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Calorimetry

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

III. Topoenergetic aspects of process of dilution of several sulphates

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The process of dilution of aqueous concentrated solutions of the series XSO_4 ($X = Cu, Na_2$, Fe, Ni, Mn, Mg) was studied calorimetrically by considering the peak height and area as eigenvalues and the initial concentration as governing potential. The experiments were carried out under standard conditions imposed by topoenergetic principles. The results obtained with the universal procedure recently established define the individual (ontogeny) and the group (phylogeny) behaviour of all the considered solutions with respect to the overall measuring system. These data agree with many other experimental facts showing the following increasing sequence of their power: $Mg < Mn < Ni < Fe < Na < Cu$. The initial concentration of hydrogen-bonds can be determined by means of standard experiments with the universal topoenergetic procedure proposed for the creation of Data Banks.

The interactions between ionic salts and polar solvents, as revealed by the dissolution processes, depend strongly on the initial concentrations of hydrogen-bonds in the two components. This assumption is supported at least by the two following experimental facts.

(i) The ionic salts include water molecules on crystallization from aqueous solutions, which indicates that these compounds allow an increase in the concentration of hydrogen-bonds. The recent structural [1, 2] and kinetic [3, 4] studies on the series of single-crystals $SnCL_2(H_2O)_x(D_2O)_{2-x}$ have shown that the included water molecules are distributed in separate crystallographic planes, alternating with $SnCl_2$ planes, in polymeric chains whose length depends on the

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concentration of hydrogen-bonds and which are responsible for the solid-solid transition at approximately 220 K [4].

(ii) The solubility of the ionic salts, especially in water, depends strongly on the water content in the crystalline structure [5], and this simple behaviour can better define the crystalline symmetry [6].

In this part of the series, the dilution process as revealed by high-resolution calorimetric measurements on aqueous solutions of hydrated sulphates XSO_4 (X = Cu, Na_2, Fe, Ni, Mn, Mg) is studied by taking into account the recently established topoenergetic principles.

The basic topoenergetic principles were thoroughly presented and applied to particular cases of measuring thermal systems by using the Arrhenius kinetic representation [4, 7, 8]. These principles were recently extended to any kind of measuring system driven by a potential U for which, under rigorous standard experimental conditions, the universal affine parameters (N, M) and a threshold value U_0 unambiguously define the individual behaviour (the ontogeny) of each tested sample with respect to the chosen measuring system [4, 6]. For a series of samples having the same nature of behaviour, the phylogenic parameters (n, m) can also be determined as defining their group behaviour (the phylogeny). The phylogeny of the series XSO_4 in the actual measurements of the dilution processes defines the relative power of cations X in producing hydrogen-bonds under standard experimental conditions.

Experimental

All calorimetric measurements were performed at 26.2±0.06° by using the previously described calorimeter [9] and technique for the dissolution process [10]. The ratio of 0.2 ml of concentrated solution (in standard-sized glass bubbles [10]) and 0.7 ml of water, previously denoted as A, was used. The specimens were prepared at 18±2° (room temperature) by using two precision syringes (±0.005 ml).

Concentrated stock solutions were also prepared at 18±2° by using the same grades of sulphates as for dissolution measurements. The concentration was established by continuous agitation and slow water addition to approximately 5% below the solubility limit.

Na_2SO_4 and $MnSO_4$ were used as anhydrous compounds, and only the initial concentrated solution of Na_2SO_4 showed a crystallization process with a short induction period, which decreased strongly on mechanical shearing (simultaneous crystallization in the needle by injection from a syringe). After complete crystallization of the solution (in approximately one hour, yielding hydrated needle-shaped crystals), a further dilution was applied, as for the other solutions. All solutions were preserved for a maximum of one week while the measurements were performed.

The calorimetric measurements were made on solutions of different concentrations, ranging between 1 and 0.4 fraction from the stock solution concentration. These solutions were prepared just before each measurement by dilution of 1 ml of the stock solution with the respective water amount. The resulting concentration, c_{st}, is expressed in grams of anhydrous salt per litre of solution.

