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Calorimetry

STUDY OF THE INTERACTION BETWEEN IONIC SALTS AND WATER AND BY HIGH-RESOLUTION CALORIMETRY

II. General remarks on several sulphates

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The solubility behaviour of several hydrated and anhydrous sulphates has been studied isothermally (26.2 ± 0.06 °C) by using the high-resolution calorimeter previously described. The notion of behaviour recently defined in terms of topoenergetic principles was adopted for these experiments by establishing standard experimental conditions (SEC), mainly covering the geometry of the measuring cell and the figure of merit of the overall calorimetric system. The previously defined parameters from the heat flow recorded at normal and high speed clearly show the oscillatory behaviour generally predicted by the topoenergetic theory. The measuring system used also allows the demonstration of a difference in behaviour for size fractions of the same solute. The overall solubility behaviour under the same SEC for all values of solute mass can be defined in accordance with the universal topoenergetic procedure applied to a large variety of composite and measuring systems. The resulting data associated with the individual (ontogenic) and the group (phylogenic) behaviour can provide Data Banks for general use.

The solubility in two-component systems is a complex problem in terms of classical thermodynamics [1], involving many experimental and theoretical aspects. A new view of this problem is provided by the topoenergetic theory of behaviour of non-equilibrium composite systems, recently developed and applied to a large variety of particular cases [2]. In fact, the notion of system behaviour is actually adopted in classical terms [1], considering that the kinetic aspects of solubility are important in the conversion of the integral heat of solution (E_s) as a function of the mass of solute (m_{st}). However, the experimental data accumulated to date involve an important disadvantage concerning the experimental conditions. It is known that the kinetics of any kind of transformation process depends strongly on the geometry and dimensions of the overall reacting system, no matter how carefully the initial components are examined as regards purity and proportion. The

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behaviour relates to a particular property of an end-product during operation or its synthesis process revealed in particular in a technological system generally called the measuring system. The kinetic aspect of this notion arises from the relationship existing between the imposed conditions and the resulting property. Onsager's theory on non-equilibrium systems involving simple properties such as thermal and electric conductivities has made such a treatment, but not taking into account their time-dependence and the influence of the exact geometry and dimensions of the measuring system [3].

Oster and Auslander initially introduced new theoretical principles as topological thermodynamics in order to express the energy circuit associated with a transforming system by simple components with elementary behaviour (e.g. dissipative, capacitive, inductive, etc.) as in electric networks [4]. Two main errors were introduced in the development of these purely formal notions [5, 6], which led the authors to abandon them, namely: (i) the neglect of physical meaning of the introduced notions, and (ii) the overall energy circuit for a particular system was expressed as a spatial distribution of an elementary circuit. Further, they started to apply this incipient formalism to very complicated cases, such as non-linear phenomena in charged membrane structures [5] and the diffusion of oxygen through a haemoglobin solution [6]. While the first error is obvious, the second one contains the key to further development of the theory. Thus, to describe the time-conversion of the considered process at different dimensions, the associated energy circuits should be essentially the same, but with different values of the elementary components which determine the process amplitude. The energy circuit is modelled as an equivalent circuit, as electric networks, regardless of the spatial distribution. This particular system becomes a measuring system in which the imposed boundary conditions can be correlated with the time-conversion of a response function [7].

The calorimetric systems were the first measuring systems these principles were applied to [7–9], and rapidly developed as working principles in the identifying, optimizing and/or scaling-up of behaviour of any kind of composite system in respect to any kind of measuring system [2]. This universal procedure involves both the exact requirements imposed by standard experimental conditions (SEC) and the procedure of data-processing and its significance [2, 10, 11].

In the present work, the physical significance of the solubility behaviour of several sulphates is reviewed on the basis of these new principles, by using the high-resolution calorimeter described previously [12]. The grain size distribution of the solute represents a new and important aspect connected to the SEC and clearly evidenced by the universal procedure. The results show that both the universal procedure and the chosen calorimetric method can be standardized with a view to unifying solubility data in Data Banks, taking into account the current IUPAC efforts in this field [2, 13].

