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ENTHALPIES OF CRYSTALLIZATION OF NACl, KCl, $LiCl\cdot H_2O$, $MgCl_2\cdot 6H_2O$, $CaCl_2\cdot 6H_2O$ AND $BaCl_2\cdot 2H_2O$ FROM AQUEOUS SOLUTION AT 298.15 K

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The enthalpies of crystallization of NaCl, KCl, $LiCl\cdot H_2O$, $MgCl_2\cdot 6H_2O$, $CaCl_2\cdot 6H_2O$ and $BaCl_2\cdot 2H_2O$ from aqueous solution were determined by means of different calculation methods on the basis of the earlier-measured differential and integral enthalpies of solution of the above salts. The obtained crystallization enthalpies are discussed and compared with the appropriate literature data.

Keywords: crystallization enthalpy

Introduction

There is still a deficiency of thermodynamic data concerning aqueous electrolyte solutions over the whole range of solute concentration. Particularly scarce are data describing the behaviour of close-to-saturation solutions. The enthalpy of crystallization is one such property. It can be accepted as a measure of the thermal balance of the crystallization process and a knowledge of its accurate value is necessary in studies of crystallization kinetics, and also in some branches of chemical technology. However, the literature data from various laboratories on the enthalpies of crystallization exhibit significant differences [1]. We therefore decided to perform calorimetric investigations on a number of anhydrous salts and also on some hydrates in aqueous solution, using the same apparatus and various experimental techniques. In recent papers [2, 3] we have presented the measured differential and integral dissolution enthalpies, $\Delta_{sol}H_2$ and $\Delta_{sol}H_m$, respectively, for NaCl, KCl, $LiCl\cdot H_2O$, $MgCl_2\cdot 6H_2O$, $CaCl_2\cdot 6H_2O$ and $BaCl_2\cdot 2H_2O$ in water at 298.15 K. In the present work, the enthalpies of crystallization of these salts are determined from the measured enthalpies by using different cal-

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culation methods, and the results are discussed and compared with the literature data.

Results and discussion

Solution calorimetry is an indirect method of determining the enthalpy of crystallization. It is based on the assumption that the least differential enthalpy of solution is numerically equal to the crystallization enthalpy, i.e.

$$|\Delta_{sol}H_2^{sat}| = |\Delta_{cryst}H_m| \tag{1}$$

The values of $\Delta_{sol}H_2^{sat}$ can be found from (a) direct measurements of $\Delta_{sol}H_2$ and (b) measurements of $\Delta_{sol}H_m$ and integral enthalpies of dilution ($\Delta_{dil}H_m$). In the former, the measured differential enthalpies of solution are extrapolated as a function of the salt concentration to the concentration of the saturated solution, $m=m_{sat}$:

$$\Delta_{cryst}H_m = \lim_{m \to m_{sat}} (\Delta_{sol}H_2) \tag{2}$$

Unfortunately, precise measurement of the differential enthalpy of solution is very complicated and often yields misleading results.

The latter requires a knowledge of $\Delta_{sol}H_m$ and the relative apparent molar enthalpy, $L_\varphi(m)$ of the salt.

Then:

$$\Delta_{sol}H_2(m) = \Delta_{sol}H_m(m) + m\cdot\left(\frac{\partial L_\varphi(m)}{\partial m}\right) \tag{3}$$

where m is the molality of the solution.

The relative apparent molar enthalpy can be calculated from the combination of dissolution and dilution enthalpies:

$$L_\varphi(m) = L_\varphi(m') + \Delta L_\varphi \tag{4}$$

$$L_\varphi(m') = \Delta_{sol}H_m(m') - \Delta_{sol}H_m^\infty \tag{5}$$

$$\Delta L_\varphi = -\Delta_{dil}H_m\,(m \to m') \tag{6}$$

where $\Delta_{sol}H_m^\infty$ is the solution enthalpy of the salt in the infinitely dilute solution. In order to find the values of derivative $\partial L_\varphi(m)/\partial m$, the relative apparent molar enthalpies as a function of the molality are fitted to the polynomial of the form

$$L_\varphi(m) = \sum_{i=1}^{n} a_i m^{i/2} \tag{7}$$

where a_i is an adjustable parameter.

