

Mean Activity Coefficients of Peroxodisulfates and Sulfates in Saturated Polycomponent Solutions

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Abstract

Activity coefficients of sodium, potassium and ammonium peroxodisulfate and sulfate in aqueous saturated polycomponent solutions at 0 – 40 °C have been derived on the basis of the thermodynamic equilibrium condition between the solid substance and its saturated solution on one hand, and on the correlation equations for the appropriate solubility data on the other hand. A good agreement between the results of both methods with maximum differences of only a few thousandths has been found. The following ternary systems without solid solutions have been treated: $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{S}_2\text{O}_8\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$, $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_8\text{-NaOH-H}_2\text{O}$, $\text{K}_2\text{S}_2\text{O}_8\text{-KOH-H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{K}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, and quaternary systems $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$.

Keywords: Activity coefficient, Sodium peroxodisulfate, Potassium peroxodisulfate, Ammonium peroxodisulfate, Sodium sulfate, Potassium sulfate, Ammonium sulfate

Introduction

In the previous contribution (Balej 2010a), estimated activity coefficients of sodium, potassium and ammonium peroxodisulfate in binary aqueous solutions at 0 – 50 °C have been presented. For the exact evaluation of thermodynamic and kinetic data of the electrosynthesis and other chemical and electrochemical reactions of peroxodisulfates, containing always sulfate ions as reaction partner, it is necessary to know the activity coefficients of these substances in the corresponding polycomponent systems, especially in solutions close to the

saturation. The aim of this contribution is to derive the values of these quantities from the known thermodynamic and solubility data in the following ternary systems:

- a) systems with a common cation: $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ (Balej and Regner 1967a), $\text{K}_2\text{S}_2\text{O}_8\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ (Balej and Regner 1960), $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$ (Balej and Regner 1963a), $\text{Na}_2\text{S}_2\text{O}_8\text{-NaOH-H}_2\text{O}$ (Balej and Regner 1970), $\text{K}_2\text{S}_2\text{O}_8\text{-KOH-H}_2\text{O}$ (Balej and Regner 1972)),
- b) systems with a common anion: $\text{Na}_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ (Balej and Regner 1966a), $\text{Na}_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ (Balej and Regner 1966b),
- c) systems without any common ion: $\text{Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Balej and Regner 1967b), $\text{K}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Balej and Regner 1969a) and $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Balej and Regner 1963b),
- d) quaternary systems: $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Balej and Regner 1965), $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Balej and Regner 1969b) and $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Balej and Regner 1968) with up to 25 wt.-% H_2SO_4 .

The mean activity coefficients of the saturated solutions of the considered peroxodisulfate or sulfate at various temperatures in ternary and quaternary systems have been calculated on the basis of the thermodynamic condition for the equilibrium between the solid electrolyte of the type 1-2, $\text{A}_2\text{B.nH}_2\text{O}$, and its saturated solution formulated by the expression (Balej 2010b)

$$\ln \gamma_s = ((\Delta_f G^\circ(\text{C}_2\text{A.nH}_2\text{O,cr}) - \Delta_f G^\circ(\text{C}_2\text{A,aq}) - n\Delta_f G^\circ(\text{H}_2\text{O,l})) / (RT) - \ln(m_{\text{C},s}^2 m_{\text{A},s} a_{\text{w},s}^n)) / 3 \quad (1)$$

The equation is valid under the assumption of a complete dissociation of the considered strong electrolytes. Here, $\Delta_f G^\circ(\text{C}_2\text{A.nH}_2\text{O,cr})$ denotes the standard formation Gibbs energy of the considered solid electrolyte and $\Delta_f G^\circ(\text{C}_2\text{A,aq})$ denotes the same quantity of the anhydrous electrolyte in its aqueous solution, respectively; $m_{\text{C},s}$, $m_{\text{A},s}$ and $a_{\text{w},s}$ represent total molality of the cation, anion and water activity of the saturated polycomponent solution at the given temperature. Values of $\Delta_f G^\circ_{\text{cr}}$ and $\Delta_f G^\circ_{\text{aq}}$ of the peroxodisulfates in the temperature range 0 - 50 °C have been taken from the previous paper (Balej 2010c), molalities of the appropriate ions in saturated polycomponent solutions have been taken from the mentioned solubility papers. Values $\Delta_f G^\circ_{\text{cr}}$ and $\Delta_f G^\circ_{\text{aq}}$ of corresponding sulfates as

coexisting solid phases present in the considered polycomponent systems at various temperatures have been obtained by the usual method with the aid of known data (Wagman et al. 1982, Knacke et al. 1991).

The other method used for the calculation of activity coefficients of saturated solutions in ternary and quaternary systems was based on the correlation equation of solubility data expressed by a series expansion of the relative activity coefficient of the crystallizing component (Nývlt 1977) as a function of the molality of other components

$$\log (\gamma_{s0}/\gamma_s) = \varphi = (\log (m_{C,s}^2 \cdot m_{A,s} / (4m_{o,s}^3))) / 3 = \sum_{i=2}^n Q_{1i} m_i + \sum_{i=2}^n \sum_{j=2}^n Q_{1ij} m_i m_j + \dots \quad (2)$$

