# Multicomponent Systems with Three-Phase Splitting Region*

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*The review of scientific publications that describe systems with three phase splitting region are presented. Mechanisms of forming of three phase splitting region are shown. All proposed classifications of diagrams with three phase splitting region are presented. Research methods of evolution of three phase splitting region are described. Problems connected with mathematical modeling of liquid – liquid – liquid equilibrium are considered. Property of mixtures to form three phase splitting regions and opportunities to separate such a mixture by special methods are analyzed. List of known systems with three and more liquid phases is presented.*

***Keywords:*** *three phase splitting, liquid – liquid – liquid equilibrium, multicomponent systems, extraction, mixing of distillation and splitting.*

## Introduction

Studying multicomponent multiphase systems containing more than two liquid phases is a rather complex task. First of all, this is due to the fact that experimental data about phase equilibrium (liquid-vapor, liquid-liquid, liquid-liquid-liquid) in such systems are extremely limited. There are certain difficulties in the description and mathematical modeling of equilibrium. There are few works devoted to systematization and search for general regularities of phase diagrams formation.

Nevertheless, the phenomenon of three-phase separation finds application in extraction (in particular, microextraction processes) and other separation processes in the technology of basic organic and petrochemical synthesis, in biotechnological processes.

Recently, sustained interest in studying multiphase systems is observed. Almost 130 years passed after the moment of discovering systems with three-phase separation (1887) [1, 2]. The number of publications in the past 30 years increased twice as compared, for example, to the period before 1980s. All this emphasizes the necessity and relevance of studying such systems.

This work is devoted to the systematization and synthesis of data on multi-component systems containing three and more liquid phases.

## The nature and mechanisms of the formation of three-phase separation regions

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If we consider a list of systems with three-phase separation, it can be seen that such systems contain components of different classes of compounds. Systems with three-phase separation can be classified for our purpose into two groups: systems with strong intermolecular interaction (a key role is played by complex formation processes) and systems with weak intermolecular interaction.

The effect of the salting-out action of various components on the solubility of mixture components and on the formation of a three-phase separation region is considered in detail in a review devoted to three-liquid systems [3]. Analysis of the dielectric permeability of components forming the three-phase separation region led to the assumption that in systems in which the difference between the values of this property of components is small a key role is played by strong affinity of molecules, i.e., the formation of new complex structures (complexes) in the solution is possible. An example can be aqueous systems containing dioxane, carbonic acids and alkali, in which the formation of gem-triol derivatives is possible. Another example can be aqueous systems containing ethyl acetate, acetic acid and sodium sulfate (a gem-triol analog is formed [4]). In fact, such complexes can act as phase forming agents. On the contrary, a large difference in dielectric permeability indicates small affinity of molecules [3]. It is possible to consider as an example water – furfural – cyclohexane system, in which all three pairs of components have limited mutual solubility. If a third component is added to one of the pairs, saturation of two phases with the third component will occur until equilibrium is attained, and then a third layer containing a surplus of this component will be formed.

There are several mechanisms of three-phase separation regions formation. Work [5] suggests two mechanisms of the formation of three-phase separation regions: with the participation of a critical phase (binodal curves contact critical and noncritical points) and without the participation of a critical phase (binodal and spinodal curves contact each other) (Figure 1).

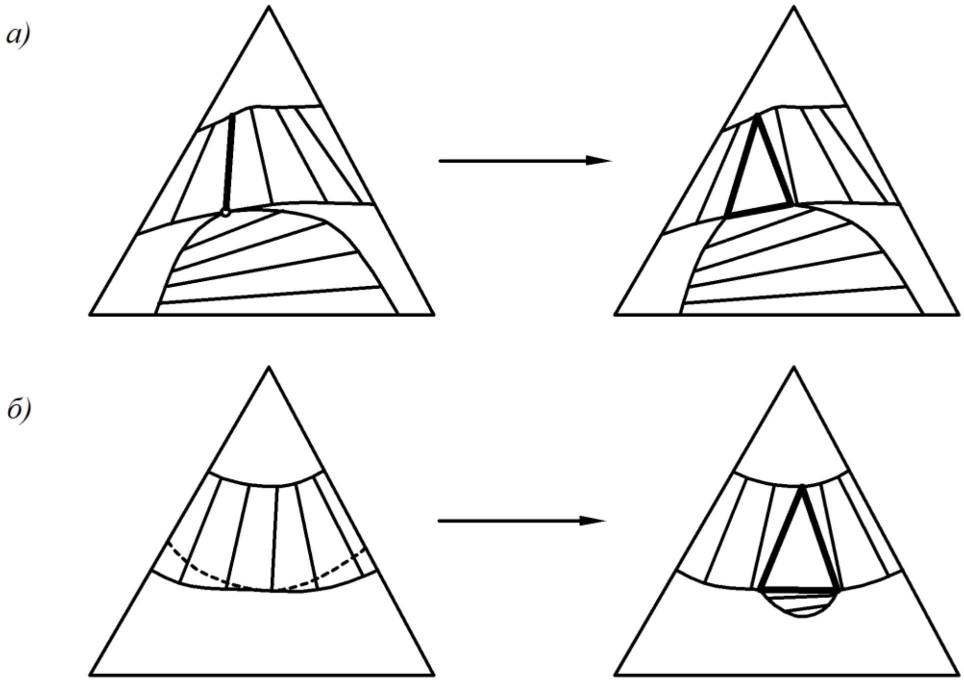

**Figure 1.** Mechanism of three-phase separation region formation [5]:
(a) with the participation of a critical phase;
(b) without the participation of a critical phase
[а means a; б means b]

