

Peculiarities of phase diagrams of reactive liquid–liquid systems*

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Abstract: The goal of this work is to consider some peculiarities of heterogeneous systems with chemical interactions. The main task is to analyze the features of liquid–liquid (LL) phase diagrams of the systems with equilibrium and nonequilibrium chemical reaction in solution. The consideration of topology of these phase diagrams should include additional elements, such as stoichiometric lines, chemical equilibrium (CE), and isoaffinity manifolds (i.e., curves, surfaces, or hypersurfaces of constant affinity). The thermodynamic conditions of mutual disposition of LL tie-lines, isoaffinity, and stoichiometric lines in ternary system are presented in the paper. Quaternary mixtures are discussed with the use of our experimental data on the solubility in the systems with ethyl acetate and *n*-propyl acetate synthesis reactions. The binodal and CE surfaces in these systems are presented. The opportunity of simultaneous LL and CE is discussed. The special aim is to consider the critical surfaces in these systems: the examples are presented on the basis of our experimental data.

Keywords: affinity; chemical equilibrium; critical phenomena; critical states; liquid–liquid equilibrium; phase diagrams; reactive systems.

INTRODUCTION

The studies of the heterogeneous systems with chemical reactions in solution are of significant importance from both basic and applied points of view. The coupled reactive and phase separation process gives well-known opportunities for the design of energy and resource-saving technological processes such as reactive distillation [1–6]. The physical-chemical study of simultaneous phase and chemical equilibrium (CE) was the object of various experimental and theoretical researches, for example, see [7–18]. Most of these works are devoted to vapor–liquid equilibrium (VLE) in reactive systems.

The aim of presented paper is to consider some peculiarities of liquid–liquid (LL) systems with chemical reactions in solution. The limited miscibility of the reacting mixture (i.e., liquid-phase splitting) leads to additional singularities of the phase diagrams. From a practical point of view, chemical interaction in solution may significantly influence the run of the LL separation process. The data on solubility and liquid–liquid equilibrium (LLE) are available for a large variety of nonreacting fluid systems [19,20] but only a few works were devoted to the thermodynamic study of LLE in reacting systems (e.g., see [21–25]).

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In the case of chemical reaction, the diagrams of the systems with LL envelope may include such additional elements as stoichiometric lines, curves (surfaces, hypersurfaces) of CE or constant affinity. A special interest for the basic thermodynamic analysis represents critical states of LLE in the case of a nonequilibrium chemical reaction or CE [23]. The critical states in multicomponent LL systems could be realized not only as critical (plait) points and curves but also as surfaces and hypersurfaces in the multidimensional thermodynamic space. One of the interesting recent results was an experimental determination of chemically equilibrium critical points of LLE in quaternary *n*-propanol–acetic acid–water–*n*-propyl acetate reacting system [23,24].

In this paper we present some of our new experimental and basic results on the behavior of LL reactive systems. For the sake of simplicity, we confine ourselves to a few types of diagrams of reacting LL systems and cases of two liquid phases with one chemical reaction in a solution.

SURFACES OF LIQUID–LIQUID AND CHEMICAL EQUILIBRIUM IN QUATERNARY SYSTEMS

The surfaces of phase and CE could be considered both for binary and multicomponent systems. According to phase rule, the numbers of degrees of freedom f in the systems with k equilibrium chemical reactions is determined by following equation [26–31]:

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

where n and r are numbers of components (chemically distinct species) and phases. Accordingly, the binary nonreactive system (or chemically nonequilibrium one) in the states of LLE has two degrees of freedom. At variable temperature (T) and pressure (P) these states of LLE are presented as surface in three-dimensional thermodynamic space “composition–temperature–pressure”.

The homogeneous binary system with one equilibrium chemical reaction (state of CE) also has two degrees of freedom. In three-dimensional thermodynamic space “composition–temperature–pressure” the CE in such systems should be presented as a surface. For simultaneous LLE and CE (i.e., CE in equilibrium two-phase binary system) the phase rule gives the following result:

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

Accordingly, in three-dimensional thermodynamic space “composition–temperature–pressure” the simultaneous LLE and CE in binary systems should be presented as a curve.

In the case of quaternary system at variable T and P the states of CE belong to hypersurface in five-dimensional thermodynamic space “composition–temperature–pressure” and the visual graphical presentation is impossible. The condition $T, P = \text{const}$ reduces the numbers of degrees of freedom

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

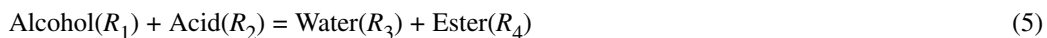
and CE could be presented as a surface in the composition tetrahedron. The same result $f = 2$ is valid for LLE in quaternary system without reaction or in the case of nonequilibrium chemical reaction: the binodal should be also presented as a surface in tetrahedron. We would remind that according to the phase rule the variance of systems in chemically nonequilibrium states should be the same as in the case of nonreactive systems.

The variance of a quaternary two-phase (LL) mixture in simultaneous LLE and CE at isothermal–isobaric conditions would be

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

such LLE and CE would correspond to the curve in composition tetrahedron.

