Aluminum Potassium Sulfate Dodecahydrate Solubility in Mixed K_2SO_4 + $Al_2(SO_4)_3$ Solutions

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Recently, the Pitzer interaction model was used to calculate aluminum potassium sulfate dodecahydrate solubility products from published solubility data. The model performed poorly, reflected by a marked increase in values with decreasing solution potassium content. Solubility measurements at 25 °C were repeated in this study. The solubility products calculated for these data show no such trend. Despite the agreement in the results of the previous studies, it appears the measurements are in error at low potassium contents. Previous workers did not analyze for potassium but calculated it using the charge balance relation. Large uncertainties and systematic errors in reported values can be introduced with this method. The solubility data reported in this study provide no basis for an adjustment of the present ion interaction parameter database for mixed K_2SO_4 + $Al_2(SO_4)_3$ solutions. An average log K_{sp} of -6.3 ± 0.1 at 25 °C is recommended for use with these data.

Introduction

In a recent paper (*1*), Pitzer ion interaction parameters for Al–SO_4 were reported and applied to the prediction of the solubility of various metal–sulfates in aluminum sulfate solutions. Although the solubility of many of these sulfates was successfully described, a problem was encountered with aluminum potassium sulfate dodecahydrate ($KAl(SO_4)_2 \cdot 12H_2O$). The binary interaction parameter data for K_2SO_4 and $Al_2(SO_4)_3$ recorded in Table I were unable to adequately represent the published solubility data for this phase in solutions of low potassium concentrations.

Three studies have reported solubility data at 25 °C over a range of potassium concentrations. The results of Britton (*2*), Khripin (*3*), and Kryzhanovskii et al. (*4*) are shown in Table II. Figure 1 is a plot of the calculated solubility products (log K_{sp}) for these data with use of the ion interaction parameters recorded in Table I. The K_{sp}'s refer to the following dissolution reaction

$$KAl(SO_4)_2 \cdot 12H_2O \rightarrow K^+ + Al^{3+} + 2SO_4^{2-} + 12H_2O \quad (1)$$

and the equilibrium constant expression is

$$K_{sp} = \gamma_{K^+}\gamma_{Al^{3+}}(\gamma_{SO_4^{2-}})^2 m_{K^+}m_{Al^{3+}}(m_{SO_4^{2-}})^2(a_{H_2O})^{12} \quad (2)$$

The log K_{sp}'s in Figure 1 are plotted versus the mole fraction of K_2SO_4 in solution given by

$$x_{K_2SO_4} = \frac{m_{K_2SO_4}}{m_{K_2SO_4} + m_{Al_2(SO_4)_3}} \quad (3)$$

where concentrations are expressed in molalities.

A useful activity coefficient model for calculating the thermodynamic solubility product of $KAl(SO_4)_2 \cdot 12H_2O$ should yield constant values as a function of the mole fraction of K_2SO_4 in the equilibrated solutions. However, Figure 1 shows a marked decrease in log K_{sp} values for the data of Britton (*2*) and Khripin

Table I. Pitzer Ion Interaction Parameters

param	K_2SO_4[a]	$Al_2(SO_4)_3$[b]	param	K_2SO_4[a]	$Al_2(SO_4)_3$[b]
β^0	0.04995	0.854	β^2		-500
β^1	0.7793	18.53	C^ϕ		-0.0911

[a] Harvie et al. (*6*). [b] Reardon (*1*).

Table II. Published Solubility Measurements of $KAl(SO_4)_2 \cdot 12H_2O$ at 25 °C[a]

Khripin (3)		Britton (2)		Kryzhanovskii et al. (4)	
K_2SO_4 mass %	$Al_2(SO_4)_3$ mass %	K_2SO_4 mass %	$Al_2(SO_4)_3$ mass %	K_2SO_4 mass %	$Al_2(SO_4)_3$ mass %
11.1 ● 0.1	1.27 ● 0.03	11.50	1.34	10.45	1.33
10.44	1.32	10.58	1.46	7.42	1.68
7.75	1.48	7.24	1.86	5.01	2.02
5.31	1.80	5.72	2.03	4.21	3.02
3.50	2.58	3.54	3.06	3.00	3.28
2.71	3.60	2.99	3.58		
2.21	4.36	2.27	4.47		
1.90	5.42	2.07	4.77		
1.66	6.29	1.86	6.14		
1.29	8.54	1.78	7.08		
1.28	11.43	1.71	8.43		
1.20	12.90	1.50	10.21		
1.14	17.24	1.45	11.29		
1.12	19.41	1.46	14.98		
1.11	24.69	1.94	27.91		
1.16	26.87	1.93	30.23		

[a] The first entry for Khripin is an average of six measurements.

