

Solubility and critical phenomena in reactive liquid–liquid systems*

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Abstract: The goal of this work is to consider solubility phenomena in reactive fluid mixtures with liquid-phase splitting. One of the main tasks is to analyze peculiarities of liquid–liquid (LL) systems with equilibrium and nonequilibrium chemical reaction. The special aim is to consider the critical states in these systems. The reactive liquid–liquid equilibrium (LLE) is treated on the base of phase rule. The topology of diagrams of reactive LLE is discussed for some types of binary and ternary systems. Examples are presented of a possible transformation of phase diagrams caused by the shifting of chemical equilibrium and by changes in the shape of the binodal. The transformations resulting in the reactive critical phase formation are considered. Quaternary mixtures are also discussed with the use of experimental data on the solubility in the system with *n*-propyl acetate synthesis reaction. The mutual crossing of the chemical equilibrium surface and binodal in the composition tetrahedron leads to the origin of the area of simultaneous chemical and LLE with two critical points (reactive critical phases). The shape of the curve of simultaneous chemical and phase equilibrium is also presented in the square of transformed composition variables.

Keywords: chemical equilibrium; critical phenomena; liquid–liquid equilibrium; reactive systems; solubility.

INTRODUCTION

Phase transitions accompanied by chemical reactions are significant from both basic and applied points of view. The simultaneous phase and chemical equilibrium has been studied in many experimental and theoretical works, for example, see [1–11]. The coupled reactive and phase separation process gives an opportunity to carry out syntheses in more effective ways. Reactive separation is the base of the development of energy- and resource-saving chemical engineering processes and is considered an important direction of green chemistry [12]. One of the well-known examples is reactive distillation, which has numerous industrial applications [13–18].

Liquid–liquid (LL) phase transitions and equilibria are the basis of separation processes such as extraction and other practices in fluid systems with limited miscibility. Thermodynamic aspects of liquid–liquid equilibria (LLE) have been investigated intensely since the beginning of the last century up to the present time, for example, see [19–21]. These investigations include experimental studies of LLE in binary and multicomponent systems, theoretical considerations such as the analysis of thermo-

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dynamic singularities, classification of LL phase diagrams, etc. One of the main aspects of the study of phase equilibrium is the determination of critical points and critical manifolds (curves, surfaces). In the case of LLE in binary systems, the critical states usually are considered as a critical (plait) point for diagrams “composition–temperature (or pressure)”. In ternary LL systems, critical points may exist for some types of immiscibility area of isothermal–isobaric phase diagrams. For ternary LLE phase diagrams at variable temperature, the critical curve can be considered (formed as a continuous set of critical points at different temperatures). In general, the critical curves are sets of critical points resulting from shifts of external conditions (e.g., temperature changes). Some recent experimental data on critical curves disposition had been presented in [22,23]. In the case of quaternary LLE, the critical curve may be realized at isothermal–isobaric conditions. Such a critical curve in the composition tetrahedron is formed by the set of critical points on the binodal surface. The critical states in multicomponent LL systems could be realized not only as critical points and curves but also as surfaces and hypersurfaces in the multidimensional thermodynamic space. The type of the manifold should be in agreement with the phase rule that is discussed in the next section of this paper.

The data on solubility and LLE are available for a large variety of fluid systems but only a few papers were devoted to the thermodynamic study of LL systems with chemical reactions in solutions (e.g., see [24–28]). Such a limited number of works on simultaneous chemical and LLE may be explained by a relatively poor database on phase equilibria in reactive systems in general. Chemical reactions in LL systems may lead to new singularities of phase diagrams and significantly influence the run of the LL separation process. Accordingly, the critical states of LLE in the case of a nonequilibrium chemical reaction or chemical equilibrium are important objects for the basic thermodynamic analysis. In this paper, we will consider some aspects of the behavior of LL reactive systems on the basis of the thermodynamic approach. For the sake of simplicity, we will consider a few examples (a few types of reactive LL systems), which would be most important in the framework of the general treatment. In particular, we will consider only cases of two (or one) liquid phases and one independent chemical reaction in a solution.

