Theoretical Derivation and Experimental Study of Ternary Water-Salt Systems with Supercritical Fluid Equilibria

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The method of continuous topological transformation of phase diagrams was used to develop systematic classifications for binary systems with components of different volatility and for the theoretical derivation of ternary phase diagrams with one volatile component [1, 2]. Several versions of phase diagrams were obtained for ternary systems with a heterogenization of homogeneous supercritical fluids. Two of these versions were confirmed by the recent experimental studies of hydrothermal equilibria.

Supercritical fluid (SCF) equilibria (where the fluid is homogeneous at any pressure) in some binary systems with volatile and nonvolatile components (in particular, in the water-salt systems) take place not only at temperatures above the critical points of both components but also at lower temperatures. Such "low-temperature" SCF equilibria arise as a result of critical phenomena in solid saturated solutions (critical endpoints ***p*** and ***Q***) in the systems of type **2**, where the melting temperature of the nonvolatile component is above the critical temperature of the volatile one, and takes place in the temperature range between points ***p*** and ***Q.*** In the case of binary systems of type **1**, the melting temperature of nonvolatile components can be above or below the critical temperature of volatile ones, and the "low-temperature" SCF equilibria are absent. If the binary subsystems with components of different volatility in the ternary system belong to the different types (types **1** and **2**), the "low-temperature" SCF equilibria spreading from the binary subsystem of type **2** should transform (as a result of heterogenization of the homogeneous SC fluid) into liquid-gas equilibria that is typical for the binary system of type **1**.

The experimental studies of ternary systems K_2CO_3 – Na_2CO_3 – H_2O and KCl – K_2SO_4 – H_2O (where the binary subsystems K_2CO_3 – H_2O and KCl – H_2O belong to type **1**, and Na_2CO_3 – H_2O and K_2SO_4 – H_2O belong to type **2**) show two versions of a heterogenization process for the SC fluid. A separation of the three-component homogeneous fluid saturated with a salt into two solutions occurs as a result of critical phenomena taking place along the critical curves starting in the nonvariant critical points ***p*** and ***Q*** of type **2** binary subsystem. Most likely, these two critical curves in the system K_2CO_3 – Na_2CO_3 – H_2O are joined in one monovariant critical curve ***pQ*** with a maximum content of K_2CO_3 in the double critical endpoint. In the case of the system KCl – K_2SO_4 – H_2O, the critical curves starting in the points ***p*** (g=l-s_{K2SO4}) and ***Q*** (l_1=l_2-s_{K2SO4}) are directed to high temperature but do not join. They end in the ternary nonvariant critical points ***pR*** (l_1=g-l_2-s_{K2SO4}) and ***QN*** (l_1=l_2-g-s_{K2SO4}), which terminate the four-phase immiscibility region l_1-l_2-g-s_{K2SO4}. The monovariant critical curves with equilibria l_1=g-l_2 and l_1=l_2-g start from the points ***pR*** and ***QN*** toward high temperatures and intersect in the tricritical point ***RN*** (l_1=l_2=g).

The work was supported by the RFBR (grant 04-03-32844) and RAS (grant 9P1.17)

[1] V.M. Valyashko, *Phys. Chem. Chem. Phys.* **4**, 1178 (2002).
[2] V.M. Valyashko, *Pure Appl. Chem.* **74**, 1871 (2002).