

# Ion-pairing in aqueous solutions of peroxodisulfates

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**Abstract:** Probable values of the degree of ion-pairing (ion-association) of aqueous solutions of alkali metal and ammonium peroxodisulfates have been calculated for various estimated values of association constants, in dependence a) on the concentration of the binary solution, b) on the concentration of the other electrolyte in the polycomponent solution with the common ion, able or not able to form ion pair, and c) on the value of the activity quotient  $Q_a$ . It followed that in the presence of another component with a common cation and neglecting the influence of activity coefficients, the ion-association degree of peroxodisulfate  $\alpha > 0.5$  in solutions with total molality  $m_t > 0.1$  mol kg<sup>-1</sup>; as mostly  $Q_a < 1.0$ , the ion-association degree is even higher so that in such cases the alkali metal and ammonium peroxodisulfates can prevalingly behave as uni-univalent electrolytes. In agreement with these results, evaluation of the solubility of sodium, potassium and ammonium peroxodisulfates in some ternary and quaternary systems has been performed under the simplified assumption of a complete ion-association to  $MS_2O_8^{1-}$  ions. It has been shown that the mean deviations between the calculated and observed solubilities of the crystallizing components are almost equally low as under the assumption of a total dissociation of the corresponding substances. The results indicated that the prevailing ion-association of more concentrated solutions of peroxodisulfates could be taken as an acceptable approach for the quantitative evaluation of physico-chemical behaviour of systems containing peroxodisulfates.

**Keywords:** Ion-pairing, Degree of ion-association, Alkali metal peroxodisulfates, Ammonium peroxodisulfate, Evaluation of solubility

## Introduction

Alkali metal and ammonium peroxodisulfates,  $M_2S_2O_8$ , are mostly considered as salts of a strong dibasic acid,  $H_2S_2O_8$ , completely dissociating in their aqueous solutions into the corresponding cations and anions, similarly as it is mostly presumed for solutions of the corresponding sulfates (Golberg 1981, Nývlt 1977). Such an approach was used e.g. for the quantitative correlation of their solubility data and for the evaluation of the concentration dependence of activity coefficients in polycomponent systems with or without common ions (Balej 1982, 2011). However, in some studies of redox reactions of peroxodisulfates of alkali metals (Chlebek and Lister 1971, Guzmán et al 1985), it was shown that their ion-pairing (ion-association)



must be taken into account. For sodium, potassium, rubidium and cesium peroxodisulfates, the following values of the ion-association constant  $K_a$  defined as (Davies 1962)

$$K_a = [m_{MS_2O_8^{1-}} / (m_{M^+} \cdot m_{S_2O_8^{2-}})] \times [\gamma_{MS_2O_8^{1-}} / (\gamma_{M^+} \cdot \gamma_{S_2O_8^{2-}})] = K_a' \cdot Q_a \quad (2)$$

have been given (Chlebek and Lister 1971) at 25 and 37 °C (see Table 1). A little higher value  $K_a = 11.5$  l mol<sup>-1</sup> at 25 °C was found for potassium salt (Guzmán et al 1985). In eqn. (2),  $Q_a$  denotes

the activity quotient  $Q_a = \gamma_{MS_2O_8^{1-}} / (\gamma_{M^+} \cdot \gamma_{S_2O_8^{2-}})$ . As can be seen, the ion-association constant  $K_a$  increases with the increasing molar mass of the cation, however, the influence of temperature is not uniform.

**Tab. 1.** Values of the ion-association constant of individual peroxodisulfates at 25 and 37 °C (Chlebek and Lister 1971).

substance	$K_a$ (kg mol <sup>-1</sup> )	
	25 °C	37 °C
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3.8	5.0
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	8.2	9.4
Rb <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	14.7	16.0
Cs <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	26.0	24.4

Analogous ion-association exists in aqueous solutions of alkali metal and ammonium sulfates, as well (Davies 1962, Masterton and Berka 1966, Jenkins and Monk 1950). Their ion-association constants at 25 °C deduced from the known values of the corresponding dissociation constants,  $K_{\text{diss}}$ , are given in Table 2 using the relation  $K_a = 1/K_{\text{diss}}$ . As can be seen, the ion-association constant for sodium sulfate from different sources exhibits a quite distinct dispersion; while for ammonium sulfate exhibits a little higher value than that for potassium sulfate. With respect to this fact and taking into account some similarity between values of  $K_a$  of

