

SOLUBILITY CORRELATIONS FOR TERNARY SYSTEMS CONTAINING PEROXODISULPHATES

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Correlations of solubility data previously measured on ternary systems containing peroxodisulphates of monovalent cations have been established using the method of relative activity coefficient expansion. The relationships obtained give a fairly good representation of experimental solubility curves for systems which do not form solid solutions. The general form of the correlation function is discussed in relation to the resultant ionic strength of saturated solution.

So far published solubility data for multicomponent systems containing alkali metal and ammonium peroxodisulphates¹⁻¹⁶ have been expressed in mass percent, allowing common materials balances to be made for technological processes based on such data. Simultaneously reported densities of the saturated solutions permit recalculations to volumetric concentrations. However, a disadvantage of solubility data expressed in this manner is a limited possibility of their use in calculating sufficiently reliable solubilities in more complicated multicomponent systems, where the experimental investigation over the whole concentration and temperature ranges required is already rather laborious and time consuming. It is therefore convenient for the given purposes to express solubilities in multicomponent systems by means of relations derived on the basis of thermodynamic description of more concentrated electrolyte solutions. Several manners of expressing the solubilities have been proposed; a survey and critical assessment of these has been given by Nývlt¹⁷.

In recalculation of solubilities in multicomponent systems containing peroxodisulphates we adhered to the method of relative activity coefficient expansion proposed by Nývlt^{17,18} and developed by modification of the relationship derived by Erdős¹⁹. The method is based on the principal thermodynamic relationship for equilibrium in multi-phase polycomponent system, defined by the equality of chemical potentials of a crystallizing component in all the co-existing phases. The method has proved successful in correlating solubility data for a number of three-component systems^{17,20-22}.

The change in the solubility of a crystallizing component induced by the presence of other components in the solution can be expressed¹⁷ in the cases of electrolytes by relationships which differ according to whether or not the crystallizing component

and the added components have a common ion (cation or anion). When there is a common ion, the change in the solubility of crystallizing component 1 due to the presence of added component 2 (beside the solvent, most frequently water, *i.e.* component 3) can be expressed for three-component systems by the general relation

$$\frac{\log [x_1^\alpha(x_1 + FB)^\beta]}{\alpha + \beta} = \varphi_1, \quad (1)$$

valid for all conceivable combinations of mono- and divalent ions, where

$$x_i = m_i/m_{0i} \quad (2)$$

$$B = x_2 m_{02}/m_{01} \quad (3)$$

$$F = v_{i\pm}/v_{1\pm} \quad (4)$$

$$\alpha = v_{1\pm} \quad (5)$$

$$\beta = v_{1\mp} \quad (6)$$

$$\varphi_1 = \log (\gamma_{01\pm}/\gamma_{1\pm}). \quad (7)$$

In Eqs (4) to (6) the upper signs in the subscripts hold for systems with a common anion, while the lower signs apply to systems with a common cation; m_1 and m_{01} represent the molalities of crystallizing component in a saturated three-component solution and in pure water, respectively, at a given temperature; m_i stands for the molality of component i in the three-component solution, v_+ and v_- signify the number of cations and anions, respectively, generated by dissociation of one molecule of the component considered, and γ_{\pm} is the mean molal activity coefficient of the component considered.

The method described is based on the fact that the quantity φ_1 is a more or less complicated function of the content of other components of polycomponent system:

$$\varphi_1 = \sum_{i=2}^n Q_{1i} m_i + \sum_{i=2}^n \sum_{j=2}^n Q_{1ij} m_i m_j + \dots, \quad (8)$$

where Q_{1i} and Q_{1ij} are the corresponding interaction coefficients.

The generalized form of Eq. (1) involving relative quantities is useful especially in computer processing of experimental data as it enables any type of system to be treated using the same program¹⁷. A disadvantage inherent in Eq. (1) is, however, that the effect of added components in changing the solubility of crystallizing compo-

ment does not emerge clearly. This is due to the fact that the method of relative activity coefficient expansion consists essentially in determining the ratio of solubility products of crystallizing component 1 in polycomponent system (S_1) and in pure solvent (S_{01}) at the same temperature, the concentrations of ions of the component considered being expressed as molalities. Taking logarithm of this ratio and rearranging, we obtain

$$(1/\nu_1) \log (S_1/S_{01}) = \varphi_1, \quad (9)$$

where

$$\nu_1 = \nu_{1+} + \nu_{1-}, \quad (10)$$

which yields the same results as Eq. (1). It is clear that for a multicomponent system involving components having some of their ions common with ions of crystallizing component 1, the total molalities of the ions must be used in determining the value of the solubility product of the crystallizing component.