PHASE RULE

For the states of simultaneous phase and chemical equilibria, the phase rule should be written in the following form [29–34]:

$$f = n + 2 - r - k \quad (1)$$

where f , n , and r are numbers of degrees of freedom, numbers of components (chemically distinct species), and phases accordingly; k is the number of equilibrium chemical reactions. For two liquid phases and one equilibrium chemical reaction, the phase rule gives

$$f = n + 2 - r - k = n + 2 - 2 - 1 = n - 1 \quad (2)$$

According to eq. 2, for varying pressure and temperature, the binary systems in the states of simultaneous phase and chemical equilibria have one degree of freedom (monovariant equilibrium), ternary systems have two degrees of freedom (bivariant equilibrium), and quaternary systems have three degrees of freedom (polyvariant equilibrium). It follows that in binary systems, simultaneous phase and chemical equilibrium should be not considered at constant temperature and pressure ($T, P = \text{const}$): at $P = \text{const}$ (or $T = \text{const}$) invariant states ($f = 0$) exist. Invariant states in ternary systems will exist at $T, P = \text{const}$. For $P = \text{const}$ (or $T = \text{const}$) ternary systems will be in a monovariant equilibrium. Simultaneous phase and chemical equilibrium in quaternary systems at isothermal–isobaric conditions ($T, P = \text{const}$) would be a monovariant state. Therefore, at isothermal–isobaric conditions the simultaneous phase and chemical equilibrium in quaternary systems is presented as a curve in the composition tetrahedron. The same curve may be in the case of ternary simultaneous phase and chemical equilibrium but at variable temperature or pressure.

In the case of the critical state of LLE, the number of degrees of freedom will be reduced by unity. It follows from the rule that for the determination of the variance the critical phase should be taken into account thrice [29,33,34]. In other words, in the case of a single critical phase the value $r = 3$ must be substituted in the phase rule (eq. 1) and the variance of the critical phase without chemical reactions is

$$f = n + 2 - r = n + 2 - 3 = n - 1 \quad (3)$$

Accordingly, the critical states of a binary nonreactive system at variable pressure and temperature are presented as the critical curve. At constant pressure, such a system is in invariant equilibrium and the critical point corresponds to this state. For ternary and quaternary systems, the variance also depends on external conditions (i.e., constant or varying pressure and temperature). For example, the critical states of a nonreactive quaternary LL system at isothermal–isobaric conditions should be presented as a curve in the composition tetrahedron.

In the case of the reactive critical phase, the variance would be reduced additionally. For the critical phase and one equilibrium chemical reaction, a number of degrees of freedom are determined by following equation:

$$f = n + 2 - r - k = n + 2 - 3 - 1 = n - 2 \quad (4)$$

At isothermal–isobaric conditions for the critical phase and one equilibrium chemical reaction, the variance is reduced (two numbers of degree of freedom less) and the following equation holds:

$$f = (n + 2 - r - k) - 2 = (n + 2 - 3 - 1) - 2 = n - 4 \quad (5)$$

Hence, in quaternary reactive system at isothermal-isobaric conditions the critical phase in chemical equilibrium is in the invariant state. Such equilibria in the systems with lesser numbers of components could not exist at isothermal-isobaric conditions.

For the thermodynamic analysis of reactive systems, it is necessary also to consider the possible geometry of chemical equilibrium manifolds. In the case of one equilibrium chemical reaction in the homogeneous solution (single-phase system), the phase rule leads to the following equation:

$$f = n + 2 - r - k = n + 2 - 1 - 1 = n \quad (6)$$

Therefore, at isothermal–isobaric conditions the manifold of chemical equilibrium in a ternary system would be a curve, in a quaternary system it would be a surface in the composition simplex (triangle or tetrahedron). Liquid-phase splitting reduces the variance and accordingly changes the geometry of the chemical equilibrium manifold. For example, the variance of a quaternary two-phase (LL) solution in chemical equilibrium states at $T, P = \text{const}$ is determined by the phase rule as follows:

$$f = n + 2 - r - k = 4 + 2 - 2 - 1 = 3 \quad (7)$$

At isothermal–isobaric conditions, the variance of simultaneous LLE and chemical equilibria of a quaternary mixture would be unity and would correspond to the curve in composition tetrahedron.

If systems are in chemically nonequilibrium states the phase rule should be considered as in the case of nonreactive systems.