**Tab. 2.** Values of  $K_d$  and  $K_a = 1/K_d$  for alkali metal and ammonium sulfates at 25 °C.

substance	$K_d$ (mol kg <sup>-1</sup> )			$K_a$ (kg mol <sup>-1</sup> )		
	Davies, 1962	Masterton and Berka, 1966	Jenkins and Monk, 1950	Davies, 1962	Masterton and Berka, 1966	Jenkins and Monk, 1950
Li <sub>2</sub> SO <sub>4</sub>	0.25	0.20		4.0	5.0	
Na <sub>2</sub> SO <sub>4</sub>	0.20	0.13	0.19	5.0	7.7	5.3
K <sub>2</sub> SO <sub>4</sub>	0.10	0.10	0.11	10.0	10.0	9.1
Rb <sub>2</sub> SO <sub>4</sub>	0.20	0.16		5.0	6.3	
Cs <sub>2</sub> SO <sub>4</sub>	0.20	0.16		5.0	6.3	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.08	0.08		12.6	12.6	

corresponding sulfates and peroxodisulfates, value  $K_a \approx 10$  mol kg<sup>-1</sup> can be assumed for ammonium peroxodisulfate at 25 °C.

Due to the fact that values of the ion-association constants  $K_a$  of individual peroxodisulfates are not sufficiently accurate, any calculation of the degree of ion-association  $\alpha$  can only be tentative. A more or less important role can play the activity quotient  $Q_a$  which, according to the analogous results at the assumption of total dissociation (Balej 2011), most probably lies at  $Q_a \leq 1.0$ . Therefore, the calculation of the degree of ion-association  $\alpha$  will be performed for more simple case  $Q_a = 1.0$  at first, followed by a discussion for the case  $Q_a < 1.0$ .

## Results and Discussion

### Aqueous binary solutions, $Q_a = 1.0$

The calculation of the degree of ion association  $\alpha$  was based on eqn. (2) in which the concentration of the associated anion  $MS_2O_8^{1-}$  was expressed as the product of the association degree  $\alpha$  and the total molality of the considered peroxodisulfate  $m$ , and the concentration of the unassociated anion  $S_2O_8^{2-}$  as the product of  $(1 - \alpha)m$  leading, after recombination, to the equation:

$$\alpha = 1.5 + 1/(2K_a m) - ((1.5 + 1/(2m))^2 - 2)^{0.5} \quad (3)$$

where  $m$  denotes the total molality of the considered peroxodisulfate. The obtained results for various solution molality and values of the ion-association constant in the range  $K_a = 4$ –25 kg mol<sup>-1</sup> are given in Table 3. As can be seen, with the exception for  $K_a = 4$  kg mol<sup>-1</sup> at  $m = 0.1$  mol kg<sup>-1</sup>, in all other cases the degree of ion-association  $\alpha > 0.5$ , i.e. the prevailing anionic specie is the associated ion-pair  $MS_2O_8^{1-}$ , the more, the higher is the concentration and  $K_a$ , as well. Consequently, with the increasing concentration, the thermodynamic behaviour of the peroxodisulfate approaches more and more to that of a 1-1 electrolyte.

**Tab. 3.** Values of the ion-association degree  $\alpha$  of pure aqueous solutions of monovalent peroxodisulfates at different values of their total molality  $m$ , various values of  $K_a$  (kg mol<sup>-1</sup>) and  $Q_a = 1.0$ .

$m$ (mol kg <sup>-1</sup> )	$\alpha$ at $K_a$		
	4	10	25
0.1	0.392	0.586	0.757
0.2	0.539	0.719	0.852
0.5	0.719	0.852	0.930
1.0	0.825	0.916	0.963
2.0	0.898	0.954	0.981
3.0	0.928	0.969	0.987
4.0	0.944	0.976	0.990
5.0	0.954	0.981	0.992
6.0	0.961	0.984	0.993

### Polycomponent solutions, $Q_{a1} = 1.0$

In the considered reaction systems, besides peroxodisulfates, also other components (most often sulfates) with or without common ions are present which can influence the degree of ion-association of peroxodisulfate in a more or less distinct extent. The presence of a component without a common ion only affects the activity quotient so that at the simplified condition  $Q_{a1} = 1.0$ , no variation of the ion-association degree can occur due to the presence of the other component.

