MULTIPHASE EQUILIBRIA IN TERNARY WATER-SALT SYSTEMS AT HIGH TEMPERATURES AND PRESSURES

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Two main types of binary systems with the distinctive solubility behavior under sub- and supercritical conditions were used to subdivide the ternary water-salt systems into three classes. Characteristic features of solubility behavior and phase equilibria in ternary water-salt systems of each class at temperatures above 200°C are discussed on the basis of available experimental data and some conclusions obtained as a result of theoretical derivation of fluid and complete phase diagrams.

INTRODUCTION

The major features of phase diagrams for the ternary systems are determined by the types of phase diagrams of constituting binary subsystems, since all binary equilibria spread into the three-component region of composition and take part in the generation of ternary phase behavior.

There are two main types of phase behavior in binary water-salt systems with solid-supercritical phase equilibria [1-5]. Binary systems of type **1** (such as $NaCl$ – H_2O, KCl – H_2O, K_2CO_3 – H_2O etc.) are characterized by increasing salt solubility in the liquid phase with temperature (positive temperature coefficient of solubility (t.c.s.)) at vapor and higher pressures up to melting point of the salt, and by the absence of critical phenomena between liquid and gas (vapor) in solid saturated solutions. The vapor pressure of solid saturated solution (L-G-S) has a maximum (Fig. 1) where the pressure can be as high as 40 MPa in some water-salt mixtures, but never reaches the critical (L=G) pressure at the same temperature. In the case of binary systems of type **2** (such as Na_2CO_3 – H_2O, Na_2SO_4 – H_2O, Na_3PO_4 – H_2O, K_2SO_4 - H_2O, SiO_2 – H_2O etc.), the salt solubility in liquid solution decreases with temperature (negative t.c.s.) under subcritical conditions. As a result the compositions of saturated liquid and vapor solutions approach each other and become identical in the first critical endpoint "p" (L=G-S) where the low temperature branch of the three-phase solubility curve (L-G-S) is terminated. Critical phenomena between liquid and gas give rise to supercritical fluid equilibria where a homogeneous supercritical fluid phase is not separated into liquid and gas at any pressure. A separation of homogeneous supercritical fluid into two solutions takes place only with increasing temperature until the high temperature branch of solubility curve originating in the melting point of the pure salt and ends at the second critical endpoint "Q" (critical phenomena in solid saturated solutions).

Binary water-salt systems of both types could be complicated by immiscibility phenomena, which appear at temperatures above 200 °C. Three-phase immiscibility regions (L_1-L_2-G) are stable in the systems of type **1** and metastable in the systems of type **2**. The immiscibility regions of two types **b** and **d** [6] were found in the water-salt systems. The binary systems of type **1b** [6] (such as H_2O – HgI_2 [7]) are characterized by stable three-phase immiscibility equilibrium (L_1-L_2-G) that ends in the upper critical endpoint N (L_1=L_2-G) where the critical phenomena between two liquids occur in equilibrium with the noncritical gas (vapor). Three-phase immiscibility region in the systems of type **1d** [6] (such as water-salt systems with $Na_2B_4O_7$ [6], PbI_2 [7], Na_2HPO_4 [8], etc) is terminated by another upper critical endpoint R (L_1=G-L_2), where one equilibrium liquid phase (L_2) is noncritical.

Two main types of constituent binary subsystems (types **1** and **2**) can be used for preliminary systematization of ternary phase behavior and for designation of the various classes of ternary systems. The binary anhydrous salt systems universally belong to type **1**. A division of binary water-salt subsystems into types **1** and **2** gives the following classification of ternary systems: (i) ternary systems with two binary water-salt subsystems of type **1** (ternary class **1-1-1**); (ii) ternary systems with binary water-salt subsystems of types **1** and **2** (ternary class **1-2-1**); (iii) ternary systems with two binary water-salt subsystems of type **2** (ternary class **2-2-1**).