BINARY REACTIVE LL SYSTEMS

The variance of a binary critical phase with the equilibrium chemical reaction



(R_i – symbol of specie i) is zero. Therefore, a critical point may exist at definite values of pressure and temperature. Three diagrams on Fig. 1 represent mutual position of the LLE curve and chemical equilibrium curve (as a function of T) for different values of pressure. Solid lines denote the LLE curves; dotted lines show the dependence of chemical equilibrium on the temperature. The dependence of

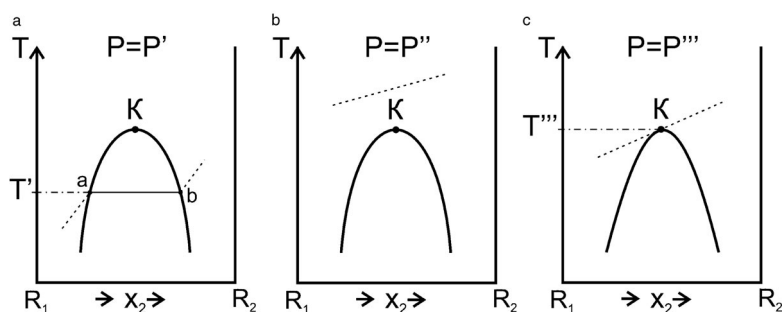


Fig. 1 Mutual disposition of LLE curve and chemical equilibrium curve (as a function of T) for different values of pressure in binary reactive system. Solid lines: curves of LLE; K : critical points; dotted lines: shifting of chemical equilibrium with temperature at different pressures: 1a: $P = P'$; 1b: $P = P''$; 1c: $P = P'''$.

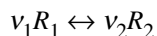
chemical equilibrium on the temperature could be determined by well-known thermodynamic relationships (e.g., Gibbs–Helmholz relations); the dotted lines on Fig. 1 correspond to possible shifting of chemical equilibrium with temperature. The position of both curves also depends on the value of pressure.

At pressure $P = P'$ (Fig. 1a), the temperature shifting of chemical equilibrium in homogeneous area to $T = T'$ will result in the state of simultaneous LL and chemical equilibrium. Hence, the state of chemical equilibrium of reaction 8 belongs to the area of liquid-phase splitting. This state is an invariant equilibrium at a given value of pressure (P'). For variable pressure and temperature, such states of simultaneous LL phase and chemical equilibria are monovariant equilibria.

At pressure $P = P''$ (Fig. 1b), the states of chemical equilibrium belong to the homogeneous region under any temperature shifts. The region of liquid-phase splitting does not correspond to the chemical equilibrium at a given value of pressure (P'').

At pressure $P = P'''$ (Fig. 1c), the temperature shifting of chemical equilibrium in the homogeneous region to $T = T'''$ will result in the critical point of LLE and chemical equilibrium. In other words, the critical phase of LLE is also the chemically equilibrium one. According to eq. 4, this state is an invariant equilibrium. Such equilibrium (binary reactive critical phase) may exist only at definite values of pressure and temperature: $P = P'''$, $T = T'''$.

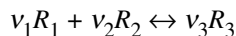
Now we had considered the reaction between two species in a form (reaction 8) when stoichiometric numbers are unit. The case of arbitrary values of stoichiometric numbers, i.e., the reaction



(where v_i is the stoichiometric number of specie i) could be considered in the same way.

TERNARY REACTIVE LL SYSTEMS

The shape of chemical equilibrium manifolds and phase diagram topology depends on the number of components (species) and on the values of stoichiometric numbers. In a ternary system with the equilibrium reversible reaction in the homogeneous liquid phase at constant pressure and temperature



chemically equilibrium states correspond to a curve in the composition triangle (Fig. 2). Hereinafter, we will use the general (algebraic) form of reaction equations

$$\sum_{i=1}^n v_i R_i = 0 \quad (9)$$

where stoichiometric numbers for reaction products are defined as positive numbers and, for reactants, negative numbers. According to eq. 6, the curve of chemical equilibrium is a monovariant equilibrium curve at $T, P = \text{const}$. An experimental example of such a system with data on the position of the chemical equilibrium curve is presented in [9] for methyl cumyl ether synthesis reaction. For systems with liquid-phase splitting, the shape of ternary phase diagrams becomes more complex, especially in the cases of the mutual crossing of binodal and chemical equilibrium curves in the composition triangle (at $T, P = \text{const}$). The points of these crossings correspond to simultaneous chemical and LL phase equilibria. Accordingly, both the condition of phase equilibrium

$$\mu_i^{(1)} = \mu_i^{(2)} \quad (10)$$

(where $\mu_i^{(r)}$ is the chemical potential of specie i in phase r) and the condition of chemical equilibrium

$$\sum_{i=1}^n v_i \mu_i = 0 \quad (11)$$

must be satisfied simultaneously. It is evident that eq. 11 is valid for all compositions belonging to the tie-line irrespective of stoichiometric numbers values.

