determined with a digital density meter (PAAR Model DMA 60), which gave a claimed precision of up to 10^{-7} g/cm^3.

The solubility and density of potassium sulfate–water solutions and potassium sulfate–water–organic cosolvent mixtures at temperatures of 15, 25, and 35 °C are listed in Table I. In all cases, both the solubility of potassium sulfate and the density of its saturated aqueous–precipitant solution are significantly reduced by the presence of the organic cosolvents. This behavior is illustrated for the new solubility data for potassium sulfate water–acetone mixtures at temperatures of 15, 25, and 35 °C shown in Figure 1.

The experimental solubility data are correlated by an expression of the form

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

where w_{eq} is the equilibrium concentration of potassium sulfate

---

[†] Permanent address: Institute of Chemical Engineering and Heating Equipment, Technical University of Wroclaw, ul. Norwida 4/6, Wroclaw, Poland.
* Author to whom correspondence should be addressed.

0021-9568/90/1735-0214$02.50/0 © 1990 American Chemical Society

Table I. Solubility and Density of Potassium Sulfate Aqueous-Organic Solutions at 15, 25, and 35 °C

concn of precipitant, kg of precipitant/kg of water	solubility of K_2SO_4, kg of K_2SO_4/100 kg of water, 15 °C	25 °C	35 °C	density of satd soln, kg/m^3, 15 °C	25 °C	35 °C
acetone						
0	10.22	12.08	13.92	1075.66	1085.49	1093.87
0.0317	8.10	9.68	11.28	1053.93	1061.68	1068.32
0.0633	6.50	7.86	9.26	1037.67	1043.45	1048.44
0.0950	5.27	6.48	7.50	1024.58	1029.00	1031.49
0.1424	3.98	4.90	5.62	1009.98	1011.80	1012.99
0.1899	3.03	3.78	4.58	998.63	998.68	998.28
0.2374		2.98			988.29	
0.2770	1.95		3.03	983.47		978.15
0.3165		2.08			974.77	
0.3957	1.15	1.45	1.81	968.63	964.04	959.04
ethanol						
0.0316	7.75	9.46	11.04	1050.48	1058.92	1065.87
0.0634	6.05	7.51	8.88	1032.23	1039.63	1044.38
0.0949	4.77	5.96	7.23	1018.12	1023.13	1027.41
0.1424	3.40	4.38	5.37	1002.73	1005.55	1007.60
0.1898	2.48	3.26	4.10	991.47	992.54	993.18
0.2373	1.87	2.50	3.19	983.08	982.68	981.76
0.3164	1.23		2.19	972.64		966.98
0.3955	0.87	1.20	1.60	964.15	959.72	955.47
methanol						
0.0317	8.00	9.66	11.31	1052.30	1060.83	1067.76
0.0635	6.39	7.80	9.25	1034.58	1041.21	1046.92
0.0952	5.16	6.39	7.61	1020.43	1025.58	1029.82
0.1428	3.86	4.82	5.85	1004.78	1007.54	1010.14
0.1904		3.73	4.55		994.16	994.95
0.2380		2.93	3.61		983.37	983.04
0.2777	1.93			977.50		
0.3173		2.05	2.54		969.76	967.53
0.3966	1.18	1.51		962.57	959.27	

Table II. Coefficients for Equation 1

precipitant	temp, °C	coefficients A	B	C
acetone	15	2.3148	-7.1635	4.2219
	25	2.4808	-6.7292	3.6020
	35	2.6253	-6.6371	3.8666
ethanol	15	2.3191	-8.5366	5.8584
	25	2.4905	-7.8529	5.1089
	35	2.6301	-7.3128	4.6974
methanol	15	2.3137	-7.4717	5.2019
	25	2.4865	-7.0294	4.5639
	35	2.6314	-6.6526	4.1068

(kg of K_2SO_4/100 kg of H_2O); x is the prevailing concentration of the precipitant in aqueous solution (kg of organic solvent/kg of water) and A, B, and C are coefficients. The values of A, B, and C determined are also presented in Table II. Again, a good fit to the data was obtained as illustrated in Figure 1.

For the purpose of comparison, both the solubility and the density data of potassium sulfate in pure aqueous solutions obtained in this work are presented in Table III together with those data available in literature (*12-17*). The solubility data of potassium sulfate in pure aqueous solutions obtained in the present study are slightly higher than those in refs 15 and 16, possibly due to the use of more pure materials.

