

PHASE EQUILIBRIA IN THE SYSTEM $\text{NH}_4\text{Al}(\text{SO}_4)_2\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$

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Abstract

Equilibrium solubility curves of the ammonium aluminium sulphate in aqueous solutions of sulphuric acid have been calculated using checked literature data and our own measurements. The concentration of sulphuric acid ranged from 0 to 23 mass%, temperature range between 20 and 60°C has been extrapolated up to 75°C by means of a thermodynamically based correlation method. The solubility correlation as well as the hydration analysis implied a possible destructuralization of solutions at higher acid concentrations.

Keywords: ammonium aluminium sulphate, solubility, sulphuric acid

Introduction

This paper is linked with a communication [1] dealing with a treatment of solutions from chemical extraction of uranium ores. The aim of this paper is to evaluate our experimental data and available literature data of the system $\text{NH}_4\text{Al}(\text{SO}_4)_2\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ and in this way to obtain an insight into possible structure changes in the solution.

Theoretical

For a phase equilibrium of the solid (') and liquid (") phase follows [2]

$$\log \frac{m_i}{m_{0i} y_i} = \log \frac{\gamma'_i \gamma''_{0i}}{\gamma''_i} \quad (1)$$

where m_i is the molality of the i -th component in the solution, m_{0i} is the molality (solubility) of the pure i -th component in water under identical conditions (temperature, pressure), y_i is mole fraction of the i -th component in solid phase and γ_i are the corresponding activity coefficients. Introducing notations for the relative molality

$$X_i = \frac{m_i}{m_{oi}} \quad (2)$$

and for the relative activity coefficient of i -th component in the liquid phase

$$\xi_i = \frac{\gamma_i''}{\gamma_{oi}''} \quad (3)$$

we obtain

$$\log \frac{x_i}{y_i} = -\log \frac{\xi_i}{\gamma_i} = \varphi_i \quad (4)$$

This relationship can be modified for a three-component system:

$$\log \frac{x_1 y_2}{x_2 y_1} = \varphi_1 - \varphi_2 \quad (5)$$

or

$$K = \frac{y_2 x_1}{y_1 x_2} \approx \frac{p'_2 p_1''}{p'_1 p_2''} \quad (6)$$

where K is a distribution coefficient.

For dissociated substances possessing a common anion, Eq. (4) converts into

$$\frac{1}{v_1} \log \left[\left(X_1 + X_2 \frac{m_{20}}{m_{10}} \right)^{v_{1-}} X_1^{v_{1+}} \right] - \log y_1 = \varphi_1 \quad (7)$$

holding for the solubility of the component 1, and the φ_1 can be approximated by the expansion

$$\varphi_1 = Q_{12} m_2 + Q_{122} m_2^2 + \dots \quad (8)$$

Solution of this equation is relatively complicated but it can be simplified [2] for the case where no solid solutions are formed

$$\frac{1}{v_1} \log \left[\left(X_1 + X_2 \frac{m_{20}}{m_{10}} \right)^{v_{1-}} X_1^{v_{1+}} \right] = \varphi_1 \quad (9)$$

A suitable shape of this equation can be obtained

$$\frac{1}{b_1 + h_1} \log \left[X_1^{b_1} \left(X_1 + \frac{h_2}{h_1} X_2 \right)^{h_1} \right] = Q_{12} m_2 + Q_{122} m_2^2 + Q_{1222} m_2^3 \quad (10)$$

where b_1 is the number of cations in the component 1 and h_1 and h_2 the number of common anions in components 1 and 2, respectively. X_i is the relative molality of the i -th component related to its solubility in pure water.

Data and their treatment

Solubility data of the ammonium aluminium sulphate in aqueous solutions of the sulphuric acid have been published in the paper [3] for temperature 30°C, in the paper [4] for temperatures 20 and 30°C. These data have been complemented by our measurements at 25, 30, 40, 50 and 60°C and by several measurements at higher temperatures.