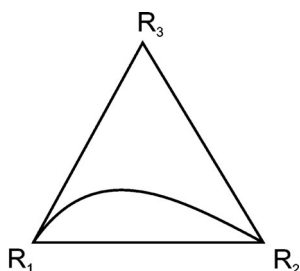


Fig. 2 Curve of chemical equilibrium of reaction 9 in composition triangle (solid line).

The LL envelope may be considered as a border between two (or a few) branches of the chemical equilibrium curve. These branches are connected by the tie-line, which may be also considered as a part of the chemical equilibrium curve in the immiscibility range. The tie-line that connects two points of LLE in chemical equilibrium is called “unique reactive tie-line” [24,25]. Some thermodynamic aspects of the theory of LLE in ternary reactive systems are discussed in [24–27]; in [26] a brief classification of ternary reactive LL systems is presented. Now we will discuss singularities in ternary reactive systems with limited miscibility for the case when critical points exist.

Figures 3 and 4 present two examples of ternary reactive systems with limited solubility where the intersection of the chemical equilibrium curve with the binodal exists. The difference between the diagrams in Figs. 3 and 4 is determined by the position of unique reactive tie-lines. The variant in Fig. 3 is the case of one unique reactive tie-line. The changing of external conditions (e.g., temperature) will lead to the shift of chemical equilibrium and the transformation of the LL envelope (binodal curve). Depending on the physical–chemical nature of the system, these changes may result in the diagram at Fig. 5 where the chemical equilibrium curve is passing through the critical point of LLE. According to eq. 4, for isobaric conditions this point corresponds to the invariant equilibrium.

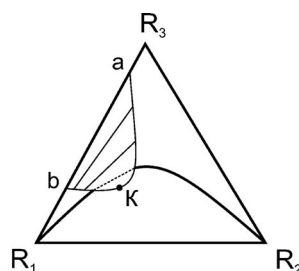


Fig. 3 Diagram of ternary reactive system with intersection of chemical equilibrium curve and binodal: case of one unique reactive tie-line (dotted line). Solid line: curve of chemical equilibrium; curve *ab*: binodal; straight lines: tie-lines; *K*: critical point.

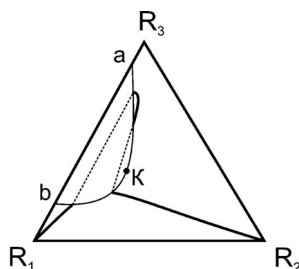


Fig. 4 Diagram of ternary reactive system with intersection of chemical equilibrium curve and binodal: case of two unique reactive tie-lines (dotted lines). Solid line: curve of chemical equilibrium; curve *ab*: binodal; *K*: critical point.

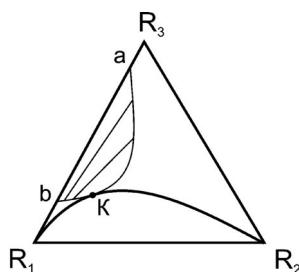


Fig. 5 Diagram of ternary reactive system: chemical equilibrium curve passing through critical point. Solid line: curve of chemical equilibrium; curve *ab*: binodal; straight lines: tie-lines; *K*: critical point.

The variant in Fig. 4 is the case of two unique reactive tie-lines. After the change of the system temperature and the subsequent shifts of the chemical equilibrium and binodal curves, the diagram can be transformed to the view in Fig. 6. As a result, one unique reactive tie-line still exists, one of the branches of the chemical equilibrium curve passes through the critical point of LLE and connects this point with the unique reactive tie-line. For isobaric conditions it is also the invariant state of the chemical equilibrium of the critical phase.

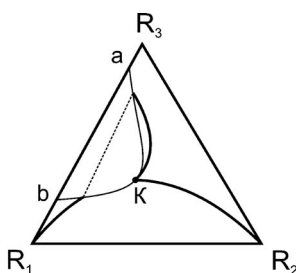
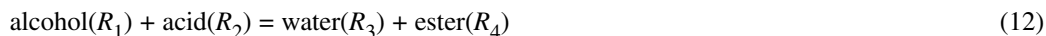


Fig. 6 Diagram of ternary reactive system: chemical equilibrium curve passing through critical point and unique reactive tie-line (dotted line). Solid lines: curve of chemical equilibrium; curve *ab*: binodal; *K*: critical point.

