Thermochimica Acta, 104 (1986) 147–152
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ENTHALPIES OF CRYSTALLIZATION OF HALOGENIDES. PART 3. INVESTIGATIONS OF TERNARY SYSTEMS

HANS-HEINZ EMONS, GERT WOLF and CHRISTA KROPP

Sektion Chemie, Bergakademie Freiberg, 9200 Freiberg (G.D.R.)

(Received 26 December 1985)

ABSTRACT

We report the indirect experimental determination of the crystallization enthalpies of AX in ternary systems of type A^+, $Mg^{2+}/X^-//H_2O$ with $A^+ = K^+$, NH_4^+, Rb^+ and $X^- = Cl^-$, Br^-. On the basis of the results obtained, the influence of the addition of MgX_2 to AX solutions is considered with respect to the lowering of the partial molar enthalpy of AX in the solution.

INTRODUCTION

The molar crystallization enthalpy $\Delta_c H_b$ of a salt b is equal to the difference between the molar enthalpy H_{b*} of the pure salt and the partial molar enthalpy H_b of salt b in the saturated solution. Thus, it corresponds to the negative partial molar dissolution enthalpy $\Delta_s H_b$ of b at the saturation molality m_{sa}

$$\Delta_c H_b = H_{b*} - H_b = -\Delta_s H_b \qquad (m_b = m_{b,sa}) \tag{1}$$

In accordance with eqn. (1), measurements of the crystallization enthalpy are useful, for example, for determining the influence of foreign salts in a solution or the influence of variations of the solvent or of its composition on H_b, because H_{b*} is constant in all these examples. Studies of $\Delta_c H_b$ consequently provide information on the interaction enthalpy in the solution. This enthalpy determines the crystallization and dissolution behaviour of the salt.

Within the framework of the present paper, $\Delta_c H_b$ is investigated for ternary systems of type A^+, $Mg^{2+}/X^-//H_2O$ with $A^+ = K^+$, NH_4^+, Rb^+ and $X^- = Cl^-$, Br^- at $T = 298.15$ K. In these systems, double salts of the carnallite type with the general formula $AX \cdot MgX_2 \cdot 6H_2O$ occur as stable solid equilibrium phases. The dissolution behaviour of double salts is incongruent ($A^+ = K^+$, NH_4^+) or congruent ($A^+ = Rb^+$), depending on the selected A^+ cation. Systematic investigations of $\Delta_c H_b$ for b = AX depending on the MgX_2 molality in the solution, which molality is considered as the foreign salt concentration, provide first results for the thermodynamic determination of the dissolution behaviour of double salts.

0040-6031/86/$03.50

Various methods for the experimental determination of $\Delta_c H_b$ have been described, and results for simple salt–water-systems have been given [1,2]. These studies clearly showed that, to determine $\Delta_c H_b$ in ternary systems, measurements of $\Delta_s H_b$ as a function of m_b near $m_{b,sa}$ are most appropriate

$$\lim_{m_b \to m_{b,sa}} \Delta_s H_b(m_b) = \Delta_c H_b \tag{2}$$

A critical analysis of our own results, and also a comparison with results from the literature, shows that the reliability of $\Delta_c H_b$ values is only in exceptional cases much better than $\pm 5\%$. This probably also applies to ternary systems and should be taken into account in discussion of the results.

For comparable systems, studies of the influence of foreign salts on the partial molar dissolution enthalpy and on the crystallization enthalpy have not been reported. Measurements of the integral dissolution enthalpy of KCl as a function of the $MgCl_2$ content of the solution [3–5] have shown that the addition of $MgCl_2$ leads to a lower value of $\Delta_s^{in} H_{KCl}$. Some values for $\Delta_c H_b$ and $\Delta_s H_b$ ($m_{b,sa}$) of the ternary system Na^+, $Rb^+/NO_3^-//H_2O$ [6] show that $\Delta_c H_{NaNO_3}$ becomes increasingly endothermic with increasing $RbNO_3$ content, whereas, for $\Delta_c H_{RbNO_3}$, the addition of $NaNO_3$ has the opposite effect.