Here, γ_{s0} represents the mean activity coefficient of the crystallizing component in the saturated solution in pure water, γ_s the mean activity coefficient of the same component in the saturated polycomponent solution, $m_{C,s}$ and $m_{A,s}$ denote the total cation and anion molalities of the crystallizing component in the saturated polycomponent solution, and $m_{o,s}$ the solubility of the same component in pure water. Knowing the concrete values of γ_{s0} and the dependence $\varphi = f(m_i, m_j, \dots)$ in the considered temperature range, values of activity coefficients of the crystallizing component in the saturated solutions of the given polycomponent system can be obtained from the expression

$$\gamma_s = \gamma_{s0} / 10^\varphi \quad (3)$$

Results and Discussion

a) Ternary systems

To calculate activity coefficients by the Eq. (1), composition of saturated solutions (in mol kg⁻¹) were taken from the appropriate solubility data. Correlation relationships $\varphi_i = f(m_j)$ for ternary systems (Balej 1982) was improved and some corrections have been performed. For individual systems, the following expressions have been used for the dependence of $\varphi_i = f(m_j)$ (at M₂S₂O₈-MOH-H₂O and M₂S₂O₈-H₂SO₄-H₂O systems, only crystallization regions of M₂S₂O₈ have been examined):

1. system Na₂S₂O₈-Na₂SO₄-H₂O, temperature range 10 – 30 °C,

a) crystallization region of Na₂S₂O₈:

$$\varphi_1 = 0.0149 m_2 - 0.00666 m_2^2 \quad (4)$$

b) crystallization region of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$:

$$\varphi_2 = (0.4284 - 0.02953 t + 0.0005086 t^2) m_1 - (0.08751 - 0.007832 t + 0.0001446 t^2) m_1^2 \quad (5)$$

2. system $\text{K}_2\text{S}_2\text{O}_8\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$, temperature range 15 – 30 °C,

a) crystallization region of $\text{K}_2\text{S}_2\text{O}_8$:

$$\varphi_1 = (0.637 - 0.0478 t + 8.91 \times 10^{-4} t^2) m_2^{0.5} - (0.128 - 0.0409 t + 9.54 \times 10^{-4} t^2) m_2 \quad (6)$$

b) crystallization region of K_2SO_4 :

$$\varphi_2 = 0.0564 m_1^{0.5} \quad (7)$$

3. system $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$, temperature range 0 – 40 °C,

a) crystallization region of $(\text{NH}_4)_2\text{S}_2\text{O}_8$:

$$\varphi_1 = (0.0195 - 0.00109 t + 1.745 \times 10^{-5} t^2) m_2 - (0.00375 - 2.02 \times 10^{-4} t + 3.01 \times 10^{-6} t^2) m_2^2 \quad (8)$$

b) crystallization region of $(\text{NH}_4)_2\text{SO}_4$:

$$\varphi_2 = (-0.02207 + 1.713 \times 10^{-4} t) m_1 \quad (9)$$

4. system $\text{Na}_2\text{S}_2\text{O}_8\text{-NaOH-H}_2\text{O}$, temperature range 10 – 30 °C,

a) crystallization region of $\text{Na}_2\text{S}_2\text{O}_8$, $m_2 \leq 8.4 \text{ mol kg}^{-1}$:

$$\varphi_1 = -0.0080 m_2 - 0.00134 m_2^2 \quad (10)$$

5. system $\text{K}_2\text{S}_2\text{O}_8\text{-KOH-H}_2\text{O}$, temperature range 10 – 40 °C,

a) crystallization region of $\text{K}_2\text{S}_2\text{O}_8$, $m_2 \leq 6.2 \text{ mol kg}^{-1}$:

$$\varphi_1 = (2.45 \times 10^{-4} - 5.55 \times 10^{-3} t + 5.47 \times 10^{-5} t^2) m_2^{0.5} + (0.281 - 3.72 \times 10^{-5} t - 6.32 \times 10^{-5} t^2) m_2 - (0.074 + 2.45 \times 10^{-6} t + 1.97 \times 10^{-5} t^2) m_2^{1.5} \quad (11)$$

6. system $\text{Na}_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$, temperature range 10 – 30 °C,

a) crystallization region of $\text{Na}_2\text{S}_2\text{O}_8$:

$$\varphi_1 = (0.007905 - 0.002556 t) m_2 + (0.3798 - 0.0006585 t) m_2^2 \quad (12)$$

b) crystallization region of $\text{K}_2\text{S}_2\text{O}_8$:

$$\varphi_2 = (0.5227 - 0.00918 t) m_1^{0.5} - (0.03266 - 0.002332 t) m_1 \quad (13)$$

7. system $\text{Na}_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$, temperature range 10 – 30 °C,

a) crystallization region of $\text{Na}_2\text{S}_2\text{O}_8$:

$$\varphi_1 = (0.03414 - 0.000407 t) m_2 - 0.00238 m_2^2 \quad (14)$$

b) crystallization region of $(\text{NH}_4)_2\text{S}_2\text{O}_8$:

$$\varphi_2 = (0.04164 - 0.001438 t) m_1 - (0.007043 - 0.00032 t) m_1^2 \quad (15)$$

8. system $\text{Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, temperature range 10 – 30 °C,

a) crystallization region of $\text{Na}_2\text{S}_2\text{O}_8$, $m_2 \leq 5 \text{ mol kg}^{-1}$:

$$\varphi_1 = (-0.1328 + 8.18 \times 10^{-4} t) m_2 - (0.00407 - 8.33 \times 10^{-5} t) m_2^2 \quad (16)$$

9. system $\text{K}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, temperature range 10 – 30 °C,

a) crystallization region of $\text{K}_2\text{S}_2\text{O}_8$, $m_2 \leq 4.5 \text{ mol kg}^{-1}$:

$$\varphi_1 = (0.2655 - 0.00566 t) m_2^{0.5} - (0.1156 - 0.00154 t) m_2 \quad (17)$$