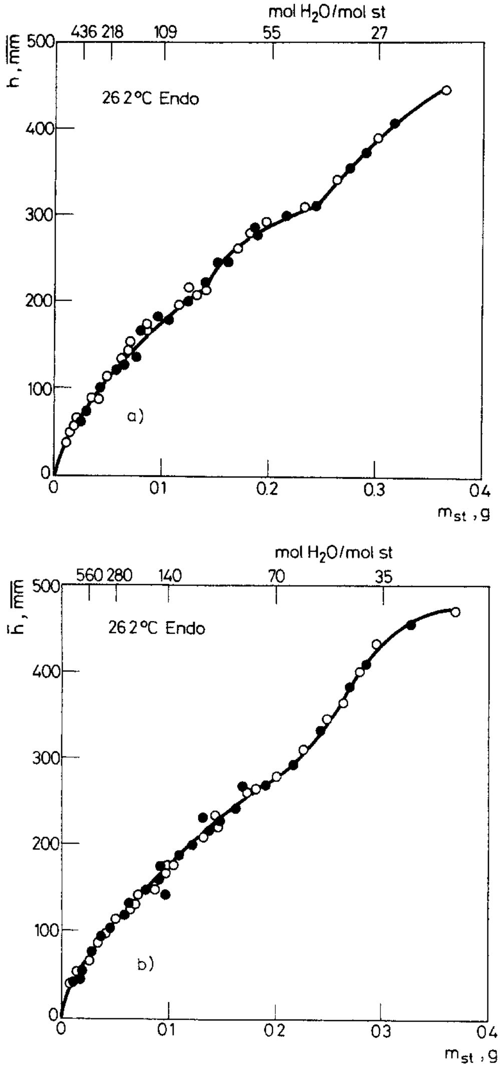

Fig. 1 Dependence of $h(m_{st})$ for the integral sample of $NiSO_4 \cdot 7H_2O$ in 0.7 (a) and 0.9 (b) ml H_2O of A (○) and B (●) type

Experimental

Measurements of the heat flow, $w(t)$, associated with the isothermal mixing of ionic salts and water were performed on the high-resolution calorimeter described previously [12]. The mixing was achieved by breaking a glass bubble having an external diameter strictly ranging between 8 and 9 mm and containing the chosen

m_{st} value. The bubble was initially located in the metallic cell containing a standard volume of 0.7 or 0.9 ml ± 0.002 ml of distilled and deionized water (see Fig. 2b in [12]). The measurements were performed only at 26.2 ± 0.06° for different m_{st} values, starting from the lower limit of sensitivity of the measuring system (approximately 10 μJ/s) up to the maximum value of m_{st} contained in the bubble. The bubble was broken with a plastic rod, and it was verified on 15 measurements with empty bubbles that there was negligible parasite heat flow. The recorded heat flows allow measurement of the peak height (h, in mm) and the integral heat of solution (E_s, in J) by using the previous calibration.

The following sulphates were considered as solute: $NiSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $MnSO_4$ and Na_2SO_4 (Reactivul, Bucharest) as pro analysis reagents. Samples of approximately 20 g were ground in a porcelain mortar and kept for a maximum of one week in a closed desiccator at room temperature (RT: 20 ± 2°) with controlled humidity (65 ± 5 RH, regulated with a saturated solution of sodium nitrite according to ISO R 483–1966) for hydrated sulphates and with P_2O_5 for anhydrous sulphates. The solubility of each

