LIQUID PHASE SPLITTING AND CRITICAL STATES IN QUATERNARY SYSTEMS WITH CHEMICAL REACTIONS: NEW EXPERIMENTAL DATA

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In this paper, we briefly present the review of experimental data on solubility, liquid-liquid equilibrium (LLE), chemical equilibrium (CE) and critical states of LLE in the systems with chemical interaction which have been obtained in our research group in recent years. These data relate to quaternary systems with reactions of esterification and hydrolysis of carboxylic acid esters. The new data sets were obtained for the following systems: formic acid + ethanol + ethyl formate + water; acetic acid + ethanol + ethyl acetate + water; acetic acid + n-propanol + n-propyl acetate + water; acetic acid + n-butyl alcohol + n-butyl acetate + water; propionic acid + ethanol + ethyl propionate + water; propionic acid + n-propanol + n-propyl propionate + water; propionic acid + n-butanol + n-butyl propionate + water. Some of the references on few recent papers are listed below [1-4]. In all systems, the presence of water as a component leads to limited mutual solubility. These results include the data both for quaternary mixtures and for binary and ternary subsystems. The compositions of critical states of LLE were also determined.

The study of solubility was carried out by "cloud-point technique" method with some modifications (as a rule, at polythermal conditions). In the LLE investigations we used gas chromatography (GC) and nuclear magnetic resonance (NMR) methods for analytical determination of phase compositions. Experimental LLE data were correlated using NRTL model and compared with the values calculated by UNIFAC model.

In this presentation, we will discuss some general features of the topology of phase diagrams of multicomponent systems with chemical reactions and limited solubility. For example, for industrial applications, the fact of establishing CE in a homogeneous area or in the region of reaction mixture splitting is of interest. The answer to this question is given by the data on the relative disposition of the binodal surface and the CE surface in the composition tetrahedron. A special case is the discussion of relatively new singularities such as manifolds of critical states. The location of these manifolds in the concentration space is also of particular interest: conducting processes in the supercritical region guarantees the absence of splitting, for instance, during a reaction. In the case of the systems with ester synthesis reaction at polythermal conditions this manifold is a surface in composition tetrahedron with a curve corresponding to chemically equilibrium critical states. The polythermal critical surfaces could be constructed on the basis of the data on the position of critical curves in a tetrahedron of composition at different temperatures. Some illustration of critical surfaces and critical curves for chemically equilibrium states will be presented.

We believe that these new data will be useful not only for the development of thermodynamic databases, but also for the industrial design of the synthesis of esters.

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[4]   A. Samarov, M. Trofimova, M. Toikka, A. Toikka, *J. Chem. Eng. Data,* 2020, 65, 2578-2582.