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Solubility of Ammonium Aluminum Sulfate Dodecahydrate in the Aluminum Sulfate + Ammonium Sulfate + Sulfuric Acid + Water System at (25, 30, 40, and 50) °C

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Solubilities of $NH_4Al(SO_4)_2 \cdot 12H_2O$ in mixed aqueous solutions of $Al_2(SO_4)_3$ and $(NH_4)_2SO_4$ were determined at (25, 30, 40, and 50) °C. At the same temperatures, solubilities of $NH_4Al(SO_4)_2 \cdot 12H_2O$ in the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ system and densities of the equilibrium solutions were measured for sulfuric acid mass fraction on the salt-free basis, w', equal to 0.1. The measured solubilities were compared with available literature data. Ammonium alum solubilities are only moderately influenced by the sulfuric acid addition up to $w'(H_2SO_4) = 0.1$. The addition of sulfuric acid to the ternary $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$ solution increases the ammonium alum solubility in solutions with a NH_4/Al molar ratio close to 1. In contrast, at either low or high NH_4/Al molar ratios, the ammonium alum solubility is suppressed by the sulfuric acid addition.

Introduction

Crystallization of $NH_4Al(SO_4)_2 \cdot 12H_2O$ (ammonium aluminum sulfate dodecahydrate, ammonium alum) is an important step in various processes aiming either at purification of alum in production of high-purity aluminum compounds[1,2] or at recovery of aluminum and sulfates from waste solutions (e.g., from anode-oxidizing solutions in the aluminum surface finishing industry).[3−5] Furthermore, the large-scale industrial crystallization of ammonium alum is implemented in the groundwater remediation technology after discontinuation of the underground uranium leaching by sulfuric acid solution (“solution mining”) in Northern Bohemia (the Czech Republic); it is envisaged that up to 150 thousand metric tons per year of ammonium alum will be produced.[6] The latter technology is of particular interest to the present authors.[7−9]

Typically, crystallization of ammonium alum proceeds from solutions where the NH_4/Al molar ratio differs from unity and excess sulfuric acid is often present (i.e., solubilities of ammonium alum in the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$ or $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ systems must be considered). A knowledge of solubility isotherms in these systems is essential for an assessment of optimum operating parameters of the crystallization process. As far as the ternary system ($(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$) is concerned, Hill and Kaplan[10] presented data on solubility of ammonium alum at 25 °C, whereas in the paper of Urazov and Kindyakov,[11] ammonium alum solubilities at (0, 25, 50, 75, and 90) °C were given. Funaki[12] and Druzhinin and Kalbaev[13] reported the ammonium alum solubility data in the same system at (30, 40, and 50) °C and at (10, 25, 40, and 60) °C, respectively. A theoretical treatment of the thermodynamics of the ternary system using the Pitzer formalism was presented by Christov.[14] As to the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ system, only the solubilities in solutions with the molar ratio NH_4/Al equal to 1 (i.e., in the $NH_4Al(SO_4)_2 + H_2SO_4 + H_2O$ subsystem) at (20, 25, 30, 40, 50, and 60) °C are available.[9]

In this work, the measurements of alum solubility were performed for the temperatures (25, 30, 40, and 50) °C (this selection was to some extent motivated by the range of final temperatures in a two-stage continuous industrial crystallization of ammonium alum[6,7]), first for the ternary system $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$, with the aim to check and supplement the published experimental data,[10−13] and then for the quaternary system $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ at a fixed value of sulfuric acid mass fraction in the salt-free mixed solvent. In addition, densities of equilibrium solutions in the quaternary system were determined.

Experimental Section

All solutions were prepared from analytical grade chemicals (ammonium aluminum sulfate dodecahydrate (min. 99 %), ammonium sulfate (min. 99 %), aluminum sulfate octadecahydrate (min. 99 %), and sulfuric acid (96.4 %)) from Lachema, a.s., Czech Republic (the numbers in parentheses give the minimum content of the title compounds as stated by the manufacturer). These materials were used as received.

