Mean Activity Coefficients of Peroxodisulfates in Saturated Solutions of the Conversion System $2NH_4^+ - 2Na^+ - S_2O_8^{2-} - SO_4^{2-} - H_2O$ at 20 °C and 30 °C
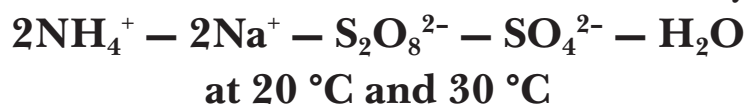
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Abstract: Solubility data of the conversion system $2NH_4^+ - 2Na^+ - S_2O_8^{2-} - SO_4^{2-} - H_2O$ at 20 °C and 30 °C for the partial pseudoternary systems $Na_2S_2O_8$—$(NH_4)_2SO_4$—H_2O, $(NH_4)_2S_2O_8$—Na_2SO_4—H_2O, $Na_2S_2O_8$—$NaNH_4SO_4$—H_2O and $(NH_4)_2S_2O_8$—$NaNH_4SO_4$—H_2O have been correlated using the relative activity coefficient expansion of the crystallizing component. The obtained correlation equations have been used for the calculation of mean activity coefficients of ammonium and sodium peroxodisulfates in their saturated solutions of the mentioned pseudoternary systems.

Keywords: mean activity coefficient, ammonium peroxodisulfate, sodium peroxodisulfate, conversion system

Introduction

In the previous contribution (Balej 2011a), mean activity coefficients (further, term "mean" is mostly omitted) of sodium, potassium and ammonium peroxodisulfates in pure aqueous solutions in the temperature region (0−50) °C have been presented. Another contribution (Balej 2011b) has brought activity coefficients of peroxodisulfates in saturated aqueous polycomponent solutions of ternary systems $Na_2S_2O_8$—Na_2SO_4—H_2O, $K_2S_2O_8$—K_2SO_4—H_2O, $(NH_4)_2S_2O_8$—$(NH_4)_2SO_4$—H_2O, $Na_2S_2O_8$—$NaOH$—H_2O, $K_2S_2O_8$—KOH—H_2O, $Na_2S_2O_8$—$K_2S_2O_8$—H_2O, $Na_2S_2O_8$—$(NH_4)_2S_2O_8$—H_2O, $Na_2S_2O_8$—H_2SO_4—H_2O, $K_2S_2O_8$—H_2SO_4—H_2O, $(NH_4)_2S_2O_8$—H_2SO_4—H_2O, and quaternary systems $(NH_4)_2S_2O_8$—$(NH_4)_2SO_4$—H_2SO_4—H_2O, $Na_2S_2O_8$—Na_2SO_4—H_2SO_4—H_2O, and $(NH_4)_2S_2O_8$—$Na_2S_2O_8$—H_2SO_4—H_2O. The aim of the present communication is to bring values of activity coefficients of ammonium or sodium peroxodisulfate in selected saturated solutions of the conversion system $2NH_4^+ - 2Na^+ - S_2O_8^{2-} - SO_4^{2-} - H_2O$ based on the solubility data at 20 °C (Balej, Čížek and Thumová 1976) and at 30 °C (Balej and Thumová 1976). From the isothermal solubility diagrams of this system, it followed that besides the four solid main substances, $(NH_4)_2S_2O_8$, $Na_2S_2O_8$, $(NH_4)_2SO_4$ and Na_2SO_4, the double sulfate $NaNH_4SO_4 \cdot 2H_2O$ also exists in the equilibrium with corresponding saturated solutions. Consequently, five different crystallization regions of the given solid substances are separated by seven binary eutonica lines crossing in three ternary eutonic points at the given temperature. It followed further that no of the crystallization regions of the four mean components touches the crystallization region of the opposite component, because they are always separated by a quite large crystallization area of the fifth component, $NaNH_4SO_4 \cdot 2H_2O$.