There is a large variety of thermodynamically possible types of LLE diagrams both for ternary and quaternary systems. In this paper we will confine ourselves to practically important types of quaternary LL systems with esterification reactions



Usually, it is a relatively simple topological type of quaternary systems with limited solubility in only one binary subsystem “ester–water”. Accordingly, there are LL envelopes in two ternary subsystems and in quaternary system. Most of the available experimental data on phase equilibria in reacting mixtures were obtained for this kind of system [32]. Nevertheless, almost all the experimental data belong to the homogeneous area of liquid-phase compositions and simultaneous CE and VLE, e.g., see [1,32–40]. Only a few experimental works on reactive mixtures include the data on phase processes in the systems with limited solubility, for example, data [41] for the residue curve map in the system lauric acid–*n*-propanol–*n*-propyl laurate–water. Most of the other research on phase transitions in LL systems with chemical reactions is related to the modeling or some theoretical aspects, e.g., see [22,41,42].

Now we consider the surfaces of LLE and CE in two quaternary systems with esterification reaction: ethyl acetate and *n*-propyl acetate synthesis reactions.

Ethanol–acetic acid–water–ethyl acetate system has well-known practical significance, and phase equilibria in this system had been intensively studied. Most of the phase equilibrium data on this system corresponds to VLE [32]. The LLE data at 342.15 K (101.325 kPa) and 363.15 K (200 kPa) and phase diagrams had been obtained in work [43]. The LLE in ternary subsystem acetic acid–ethyl acetate–water at 283.15, 298.15, and 313.15 K had been studied in work [44]. The data on LLE in ternary subsystem ethanol–ethyl acetate–water at the same temperatures (283.15, 298.15, and 313.15 K) are presented in paper [45]. The ethanol–ethyl acetate–water system was also studied in work [46] at 303.15 K and in [47] at 298.15, 308.15, and 318.15 K (atmospheric pressure).

The *n*-propanol–acetic acid–water–*n*-propyl acetate system had been also studied in numerous theoretical and experimental works, e.g., kinetics of *n*-propyl acetate synthesis [48], CE and VLE [49,50], solubility and LLE [24], residue curve map [51], and modeling and theoretical consideration [51,41]). The detailed discussion of phase transition in this system and comparison of azeotropic data has been carried out in [52].

The surfaces of CE for both systems are presented on Fig. 1: we used our experimental data for ethanol–acetic acid–water–ethyl acetate system [53] and for *n*-propanol–acetic acid–water–*n*-propyl acetate system [54]. The view of surface of the CE of both systems is similar and typical for this kind of system [55]. As usual, the compositions of quaternary systems are presented in the tetrahedron; we use grid (Cartesian) coordinates and composition space is the irregular tetrahedron. According to the equation of reaction 5, four binary subsystems ($R_1 - R_3$, $R_1 - R_4$, $R_2 - R_3$, $R_2 - R_4$) are nonreactive and should be considered as parts and borders of the surface of CE. Two binary systems ($R_1 - R_2$ and

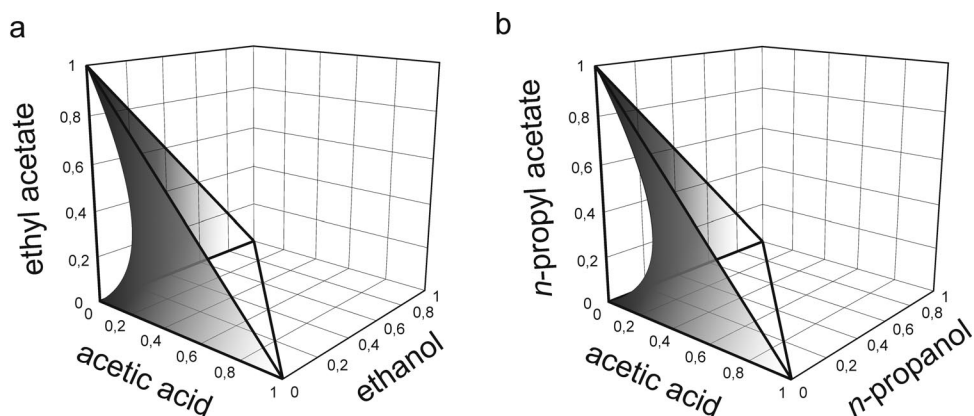


Fig. 1 The surface of CE (molar fractions, $T = 293.15$ K): 1a: ethanol–acetic acid–water–ethyl acetate system; 1b: *n*-propanol–acetic acid–water–*n*-propyl acetate system.

$R_3 - R_4$) and all four ternary subsystems are in chemically nonequilibrium states and do not belong to this surface.

The surfaces of solubility (the binodal surface) in both systems are presented in Fig. 2: we used our experimental data for ethanol–acetic acid–water–ethyl acetate system at 293.15 K [56] and for *n*-propanol–acetic acid–water–*n*-propyl acetate system at the same temperature [54]. The view of surfaces of solubility is also similar. Nevertheless, mutual consideration of both surfaces (CE and solubility) for these systems leads to different conclusions. In the case of *n*-propanol–acetic acid–water–*n*-propyl acetate system the mutual position of binodal and CE surface gives the area of their intersection: the region of simultaneous phase and CE (Fig. 3). The diagram in Fig. 3 is given from two viewpoints which present the effect of intersection more clearly. The curve (the border) of surfaces intersection is the part of binodal that corresponds to CE of heterogeneous (LL) mixture. The area of immiscibility of CE mixture at 293.15 K is small and almost the same as at 313.15 K [23]: the temperature shift does not lead to significant change in the size of the region of simultaneous phase and CE.

