A Contribution to the Study of Ternary Saturated Electrolyte Solutions

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A quantity has been introduced, whose dependence on the composition along the branches of the solubility isotherms of ternary systems consisting of two salts with a common ion and water exhibits breaks, which can be explained by the introduction of a previously unobserved configuration of the ternary saturated solution. In the respective region, a saturated solution in a ternary system may undergo second-order phase transitions to achieve specific configurations that are not derived from the structure of the binary saturated solution of the particular solute. It is assumed that further study of this phenomenon could contribute to a better understanding of the processes occurring in concentrated electrolyte solutions.

Key words: Saturated Electrolyte Solutions; Solubility Isotherms; Hydration Analysis; Second Order Phase Transitions; Ternary Systems.

On the basis of the assumption that the solubility is determined by the energy balance at equilibrium between a solid salt and its saturated solution, our group has recently undertaken a search for a method of computer analysis of solubility isotherms that would provide information on the individual factors affecting this equilibrium (the lattice energy of the solid phase, the hydration of ions in the saturated solution, and possibly other ionic processes in this solution, such as hydrolysis, formation of associates or complex ions, etc.). The proposed method termed hydration analysis [1], permits the calculation and, for the required treatment, the use of an amount of water that attains different properties in the three-component saturated solution that in a saturated binary solution. It is also straightforward to obtain the ratio γ/γ_0 (γ is the activity coefficient of the solute in the ternary saturated solution and γ_0 the activity coefficient of the same solute in its saturated solution in water under the same conditions) [2]. This possibility leads to the consideration of the transfer of electrolyte I from its saturated solution in water to a saturated solution that also contains a certain concentration of electrolyte II. In this connection it has been found that an unexpected conclusion follows from the expression

$$\Xi = m_s \, RT \ln \gamma/\gamma_0 . \qquad (1)$$

Without detailed consideration of the pertinent standard states, this quantity can be assigned the significance of the residual Gibbs energy for the transfer of m_s moles of electrolyte I from its saturated solution to a solution containing 1 kg of water and having a concentration of electrolyte II such that the ternary solution formed at the temperature T is exactly saturated in electrolyte I. The dependence of Ξ on the concentration of electrolyte II, m_1, was studied for a number of systems containing the chlorides and sulfates of the alkali and alkaline earth metals. A dependence with a surprising, previously unobserved shape was obtained, which is depicted in Fig. 1 as an example for the KCl–$CaCl_2$–H_2O system.

An explanation of these observations can only be based on a new interpretation of the conditions in the three-component saturated solutions. Our interest is concentrated on the amount of water that is directly affected by the individual ions and/or ion pairs, water participating in the formation of a solvent-shared ion pair, destructured water, and bulk water in the sense of the concepts of Frank and Wen [3]. Than, our approach can be explained in the following manner: Consider a saturated solution of electrolyte I. This solution may already contain a certain amount of electrolyte II and thus may be either binary ($m_1 = 0$, i.e. point B in Fig. 1) or ternary ($m_1 > 0$, i.e. the other points in Figure 1). The addition of an infinitesimal amount of electrolyte II to this saturated solution of electrolyte I can lead to any of the following phenomena:

i. An infinitesimal change in the composition of the saturated solution along the solubility isotherms with the corresponding crystallization or dissolving of electro-