10. system $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, temperature range 10 – 30 °C,

a) crystallization region of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $m_2 \leq 6 \text{ mol kg}^{-1}$:

$$\varphi_1 = (-0.110 + 0.0010 t) m_2 \quad (18)$$

Selected values of activity coefficients of individual crystallizing components in the mentioned ternary system calculated by the both methods are given in Table 1, simultaneously with the composition of the appropriate eutonic solutions limiting the crystallization regions of the coexisting solid phases. For systems $\text{M}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ with no eutonics, solubility data are available up to ca. 25-30 wt.-% H_2SO_4 . For the system $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$, the calculation of activity coefficients of the crystallizing substance $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ by the first method could not be performed because no data of water activity of the corresponding saturated ternary solutions are available. In this case, therefore, activity coefficients have only been calculated using the second method. The agreement of all results calculated by both methods was very good, with mean deviations 1.06 rel.-% and with a maximum deviation attaining 5.9 rel.-% for the system $\text{Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$. Results of the first method are to be preferred, as they directly correspond to the measured solubility data, while the results of the second method can depict some deviations due to the possibly not completely consistent form of the used correlation equations, especially at high ionic strength of the saturated polycomponent solutions.

Table 1. Selected values of activity coefficients of saturated solutions of sodium, potassium and ammonium peroxodisulfates and sulfates in the considered ternary systems.

<i>t</i> °C	<i>m</i> ₁ mol kg ⁻¹	<i>m</i> ₂ mol kg ⁻¹	γ_1		γ_2		solid phase
			a	b	a	b	
<i>system Na₂S₂O₈-Na₂SO₄-H₂O</i>							
10	2.6687	0.2182	0.119	0.121	--	--	Na ₂ S ₂ O ₈
	2.6013	0.2813	0.120	0.121	--	0.110	Na ₂ S ₂ O ₈ +Na ₂ SO ₄ ·10H ₂ O
	1.3085	0.3617	--	--	--	0.145	Na ₂ SO ₄ ·10H ₂ O
20	2.7003	0.4369	0.132	0.131	--	--	Na ₂ S ₂ O ₈
	2.5455	0.7500	0.130	0.131	--	0.115	Na ₂ S ₂ O ₈ +Na ₂ SO ₄ ·10H ₂ O
	1.2137	0.8593	--	--	--	0.148	Na ₂ SO ₄ ·10H ₂ O
30	2.4676	1.2006	0.144	0.142	--	--	Na ₂ S ₂ O ₈
	1.8912	2.2413	0.145	0.145	--	0.120	Na ₂ S ₂ O ₈ +Na ₂ SO ₄ ·10H ₂ O
	0.9240	2.3803	--	--	--	0.134	Na ₂ SO ₄ ·10H ₂ O
<i>system K₂S₂O₈-K₂SO₄-H₂O</i>							
15	0.0523	0.3281	0.278	0.271	--	--	K ₂ S ₂ O ₈
	0.0411	0.5668	0.220	0.222	0.235	0.234	K ₂ S ₂ O ₈ +K ₂ SO ₄
	0.0227	0.5741	--	--	0.238	0.238	K ₂ SO ₄
20	0.0887	0.2666	0.286	0.285	--	--	K ₂ S ₂ O ₈
	0.0571	0.6209	0.215	0.216	0.226	0.221	K ₂ S ₂ O ₈ +K ₂ SO ₄
	0.0324	0.6304	--	--	0.229	0.231	K ₂ SO ₄
25	0.1173	0.3015	0.272	0.272	--	--	K ₂ S ₂ O ₈
	0.0816	0.6578	0.210	0.213	0.222	0.221	K ₂ S ₂ O ₈ +K ₂ SO ₄
	0.0410	0.6778	--	--	0.223	0.223	K ₂ SO ₄
30	0.1620	0.3219	0.257	0.258	--	--	K ₂ S ₂ O ₈
	0.1081	0.7080	0.207	0.208	0.213	0.214	K ₂ S ₂ O ₈ +K ₂ SO ₄
	0.0539	0.7273	--	--	0.218	0.217	K ₂ SO ₄
<i>system (NH₄)₂S₂O₈-(NH₄)₂SO₄-H₂O</i>							
10	1.9586	1.8916	0.107	0.106	--	--	(NH ₄) ₂ S ₂ O ₈
	0.8508	4.7726	0.110	0.108	0.113	0.113	(NH ₄) ₂ S ₂ O ₈ +(NH ₄) ₂ SO ₄
	0.5035	5.0429	--	--	0.113	0.112	(NH ₄) ₂ SO ₄
20	2.3811	2.0547	0.114	0.114	--	--	(NH ₄) ₂ S ₂ O ₈
	1.2344	4.6850	0.118	0.115	0.117	0.116	(NH ₄) ₂ S ₂ O ₈ +(NH ₄) ₂ SO ₄
	0.5325	5.2596	--	--	0.114	0.114	(NH ₄) ₂ SO ₄
30	2.6305	2.5912	0.122	0.122	--	--	(NH ₄) ₂ S ₂ O ₈
	1.8130	4.4149	0.123	0.122	0.119	0.118	(NH ₄) ₂ S ₂ O ₈ +(NH ₄) ₂ SO ₄
	0.9512	5.1115	--	--	0.116	0.115	(NH ₄) ₂ SO ₄
40	3.0828	2.7668	0.131	0.130	--	--	(NH ₄) ₂ S ₂ O ₈
	2.4592	4.1813	0.130	0.130	0.118	0.119	(NH ₄) ₂ S ₂ O ₈ +(NH ₄) ₂ SO ₄
	0.9109	5.3707	--	--	0.113	0.113	(NH ₄) ₂ SO ₄