For the saturated solution, we obtain

$$-\Delta_{sol}H_2^{sat}=\Delta_{cryst}H_m = \Delta_{sol}H_m^{sat} + m_{sat}\left(\frac{\partial L_\varphi(m)}{\partial m}\right)_{m=m_{sat}} \tag{8}$$

This is a very time-consuming method, since it calls not only for measurements of the enthalpies of solution and dilution within the whole range of salt concentration, but also for precise determination of the standard solution enthalpy of the salt. Therefore, we decided to modify this calculation method in some respects. The values of $\Delta_{sol}H_2^{sat}$ were determined from several pairs of measurements of dilution and solution enthalpies. Firstly, the saturated solution was diluted to some final concentration, m_f, and next the enthalpy of solution of the salt at the same concentration, $\Delta_{sol}H_m(m_f)$, was measured.

Hence:

$$\Delta_{sol}H_m^{sat} = \Delta_{sol}H_m(m_f) - \Delta_{dil}H_m\ (m_{sat}\rightarrow m_f) \tag{9}$$

Additionally, several successive measurements of the dilution enthalpy were carried out, starting from the saturated solution, in order to obtain $\Delta L_\varphi = L_\varphi(m_f) - L_\varphi(m_{sat})$ as a function of m_f within the concentration range near saturation. Assuming that

$$\left(\frac{\partial \Delta L_\varphi(m_f)}{\partial m_f}\right)_{m_f = m_{sat}} = \left(\frac{\partial L_\varphi(m)}{\partial m}\right)_{m=m_{sat}} \tag{10}$$

we are able to calculate $\Delta_{sol}H_2^{sat}$ by using Eq. (8).

We found that the enthalpies of crystallization determined from the integral enthalpies of solution by means of the two above-mentioned methods differ from each other by at most 3%. However, for the hydrates, the values of $\Delta_{cryst}H_m$ obtained from the integral enthalpies of solution (both methods) and from direct measurements of differential enthalpies of solution differ significantly. In this case, the calculated values of $\Delta_{sol}H_2$ were close to those obtained from direct measurements only after modification of Eq. (3) to the form

$$\Delta_{sol}H_2 = \Delta_{sol}H_m + \frac{M_a}{M_h}\cdot m\cdot\left(\frac{\partial L_\varphi}{\partial m}\right) \tag{11}$$

where M_a and M_h are the molecular masses of anhydrous and hydrated salts, respectively.

Figure 1 presents the differential enthalpies of solution of $LiCl\cdot H_2O$ in water, in the range of high salt concentration. The continuous lines illustrate the data obtained from direct measurements of $\Delta_{sol}H_2$ by Wolf and coworkers [4] (curve 1) and in our laboratory [2] (curve 2). The interrupted and dashed lines refer to the $\Delta_{sol}H_2$ values calculated from the enthalpy of solution data [3–5] according to Eq. (3) (curves 3–5) and on the basis of Eq. (11) (curves 6–8). It can be seen from the graph that only in the latter case is there good agreement between the $\Delta_{sol}H_2$ data for $LiCl\cdot H_2O$ determined by the direct and indirect methods.