In the presence of a component with a common ion, it must be distinguished between the case when this component is completely dissociated into ions, i.e. when it does not form any ion-pair ( $\alpha_2 = 0$ ), and between the case when the ionic component does form ion-pair. In the presence of a component of the type  $M_2A$  with a common cation and completely dissociating into ions  $M^+$  and  $A^{2-}$  (i.e.  $\alpha_2 = 0$ ), the degree of ion-association of peroxodisulfate into an ion-pair  $MS_2O_8^{1-}$  can be computed using the equation

$$\alpha_1 = 1.5 + m_2/m_1 + 1/(2K_{a1}m_1) - ((1.5 + m_2/m_1 + 1/(2K_{a1}m_1))^2 - 2 - 2m_2/m_1)^{0.5} \quad (4)$$

where  $m_1$  denotes the molality of the considered peroxodisulfate with the ion-association constant  $K_{a1}$ ,  $m_2$  denotes the molality of the other uni-bivalent electrolyte with a common cation. The results for various values of  $m_1$  and  $m_2$  and for the presumed ion-association constant  $K_{a1} = 10 \text{ mol kg}^{-1}$  are given in Table 4. As can be seen, even a quite low concentration of the other component with a common cation causes a distinct rise of the ion-association degree  $\alpha_1$ . Consequently, at all solution compositions given in Table 4, the ion-association degree  $\alpha_1 > 0.75$  so that the thermodynamic behaviour of peroxodisulfates approaches to that of the type 1-1, the more, the higher is the concentration of the other component with a common cation. Analogous results can be obtained for the case of the presence of another component with a common anion.

A more complicated case arises when the other component  $M_2A$  with a common cation  $M^+$  and total molality  $m_2$  can form an ion-pair  $MA^-$  with the ion-association constant  $K_{a2}$  and association degree  $\alpha_2$ . The ion-association degree of peroxodisulfate,  $\alpha_1$ , can be calculated (under a further simplified condition  $Q_{a2} = 1.0$ ) by a common solution of two equations with two unknown values  $\alpha_1$  and  $\alpha_2$  given by expressions

$$\alpha_1 = 1.5 + m_2(2 - \alpha_2)/(2m_1) + 1/(2K_{a1}m_1) - ((1.5 + m_2(2 - \alpha_2)/(2m_1) + 1/(2K_{a1}m_1))^2 - 2 - m_2(2 - \alpha_2)/m_1)^{0.5} \quad (5)$$

and

$$\alpha_2 = 1.5 + m_1(2 - \alpha_1)/(2m_2) + 1/(2K_{a2}m_2) - ((1.5 + m_1(2 - \alpha_1)/(2m_2) + 1/(2K_{a2}m_2))^2 - 2 - m_1(2 - \alpha_1)/m_2)^{0.5} \quad (6)$$

for given values  $m_1$ ,  $m_2$ ,  $K_{a1}$  and  $K_{a2}$ . Without solving this problem for concrete values of the given

quantities, it can be expected that values of the ion-association degree  $\alpha_1$  are in every case lower than those for  $\alpha_2 = 0$ , but higher than in the absence of a component with a common ion.

#### **Aqueous binary and polycomponent solutions, $Q_a < 1.0$**

In this case, if values of the activity quotient  $Q_a$  at a concrete solution composition are known, values of the ion-association degree  $\alpha_1$  could be computed using analogous expressions as in the case at  $Q_a = 1.0$ , using  $K'_a = K_a/Q_a$ . However, as the concrete values of the activity quotient  $Q_a$  of individual peroxodisulfates in the considered binary and polycomponent solutions are unknown up to today, values of  $\alpha_1$  can only be estimated. As has been given above, in all real cases  $Q_a < 1.0$ , so that always  $K'_a > K_a$ . With respect to the results at  $Q_a = 1.0$  given in Tables 3 and 4, it can be concluded that at  $Q_a < 1.0$ , values of the ion-association degree  $\alpha_1$  should be always even higher than those at  $Q_a = 1.0$ , i.e. the thermodynamic behaviour of sodium, potassium and ammonium peroxodisulfates in their aqueous binary and polycomponent solutions at concentrations with  $m \geq 0.1 \text{ mol kg}^{-1}$  could be taken as a 1-1 electrolyte.