Table 1 Solubility data in the system ammonium aluminium sulphate (AAS)–sulphuric acid (SA)–H₂O

$T/^\circ\text{C}$	$p/\text{mass}\%$					$a_{\text{AAS}_{\text{anh}}}$	w_{hyd}	Source
	H ₂ SO ₄	AAS _{anh}	AAS _{hyd}	H ₂ O _{tot}	H ₂ O _{free}			
20	0	5.28	10.10	94.72	89.90	5.57	0.112	2
	1.05	5.56	10.63	93.39	88.32	5.95	0.120	
	5.5	6.03	11.53	88.47	82.97	6.82	0.139	
	7.2	6.03	11.53	86.77	81.27	6.95	0.142	
	9.2	5.97	11.41	84.83	79.39	7.04	0.144	
	10.1	5.91	11.30	83.99	78.60	7.04	0.144	
	13	5.63	10.76	81.37	76.24	6.92	0.141	
	17	5.22	9.98	77.78	73.02	6.71	0.137	
	22.8	4.47	8.57	72.72	68.63	6.16	0.125	
	25	0	5.85	11.19	94.15	88.81	6.21	
1.25		6.05	11.57	92.7	87.18	6.53	0.133	this work
2		6.4	12.24	91.6	85.76	6.99	0.143	
2.6		6.6	12.62	90.8	84.78	7.27	0.149	this work
4		6.75	12.91	89.25	83.09	7.56	0.155	
5.2		6.9	13.19	87.9	81.61	7.85	0.162	
6.6		7	13.38	86.4	80.02	8.10	0.167	
7.05		7	13.38	85.95	79.57	8.14	0.168	
8.35		6.95	13.29	84.7	78.36	8.21	0.170	
9.8		6.8	13.00	83.4	77.20	8.15	0.168	
10.5		6.7	12.81	82.8	76.69	8.09	0.167	
13		6.1	11.66	80.9	75.34	7.54	0.155	
14.3		6.05	11.57	79.65	74.13	7.60	0.156	
16	5.8	11.09	78.2	72.91	7.42	0.152		

Table 1 Continued

$T/^\circ\text{C}$	$p/\text{mass}\%$					a AAS _{anh}	w_{hyd}	Source
	H_2SO_4	AAS _{anh}	AAS _{hyd}	$\text{H}_2\text{O}_{\text{tot}}$	$\text{H}_2\text{O}_{\text{free}}$			
25	17.85	5.45	10.42	76.7	71.73	7.11	0.145	
	19.6	5	9.56	75.4	70.84	6.63	0.135	
	20.55	4.85	9.27	74.6	70.18	6.50	0.132	
	21.85	4.65	8.89	73.5	69.26	6.33	0.128	
30	0	7.15	13.67	92.85	86.33	7.70	0.158	2
	2	7.77	14.86	90.23	83.14	8.61	0.179	
	8.1	8.11	15.51	83.79	76.39	9.68	0.203	
	10	7.89	15.09	82.11	74.91	9.61	0.201	
	11.8	7.77	14.86	80.43	73.34	9.66	0.203	
	15.7	7.21	13.79	77.09	70.51	9.35	0.195	
	15.7	7.33	14.01	76.97	70.29	9.52	0.199	
	17	7.12	13.61	75.88	69.39	9.38	0.196	
	17	7.43	14.21	75.57	68.79	9.83	0.207	
	18.6	6.84	13.08	74.56	68.32	9.17	0.191	
	20.5	6.62	12.66	72.88	66.84	9.08	0.189	
	30	0	7.08	13.54	92.92	86.46	7.62	0.157
2.1		7.69	14.71	90.21	83.19	8.53	0.177	
4.12		7.89	15.08	87.99	80.80	8.96	0.187	
6.06		8.11	15.51	85.83	78.43	9.45	0.198	
7.96		8.09	15.46	83.95	76.58	9.63	0.202	
9.85		7.90	15.11	82.25	75.04	9.61	0.201	
11.69		7.76	14.84	80.55	73.47	9.64	0.202	
13.52		7.55	14.43	78.93	72.05	9.56	0.200	3
15.36		7.20	13.77	77.44	70.87	9.30	0.194	
15.35		7.23	13.83	77.42	70.82	9.34	0.195	
17.07		7.14	13.66	75.79	69.27	9.43	0.197	
17.19		6.84	13.07	75.97	69.74	9.00	0.187	
18.93		6.66	12.73	74.41	68.34	8.95	0.186	
18.89		6.78	12.97	74.33	68.14	9.13	0.190	
20.7		6.36	12.16	72.94	67.14	8.72	0.181	
22.4		6.16	11.78	71.44	65.82	8.62	0.179	
30	0	7	13.38	93	86.62	7.53	0.155	this work
	1.25	7.2	13.76	91.55	84.98	7.86	0.162	
	2.3	7.45	14.24	90.25	83.46	8.25	0.171	

