# DIFFERENTIAL ENTHALPIES OF SOLUTION OF LiCl·H₂O, NaCl, KCl, MgCl₂·6H₂O, CaCl₂·6H₂O, AND BaCl₂·2H₂O IN WATER AT 298.15 K, NEAR THE SATURATION CONCENTRATION
## Enthalpies of crystallization

## A. Chmarzyński

Faculty of Chemistry N. Copernicus University, ul. Gagarina 7, 87-100 Toruń, Poland

## Abstract

The direct measurements of differential enthalpies of solution $\Delta_{sol}H_2$, of LiCl·H₂O, NaCl, KCl, MgCl₂·6H₂O, CaCl₂·6H₂O and BaCl₂·2H₂O, as the function of molality, $m$, in the region of concentrated solutions were performed. On this basis the enthalpies of crystallization, $\Delta_{cryst}H_m$, were calculated and compared to the appropriate literature data.

**Keywords:** crystallization enthalpy, enthalpy of solution

## Introduction

For thermodynamic calculations and for the study of electrolyte-solution models, the knowledge of the concentration dependence of the solution enthalpy is necessary [1, 2]. Unfortunately, the available information is far from complete up to molality of the saturated solution even at 298.15 K, with the exception of the more common solutes (e.g. NaCl, CaCl₂) [3, 4]. But even for KCl solutions there is a lack of data at higher molalities [3, 4] and the thermodynamic treatment is not complete [1, 3, 5]. Particularly scarce are data describing the behaviour of close-to-saturation solutions. The enthalpy of crystallization is one such property. However, the literature data from various laboratories on the enthalpies of crystallization exhibit significant differences [6]. Therefore, the aim of this work was to begin a systematic investigations on a number of salts in aqueous solutions using the same apparatus and various experimental techniques. The investigated systems include all three kinds of isotherms of solution enthalpies (according to Mishchenko and Pronina classification [7]) and the solid phases are both anhydrous salts and hydrates.

## Experimental

The experiments were carried out with a solution calorimeter of "isoperibol" type, made in Technical University of Gdańsk [8, 9].

Analytical grade salts (POCh, Gliwice, Poland) were used. The anhydrous salts were dried 3 to 4 h at 375–385 K and then stored in a desiccator over phosphorus pentoxide. The hydrates were prepared by solution of salts in redistilled water at 333–343 K, recrystallization at 298.15 K and then dried. Hydrates received that way were kept in desiccators maintaining suitable water's vapour pressure. The compositions of the solid phases were determined using X-ray diffractometer analysis and derivatography.

All solutions were prepared by weighing. Double distilled water was used throughout the experiment.

The calculations were performed with an IBM PC/AT microcomputer using the program Statgraphics (Statistical Graphics System by Statistical Graphics Corporation, vers. 2.6).

The experimental data are available on request.

## Results and discussion

Direct measurements of molar differential enthalpies of solution, $\Delta_{sol}H_2$, were taken for the above mentioned salts in water at 298.15 K. These experiments were conducted for concentrated solutions, trying to a maximum approach the saturated solution.

The time of dissolving of the salt samples depended on the concentration of solutions and it ranged between 0.5 min for the less concentrated solutions, to several minutes for the solutions close to saturation. The used amounts of soluted salts changed between 0.1–0.4 g, while the mass of solutions between 100–115 g.

It is obvious that the values of crystallization enthalpies taken from direct measurements of differential enthalpies of solution depend on the size of the dissolved salt doses. In order to reduce the dependence, the smallest possible samples of the dissolved salts were used. At the same time, they had to be as big as to keep the error of the single measurements within 1%. That, however, could not be used in the case of the system NaCl–$H_2O$ because of the relatively small thermal effect of a dissolution process.

Therefore the influence of the size of the salt sample for the value of $\Delta_{cryst}H_m$, for that system, was examined. Thus, the data defined as NaCl (1) denote the doses 1.0 g, the data NaCl (2) refer to the doses 0.5 g and the data described as NaCl (3) concern the doses about 0.3 g.