QUATERNARY REACTIVE LL SYSTEMS

The quaternary reactive LL systems will be also considered on the basis of some examples. One should take into account the large variety of thermodynamically possible types of LLE diagrams both for ternary and quaternary systems. Therefore, we will confine ourselves to a relatively simple but important type of quaternary systems with limited solubility in only one binary subsystem (and accordingly, two ternary subsystems).

One of the practically important types of quaternary LL reactive systems is the system with esterification reactions



The absolute majority of available experimental data on phase equilibria were obtained for this kind of systems. Accordingly, we will consider quaternary LL reactive systems on the base of singularities of systems with the esterification reaction as an example. Due to typical immiscibility of water and esters, such quaternary systems (alcohol–acid–water–ester) have the limited solubility area in the composition tetrahedron. Nevertheless, most results of the studies of these reactive systems, practically all experimental data on the simultaneous chemical and phase equilibria, belong to the homogeneous area of liquid-phase compositions. The goal of these works first of all was the determination of vapor–liquid equilibria for all chemically equilibrium compositions of solutions; practically all datasets are related to completely miscible liquid mixtures (e.g., see [1,11,35–40]). The review of the data on phase equilibria in the systems with the esterification reaction is presented in [41]. Only a few experimental works include the datasets on phase processes in the reactive systems with limited miscibility, for example, data [42] for the residue curve map in the system lauric acid–*n*-propanol–*n*-propyl laurate–water. Most of the other works on phase transitions in LL reactive systems with the esterification reaction are related to some theoretical aspects or modeling, for example, see [8,14,43,44].

From our point of view, there are a few possible explanations for the existence of only very limited sets of data on the solubility in reacting systems (with the esterification reaction), i.e.,

- the esterification reaction usually has the equilibrium in the homogeneous area of the composition tetrahedron;
- the determination of chemical equilibrium (belonging to the homogeneous area only) is an experimental artifact or error.

The origin of the experimental error may be caused by the complex processes in LL reactive systems. One should take into account the rates of three processes: phase transition and chemical reactions in two liquid phases. All these factors significantly influence the coupled process. The rate of the establishment of LL phase equilibrium may be of the same order as of the establishment of chemical equilibrium (especially without shaking the solution). Moreover, the reaction rates in the phases (for the esterification—“water” and “organic” medium) also may significantly differ from one another. Because

of these factors, the reacting LL systems are also of great interest from the thermodynamic point of view: one could expect various coupled phenomena.

The compositions of the system with the equilibrium reaction of esterification–ester hydrolysis (eq. 12) should be presented in the composition tetrahedron. Solutions in chemical equilibrium belong to a surface inside this tetrahedron. According to the equation of reaction (eq. 12) all four ternary subsystems of the quaternary system are in chemically nonequilibrium states. Two binary systems ($R_1 - R_2$ and $R_3 - R_4$) are also in chemically nonequilibrium states, but the other four binary subsystems ($R_1 - R_3$, $R_1 - R_4$, $R_2 - R_3$, $R_2 - R_4$) are nonreactive. These four binary subsystems (and points of pure substances) should be considered as parts and borders of the surface of chemical equilibrium in the composition tetrahedron. The typical shape of the chemical equilibrium surface is presented in Fig. 7 for the equilibrium of *n*-propyl acetate synthesis reaction ($T = 313,15$ K) [45,46]. We use Cartesian coordinates, and accordingly the composition space is the irregular tetrahedron.

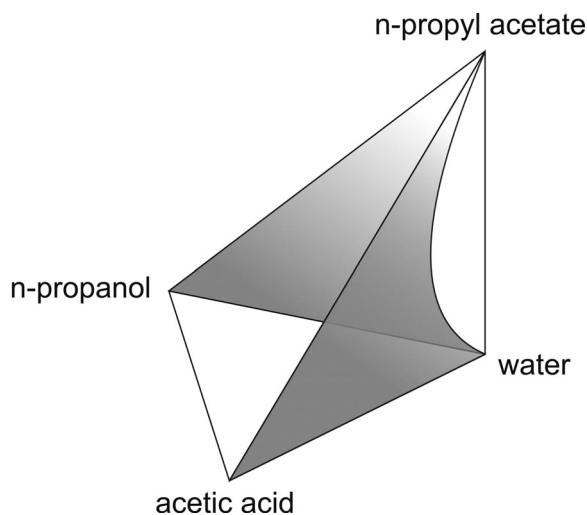


Fig. 7 Surface of chemical equilibrium of *n*-propyl acetate synthesis reaction ($T = 313.15$ K).