TERNARY SYSTEMS

*Ternary class **1-1-1**.* The simplest ternary phase behavior is observed in ternary water-salt systems of class **1-1-1**, where the both binary water-salt and anhydrous subsystems belong to type **1** without immiscibility phenomena (type **1a**). Solubility of the both salts in equilibrium with vapor (eutonic equilibrium L-G-S_1-S_2) increases with temperature up to the eutectic point in the anhydrous binary subsystem. Such phase behavior one can see in Fig. 2, where the solubility surfaces for the system NaCl – KCl – H_2O [3] are shown. Vapor pressure of the eutonic solutions passes through a maximum, which is much lower than the similar maximum on the three-phase solubility curves in binary water-salt subsystems (Fig. 1). Critical phenomena in solid saturated solutions are absent at any ratio of salt components in ternary mixtures of class **1-1-1**.

If only one of constituting binary water-salt subsystem has the immiscibility phenomena, the ternary system is complicated by three-phase immiscibility region that should disappear in the ternary nonvariant critical point. The system $Na_2B_4O_7$ – NaCl – H_2O belongs to ternary class **1-1-1** with the binary subsystem $Na_2B_4O_7$ – H_2O of type **1d** [6]. The immiscibility region spreading from this binary subsystem is bounded by two monovariant critical curves N-RN (L_1=L_2-G) and R-RN (L_1=G-L_2) and ends in the tricritical point RN (L_1=L_2=G) (Fig. 3a).

Ternary system HgI_2 – PbI_2 – H_2O [7] also belongs to ternary class **1-1-1** but already both binary water-salt subsystems have the immiscibility regions of different types (Fig. 3b). The immiscibility region of type **d**, spreading from the subsystem PbI_2 – H_2O, ends in the tricritical point RN. Another immiscibility region of type **b** spreading from the subsystem HgI_2 - H_2O is terminated by the invariant critical point LN (L_1=L_2-G-S) in solid saturated solutions. The immiscibility region of type **b** can be terminated also by the double critical endpoint N'N (L_1=L_2-G) in ternary systems when two critical endpoints of the same nature L_1=L_2-G coincide. However, the experimental examples of such phase behavior were found only in nonaqueous systems, see for instance [9]. Fig. 3b shows also the eutonic behavior of solubility surface of HgI_2 and PbI_2 (both surfaces have a slope directed onto the eutonic composition at temperature minimum) and the immiscibility phenomena in solid saturated solutions (curves L-LN).

*Ternary class **1-2-1**.* Solubility behavior in this ternary class is characterized by the increasing of solubility of type **2** salt with increasing a concentration of the second salt (type **1** salt) and by the change of sign of temperature coefficient of salt solubility (t.c.s.) from negative to positive in ternary solutions. Such phase behavior was observed in the system NaCl – Na_2SO_4 – H_2O, KCl – K_2SO_4 – H_2O, K_2CO_3 – Na_2CO_3 – H_2O, Na_2HPO_4 – Na_3PO_4 –

H_2O etc. Fig. 4 show the intersection of solubility isotherms in the systems NaCl – Na_2SO_4 – H_2O and KCl – K_2SO_4 – H_2O [3, 4], where the negative t.c.s of a salt of type **2** in the dilute solutions becomes positive as the concentration of salts increases. Eutonic solutions, as well as in ternary systems of class **1-1-1**, are characterized by increasing of salt concentration with temperature (Fig. 4) and by pressure maximum (curves for NaCl – Na_2SO_4 – H_2O, KCl – K_2SO_4 – H_2O and KF – LiF– H_2O systems shown in Fig. 1).

The metastable immiscibility region, spreading from the binary subsystem of type **2**, usually does not transform into stable equilibria. Nevertheless, the tie-line form of solubility isotherms (such as the 360 and 370 ^oC isotherms in Fig. 4b) shows that the metastable immiscibility region takes place very close to the stable solubility surface. A transition of the metastable immiscibility region into stable equilibria through the immiscibility of solid saturated solutions at vapor pressure was established in the system Na_2HPO_4 – Na_3PO_4 – H_2O [8], where both water-salt subsystems have the immiscibility regions of type **d** that is stable in the Na_2HPO_4 – H_2O system (type **1d**) and metastable in the Na_3PO_4 – H_2O system (type **2d**).