Using the experimental data, there were ranged out the curves of concentration dependence of differential enthalpies of solution, describing its by the polynomial:

$$\Delta_{sol}H_2(m) = \sum_{i=0}^{2} a_i m^i \qquad (1)$$

where $a_i$ is an adjustable parameter, and $m$ – molality of the solution.

The coefficients of this polynomial were calculated for each of the salts being tested and put in Table 1 as well as values of the minimal solutions molalities, $m_{min}$.

Taking advantage of the dependencies calculated according to Eq. (1), the molar enthalpies of crystallization, $\Delta_{cryst}H_m$, were calculated. For that purpose the well known dependence was used:

$$\left| \Delta_{sol}H_2^{sat} \right| = \left| \Delta_{cryst}H_m \right| \qquad (2)$$

where $\Delta_{sol}H_2^{sat}$ is the last differential enthalpy of solution.

The measured values of $\Delta_{sol}H_2$ were extrapolated to the molalities of the saturated solutions, $m = m_s$:

$$\Delta_{sol}H_2^{sat} = \lim_{m \to m_s} (\Delta_{sol}H_2) \qquad (3)$$

using Eq. (1) and coefficients from Table 1.

**Table 1** Coefficients of Eq. (1); $N$ – number of experimental points used in each fit, $m_{min}$ denotes the least molality, $R$ – correlation coefficient

| Salt | $N$ | $m_{min}$ / mol·kg$^{-1}$ | $a_0$ / J·mol$^{-1}$ | $a_1$ / J·kg·mol$^{-2}$ | $a_2$ / J·kg$^2$·mol$^{-3}$ | $R$ |
|------|-----|------|------|------|------|------|
| LiCl·H$_2$O | 27 | 16.6114 | –27289.7 | 3.3180E3 | –0.07253E3 | 0.9947 |
| NaCl (1) | 18 | 4.1732 | 2074.9 | –0.6264E3 | 0.08465E3 | 0.9697 |
| NaCl (2) | 17 | 4.5317 | 1317.7 | –0.3874E3 | 0.07042E3 | 0.9690 |
| NaCl (3) | 17 | 4.3012 | 4120.0 | –1.4761E3 | 0.17555E3 | 0.9845 |
| KCl | 24 | 2.0214 | 18873.0 | –2.0994E3 | 0.23520E3 | 0.9552 |
| MgCl$_2$·6H$_2$O | 31 | 2.5017 | 192.8 | 0.9919E3 | 0.18115E3 | 0.9956 |
| CaCl$_2$·6H$_2$O | 35 | 3.9817 | 24188.3 | –1.4254E3 | 0.43383E3 | 0.9653 |
| BaCl$_2$·2H$_2$O | 18 | 1.3119 | 25574.4 | –9.4888E3 | 4.00571E3 | 0.9652 |

The values calculated that way as well as the saturation molalities are given in Table 2.

In addition, by this means the enthalpies of crystallization of NaCl and KCl were calculated, taking to calculation differential enthalpies of solution from works of Sanahuya and Gomez-Estevez [10, 11], and LiCl·H$_2$O, from work of Wolf et al. [12]. Those values are shown in Table 3.

**Table 2** The molar enthalpies of crystallization of investigated salts in water at 298.15 K; $m_s$ denotes the molality of saturated solutions [16], $\Delta\overline{m}$ is an arithmetic average of $\Delta m$ in a given series of measurements and $\Delta m$ means increasing of molality after dissolution process

| Salt | $m_s$ / mol·kg$^{-1}$ | $\Delta\overline{m}$ / mol·kg$^{-1}$ | $-\Delta_{cryst}H_m$ / J·mol$^{-1}$ |
|------|------|------|------|
| LiCl·H$_2$O | 19.9003 | 0.0189 | 10016±42 |
| NaCl (1) | 6.1507 | 0.2205 | 1425±19 |
| NaCl (2) | 6.1507 | 0.1145 | 1599±27 |
| NaCl (3) | 6.1507 | 0.0575 | 1682±22 |
| KCl | 4.8204 | 0.0200 | 14218±178 |
| MgCl$_2$·6H$_2$O | 5.8614 | 0.0104 | 12230±139 |
| CaCl$_2$·6H$_2$O | 7.4669 | 0.0100 | 37733±362 |
| BaCl$_2$·2H$_2$O | 1.8556 | 0.0139 | 21760±164 |

For NaCl, KCl and LiCl·H$_2$O there were also calculated values of $\Delta_{cryst}H_m$ using the integral enthalpies of solution data given by Parker [3] and Wolf et al. [12]. Those values were calculated in the way given below.