Due to a high number of the original solubility data (totally 205 measurements) bringing results of four diagonal sections, seven binary eutonica lines and three ternary eutonic points at the given temperature, this communication is only limited to the correlation of the previous solubility data of corresponding peroxodisulfates in four diagonal sections, i.e. $(NH_4)_2S_2O_8$—Na_2SO_4—H_2O, $Na_2S_2O_8$—$(NH_4)_2SO_4$—H_2O, $(NH_4)_2S_2O_8$—$NaNH_4SO_4$—H_2O, and $Na_2S_2O_8$—$NaNH_4SO_4$—H_2O at both considered temperatures. The first two systems represent pseudoternary systems without any common ion, whereas the last two belong to such ones with a common and an uncommon cation. The obtained results have been used for the calculation of activity coefficients of the corresponding peroxodisulfates in their saturated polycomponent solutions.

The solubility correlation of the considered systems was based on the relative activity coefficient expansion (Nývlt 1977, Balej 1982)

$$\ln\left(\frac{\gamma_{s0}}{\gamma_s}\right) = \varphi = \frac{\ln\left(\frac{m_{C,S}^2 m_{A,S}}{4 m_{0,S}^3}\right)}{3} = \sum_{i=2}^{n} Q_{1i} m_i + \sum_{i=2}^{n}\sum_{j=2}^{n} Q_{1ij} m_i m_j + ... \quad (1)$$

Here, γ_{so} and γ_s denotes the activity coefficient of the crystallizing substance in the saturated solution in pure water and in the polycomponent solution, respectively, $m_{C,S}$ and $m_{A,S}$ denotes the molality of

the cation and anion of the crystallizing substance in the saturated polycomponent solution, and $m_{0,S}$ represents the solubility of the crystallizing substance in pure water, all at the given temperature.

The activity coefficients of the considered peroxodisulfate in the saturated solutions of the considered pseudoternary systems have been calculated by two different methods. The first one consists on the mentioned method of the relative activity coefficient expansion of the crystallizing component defined by Eq. (1), according to which the activity coefficient of the considered substance in its saturated polycomponent solution is given by the equation

$$\gamma_{1S} = \frac{\gamma_{1S0}}{\exp \varphi_1} \qquad (2)$$

The second method is based on the thermodynamic condition of the equilibrium between the solid anhydrous electrolyte of the type 1-2, A_2B, and its saturated solution formulated by the expression (Balej 2010a)

$$\ln \gamma_S = \\ = \left(\frac{\Delta_f G^* (C_2A, cr) - \Delta_f G^* (C_2A, aq)}{RT} - \ln(m_{C,S}^2 m_{A,S}) \right) \qquad (3)$$

The equation is valid under the assumption of a complete dissociation of the considered strong electrolyte. Here, $\Delta_f G^\circ (C_2A, cr)$ denotes the standard formation Gibbs energy of the anhydrous solid electrolyte and $\Delta_f G^\circ (C_2A, aq)$ denotes the same quantity of the same electrolyte in its aqueous solution, respectively. Values of $\Delta_f G^\circ_{cr}$ and $\Delta_f G^\circ_{aq}$ of the peroxodisulfates at the given temperatures have been taken from the previous paper (Balej 2010b), molalities of the appropriate ions in saturated polycomponent solutions have been calculated from the mentioned solubility data originally given in wt. %.