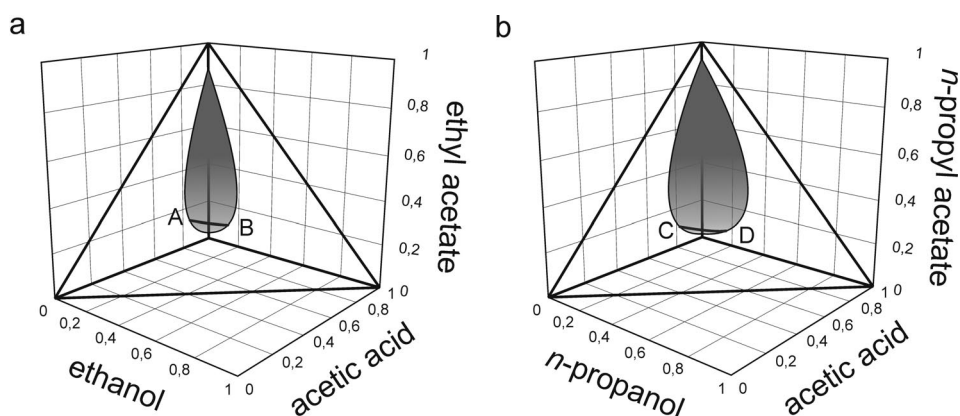


Fig. 2 The binodal surface (molar fractions, $T = 293.15$ K): 2a: ethanol–acetic acid–water–ethyl acetate (AB – critical curve); 2b: *n*-propanol–acetic acid–water–*n*-propyl acetate (CD – critical curve).

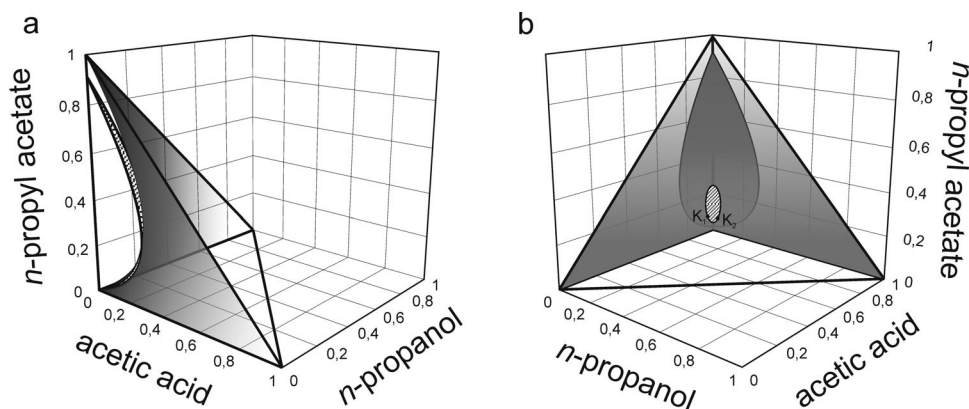


Fig. 3 The simultaneous CE and LLE for the *n*-propanol–acetic acid–water–*n*-propyl acetate system (molar fractions, $T = 293.15$ K), diagrams from different viewing angles: 3a: shaded surface – binodal; 3b: white stroked region – the area of the intersection, K_1 and K_2 – critical points on the border of this area.

In the case of ethanol–acetic acid–water–ethyl acetate system the experimental data at 293.15 K [53,56] indicate that the binodal and CE surface do not intersect one another. Accordingly, the CE of ethyl acetate synthesis reaction is settled in the homogeneous area only. The analysis of mutual position of surfaces (CE and LLE) leads also to the following conclusion: all stoichiometric lines of esterification reaction (ethyl acetate synthesis) at 293.15 K belong to the homogeneous region of compositions. In another word, the reaction mixture should always be homogeneous at 293.15 K. The last conclusion is valid for esterification only. The process of ethyl acetate hydrolysis may be accompanied by solution splitting.

The area of simultaneous CE and LLE in *n*-propanol–acetic acid–water–*n*-propyl acetate system at 293.15 K could also be presented in the complex of the transformed composition variables α_i [57,58] (Fig. 4). In the case of reaction 5, this 2D composition complex is a square and these variables have become

$$\alpha_1 = x_1 + x_4$$

$$\alpha_2 = x_2 + x_4$$

$$\alpha_3 = x_3 + x_4$$

where x_i is the molar fraction of specie i . The area of simultaneous LLE and CE both in the tetrahedron and in the square of α_i -variables represents a continuous set of tie-lines. All these tie-lines are analogous to the “unique reactive tie-line” in ternary systems [21]. In the ternary system, the unique reactive tie-lines are the part of the CE curve in the area of solution splitting. In the quaternary system, CE in the area of immiscibility could be considered as a linear surface formed by the set of unique reactive tie-lines.

