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ENTHALPY OF SOLUTION AND EFFECT OF TEMPERATURE ON ACTIVITY COEFFICIENTS IN MSO_4–H_2SO_4–H_2O SYSTEM

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Results of calorimetric determination of integral enthalpies of solution of some hydrates (monohydrates and heptahydrates) of 3*d* transition metal sulphates such as $FeSO_4$, $NiSO_4$ and $MnSO_4$ in three-component systems at sulphuric acid concentrations up to 2*M* are reported. Measured values of integral enthalpies of solution are the basis for calculation of activity coefficient temperature dependences according to Pitzer's model.

Keywords: activity coefficients, MSO_4–H_2SO_4–H_2O systems

Introduction

In recent years there has been interest in the thermodynamic properties of mixed aqueous electrolyte solutions [1, 2]. Among these enthalpies of solution of transition metal sulphates in sulphuric acid solutions (MSO_4–H_2SO_4–H_2O systems) are especially important.

Integral enthalpies of solution of transition metal sulphates in water and in sulphuric acid solutions are necessary for determination and prediction of the temperature-dependence of salt activity coefficients and solubility equilibria in multicomponent mixed electrolyte systems.

The calorimetric determinations of integral enthalpies of solution of transition metal sulphates in sulphuric acid solutions presented in this paper are a continuation of a project carried out in CSChN PAN and presented earlier [3, 4].

Experimental

Analytical-grade transition metal sulphate hydrates $FeSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$ and $MnSO_4 \cdot H_2O$ were double recrystallized, dried and ground. The 0.020–0.028 mm size fraction was separated for experiments. The nonadiabaticnonisothermic calorimeter (constructed in Department of Calorimetry, Institute of Physical Chemistry of PAS) was used to determine integral enthalpies of solution at 298.15 K. The internal temperature of the calorimetric system was stabilized with a precision of 0.001 K.

Salt samples were dissolved in about 100 ml water or sulphuric acid. In all experiments a constant mass ratio of salt to water in solution was established. This ratio was $1\cdot10^{-3}$ for $MnSO_4\cdot H_2O$ and $5\cdot10^{-4}$ for $FeSO_4\cdot 7H_2O$ and $NiSO_4\cdot 7H_2O$. The electric heater of the calorimeter was calibrated from the heat of solution of potassium chloride in water. Results of calorimetric measurements were evaluated using the Dickinson method [5, 6].

Table 1 Integral dissolution enthalpy of some transition metal sulphates in sulphuric acid solutions

No	H_2SO_4 concentration / $\frac{\text{mol } H_2SO_4}{\text{kg } H_2O}$	ΔH_s / kJ·mol^{-1}		
		$FeSO_4\cdot 7H_2O$	$MnSO_4\cdot H_2O$	$NiSO_4\cdot 7H_2O$
1	0.0000	13.808	- 20.191	15.644
2	0.0256	14.486	- 19.221	18.635
3	0.1030	16.371	- 17.594	22.696
4	0.5032	17.932	- 14.985	27.265
5	1.0030	19.391	- 13.465	28.973
6	2.0901	19.933	- 12.443	30.577

Results

Measured integral enthalpies of solution of $FeSO_4\cdot 7H_2O$, $NiSO_4\cdot 7H_2O$ and $MnSO_4\cdot H_2O$ in sulphuric acid solutions in the concentration range 0–2 *M* are summarized in Table 1. Results showed significant differences between kinetics of dissolution of mono- and heptahydrated salts, as illustrated by the calorimetric curves in Fig. 1. The dissolution process of the heptahydrates $FeSO_4\cdot 7H_2O$ and $NiSO_4\cdot 7H_2O$ is relatively fast and strongly endothermic whereas the dissolution process of the monohydrate $MnSO_4\cdot H_2O$ is slow and exothermic. The concentration dependence of enthalpies of solution as a function of sulphuric acid concentration is illustrated in Figs 2 to 4.

This concentration-salt enthalpies solution dependence can be described by the empirical equation:

$$H_s(m) = a_0 + a_1\sqrt{m} + a_2(\sqrt{m})^2 + \ldots$$

where m denotes the sulphuric acid molality.

Calculated values of regression coefficients are listed in Table 2. On the basis of experimentally determined enthalpies of transition metal sulphate solution, the *apparent relative enthalpy of solution can be calculated.* By application of Pitzer's correlation equation [7] for the apparent relative enthalpy of mixed electrolyte solution of three-component systems with a common anion, the Pitzer's virial coefficients β_0, β_1, β_2, θ and ψ temperature derivatives necessary for calculation of activity coefficients at higher temperatures can be calculated.