Differential enthalpy of solution may be calculated from concentration dependence of integral enthalpy of solution:

$$\Delta_{sol}H_2(m) = \Delta_{sol}H_m(m) + m\left(\frac{\partial L_\varphi(m)}{\partial m}\right) \tag{4}$$

where $L_\varphi$ is relative apparent molar enthalpy and $\Delta_{sol}H_m$ denotes integral enthalpy of 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 were fitted to the polynomial of the form;

$$L_\varphi(m) = \sum_{i=1}^{n} a_i m^{i/2} \tag{5}$$

where $a_i$ is an adjustable parameter.

For the saturated solution we obtain:

$$\Delta_{sol}H_2^{sat} = \Delta_{sol}H_m^{sat} + m_s\left(\frac{\partial L_\varphi(m)}{\partial m}\right)_{m=m_s} \tag{6}$$

where

$$\Delta_{sol}H_m^{sat} = \Delta_{sol}H_m^{\infty} + L_{\phi}(m_s) \tag{7}$$

and $\Delta_{sol}H_m^{\infty}$ is the solution enthalpy of the salt in an infinitely diluted solution. For calculations, $\Delta_{sol}H_m^{\infty}$ values taken from Parker's work [3] were used.

The values calculated that way, values obtained in this work and literature data are compiled in Table 3. It is divided into two groups – received from direct measurements of crystallization enthalpies, and the calculated ones.

As it can be seen from Table 3 there appear great differences in values of $\Delta_{cryst}H_m$. Even for NaCl and KCl, the most thoroughly tested salts the differences amount to about 15% and 20%, respectively. An unexpectedly great difference may be observed for LiCl·H₂O. The values obtained from direct measurements of $\Delta_{sol}H_2$ and from $\Delta_{sol}H_m$ differ from each other by almost 67%.

It also can be seen from this Table that enthalpies of crystallization obtained in this work for NaCl and KCl are generally in a good agreement with the available literature data. This shows a proper choice of measurement method, as well as satisfying precision of apparatus. For the rest of the systems there is little literature data available, which differs from each other to the large enough extent, as to be able to compare them.

Looking for the main reasons of the appearance of such great differences between literature data, the influence of a weighed amount of soluted salt on the value of $\Delta_{cryst}H_m$ was examined. The investigations for the system NaCl–H₂O were carried out, for the reasons explained earlier.

The experiments were carried out in three series, starting from mean value of $\Delta\overline{m} = 0.2205$, for NaCl(1), over $\Delta\overline{m} = 0.1145$, for NaCl(2), up to $\Delta\overline{m} = 0.0575$, for NaCl(3). It turned out that obtained points lay on a line described by the equation:

$$\Delta_{cryst}H_m(\Delta\overline{m}) = -1766.9 + 1514.2(\Delta\overline{m}), \tag{8}$$

where $\Delta\overline{m}$ is an arithmetic average of $\Delta m$ values in a given series of measurements and $\Delta m$ means increasing of molality after dissolution process (Table 2).

It shows that for $\Delta m = 0$, the values of $\Delta_{cryst}H_m = -1767 \pm 27$ J·mol⁻¹, being different by about 23% from the value obtained for $\Delta\overline{m} = 0.2205$.