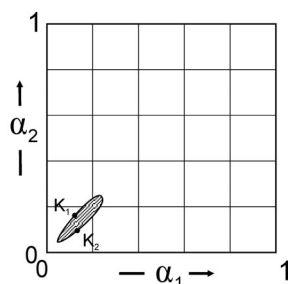


Fig. 4 The area of simultaneous CE and LLE in *n*-propanol–acetic acid–water–*n*-propyl acetate system in the square of transformed composition variables α_i at 293.15 K; white stroked region – the area of the intersection, K_1 and K_2 – critical points on the border of this area.

CRITICAL SURFACES OF LIQUID–LIQUID EQUILIBRIUM IN QUATERNARY REACTING SYSTEMS: EXPERIMENTAL RESULTS

In binary systems, the critical states of LLE usually are considered as a critical (plait) point for diagrams “composition–temperature”. In ternary systems, critical points of LLE may exist for some types of immiscibility region of isothermal–isobaric phase diagrams. At variable temperature, the set of critical points composes the critical curve in composition triangle [19,26,27]. In quaternary systems at isothermal–isobaric conditions, the critical states of LLE could be represented as a curve in composition tetrahedron (the set of critical points on the binodal surface). In the general case of multicomponent LL systems, the critical states correspond to various manifolds (points, curves, surfaces, or hypersurfaces) in the multidimensional thermodynamic space. The type of the manifold should be in agreement with the phase rule

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

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. In the case of the critical state, the number of degrees of freedom will be reduced: the critical phase should be taken into account thrice [26,30,31]. For the quaternary LL system in the state of simultaneous phase and CE the variance of single critical phase at constant T and P is determined as

$$r = 3, n = 4, k = 1$$

$$f = n + 2 - r - k = 4 + 2 - 3 - 1 - 2 = 0 \quad (7)$$

i.e., it is an invariant state. At variable T these states correspond to the curve in composition tetrahedron.

The critical states of a nonreactive quaternary LL system (or a reacting system in chemically non-equilibrium states) at constant T and P should be presented as a curve in the composition tetrahedron (monovariant state). At variable T the numbers of degrees of freedom is 2

$$f = n + 2 - r - k = 4 + 2 - 3 - 0 - 1 = 2 \quad (8)$$

these states correspond to the critical surface in composition tetrahedron.

Now we will present some experimental examples of critical states in quaternary LL systems with chemical reactions. Critical surface of LLE in the ethanol–acetic acid–water–ethyl acetate system is presented in Fig. 5. The surface had been constructed on the base of experimental data at polythermal condition, 293.15, 303.15, and 313.15 K [56,59]. The critical curve at 293.15 K (Fig. 2a) belongs to this surface.

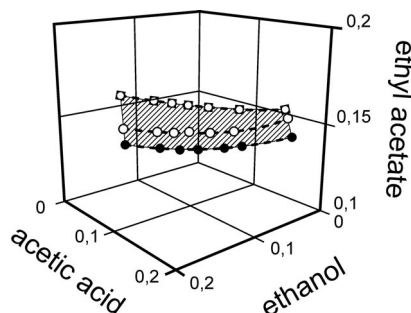


Fig. 5 Critical surface of LLE in the ethanol–acetic acid–water–ethyl acetate system at atmospheric pressure and polythermal conditions: ● – critical curve at 293.15 K, ○ – critical curve at 303.15 K, ■ – critical curve at 313.15 K.

The location of the critical surface in the system with n -propyl acetate synthesis reaction (Fig. 6) is like the previous case of ethanol–acetic acid–water–ethyl acetate system. The differences in these diagrams are caused by the position of CE surface in n -propanol–acetic acid–water– n -propyl acetate system, namely, the intersection of this surface and binodal in composition tetrahedron. As a result, at 293.15–313.15 K there are critical points of LLE which are in CE states. These points are presented in Figs. 3 and 4 at 293.15 K. The set of them generates the critical curve of LLE for CE states. This curve was constructed on the base of experimental data [23,24,54]. Gray points in Fig. 6 correspond to critical states of LLE which are in CE. Evidently, these points form two critical curves of simultaneous LLE and CE in composition tetrahedron.

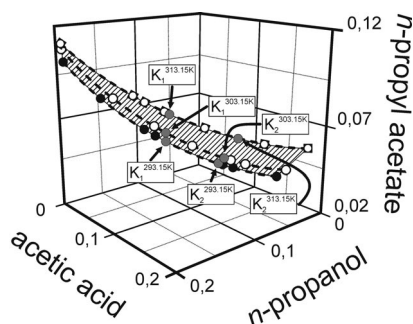


Fig. 6 Critical surface of LLE in the *n*-propanol–acetic acid–water–*n*-propyl acetate system at atmospheric pressure and polythermal conditions: ● – critical curve at 293.15 K, ○ – critical curve at 303.15 K, ■ – critical curve at 313.15 K; ● – critical points of LLE for chemically equilibrium compositions.

TIE-LINES AND STOICHIOMETRIC LINES IN REACTIVE LIQUID–LIQUID SYSTEMS

The mutual position of the binodals and CE manifolds may be discussed on the base of thermodynamic analysis. In the general case of nonequilibrium chemical reaction, some problems may be connected with determination of the values of thermodynamic parameters in the course of the chemical process. The correct solution of these and related problems is described in [30]. Thermodynamic description of the systems with nonequilibrium reactions is presented in a well-known book [27]. The systems with chemical reaction could be also considered in the state of partial equilibrium (see, e.g., [30,60,61]) when the deviations from equilibrium statistical distribution are small. In this case, the conditions of internal equilibrium (thermal, mechanical, diffusion, etc.) are fulfilled in the run of reaction.