Solutions were prepared gravimetrically using an AND model GR-300 analytical balance (repeatability of weighing expressed as ± 1 SD was ± 0.1 mg). The salts (ammonium alum and ammonium sulfate or ammonium alum and aluminum sulfate, respectively) and distilled water (or distilled water and sulfuric acid) were weighed into 100 cm^3 polypropylene screw-cap conical flasks. The masses of respective components were estimated from the previously published solubility data.[10−13] An excess amount of about 4 g of ammonium alum octahedral crystals (size range of ≈ (70 to 200) μm as determined by optical microscopy) was added into the flasks to maintain the state of equilibrium between solution and the solid phase. The flasks were tightly sealed and immersed into a thermostated shaking water bath; the equilibrium was thus approached from the undersaturation side. To minimize attrition of alum crystals, gentle horizontal shaking operation was performed so that the alum crystals were slowly moving at the bottom of the flask. The equilibration period was at least 72 h at constant temperature, which was sufficient for reaching the equilibrium

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Table 1. Compositions of the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$ Solutions in Equilibrium with $NH_4Al(SO_4)_2 \cdot 12H_2O$ Crystals at t = (25, 30, 40, and 50) °C

$100w^a$ at t							
25 °C		30 °C		40 °C		50 °C	
$(NH_4)_2SO_4$	$Al_2(SO_4)_3$	$(NH_4)_2SO_4$	$Al_2(SO_4)_3$	$(NH_4)_2SO_4$	$Al_2(SO_4)_3$	$(NH_4)_2SO_4$	$Al_2(SO_4)_3$
0.029	27.5	0.079	27.9	0.128	28.9	0.231	30.0
0.129	21.8	0.160	23.6	0.228	25.6	0.538	26.1
0.276	15.8	0.838	10.6	0.940	13.5	1.59	15.8
0.478	12.2	2.20	4.88	1.77	9.61	2.57	11.3
0.944	7.50	12.3	1.37	2.14	8.23	4.16	8.65
1.67	4.49	25.9	0.897	2.91	6.92	10.85	5.16
3.95	2.06	37.8	0.682	8.24	3.35	20.8	3.80
8.73	1.18	41.5	0.719	26.5	1.70	33.4	3.09
14.5	0.907	42.2	0.646	35.7	1.35	42.0	2.49
21.1	0.765	41.8	0.641	43.4	1.13	43.6	2.24
32.6	0.514	43.1	0.606				
42.8	0.368	43.1	0.605				

[a] w, mass fraction of the respective component in the solution saturated by $NH_4Al(SO_4)_2 \cdot 12H_2O$.

concentrations (as determined by preliminary experiments). Then the shaking operation was discontinued, and the thermostated system was allowed to rest for (4 to 7) h. Samples of the clear solution were taken by a glass pipet (preheated in the experiments with solution temperatures greater than 25 °C) for the chemical analysis and for the determination of solution density.

At the experimental temperatures, the viscosity of the saturated solution was still low enough to obtain clear liquid through sedimentation within several hours. No turbidity due to hydrolytic formation of $Al(OH)_3$ was observed. As follows from speciation and saturation-index calculations using the PHREEQC computer program[15] with the phreeqc.dat database file, hydrolysis of aluminum ions is almost completely suppressed in saturated solutions of ammonium alum in the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$ system. The degree of hydrolysis increases with decreasing concentration of aluminum in solution, but even for the solution with the lowest aluminum concentration in the present work (mass fractions of $Al_2(SO_4)_3$ and $(NH_4)_2SO_4$ equal to 0.0037 and 0.428, respectively; see Table 1), only 0.05 % of aluminum should be precipitated as amorphous aluminum hydroxide according to the PHREEQC prediction. Moreover, the slightly supersaturated $Al(OH)_3$ solutions may stay in a metastable state and spontaneous precipitation need not occur. Schlain et al.[16] explicitly neglected the effect of hydrolysis upon the solubility of ammonium alum in pure water since they experimentally determined that in the temperature range from (25 to 80) °C, only 0.01 % to 0.1 % of the alum in some saturated solutions had hydrolyzed. In the other earlier studies on the solubilities in the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$ system,[10−12] the occurrence of aluminum hydrolysis was not reported.