Table 1. Continued

<i>t</i> °C	<i>m</i> ₁ mol kg ⁻¹	<i>m</i> ₂ mol kg ⁻¹	γ_1		γ_2		solid phase
			a	b	a	b	
<i>system Na₂S₂O₈-NaOH-H₂O</i>							
10	1.9961	2.0890	0.126	0.128	--	--	Na ₂ S ₂ O ₈
	1.1096	4.7856	0.140	0.143	--	--	Na ₂ S ₂ O ₈
	0.7392	6.4630	0.147	0.156	--	--	Na ₂ S ₂ O ₈
20	1.9108	2.8477	0.142	0.144	--	--	Na ₂ S ₂ O ₈
	0.9179	5.7945	0.166	0.164	--	--	Na ₂ S ₂ O ₈
	0.4252	8.3639	0.189	0.192	--	--	Na ₂ S ₂ O ₈
30	2.0996	2.7923	0.156	0.156	--	--	Na ₂ S ₂ O ₈
	1.0770	5.6045	0.182	0.177	--	--	Na ₂ S ₂ O ₈
	0.5650	7.8380	0.205	0.202	--	--	Na ₂ S ₂ O ₈
<i>system K₂S₂O₈-KOH-H₂O</i>							
10	0.0359	0.4103	0.363	0.367	--	--	K ₂ S ₂ O ₈
	0.0069	2.8923	0.190	0.187	--	--	K ₂ S ₂ O ₈
	0.00406	5.9932	0.140	0.145	--	--	K ₂ S ₂ O ₈
20	0.0647	0.5762	0.319	0.321	--	--	K ₂ S ₂ O ₈
	0.0201	2.1794	0.219	0.221	--	--	K ₂ S ₂ O ₈
	0.00868	5.2949	0.145	0.148	--	--	K ₂ S ₂ O ₈
30	0.1319	0.5804	0.301	0.299	--	--	K ₂ S ₂ O ₈
	0.0370	2.3632	0.227	0.223	--	--	K ₂ S ₂ O ₈
	0.0101	6.1602	0.188	0.186	--	--	K ₂ S ₂ O ₈
40	0.2478	0.5848	0.275	0.281	--	--	K ₂ S ₂ O ₈
	0.0901	2.0268	0.239	0.242	--	--	K ₂ S ₂ O ₈
	0.0196	6.0492	0.202	0.207	--	--	K ₂ S ₂ O ₈
<i>system Na₂S₂O₈-K₂S₂O₈-H₂O</i>							
10	2.7345	0.1272	0.120	0.121	--	--	Na ₂ S ₂ O ₈
	2.7590	0.2289	0.118	0.117	0.086	0.085	Na ₂ S ₂ O ₈ +K ₂ S ₂ O ₈
	1.5925	0.1714	--	--	0.124	0.123	K ₂ S ₂ O ₈
20	2.8828	0.2062	0.134	0.131	--	--	Na ₂ S ₂ O ₈
	2.9383	0.3659	0.129	0.125	0.084	0.084	Na ₂ S ₂ O ₈ +K ₂ S ₂ O ₈
	0.6874	0.2204	--	--	0.181	0.183	K ₂ S ₂ O ₈
30	3.0578	0.2824	0.146	0.142	--	--	Na ₂ S ₂ O ₈
	3.1313	0.5040	0.140	0.137	0.089	0.085	Na ₂ S ₂ O ₈ +K ₂ S ₂ O ₈
	0.8870	0.3424	--	--	0.165	0.166	K ₂ S ₂ O ₈

Table 1. Continued

<i>t</i> °C	<i>m</i> ₁ mol kg ⁻¹	<i>m</i> ₂ mol kg ⁻¹	γ_1		γ_2		solid phase
			a	b	a	b	
<i>system Na₂S₂O₈-(NH₄)₂S₂O₈-H₂O</i>							
10	2.5706	1.5517	0.111	0.111	--	--	Na ₂ S ₂ O ₈
	2.4971	2.6731	0.105	0.105	0.099	0.099	Na ₂ S ₂ O ₈ +(NH ₄) ₂ S ₂ O ₈
	1.2518	2.8207	--	--	0.103	0.102	(NH ₄) ₂ S ₂ O ₈
20	2.8187	1.1991	0.124	0.125	--	--	Na ₂ S ₂ O ₈
	2.5752	3.0934	0.118	0.116	0.109	0.108	Na ₂ S ₂ O ₈ +(NH ₄) ₂ S ₂ O ₈
	1.5562	3.2410	--	--	0.112	0.111	(NH ₄) ₂ S ₂ O ₈
30	2.9728	1.5963	0.134	0.136	--	--	Na ₂ S ₂ O ₈
	2.7155	3.5170	0.129	0.130	0.120	0.119	Na ₂ S ₂ O ₈ +(NH ₄) ₂ S ₂ O ₈
	1.4906	3.7169	--	--	0.122	0.122	(NH ₄) ₂ S ₂ O ₈
<i>system Na₂S₂O₈-H₂SO₄-H₂O</i>							
10	1.2876	2.4661	0.259	0.258	--	--	Na ₂ S ₂ O ₈
	0.6941	4.2441	0.481	0.470	--	--	Na ₂ S ₂ O ₈
	0.5090	5.1985	0.655	0.661	--	--	Na ₂ S ₂ O ₈
20	1.8615	1.7061	0.212	0.213	--	--	Na ₂ S ₂ O ₈
	1.0545	3.6230	0.374	0.378	--	--	Na ₂ S ₂ O ₈
	0.6506	5.3003	0.605	0.643	--	--	Na ₂ S ₂ O ₈
30	1.9021	2.0392	0.243	0.245	--	--	Na ₂ S ₂ O ₈
	0.9993	4.3430	0.462	0.458	--	--	Na ₂ S ₂ O ₈
	0.7411	5.3891	0.622	0.617	--	--	Na ₂ S ₂ O ₈
<i>system K₂S₂O₈-H₂SO₄-H₂O</i>							
10	0.1329	0.3087	0.349	0.348	--	--	K ₂ S ₂ O ₈
	0.1426	0.9710	0.329	0.330	--	--	K ₂ S ₂ O ₈
	0.1346	2.3274	0.348	0.348	--	--	K ₂ S ₂ O ₈
	0.1084	4.3977	0.428	0.426	--	--	K ₂ S ₂ O ₈
20	0.2026	0.3446	0.316	0.314	--	--	K ₂ S ₂ O ₈
	0.2096	0.9700	0.305	0.308	--	--	K ₂ S ₂ O ₈
	0.1949	2.3536	0.328	0.333	--	--	K ₂ S ₂ O ₈
	0.1596	3.8781	0.401	0.395	--	--	K ₂ S ₂ O ₈
30	0.2923	0.1735	0.295	0.291	--	--	K ₂ S ₂ O ₈
	0.3021	0.3446	0.286	0.288	--	--	K ₂ S ₂ O ₈
	0.2953	0.9910	0.292	0.292	--	--	K ₂ S ₂ O ₈
	0.2653	2.4895	0.325	0.326	--	--	K ₂ S ₂ O ₈
	0.2193	4.5019	0.394	0.399	--	--	K ₂ S ₂ O ₈