Results and discussion

For all solution except Na_2SO_4, the effect associated with the dilution process is exothermic. Naturally, the amplitude of the effect increases with c_{st}, and the standard experimental conditions used allow us to consider this amplitude expressed in terms of h (the peak height in mm) or E_d (the peak area in joules) [9, 10] as the eigenvalue θ, and c_{st} as the governing potential, so that the following affine relationship should exist [4, 6]:

$$\ln \theta = N \ln (c_{st} - c_{st}^0) + M \qquad (1)$$

c_{st}^0 is the threshold value of c_{st} at which the dilution process is inhibited; this can be considered zero for sulphates. For both eigenvalues h and E_d, the ontogenic parameters (N, M) can be determined by linear regression of 8–10 pairs of values (θ, c_{st}) according to Eq. (1). The associated correlation coefficients lie in the range 0.990–0.9990. For all systems and experiments, the values of h and E_d are in the same linear correlation as for the calibration experiments [9].

In Table 1 the ontogenic and phylogenic parameters corresponding to $\theta = E_d$ for all series are given with their associated standard deviations. The chosen eigenvalues are proportional to the transforming component (C_{tr}) in each tested sample, but the (N, M) standard values represent C_{tr} or C_{in} (iner component) on the logarithmic scale, depending on the process polarity [4, 6, 8]. According to the general significances of the affine parameters established in a large number and variety of particular cases, the polarity of the dilution process for all the considered solutions is negative $(N > 0, n < 0, \theta \sim C_{tr})$, and $M, m \sim \ln C_{tr}$, $-M/N \sim \ln c_{tr} (c_{tr}$ is the value of the kinetic entity responsible for the transformation process) and $-N^2/M \sim CS$ (CS is the compatibility-stability coefficient or the strength of the coupling between C_{tr} and C_{in}). These values are expressed in units derived from the basic units of θ and U.

In Fig. 1 the phylogeny with respect to $\theta = h$ of the overall series of XSO_4 is

Table 1 The ontogenic and phylogenic parameters of several sulphates with respect to the process of dilution of aqueous solutions in the isothermal calorimetric system with $\theta = E_d$ (J), $U = c_{st}$ (g anh/l), $U_0 = 0$

X	N	$-M$
Mg	3.12 ± 0.2	8.45 ± 0.5
Mn	2.75 ± 0.1	7.22 ± 0.2
Ni	2.25 ± 0.1	4.21 ± 0.2
Fe	1.91 ± 0.07	2.68 ± 0.1
Na_2	1.77 ± 0.1	1.71 ± 0.1
Cu	1.66 ± 0.1	1.21 ± 0.1
	$n = -(0.195 \pm 0.008)$	$m = 1.42 \pm 0.06$

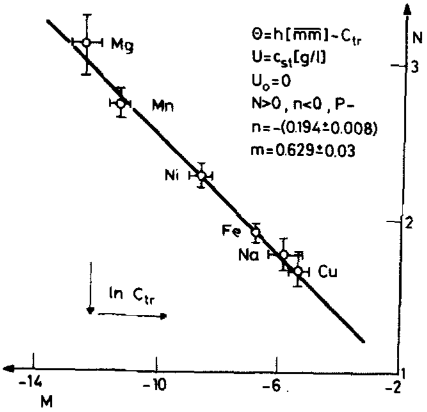

Fig. 1 Phylogenic representation of process of dilution at 26.2° of several sulphate solutions in water with respect to the isothermal calorimetric system with $\theta = h\ (\overline{mm})$ as eigenvalue and $U = c_{st}$ (g/l) as the driving potential

represented. As for $\theta = E_d$, the standard amplitude increases in the following sequence:

$$\mathrm{Mg} < \mathrm{Mn} < \mathrm{Ni} < \mathrm{Fe} < \mathrm{Na} < \mathrm{Cu} \tag{2}$$