EXPERIMENTAL

The crystallization enthalpy of AX was determined as a function of the MgX_2 content for solutions of composition according to the saturation line of AX in the solubility curve. The solubility data required for this purpose were known for the systems studied [7]. For each selected MgX_2 content, numerous measurements of $\Delta_s H_{AX}$ at various AX concentrations would be necessary to determine $\Delta_c H_{AX}$ according to eqn. (2). Since $d\Delta_s H_{AX}/dm_{AX}$ is small near $m_{AX,sa}$ [2], only $\Delta_s H_{AX}$ was measured for $m_{AX}/m_{AX,sa} = 0.95$, and the result was equated with a negative crystallization enthalpy. Through this simplification, the number of necessary measurements can be considerably reduced without severely limiting the validity of the results. In the following report, the symbol $\Delta_c H_{AX}^*$ will be used for the respective values.

The calorimetric measurements were performed at $T = 298.15$ K in a modified LKB calorimeter (type 8700) [1]; a detailed description of our method for measuring partial molar dissolution enthalpies $\Delta_s H_b$ is given in ref. 2. The solutions were produced by the addition of weighed portions of AX, of a MgX_2 stock solution and of bidistilled water into the calorimetric measuring cell. In the experiments, we used KCl (p.a.), KBr (DAB 7), NH_4Cl (p.a.), NH_4Br (p.a.) and $MgCl_2 \cdot 6H_2O$ (DAB 7) (VEB Jenapharm, Laborchemie Apolda) and $MgBr_2 \cdot 6H_2O$, obtained by reacting MgO with a

48% HBr solution, after double recrystallization. The sample (0.2 g AX salt) to be dissolved in 60 cm^3 of solution in the calorimetric experiment was dried for several days at $T = 323$ K and placed in glass ampoules in a manipulator box. The low rate of dissolution of AX near $m_{\mathrm{AX,sa}}$, poses problems for the calorimetric measurements [2], and was further decreased by the foreign salt content (MgX_2) in the solution. As a result, duration of the principal calorimetric period was, on average, increased to 90 min, but did not exceed the limit [2] beyond which the measuring accuracy of ±5% was invalid.

RESULTS AND DISCUSSION

The results from the measurement of molar crystallization enthalpy $\Delta_c H_{AX}^*$ are plotted versus the composition of the ternary systems examined (Fig. 1). To permit comparisons, $\Delta_c H_{AX}$ values measured for the binary systems are

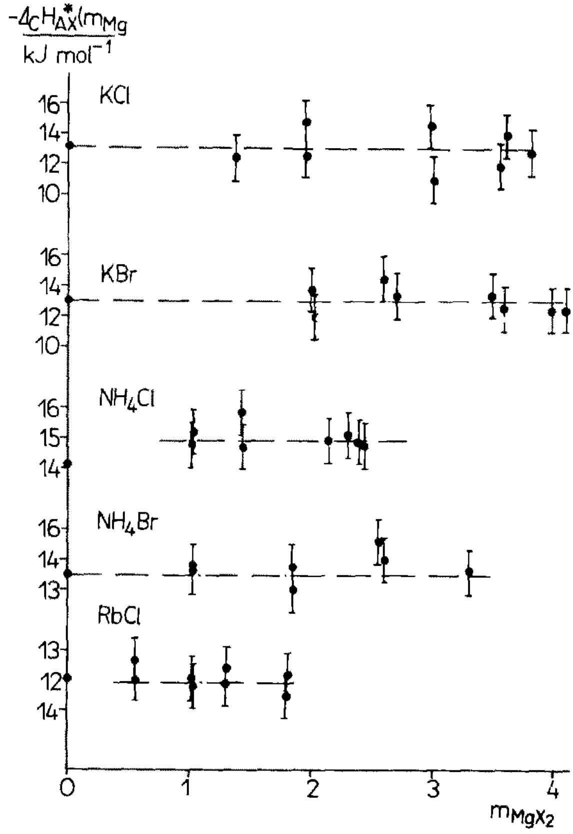

Fig. 1. Molar crystallization enthalpy $\Delta_c H_{AX}^*$ for AX = KCl, KBr, NH_4Cl, NH_4Br and RbCl at different MgX_2 contents of the solution at $T = 298.15$ K.