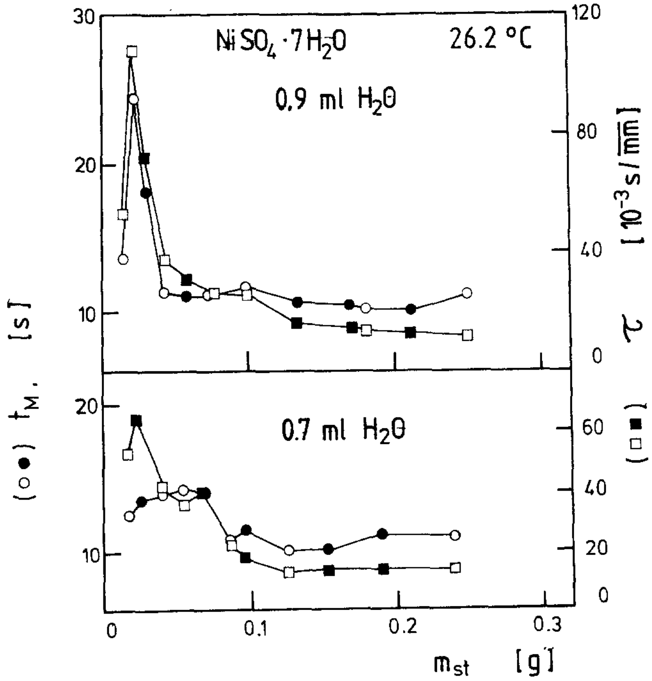

Fig. 2 Dependence of t_M (●, ○) and τ (□, ■) on m_{st} for the integral sample of $NiSO_4 \cdot 7H_2O$ determined at high speed of recording [12] for 0.7 and 0.9 ml H_2O of A (○, □) and B (●, ■) type

sulphate was tested on the integral ground sample (*I*) and on different size fractions (*F*) obtained by sifting with square-mesh sieves. The gravimetric distributions of freshly ground samples are given in Table 1. The size distributions of integral samples were also determined with an optical microscope by using a calibrated scale with 0.01 mm divisions.

Table 1 Gravimetric distribution of freshly grinded salts obtained by sifting with square-mesh sieves (% wt for each $\langle D \rangle$ range) and shape factor of solubility endotherm or hydration exotherm for integral (I) and fractionated samples

$\langle D \rangle$ mm	$NiSO_4 \cdot 7H_2O$	$MgSO_4 \cdot 7H_2O$	$CuSO_4 \cdot 5H_2O$	$FeSO_4 \cdot 7H_2O$	$MnSO_4$	Na_2SO_4
<0.102	1.2	4.2	8.7	31.1	82	76
0.102–0.315	53.6	32.5	51.0	22.0	18	24
0.315–0.500	41.5	50.4	30.8	25.0	—	—
0.500–0.600	3.7	12.9	9.5	21.9	—	—
$\langle h/E_s \rangle$ $\overline{mm}$/J						
I	61.4 ± 4	54.2 ± 6	49 ± 4	39.3 ± 2	35.2 ± 2	52.5 ± 8
0.102–0.315	64.6 ± 10	56.7 ± 10	51.6 ± 9	43.2 ± 4	—	—
0.315–0.500	51.8 ± 6	50.8 ± 8	52.5 ± 6	47.1 ± 6	—	—

For each solute sample, two water samples denoted *A* and *B* were analysed. The two water samples, originating from the same plastic receiver, were transferred and preserved in two containers made from different glass grades (Pyrex – *A*, and Turdaterm – *B*) with a view to revealing any differences in ionic salt-water interactions.

Results and discussion

The high resolution of the calorimeter was revealed by the calibration experiments on a standard measuring cell having a chosen geometry of the heating element (Fig. 2a in [12]). Under these SEC, a linear relationship exists between the height and the area of the standard exotherms, so that h and E_s represent two distinct eigenvalues [2, 10, 11] of the time conversion $w(t)$ for the particular solution process. On the other hand, the figure of merit of the calorimeter [12] is much better than those for the commercial types actually used for this kind of experiment. For instance, the solution endotherm of KCl in H_2O (at molarity $n \simeq 4 \times 10^3$ mol H_2O/mol KCl) in the SETARAM C 80 extends to approximately 35 minutes with $h/E_s \simeq 0.3$ $\overline{mm}$/J (Fig. 5 in [14]), while for similar experiments the actual calorimeter shows a sharp endotherm extending to approximately 5 minutes with