#### **Evaluation of solubility data assuming $\alpha_1 = \alpha_2 = 1.0$**

It seemed therefore just as interesting to evaluate the solubilities of sodium, potassium and ammonium peroxodisulfates under the simplified assumption of a complete ion-association to  $MS_2O_8^{1-}$  and  $MSO_4^{1-}$  ions in the following polycomponent systems:  $Na_2S_2O_8$ - $Na_2SO_4$ - $H_2O$  (Balej and Regner 1967b),  $Na_2S_2O_8$ - $H_2SO_4$ - $H_2O$  (Balej and Regner 1967a),  $Na_2S_2O_8$ - $K_2S_2O_8$ - $H_2O$  (Balej and Regner 1966a),  $Na_2S_2O_8$ - $(NH_4)_2S_2O_8$ - $H_2O$  (Balej and Regner 1966b),  $K_2S_2O_8$ - $K_2SO_4$ - $H_2O$  (Balej and Regner 1960),  $(NH_4)_2S_2O_8$ - $(NH_4)_2SO_4$ - $H_2O$  (Balej and Regner 1963a),  $(NH_4)_2S_2O_8$ - $H_2SO_4$ - $H_2O$  (Balej and Regner 1963b),  $Na_2S_2O_8$ - $Na_2SO_4$ - $H_2SO_4$ - $H_2O$  (Balej and Regner 1969),  $(NH_4)_2S_2O_8$ - $(NH_4)_2SO_4$ - $H_2SO_4$ - $H_2O$

**Tab. 4.** Values of the ion-association degree  $\alpha$  of the aqueous solutions of peroxodisulfate with presumed association constant  $K_a = 10 \text{ kg mol}^{-1}$  and  $Q_a = 1.0$  in the presence of a completely dissociated component  $M_2A$  with a common cation.

$m_1$ (mol kg <sup>-1</sup> )	$\alpha_1$ at $m_2$						
	0.1	0.2	0.5	1	2	3	4
0.1	0.7639	0.8377	0.9172	0.9546	0.9762	0.9839	0.9878
0.2	0.8139	0.8625	0.9240	0.9566	0.9768	0.9841	0.9880
0.5	0.8835	0.9046	0.9387	0.9618	0.9783	0.9849	0.9884
1.0	0.9271	0.9361	0.9534	0.9681	0.9805	0.9859	0.9890
2.0	0.9581	0.9612	0.9684	0.9759	0.9837	0.9877	0.9901
3.0	0.9705	0.9721	0.9760	0.9806	0.9860	0.9891	0.9910
4.0	0.9772	0.9782	0.9807	0.9838	0.9877	0.9901	0.9918
5.0	0.9815	0.9821	0.9838	0.9861	0.9891	0.9910	0.9924

(Balej and Regner 1965) and  $\text{Na}_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  (Balej and Regner 1968). For the evaluation of the correlation equations, the same method of the relative activity coefficient expansion as previously (Balej 1982) has been used. In systems with a common ion, the expression of the relative activity coefficients expansion has the following form

$$\begin{aligned} \log(\gamma_{\text{so}}/\gamma_{\text{s}}) = \varphi &= (\log(m_{\text{c},\text{s}} \cdot m_{\text{A},\text{s}}/(m_{\text{o},\text{s}}^2)))/2 = \\ &= \sum Q_{\text{i}} m_{\text{i}} + \sum \sum Q_{\text{ij}} m_{\text{i}} m_{\text{j}} + \dots \end{aligned} \quad (7)$$

where sums are from 1 to n for i and j, respectively. In systems without a common ion, it has a simple form

$$\log(\gamma_{\text{so}}/\gamma_{\text{s}}) = \varphi = \log(m_{\text{s}}/m_{\text{os}}) \quad (8)$$

At the presented approach, it must be pointed out that systems  $\text{Na}_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ ,  $\text{Na}_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$  and  $\text{Na}_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  belong to systems without any common ion.