For the sake of simplicity, we will consider the ternary LL system with one chemical reaction. Our analysis includes not only CE but also states of constant affinity: in ternary system at isothermal–isobaric conditions it would be isoaffinity curves in composition triangle. The conception of affinity is useful for the analysis of thermodynamic peculiarities of the systems with chemical interactions, e.g., see [27] or recent works [62,63]. We use the approach that is similar to the method of the analysis of chemical potentials in the nonreactive system proposed by Storonkin and Shults [31,64]. This method was subsequently generalized in [65,66].

The affinity *A* is determined by [27]

$$A = -\sum_i v_i \mu_i \quad (9)$$

where μ_i and v_i are chemical potential and stoichiometric number of specie *i*; v_i are positive for reaction products and negative for initial reagents. The values of affinity determine the run of reactions. On the other hand, it follows from eq. 9 that the affinity is equilibrium thermodynamic parameters [27]. It gives the opportunity to consider the phase properties and singularities of the diagram of reacting systems on the basis of equilibrium approach.

According to conditions of equilibrium and stability, the affinity in CE has an extreme value and the following relationships hold [27]:

$$A = 0 \quad (10)$$

$$\frac{\partial A}{\partial \xi} < 0 \quad (11)$$

In equilibrium LL system (reactive or nonreactive), the following conditions for chemical potential are valid [26–31]:

$$\mu_i^{(1)} = \mu_i^{(2)} \quad (12)$$

(superscript is index of phase) and consequently the affinity should have the equal value in both phases

$$A^{(1)} = A^{(2)} \quad (13)$$

The condition of CE is valid both for homogeneous and heterogeneous (multiphase) systems [27]. The stability condition 11 is written for homogeneous states. In the case of heterogeneous systems, the necessary stability condition could be presented in form [31]

$$dTdS^{(g)} - dPdV^{(g)} + d\mu_1 dm_1^{(g)} + d\mu_2 dm_2^{(g)} + \dots + d\mu_n dm_n^{(g)} > 0 \quad (14)$$

where $dS^{(g)}$, $dV^{(g)}$, $dm_1^{(g)}$, $dm_2^{(g)}$, ..., $dm_n^{(g)}$ are total changes of entropy, volume, and mass of heterogeneous system (heterogeneous complex of phases). At constant T and P the following equation holds:

$$d\mu_1 dm_1^{(g)} + d\mu_2 dm_2^{(g)} + \dots + d\mu_n dm_n^{(g)} > 0 \quad (15)$$

The condition $P = \text{const}$ is not necessary because usually we have the opportunity to neglect by the influence of the pressure on chemical potentials of components in condensed (liquid) phases.

If values $m_i^{(g)}$ change only in the run of chemical reaction the differential $dm_i^{(g)}$ could be presented by means of the extent of reaction ξ

$$\frac{dm_i^{(r)}}{v_i} = \frac{dm_1^{(r)}}{v_1} = \frac{dm_2^{(r)}}{v_2} = \dots = \frac{dm_n^{(r)}}{v_n} = d\xi^{(r)} \quad (16)$$

$$\frac{d\sum m_1^{(r)}}{v_1} = \frac{d\sum m_2^{(r)}}{v_2} = \dots = \frac{d\sum m_n^{(r)}}{v_n} = \frac{dm_i^{(g)}}{v_i} = d\xi^{(g)} \quad (17)$$

where subscript (r) is an index of phase r , $\xi^{(g)}$ is the extent of reaction related to the heterogeneous complex. Thereby inequality 15 is transformed to the following equations:

$$v_1 d\mu_1 d\xi^{(g)} + v_2 d\mu_2 d\xi^{(g)} + \dots + v_n d\mu_n d\xi^{(g)} > 0 \quad (18)$$

$$dA d\xi^{(g)} > 0 \quad (19)$$

Therefore, stability condition at constant T and P could be presented by

$$\frac{\partial A}{\partial \xi^{(g)}} < 0 \quad (20)$$

Equations 9–20 could be applied to multicomponent system but to avoid problems with graphic representation we will confine ourselves by a few examples of ternary systems with chemical reactions ($T, P = \text{const}$)

$$v_1 R_1 + v_2 R_2 = v_3 R_3 \quad (21)$$

Two diagrams in Fig. 7 are possible variants of systems with unique reactive tie-lines. For the first time the diagram of reactive system with “unique reactive liquid–liquid tie-line” was considered in the paper [21] with the use of Margules solution model for the reaction $R_1 + R_2 = R_3$. The qualitative view of such a diagram is presented in Fig. 7a. The diagram with similar tie-line was also discussed in paper [22] for the system with cyclohexanol synthesis reaction.

In papers [23,53,67] some other types of diagrams of reactive LL systems had been proposed and discussed. The case of two unique reactive tie-lines is shown in Fig. 7b. According to reaction eq. 21, stoichiometric lines are the straight ones. CE states correspond to curves in the composition triangle (Fig. 7).