(*3*) at mole fractions less than 0.3. Because the data from both authors are in agreement, we ruled out possible analytical error and considered that there were only two explanations for this effect. One was that the Pitzer ion interaction parameters used to calculate the ion and water activities in eq 2 are either incorrect or incomplete. It is possible, for example, the ternary interaction parameters, such as $\theta_{K^+-Al^{3+}}$ or $\psi_{K^+-Al^{3+}-SO_4^{2-}}$, which were set to zero in the construction of Figure 1, may account for the observed decrease in log K_{sp} at low mole fractions of K_2SO_4. We found, though, that no reasonable set of values for these parameters could be assembled to remove this trend. An alternate explanation is that a phase change occurs at a mole fraction of K_2SO_4 near 0.3 that went unnoticed by both Britton and Khripin. That is, a solid phase other than $KAl(SO_4)_2 \cdot 12H_2O$ might control the solution composition at low potassium concentration and, if the solubility product for this hypothetical new phase were to be calculated, the values would be constant, as they are above $x_{K_2SO_4} = 0.3$.

The purpose of this investigation was to repeat the solubility determinations of $KAl(SO_4)_2 \cdot 12H_2O$ at 25 °C in order to corroborate the previously published data and to examine the equilibrated solid phase at low mole fractions of K_2SO_4.

Experimental Section

Reactant solutions for this experiment were prepared by adding Baker reagent-grade $KAl(SO_4)_2 \cdot 12H_2O$ to solutions of known concentration of aluminum sulfate. The solutions were prepared with Baker reagent-grade $Al_2(SO_4)_3 \cdot 18H_2O$ and distilled–deionized water. Twenty reaction solutions, representing
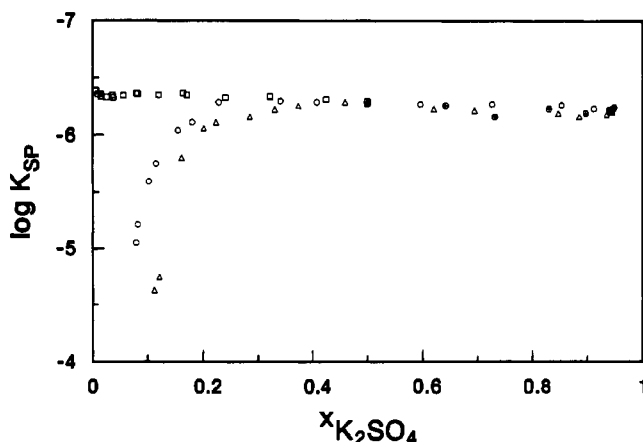
Figure 1. log K_{sp} values for aluminum potassium sulfate dodecahydrate as a function of mole fraction of K_2SO_4 ($x_{K_2SO_4}$): ⊕, Kryzhanovskii et al. (4); ⊙, Khripin (3); △, Britton (2); □, this work.

a range of K_2SO_4 mole fractions from 0.5 to 0.006, were equilibrated with the solid in 40-mL glass vials.

To prevent possible enhancement in solubility from grinding effects, the solutions were not stirred during equilibration. Instead the reaction vessels were secured on a circular carousel. The carousel was completely immersed in a water bath, and the effluent from a heater/circulatory pump, which maintained the bath at 25 ± 0.1 °C, was directed at the carousel to cause its rotation at 10–20 rpm. This resulted in a gentle tumbling action to the precipitate and thorough mixing in each reaction vial.

After an equilibration period of 10 days, approximately 2 mL of the supernatant from each reactant vessel was removed. The samples were diluted gravimetrically and then analyzed for potassium with a Varian Model 1475 atomic absorption spectrophotometer (AAS). The reproducibility of the measurements was estimated to better than 2% on analyzing replicate samples at different times. Analyses of samples withdrawn after 18-days equilibration agreed with the first set within experimental error. The possible interference of high aluminum and sulfate concentrations on potassium analysis by AAS was investigated and found not to be a problem. The final aluminum and sulfate concentrations were determined by adding the expected stoichiometric increase in their concentrations from the dissolution of the solid (based on the potassium analyses) to their known initial concentrations in the prepared solutions. Crystals were also removed from each reaction vessel at the end of the experiment and examined under the microscope. $KAl(SO_4)_2 \cdot 12H_2O$ was confirmed as the equilibrated solid phase for all solutions.