In the case when the metastable three-phase immiscibility region of type **d** spreading from the binary subsystem of type **2d** does not transform into stable equilibria, a homogeneous supercritical fluid region is bounded by the continuous monovariant critical curve pQ. The first experimental data on a behavior of the critical curve pQ in a ternary system with metastable three-phase immiscibility region were obtained recently for the system H_2O – Na_2CO_3 – K_2CO_3. Fig. 5a shows that the curve pQ starts in the critical endpoint "p" as a critical endpoint locus of the nature L=G-S and transforms continuously into the equilibrium L_1=L_2-S with increasing of pressure (and temperature) on the way to the critical endpoint Q. Vapor pressure measurements of unsaturated ternary solutions at 425^{o}C show that the vapor pressure is increasing upon addition of Na_2CO_3 to the aqueous K_2CO_3 solutions in spite of a general increase in concentration (Fig. 5b). As a result the critical curve L=G, which is originated in the critical point K (L=G) of the aqueous K_2CO_3 solution and bounded the isothermal two-phase region L-G spreading from the binary K_2CO_3 - H_2O system, is directed toward higher pressure with increasing of the Na_2CO_3 content. This critical curve interests the solubility surface of Na_2CO_3 at the point pQ (L=G-S or L_1=L_2-S), which belongs to the ternary critical curve pQ (Fig. 5b). Critical point pQ corresponds to the maximum pressure of three-phase region L-G-S (or L_1-L_2-S at the highest pressures) in isothermal conditions (Fig. 5a).

*Ternary class **2-2-1**.* Two types of ternary phase behavior were established in the experimental studies of ternary systems with two binary water-salt subsystems of type **2** complicated with immiscibility phenomena (type **2d**) [3, 4]. In the first case the three-phase immiscibility region of ternary mixtures is retained in metastable conditions at any ratio of salt components including the eutonic solution. Another type of phase behavior takes place when the metastable immiscibility region becomes stable in ternary solutions. As a result the joint solubility of two salt components increases drastically, because the immiscibility region separates the eutonic and the solubility curves. The t.c.s in eutonic solutions becomes positive and critical phenomena in these solutions saturated with two solid phases are absent. Such behavior was found in the ternary systems H_2O – K_2SO_4 – $KLiSO_4$ and H_2O – SiO_2 – $Na_2Si_2O_5$ [4]. As one can see from Fig. 6, a transition of metastable immiscibility region into stable equilibria in the systems H_2O – SiO_2 (Qz) – $Na_2Si_2O_5$ (Ds) is indicated as a strong decrease of critical temperature and pressure (critical curve $N_{Ds}N_{Qz}$) up to 200 ^oC at vapor pressures and in appearance of the continuous eutonic curve (L-G-S_{Qz}-S_{Ds}) with a maximum of vapor pressure. Fig. 6 also depicts another type of phase behavior in the ternary system $Na_2Si_2O_5$ (Ds) – Na_2SiO_3 (Ms) – H_2O, where the eutonic solution is terminated by the second critical endpoint Q_{DsMs} similar to the solubility curves in the binary subsystems H_2O –

$Na_2Si_2O_5$ and H_2O – Na_2SiO_3 that are terminated in the critical endpoints Q_{Ds} and Q_{Ms}.

This example demonstrates that one ternary class can have various types of phase behavior and several versions of phase diagram even in the case when the types of phase diagrams of constituting binary subsystems are exactly the same.

CONCLUSION

The review of available experimental data on sub- and supercritical phase behavior in ternary water-salt systems not only confirms a general position formulated in the first sentence of the paper, but permits to conclude that all ternary phase equilibria are the stable and metastable equilibria spreading from the constituting binary subsystems and the equilibria, which are a result of an intersection of these "spreading" equilibria between each other. Totally new equilibria appear only in the case when the ternary solid phase is generated as a product of chemical reaction between three components.