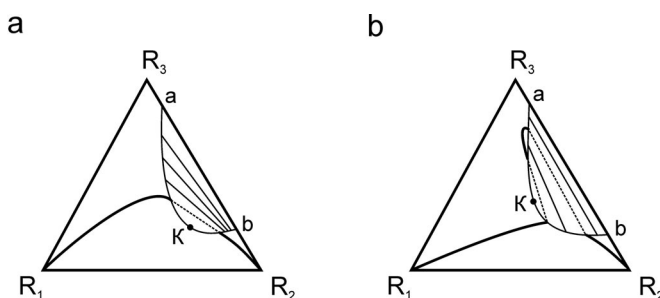


Fig. 7 Two examples of diagrams of ternary systems with one (7a) and two (7b) unique reactive LL tie-lines (---), *ab* – binodals, *K* – critical points.

For further analysis it would be sufficient to consider the fragments of diagrams: segments of CE curves, stoichiometric lines, binodals, and a few LL tie-lines (Fig. 8). In concordance with inequality 20, the affinity on stoichiometric lines for direct and reverse reactions in the vicinity of CE should go down. Accordingly, the shifting along binodal branches toward the unique reactive tie-line should be also accompanied by the decreasing of affinity. The affinity on unique reactive tie-line (i.e., CE state) possesses the zero value. Of course, this evident conclusion follows also from general condition of CE.

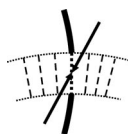


Fig. 8 Binodal (.....), tie-lines (----), CE curve (—), stoichiometric lines (→) for direct and reverse reactions: fragment of diagram of ternary LL system; ■■■ – the unique reactive tie-line.

Due to the differential form of eq. 20, this result is strictly valid for the infinitesimal vicinity of CE. It will be also correct for finite deviation of affinity from CE in the limits of monotonous dependence of affinity on extent of reaction, e.g., when

$$\frac{\Delta A}{\Delta \xi^{(g)}} < 0 \quad (22)$$

where Δ means a finite change of *A* and ξ . An assumption concerning such monotonous dependence gives the opportunity to consider the link between affinity and positions of tie-lines and stoichiometric lines in composition simplex. A few examples are presented in Fig. 9, where the arrows indicate the direction of stoichiometric lines that is the change of solution composition in the course of the reaction. In assumption of validity of eq. 22 the affinity diminishes in this direction.

Let us consider the case of Fig. 9a. According to eqs. 13 and 22 the affinity on tie-line “*c*” has a greater value in comparison with tie-line “*a*” and “*b*”. Thus, on both branches of the binodal the value of affinity falls when the state changes from tie-line “*c*” to “*a*” (“right to left” in Fig. 9a).

The opposite case is illustrated by Fig. 9b where tie-lines have another slope. The same consideration will lead to the conclusion that the value of affinity on binodal increases from tie-line “*c*” to “*a*”.

The case when tie-line coincides with stoichiometric line (tie-line “*b*” in Fig. 9c) corresponds to the extremum of affinity on binodal. It could be also a special case of unique reactive tie-line. The type of extremum could be determined by a slope of neighboring tie-lines relatively to stoichiometric line. One may also consider adjacent stoichiometric lines. Again, the same consideration gives that the affi-

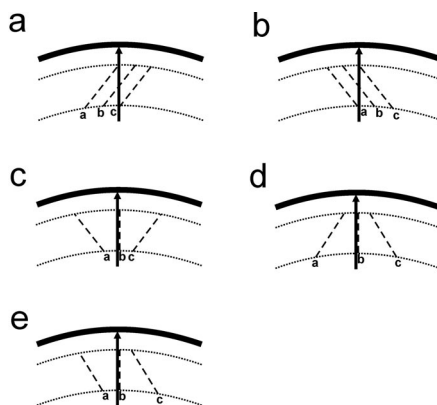


Fig. 9 Different cases of disposition of binodals, tie-lines, CE curves, stoichiometric lines for direct and reverse reactions: fragment of diagrams of ternary LL system. The notation for lines and curves is the same as in Fig. 8. The description of cases 9a, 9b, 9c, 9d, and 9e is given in the text.

ity should decrease when the state changes to binodal “b” from both sides (left and right). Thereby, the case of Fig. 9c corresponds to the minimum of affinity value on binodal. In the case of the diagram in Fig. 9d affinity on binodal has a maximum value. At last, the case of Fig. 9e corresponds to inflection point with horizontal tangent on the curve of the dependence of affinity on phase compositions (along binodal).

Thereby, the condition of thermodynamic equilibrium and stability leads to the following conclusions for the LL systems with chemical reaction in immiscibility area: (i) the change of the affinity on binodal is determined by the slope angle between tie-lines and stoichiometric lines and (ii) the concordance of tie-line with the run of stoichiometric line corresponds to extreme value of affinity on binodal curve. We would remind that these conclusions are valid for the states closed to CE. In the case of monotonous dependence of affinity on extent of reaction (eq. 22) they also would be valid for the states which are far from the vicinity of CE.

These conclusions could be generalized for the systems with arbitrary numbers of components. Particularly, the approach proposed in paper [66] may be applied. In the presented paper we had limited ourselves by a more illustrative case of ternary systems. Generally, the inclusion in the consideration of diagrams of LL reactive systems of the additional elements (stoichiometric lines, CE, and isoaffinity manifolds) gives the opportunity to set new thermodynamic conditions and to specify the topological structure of these diagrams.