The results of this treatment could be presented by the following expressions, simultaneously with values of the mean deviation of the calculated solubility of the crystallizing component:

*system*  $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ , temperature range 10–40 °C, crystallization area  $\text{Na}_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi &= (-0.00025 - 0.000625t)m_2 \\ \sigma &= \pm 0.77 \text{ rel. \%} \end{aligned} \quad (9)$$

*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, crystallization area  $\text{Na}_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi &= (-0.1307 + 0.000706t)m_2 - \\ &- (0.0046 - 0.000105t)m_2^2 \\ \sigma &= \pm 1.1 \text{ rel. \%} \end{aligned} \quad (10)$$

*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, crystallization area  $\text{Na}_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_1 &= (0.0065 - 0.0039t)m_2 + (0.214 - 0.001t)m_2^2 \\ \sigma &= \pm 0.33 \text{ rel. \%} \end{aligned} \quad (11)$$

crystallization area  $\text{K}_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_2 &= (0.138 - 0.0018t)m_1 \\ \sigma &= \pm 3.30 \text{ rel. \%} \end{aligned} \quad (12)$$

*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, crystallization area  $\text{Na}_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_1 &= (-0.0158 - 0.000189t)m_2 \\ \sigma &= \pm 0.56 \text{ rel. \%} \end{aligned} \quad (13)$$

crystallization area  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_2 &= (-0.0164 - 0.00041t)m_1 \\ \sigma &= \pm 0.67 \text{ rel. \%} \end{aligned} \quad (14)$$

*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, crystallization area  $\text{K}_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_1 &= 0.0473m_2 \\ \sigma &= \pm 4.25 \text{ rel. \%} \end{aligned} \quad (15)$$

crystallization area  $\text{K}_2\text{SO}_4$ :

$$\begin{aligned} \varphi_2 &= 0.1443m_1 - 0.8119m_1^2 \\ \sigma &= \pm 0.45 \text{ rel. \%} \end{aligned} \quad (16)$$

*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 10–40 °C, crystallization area  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_1 &= (-0.0178 + 0.000358t)m_2 - \\ &- (0.00286 - 0.0000107t)m_2^2 \\ \sigma &= \pm 1.27 \text{ rel. \%} \end{aligned} \quad (17)$$

crystallization area  $(\text{NH}_4)_2\text{SO}_4$ :

$$\begin{aligned} \varphi_2 &= (-0.03383 + 0.000162t)m_1 \\ \sigma &= \pm 0.27 \text{ rel. \%} \end{aligned} \quad (18)$$

*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, crystallization area  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_1 &= (-0.1426 + 0.0021t)m_2 + \\ &+ (0.00807 - 0.00027t)m_2^2 \\ \sigma &= \pm 1.32 \text{ rel. \%} \end{aligned} \quad (19)$$

*system*  $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ , temperature range 10–40 °C, crystallization area  $\text{Na}_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_1 &= (-0.00025 - 0.000625t)m_2 - \\ &- (0.1307 - 0.000706t)m_2 - \\ &- (0.0046 - 0.000105t)m_2^2 + \\ &+ (0.0017 + 0.000348t)m_2m_3 \\ \sigma &= \pm 6.0 \text{ rel. \%} \end{aligned} \quad (20)$$

*system*  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ , temperature range 10–40 °C, crystallization area  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_1 &= (-0.0178 + 0.000358t)m_2 - \\ &- (0.00286 - 0.0000107t)m_2^2 - \\ &- (0.1426 - 0.0021t)m_3 + \\ &+ (0.00807 - 0.00027t)m_3^2 + \\ &+ (0.0137 - 0.0000865t)m_2m_3 - \\ &- (9.1 \times 10^{-5} - 2.08 \times 10^{-6}t)m_2^2m_3^2 \\ \sigma_1 &= \pm 6.61 \text{ rel. \%} \end{aligned} \quad (21)$$

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

$$\begin{aligned} \varphi_1 &= (-0.0158 - 0.000189t)m_2 - \\ &- (0.1307 - 0.000706t)m_3 - \\ &- (0.0046 - 0.000105t)m_3^2 - \\ &- (0.00962 - 0.000671t)m_2m_3 + \\ &+ (0.00177 - 0.0000884t)m_2^2m_3^2 \\ \sigma &= \pm 2.61 \text{ rel. \%} \end{aligned} \quad (22)$$

crystallization area  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ :

$$\begin{aligned} \varphi_2 &= (-0.0164 - 0.00041t)m_1 - \\ &- (0.1426 - 0.0021t)m_3 + \\ &+ (0.00807 - 0.00027t)m_3^2 + \\ &+ (0.02224 - 0.000352t)m_2m_3 \\ \sigma &= \pm 2.39 \text{ rel. \%} \end{aligned} \quad (23)$$