Table 1 Continued

$T/^\circ\text{C}$	$p/\text{mass}\%$					a AAS _{anh}	w_{hyd}	Source
	H_2SO_4	AAS _{anh}	AAS _{hyd}	$\text{H}_2\text{O}_{\text{tot}}$	$\text{H}_2\text{O}_{\text{free}}$			
	3.55	7.6	14.53	88.85	81.92	8.55	0.177	
	5.55	7.85	15.00	86.6	79.44	9.06	0.189	
	6	7.9	15.10	86.1	78.90	9.18	0.191	
	7.15	7.85	15.01	85	77.84	9.24	0.193	
	8.3	7.85	15.01	83.85	76.69	9.36	0.196	
	9.5	7.75	14.82	82.75	75.68	9.37	0.196	
	10.4	7.7	14.72	81.9	74.88	9.40	0.197	
	11.9	7.55	14.44	80.55	73.66	9.37	0.196	
	14.35	7.25	13.86	78.4	71.79	9.25	0.193	
	16.7	6.9	13.19	76.4	70.11	9.03	0.188	
	18.4	6.6	12.62	75	68.98	8.80	0.183	
	19.8	6.35	12.14	73.85	68.06	8.60	0.178	
	21.05	6.1	11.66	72.85	67.29	8.37	0.173	
40	0	9.6	18.35	90.4	81.64	10.62	0.225	this work
	1.2	9.75	18.64	89.05	80.16	10.95	0.233	
	2.1	9.9	18.93	88	78.97	11.25	0.240	
	3.05	10.05	19.22	86.9	77.73	11.57	0.247	
	5.1	10.35	19.73	84.55	75.11	12.24	0.263	
	7.2	10.45	19.98	82.35	72.82	12.69	0.274	
	9.08	10.42	19.92	80.5	71.00	12.94	0.281	
	10.8	10.3	19.69	78.9	69.51	13.05	0.283	
	12	10.2	19.50	77.8	68.50	13.11	0.285	
	14.35	9.95	19.02	75.7	66.63	13.14	0.286	
	15.55	9.8	18.74	74.65	65.71	13.13	0.285	
	17.95	9.45	18.07	72.6	63.98	13.02	0.282	
	19.7	9.25	17.69	71.05	62.61	13.02	0.282	
50	0	13.25	25.33	86.75	74.67	15.27	0.339	this work
	1.2	13.05	24.95	85.75	73.85	15.22	0.338	
	2.45	13.15	25.14	84.4	72.41	15.58	0.347	
	3.6	13.25	25.3	83.15	71.07	15.94	0.356	
	5.3	13.4	25.62	81.3	69.08	16.48	0.371	
	6.15	13.5	25.8	80.35	68.04	16.80	0.379	
	7.6	13.55	25.91	78.85	66.49	17.18	0.390	

Table 1 Continued

$T/^\circ\text{C}$	$p/\text{mass}\%$					$a_{\text{AAS}_{\text{anh}}}$	w_{hyd}	Source
	H_2SO_4	AAS_{anh}	AAS_{hyd}	$\text{H}_2\text{O}_{\text{tot}}$	$\text{H}_2\text{O}_{\text{free}}$			
50	9.85	13.5	25.81	76.65	64.34	17.61	0.401	
	11.05	13.45	25.72	75.5	63.23	17.81	0.407	
	13	13.4	25.62	73.6	61.38	18.21	0.417	
	14.8	13.2	25.23	72	59.96	18.33	0.421	
	15.95	13.1	25.04	70.95	59.00	18.46	0.425	
	17.1	13.1	25.04	69.8	57.85	18.77	0.433	
	18.45	12.95	24.76	68.6	56.79	18.88	0.436	
58	1.6	17.2						this work
58.5	0	17.17						
60	0	17.17	32.82	82.83	67.17	20.73	0.489	this work
	1.9	17.15	32.79	80.95	65.31	21.19	0.502	
	4.4	17.1	32.70	78.5	62.90	21.78	0.520	
	5.95	17.2	32.89	76.85	61.16	22.38	0.538	
	7.2	17.25	32.98	75.55	59.82	22.83	0.551	
	9.55	17.4	33.27	73.05	57.18	23.82	0.582	
	11.95	17.5	33.46	70.55	54.59	24.81	0.613	
	13.45	17.55	33.56	69	52.99	25.43	0.633	
	14.7	17.5	33.46	67.8	51.84	25.81	0.645	
	16	17.35	33.17	66.65	50.83	26.03	0.653	
62.5	1.0	21.0						this work
67.7	2.5	24.5						
68.3	5.0	24.0						
71.7	3.0	26.0						
72.0	7.0	69.0						this work
72.0	7.0	23.0						
73.5	1.0	26.0						

