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THE STRATEGY OF STUDY OF THREE-LIQUID PHASE EQUILIBRIA IN QUATERNARY MIXTURES*

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In the separation of multicomponent heterogeneous mixtures in units consist a distillation column and decanter, is a fundamental question about the location of delamination region with different numbers of liquid phases in a concentration simplex. Solution of this issue is based on data on the vapor–liquid equilibria and liquid–liquid of mixture and its components, as well as on the general laws of formation of the topological structure of delamination areas. The strategy of the study three-liquid phase equilibrium area in the quaternary mixtures are proposed. The strategy based on the formula of a topological invariant separation region and mathematical concepts centroid – the point of the intersection of the three medians. The presence of three-liquid phase areas of delamination of open and closed types, differing in the absence (presence) of degeneracy region through the critical node.

Keywords: *three-phase delamination region, phase diagram structure, mathematical simulation*

Introduction

Thermodynamic-topological analysis of the structure of the phase diagram of the studied system [1–5] is obligatory when designing basic technological schemes for the separation of multicomponent multiphase mixtures of organic substances. This analysis allows to find out the main restrictions imposed on the separation process and to suggest methods of overcoming them.

Work [6] suggests a formula of topological invariant as the main tool enabling to analyze the phase separation diagrams characterized by phase separation regions of different dimension:

$$R + f = n - 1, \quad (1)$$

where R is the dimension of the phase simplex (phase separation simplex), f is the system variance, n is the number of components in the system.

Formula (1) is the direct sum of two varifolds: linear varifold R depending on the number of liquid phases ($R = \varphi^l - 1$) and nonlinear varifold f, the dimension of which is equal to the number of degrees of freedom of the phase separation region. In case of quaternary systems the number of liquid phases can vary from 1 to 4 (φ^l_{max}), and the structure of the phase separation regions is as presented in Table 1.

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Table 1. Characteristics of phase separation regions of a quaternary system (n = 4)

The number of liquid phases, φ^l	Dimension of phase simplex, R	System variance, f
1	0	3
2	1	2
3	2	1
4	3	0

Figure 1 shows as examples some structures of the phase separation diagrams of quaternary systems.

It is noted in [7] that when studying the evolution of the equilibrium region of three liquid phases (R = 2), an indispensable condition is that the gross composition point X^* be in the three-phase separation region. In this case f = 1, and this degree of freedom is completed by setting the concentration of the i-th component (at a specific step). Otherwise, when point X^* is in the two-phase separation region (R = 1), f = 2, and an additional degree of freedom appears. When this state is attained, the gross composition should be changed in a certain manner.

This situation appears due to the nonlinearity of f participating in the formation the three-phase region in the tetrahedron (the flat triangle of phase separation is shifted along the curve [6]). At the same time the addition of a component to the mixture is described by the material balance equation, which is always linear.