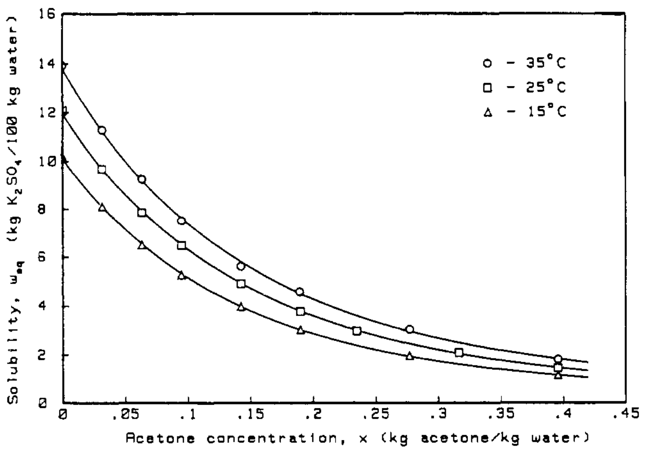

Figure 1. Solubility of potassium sulfate in aqueous acetone at 15, 25, and 35 °C.

Table III. Solubility and Density of Potassium Sulfate Aqueous Solutions at 10, 15, 20, 25, 30, 35, 40, and 50 °C

temp, °C	solubility, kg of K_2SO_4/kg of H_2O, this study	ref 13	ref 14	ref 15	ref 12	ref 16[a]	density, kg/m^3, this study	ref 13	ref 14	ref 17	ref 12
0		0.074				0.0735		1060			
10		0.092		0.0924		0.0922		1070			
15	0.1022			0.1014			1075.66				
20		0.109	0.1106	0.1105	0.1119	0.1111		1080	1082		1081.16
25	0.1208			0.1198		0.1203	1085.49				
30		0.130	0.1303	0.1291	0.1300	0.1297		1090		1086.64	1090.12
35	0.1392			0.1385			1093.87				
40		0.148	0.1494	0.1478	0.1479	0.1476		1100			1097.56
50			0.1670	0.1661	0.1652	0.1650		1105			1103.74

[a] Solubilities of inorganic and organic compounds.

Registry No. K_2SO_4, 7778-80-5; acetone, 67-64-1; ethanol, 64-17-5; methanol, 67-56-1.

Literature Cited

(1) Budz, J.; Mydlarz, J.; Mozolowski, F. *Przem. Chem.* **1985**, *64* (10), 489.
(2) Budz, J.; Mydlarz, J.; Mozolowski, F. *Przem. Chem.* **1986**, *65* (10), 554.
(3) Harano, Y.; Nakano, K.; Saito, M.; Imoto, T. *J. Chem. Eng. Jpn.* **1976**, *9*, 373.
(4) Hoppe, H. *Chem. Proc. Eng.* **1968**, *49*, 61.
(5) Lozano, J. A. F. *Ind. Eng. Chem. Process Des. Dev.* **1976**, *15*, 445.
(6) Karpinski, P. H.; Budz, J.; Mydlarz, J. Presented at the International Symposium-Workshop on Particulate and Multi-Phase Processes and the 16th Annual Meeting of the Fine Particle Society, Miami Beach, FL, 1985.
(7) Budz, J.; Karpinski, P. H.; Mydlarz, J.; Nyvlt, J. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 657.
(8) Mydlarz, J.; Budz, J. *Zesz. Nauk. Politech. Poznańskiej* (Poznań) **1986**, *No. 18*, 323.
(9) Mydlarz, J.; Budz, J. Presented at the AIChE Annual Meeting, New York, 1987.
(10) Jones, A. G.; Mydlarz, J. *Chem. Eng. Res. Des.* **1989**, *67*, 283.
(11) Jones, A. G.; Mydlarz, J. *Can. J. Chem. Eng.*, in press.
(12) Mydlarz, J.; Jones, A. G.; Millan, A. *J. Chem. Eng. Data* **1989**, *34*, 124.
(13) Mullin, J. W. *Crystallisation*, 2nd ed.; Butterworths: London, 1972.
(14) Mullin, J. W.; Gaska, C. *J. Chem. Eng. Data* **1973**, *18*, 217.
(15) Broul, M.; Nyvlt, J.; Sohnel, O. *Solubility in Inorganic Two-Component Systems*; Academia, Praque-Elsevier: Amsterdam, 1981; p 89.
(16) *Solubilities of Inorganic and Organic Compounds. Part I. Binary Systems*, Stephen, H., Stephen, T., Eds.; Pergamon Press: Oxford-London-New York-Paris, 1963; Vol. I, p 163.
(17) Ishii, T.; Fujita, S. *J. Chem. Eng. Data* **1978**, *23*, 19.