CONCLUSION

The chemical reaction in the systems with liquid-phase splitting leads to additional peculiarities in comparison with nonreacting systems. In quaternary reactive system, in addition to the surface of phase equilibria the surface of CE should also be considered. In this paper we presented our experimental results on the position of the surfaces of LLE and CE in composition tetrahedron for the systems with ethyl acetate and *n*-propyl acetate synthesis reactions. According to experimental data, the intersection of the surfaces of LLE and CE exists only in the system with *n*-propyl acetate synthesis reactions: it means that CE in this system is settled both in the homogeneous and heterogeneous regions.

For both systems, the surfaces of critical states had been constructed in composition tetrahedron for 293.15–313.15 K. In the case of *n*-propanol–acetic acid–water–*n*-propyl acetate system the phase diagram also includes the critical curve of LLE for CE states.

In this paper we also presented some thermodynamic results for ternary reacting systems when the location of CE curves determines the mutual position of stoichiometric lines, binodals, and tie-lines. The thermodynamic analysis was based on the conditions of equilibrium and stability. The analogous consideration had been carried out for isoaffinity curves (curves of constant affinity), particularly, for the vicinity of CE and for the case of monotonous dependence of affinity on reaction extent.

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REFERENCES

1. K. Sundmacher, A. Kienle (Eds.). *Reactive Distillation*, Wiley-VCH, Weinheim (2003).
2. M. F. Doherty, M. F. Malone. *Conceptual Design of Distillation Systems*, McGraw-Hill, New York (2001).
3. R. Taylor, R. Krishna. *Chem. Eng. Sci.* **55**, 5183 (2000).
4. E. Y. Kenig, H. Bäder, A. Górak, B. Beßling, T. Adrian, H. Schoenmakers. *Chem. Eng. Sci.* **56**, 6185 (2001).
5. S. Steinigeweg, J. Gmehling. *Ind. Eng. Chem. Res.* **41**, 5483 (2002).
6. Yu. A. Pisarenko, L. A. Serafimov, N. N. Kulov. *Theor. Found. Chem. Eng.* **43**, 591 (2009).
7. V. T. Zharov, O. K. Pervukhin. *Zh. Fiz. Khim.* **46**, 1970 (1972).
8. A. V. Solokhin, S. A. Blagov, L. A. Serafimov, V. S. Timofeev. *Theor. Found. Chem. Eng.* **24**, 103 (1990).
9. G. Maurer. *Fluid Phase Equilib.* **116**, 39 (1996).
10. E. S. Peres-Cisneros, R. Gani, M. L. Michelsen. *Chem. Eng. Sci.* **52**, 527 (1997).
11. L. A. Serafimov, Yu. A. Pisarenko, N. N. Kulov. *Chem. Eng. Sci.* **54**, 1383 (1999).
12. S. A. Blagov, B. Bessling, H. Schoenmakers, H. Hasse. *Chem. Eng. Sci.* **55**, 5421 (2000).
13. S. K. Wasylkiewicz, S. Ung. *Fluid Phase Equilib.* **175**, 253 (2000).
14. A. Heintz, S. P. Verevkin. *Fluid Phase Equilib.* **179**, 85 (2001).
15. M. Teodorescu, K. Aim, I. Wichterle. *J. Chem. Eng. Data.* **46**, 261 (2001).
16. S. Yu. Shalunova, Yu. A. Pisarenko, A. S. Shuvalov, L. A. Serafimov. *Theor. Found. Chem. Eng.* **38**, 31 (2004).
17. S. Bernatová, K. Aim, I. Wichterle. *Fluid Phase Equilib.* **247**, 96 (2006).
18. G. Maurer. *J. Chem. Thermodyn.* **43**, 147 (2011).
19. J. P. Novák, J. Matouš, J. Pick. *Liquid–Liquid Equilibria*, Elsevier, Amsterdam (1987).
20. J. M. Sørensen, W. Arlt. *Liquid–Liquid Equilibrium Data Collection. Ternary and Quaternary Systems*, Part 3, Vol. V, Dechema Chemistry Data Series, Frankfurt (1980).
21. S. Ung, M. Doherty. *Chem Eng. Sci.* **50**, 3201 (1995).
22. Z. Qi, A. Kolah, K. Sundmacher. *Chem. Eng. Sci.* **57**, 163 (2002).
23. A. Toikka, M. Toikka. *Pure Appl. Chem.* **81**, 1591 (2009).
24. M. A. Toikka, B. I. Gorovitz, A. M. Toikka. *Russ. J. Appl. Chem.* **81**, 223 (2008).
25. A. M. Toikka, M. A. Toikka, M. A. Trofimova. *Russ. Chem. Bull.* (Russian version) **61**, 659 (2012).
26. J. W. Gibbs. *The Collected Works, Vol. 1, Thermodynamics*, Longmans, Green, London (1931).
27. I. Prigogine, R. Defay. *Chemical Thermodynamics*, Longmans, Green, London (1954).
28. J. M. Prausnitz, R. N. Lichtenthaler, E. G. Azevedo. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice-Hall, Englewood Cliffs, NJ (1999).
29. J. W. Tester, M. Modell. *Thermodynamics and its Applications*, 3rd ed., Prentice Hall PTR, Upper Saddle River, NJ (1997).