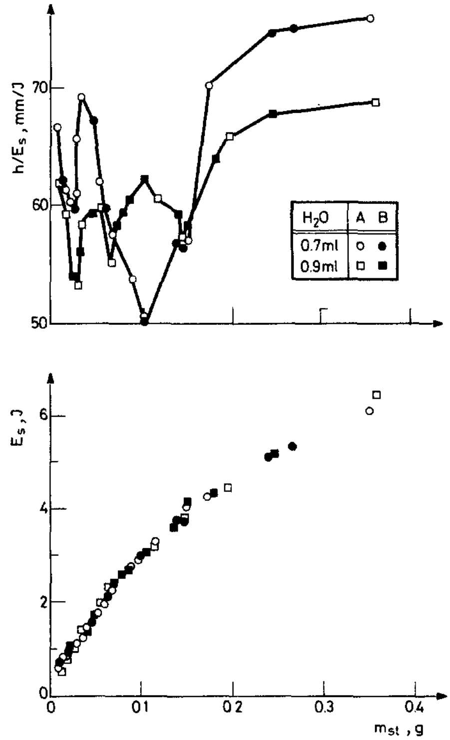

Fig. 3 Dependence of E_s and h/E_s on m_{st} for the integral sample of $NiSO_4 \cdot 7H_2O$

$h/E_s \simeq 50$ mm/J. The average values and standard deviations of ratio $\overline{H/E_s}$ are given in Table 1 for integral samples and their fractions for the overall range of m_{st} values 30–50 values for each sample or fraction.

The chosen SEC for solution experiments involve a standard mixing effect associated with the breaking of the glass bubble, which acts differently for each m_{st} value, the size distribution of the sample and the nature of the solute-solvent interaction. Thus, it is expected that ratio h/E_s should be a sensitive parameter for these characteristics. Since the SEC involve standard geometry and standard energy perturbation, it is easy to conclude that oscillatory phenomena will result in $h(m_{st})$ and $E_s(m_{st})$ dependences as in any mechanically excited tube [11]. The amplitude of the solution process expressed by these eigenvalues, as by their ratio, should reveal a series of harmonics depending on the calorimeter resolution.

The solubility behaviour of $NiSO_4 \cdot 7H_2O$ as revealed by the calorimeter system and its associated SEC is described in detail below; only particular aspects will be mentioned for the other salts analysed. Figures 1a and 1b present the dependence of $h(m_{st})$ for 0.7 and 0.9 ml water, respectively, for the integral sample. At first sight no difference can be observed between the two volumes and water samples, but a

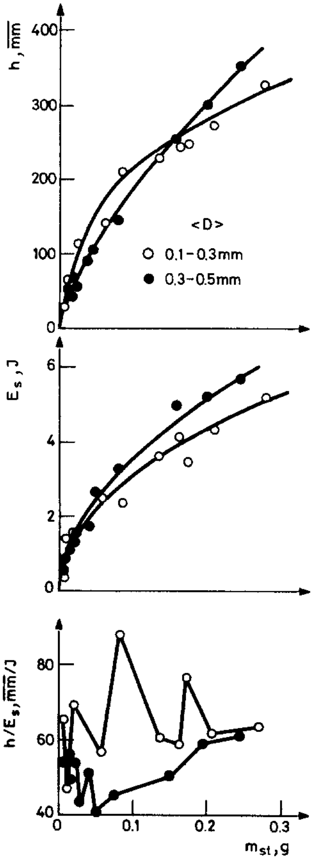

Fig. 4 Dependence of h, E_s and h/E_s on m_{st} for size fractionated samples of $NiSO_4 \cdot 7H_2O$ in 0.7 ml H_2O (A)

separate representation reveals that the two dependences have different harmonics, with the maximum slope at $m_{st} = 0$, as generally observed [1]. This domain corresponds to dilute solutions with molarity above $n = 400$ for which the differential heat of solution (E_s^d) can be determined. The oscillatory behaviour can also be observed in $t_M(m_{st})$ and $\tau(m_{st})$ determined by high-speed recording of $w(t)$, as defined in Fig. 8 in [12]. Figure 2 shows a sharp basic harmonic for 0.9 ml H_2O for both parameters in the above range of dilute solutions. The ratio h/E_s proves to be more sensitive to these oscillations (Fig. 3), as expected. The dependence of $E_s(m_{st})$ is similar to that of $h(m_{st})$, but tends to saturation more rapidly.