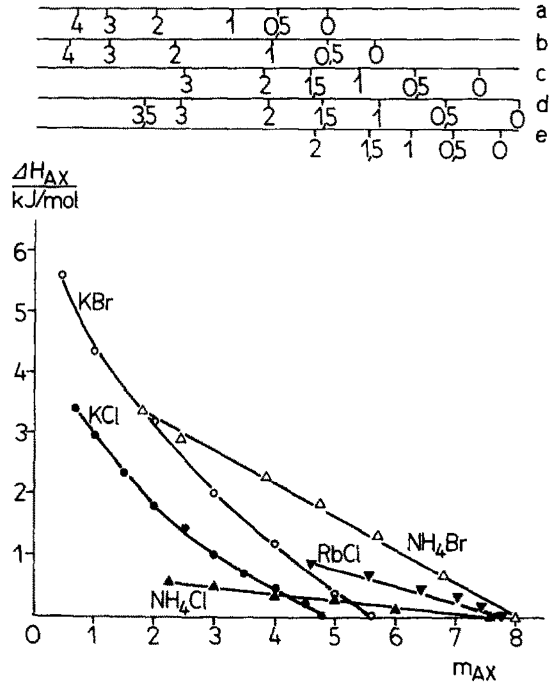

Fig. 2. Difference $\Delta H_{AX} = H_{AX}^{\text{binary}}(m_{AX}) - H_{AX}^{\text{ternary}}(m_{AX})$ as a function of m_{AX}, with an indication of the corresponding MgX_2 solubility in the systems: (a) K^+, $Mg^{2+}/Cl^-//H_2O$; (b) K^+, $Mg^{2+}/Br^-//H_2O$; (c) NH_4^+, $Mg^{2+}/Cl^-//H_2O$; (d) NH_4^+, $Mg^{2+}/Br^-//H_2O$; (e) Rb^+, $Mg^{2+}/Cl^-//H_2O$.

also given, The illustration clearly shows that, within the given error limit and independent of the MgX_2 concentration and, thus of the AX concentration, the crystallization enthalpy along the saturation line for AX is equal to the value measured in the binary system in all the systems investigated. Since H_{AX*} is constant in all the investigations, H_{AX} is also independent of the composition in spite of a decreasing AX concentration along the saturation line. In contrast to this, a distinct decrease of H_{AX} with m_{AX} has been observed for the corresponding binary systems [2,8]. Figure 2 shows the difference (ΔH_{AX}) of the partial molar enthalpies in the binary and ternary systems

$$\Delta H_{AX} = H_{AX}^{\text{binary}}\,(m_{AX}) - H_{AX}^{\text{ternary}}\,(m_{AX}) \tag{3}$$

for identical m_{AX} values as a function of m_{AX} and m_{MgX_2}, respectively. The data for $\Delta_s H_{AX} = f(m_{AX})$ have been taken from refs. 2,5 and 7.

In the binary system, H_{AX} is principally exothermic but to a lesser degree for solutions with AX isomolality. This tendency becomes more obvious with decreasing m_{AX} or increasing m_{MgX_2}. From the relationship between the enthalpy and entropy in the equilibrium state it can be deduced that in solutions with AX isomolality the partial molar entropy of AX, starting from the binary system, is lowered to a greater extent with increasing content of foreign salt, similar to the decrease in entropy observed in the binary system with increasing m_{AX} up to $m_{AX,sa}$.

Decrease in entropy is more pronounced in the bromide systems than in the chloride systems. A comparable graduation can be shown for the cations in the order K^+, Rb^+, NH_4^+. The observed decrease in the partial molar entropy of AX because of the addition of MgX_2 could be a consequence of the modified solution structure with the resulting decrease in the moveability of the ions. The formation of complex particles in the solution with increasing MgX_2 content, assumed in ref. 9, affords a similar explanation of the entropy reduction.

The more exothermic partial molar enthalpy of AX in the ternary system, which corresponds to the difference ΔH_{AX}, may be caused by various interionic interactions which, however, are probably due to the foreign salt concentration m_{MgX_2} present in the ternary system. Therefore, it appears