Eq. (9) was used as a starting point in deriving concrete expressions correlating solubility data previously measured on ternary systems involving alkali metal and ammonium peroxodisulphates. The results of the evaluation are reported in the present communication.

RESULTS AND DISCUSSION

The ternary systems containing alkali metal and ammonium peroxodisulphates for which experimental data are available^{1-4,6-9,11-14*} can be divided into three groups which may further be subdivided according to whether the two components crystallize in the solid phase separately in their pure forms or as solid solutions: a_1) systems with a common anion which do not form solid solutions: $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ (ref.⁶) and $\text{Na}_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ (ref.⁷), a_2) systems with a common anion which form solid solutions: $\text{K}_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ (ref.²), b) systems with a common cation which do not form solid solutions: $\text{K}_2\text{S}_2\text{O}_8\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ (ref.¹), $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ (ref.⁹), $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$ (ref.³), $\text{Na}_2\text{S}_2\text{O}_8\text{-NaOH-H}_2\text{O}$ (ref.¹³), $\text{K}_2\text{S}_2\text{O}_8\text{-KOH-H}_2\text{O}$ (ref.¹⁴), c) systems with no common ion: $\text{Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (ref.⁸), $\text{K}_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (ref.¹²), $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (ref.⁴).

In the case of group a_1) the effect of component 2 on the solubility of crystallizing component 1 in saturated solution was evaluated using the relation

$$\frac{1}{3} \log [m_1^2(m_1 + m_2)/m_{01}^3] = \varphi_1. \quad (11)$$

* For the system $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$, the recently determined solubility data at 0°C, not yet published, have been included into the correlations, too.

The solubility correlation for group (a_2) will be the subject of a separate communication.

With group (b) systems with differing divalent anions ($S_2O_8^{2-}$ and SO_4^{2-}) were treated using the relation

$$\frac{1}{3} \log [m_1(m_1 + m_2)^2/m_{01}^3] = \varphi_1, \quad (12)$$

while the relationship

$$\frac{1}{3} \log [m_1(2m_1 + m_2)^2/4m_{01}^3] = \varphi_1 \quad (13)$$

was used for unlike mono- and divalent anions (OH^- and $S_2O_8^{2-}$).

Finally, data for systems belonging to group (c) were treated with the use of the relation

$$\log (m_1/m_{01}) = \varphi_1. \quad (14)$$

The interaction coefficients Q of expansion (8) were determined following the procedures described in refs¹⁷⁻²²: the quantity φ_1/m_2 was calculated using one of the relations (11) to (14) and its dependence on m_2 was established by the regression analysis. For systems containing potassium peroxodisulphate as the crystallizing component 1 it turned out to be preferable to use a function in the form $\varphi_1 = f(m_2^{0.5})$ for the expansion (8) since the original form based on m_2 exhibited a strong non-linearity, unlike the other systems studied.

In calculations according to Eqs (11) to (14), values resulting from correlations presented in our previous papers²³ were used for the solubilities of pure peroxodisulphates. Solubilities of other components in pure water were taken from smoothed data tabulated in ref.²⁴.

The method described was used to evaluate solubilities in the above ternary systems containing peroxodisulphates, with the exception of the system $K_2S_2O_8-(NH_4)_2 \cdot S_2O_8-H_2O$ which forms solid solutions. Where the relevant data were available, the interaction coefficients Q were calculated for the crystallization regions of both components. In the case of ternary systems with sulphuric acid or alkali metal hydroxide as the added component, the above method was only used to evaluate the solubility data for the peroxodisulphate involved, because here the added component either did not crystallize at all in the temperature range covered (H_2SO_4) or its crystallization occurred only at high concentrations, which were beyond the region of technical interest, and moreover, made a reliable solubility determination difficult.

