

The Influence of the Degree of Organization of Saturated Solutions on the Shape of the Solubility Isotherm

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Z. Naturforsch. **56 a**, 865–868 (2001); received November 14, 2001

Special features of solubility isotherms of salt hydrates have been observed, from which the evidence of strong organization of saturated solutions of hydrates may be deduced. Often observed low contents of the non saturating component in the eutonic solution limiting the crystallization branch of hydrated salts is put into connection with this result. The composition of the respective eutonic solutions exhibits a correlation with the hydration entropy of the ions present in the ternary saturated solution.

Key words: Computer Chemistry; Concentrated Electrolyte Solutions; Phase Diagrams; Salt Hydrates; Thermodynamics.

During the past decades, the combination of that diffraction studies [1] and large scale computational calculations [2] has brought a significant improvement in our understanding of the structure of aqueous electrolyte solutions. The authors of these investigations, however, stress [3] that there are several technical disadvantages in the practical implementation of these direct methods, especially in the case of concentrated solutions. Therefore the respective field is benefiting also from contributions of indirect investigations.

In recent years [4 - 7] we have tried to prove that information on the ionic processes in saturated aqueous electrolyte solutions is included in the solubility isotherms of ternary systems consisting of two electrolytes with a common ion. Therefore we started searching for a method of computer analysis of solubility curves that would elucidate this information. The proposed method, called hydration analysis [4], permits the calculation and, for the required treatment, use of the amount of water that attains different properties in the three component saturated solution from those in the saturated binary solution.

In hydration analysis, the amount of water which preserved in ternary solution the properties of water in binary saturated solution of the uni-univalent electrolyte MX (the effective water w_{eff}) is calculated so

$$m_0^2 = m_{\text{MX}}(m_{\text{MX}} + m_{\text{MX}'}). \quad (1)$$

This may be done by expressing the molalities via mass %:

$$\left(\frac{1000w_0}{(M_r)_{\text{MX}}(w_{\text{H}_2\text{O}})_0} \right)^2 = \quad (2)$$

$$\frac{1000w_{\text{MX}}}{(M_r)_{\text{MX}}w_{\text{eff}}} \frac{1000}{w_{\text{eff}}} \left(\frac{w_{\text{MX}}}{(M_r)_{\text{MX}}} + \frac{w_{\text{MX}'}}{(M_r)_{\text{MX}'}} \right),$$

where w_0 is the concentration in mass % (or molality m_0) of the binary saturated solution serving as our reference point, and $(w_{\text{H}_2\text{O}})_0$ is the concentration of water in that solution. From (2) follows

$$w_{\text{eff}} = \frac{(w_{\text{H}_2\text{O}})_0(M_r)_{\text{MX}}}{w_0} \sqrt{n_{\text{MX}}(n_{\text{MX}} + n_{\text{MX}')}}, \quad (3)$$

where $n_i = w_i/(M_r)_i$ is the amount of substance of the component i in 100 g of the saturated solution. Therefore, the amount of water that attains different properties in the three component saturated solution

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from those in the saturated binary solution $w_{\text{changed}} = w_{\text{H}_2\text{O}} - w_{\text{eff}}$ is expressed as the parameter P :

$$P = \frac{w_{\text{H}_2\text{O}} - w_{\text{eff}}}{(M_r)_{\text{H}_2\text{O}}(n_{\text{H}_2\text{O}} + n_{\text{MX}} + n_{\text{MX}})}, \quad (4)$$

where $w_{\text{H}_2\text{O}} = 100 - w_{\text{MX}} - w_{\text{MX}}$ answers to the concentration of water in the ternary saturated solution under consideration (in mass %). For the sake of clarity, the parameter P is expressed relative to one mole of the non-saturating component, i. e. P/x_2 .

From the values obtained by hydration analysis, the concentration dependence of the relation P/x_2 and the total amount of water available per ion of salt components Aq were found most suitable for the description of ionic processes [4]. Therefore, only these dependences have been depicted on the relevant figures also in this paper. Further, the points depicting the values of the variables have not been connected by curves, as no theory exists to describe the shape of the concentration dependence of P/x_2 as yet.