In Fig. 4, dependences of h, E_s and h/E_s on m_{st} for the two main size fractions of $NiSO_4 \cdot 7H_2O$ are presented for 0.7 ml H_2O (A). A clear difference between their behaviour is seen for all parameters, namely: the small size fraction tends more

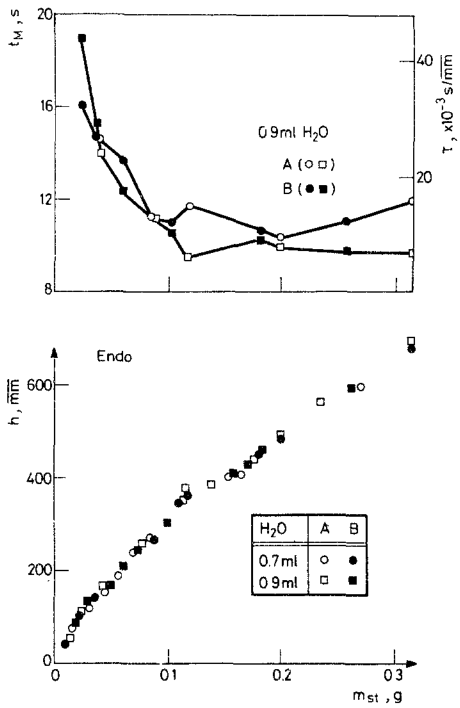

Fig. 5 Dependence of h, t_M (○, ●) and τ (□, ■) on m_{st} for the integral sample of $MgSO_4 \cdot 7H_2O$

rapidly to saturation, but shows marked oscillatory behaviour due to the greater mixing effect on the solute.

Basically the same behaviour is revealed for the other sulphates. In Figs 5 and 6, these parameters are presented as a function of m_{st} for the integral sample of $MgSO_4 \cdot 7H_2O$. All hydrated sulphates show an endothermal effect of dissolution of approximately 60–100 J/g, while the anhydrous sulphates are characterized by a strong exothermal heat of hydration-crystallization. Anhydrous $MnSO_4$ and Na_2SO_4 have a grain size distribution centered on $\langle D \rangle \simeq 0.1$ mm. In Fig. 7 the hydration behaviour of $MnSO_4$ is presented as a function of m_{st} by considering several basic parameters. Oscillatory effects and clear differences between the two water volumes are due to the large heat effects. Samples of Na_2SO_4 systematically show the splitting of the exothermal process clearly revealed at high recording speed (Fig. 8). This phenomenon can be explained either by the coexistence of five crystalline forms [15] for which two forms of behaviour are distinguished, or by a distinct succession of hydration and crystallization processes, taking into account that a crystalline material results.

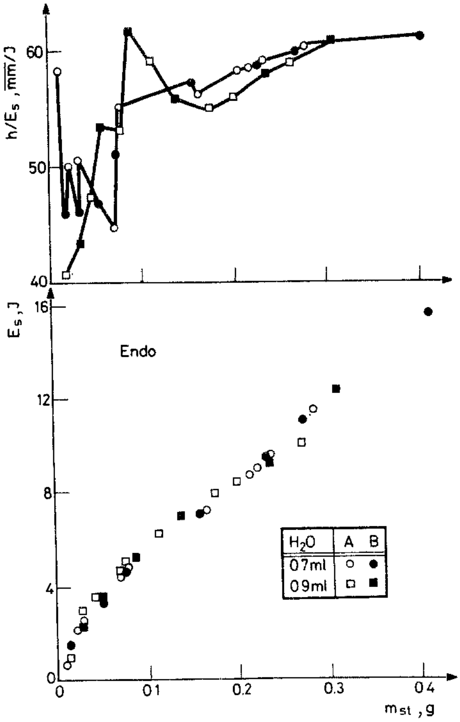

Fig. 6 Dependence of E_s and h/E_s on m_{st} for the integral sample of $MgSO_4 \cdot 7H_2O$