Table 1. Continued

t °C	m_1 mol kg ⁻¹	m_2 mol kg ⁻¹	γ_1		γ_2		solid phase
			a	b	a	b	
<i>system (NH₄)₂S₂O₈-H₂SO₄-H₂O</i>							
10	1.6260	2.5057	0.202	0.199	--	--	(NH ₄) ₂ S ₂ O ₈
	1.1153	4.4289	0.295	0.300	--	--	(NH ₄) ₂ S ₂ O ₈
	0.7675	6.9767	0.428	0.434	--	--	(NH ₄) ₂ S ₂ O ₈
20	2.8274	1.0442	0.146	0.143	--	--	(NH ₄) ₂ S ₂ O ₈
	2.3322	2.0820	0.177	0.178	--	--	(NH ₄) ₂ S ₂ O ₈
	1.6220	3.8148	0.254	0.255	--	--	(NH ₄) ₂ S ₂ O ₈
30	1.2780	5.1520	0.323	0.326	--	--	(NH ₄) ₂ S ₂ O ₈
	3.0958	1.5068	0.164	0.163	--	--	(NH ₄) ₂ S ₂ O ₈
	2.1598	3.4253	0.236	0.233	--	--	(NH ₄) ₂ S ₂ O ₈
	1.3763	6.0335	0.370	0.375	--	--	(NH ₄) ₂ S ₂ O ₈

a... Eq. (1); b... Eq. (3);

The results showed that the activity coefficients of the crystallizing component in saturated solutions of the ternary systems were influenced by the added components in a different manner. In systems with a common cation, at the system Na₂S₂O₈-Na₂SO₄-H₂O, the presence of Na₂SO₄ caused a very small increase of the activity coefficients of saturated solutions of Na₂S₂O₈, while in the reciprocal case, a decrease of activity coefficients of saturated solutions of Na₂SO₄ with an increasing content of Na₂S₂O₈ could be observed. A negligible change of activity coefficients of saturated solutions of (NH₄)₂S₂O₈ was also caused by the addition of (NH₄)₂SO₄, while the addition of (NH₄)₂S₂O₈ to the saturated solutions of (NH₄)₂SO₄ led to a small increase of its activity coefficients. At the system K₂S₂O₈-K₂SO₄-H₂O, a monotonous decrease of activity coefficients of saturated solutions of K₂S₂O₈ and an increase of activity coefficients of saturated solutions of K₂SO₄ by the addition of the other component has been observed. The addition of NaOH to the saturated solutions of Na₂S₂O₈ caused a monotonous increase of its activity coefficients, in contradiction to the system K₂S₂O₈-KOH-H₂O where the activity coefficients of potassium peroxodisulfate decreased monotonously with an increasing content of KOH.

For the systems with the common S₂O₈²⁻ anion, an increasing content of the other component always led to a decrease of the activity coefficient of the crystallizing component. The same effect has been observed at the system (NH₄)₂SO₄-H₂SO₄-H₂O with a common

anion SO_4^{2-} . On the other hand, the addition of sulfuric acid to saturated solutions of sodium or ammonium peroxodisulfate caused a great increase of activity coefficients in both cases, while at the potassium salt, its activity coefficient has initially decreased to a minimum and then increased with an increasing content of sulfuric acid. These findings can be explained by the actual change of the position of the corresponding point on the plot $\ln \gamma_s$ vs. I (total ionic strength) of the saturated polycomponent solution of the salt with a higher or lower solubility caused by the addition of another component.

b) Quaternary systems

The derivation of activity coefficients of saturated solutions in the corresponding quaternary systems with up to 25 wt.-% H_2SO_4 using Eq. (3) was based on the following correlation equations obtained by a similar manner (Balej 1982) and valid with an acceptable reliability for the whole measured range of molalities of individual components and temperatures:

1. System $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $(\text{NH}_4)_2\text{SO}_4$ - H_2SO_4 - H_2O , temperature range 0 – 40 °C,

- a) crystallization region of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $y_{\text{H}_2\text{SO}_4} \leq 25$ wt.-%:

$$\begin{aligned} \varphi_1 = & (0.0195 - 0.00109 t + 1.745 \times 10^{-5} t^2) m_2 - \\ & - (0.00375 - 2.02 \times 10^{-4} t + 3.01 \times 10^{-6} t^2) m_2^2 - (0.110 - 0.0010 t) m_3 - \\ & - (0.006 - 0.00104 t - 2.338 \times 10^{-5} t^2 + 1.016 \times 10^{-6} t^3) (m_2 m_3)^{0.5} + \\ & + (0.0182 - 6.06 \times 10^{-4} t + 3.085 \times 10^{-6} t^2 + 1.2 \times 10^{-7} t^3) m_2 m_3 \end{aligned} \quad (19)$$

where index 2 and 3 relates to $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 , respectively.

2. System $\text{Na}_2\text{S}_2\text{O}_8$ - Na_2SO_4 - H_2SO_4 - H_2O , temperature range 10 – 30 °C,

- a) crystallization region of $\text{Na}_2\text{S}_2\text{O}_8$, $y_{\text{H}_2\text{SO}_4} \leq 25$ wt.-%:

$$\begin{aligned} \varphi_1 = & 0.0149 m_2 - 0.00666 m_2^2 - (0.1445 - 0.00104 t) m_3 + \\ & + 0.01727 (m_2 m_3)^{0.5} + 0.0151 m_2 m_3 \end{aligned} \quad (20)$$

where index 2 and 3 relates to Na_2SO_4 and H_2SO_4 , respectively.

3. System $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $\text{Na}_2\text{S}_2\text{O}_8$ - H_2SO_4 - H_2O , temperature range 10 – 30 °C,

- a) crystallization region of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $y_{\text{H}_2\text{SO}_4} \leq 25$ wt.-%:

$$\begin{aligned} \varphi_1 = & (0.0416 - 0.00144 t) m_2 - (0.00704 - 0.00032 t) m_2^2 - \\ & - (0.110 - 0.0010 t) m_3 - (0.0437 - 0.00338 t + 8.704 \times 10^{-5} t^2) m_2 m_3 + \\ & + (0.0631 - 0.00211 t + 3.765 \times 10^{-5} t^2) (m_2 m_3)^2 - \\ & - (0.0164 - 6.216 \times 10^{-4} t + 9.17 \times 10^{-6} t^2) (m_2 m_3)^3 \end{aligned} \quad (21)$$

where index 2 and 3 relates to $\text{Na}_2\text{S}_2\text{O}_8$ and H_2SO_4 , respectively;

b) crystallization region of $\text{Na}_2\text{S}_2\text{O}_8$:

$$\begin{aligned} \varphi_2 = & (0.0341 - 0.00407 t) m_1 - 0.00348 m_1^2 - (0.145 - 0.00104 t) m_3 - \\ & - (0.162 - 0.0112 t + 2.594 \times 10^{-4} t^2) (m_1 m_3)^{0.5} + \\ & + (0.198 - 0.0129 t + 2.913 \times 10^{-4} t^2) m_1 m_3 - \\ & - (0.0541 - 0.00387 t + 8.55 \times 10^{-5} t^2) (m_2 m_3)^{1.5} \end{aligned} \quad (22)$$

where index 1 and 3 relates to $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and H_2SO_4 , respectively. Because the main attention has been given to the crystallization region of the peroxodisulfates, no correlation equations could be derived for the corresponding sulfates as the crystallizing components. Therefore, their activity coefficients in the binary and ternary eutonica were calculated using Eq. (1). The same manner has also been used for the calculation of activity coefficients of saturated solutions of eutonica coexisting with the solid decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, because no data of water activities of the corresponding saturated polycomponent solutions are available.

Selected values of activity coefficients of saturated solutions of the considered peroxodisulfates in the experimentally examined regions of the system $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $(\text{NH}_4)_2\text{SO}_4$ - H_2SO_4 - H_2O are summarized in Table 2, of the system $\text{Na}_2\text{S}_2\text{O}_8$ - Na_2SO_4 - H_2SO_4 - H_2O in Table 3, and of the system $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $\text{Na}_2\text{S}_2\text{O}_8$ - H_2SO_4 - H_2O in Table 4. Here, coexisting solid phases are also given indicating simultaneously the composition of the corresponding binary and ternary eutonica limiting the crystallization regions of individual components.

Table 2. Mean activity coefficients of ammonium peroxodisulfate and sulfate in the saturated solutions of the system $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $(\text{NH}_4)_2\text{SO}_4$ - H_2SO_4 - H_2O

$(\text{NH}_4)_2\text{S}_2\text{O}_8$	$(\text{NH}_4)_2\text{SO}_4$	H_2SO_4	γ_1		γ_2	solid
mol kg^{-1}	mol kg^{-1}	mol kg^{-1}	a	b	a	
0 °C						
0.918	2.617	0.870	0.114	0.115	--	A
1.065	0.949	2.008	0.158	0.159	--	A
0.397	2.354	3.446	0.178	0.175	--	A
0.335	2.629	3.904	0.179	0.179	--	A
0.217	4.405	5.059	0.154	0.150	--	A