There might also be other sources of mistakes. It should be noticed, that many authors do not present the concentration of saturated solutions. It may cause considerable divergences, particularly for hydrates, in which occur great differences in determinated values of saturated solutions concentrations. For example, the values of $m_s$ for CaCl₂·6H₂O range between 7.195–8.588 mol·kg⁻¹ [16] and enthalpies of crystallization calculated according to my data, take the

**Table 3** The molar enthalpies of crystallization from aqueous solutions at 298.15 K; comparison of values from different sources

| Salt | $-\Delta_{cryst}H_m$ / $J \cdot mol^{-1}$ | | | |
|---|---|---|---|---|
| | calculated | Ref. | measured | Ref. |
| LiCl·H$_2$O | 95401–13140 | [12] | | |
| | 13095 | [14] | | |
| | 10016±42[a] | | | |
| | 9538±2[b] | [12] | | |
| | 14001±418[c] | [3] | | |
| | 15928±418[c] | [12] | | |
| NaCl | 1590–1757 | [13] | | |
| | 1536 | [15] | | |
| | 1767±27[a] | | 1506 | [15] |
| | 1610±64[b] | [10] | | |
| | 1637±11[c] | [3] | | |
| KCl | 13220–14130 | [6] | | |
| | 13770–14144 | [13] | | |
| | 13556 | [15] | 13619 | [15] |
| | 14016 | [14] | 15889 | [13] |
| | 14218±178[a] | | | |
| | 13911±84[b] | [11] | | |
| | 13681±12[c] | [3] | | |
| MgCl$_2$·6H$_2$O | 11673 | [13] | | |
| | 11046 | [15] | 12552 | [13] |
| | 12230±139[a] | | | |
| CaCl$_2$·6H$_2$O | 38325 | [15] | | |
| | 38284 | [14] | 37572 | [15] |
| | 37733±362[a] | | | |
| BaCl$_2$·2H$_2$O | 19497 | [15] | | |
| | 20585 | [14] | 18200 | [15] |
| | 21760±164[a] | | | |

a) this work, b) calculated from differential enthalpies of solution [10–12] using Eq. (1),
c) calculated from integral enthalpies of solution [3, 12] using Eq. (6)

values $-36391$ and $-43941$ J·mol$^{-1}$, respectively. This happens similarly in case of MgCl$_2$·6H$_2$O and LiCl·H$_2$O.

It was also noticed, that for hydrates, in the region of concentrations close to saturation, the obtained points differ considerably from the rest in a given run of measurements. That phenomenon occurred in spite of complete dissolution of hydrate and was most evident in the case of the LiCl–H$_2$O system. During solution of LiCl·H$_2$O, starting from the molality equal to 19.3407 mol·kg$^{-1}$ a small but distinct exothermic effect occurred, nevertheless the total effect of dissolution process was endothermic. This phenomenon was increasing during rise of solution concentration and ranged between 7–10% of total thermal effect of the dissolution process. It occurred in the beginning of the solution and continued ca 0.5 min; and the total solution time of the sample in those solutions was ca. 8–10 min. For the rest of the systems appearance of the additional exothermic effect was not observed. Nevertheless, for hydrates, in the region of concentrations close to saturation the obtained points differed considerably from the previous ones and were always more exothermic. This points out the similarity of the phenomena occurring in these systems. It also allows for supposition that there are such interactions in these solutions which enable creation of quasi-crystalline structures. The addition of the solid phase to this solution causes destruction of its structure, which influence the change in the total thermal effect of dissolution process.

Rychly and Nyvlt in their work [13] point out the possibility of occurrence the similar phenomenon (destruction of solution structure) during homogeneous crystallization of saccharose and sodium acetate from aqueous solutions. In this case we have to do with still more concentrated solutions, because crystallization occurs from supersaturated solutions.

However, the carried out investigations of solution enthalpies only, are not sufficient for clear explanation of the observed phenomenon nature. Nevertheless, that phenomenon has distinct influence for obtained values of crystallization enthalpies.

As it can be seen from Table 3 there appear considerable divergences between crystallization enthalpies values. Taking into consideration the reasons given above and also others, for example, various experimental techniques or ways of calculation of $\Delta_{cryst}H_m$ values, that fact seems to be justified.

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**Zusammenfassung** — Für $LiCl \cdot H_2O$, $NaCl$, $KCl$, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$ und $BaCl_2 \cdot 2H_2O$ wurden im Bereich konzentrierter Lösungen die differentiellen Lösungsenthalpien $\Delta_{sol}H_2$ in Abhängigkeit von der Konzentration direkt gemessen. Ausgehend von diesen Messungen wurden die Kristallisationsenthalpien $\Delta_{cryst}H_m$, berechnet und mit den entsprechenden Literaturangaben verglichen.