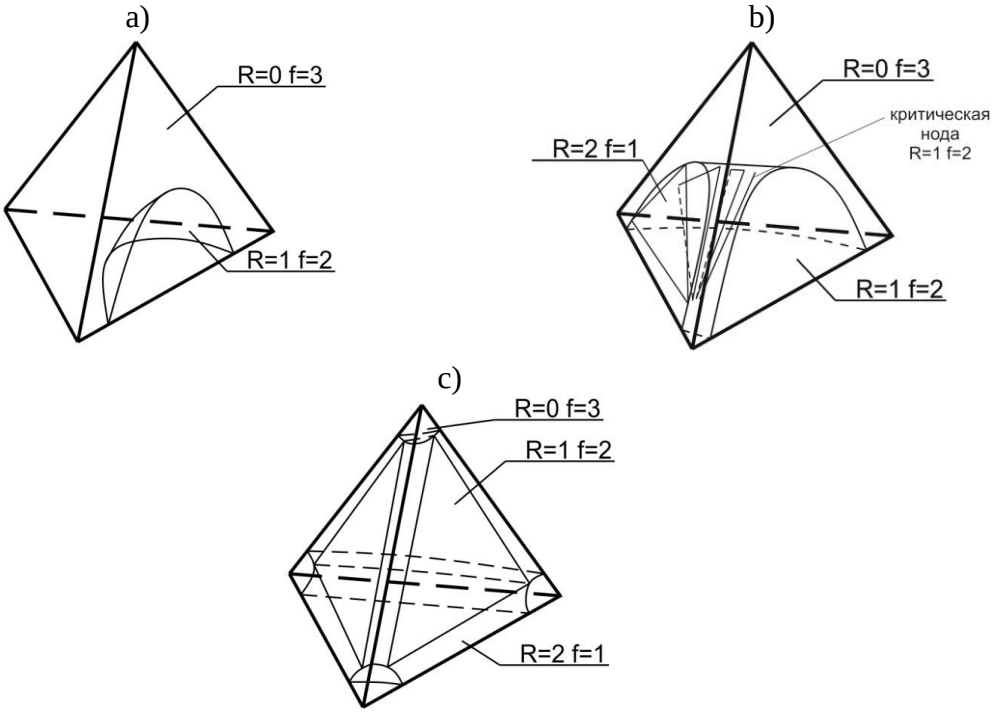

Figure 1. Examples of diagrams of quaternary systems undergoing phase separation with different topology of phase separation regions
[критическая нода means critical node]

Calculation and Theory Part

We studied previously [7] the structure of the phase equilibrium diagram of a quaternary system: 2-methyl-1,3-butadiene – 2-methyl-2-butene – acetonitrile – water. The diagram includes a region of equilibrium of three liquid phases. The transition of the three-phase separation region in the concentration tetrahedron through the critical node to the two-phase region (Figure 1b) is shown. The study technique was restricted to step-by-step addition of a homogenizing substance (2-methyl-1,3-butadiene) to the triple 2-methyl-2-butene – acetonitrile – water component characterized by the presence of a region of equilibrium of three liquid phases until the acetonitrile layer disappears. Disadvantages of this technique are: 1) the uncertainty arising when one of the layers is exhausted and 2) the difficulty of determining exactly the gross composition corresponding to the transition of the three-phase separation into two-phase one and *vice versa* through the critical node.

The aim of this work is to improve the technique and to create an algorithm for studying the regularities of three-phase regions formation. The condition of gross composition point *X** location in the phase separation region remains. It is known from mathematics that any triangle has a point (centroid) [8] where three medians cross. In our case, the coordinate of this point corresponds to the equality of liquid layers quantities: $r' = r'' = r'''$.

Let us assume that there is *i-j-k-l* mixture, in which *i-j-k* component is characterized by the existence of a region of three liquid phases equilibrium. Then the algorithm of studying the evolution of three-phase separation is restricted to the form presented in Figure 2.

In order to input basic data (step 1) it is necessary to preset the gross composition $X_0^*(x_{0,i}; x_{0,j}; x_{0,k})$ of triple mixture *i-j-k* at the initial iteration 0. This composition is related to the region of three liquid phases equilibrium $(x_{0,l} = 0)$ at preset temperature and pressure. Then the phase equilibrium liquid–liquid–liquid of this mixture (step 2) is simulated. This is followed by obtaining and comparing the structures of equilibrium layers $X'_0(x'_{0,i}; x'_{0,j}; x'_{0,k})$, $X''_0(x''_{0,i}; x''_{0,j}; x''_{0,k})$ and $X''_0(x''_{0,i}; x''_{0,j}; x''_{0,k})$ (steps 3–5). If experimental data on the phase equilibrium liquid–liquid–liquid in triple component *i-j-k* are available, steps 1–3 can be omitted.