The solid phase was isolated by filtration, dried at the room temperature, and pulverized for the X-ray analysis with a Siemens D 5005 X-ray diffraction analyzer. The diffraction patterns were compared with the data listed in the Powder Diffraction File.[17]

Aluminum in the liquid samples was determined by chelatometric titrations (a fixed amount of an EDTA solution was added to a sample and the unreacted part of EDTA was titrated with an $ZnSO_4$ solution using the xylenol orange indicator). Concentrations of sulfate ions were determined by a gravimetric method (weighing $BaSO_4$ after precipitation with $BaCl_2$). Concentrations of ammonium ions were determined by a distillation method—ammonia liberated from the solution sample by NaOH was absorbed in a known volume of HCl solution. Sulfuric acid concentrations in the quaternary system $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ were determined by potentiometric titrations with a sodium hydroxide solution. On titration curves (pH versus added volume of NaOH solution), it was possible to distinguish two separate end points corresponding to the reaction of NaOH with sulfuric acid and with aluminum, respectively, as long as the Al/H_2SO_4 molar ratio in solution was greater than $\approx$0.08. When that condition was not fulfilled, only the endpoint corresponding to the sum of Al and H^+ was observed; the volume of titrant corresponding to sulfuric acid was then obtained by subtracting the volume of NaOH equivalent to the aluminum content (using the Al concentration determined by the chelatometric titration).

The estimates of the repeatabilities[18] of the concentration determinations by the analytical methods (expressed as ± 1 SD/average value) are based upon evaluation of triplicate analyses of 10 samples of equilibrium solutions. Repeatability of the aluminum, sulfate ion and ammonium determination was ± 0.7 %, ± 0.6 %, and ± 1.1 %, respectively. Repeatability of sulfuric acid determination was ± 1 % for the solutions with the Al/H_2SO_4 molar ratio greater than $\approx$0.08; for 12 solution samples (denoted in Table 2), which did not fulfill that condition, the repeatability was estimated as 1.5 %.

The water temperature in the thermostated shaking bath was measured by a 100 Ω platinum resistance thermometer. The maximum temperature instability of the thermostated bath did not exceed ± 0.05 °C and the standard uncertainty[18] (the coverage factor $k = 1$) of the bath temperature is estimated to be ± 0.1 °C.

The densities of the saturated solutions at (25, 30, 40, and 50) °C were measured with 10 cm^3 pycnometers calibrated with distilled water at the temperatures at which they were to be used. The same thermostated shaking bath as for the solubility measurements was used for the density measurements. The estimated standard uncertainty (the coverage factor $k = 1$) of the density determinations is ± 0.001 $g \cdot cm^{-3}$.

Results and Discussion

As determined by X-ray diffraction analysis, the equilibrium solid phase in all solubility experiments was composed of ammonium alum crystals. Measured solubilities of ammonium alum in the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$ system are summarized in Table 1 and in Figures 1 and 2. The composition of each solution in equilibrium with $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystals is characterized by mass fractions $w((NH_4)_2SO_4))$ and $w(Al_2(SO_4)_3$. These values were calculated from the analytic determinations of ammonium and aluminum concentrations,

Table 2. Compositions of the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ Solutions in Equilibrium with $NH_4Al(SO_4)_2\cdot 12H_2O$ Crystals at (25, 30, 40, and 50) °C