For the dissolution process, the standard amplitude according to the affine parameter $m \sim \ln C_{tr}$ (as defined on the (N, M) values of all size fractions (Table 3 in [10])) leads to:

$$\mathrm{Cu} < \mathrm{Ni} < \mathrm{Mg} < \mathrm{Fe} \tag{3}$$

which generally shows an opposite sequence. Both processes are essentially based on hydrogen-bond formation and/or destruction, but from the topoenergetic point of view their natures differ. More exactly, the n values are practically the same, but the m values are different, namely m(dissolution) $<$ m(dilution) and, taking into account that for both cases $m \sim \ln C_{tr}$, it results that the C_{tr} involved in the dilution process is greater than that in the dissolution process. Furthermore, the opposite directions of the thermal flows for the two processes means another important difference. The endothermic effect of the dissolution process shows the hydrogen-bond breaking, while the exothermic effect of the dilution process represents the hydrogen-bond formation. These facts are in good agreement with the structural image of hydrated crystals which include polymeric water with a high concentration of hydrogen-bonds. The coexistence of ionic molecules in concentrated solution catalyses the formation of water chains by dilution.

Na_2SO_4 solutions show that at low concentrations this type of cation involves a high number of hydrogen-bonds. The fact that this salt can contain 10 H_2O molecules per 1 Na_2SO_4 molecule in the crystalline structure is a consistent argument for this assumption. Furthermore, the anhydrous compounds show strong exothermic effects of dissolution. This exothermic effect should be proportional to the power of each cation in forming hydrogen-bonds.

If these facts are taken into account, a direct relationship should exist between the standard values of the dilution process and the limiting concentration, c_{st}^{∞}, of solubility at a near temperature. Figure 2 shows the most important affine parameters as functions of $\ln c_{st}^{\infty}$ (c_{st}^{∞} values determined at 25° [11]). The following observations must be pointed out: (i) all dependences exhibit monotonous variations in the same sequence as in (2); (ii) the kinetic entity and CS coefficient increase with decrease of $\ln C_{tr}$. c_{st}^{∞} is expressed in moles of anhydrous salt per moles of H_2O, so that these dependences can be expressed directly by molecular contributions in the amplitude of the dilution process.

The initial concentration of hydrogen-bonds can be controlled in the solvent-solute system by solvent modification. Figure 3 illustrates the dependence of the solution amplitude expressed by h/m_{st}, E_s/m_{st} and the shape coefficient h/E_s for the dissolution process of $MgSO_4 \cdot 7H_2O$ ($m_{st} = 0.03$–0.05 g) in 0.7 ml solvent with different ethanol contents. The copolymer chains in the solvent contain hydrogen-bonds, which drastically decrease from approximately 25 volume % ethanol. These experiments depend strongly on the grain size of the solute, which agrees with the increase in the shape coefficient h/E_s with the ethanol content.

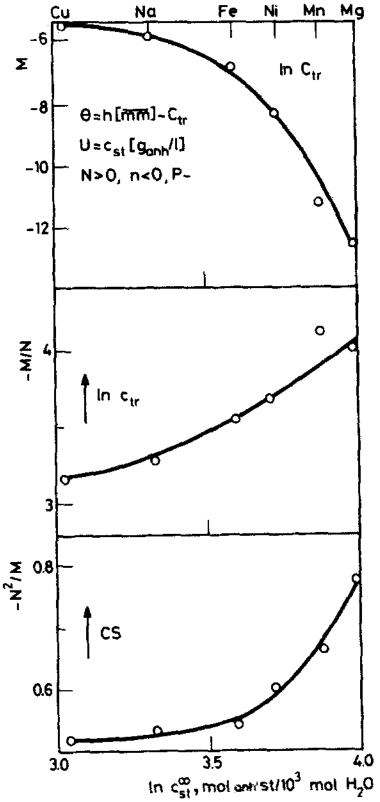

Fig. 2 Dependence of the derivative ontogenic parameters M, $-M/N$ and $-N^2/M$ as functions of the saturation concentration at 25° in water for the process of dilution of several sulphates, as revealed by the isothermal calorimetric system

Concluding remarks

As for any other kinetic data, the dissolution and dilution results for a series of solute-solvent systems should be determined under standard experimental conditions with a view to comparing and identifying the nature and the amplitude of the triggered process [4, 6–8]. These data can be stored in Data Banks if the exact experimental conditions are categorized.