As can be seen, values of mean deviations of the cal-

culated solubilities of the crystallizing component of ternary systems are low and mostly do not exceed 1 rel. %. Higher value of this quantity at the system  $K_2S_2O_8$ - $K_2SO_4$ - $H_2O$  attaining  $\pm 4.25$  rel. % for the crystallization area of  $K_2S_2O_8$  is probably caused by a low solubility of this salt in the considered system leading to a lower accuracy of the analysed contents.

A comparison of the mean deviation at the considered quaternary systems under the assumption of a total ion-association and total dissociation of individual components is given in Table 5. As can be seen, at the system  $Na_2S_2O_8$ - $Na_2SO_4$ - $H_2SO_4$ - $H_2O$ , the difference between both values is quite low, a little higher is at the system  $(NH_4)_2S_2O_8$ - $(NH_4)_2SO_4$ - $H_2SO_4$ - $H_2O$ . A hardly understandable difference has been observed at the system  $Na_2S_2O_8$ - $(NH_4)_2S_2O_8$ - $H_2SO_4$ - $H_2O$  for the crystallization area  $Na_2S_2O_8$ , while for the crystallization area  $(NH_4)_2S_2O_8$ , values of the mean deviation by both methods were practically identical.

**Tab. 5.** Values of mean deviations of measured and calculated solubilities of crystallizing peroxodisulfates in the considered quaternary systems under assumption of a total association and total dissociation of the electrolytes.

system	$\sigma$ (rel. %)	
	total associa- tion	total dissocia- tion
$Na_2S_2O_8$ - $Na_2SO_4$ - $H_2SO_4$ - $H_2O$	$\pm 6.00$	$\pm 5.67$
$(NH_4)_2S_2O_8$ - $(NH_4)_2SO_4$ - $H_2SO_4$ - $H_2O$	$\pm 6.61$	3.33
$Na_2S_2O_8$ - $(NH_4)_2S_2O_8$ - $H_2SO_4$ - $H_2O$ : crystallization area $Na_2S_2O_8$	$\pm 2.61$	$\pm 8.30$
crystallization area $(NH_4)_2S_2O_8$	$\pm 2.35$	$\pm 2.39$

## Conclusions

Values of the ion-association degree  $\alpha$  have been calculated of sodium, potassium and ammonium peroxodisulfates in their aqueous binary and polycomponent solutions for selected presumed values of the ion-association constants  $K_a$  under the simplified assumption that the activity quotients of corresponding solution components  $Q_a = 1.0$ . All presented results led to the conclusion that a very simplified assumption about a complete ion-association of the considered peroxodisulfates and sulfates in the form of associated anions  $MS_2O_8^{1-}$  and  $MSO_4^{1-}$  may be used for the quantitative evaluation of the solubility of these substances in the considered polycompo-

nent systems. Very low mean deviations between the calculated and measured solubilities of crystallizing components at the most considered ternary systems and acceptable low ones at all considered quaternary systems are almost identical with those observed previously (Balej 1982, 2011) under the assumption of a total dissociation of the considered peroxodisulfates and sulfates. Accordingly, the concept of a quite extensive ion-association of sodium, potassium and ammonium peroxodisulfates in their sufficiently concentrated binary and polycomponent solutions seems to be sufficiently probable. However, due to the low accuracy of the considered values of  $K_a$ , it must be reminded that the presented values of the ion-association degrees of peroxodisulfates only represent tentative values. Nevertheless, the results show that the concept of ion-association to  $MS_2O_8^{1-}$  is well acceptable and could be taken into account in scientific communications dealing with the physico-chemical behaviour of systems containing peroxodisulfates. However, clear evidence about the true composition and amount of the considered anions in the corresponding systems must be obtained by suitable additional, most probably spectroscopic measurements leading to sufficiently reliable and accurate values of the individual ion-association constants.

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