It is also straightforward [5] to obtain the ratio γ_{\pm}/γ_0 (γ_{\pm} and γ_0 are, respectively, activity coefficients of the solute in the ternary saturated solution and in its binary saturated solution in water under the same conditions), as

$$P = \frac{w_{\text{H}_2\text{O}}}{(M_r)_{\text{H}_2\text{O}}(n_{\text{H}_2\text{O}} + n_{\text{MX}} + n_{\text{MX}})} \left(1 - \frac{\gamma_0}{\gamma_{\pm}}\right) = x_{\text{H}_2\text{O}} \left(1 - \frac{\gamma_0}{\gamma_{\pm}}\right), \quad (5)$$

where $x_{\text{H}_2\text{O}}$ is the mole fraction of water in the ternary saturated solution under consideration.

Recently [6] the quantity Ξ has been introduced as

$$\Xi = m_1 RT \ln \gamma_{\pm}/\gamma_0. \quad (6)$$

Without detailed considerations of the pertinent standard states, this quantity can be assigned the significance of the residual Gibbs energy for the transfer of m_1 moles of electrolyte 1 from its saturated solution to a solution containing 1 kg of water and a concentration of electrolyte 2 such that the ternary solution formed at the temperature T is exactly saturated in electrolyte 1.

It has been proven [7] that the dependence of the quantity Ξ on the composition along the branches of the solubility isotherm of a ternary system follows the changes of configuration of the ternary saturated solution.

All these treatments are especially effective if applied to families of homologous systems. In selecting such families of systems, both by literature search and own measurement [7], special features of solubility isotherms of salt hydrates have been observed.

Prior to the present considerations, some evidence of strong organization of saturated solutions of hydrates was deduced directly from the results of the hydration analysis. The 25 °C solubility isotherms in the systems $\text{MnCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ [8], $\text{CoCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ [9] and $\text{CuCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ [10] were analyzed. When magnesium chloride is added to saturated solutions of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$, hydration of the Mg^{2+} ion added by the water molecules available in the saturated solution proceeds. The parameter P/x_2 giving a quantitative characterization of the competition is approximately 3, 4, and 5.5, respectively. This sequence ($\text{CoCl}_2 \cdot 6 \text{H}_2\text{O} < \text{MnCl}_2 \cdot 4 \text{H}_2\text{O} < \text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$) does not reflect the amount of water available in the respective saturated solutions which increases in the order $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O} < \text{CuCl}_2 \cdot 2 \text{H}_2\text{O} < \text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$. Instead, the parameter P/x_2 seems to be the larger, the lower the water content in the hydrate at equilibrium. This means: the higher hydrate is present in the equilibrium solid phase, the less the respective saturated solution is willing to let the Mg^{2+} ion build its hydration sphere.

However, in the systems with hydrated salts, quite often the solubility branches of the hydrated components are too short to meet the criteria established for the applicability of hydration analysis [11]. The phenomenon itself can be put into connection with the problem under discussion. Let us assume that a saturated solution of a hydrate has its own configuration, more or less related to the structure of the respective crystal hydrate. Such a relation between concentrated electrolyte solutions and solid crystal hydrate was assumed earlier in some considerations of Mishchenko [14] and was also reflected by using ionic radii based on solid hydrate data in attempts to use the Born equation for the consideration of ion hydration [15]. Such a configuration represents the minimum potential energy of the system. Adding the other solute causes a perturbation of this state and hence a potential energy increase. In the above systems with MgCl_2 added to the liquid phase, the added component has the ability to organize the solution also due to the strong hydration of the magnesium cation. Therefore, the respective hydration energy contributes to the compensation