The solubility data at present compiled in the IUPAC series involve the results obtained for different scales and hydrodynamic conditions. Another important characteristic seems to be the initial structure of the solvent, which can be given by standard experiments [6].

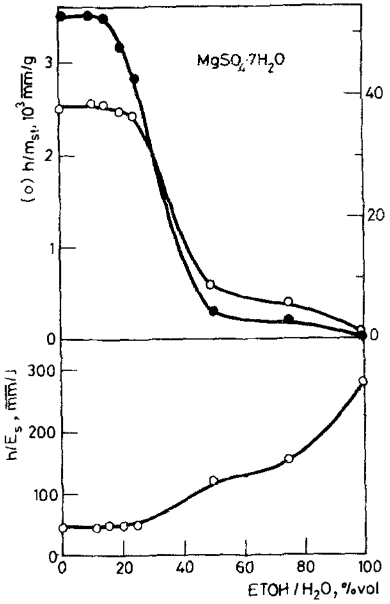

Fig. 3 Dependence of h/m_{st}, E_s/m_{st} and h/E_s on ethanol concentration in the solvent for the dissolution process of $MgSO_4 \cdot 7H_2O$ (grain size fraction 0.20–0.312 mm) in 0.7 ml solvent

In further work, the powers of cations in forming hydrogen-bonds will be determined in dissolution experiments on anhydrous salts under standard conditions and by considering different solvent systems with different initial concentrations of hydrogen-bonds.

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Zusammenfassung — Der Prozeß der Verdünnung konzentrierter wässriger Lösungen der Serie XSO_4 ($X = Cu, Na_2, Fe, Ni, Mn, Mg$) wurde kalorimetrisch untersucht, indem Höhe und Fläche des Peaks als Eigenwerte und die Ausgangskonzentration als dominierendes Potential angesehen wurden. Die Experimente wurden unter von topochemischen Prinzipien auferlegten Standardbedingungen ausgeführt. Die mit der kürzlich eingeführten universellen Prozedur erhaltenen Ergebnisse kennzeichnen das (ontogene) individuelle und das (phylogene) Gruppenverhalten aller in Betracht genommenen Lösungen in Bezug auf das Gesamtmeßsystem. Diese Daten stimmen mit anderen experimentellen Fakten überein. Die von den Kationen ausgehende Wirkung nimmt in der Reihenfolge $Mg < Mn < Ni < Fe < Na < Cu$ zu. Die Ausgangskonzentration der Wasserstoffbindungen kann mittels Standardexperimenten nach der für die Schaffung einer Datenbank vorgeschlagenen universellen topoenergetischen Prozedur bestimmt werden.

Резюме — Калориметрически изучен процесс растворения концентрированных водных растворов ряда солей общей формулы XSO_4 ($X = Cu, Na_2, Fe, Ni, Mn, Mg$), считая высоту пика и его поверхность как эйгеновские величины, а начальную концентрацию — как регулирующий потенциал. Эксперименты были проведены в стандартных условиях на основе топоэнергетических принципов. Результаты, полученные с помощью недавно установленной универсальной методики, определяют индивидуальное (онтогенное) и групповое (филогенное) поведение вышеприведенных растворов относительно общей измерительной системы. Эти данные согласуются со многими другими экспериментальными данными, показывая увеличение их силы в ряду $Mg < Mn < Ni < Fe < Na < Cu$. Начальная концентрация водородных связей может быть определена с помощью стандартных экспериментов на основе универсального топоэнергетического метода, предложенного для создания банка данных.