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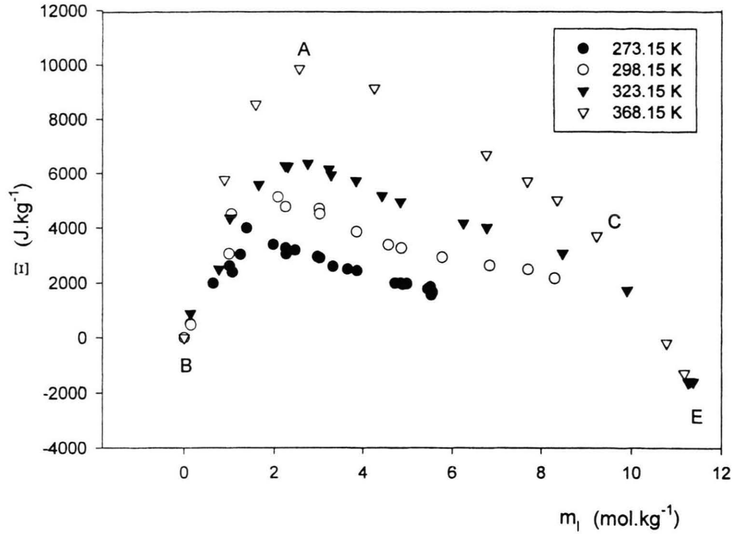

Fig.1. Concentration dependence of the quantity Ξ in the KCl–$CaCl_2$–H_2O system at 273.15, 298.15, 323.15 and 368.15 K. The points A, B, C, E are defined in the text.

lyte I, where the ions are only incorporated into the structure of the original solution (parts BA, AC and CE in Figure 1).

ii. An infinitesimal change in the composition of the saturated solution along the solubility isotherms with the corresponding crystallization or dissolving of electrolyte I, with a fundamental change in the organization of the original saturated solution. In this way, the more or less modified structure of the binary saturated solution of electrolyte I could be reorganized to a unique configuration of the ternary saturated solution that would differ fundamentally from this structure (point A in Fig. 1) or from the more or less modified configuration of the ternary saturated solution to a configuration resembling the closest solution saturated with two solid phases, if this configuration is different from the two previous structures (point C in Figure 1).

iii. An infinitesimal change in the composition of the saturated solution to an eutonic or a peritonic solution (point E in Fig. 1), and crystallization of the first fraction of the neighbouring solid phase in the pertinent phase diagram. This phase can be a different hydrate of electrolyte I, the anhydrous electrolyte I, a ternary compound, a hydrate of electrolyte II or the anhydrous electrolyte II).

It follows from the analysis of the first group of systems that all the individual structural regions (the region of the modified structure of the binary saturated solution, the region of the configuration of the ternary saturated solution, and the region of the modified structure of a solution saturated in two solid phases) need not appear on the given crystallization branch, or could be very narrow. The configuration of the ternary solution, for example, can appear at very low m_1 values, which frequently occurs in systems where significant association can be expected. A solution saturated in two solid phases may have its own structure. The crystallization of another solid phase, however, can also occur from a solution with the modified structure of a binary saturated solution or from a solution having the configuration of a ternary solution. It appears that future attention should concentrate on the search for a connection between the size, the charge and similar characteristics of participating ions on the one hand, and the existence and concentration range of the individually predicted regions in the pertinent saturated solutions on the other, and the effect of temperature on these relations.

Therefore, we propose a concept of fundamental reorganizations in the liquid phase with a composition that continuously changes along the solubility curve. We are not in slightest doubt regarding to the smoothness of the respective solubility branch and thus the possibility, e.g., of its simulation by the Pitzer method [4]. The situation observed is somewhat reminiscent of older observations [5, 6] of discontinuities in the temperature derivatives of the solubilities of some salts. The authors designated these phenomena as second-order phase transitions in solutions and associated them with “concentration fluctuations” and the degree of ordering of the species in solution. It is difficult to find more modern data for comparison, since X-ray and neutron diffraction studies, as well as computer simulations are mostly limited to binary systems and unsaturated solutions. Mention is made of the possibility of fundamental changes in the structure of solutions in dependence of the concentration in the work of Caminiti et al. [7], concerned with the X-ray determination of the structures of the solutions of chlorides of some bivalent metals. The only studies dealing with ternary systems [8, 9] are limited to a single composition of the solution. The above concept of a unique configuration of ternary solutions that is fundamentally different from the structure of a binary saturated solution could provide an explanation, e.g., for the role of admixtures in crystallization process [10] and could also provide an explanation of the concentration dependence of properties in saturated and, in general, concentrated electrolyte solutions.

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