The surface of solubility (binodal) in the composition tetrahedron is presented in Fig. 8. This surface is constructed on the base of our experimental data for 313.15 K [28]. The mutual position of both surfaces, chemical equilibrium and solubility, gives the area of their intersection that is presented in Fig. 9. This is a region of simultaneous phase and chemical equilibria. The border of this region (i.e., the curve of surface intersections) is a binodal that corresponds both to LLE and chemical equilibrium. The LLE critical curve is running from one ternary critical point to another and also passes through the region of simultaneous LL and chemical equilibrium. Accordingly, there are two critical points at the surfaces intersection curves (Fig. 9). Only these two points correspond to the reactive critical phases in chemical equilibrium. All other points on the critical curve belong to the chemically nonequilibrium area. The composition area of immiscibility at the chemical equilibrium surface is rather small; probably it is a reason why the effect of the splitting of chemically equilibrium solutions in this system was not experimentally determined before.

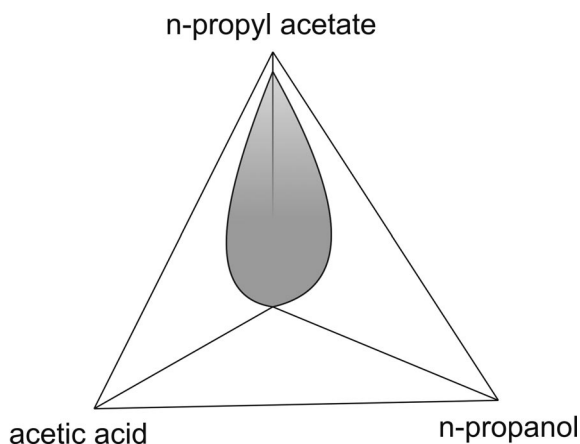


Fig. 8 Binodal surface in the system acetic acid–*n*-propanol–water–propyl acetate ($T = 313.15$ K).

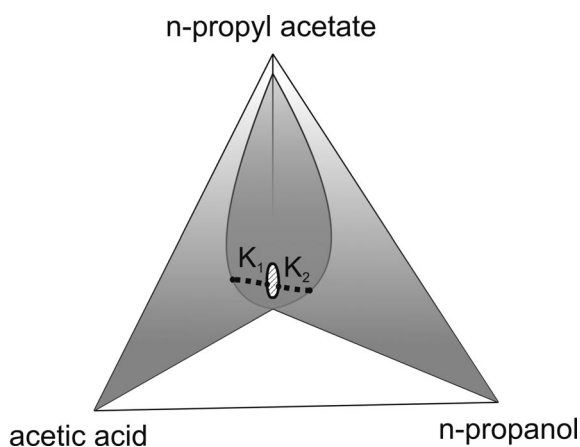


Fig. 9 Area of simultaneous chemical equilibrium and LLE in the system acetic acid–*n*-propanol–water–*n*-propyl acetate at $T = 313.15$ K (white stroked region at binodal surface in composition tetrahedron). Dotted line: critical curve of LLE; K_1 and K_2 : critical points on the border of the area of simultaneous chemical equilibrium and LLE.

The *n*-propanol–acetic acid–water–*n*-propyl acetate system had been studied in numerous works, both in theoretical (modeling) and experimental research (e.g., kinetic study [47], chemical and vapor-liquid equilibria [48,49], solubility and LLE [28], residue curve map [50], modeling, and theoretical consideration [44,50]). In [44] the existence of the heterogeneous reactive azeotrope was predicted at the normal pressure on the base of the experimental data [48] and modeling; it also means that chemically equilibrium solutions should separate at least in the vicinity of the predicted azeotropic point. On the other hand, in the experimental study of the residue curve map [51] it has been noted that phase splitting was not observed through the whole experiments. In [44] it was also proposed that the experimental verification of reactive azeotrope LL transitions should be conducted at reduced pressure and temperature. This conclusion partly agrees with our experimental results [28]; at $T = 313.15$ K, the splitting of chemically equilibrium solutions has been determined but the reactive azeotrope is still in the homogeneous area. The detailed discussion and comparison of the data on the system with *n*-propyl acetate synthesis reaction has been carried out in [46].