The ammonium aluminium sulphate used for our measurements was produced in Spolchemie for the production of synthetic corundum single crystals, several times recrystallized from demineralized water and its purity checked by atomic absorption (Varian AA-30) and X-ray spectrography (Philips PV-1404). Its purity has been found as 99.966 mass%. The sulphuric acid used was reagent grade product by Spolchemie. The conductivity of the demineralized water was about 5 μS . Isothermal data as well as the literature data were obtained using an analytical method, our measurements were based on a polythermal method (components altogether 100 g weighted into a closed bottle and heated with the rate 1 K h^{-1} until the last crystals dis-

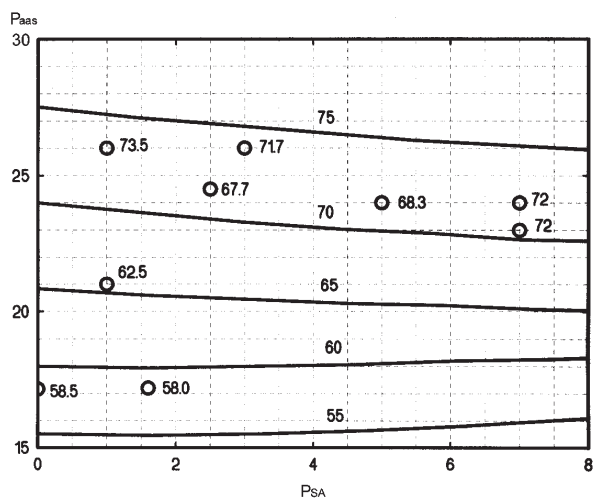


Fig. 1 Polythermic measurement of the solubility in the system: ammonium aluminium sulphate (AAS)–sulphuric acid (SA)–water. Number at the points denote the measured temperature of solubility, the curves have been calculated by the correlation method [5] using constants from Table 2

appeared); polytherms were obtained by interpolation of close lying data. Their accuracy is lower at higher temperatures, as can be seen from Fig. 1. Literature data as well as the results of the analytical method of our measurement show clearly that in the investigated concentration range the ammonium aluminium sulphate dodecahydrate is the sole existing solid phase. All data are summarized in Table 1.

Table 2 Interaction constants Q of the system ammonium aluminium sulphate–sulphuric acid–water

$T/^\circ\text{C}$	Q_{12}	Q_{122}	Q_{1222}	Source
20	0.6419 ₆₇₆	−0.3811 ₅₆₅	0.0726 ₇₄₀	3
25	0.5770 ₉₂₁	−0.3082 ₁₀₀	0.0554 ₉₈₃	this work
30	0.5254 ₂₈₇	−0.2902 ₀₀₇	0.0567 ₉₇₈	3
	0.4898 ₄₂₄	−0.2410 ₁₈₅	0.0418 ₇₆₁	2
	0.4625 ₇₀₆	−0.2245 ₃₉₅	0.0397 ₈₃₀	this work
40	0.3358 ₆₈₃	−0.1309 ₅₀₇	0.0206 ₄₇₅	this work
50	0.1837 ₄₃₁	−0.0255 ₅₀₆	0	this work
55	0.170	−0.0150	0	interpolation
60	0.1545 ₈₀₈	−0.0195 ₅₃₉	0	this work
65	0.110	−0.010	0	extrapolation
70	0.080	−0.0018	0	extrapolation
75	0.070	−0.0010	0	extrapolation

The values of the constants Q evaluated using the method described in detail and checked on many inorganic systems in the book [2] are summarized Table 2 and shown in Fig. 2.

Using known values Q we can recalculate the smoothed solubilities of component 1 for any given concentration of the component 2 using Eq. (10), (Fig. 2).

Hydration analysis [6, 7], based on Eq. (11), can provide some information on the intrinsic structure of the solution.

$$P = \frac{1 - w_1 - w_2 - w_{\text{vol}}}{M_0(n_1 + n_2)} \quad (11)$$

From this equation, values of the hydration parameter P and of the ratio P/x_2 shown in Fig. 3 and given in Table 3 for three values chosen for each system, were obtained.