Results and Discussion

The composition (in mol kg^{-1}) of the saturated solutions of the considered ternary systems without a common ion, $(NH_4)_2S_2O_8$—Na_2SO_4—H_2O, at both temperatures is presented in Table 1. The last data at every temperature correspond to the eutonic solution at which two solid substances coexist with the saturated solution. The evaluation of solubility data according to Eq. (1) led to the expression

$$\varphi_1 = \ln\left(\frac{\gamma_{1S0}}{\gamma_{1S}}\right) = \ln\left(\frac{m_{1S}}{m_{1S0}}\right) = \\ = (0.02807 - 0.000726t)m_2 \qquad (4)$$

so that the solubility dependence of the ammonium peroxodisulfate (m_{1S}) on the content of sodium sulfate (m_2) is given by the equation

$$m_{1S} = (2.4383 + 0.05564t)\exp((0.02807 - \\ - 0.000726t)m_2) \qquad (5)$$

Here, m_{1S0} denotes the solubility of the crystallizing componen in pure water, t the temperature in °C. The same dependence with almost the same accuracy could be expressed by an empirical equation

Tab. 1. Solubility data and activity coefficients in the system $(NH_4)_2S_2O_8$—Na_2SO_4—H_2O.

	m_{1S}		m_2	γ_{1S}		solid
exp	Eq. (5)	Eq. (6)		Eq. (2)	Eq. (3)	
		20 °C				
3.551	3.551	3.551	0.000	0.116	0.116	$(NH_4)_2S_2O_8$
3.567	3.568	3.568	0.358	0.115	0.116	$(NH_4)_2S_2O_8$
3.579	3.579	3.579	0.581	0.115	0.115	$(NH_4)_2S_2O_8$
3.597	3.597	3.597	0.953	0.115	0.115	$(NH_4)_2S_2O_8$
3.620	3.619	3.619	1.391	0.114	0.114	$(NH_4)_2S_2O_8$
3.624	3.624	3.624	1.499	0.114	0.114	$(NH_4)_2S_2O_8$
3.627	3.626	3.626	1.533	0.114	0.114	$(NH_4)_2S_2O_8$
3.648	3.645	3.645	1.929	0.113	0.113	$(NH_4)_2S_2O_8$
3.670	3.667	3.666	2.366	0.112	0.112	$(NH_4)_2S_2O_8 + NaNH_4SO_4 \cdot 2H_2O$
		30 °C				
4.108	4.108	4.108	0.000	0.124	0.124	$(NH_4)_2S_2O_8$
4.127	4.126	4.126	0.700	0.123	0.123	$(NH_4)_2S_2O_8$
4.143	4.143	4.143	1.376	0.123	0.123	$(NH_4)_2S_2O_8$
4.157	4.158	4.158	1.949	0.123	0.123	$(NH_4)_2S_2O_8$
4.170	4.173	4.172	2.501	0.122	0.122	$(NH_4)_2S_2O_8 + NaNH_4SO_4 \cdot 2H_2O$

$$m_{1S} = 2.4383 + 0.05564t + (0.09383 - 0.002264t)m_2 \quad (6)$$

Results of the corresponding calculations are given in Tab. 1 as well. As can be seen, the agreement between the measured and calculated values according to different equations is very good and the mean deviation is always below 0.1 rel. %.

Solubility data of the pseudoternary system $Na_2S_2O_8$—$(NH_4)_2SO_4$—H_2O at the both considered temperatures are given in Table 2, from which the following correlation equation has been obtained:

$$\varphi_1 = \ln\left(\frac{\gamma_{1S0}}{\gamma_{1S}}\right) = \ln\left(\frac{m_{1S}}{m_{1S0}}\right) = (-0.04339 + 0.003439t)m_2 \quad (7)$$

so that

$$m_{1S} = (2.5063 + 0.02287t)\exp((-0.04339 - 0.003439t)m_2) \quad (8)$$

The solubility could also be expressed by a simpler empiric equation

$$m_{1S} = 2.5063 + 0.02287t - (-0.1685 - 0.01226t)m_2 \quad (9)$$

Results of the corresponding calculations are given in Tab. 2 as well. As can be seen, the agreement between the measured and calculated values according to different equations is in this case also very good and the mean deviation is always below 0.1 rel. %.