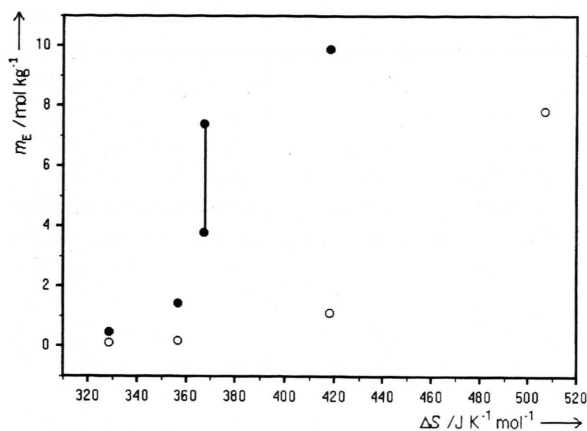


Fig. 1. Plot of the length of the crystallization branch of hydrates against the entropy of hydration of the alkaline earth cations in the systems $\text{LiCl} \cdot \text{M}^{\text{II}}\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{LiNO}_3 \cdot \text{M}^{\text{II}}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. ●: $\text{LiNO}_3 \cdot 3 \text{H}_2\text{O}$ in solid phase^a, M = Mg, Ca, Sr, Ba; ○: $\text{LiCl} \cdot \text{H}_2\text{O}$ in solid phase [12, 13], M = Be, Mg, Sr, Ba.

^a The two values for the calcium system are the boundaries of the area of the liquid phase observed on the respective solubility isotherm [7].

of breaking the original configuration. In most other cases, the system maintains its potential energy by expelling the added component into the solid phase, regardless of whether in the pure form (forming an eutonic i. e. eutectic system of unsymmetrical shape) or as a double salt (often, e. g., in the case of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ in systems with alkali metal chlorides). Such a phenomenon is reflected in the shape of the solubility isotherm under consideration as a low concentration of the non-saturating component in the respective eutonic point, or, in other words, as a very short crystallization branch of the hydrate.

From the thermodynamic point of view, the entropy of the system clearly reflects the phenomenon under discussion and should be examined. However, in the respective calculation a term characterizing the difference between a saturated solution of the anhydrous salt and that of the hydrate should be introduced, the derivation of which remains unclear. Nevertheless, our statements are supported by Figure 1. In Fig. 1, the concentration of the added salt in the eutonic solution limiting at 25 °C the crystallization branch of $\text{LiCl} \cdot \text{H}_2\text{O}$, and $\text{LiNO}_3 \cdot 3 \text{H}_2\text{O}$ in ternary systems consisting of these solutes, the chlorides respectively nitrates of alkaline earth metals and water is plotted against the entropy of hydration of the added ions. The entropy of hydration was chosen as the independent

variable, as the literature yields a very reliable set of data. The values used in this article were the “experimental” ones taken from the book of Krestov [16]. Plots of analogous shapes are found for other thermodynamic characteristics of the hydration as well as for the viscosity parameter B , where the connection to the hydration sphere(s) of the ions involved was suggested [17]. Plots of very similar shapes were found also when the respective eutonic concentrations were plotted against the water-structural contribution to the entropy and even for the ΔG_{HB} values on the structure breaking and making scale given by Marcus [18]. However, only the plot against the hydration entropy has been demonstrated here, as a mutual correlation of the entropy of hydration and other characteristics of hydration was proved [18, 19].

The attempt to depict an analogous correlation for other families of added ions, such as for transition metals, is less illustrative due to the close values of their hydration entropies and lack of precise data. The longest crystallization branches of hydrated chlorides such as $\text{LiCl} \cdot \text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$, have been observed in solutions of zinc and mercury chlorides [12, 20], where an energetic contribution of complexation may be expected. Nevertheless, involving complex formation in these considerations seems quite subtle and needs further material for comparison.