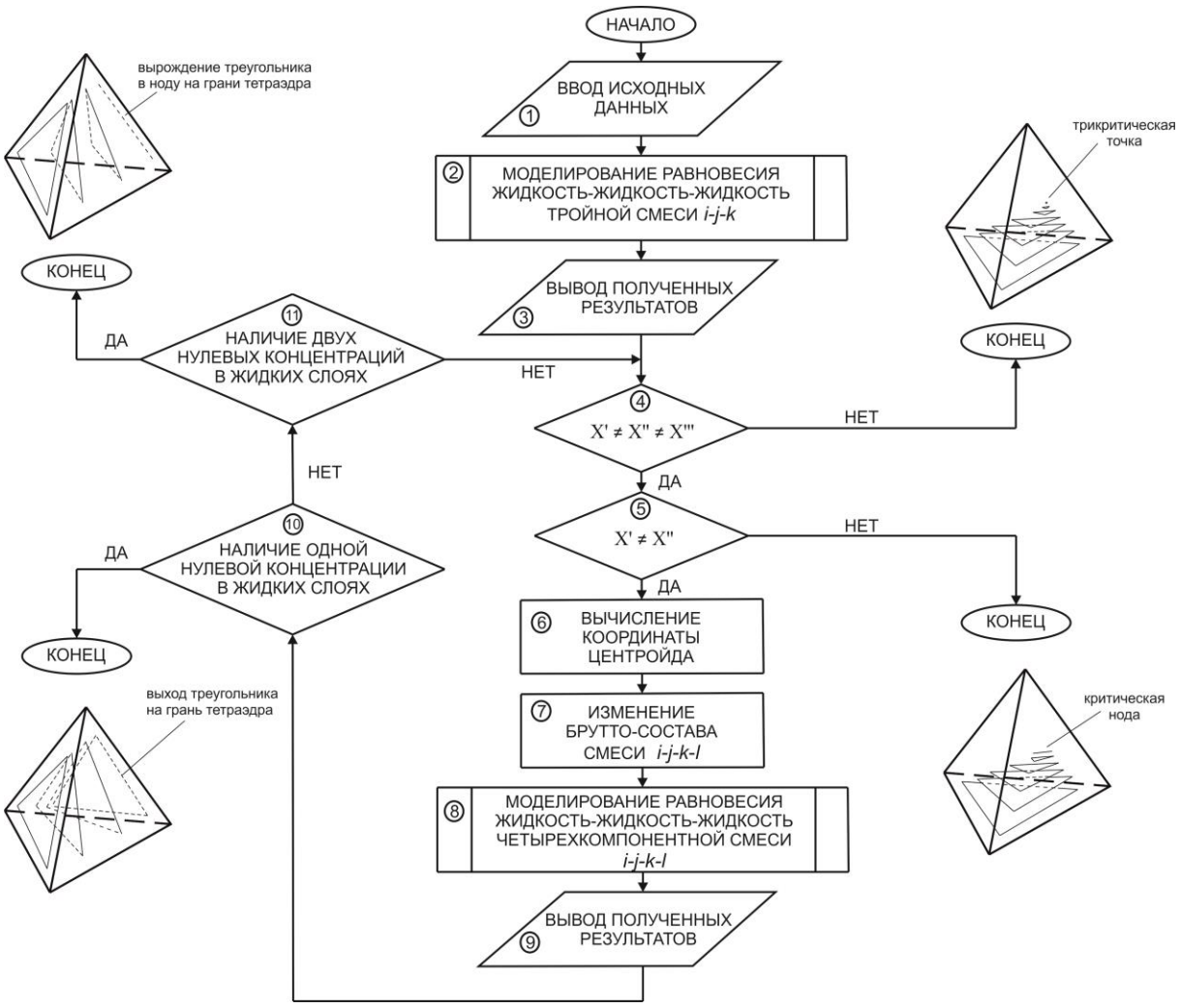

Figure 2. Algorithm for studying the evolution of the three-phase separation region inside the concentration tetrahedron.

Because the equality of layer compositions is impossible at the initial iteration (steps 4, 5), the centroid coordinate is calculated (step 6): $x_{1,i} = \frac{x'_{0,i} + x''_{0,i} + x'''_{0,i}}{3}$; $x_{1,j} = \frac{x'_{0,j} + x''_{0,j} + x'''_{0,j}}{3}$; $x_{1,k} = \frac{x'_{0,k} + x''_{0,k} + x'''_{0,k}}{3}$. Then it is necessary to change the gross composition X_1^* (iteration 1) with the addition of the first component at a certain step $(x_{1,l})$ to the mixture corresponding to the centroid, i.e., to reduce the content of components *i*, *j*, *k* by the value of 1/3 steps. Thus, the coordinate of point X_1^* in the first iteration takes the following form: $x_{1,i} = \frac{x'_{1,i} + x''_{1,i} + x'''_{1,i}}{3} - \frac{x_{1,l}}{3}$; $x_{1,j} = \frac{x'_{1,j} + x''_{1,j} + x'''_{1,j}}{3} - \frac{x_{1,l}}{3}$; $x_{1,k} = \frac{x'_{1,k} + x''_{1,k} + x'''_{1,k}}{3} - \frac{x_{1,l}}{3}$; $x_{1,l}$ (step 7). The approach in the subsequent iterations is similar.