We can now start the quantitative evaluation of the salt-water interaction in the considered measuring system, with E_s^d values determined by averaging values of E_s in the high-dilution domain and separately reported for the integral and fractionated samples. In Table 2 the mean values with the standard deviations are given for all analysed sulphates, in comparison with reference data recently reported [1, 16]. The present data are systematically higher, due to the high resolution of the measuring system, but differences normally appear because of different experimental conditions. It is interesting to note the great differences for Na_2SO_4, due to the superposition of many processes which specifically appear under different experimental conditions.

The problem which arises is: if the chosen SEC are preserved for all experiments, how can the behaviour be characterized in the overall m_{st} range for each sample? The universal procedure established on the topoenergetic principles gives the answer [2, 10, 11]. For the eigenvalue 0 determined by experiment with the stepwise applied perturbation with amplitude ΔU (U is the governing potential of the process), the following affine relationship exists:

$$\ln \theta = N \ln |\Delta U| + M \tag{1}$$

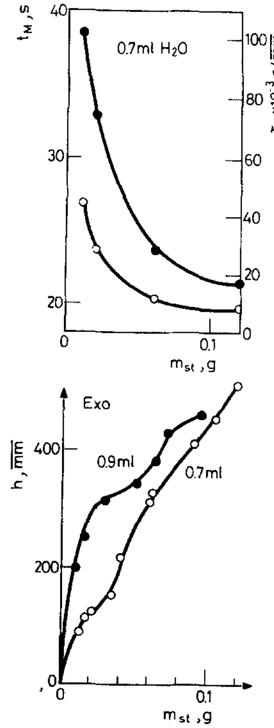

Fig. 7 Dependence of h, t_M (○) and τ (●) on m_{st} for the integral sample of $MnSO_4$ in A type of water

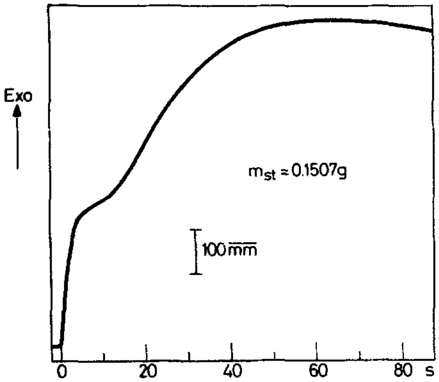

Fig. 8 Typical solution exotherm of the integral sample of Na_2SO_4/0.9 ml H_2O recorded at high speed

Table 2 Comparative values of E_s^d (J/g) for diluted solutions ($n \leqslant 400$) of integral (I) and fractionated (F) sulphates

	26.2 °C present work	RT J. W. Mullin [16]	G. Beggerow Landolt–Börnstein [1]
$NiSO_4 \cdot 7H_2O$	I 72± 8 F 81±10	62.6	36.0 (18 °C, $n=400$)
$MgSO_4 \cdot 7H_2O$	I 75±18 F 97± 5	54.0	77.1 (25 °C, $n=25$) 68.2 (25 °C, $n=700$) 63.2 (30 °C, $n=400$)
$FeSO_4 \cdot 7H_2O$	I 72±10 F 85± 8	66.3	—
$CuSO_4 \cdot 5H_2O$	I 54± 2 F 65± 2	48.8	81.7 (18 °C, $n=400$)
$MnSO_4$	I −(457±22)	−382	−21.9 (18 °C, $n=20$–200) −376 (RT, $E_{s\infty}$)
Na_2SO_4	I −(90±10)	−8.24	−17.4 (25 °C, $n=400$)