10 °C

1.911	1.243	0.859	0.123	0.124	--	A
0.989	3.808	0.928	0.116	0.116	--	A
0.601	5.466	0.998	0.117	0.114	0.103	A+B
1.017	2.783	1.812	0.134	0.135	--	A
0.628	4.517	1.965	0.129	0.127	--	A
0.450	6.338	2.198	0.120	0.121	0.091	A+B
1.152	1.316	2.585	0.172	0.171	--	A
0.628	3.687	2.934	0.145	0.148	--	A
0.392	6.060	3.401	0.130	0.130	--	A+C
0.871	1.214	3.465	0.211	0.204	--	A
0.447	4.051	4.175	0.158	0.165	--	A
0.344	6.274	4.862	0.133	0.137	--	A+C
0.646	1.302	4.485	0.244	0.245	--	A
0.306	3.766	5.327	0.191	0.195	--	A
0.269	5.235	5.959	0.163	0.167	--	A
0.259	6.824	6.664	0.140	0.137	--	A+C
0.420	6.360	2.309	0.123	0.121	0.091	A+B+C

20 °C

2.448	1.152	0.918	0.130	0.128	--	A
2.016	2.230	0.942	0.125	0.124	--	A
1.112	4.707	1.007	0.123	0.118	--	A
0.911	5.516	1.039	0.123	0.117	0.105	A+B
2.025	1.187	1.833	0.150	0.150	--	A
1.314	3.206	1.953	0.138	0.139	--	A
0.913	5.054	2.124	0.129	0.132	--	A
0.677	6.412	2.268	0.127	0.127	0.093	A+B
1.552	1.322	2.751	0.176	0.174	--	A
0.961	3.460	3.017	0.155	0.158	--	A
0.581	6.644	3.617	0.132	0.140	--	A+C
1.224	1.297	3.697	0.208	0.206	--	A
0.644	4.239	4.352	0.169	0.178	--	A
0.563	5.507	4.732	0.150	0.167	--	A
0.490	6.898	5.158	0.138	0.153	--	A+C
0.656	2.470	5.017	0.222	0.229	--	A
0.511	3.809	5.506	0.195	0.213	--	A
0.422	6.431	6.614	0.152	0.157	--	A
0.429	7.835	7.250	0.134	0.159	--	A+C
0.604	6.750	2.610	0.129	0.129	0.089	A+B+C

30 °C						
2.885	1.233	0.977	0.139	0.135	--	A
1.867	3.806	1.034	0.130	0.127	--	A
1.291	5.572	1.090	0.129	0.123	0.103	A+B
2.110	2.122	1.996	0.152	0.152	--	A
1.570	3.919	2.126	0.141	0.144	--	A
0.995	6.922	2.416	0.128	0.134	0.087	A+B
1.734	2.151	3.023	0.171	0.176	--	A
1.259	4.149	3.303	0.153	0.165	--	A
0.815	7.414	3.897	0.134	0.147	--	A+C
1.397	2.211	4.107	0.194	0.205	--	A
0.983	4.489	4.633	0.165	0.188	--	A
0.754	8.074	5.708	0.131	0.160	--	A+C
1.067	2.368	5.290	0.219	0.241	--	A
0.746	4.620	6.052	0.183	0.219	--	A
0.637	9.594	8.202	0.126	0.117	--	A+C
0.872	0.939	7.549	0.359	0.393	0.455	A+B+C

a... Eq. (1); b... Eq. (3); A... $(\text{NH}_4)_2\text{S}_2\text{O}_8$, B... $(\text{NH}_4)_2\text{SO}_4$, C... $3(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$

Table 3. Mean activity coefficients of sodium peroxodisulfate and sulfate in the saturated solutions of the system $\text{Na}_2\text{S}_2\text{O}_8$ - Na_2SO_4 - H_2SO_4 - H_2O

$\text{Na}_2\text{S}_2\text{O}_8$	Na_2SO_4	H_2SO_4	γ_1		γ_2	solid
mol kg^{-1}	mol kg^{-1}	mol kg^{-1}	a	b	a	
10 °C						
2.076	0.226	0.819	0.150	0.152	--	A
1.307	1.026	1.650	0.173	0.178	--	A
1.172	1.393	1.673	0.169	0.174	--	A+B
0.544	2.447	2.659	0.197	0.201	--	A
0.314	2.523	3.653	0.245	0.245	--	A
0.173	2.665	4.825	0.299	0.305	--	A

20 °C						
2.162	0.469	0.849	0.160	0.161	--	A
1.810	1.319	0.868	0.151	0.154	--	A
1.626	1.745	0.877	0.149	0.152	--	A+B
1.636	0.575	1.667	0.197	0.196	--	A
0.994	2.488	1.801	0.172	0.176	--	A

1.272	0.573	2.491	0.242	0.242	--	A
0.878	1.824	2.641	0.212	0.216	--	A
0.939	0.574	3.327	0.305	0.299	--	A
0.564	1.843	3.559	0.265	0.261	--	A
0.349	1.906	4.601	0.325	0.320	--	A
0.186	3.676	5.324	0.280	0.279	--	A
30 °C						
2.295	0.605	0.876	0.172	0.171	--	A
1.738	1.866	0.901	0.164	0.163	--	A
1.430	2.643	0.921	0.161	0.162	0.081	A+C
1.830	0.594	1.722	0.209	0.208	--	A
1.371	1.868	1.803	0.190	0.190	--	A
1.158	2.566	1.858	0.183	0.185	--	A
0.966	3.386	1.938	0.175	0.183	0.071	A+C
1.033	1.880	2.722	0.224	0.223	--	A
0.708	3.428	2.979	0.201	0.207	--	A
1.100	0.592	3.431	0.315	0.308	--	A
0.902	1.222	3.539	0.289	0.284	--	A
0.568	2.664	3.858	0.255	0.249	--	A
0.326	4.552	4.395	0.233	0.224	--	A
0.372	2.787	5.045	0.298	0.292	--	A
0.226	4.946	5.969	0.253	0.244	--	A
0.712	3.103	0.864	--	--	0.080	C
0.786	3.497	1.908	--	--	0.071	C

a... Eq.(1); b... Eq. (3); A... Na₂S₂O₈; B... Na₂SO₄.10H₂O; C... Na₂SO₄;