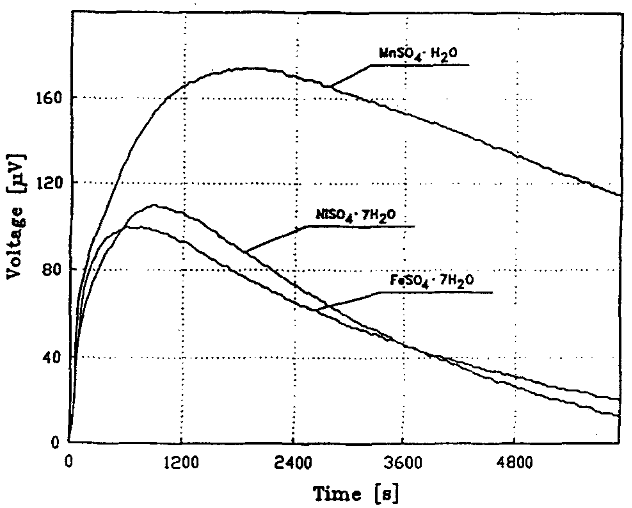

Fig. 1 Calorimetric curves of dissolution process of some transition metal sulphates in water

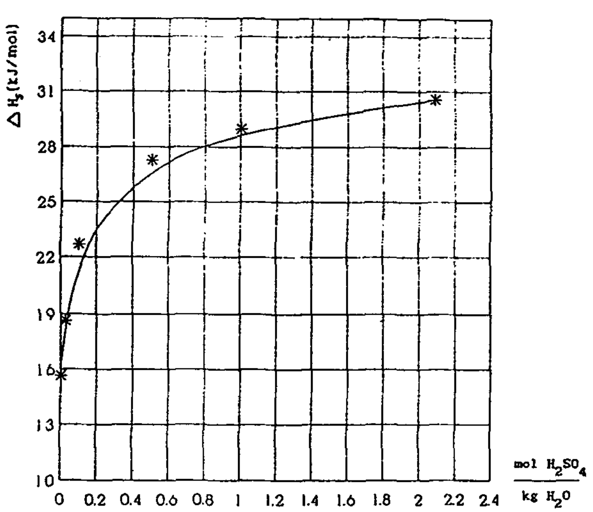

Fig. 2 Integral dissolution enthalpy of $NiSO_4 \cdot 7H_2O$ in sulphuric acid solutions

Table 2 Coefficiens of equation $\Delta H_s = a_0 + a_1 \cdot \sqrt{m} + a_2 \cdot (\sqrt{m})^2$

Salt	a_0	a_1	a_2	R^2
$FeSO_4 \cdot 7H_2O$	13.6500	8.2479	– 2.6800	0.9876
$MnSO_4 \cdot H_2O$	– 20.4025	9.6413	– 2.8334	0.9971
$NiSO_4 \cdot 7H_2O$	15.7657	21.8419	– 8.1167	0.9939

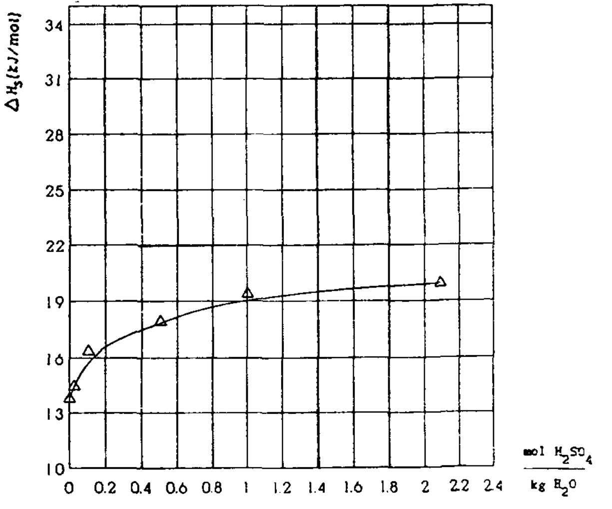

Fig. 3 Integral dissolution enthalpy of $FeSO_4 \cdot 7H_2O$ in sulphuric acid solutions

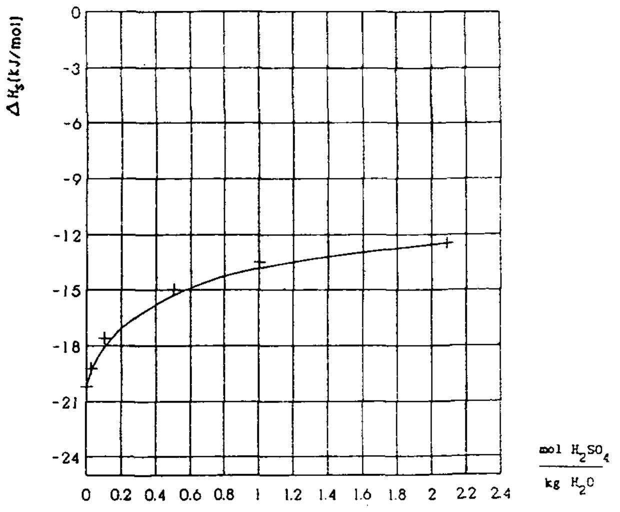

Fig. 4 Integral dissolution enthalpy of $MnSO_4 \cdot H_2O$ in sulphuric acid solutions

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Zusammenfassung — Es werden die Ergebnisse der kalorimetrischen Bestimmung der integralen Lösungsenthalpien einiger Hydrate (Monohydrate und Heptahydrate) von Sulfaten einiger 3*d* Übergangsmetalle wie z.B. von $FeSO_4$, $NiSO_4$ und $MnSO_4$ in Dreikomponentensystemen mit einer Schwefel-säurekonzentration bis 2*M* beschrieben. Die gemessenen Werte der integralen Lösungsenthalpien stellen die Grundlage für die Berechnung der Temperatur-abhängigkeit von Aktivitätskoeffizienten nach dem Pitzer'schen Modell dar.