where parameters (N, M) define the individual behaviour (ontogeny) of the tested sample in the chosen SEC and measuring system. The (N, M) values can be determined by linear regression of pairs of values (θ, ΔU) ranging in the domain of values characterizing the same nature of the triggered transformation process, but with different amplitudes. In the present experiments, θ: h and E_s, which are proportional to the transforming component C_{tr} in the overall sample of (salt + water), and $U = m_{st}$ can be considered. In Fig. 9 the basic parameters (N, M) and their derivatives $-M/N$ (proportional to the mass of the kinetic entity in the logarithmic scale, $\ln c_{tr}$) and $-N^2/M$ (proportional to the strength of the coupling between the inert, C_{in}, and the transforming components, CS) [2, 10, 11] determined for $\theta = h\,[\overline{mm}]$ are represented for the series of integral samples and size fractions of $NiSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 7H_2O$. The significances of these parameters were previously established in a large variety of standard reacting and measuring systems [2, 10, 11]. Since the phylogenic series has a transformation process of the same nature, a further affine relationship exists:

$$N = nM + m \tag{2}$$

The mutual signs of parameters (N, n) define the polarity of the process [9], also established on standard systems [2, 9–11]. For each phylogenic series the standard amplitude (M) and the kinetic entity ($-M/N$) decrease with the $\langle D \rangle$ of the fraction, and this is more pronounced for $NiSO_4 \cdot 7H_2O$. This result is in good

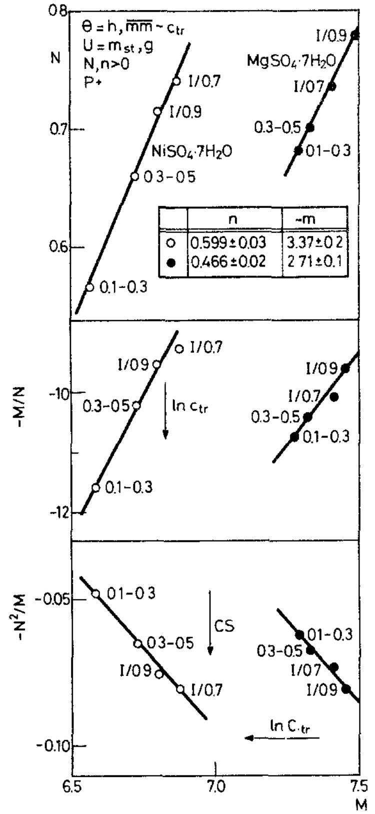

Fig. 9 Dependence of N, M, $-M/N$ and $-N^2/M$ parameters obtained by the universal procedure [2, 10, 11] for the overall solution process of $NiSO_4 \cdot 7H_2O$ (○) and $MgSO_4 \cdot 7H_2O$ (●) series of samples with $\theta = h$ [$\overline{mm}$]

Table 3 Phylogenic parameters (n, m) and (n_1, m_1) for fractionated samples and overall hydrated sulphates, respectively, obtained by linear regression according to the universal procedure for θ: h and E_s ($U = m_{st}$ in g, $U_0 = 0$) from isothermal (26.2 °C) solubility endotherms in 0.7 ml H_2O

	$\theta = h$ ($\overline{mm}$)		$\theta = E_s$ (J)	
	n	$-m$	n	m
$NiSO_4 \cdot 7H_2O$	0.599±0.03	3.37±0.2	0.266±0.01	−(0.150±0.01)
$MgSO_4 \cdot 7H_2O$	0.466±0.02	2.71±0.1	0.350±0.01	−(0.501±0.02)
$CuSO_4 \cdot 5H_2O$	0.666±0.02	3.55±0.1	−(0.405±0.01)	2.65±0.1
$FeSO_4 \cdot 7H_2O$	0.098±0.006	0.029±0.005	−(0.0396±0.006)	0.643±0.01
(n_1, m_1)	−(0.154±0.009)	0.0839±0.005	−(0.237±0.02)	0.197±0.02