After this the liquid–liquid–liquid phase equilibrium of the four-component mixture *i*-*j*-*k*-*l* (step 8) is simultated with repeated determination (step 9) and analysis of the structures of the equilibrium layers X'_1, X''_1, X'''_1 (steps 10, 11). It is necessary to check whether zeroing of one (or two) concentrations in the equilibrium layers occurs. These cases correspond to: 1) transition of the three-phase separation region to the other triple component; 2) degeneration of the three-phase region into a two-phase one on the sides of the tetrahedron edges (Table 2). If these conditions are fulfilled, the algorithm comes to an end. If these conditions are not fulfilled, it is necessary to repeat the comparison of the equilibrium layers compositions (step 4). If they are not equal, the next iteration should be made. The fulfillment of the condition $X'_z = X''_z = X'''_z$ means that this gross composition $X_z^*(x_{z,i}; x_{z,j}; x_{z,k}; x_{z,l})$ is associated with so-called tricritical point [9]. In contrast, the fulfillment of the condition of two equilibrium layers equality $X'_z = X''_z$ is associated with the critical node of transition to the three-phase separation into the two-phase one in the tetrahedron. The algorithm comes to an end, i.e., the three-phase separation region degenerates into a two-phase region.

The three-phase separation region evolution was studied in a computing experiment with model and real systems [7, 10] as examples with the use of the NRTL equation and AspenPlus software system. A closed type evolution is modelled in 2-methyl-1,3-butadiene – 2-methyl-2-butene – acetonitrile – water system as shown in Figure 1b. An open type evolution is modelled in *n*-hexane (*n*-heptane, *n*-octane) – cyclohexane – furfural – water system as shown in Figure 1c. The obtained data confirmed the operability of the suggested algorithm.

Table 2. Characteristics of iterative procedures for studying three-phase separation evolution in concentration tetrahedron

Iteration	Components concentration				Note
	i	*j*	*k*	*l*	
0	$x_{0,i}$	$x_{0,j}$	$x_{0,k}$	$x_{0,l}$	Original composition of three-component system
1	$x_{1,i}$	$x_{1,j}$	$x_{1,k}$	$x_{1,l}$	Intermediate four-component compositions
2	$x_{2,i}$	$x_{2,j}$	$x_{2,k}$	$x_{2,l}$	
…	…	…	…	…	
z – 1	$x_{z-1,i}$	$x_{z-1,j}$	$x_{z-1,k}$	$x_{z-1,l}$	
z	$x_{z,i}$	$x_{z,j}$	$x_{z,k}$	$x_{z,l}$	Degeneration of phase separation triangle into liquid–liquid node in concentration tetrahedron ($\varphi^l = 2$) or degeneration into tricritical point ($\varphi^l = 0$)
	0	$x_{z,j}$	$x_{z,k}$	$x_{z,l}$	Phase separation triangle shift to tetrahedron side($\varphi^l = 3$)
	$x_{z,i}$	0	$x_{z,k}$	$x_{z,l}$	
	$x_{z,i}$	$x_{z,j}$	0	$x_{z,l}$	
	0	0	$x_{z,k}$	$x_{z,l}$	Degeneration of phase separation triangle into liquid–liquid node on tetrahedron side or edge ($\varphi^l = 2$)
	0	$x_{z,j}$	0	$x_{z,l}$	
	$x_{z,i}$	0	0	$x_{z,l}$	

Conclusion

A technique and algorithm for studying the evolution of the three-phase separation region in the concentration tetrahedron were suggested. It was found that two essentially different types of evolution are possible. They result in: 1) the formation of a closed region of three-phase liquid separation with its transition through the critical node into the two-phase region; 2) the formation of an open region of three liquid phases equilibrium. The latter region is based on phase separation triangles in different triple components of the tetrahedron.

Acknowlegment

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Designations:

R – the phase simplex dimension; *f* – the system variance, *n* – the number of components in the system, φ^l – the number of liquid phases; X', X'', X''' (r', r'', r''') – the compositions (quantities) of equilibrium liquid phases; X_z^* – the gross composition of the four-component mixture in the z-th iteration; $x_{i(j,k,l),z}$ – the concentration of component *i (j,k,l)* in the z-th iteration.

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