At the other two considered pseudoternary systems with a common cation, the solubility correlation equation has the following common form

$$\varphi_1 = \frac{\ln\frac{(2m_{1S} + m_2)^2 m_1}{4m_{1S0}^3}}{3} \quad (10)$$

Accordingly, the calculation of the solubility of crystallizing peroxodisulfate (m_{1S}) must be performed by the solution of the polynomic equation of the following form

$$m_{1S}^3 + m_2 m_{1S}^2 + 0.25 m_2^2 m_{1S} - m_{1S0}^3 \exp(3\varphi_1) = 0 \quad (11)$$

The solubility data of the system $(NH_4)_2S_2O_8$—$NaNH_4SO_4$—H_2O are given in Table 3. The evaluation of solubility data according to Eq. (1) led to the following expression for the solubility dependence of the ammonium peroxodisulfate (m_{1S}) on the content of sodium ammonium sulfate (m_2)

$$\varphi_1 = \frac{\ln\frac{(2m_1 + m_2)^2 m_1}{4m_{1S0}^3}}{3} = (0.01493 - 0.0002991t)m_2 + (0.003053 - 0.0001676t)m_2^2 \quad (12)$$

so that the molality of ammonium peroxodisulfate in the saturated polycomponent solutions has been calculated by the solvation of the polynomic equation

$$m_{1S}^3 + m_2 m_{1S}^2 + 0.25 m_2^2 m_{1S} - m_{1S0}^3 \exp((0.04479 - 0.0008973t)m_2 - (0.000916 - 0.000503t)m_2^2) = 0 \quad (13)$$

Values of m_{1S} could also be obtained using a simpler empiric equation

$$m_{1S} = 2.4383 + 0.05564t - (0.283 + 0.000933t)m_2 \quad (14)$$

The results of calculations are given in Table 3 as well. As can be seen, the agreement between the measured and calculated values of m_{1S} is very good and the mean deviation $\sigma \leq 0.1$ rel. %.

The solubility data of the system $Na_2S_2O_8$—$NaNH_4SO_4$—H_2O are given in Table 4. The evaluation of solubility data according to Eq. (1) led to the following common expression

Tab. 2. Solubility data and activity coefficients in the system $Na_2S_2O_8$—$(NH_4)_2SO_4$—H_2O.

	m_{1S}		m_2	γ_{1S}		coexisting solid substance
exp	Eq. (8)	Eq. (9)		Eq. (2)	Eq. (3)	
		20 °C				
2.964	2.964	2.964	0.000	0.133	0.133	$Na_2S_2O_8$
3.011	3.013	3.013	0.649	0.131	0.131	$Na_2S_2O_8$
3.084	3.082	3.082	1.536	0.128	0.128	$Na_2S_2O_8$
3.133	3.130	3.129	2.149	0.126	0.126	$Na_2S_2O_8 + NaNH_4SO_4 \cdot 2H_2O$
		30 °C				
3.192	3.192	3.192	0.000	0.145	0.144	$Na_2S_2O_8$
3.271	3.267	3.269	0.384	0.142	0.141	$Na_2S_2O_8$
3.392	3.387	3.390	0.989	0.136	0.136	$Na_2S_2O_8$
3.580	3.580	3.575	1.917	0.129	0.129	$Na_2S_2O_8$
3.677	3.680	3.671	2.399	0.126	0.125	$Na_2S_2O_8 + NaNH_4SO_4 \cdot 2H_2O$

Tab. 3. Solubility data and activity coefficients in the system $(NH_4)_2S_2O_8$—$NaNH_4SO_4$—H_2O.