agreement with the behaviour revealed qualitatively by different oscillatory behaviour (see h/E_s in Figs 3 and 6). The compatibility-stability of the overall samples (CS) increases with $\langle D \rangle$, revealing that the solution process tends to be inhibited for high values of $\langle D \rangle$. Phylogenic parameters (n, m) and their standard deviations determined by linear regression in the overall m_{st} domain are given in Table 3 for all series of hydrated sulphates and corresponding to θ: h and E_s. No clear difference between the two water samples was detected in the ontogenic or phylogenic parameters. Furthermore, the phylogenic parameters show a second-order phylogeny [2, 10, 11]:

$$n = n_1 m + m_1 \qquad (3)$$

for all the hydrated sulphates, revealing a common feature in the nature of the solubility process.

Concluding remarks

From the data resulting from the dissolution experiments for the series of sulphates in water by using the high-resolution calorimeter and by strict preservation of the SEC, the following aspects were revealed:

The solute-solvent interaction can be determined in the overall m_{st} domain by the universal procedure established on the topoenergetic principles by considering eigenvalues determined from the time-conversion of $w(t)$. This new aspect of solubility behaviour is more realistic relative to the classical one, for which particular E_s data strongly dependent on the experimental conditions are given.

The resulting ontogenic and phylogenic parameters can provide Data Banks for a large number of solute-solvent systems with a view to unifying current efforts [13] in a more effective and concentrated form.

The ionic salt-water interactions depend strongly on the characteristics of the two components, so that with a view to a better definition of the ionic salts a standard water should be used, and vice versa.

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Zusammenfassung — Das Löslichkeitsverhalten verschiedener wasserhaltiger und wasserfreier Sulfate wird isotherm (26.2 ± 0.06 °C) mit dem kürzlich beschriebenen hochauflösenden Kalorimeter untersucht. Der vor kurzem auf der Basis topoenergetischer Prinzipien definierte Begriff des Verhaltens wird diesen Experimenten durch Festlegung der experimentellen Standardbedingungen, die sich im wesentlichen auf die Geometrie der Meßzelle und auf die Vorzüge des ganzen kalorimetrischen Systems beziehen, angepaßt. Die vorangehend definierten Parameter des bei normaler und hoher Geschwindigkeit registrierten Wärmestromes zeigen deutlich ein im allgemeinen von der topoenergetischen Theorie vorausgesagtes Oscillationsverhalten. Das angewandte Meßsystem erlaubt auch Unterschiede im Verhalten von Größenfraktionen der gleichen zu lösenden Substanz festzustellen. Das Löslichkeitsverhalten kann bei gleichen experimentellen Standardbedingungen für jede Menge der zu lösenden Substanz entsprechend der auch für eine größere Anzahl von Bestandteilen und Meßsystemen angewandten universellen energetischen Prozedur definiert werden. Die erhaltenen, sich auf das individuelle (ontogene) und (phylogene) Gruppenverhalten beziehenden Daten können Datenbanken zur allgemeinen Benutzung bilden.

Резюме — В изотермических условиях (26,2 ± 0,06°), используя ранее описанный калориметр высокого разрешения, изучено поведение растворимости нескольких гидратных и безводных сульфатов. Понятие поведения, недавно сформулированное на основе топоэнергетических принципов, адаптировано для этих экспериментов, определением стандартных экспериментальных условий (СЭУ), которые включают, главным образом, геометрию измерительной ячейки и критерий полной калориметрической системы. Параметры, определенные из теплового потока при нормальной и высокой скорости, ясно показали колебательный характер, установленный на основе топоэнергетической теории. Используемая измерительная система позволила также обнаружить различное поведение растворимости того же самого вещества в зависимости от размеров частиц. Общее поведение растворимости в одинаковых стандартных экспериментальных условиях для всех значений массы растворенного вещества может быть определена на основе универсального топоэнергетического метода, используемого также для разнообразных составов и измерительных систем. На основе полученных результатов, связанных с индивидуальным (отногенным) и групповым (филогенным) поведением, может быть создан банк данных для общего пользования.