$100w^a$			$100w'^b$	solution density
$(NH_4)_2SO_4$	$Al_2(SO_4)_3$	H_2SO_4	H_2SO_4	$g\cdot cm^{-3}$
25 °C				
0.080	19.7	8.91	11.1	1.309
0.0795	20.0	7.84	9.81	1.312
0.330	14.4	8.25	9.67	1.223
1.02	7.60	8.70	9.52	1.147
1.72	5.24	8.36	8.98	1.126
2.24	4.33	8.76	9.38	1.116
5.28	1.93	10.05	10.8	1.108
8.57	1.11	8.54	9.45	1.116
14.5	0.569	7.95[c]	9.36	1.140
21.5	0.334	7.54[c]	9.64	1.176
32.5	0.205	6.59[c]	9.79	1.224
42.8	0.146	5.61[c]	9.83	1.279
30 °C				
0.145	20.2	9.47	11.9	1.311
0.147	21.7	7.69	9.84	1.320
0.365	16.2	8.00	9.58	1.244
0.773	10.5	8.60	9.69	1.180
1.47	7.45	8.89	9.76	1.147
2.26	5.47	8.80	9.54	1.139
4.36	3.30	8.99	9.74	1.115
6.85	1.81	9.06	9.92	1.113
11.8	1.03	8.62[c]	9.90	1.132
19.5	0.565	7.68[c]	9.62	1.171
27.8	0.389	6.80[c]	9.47	1.208
43.3	0.238	5.22[c]	9.26	1.280
40 °C				
0.227	22.9	8.04	10.5	nm[d]
0.807	14.0	8.42	9.89	1.215
0.273	21.4	9.34	11.9	nm
2.01	9.43	8.49	9.59	1.167
2.77	8.08	8.41	9.43	1.152
3.38	6.66	8.55	9.50	1.144
5.74	4.24	8.67	9.63	1.131
8.30	2.86	8.13	9.15	1.127
17.7	1.17	8.03[c]	9.90	1.155
26.0	0.741	6.96[c]	9.51	1.200
36.5	0.535	5.96[c]	9.46	1.250
44.3	0.393	5.25[c]	9.49	nm
50 °C				
0.490	22.4	8.97	11.6	1.326
0.398	23.6	7.85	10.3	1.330
1.34	16.1	8.01	9.70	1.238
2.28	12.3	7.88	9.23	1.195
3.17	10.9	8.22	9.57	1.181
4.05	9.03	8.47	9.74	1.168
6.93	5.96	8.42	9.66	1.145
10.6	3.84	8.60	10.1	1.150
19.4	2.05	7.54	9.58	1.169
34.6	1.20	6.20	9.66	1.241
39.8	1.03	5.42	9.19	1.271
44.4	0.838	5.03	9.27	1.292

[a] w, mass fraction of the respective component in the solution saturated by $NH_4Al(SO_4)_2\cdot 12H_2O$. [b] w', mass fraction of H_2SO_4 on a salt-free basis; $w' = w(H_2SO_4)/[w(H_2SO_4) + w(H_2O)]$. [c] Calculated from the sum of moles of H^+ and Al in the unit mass of solution (obtained by the potentiometric titration with NaOH solution) and the concentration of Al determined by chelatometric titration; relative combined standard uncertainty ($k = 1$) estimated as 2.0 %. [d] nm, not measured.

respectively. The results of determinations of sulfate concentrations were used for an independent check of the consistency of results by means of the charge balance. The relative charge imbalance for each experimental point in Table 1 was calculated as the ratio $\Sigma z_i m_i/\Sigma|z_i|m_i$, where m_i is the number of moles of the respective ion in a mass unit of solution and z_i is the ion charge. The average value of the charge imbalance and its standard deviation for 44 experimental points in Table 1 was (−0.1 ± 1.2) %. Taking into account the repeatability of the analytical measurement and the uncertainty of the measurement of temperature (as given in the Experimental Section), as well as the standard deviation of the average value of the charge imbalance, we estimate the relative combined standard uncertainty ($k = 1$) of $w((NH_4)_2SO_4)$) and $w(Al_2(SO_4)_3$ in Table 1 as 1.5 and 1.2 %, respectively.