On the other hand, it should be stressed that it is not only the ion hydration in the saturated solution, but also the overall configuration of the respective solution, involving packing of its ions and water molecules in space, which is responsible for the phenomena under consideration. This may be illustrated by the following example: as mentioned above, of the chloride systems, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ is the hydrate which exhibits very often a short crystallization branch due to organization of its saturated solution. However, in the $\text{CaBr}_2 \cdot \text{MgBr}_2 \cdot \text{H}_2\text{O}$ system at 25 °C [21], the solubility isotherm is highly unsymmetrical, with the eutonic point at 52.6 mass % $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ and 6.7 mass % $\text{CaBr}_2 \cdot 6 \text{H}_2\text{O}$, in spite of the fact that the solubility of both salts does not differ much ($\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ 50.8 mass %, i. e. 5.62 mol kg^{-1} , $\text{CaBr}_2 \cdot 6 \text{H}_2\text{O}$ 60.5 mass %, i. e. 7.66 mol kg^{-1}). This means that in this case $\text{CaBr}_2 \cdot 6 \text{H}_2\text{O}$ is the component which exhibits the more organized saturated solution, expelling the added MgBr_2 into the solid phase. This fact may be accepted and understood if we take into account the size of the ions involved ($r_{\text{Mg}^{2+}} = 65 \text{ pm}$, $r_{\text{Ca}^{2+}} = 99 \text{ pm}$, $r_{\text{Cl}^-} = 181 \text{ pm}$ and $r_{\text{Br}^-} = 196 \text{ pm}$). From

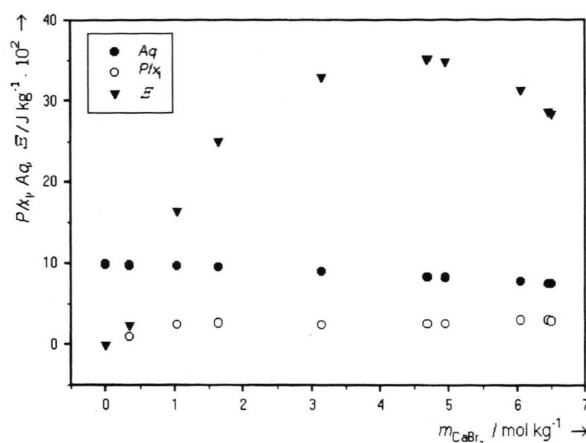


Fig. 2. Hydration analysis of the solubility branch of $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ in the system $\text{MgBr}_2\text{-CaBr}_2\text{-H}_2\text{O}$ at 25 °C.

this point of view, the dimensions of Mg^{2+} and Br^- ions differ too much to ensure a favorable filling of the space, the situation being more favorable in the case of calcium.

The respective solubility isotherm was treated by hydration analysis; on the solubility branch depicting the solubility of $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ in CaBr_2 solutions, additional support for the above conclusions was found. In Fig. 2, the dependences of the amount of available water A_q , the hydration parameter P/x_2 and the variable Ξ on the concentration of the added Ca^{2+} ion are presented. As we can see, the ions of the

added electrolyte build their hydration spheres from the water available in a saturated solution of the solute. Moreover, a structure change characterized by a break on the concentration dependence of Ξ is demonstrated. This may be understood as adaptation of the structure to that one more related to the energetically advantageous structure of the saturated solution of $\text{CaBr}_2 \cdot 6 \text{H}_2\text{O}$ as the calcium concentration in the solution grows. On the shorter solubility branch depicting the solubility of $\text{CaBr}_2 \cdot 6 \text{H}_2\text{O}$ in MgBr_2 solutions, the added magnesium bromide is smoothly incorporated into the structure of the binary saturated solution and soon expelled into the solid phase.

On the basis of the above arguments, high organization in saturated solutions of hydrates is very probable and should be taken into account in discussions of their physico-chemical properties together with the structure and energetic considerations on the molecular level. In all probability, this organization is responsible for what is called “inter- and intramolecular weak interactions” e. g. in the discussion of crystallization processes [22] performed by the Ohtaki group and should be considered as the medium, in which their nuclei are formed. In addition, the mutual connection between the shape of the solubility isotherm in a ternary system consisting of two salts with a common ion and the degree of organization of the respective saturated solutions may be considered to be proven.

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