ACKNOWLEDGEMENTS

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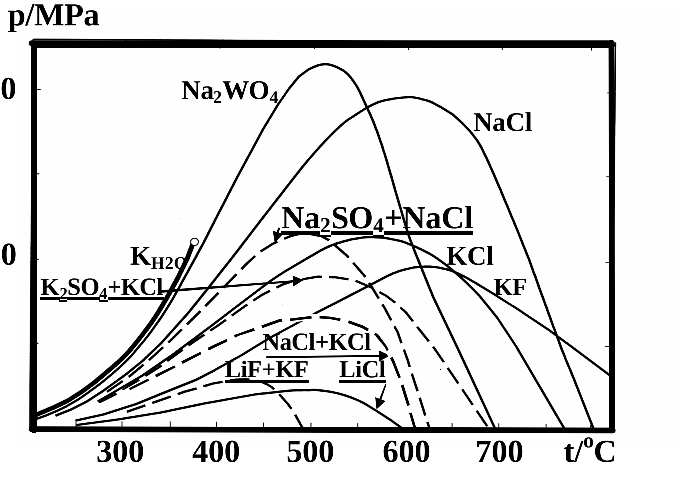

Figure 1 p-t projections of the 3-phase solubility (solid lines) and eutonic (dashed lines) curves.

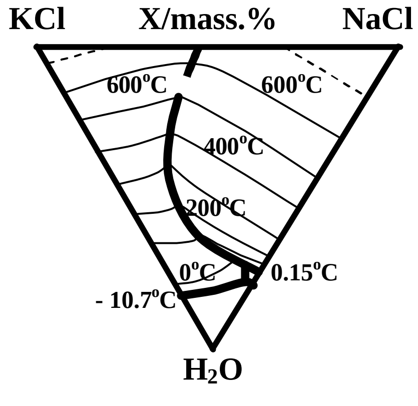

Figure 2 Solubility isotherms at vapor pressure in the system NaCl – KCl – H_2O

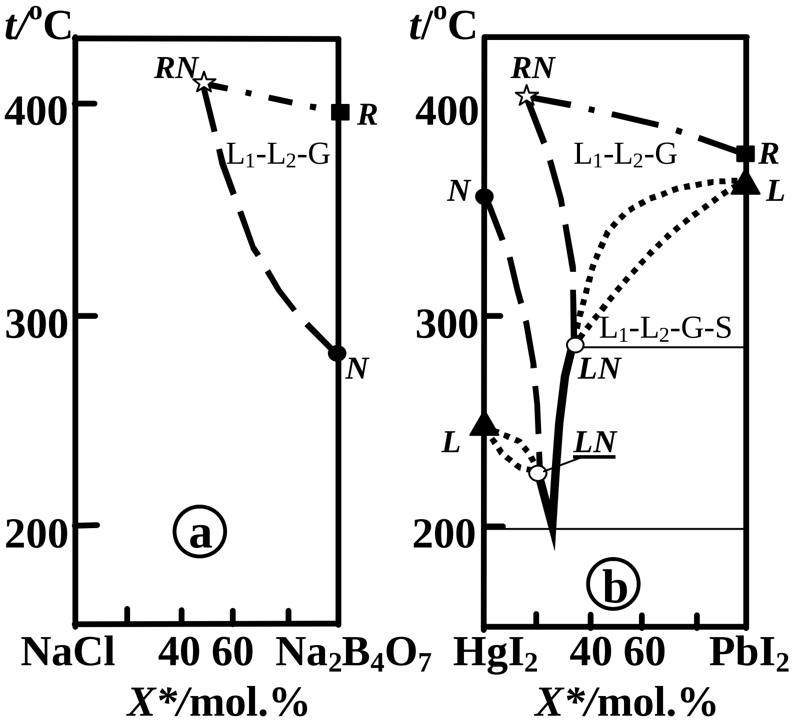

Figure 3 **t-X*** projections of immiscibility regions in ternary systems NaCl – $Na_2B_4O_7$ – H_2O (a) [6] and HgI_2 – PbI_2 – H_2O (b) [7].
X* = 100 $X_1/(X_1+X_2)$, where X_1 and X_2 are the molar amounts of salts in aqueous solutions.