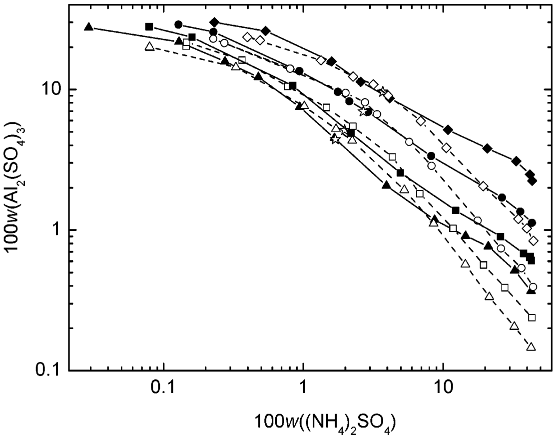

Figure 1. Compositions of solutions in equilibrium with $NH_4Al(SO_4)_2\cdot 12H_2O$ crystals. The $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$ solutions (solid lines): filled triangles, 25 °C; filled squares, 30 °C; filled circles, 40 °C; filled diamonds, 50 °C. The $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ solutions (dashed lines): open triangles, 25 °C; open squares, 30 °C; open circles, 40 °C; open diamonds, 50 °C; the experimental values from Table 2 were adjusted to the reference mass fraction $w'(H_2SO_4) = w(H_2SO_4)/[w(H_2SO_4) + w(H_2O)] = 0.1$ by linear interpolation. Stars, solubility of $NH_4Al(SO_4)_2\cdot 12H_2O$ in pure water.[16] The lines, drawn point to point, are only guides to the eye.

In Figures 1 and 2, equilibrium isotherms ($w(Al_2(SO_4)_3)$ versus $w((NH_4)_2SO_4)$) are plotted in rectangular logarithmic coordinates in order to show more distinctly the solubility values in the whole concentration range of both components. The data obtained in this work are compared with the available literature data in Figure 2. At 25 °C, the data of Hill and Kaplan[10] as well as those of Urazov and Kindyakov[11] generally agree with the present data (Figure 2a); nevertheless, it should be noted that the literary data[10,11] exhibit a large spread near $w((NH_4)_2SO_4) \approx 0.006$. The data of Druzhinin and Kalbaev[13] at 25 °C in Figure 2a (as well as the data of those authors at 40 °C in Figure 2c) fluctuate widely and should not be considered reliable. Most of the points of the solubility isotherms at 30 °C and 40 °C reported by Funaki[12] lie above our measurements (Figure 2b,c). The Funaki's data at 30 °C and 40 °C lie too high to be consistent with the solubilities of ammonium alum in pure water[16] at these temperatures which are also plotted in Figure 2a to 2d (ammonium alum solubility in pure water[16] serves as an independent check of the relative position of the solubility isotherm in the more complex ternary system). At 50 °C (Figure 2d), data of Urazov and Kindyakov[11] and Funaki[12] agree very well with our results in the central part of the solubility isotherm, they scatter quite a bit, however, near the both ends of the solubility curve.

Measured solubilities of ammonium alum in $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ solutions are given in Table 2 and in Figure 1. They are compared with the solubilities in the ternary system. In Figure 1, the experimental mass fractions $w(Al_2(SO_4)_3)$ from Table 2 were adjusted to the reference mass fraction of the sulfuric acid on a salt-free basis, $w'(H_2SO_4)$, equal to 0.1 by linear interpolation, making use of the smoothed isotherms of the ternary system (where $w'(H_2SO_4) = 0$); these small adjustments which were made for the graphical presenta-