A summary of the resulting correlations between the relative activity coefficient, φ_1 , of crystallizing component and the molality of added component for various ternary systems containing alkali metal and ammonium peroxodisulphates is given in Table I. The relations for φ_1 are valid in the temperature range 10–30°C, except

TABLE I
Relative activity coefficient expansions for saturated solutions of ternary systems containing peroxodisulphates

Group	Component 1	Component 2	Cryst. comp.	φ_1	Note
a	Na ₂ S ₂ O ₈	K ₂ S ₂ O ₈	1	$(0.007905 - 0.002556 t)m_2 + (0.3798 - 0.0006585 t)m_2^2$	
			2	$(0.5277 - 0.00918 t)m_1^{0.5} - (0.03266 - 0.002332 t)m_1$	
	Na ₂ S ₂ O ₈	(NH ₄) ₂ S ₂ O ₈	1	$(0.03414 - 0.000407 t)m_2 - 0.00238m_2^2$	
			2	$(0.04164 - 0.001438 t)m_1 - (0.007043 - 0.00032 t)m_1^2$	
	Na ₂ S ₂ O ₈	Na ₂ SO ₄	1	$0.0149m_2 - 0.006666m_2^2$	m_2 calculated
			2(10 H ₂ O)	$(0.4284 - 0.02953 t + 0.0005086 t^2)m_1 -$ $-(0.08751 - 0.007832 t + 0.0001446 t^2)m_1^2$	for anhydrous salt
b	K ₂ S ₂ O ₈	K ₂ SO ₄	1	$(0.266 - 0.011 t)m_1^{0.5} + 0.294m_2$	
			2	$(0.2251 - 0.008092 t)m_1^{0.5} + (0.3184 - 0.000636 t)m_1$	
	(NH ₄) ₂ S ₂ O ₈	(NH ₄) ₂ SO ₄	1	$(0.0195 - 0.00109 t + 1.745 \times 10^{-5} t^2)m_2 -$ $-(0.00375 - 2.02 \times 10^{-4} t + 3.01 \times 10^{-6} t^2)m_2^2$	
			2	$-0.01339m_1$	
	Na ₂ S ₂ O ₈	NaOH	1	$-0.0080m_2 - 0.00134m_2^2$	
	K ₂ S ₂ O ₈	KOH	1	$(0.02168 - 0.004756 t)m_2 - (0.0213 - 0.000512 t)m_2^2$ $(0.1307 - 0.00404 t)m_1^{0.5} + (0.06024 - 0.000532 t)m_2$	applies to $2 < m_2 \leq 6$ $m_2 < 2$
c	Na ₂ S ₂ O ₈	H ₂ SO ₄	1	$(-0.1445 + 0.00104 t)m_2$	for $m_2 \leq 5$
	K ₂ S ₂ O ₈	H ₂ SO ₄	1	$(0.2655 - 0.00566 t)m_1^{0.5} - (0.1156 - 0.00154 t)m_2$	for $m_2 \leq 4.5$
	(NH ₄) ₂ S ₂ O ₈	H ₂ SO ₄	1	$(-0.110 + 0.0010 t)m_2$	for $m_2 \leq 6$

for the systems $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $(\text{NH}_4)_2\text{SO}_4$ - H_2O , $\text{K}_2\text{S}_2\text{O}_8$ - K_2SO_4 - H_2O , and $\text{K}_2\text{S}_2\text{O}_8$ - KOH - H_2O , for with they hold within 0–40°C, 15–30°C and 10–40°C, respectively.

As has been mentioned, for systems containing potassium peroxodisulphate as the crystallizing component it proved to be appropriate to expand φ_1 as a polynomial in $m_2^{0.5}$, and not in m_2 recommended by Nývlt¹⁷. This is apparently due to the fact that unlike other peroxodisulphates and components involved in the systems investigated, potassium peroxodisulphate is little soluble. In this connection it is to be realized that the quantity φ_1 is defined by Eq. (7) which can be written in the form

$$\varphi_1 = -(\log \gamma_{1\pm} - \log \gamma_{01\pm}) = -\log \gamma_{1\pm} + \text{constant}. \quad (15)$$

It is well-known that the value of $-\log \gamma_{1\pm}$ is a relatively complicated function of the total ionic strength, I , of solution, involving always, beside higher terms, the basic Debye-Hückel term in $I^{0.5}$ valid up to ionic strength of the order of 10^{-1} mol/kg.