Table 4. Mean activity coefficients of ammonium and sodium peroxodisulfate in the saturated solutions of the system (NH₄)₂S₂O₈-Na₂S₂O₈-H₂SO₄-H₂O

(NH ₄) ₂ S ₂ O ₈ mol kg ⁻¹	Na ₂ S ₂ O ₈ mol kg ⁻¹	H ₂ SO ₄ mol kg ⁻¹	γ_{s1}		γ_{s2}		solid
			a	b	a	b	
10 °C							
2.033	0.814	1.572	0.145	0.140	--	--	A
1.618	0.277	2.599	0.193	0.192	--	--	A
1.128	0.326	4.365	0.268	0.270	--	--	A
1.253	0.726	3.878	0.225	0.221	0.329	0.330	A+B
1.805	1.391	2.036	0.150	0.141	0.182	0.184	A+B

2.189	1.849	1.006	0.122	0.112	0.139	0.138	A+B
0.960	1.638	1.504	--	--	0.175	0.178	B
0.613	1.168	2.575	--	--	0.248	0.240	B
0.689	0.613	4.336	--	--	0.423	0.416	B
20 °C							
2.569	0.772	1.484	0.147	0.146	--	--	A
2.014	0.445	2.775	0.192	0.192	--	--	A
1.411	0.246	4.679	0.277	0.286	--	--	A
1.404	0.616	4.989	0.260	0.262	0.430	0.427	A+B
1.606	0.853	4.091	0.223	0.220	0.324	0.324	A+B
1.873	1.170	3.166	0.187	0.184	0.245	0.250	A+B
2.982	2.449	0.280	0.113	0.113	0.123	0.126	A+B
1.215	2.218	0.961	--	--	0.154	0.161	B
0.818	1.565	2.141	--	--	0.219	0.213	B
0.585	0.730	4.479	--	--	0.443	0.435	B
0.382	0.675	4.701			0.502	0.474	B
30 °C							
2.987	0.815	1.484	0.157	0.157	--	--	A
2.367	0.562	2.848	0.200	0.195	--	--	A
1.661	0.408	5.179	0.285	0.285	--	--	A
1.669	0.643	5.467	0.274	0.277	0.468	0.466	A+B
2.281	1.355	3.135	0.191	0.188	0.245	0.244	A+B
2.979	2.122	1.135	0.143	0.129	0.162	0.158	A+B
1.528	2.180	1.248	--	--	0.177	0.180	B
0.692	1.461	2.838	--	--	0.277	0.281	B

a... Eq. (1); b... Eq. (3); A... $(\text{NH}_4)_2\text{S}_2\text{O}_8$; B... $\text{Na}_2\text{S}_2\text{O}_8$;

As can be seen, the influence of individual added components on the activity coefficients of saturated solutions of peroxodisulfates and sulfates in the considered quaternary systems is similar as it was observed for the ternary systems. The addition of sulfate and/or peroxodisulfate at constant content of sulfuric acid always diminishes and any addition of sulfuric acid always increases the corresponding activity coefficient of the crystallizing peroxodisulfate or sulfate at the given temperature. This different effect of neutral salts and sulfuric acid at the same total ionic strength of the saturated solutions (lying

between ca. 10 to 56 mol kg⁻¹) must evidently be ascribed to a specific action of sulfuric acid. Its theoretical explanation, however, did not form the subject of this contribution.

The agreement of activity coefficients of saturated solutions of the considered peroxodisulfates and/or sulfates in the mentioned quaternary systems derived by both methods was sufficiently good: at the system (NH₄)₂S₂O₈-(NH₄)₂SO₄-H₂SO₄-H₂O, the mean deviation of all results attained 1.5 rel.-%, at systems Na₂S₂O₈-Na₂SO₄-H₂SO₄-H₂O and (NH₄)₂S₂O₈-Na₂S₂O₈-H₂SO₄-H₂O, the mean deviations of all results attained 2.4 rel.-% in both cases. This finding can be held as a surprisingly positive result, because the correlation equations were based on the commonly accepted assumption about the total dissociation of all considered substances, although it is known that in systems containing sulfuric acid, also HSO₄¹⁻ ions are always present, and, in addition, formation of ion pairs, MSO₄¹⁻ (Marcus and Hefter 2006), and even MS₂O₈¹⁻ (Chlebek and Lister 1971) should be considered in a rigorous thermodynamic treatment of such systems. The appropriate thermodynamic data of all such equilibria in the considered concentrated polycomponent solutions are, however, not yet known.

Conclusion

It can be concluded that the presented activity coefficients of saturated solutions of the considered peroxodisulfates and sulfates in the mentioned ternary and quaternary systems, derived from corresponding solubility data, can be used as a sufficiently reliable basis for a more detailed evaluation of the thermodynamics and kinetics of chemical and electrochemical reactions of these substances at real industrial reaction conditions existing in various their applications.

Acknowledgement

Financial support of the Czech Science Foundation (grant No. 203/09/1343) is gratefully appreciated. Dr. Ivo Paseka is kindly acknowledged for the critical reading of the manuscript and for valuable advices.

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