Table 3 Selected results of the hydration analysis

$T/^\circ\text{C}$	Source	% H_2SO_4	P	P/x_2
20	3	1.05	-0.182	-89.02
		9.20	-1.11	-57.09
		22.8	-1.84	-33.99
25	this work	1.25	-0.171	-70.41
		9.80	-1.14	-54.40
		20.55	-1.51	-31.43
30	3	2.00	-0.28	-68.95
		10.00	-0.96	-44.10
		20.50	-1.48	-30.40
	2	2.10	-0.29	-67.95
		9.85	-0.97	-45.32
		20.70	-1.46	-29.61
		this work	1.25	-0.15
40	this work	9.50	-0.93	-45.58
		21.05	-1.44	-28.85
		1.20	-0.10	-42.48
50	this work	10.80	-0.82	-33.88
		19.70	-1.24	-25.90
		1.20	-0.05	-19.59
60	this work	9.85	-0.56	-24.68
		18.45	-0.98	-21.06
		1.90	-0.09	-20.51
		9.56	-0.46	-20.09
		16.00	-0.78	-18.75

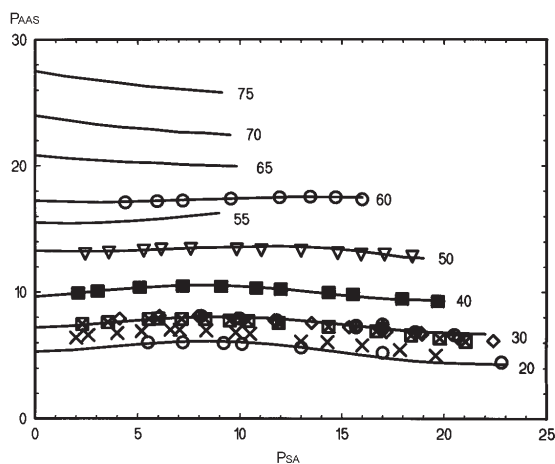


Fig. 2 Solubility in the system: ammonium aluminium sulphate (AAS)–sulphuric acid (SA)–water. Individual curves have been calculated from Eq. (9)

Discussion

Literature data used for the treatment have been limited up to sulphuric acid concentration below 23%. Results with higher acid concentrations couldn't be correlated with sufficient accuracy using given Q constants. This may be explained by a more complicated interactions in the solution and probably also by a lower data precision [3]. It has been shown [4] as well that the character of the solubility at acid concentrations above 30% is changed: the solubility up to 8% H_2SO_4 slightly rises, between 8 and 32% H_2SO_4 diminishes, passes through a minimum and at higher acid concentrations rises again.

It can be seen from Table 2 that the absolute values of the interaction constants Q decrease with rising the temperature. This is not unexpected, as the behaviour of the solution approaches ideality with higher temperatures. Up to 50°C three constants are required for the correlation, at higher temperatures $Q_{122}=0$, and just two constants are sufficient. The constants for temperatures above 60°C were obtained by a graphical extrapolation. At the same time, no new interactions can be expected at slightly higher temperatures so that the extrapolation seems to be safe in this case; its acceptance is checked by polythermal data shown in Fig. 1.

It can be concluded from the interaction constants [7] $Q_{12}>0$ a $Q_{122}<0$ that in particular at higher acid concentrations occurs some destructuralization of the solution. This corroborates as well the values of the hydration parameter $P<0$ approaching a constant value and slightly rising values of $P/x_2<0$ at lower temperatures. On the other hand we can conclude from almost constant values of x_0/s that the sulphuric acid up to 20% doesn't remove water from the hydration sphere of the alum.