TABLE II

Calculated and experimentally determined compositions, m_1 , m_2 (mol/kg), of eutonic solutions in ternary systems containing peroxodisulphates

Component 1	Component 2	Temperature °C	$m_{1,\text{calc}}$	$m_{1,\text{exp}}$	$m_{2,\text{calc}}$	$m_{2,\text{exp}}$
$\text{Na}_2\text{S}_2\text{O}_8$	$\text{K}_2\text{S}_2\text{O}_8$	10	2.760	2.760	0.234	0.230
		20	2.935	2.938	0.366	0.366
		30	3.131	3.131	0.537	0.504
$\text{Na}_2\text{S}_2\text{O}_8$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	10	2.490	2.497	2.688	2.673
		20	2.606	2.575	3.098	3.094
		30	2.681	2.716	3.514	3.517
$\text{Na}_2\text{S}_2\text{O}_8$	Na_2SO_4	10	2.580	2.614	0.288	0.282
		20	2.530	2.546	0.758	0.750
		30	2.205	2.241	1.903	1.891
$\text{K}_2\text{S}_2\text{O}_8$	K_2SO_4	15	0.040	0.041	0.570	0.567
		20	0.057	0.057	0.617	0.621
		25	0.080	0.082	0.658	0.658
		30	0.107	0.108	1.708	0.708
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	$(\text{NH}_4)_2\text{SO}_4$	0	0.513	0.513	4.893	4.894
		10	0.851	0.851	4.799	4.773
		20	1.285	1.234	4.643	4.685
		30	1.813	1.813	4.417	4.415
		40	2.422	2.459	4.187	4.182

Thus, when the solubility of a pure crystallizing component is considerably higher than the limit of validity of the Debye-Hückel limiting law, and the ionic strength is further enhanced due to the presence of another component in the solution, the basic Debye-Hückel term loses its dominating influence and the dependence of φ_1 on the content of the added component (or components) may apparently be expressed with sufficient accuracy only by a polynomial in m_j . If, on the other hand, the solubility of crystallizing component is so low as to fall into the concentration range within which the variation of its activity coefficient with the total ionic strength of the solution is determined to a large extent by the basic Debye-Hückel term, then it is undoubtedly more adequate to expand φ_1 as a polynomial in $m_j^{0.5}$. Such is the case with potassium peroxodisulphate as the crystallizing component, whose solubility at 10°C, $m_0 = 0.1096$ mol/kg, and at 40°C, $m_0 = 0.4244$ mol/kg. With an addition of another component, the total concentration falls into the range of validity of Brønsted relationship, $-\log \gamma_{\pm} = AI^{0.5} + BI$, which holds for electrolytes of 1-1 type up to ionic strength $I = 3$, and possibly even higher.

In order to test the correctness of the correlations obtained, back-calculations of the solubilities of crystallizing components were made by substituting the corresponding equations for the quantity φ_1 in the basic relations (11) to (14). Figs 1-10 provide comparison between solubilities calculated in this way and experimentally found values for all the systems studied. Further comparison between calculated and

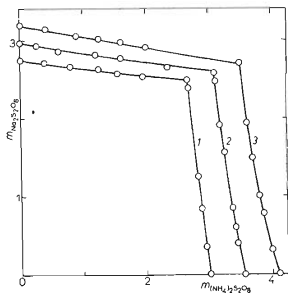


FIG. 1

Comparison between calculated solubility curves (full lines) and experimental points for the ternary system $\text{Na}_2\text{S}_2\text{O}_8$ - $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - H_2O at 10 1, 20 2, and 30°C 3

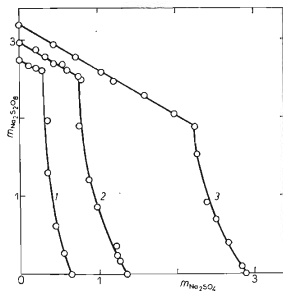


FIG. 2

Comparison between calculated solubility curves (full lines) and experimental points for the ternary system $\text{Na}_2\text{S}_2\text{O}_8$ - Na_2SO_4 - H_2O at 10 1, 20 2, and 30°C 3

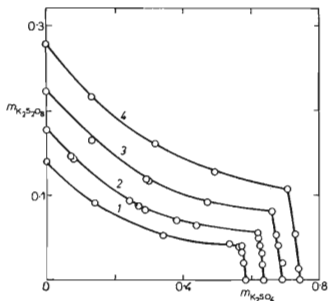


FIG. 3

Comparison between calculated solubility curves (full lines) and experimental points for the ternary system $K_2S_2O_8$ - K_2SO_4 - H_2O at 15 1, 20 2, 25 3, and 30°C 4