The 3D graphs in Figs. 6–8 give mostly qualitative description of reactive phase diagrams. For quaternary reactive systems, 2D diagrams may be applied with the use of transformed composition vari-

ables [51,52]. In the case of reaction 12, all stoichiometric numbers are unit (+1 and -1) and transformed composition variables (α_i) are

$$\alpha_1 = x_1 + x_4$$

$$\alpha_2 = x_2 + x_4$$

$$\alpha_3 = x_3 - x_4$$

where x_i is the molar fraction of specie i . For the sum of variables, these equations yield

$$\alpha_1 + \alpha_2 + \alpha_3 = 1$$

Hence the composition space for α_i -variables would be a square. This 2D composition complex is convenient for the presentation of properties of reactive systems but for chemical equilibrium only. The area of simultaneous chemical equilibrium and LLE is presented in Fig. 10 in the square of the transformed composition variables. The border of this area is a binodal curve that belongs to both binodal and chemical equilibrium surfaces in the composition tetrahedron. Two critical points on this curve also correspond to the critical curve in the composition tetrahedron (Fig. 9).

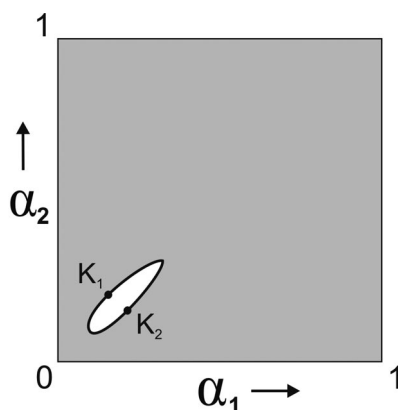


Fig. 10 Area of simultaneous chemical equilibrium and LLE in the square of transformed composition variables α_i (white region). Two critical points K_1 and K_2 also correspond to the critical line in composition tetrahedron.

The area of simultaneous LLE and chemical equilibrium both in the composition tetrahedron and in the square of the transformed composition variables may be considered as analogous to unique reactive tie-lines in ternary systems. Really, the composition spaces corresponding to the area of simultaneous equilibrium (in tetrahedron and square) represent a continuous set of tie-lines. Every tie-line connects two points of LLE at the surface of chemical equilibrium.

In spite of the scantiness of experimental data, such topological peculiarities of quaternary reactive systems with limited solubility should be considered as a possible variant of their phase behavior. One of the examples may be systems with the esterification reaction at different conditions considered in this chapter.

CONCLUSION

The liquid-phase splitting in the course of a chemical reaction leads to some new peculiarities of both chemical and LL phase equilibria. The conditions of simultaneous phase and chemical equilibria reduce the variance of the system, and accordingly the existence of critical states should be under special lim-

itations. For example, a nonreactive critical phase in a ternary system at isothermal–isobaric conditions is in the invariant state. In the case of a reactive system (in chemical equilibrium), the number of degrees of freedom is reduced; accordingly, the invariant equilibrium of a reactive critical phase in ternary systems at $T, P = \text{const}$ does not exist. In general, the topology of diagrams of LL reactive systems comprises new elements. Some of them were discussed for a few types of LL systems. At isothermal–isobaric conditions, the diagrams of quaternary reactive systems in simultaneous LL and chemical equilibrium include new elements (in comparison with nonreactive mixtures), e.g.,

- a binodal curve in the composition tetrahedron that belongs to the simultaneous phase and chemical equilibrium,
- critical points that correspond to reactive critical phases and belong to both surfaces (LLE and chemical equilibrium),
- a composition area of simultaneous LLE and chemical equilibrium, which may be considered as analogous to unique reactive tie-lines in ternary systems.

The solubility phenomena in fluid reactive systems are the subject of interest from both basic and applied points of view. The data on LLE and chemical equilibrium should be taken into account for such processes as chemical synthesis in splitting solutions, extraction in reactive systems, etc. The contemporary database on thermodynamic properties of reactive LL systems is rather limited and needs to be developed.

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