	m_{1S}		m_2	γ_{1S}		coexisting solid substance
exp	Eq. (13)	Eq. (14)		Eq. (2)	Eq. (3)	
		20 °C				
3.551	3.551	3.551	0.000	0.116	0.116	$(NH_4)_2S_2O_8$
3.099	3.099	3.099	1.497	0.115	0.115	$(NH_4)_2S_2O_8$
2.559	2.557	2.558	3.293	0.113	0.116	$(NH_4)_2S_2O_8 + NaNH_4SO_4 \cdot 2H_2O$
		30 °C				
4.108	4.108	4.108	0.000	0.124	0.124	$(NH_4)_2S_2O_8$
3.753	3.754	3.755	0.877	0.124	0.126	$(NH_4)_2S_2O_8$
3.622	3.622	3.621	1.563	0.123	0.123	$(NH_4)_2S_2O_8$
3.343	3.343	3.343	2.459	0.124	0.124	$(NH_4)_2S_2O_8$
3.014	3.013	3.016	3.511	0.124	0.124	$(NH_4)_2S_2O_8 + NaNH_4SO_4 \cdot 2H_2O$

$$\varphi_1 = \frac{\ln\dfrac{(2m_1 + m_2)^2 m_1}{4m_{1S0}^3}}{3} =$$
$$= (0.08984 - 0.002103t)m_2 +$$
$$+ (0.006101 - 0.0003009t)m_2^2 \qquad (15)$$

so that the molality of sodium peroxodisulfate in the saturated polycomponent solutions has been calculated by the solvation of the polynomic equation

$$m_{1S}^3 + m_2 m_{1S}^2 + 0.25 m_2^2 m_{1S} -$$
$$- m_{1S0}^3 \exp((0.2695 - 0.006309t)m_2 + \qquad (16)$$
$$+ (0.0183 - 0.0009027t)m_2^2) = 0$$

The same quantity could be calculated using a simpler empiric equation

$$m_{1S} = 2.5063 + 0.02287t -$$
$$- (0.0501 + 0.006584t)m_2 \qquad (17)$$

with a mean deviation $\sigma \leq 0.08$ rel. %.
Mean activity coefficients of the corresponding peroxodisulfates in their saturated polycompo-

nent solutions have been calculated using Eq. (2) and Eq. (3). The obtained results are given in Tab. 1—4 as well. As can be seen, the individual values of the mean activity coefficients of the considered peroxodisulfates computed by both mentioned methods are practically identical in all cases.

From the results, it further follows that in the both pseudoternary systems without a common cation, the added components enlarge the solubility of the crystallizing peroxodisulfate and consequently decrease its activity coefficient, because the product $m_{1S}\gamma_{1S}$ = const. (see Eq. 4). This behaviour is totally opposite to that observed at the systems $M_2S_2O_8$—H_2SO_4—H_2O with M = Na or NH_4 (Balej 2011b) where the increasing content of H_2SO_4 caused a decrease of the solubility and consequently an increase of the activity coefficients of the corresponding peroxodisulfate.

Very interesting is the mutual comparison of the influence of individual additives on the final effects expressed as the specific increase or decrease of the

Tab. 4. Solubility data and activity coefficients in the system $Na_2S_2O_8$—$NaNH_4SO_4$—H_2O.

	m_{1S}		m_2	γ_{1S}		coexisting solid substance
exp	Eq. (16)	Eq. (17)		Eq. (2)	Eq. (3)	
		20 °C				
2.964	2.964	2.964	0.000	0.133	0.133	$Na_2S_2O_8$
2.853	2.853	2.854	0.601	0.129	0.129	$Na_2S_2O_8$
2.797	2.798	2.795	0.930	0.127	0.127	$Na_2S_2O_8 + NaNH_4SO_4 \cdot 2H_2O$
		30 °C				
3.192	3.192	3.192	0.000	0.145	0.144	$Na_2S_2O_8$
3.107	3.107	3.107	0.344	0.144	0.143	$Na_2S_2O_8$
2.933	2.932	2.933	1.048	0.141	0.141	$Na_2S_2O_8$
2.785	2.786	2.782	1.658	0.140	0.139	$Na_2S_2O_8$
2.755	2.753	2.756	1.762	0.140	0.139	$Na_2S_2O_8$
2.729	2.728	2.730	1.865	0.139	0.139	$Na_2S_2O_8 + NaNH_4SO_4 \cdot 2H_2O$