30. A. Münster. *Chemische Thermodynamik*, Akademie-Verlag, Berlin (1969).
31. A. V. Storonkin. *Thermodynamics of Heterogeneous Systems* (in Russian), Parts 1 & 2, Publishing House of Leningrad University, Leningrad (1967).
32. A. M. Toikka, M. A. Toikka, Yu. A. Pisarenko, L. A. Serafimov. *Theor. Found. Chem. Eng.* **43**, 129 (2009).
33. E. A. Campanella, B. A. Mandagaran. *Latin Am. Appl. Res.* **33**, 223 (2003).
34. M. Teodorescu, K. Aim, I. Wichterle. *J. Chem. Eng. Data* **46**, 261 (2001).
35. L.-s. Lee, M.-zh. Kuo. *Fluid Phase Equilib.* **123**, 147 (1996).
36. N. Calvar, A. Dominguez, J. Tojo. *Fluid Phase Equilib.* **235**, 215 (2005).
37. L. Lee, S. Liang. *Fluid Phase Equilib.* **149**, 57 (1998).
38. S. Bernatová, K. Aim, I. Wichterle. *J. Chem. Eng. Data* **52**, 20 (2007).
39. A. C. Dimian, F. Omota, A. Bliet. *Chem. Eng. Proc.* **43**, 411 (2004).
40. E. Lladosa, J. B. Montón, M. C. Burguet, R. Muñoz. *J. Chem. Eng. Data* **53**, 108 (2008).
41. M. J. Okasinski, M. F. Doherty. *Chem. Eng. Sci.* **55**, 5263 (2000).
42. N. Chadda, M. F. Malone, M. F. Doherty. *AIChE J.* **47**, 590 (2001).
43. I. A. Furzer. *Chem. Eng. Sci.* **49**, 2544 (1994).
44. A. Colombo, P. Battilana, V. Ragaini, C. L. Bianchi. *J. Chem. Eng. Data* **44**, 35 (1999).
45. H. M. Lin, C. E. Yeh, G. B. Hong, M. J. Lee. *Fluid Phase Equilib.* **237**, 21 (2005).
46. M. U. Pai, K. M. J. Rao. *Chem. Eng. Data* **11**, 353 (1966).
47. A. Arce, L. Alonso, I. Vidal. *J. Chem. Eng. Jpn.* **32**, 440 (1999).
48. H. J. Bart, W. Kaltenbrunner, H. Landschützer. *Int. J. Chem. Kinet.* **28**, 649 (1996).
49. V. A. Sokolov, N. P. Markuzin. *Experimental data on vapour-liquid equilibrium and chemical reaction in the system acetic acid-n-propanol-water-n-propyl acetate*, Paper No. 35-82 (in Russian), Soviet Institute of Scientific Information (1982).
50. V. V. Kocherbitov, A. M. Toikka. *Russ. J. Appl. Chem.* **72**, 1706 (1999).
51. Y.-S. Huang, K. Sundmacher, S. Tulashie, E.-U. Schlünder. *Chem. Eng. Sci.* **60**, 3363 (2005).
52. A. Toikka, M. Toikka. *Fluid Phase Equilib.* **250**, 93 (2006).
53. A. M. Toikka, M. A. Trofimova, M. A. Toikka. *Russ. Chem. Bull.* (Russian version) **61**, 737 (2012).
54. M. Toikka. Ph.D. Thesis, Saint-Petersburg State University, Russia (2010).
55. A. M. Toikka, J. D. Jenkins. *Chem. Eng. J.* **89**, 1 (2002).
56. M. Trofimova, M. Toikka, A. Toikka. *Fluid Phase Equilib.* **313**, 46 (2012).
57. V. T. Zharov, *Zh. Fiz. Khim.* **44**, 1967 (1970).
58. D. Barbosa, M. F. Doherty. *Proc. R. Soc. London, Ser. A* **413**, 459 (1987).
59. M. Trofimova. Ph.D. Thesis, Saint-Petersburg State University, Russia (2012).
60. O. K. Pervukhin. *Zh. Fiz. Khim.* **65**, 2891 (1991).
61. V. T. Zharov, O. K. Pervukhin. *Vestnik Leningrad. Univ. Ser. 4, Physics, Chemistry Issue 4*, 97 (1977).
62. P. Koukkari, L. Laukkanen, S. Liukkonen. *Fluid Phase Equilib.* **136**, 345 (1997).
63. P. Koukkari, R. Pajarre. *Pure Appl. Chem.* **83**, 1243 (2011).
64. A. V. Storonkin, M. M. Shults. *Zh. Fiz. Khim.* **34**, 2167 (1960).
65. V. K. Filippov, M. M. Shults. *Dokl. Akad. Nauk SSSR* **235**, 414 (1977).
66. A. M. Toikka. *J. Appl. Chem. USSR* **65**, 900 (1992).
67. V. V. Kocherbitov, A. M. Toikka. *Vestnik St. Petersburg Univ. Ser. 4, Physics, Chemistry Issue 3*, 120 (1998).