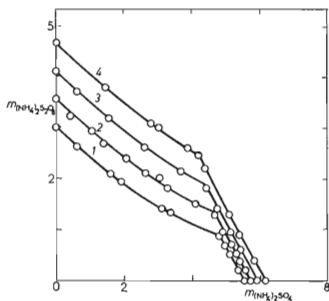


FIG. 4

Comparison between calculated solubility curves (full lines) and experimental points for the ternary system $(NH_4)_2S_2O_8$ - $(NH_4)_2SO_4$ - H_2O at 10 1, 20 2, 30 3, and 40°C 4

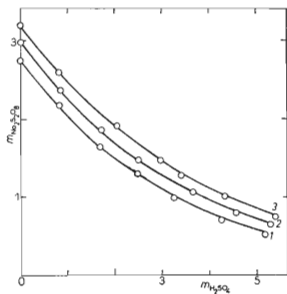


FIG. 5

Comparison between calculated solubility curves (full lines) and experimental points for the ternary system $Na_2S_2O_8$ - H_2SO_4 - H_2O at 10 1, 20 2, and 30°C 3

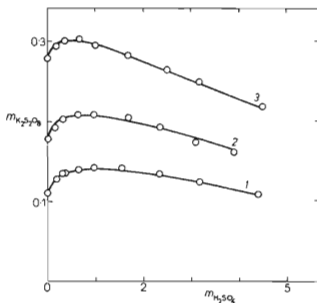


FIG. 6

Comparison between calculated solubility curves (full lines) and experimental points for the ternary system $K_2S_2O_8$ - H_2SO_4 - H_2O at 10 1, 20 2, and 30°C 3

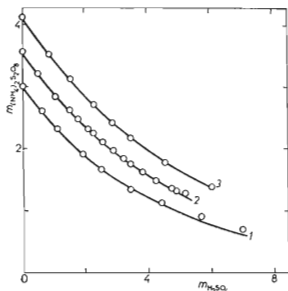


FIG. 7

Comparison between calculated solubility curves (full lines) and experimental points for the ternary system $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ at 10, 20, 2, and 30°C 3

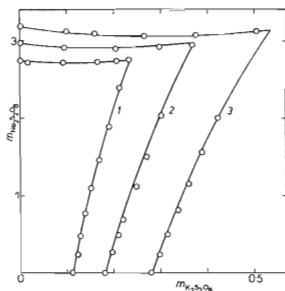


FIG. 8

Comparison between calculated solubility curves (full lines) and experimental points for the ternary system $\text{Na}_2\text{S}_2\text{O}_8\text{-K}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ at 10, 20, 2, and 30°C 3

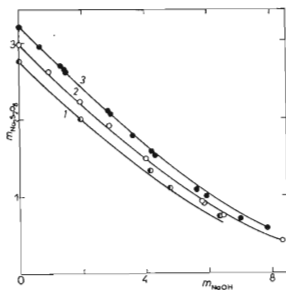


FIG. 9

Comparison between calculated solubility curves (full lines) and experimental points for the ternary system $\text{Na}_2\text{S}_2\text{O}_8\text{-NaOH-H}_2\text{O}$ at 10, 20, 2, and 30°C 3

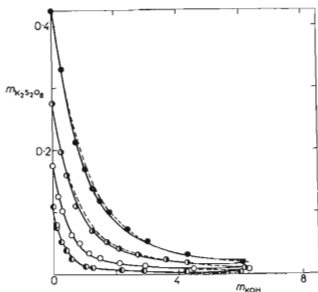


FIG. 10

Comparison of solubility curves calculated according to equations for $m_2 \leq 2$ (full line) and for $2 < m_2 \leq 6$ (broken line) with experimental points of the ternary system $\text{K}_2\text{S}_2\text{O}_8\text{-KOH-H}_2\text{O}$ at 10 (○), 20 (○), 30 (◐), and 40°C (●)

experimental solubilities is given in Table II which summarizes calculated and experimentally determined eutonic compositions for the systems studied. The figures as well as Table II show that in the majority of cases the calculated solubility curves and the coordinates of eutonic points are in very good agreement with the experimental data. It is gratifying to see that the best agreement has been obtained for systems of primary technical importance, containing ammonium peroxodisulphate and/or sodium peroxodisulphate as crystallizing component. It may be assumed that these relationships would yield sufficiently reliable results in solubility calculations for even more complicated systems involving these peroxodisulphates, such as may be encountered in various processes of peroxodisulphate manufacture or further processing.

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