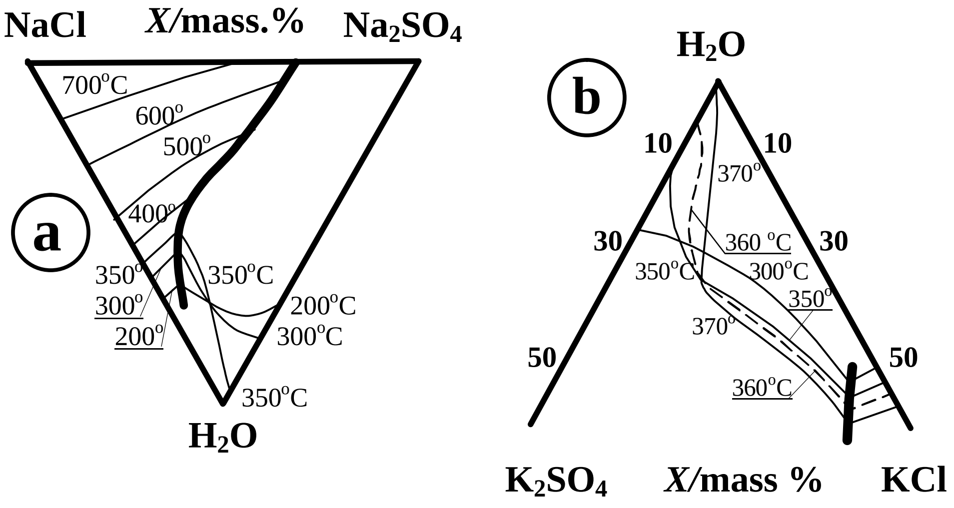

Figure 4 Solubility isotherms at vapor pressure in the systems NaCl – Na_2SO_4 – H_2O (a) and KCl – K_2SO_4 – H_2O (b) [3, 4].
Solid and dashed lines show the composition of solid saturated liquid solutions; heavy lines are the composition of liquid solutions saturated with two solid phases.