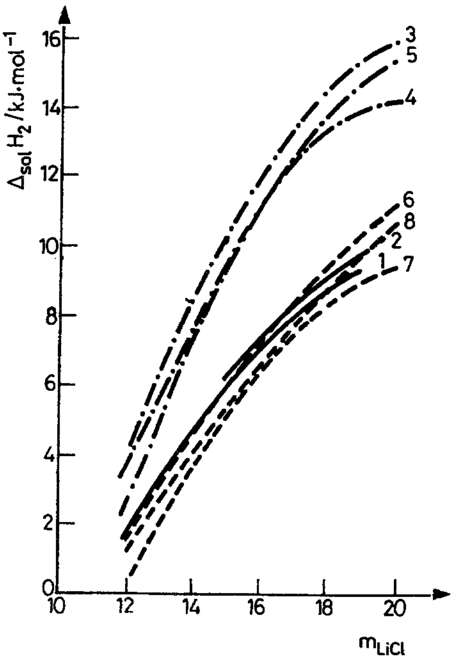

Fig. 1 Differential enthalpies of solution of $LiCl\cdot H_2O$ in water at 298.15 K as a function of molality for $m \geq 12$, determined directly (curves 1 and 2), and calculated from the dissolution enthalpies with the use of Eq. (3) (curves 3–5) or Eq. (11) (curves 6–8)

The enthalpies of crystallization of the salts examined here are compiled in Table 1. The first column gives the values obtained from the differential enthalpies of solution (Eq. 2) measured directly. The second and third columns present the analogous data derived from the integral enthalpies of solution, according to Eqs (8) and (11). For the sake of comparison, the literature data obtained by using different experimental techniques [5–12] are also included in the Table. Since they are widely scattered, in the last column we additionally present the crystal-

Table 1 Molar enthalpies of crystallization of salts from aqueous solution at 298.15 K. Comparison of values obtained from different sources

Salt	$-\Delta_{\mathrm{cryst}}H_{\mathrm{m}}$ / J·mol^{-1}				
	Eq. (2)	Eq. (8)	Eq. (11)	Literature	Pekárek
NaCl	1767±27	1600±39	1600±39	1590–11757	1500
KCl	14218±178	13779±143	13779±143	13220–14144	13600
$LiCl{\cdot}H_2O$	10016±42	15536±58	10634±101	9540–13140	9540
$MgCl_2{\cdot}6H_2O$	12230±139	23760±241	12766±163	11046–12552	12500
$CaCl_2{\cdot}6H_2O$	37733±362	59944±437	40344±303	37572–38325	37600
$BaCl_2{\cdot}2H_2O$	21760±164	19654±245	19573±194	18200–20585	19500

lization enthalpies selected by Pekárek [13] and accepted by the U.S. National Bureau of Standards as the "best" standard values.

The crystallization enthalpies calculated in this work appeared to depend on the calculation method, as mentioned earlier. The values obtained by using Eq. (11) are generally in good agreement with the selected NBS data, while those calculated from Eq. (8) exhibit large deviations from the standard data. The above observations are confirmed by the results concerning $KF \cdot 2H_2O$, a salt not investigated in our work. The value of $\Delta_{sol}H_2^{sat}$ calculated from Parker's data [5] by means of Eq. (8) is 24589±112 J·mol^{-1}, while that obtained from Eq. (11) is 20533±112 J·mol^{-1}, which is very close to the "best" value calculated from the Williamson and Nakayama dependence [14–16]: 20640±230 J·mol^{-1}.

Conclusions

It can be concluded that determination of the crystallization enthalpies in the manner proposed in this paper (i.e. measurement of the dilution enthalpy of saturated salt solution, followed by measurement of the dissolution enthalpy of this salt to the same final molality and then the use of Eq. (11) for the $\Delta_{crys}H_m$ calculation) shortens the time needed to obtain the necessary number of experimental data. Moreover, it yields $\Delta_{crys}H_m$ values that are in good agreement with those obtained from the Williamson and Nakayama relation and accepted as standard ones.

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Zusammensetzung — Es wurden die Kristallisationenthalpien des NaCl, KCl, $LiCl\cdot H_2O$, $MgCl_2\cdot 6H_2O$, $CaCl_2\cdot 6H_2O$ und $BaCl_2\cdot 2H_2O$ aus wässerigen Lösungen bestimt. Es wurden vorher gemessene differenzierte und integrale Enthalpien von oben genannten gelösten Sälze ausgenutzt, bei denen verschiedene Berechnungsmethoden angewandt wurden. Die gewonenen Kristallisationenthalpien wurden mit entsprechenden Literaturangaben erörtert und vergliechen.