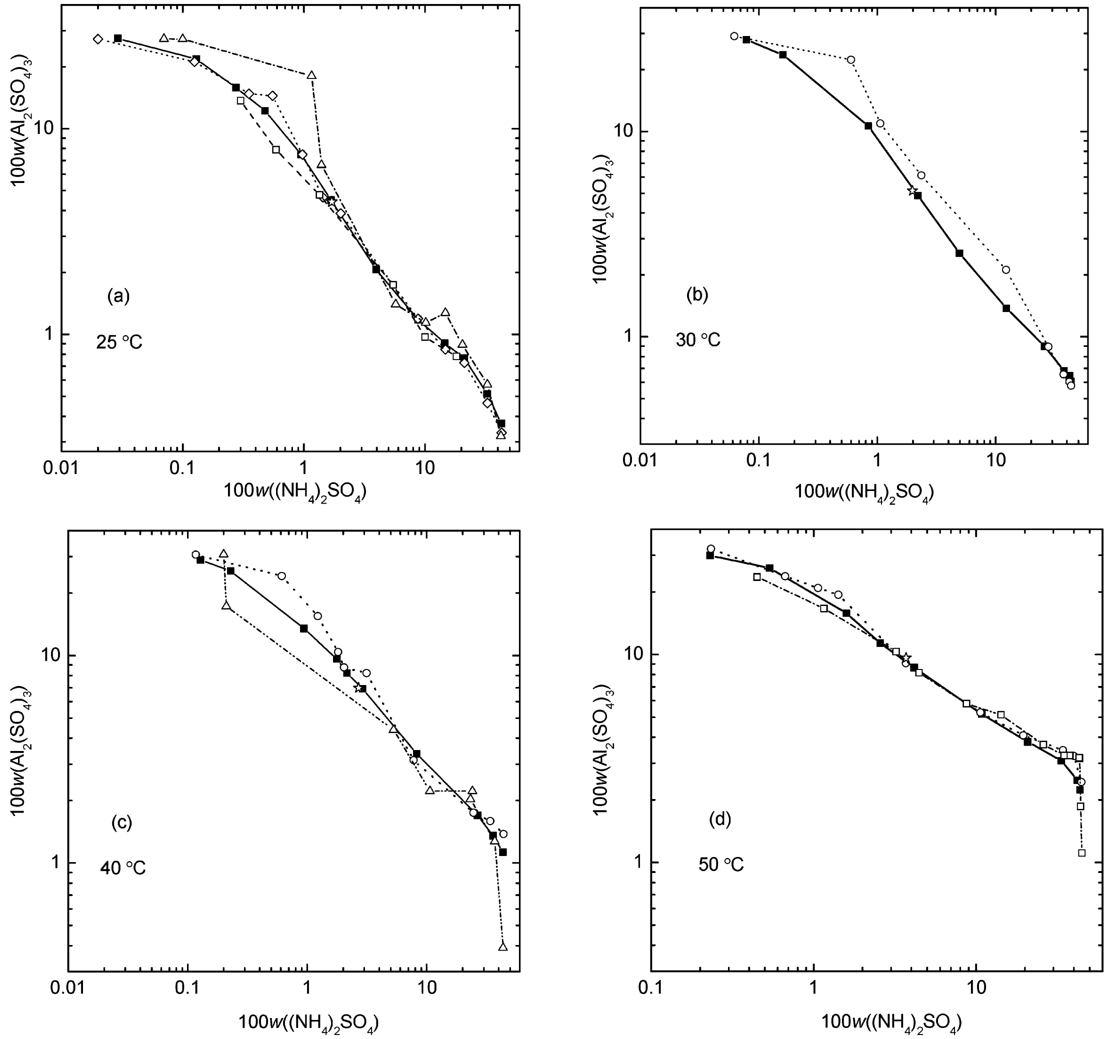

Figure 2. Compositions of the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$ solutions in equilibrium with $NH_4Al(SO_4)_2 \cdot 12H_2O$ crystals. Comparison of the present work with the available literature data for temperatures: a, 25 °C; b, 30 °C; c, 40 °C; d, 50 °C. Symbols: filled squares, this work; open diamonds, Hill and Kaplan[10], 25 °C; open squares, Urazov and Kindyakov,[11] 25 °C and 50 °C; open triangles, Druzhinin and Kalbaev,[13] 25 °C and 40 °C; open circles, Funaki,[12] (30, 40, and 50) °C; stars, solubility of $NH_4Al(SO_4)_2 \cdot 12H_2O$ in pure water[16] (the lines, drawn point to point, are only guides to the eye).

tion only, did not change the overall character of the plot. The average value of the charge imbalance and its standard deviation for 48 experimental points in Table 2 was (−0.6 ± 1.5) %. The relative combined standard uncertainty ($k = 1$) of $w((NH_4)_2SO_4)$, $w(Al_2(SO_4)_3)$, and $w(H_2SO_4)$ given in Table 2 was estimated as 1.7 %, 1.4 %, and 1.6 %, respectively (for 12 experimental solubilities with the Al/H_2SO_4 molar ratio less than ≈ 0.08, the relative combined standard uncertainty of $w(H_2SO_4)$ was estimated as 2.0 %; those concentrations are denoted by the superscript *c* in Table 2).