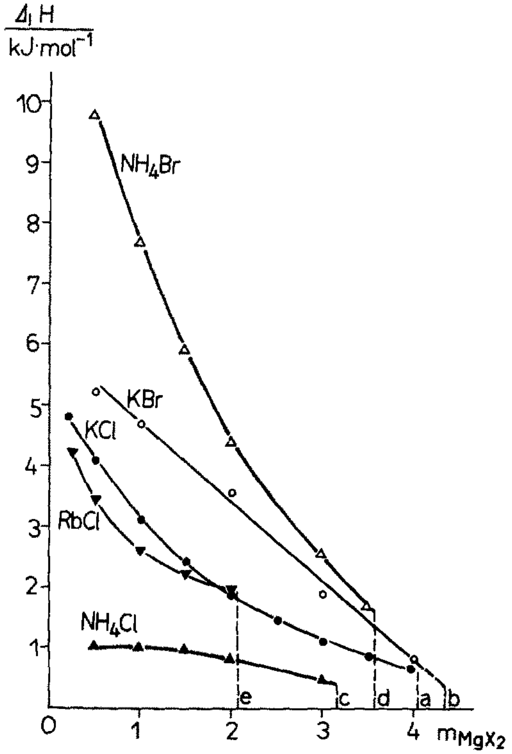

Fig. 3. Interaction enthalpy $\Delta_I H$ versus m_{MgX_2}. (— — —) Designates the solution composition in the equilibrium solution of the two-salt paragenesis $AX + AX \cdot MgX_2 \cdot 6H_2O$ in the systems: (a) K^+, $Mg^{2+}/Cl^-//H_2O$; (b) K^+, $Mg^{2+}/Br^-//H_2O$; (c) NH_4^+, $Mg^{2+}/Cl^-//H_2O$; (d) NH_4^+, $Mg^{2+}/Br^-//H_2O$; (e) Rb^+, $Mg^{2+}/Cl^-//H_2O$.

reasonable to convert ΔH_{AX} into a molar interaction enthalpy $\Delta_I H$ on the basis of the number of mol of MgX_2 existing per mol of AX

$$\Delta_I H = \Delta H_{AX}(m_{AX}/m_{MgX_2}) \qquad (4)$$

$\Delta_I H$ indicates the change in the partial enthalpy h_{AX} of a binary system of concentration m_{AX} caused by the addition of 1 mol of MgX_2.

In Fig. 3, $\Delta_I H$ is plotted for the systems investigated as a function of the composition. It is evident that the influence of the MgX_2 addition is most pronounced in the ternary systems with a high AX (low MgX_2) molality. $d\Delta_I H/dm_{AX}$ is always positive. $\Delta_I H$ has distinctly higher values in the bromide systems compared with the chloride systems investigated. However, there is no evidence of a corresponding definite dependence on the selected A^+ cation.

An essential finding of the present investigations is that, in the ternary systems investigated, $\Delta_I H$ increases the partial molar enthalpy H_{AX} exothermically, in such a way that, at the saturation concentration $m_{AX,sa}$, irrespective of the pertaining m_{MgX_2}, and H_{AX} value is obtained, which leads to a $\Delta_c H_{AX}$ value corresponding to that for the binary systems. Saturation is achieved when $H_{AX}^{ternary}(m_{AX}) = H_{AX}^{binary}\ (m_{AX,sa})$. Whether this finding holds true also for other systems needs to be established by further investigation. Similarly, it would be helpful to determine H_{MgX_2} along the saturation line for AX up to the two-salt paragenesis in order to assist the clarification of the thermodynamic processes taking place in double-salt crystallization. Studies in this field are being prepared.

REFERENCES

1 H.-H. Emons, G. Wolf and C. Kropp, Thermochim. Acta, 81 (1984) 59.
2 H.-H. Emons, G. Wolf and C. Kropp, Thermochim. Acta, 104 (1986) 139.
3 I.E. Voskresenskaya, Usp. Khim., 5 (1936) 1019.
4 T.I. Gaidukova and A.B. Sdanovskij, Zh. Fiz. Khim., 46 (1972) 2905.
5 K.P. Mishchenko and G.M. Poltoratskij, Termodinamika i stroenie vodnykh rastvorov elektrolitov, Khimiya, Leningrad, 1976.
6 B.D. Stepin, G.A. Lovetskaya and O.V. Ioffe, Zh. Fiz. Khim., 23 (1978) 2247.
7 Spravochnik eksperimentalnykh dannykh po rastvorimosti mnogokomponentnykh vodno-solevykh sistem, Khimiya, Leningrad, 1975.
8 J. Wüst and E. Lange, Z. Phys. Chem., 116 (1925) 161.
9 A.B. Sdanovskij and L.D. Deryabina, Zh. Fiz. Khim., 39 (1965) 1464.