Tab. 5. Specific change of the solubility Δm_{1S} and activity coefficient $\Delta\gamma_{1S}$ of the crystallizing component of the considered systems caused by the added substance.

system	$\Delta\mathbf{m_{1S}}$		$\Delta\boldsymbol{\gamma_{1S}}$	
	20 °C	30 °C	20 °C	30 °C
$(NH_4)_2S_2O_8-Na_2SO_4-H_2O$	0.0503	0.0248	-0.0017	-0.0008
$Na_2S_2O_8-(NH_4)_2SO_4-H_2O$	0.0786	0.2017	-0.0033	-0.0079
$(NH_4)_2S_2O_8-NaNH_4SO_4-H_2O$	−0.301	−0.312	~0	~0
$Na_2S_2O_8-NaNH_4SO_4-H_2O$	−0.180	−0.248	−0.0065	−0.0032

solubility Δm_{1S} and activity coefficients $\Delta\gamma_{1S}$ of the crystallizing substance formulated as followed

$$\Delta m_{1S} = \frac{m_{1Se} - m_{1S0}}{m_{2e}} \qquad (18)$$

and

$$\Delta\gamma_{1S} = \frac{\gamma_{1Se} - \gamma_{1S0}}{m_{2e}} \qquad (19)$$

where index "e" denotes eutonic solution. From the obtained results given in Table 5 it follows that the influence of added ammonium sulfate on the solubility of sodium peroxodisulfate is totally different from that of sodium sulfate addition on the solubility of ammonium peroxodisulfate. While in the first case the solubility increase of sodium peroxodisulfate with ammonium sulfate addition at 30 °C was more than twice higher than at 20 °C, the solubility increase of ammonium peroxodisulfate with sodium sulfate addition was about twice lower at the same conditions.

At systems with a common cation, the addition of sodium ammonium sulfate to the crystallizing ammonium peroxodisulfate solution caused a quite distinct decrease of its solubility, with an almost negligible influence of temperature. The addition of the same double sulfate to the crystallizing sodium peroxodisulfate solution also caused its solubility decrease, however, in this case, the effect was more distinct and higher at a higher temperature.

What about the influence of the added sulfates on the specific change of activity coefficients of the crystallizing peroxodisulfates, the final effect was always opposite in comparison to their influence on the solubility change, in accordance with the theoretical expectation. However, it can commonly be stated that the values of activity coefficients of ammonium or sodium peroxodisulfate in their saturated polycomponent solution differ not too much from those in pure water at the same temperature, the maximum deviation σ = 13 rel. % has been observed at the eutonic solution of the system $Na_2S_2O_8-(NH_4)_2SO_4-H_2O$ at 30 °C.

Conclusion

The presented results brought the evaluation of the previous solubility data of the conversion system $2NH_4^+ - 2Na^+ - S_2O_8^{2-} - SO_4^{2-} - H_2O$ at 20 °C and 30 °C for four selected pseudoternary systems $Na_2S_2O_8-(NH_4)_2SO_4-H_2O$, $(NH_4)_2S_2O_8-Na_2SO_4-H_2O$, $Na_2S_2O_8-NaNH_4SO_4-H_2O$ and $(NH_4)_2S_2O_8-NaNH_4SO_4-H_2O$ in the form of suitable correlation equations using the relative activity coefficient expansion of the crystallizing component. The obtained equations have been used for the calculation of mean activity coefficients of sodium and ammonium peroxodisulfates in their saturated solutions of the mentioned pseudoternary systems. It was observed that the values of activity coefficients of ammonium or sodium peroxodisulfate in their saturated polycomponent solutions differ not too much from those in pure water. The presented results represent a supplement of previous papers about the same theme (Balej 1982, 2011a, b).

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