Results

The results of the solubility measurements in the K_2SO_4 + $Al_2(SO_4)_3$ solutions at 25 °C are shown in Table III. The logarithms of the solubility product using the interaction parameter data in Table I and eq 2 are also included. Figure 1 presents the calculated solubility products (log K_{sp}) versus mole fraction of K_2SO_4 for both the previously published solubility data and those from this study.

The analytical uncertainty of the solubility measurements is ±2% of the recorded values in Table III. This is based on the reproducibility of the AAS measurements themselves for individual solutions. There are, however, six pairs of samples in Table III that had close to the same initial aluminum sulfate concentration. Members of each pair should have yielded similar potassium mass percents. The largest difference between these replicate runs is 5%, and this probably represents more accurately the maximum absolute uncertainty in the tabulated measurements.

Table III. Measured Solubility of $KAl(SO_4)_2 \cdot 12H_2O$ at 25 °C

K_2SO_4 mass %	$Al_2(SO_4)_3$ mass %	log K_{sp}	K_2SO_4 mass %	$Al_2(SO_4)_3$ mass %	log K_{sp}
2.21	4.34	−6.28	0.163	20.85	−6.33
1.89	5.02	−6.31	0.109	22.92	−6.36
1.51	6.24	−6.33	0.072	25.04	−6.39
1.27	7.83	−6.32	2.23	4.38	−6.28
0.940	9.43	−6.36	1.51	6.23	−6.33
0.768	11.11	−6.35	0.980	9.36	−6.35
0.581	12.88	−6.36	0.565	12.93	−6.36
0.441	14.82	−6.34	0.316	16.78	−6.35
0.333	16.76	−6.32	0.156	20.77	−6.36
0.236	18.71	−6.33	0.073	25.04	−6.38

Discussion

Figure 1 shows that the solubility products calculated from the experimental data in this study are quite constant with decreasing mole fraction of K_2SO_4 and do not show the precipitous decrease evidenced in the data of Britton (2) and Khripin (3). The results from this study are therefore consistent with the thermodynamic prediction of a constant solubility product with changes in solution composition. These results strongly suggest that the solubility data of Britton (2) and Khripin (3) are incorrect at low mole fractions of K_2SO_4.

It is useful to review the analytical procedures used by Britton (2) and Khripin (3). Both authors analyzed their equilibrated solutions for SO_4^{2-} and Al^{3+}. SO_4^{2-} was determined gravimetrically in each study by weighing $BaSO_4$ after precipitation with $BaCl_2$. Britton (2) determined Al^{3+} by precipitation as aluminum hydroxides with NaOH in the presence of phenolphthalein at 100 °C. Khripin (3) determined the concentration of Al^{3+} gravimetrically by precipitation with 8-hydroxyquinoline. Neither of the authors determined the concentration of K^+ directly, as was done in the present study. Rather the concentration of K^+ in both studies was found by applying the charge balance relation:

$$m_{K^+} = 2m_{SO_4^{2-}} - 3m_{Al^{3+}} \qquad (4)$$

Britton (2) noted a problem that led to the underestimation of aluminum concentrations due to the incorporation of some aluminum sulfate in the aluminum hydroxide precipitate. He tried to minimize this interference by substantially diluting his solutions before analysis. Churchill and Moss (5) pointed out that the principal problem with aluminum precipitation techniques such as that used by Khripin (3) is underestimation due to incomplete precipitation. If this were the case, i.e. if the concentration of aluminum was underestimated with respect to sulfate in these previous solubility studies, then the concentration of potassium would be overestimated, since it is calculated as the difference in equivalents between sulfate and aluminum. At high mole fractions of K_2SO_4, this difference is large and the overestimation error imparted to the calculated potassium concentration would be small. Under these conditions, the calculated solubility products would not be significantly affected by this source of error. Toward low mole fractions of K_2SO_4, on the other hand, the overestimation of potassium would become increasingly larger as the difference in the equivalent concentration of SO_4^{2-} and Al^{3+} becomes smaller. Thus the calculated solubility product would be expected to increase (−log K_{sp} decrease) as $x_{K_2SO_4}$ decreases. This explanation is consistent with the sharp decline in log K_{sp} values observed in Figure 1 for the data of both Britton (2) and Khripin (3) as compared to the results of the present investigation.