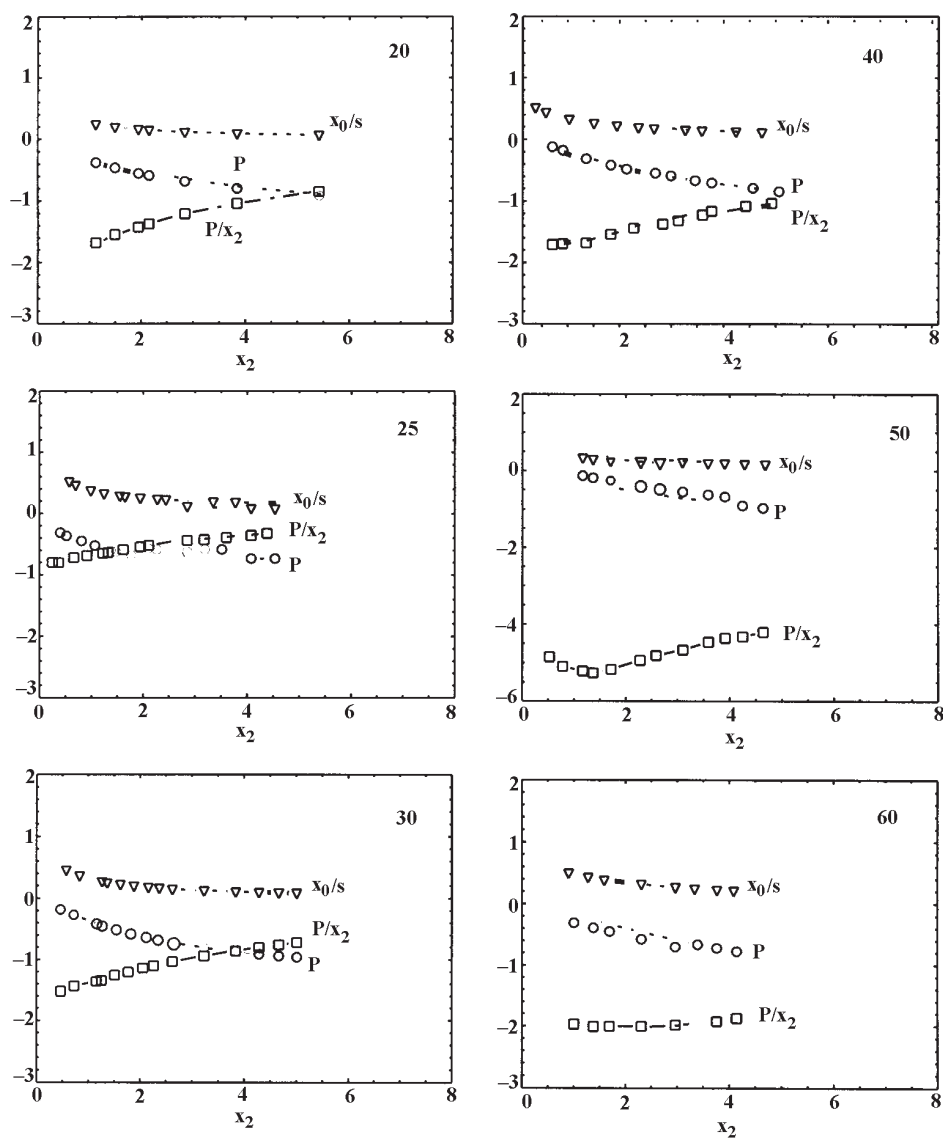


Fig. 3 Hydration analysis of the system: ammonium aluminium sulphate (AAS)–sulphuric acid (SA)–water. Corresponding temperatures are given in the right upper corner. Plotted are relative values related to the rounded maxims

The value of the hydration parameters P and P/x_2 is extremely sensitive [6] to the quality of experimental data. The smooth curves on Fig. 3 thus demonstrate that the data obtained are sufficiently reliable.

Notations

a	concentration (g/100 g H_2O)
b_1	number of different cations in component 1
h_1	number of common anions in component 1
K	distribution coefficient
M_{anh}, M_i	molecular mass of anhydrous substance (g mol^{-1})
M_0	molecular mass of water (g mol^{-1})
m_i	molality of the i -th component ($\text{mol kg}^{-1} \text{H}_2\text{O}$)
m_{0i}	molality of the i -th component in pure water ($\text{mol kg}^{-1} \text{H}_2\text{O}$)
n_i	number of moles in $100 \text{ cm}^3 \text{H}_2\text{O}$ mol/100 $\text{cm}^3 \text{H}_2\text{O}$
P	hydration parameter
p, p_i	concentration (mass%)
Q_{ij}, Q_{122}	interaction constants
s	number of components
T	temperature ($^\circ\text{C}$)
w_i	concentration (kg kg^{-1})
$w_{0\text{vol}}$	concentration of free water (kg kg^{-1})
X	relative molality
x_i	mole fraction in liquid
x_0	amount of water outside the hydration sphere (kg/kg)
y_i	mole fraction in solid
γ_i	activity coefficient
Φ_i	expansion function
v_i	number of ions
ξ_i	relative activity coefficient
Subscripts:	
anh	anhydrous
free	free water
hyd	hydrate
tot	total

* * *

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