As already noted in the Introduction, solubilities of ammonium alum in the quaternary system $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ are available in the literature only for the $NH_4Al(SO_4)_2 + H_2SO_4 + H_2O$ subsystem.[9] The solubility values in Table 2 were interpolated to the molar ratio $NH_4/Al = 1$; the $NH_4Al(SO_4)_2$ solubility values (the sum of $w(Al_2(SO_4)_3)$ and $w((NH_4)_2SO_4)$) obtained by this procedure are in good agreement with the solubility data[9] for the $NH_4Al(SO_4)_2 + H_2SO_4 + H_2O$ system, as can be seen in Figure 3.

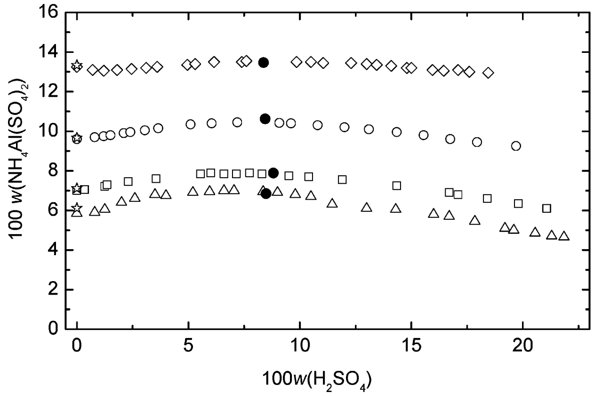

Figure 3. Comparison of the measured data for the $NH_4Al(SO_4)_2 \cdot 12H_2O$ solubilities in the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ system with the available literature data. Data of Nývlt et al.[9] for the solubility of $NH_4Al(SO_4)_2 \cdot 12H_2O$ in aqueous solutions of H_2SO_4 (i.e., for the above quaternary system with the NH_4/Al molar ratio equal to 1): open triangles, 25 °C; open squares, 30 °C; open circles, 40 °C; open diamonds, 50 °C. Filled circles, this work, data for the $NH_4Al(SO_4)_2 \cdot 12H_2O$ solubility in the $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2SO_4 + H_2O$ system at (25, 30, 40, and 50) °C interpolated to the NH_4/Al molar ratio equal to 1. Stars, solubilities of $NH_4Al(SO_4)_2 \cdot 12H_2O$ in pure water[16] at (25, 30, 40, and 50) °C.

From Figure 1, it is apparent that the addition of sulfuric acid to the ternary $(NH_4)_2SO_4 + Al_2(SO_4)_3 + H_2O$ solution increases the ammonium alum solubility in the central part of the solubility isotherms (i.e., in solutions with a NH_4/Al molar ratio close to 1). This may be seen also in Figure 3 where the dependence between ammonium alum solubility and H_2SO_4 concentration exhibits a flat maximum at $w'(H_2SO_4) \approx 0.08$ to 0.1. On the other hand, at low NH_4/Al ratios and, more significantly, at high

NH_4/Al ratios, the ammonium alum solubility is suppressed by the H_2SO_4 addition. In general, the ammonium alum solubilities are only moderately influenced by the sulfuric acid addition up to $w'(H_2SO_4) = 0.1$. This finding is of importance for several practical applications, where moderately acidic solutions of ammonium alum with the NH_4/Al molar ratio $\neq 1$ are crystallized,[2,5−7] since the necessary solubilities may be obtained by interpolation in Tables 1 and 2.

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