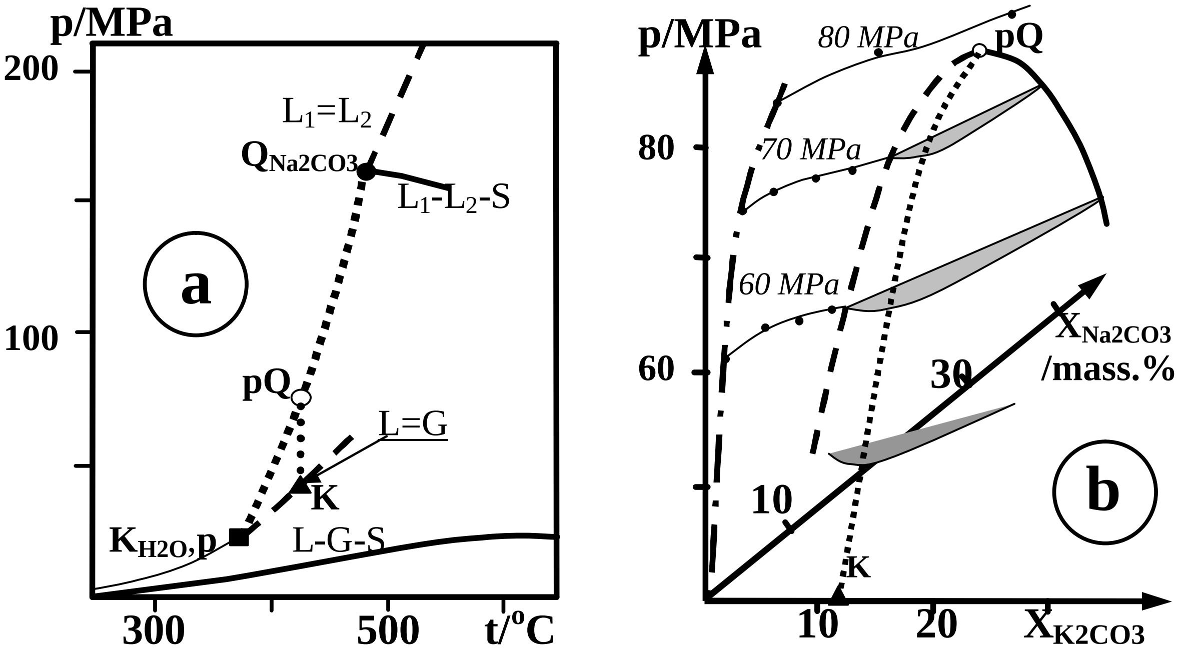

Figure 5 **p-t** projection of supercritical phase equilibria (a) and three-dimensional **p-X** isotherm (425 °C) (b) of the systems Na_2CO_3 – H_2O, K_2CO_3 – H_2O and Na_2CO_3 – K_2CO_3 – H_2O.

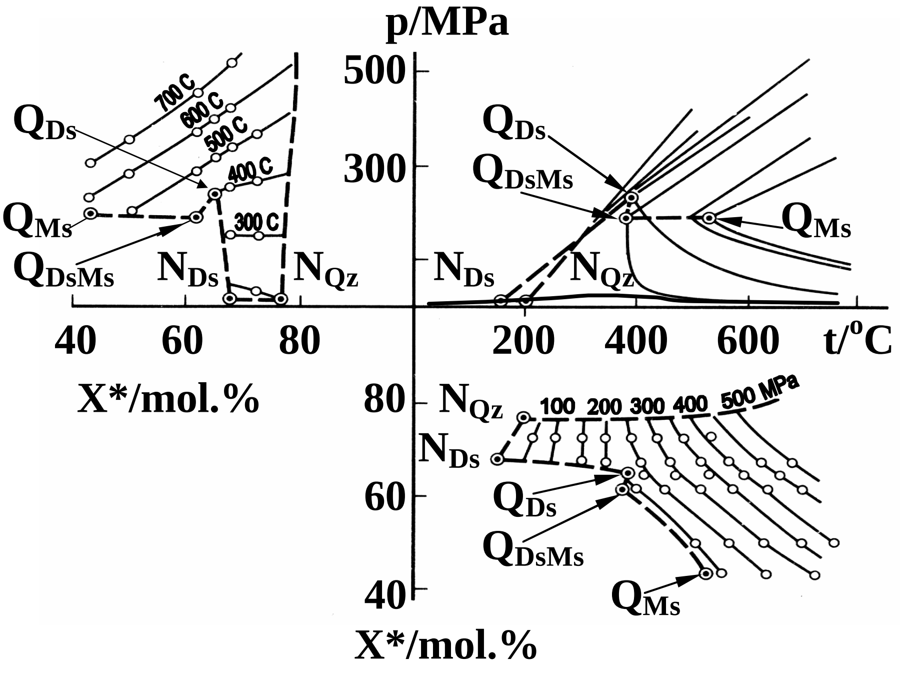

Figure 6 **p-X***, **p-t** and **t-X*** projections of the critical surfaces in ternary systems SiO_2 – $Na_2Si_2O_5$ – H_2O and $Na_2Si_2O_5$ – Na_2SiO_3 – H_2O [4].
$X^* = 100\ X_{SiO2}/(X_{SiO2} + X_{Na2O}$, where X_{SiO2} and X_{Na2O} are the molar amounts of SiO_2 and Na_2O in aqueous solution.