Received for review June 5, 1989. Accepted November 9, 1989.

Isobaric Vapor–Liquid Equilibrium of Methyl Butanoate with Ethanol and 1-Propanol Binary Systems

Juan Ortega,* Pedro Susial, and Casiano de Alfonso

Cátedra de Termodinâmica y Fisicoquimica, Escuela Superior de Ingenieros Industriales, Polytechnic University of Canarias, 35071 Las Palmas, Canary Islands, Spain

Binary *T–p–c–y* vapor–liquid equilibria (VLE) at 101.32 kPa are reported for methyl butanoate + ethanol or 1-propanol. The experimental VLE data of both systems were verified and found to be thermodynamically consistent. The azeotropic coordinates (mole fraction of the ester and temperature) are 0.091 and 350.97 K, for methyl butanoate + ethanol, and 0.409 and 366.77 K, for methyl butanoate + 1-propanol. The data were then compared with those obtained by using the UNIFAC and ASOG models.

Introduction

In continuation of our vapor–liquid equilibrium (VLE) studies on ester + alkanol binary mixtures (*1–4*), we present here VLE measurements at 101.32 kPa for methyl butanoate + ethanol or + 1-propanol.

Another aim of this paper is to compare the experimental data with those predicted with the ASOG model (OH/COO, Kojima and Tochigi (*5*)) and the different values for the ester group from the classical UNIFAC model (COH/COO, Fredenslund et al. (*6*); OH/COOC, Skjold-Jorgensen et al. (*7*); CCOH/COOC, Fredenslund et al. (*8*)).

Experimental Section

Materials. The compounds used in the present study were from Fluka AG. The physical properties of the alkanols used in this work were described earlier (*4*). "Purum" grade methyl butanoate of commercial purity greater than 99 mol % was degassed ultrasonically and stored in the dark for several days over a molecular sieve, type 4A from Fluka. The physical properties determined experimentally after this treatment were as follows: density, ρ(298.15 K) = 892.37 kg·m^{-3}; refractive index, n_D(298.15 K) = 1.3851; normal boiling point, T_b = 375.3 K. These can be compared with the following literature values (*9*): 892.9 kg·m^{-3}, 1.3847, and 375.90 K, respectively.

Apparatus and Procedure. The experimental equipment and method of operation were as described previously (*1, 4*). Pressure was maintained constant to within 0.02 kPa, and the equilibrium temperature was measured in a digital thermometer (Comark, Model 6800), giving a reading of ±0.01 K and whose mean error was estimated to be 0.01% of the reading. The compositions of the coexisting phases were determined from the densities of liquid samples removed from the equilibrium still. The density vs ester mole fraction x_1 curves, $\rho(x_1)$, were established previously for each system (see ref 10). The accuracy of the mole fraction is 0.001 for the liquid phase and 0.002 for the vapor phase.

Experimental Results and Treatment of Data

Pure Compounds. The experimental vapor pressure of the pure liquids vs temperature T were correlated with use of the Antoine equation

$$\log (p^\circ_i/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) - C] \qquad (1)$$

The constants A and B were determined for various values of C, by applying Marquardt's algorithm (*11*) for nonlinear functions (method 1), retaining the value of C that minimized the standard deviation $s(p^\circ_i) = [\sum(p_{i,\mathrm{exp}} - p_{i,\mathrm{cal}})^2/N]^{1/2}$, where N is the number of experimental points. Nonlinear simplex regression, as modified by Nelder and Mead (*12*) (method 2), was also used to obtain the constants A, B, and C. The results of both methods, along with the $s(p_i)$ values are set out in Table II.

Mixtures. The isobaric vapor–liquid equilibrium data at 101.32 kPa for methyl butanoate (1) + ethanol (2) or 1-propanol are presented in Table III. The activity coefficients γ_i of the components in the liquid phase, calculated from the experimental $p-T-x-y$ data, are shown in Figure 1. Vapor-phase nonideality was accounted in terms of the second virial coefficients B_{ij} estimated by the method of Tsonopoulos (*15*) and the liquid molar volumes v_i^L estimated with the Spencer and Danner (*16*) form of the Rackett equation. The quality of the experimental data was verified by means of several consistency tests published in the literature. The data for the two systems studied satisfied Herington's test (*17*). However, the same did

0021-9568/90/1735-0216$02.50/0