Despite the consistency of the calculated solubility products for $KAl(SO_4)_2 \cdot 12H_2O$ derived in this study, there is still a discernible trend in the values in Figure 1. The values range from log K_{sp} = −6.28 at a K_2SO_4 mole fraction of 0.5 to −6.38 at a mole fraction near 0.0. If the high K_2SO_4 mole fraction data

of Britton (2) and Khripin (3) are included (Figure 1), there is an overall change in log K_{sp} from −6.22 to −6.38 from high to low potassium concentrations, respectively. In our analysis, we have ignored the effects of the ternary interaction parameters $\theta_{K^+-Al^{3+}}$ and $\psi_{K^+-Al^{3+}-SO_4^{2-}}$, setting them to zero in our calculations. We tried to derive values for these parameters by performing a regression analysis on the solubility data. However, we found that only 40% of the total variation can be explained by invoking these parameters and therefore do not recommend this approach. It is possible that the slight systematic variation observed in the solubility product may be due to uncertainties in the binary interaction parameters for K_2SO_4 or $Al_2(SO_4)_3$ that are recorded in Table I. One possible explanation is that the K_2SO_4 interaction parameters are applied to inappropriate solution concentration conditions in this study. The K_2SO_4 parameters were determined by Pitzer and Mayorga (6) from analysis of isopiestic data up to concentrations of 0.7 m, i.e. saturation with respect to arcanite (K_2SO_4). No C^ϕ parameter could be derived by these authors at such low concentrations. In this study, however, the parameters are applied to calculate solubility products at sulfate concentrations as high as 3 m at the low K_2SO_4 mole fraction end of Figure 1.

At this time, no conclusion can be drawn as to the cause of the trend in the solubility products and no recommendation is made to add or adjust any parameters in Table I that describe equilibria in mixed K_2SO_4 + $Al_2(SO_4)_3$ solutions. In modeling aluminum potassium sulfate dodecahydrate solubility in mixed salt solutions, we recommend using an average log K_{sp} of −6.3 ± 0.1 for 25 °C. From the standard chemical potentials ($\mu°/RT$) of H_2O, K^+, Al^{3+}, and SO_4^{2-} listed in Reardon (1), a $\mu°/RT$ value of −2074.62 ± 0.23 for $KAl(SO_4)_2 \cdot 12H_2O$ is derived, only slightly and not significantly different than the value recommended in this reference.

Conclusions

A marked trend in the solubility product of $KAl(SO_4)_2 \cdot 12H_2O$ with decreasing mole fraction of potassium in solution has been observed for previously published solubility data. This trend is noted for the solubility measurements of two independent studies when the Pitzer ion interaction model is used to calculate ion activity coefficients. The experimental results of this study show that the calculated solubility products are very consistent and do not vary substantively with potassium concentration. In examining the experimental techniques used in previous studies, it appears that the method used to evaluate the potassium content of the solution is the reason for this disparity. Previous authors determined the concentration of Al^{3+} and SO_4^{2-} analytically and then found the concentration of K^+ by charge balance difference. This method can produce large uncertainties in the estimation of potassium content when the concentrations of Al^{3+} and SO_4^{2-} are large compared with K^+.

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Partial Molar Volumes of Ethylene Glycol and Water in Their Mixtures

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The densities of ethylene glycol (EG)–water (W) mixtures were measured over the whole composition range at 5, 15, 25, 35, and 45 °C. The apparent and partial molar volumes and partial molar thermal expansions were evaluated for both components. The limiting partial molar volumes of EG and W are smaller than the molar volumes of pure EG and W, respectively, at all temperatures. A characteristic minimum or maximum was observed in the partial molar volume or thermal expansion of EG vs composition curve at low mole fraction. Mostly the volumetric behavior of EG–W mixtures exhibits a minor deviation from ideality compared to monohydric alcohol–water mixtures.

Introduction

In the previous papers, we reported the partial molar volumes of some alcohols V_A and of water V_W in their solutions (1–3). At low mole fraction X of alcohol the V_A vs X curve passes through a sharp minimum, as has been well-known for

Table I. Densities of Pure Ethylene Glycol

t/°C	$\rho/(g\ cm^{-3})$			
	this work	lit.		
5	1.124 265			
15	1.117 244	1.117 10[a]	1.116 93[b]	
25	1.110 212	1.110 0[a]	1.109 97[b]	1.109 89[c]
35	1.103 164	1.102 68[b]		
45	1.096 021			

[a] Reference 7. [b] Reference 8. [c] Reference 9.

a number of aqueous solutions of nonelectrolytes. In the alcohol-rich region, on the other hand, a similar minimum was found for the V_W vs X curve in *tert*-butyl alcohol, but not in the other alcohol solutions. These peculiarities of the volumetric behavior appear to be observed in the aqueous mixtures of nonelectrolytes with a polar group. Little anomaly has been observed in the partial molar volume for the mixtures of water with hydrophobic compounds such as benzene or alkylbenzenes (4). In this paper we present the density data for the mixtures of water with ethylene glycol, which is bifunctional