Work [6] describes 28 mixtures of water-organic and non-aqueous ternary systems. In 11 of them, a region of three-phase separation is formed according to scheme (a) of Figure 1 (nitromethane – nonanol – water, nitromethane – ethylene glycol – nonanol), in 15 of them – according to scheme (b) of Figure 1 (heptane – aniline – water, cyclohexane – aniline – water). The mechanism of the three-phase separation region formation in ternary and quaternary systems is described. The author [6] investigates the change of solubility in the initial separating binary (ternary) mixture upon the addition of a third (fourth) component. If the increase in the concentration of the introduced component increases the solubility of the components in the original mixture, this is called salting-out effect of the component (for example, when heptane is added to nitromethane – ethylene glycol binary mixture). If solubility decreases, this is called salting-in effect (for example, when dodecanol is added to nitromethane – ethylene glycol binary mixture) [6]. According to the results of this work, a sufficient condition of three-phase separation in ternary systems is the existence of a two-phase separation region with top critical solution temperature in binary components. However, the emergence of three liquid phases is also possible, when one or more binary components are homogeneous.

One more mechanism of the formation of a three-phase separation region is described in [2]. According to this mechanism the emergence of a three-phase separation region in a ternary system containing only one couple of components with limited mutual solubility is possible. This mechanism is implemented in water mixtures of succinonitrile and hexane, succinonitrile and benzene and some other systems [2].

Phase separation diagrams containing three-phase separation regions are very diverse. One of independent tasks is to determine the signs of diagrams equivalence for the purpose of their classification. Much attention was paid to this problem for a long time [7–10]. Today there are several classifications of separation diagrams of ternary and quaternary systems [6, 11–15].

The simplest classification is presented in [11]. It is a classification numbering several types of diagrams that differ from one another in the existence of regions of states of different type (liquid–liquid, liquid–liquid–liquid, liquid–liquid–solid). Systems with regions of three-phase separation belong to type 3 of this classification.

Work [12] suggests a classification of phase separation diagrams of ternary systems, and also bases for the classification of systems with a large number of components. Beregovykh V.V. considered a phase separation diagram as a simplex with lines, faces and hyperfaces of solubility limits placed in it. They break the simplex into a number of cells. Thus, he considered a phase separation diagram as a figure related to the category of multicellular topological formations. A number of diagrams of ternary systems were synthesized on the basis of solving the Cauchy problem. This classification is limited to systems, where the concentration simplex element can have only one separation region with the number of phases depending on the number of components of this element. The total amount of diagrams is 23, and 11 of them contain a three-phase separation region. It should be noted that some of the provided charts will be related rather to fine structures, i.e., they will exist only under certain conditions.

The classification suggested in [13] for the first time takes into account critical manifolds of separation diagrams, as well as island-type separation regions (cycles). Considering and grouping all the possible geometrical elements of a separation diagram the authors [13, 16] obtained an equation of non-local regularities for multi-component multiphase systems. On the basis of this equation a classification of separation diagrams of ternary systems was suggested. Diagrams in which two biphase regions are missing on one binary component are considered. They contain only one unbound cycle of two-phase separation. The number of phase triangles is no more than three. As a result, 25 classes of diagrams (103 types) of ternary systems separation were found; 23 of them contain one, and 68 – two regions of three-phase separation.

The most complete classification of separation diagrams of ternary systems is the classification suggested in [14, 15, 17]. This classification leaves room for the formation of two separation regions in binary components and up to three regions of three-phase separation in the concentration triangle. The classification is based on the Euler's equation determining the interrelation between the geometrical elements of the separation diagram. On the basis of the equations of geometrical thermodynamics, and also of the rule of separation regions contact [18] an atlas of possible types of diagrams was synthesized. The total number of diagram types was 327; 33, 114 and 171 of them contain one, two and three separation regions, respectively. The possibility of extending this classification to systems with a large number of components is shown. Note that this classification of diagrams does not consider the existence of island regions of two-phase separation in the system.

Work [6] presents a classification of separation diagrams of quaternary systems containing three-phase separation regions. The classification is based on information about the existence of three-phase regions in one, two or more three-component components, and also on information about the mechanism of the origin of the three-phase separation region. However, of course, the presented set of diagram types does not exhaust all the variety of separation diagrams of quaternary systems.

Considering quaternary systems containing three-phase separation regions the author [6] described four types of evolution of the three-phase separation region in the concentration simplex of quaternary systems (Figure 2). It is important to note that the evolution of the three-phase separation region is understood as the geometrical features of the region inclusion in the concentration simplex.

The case presented in Figure 2a is related to systems, two ternary components of which include a three-phase separation region. In case of Figure 2b degeneration of the three-phase separation region via the critical liquid-liquid node occurs.

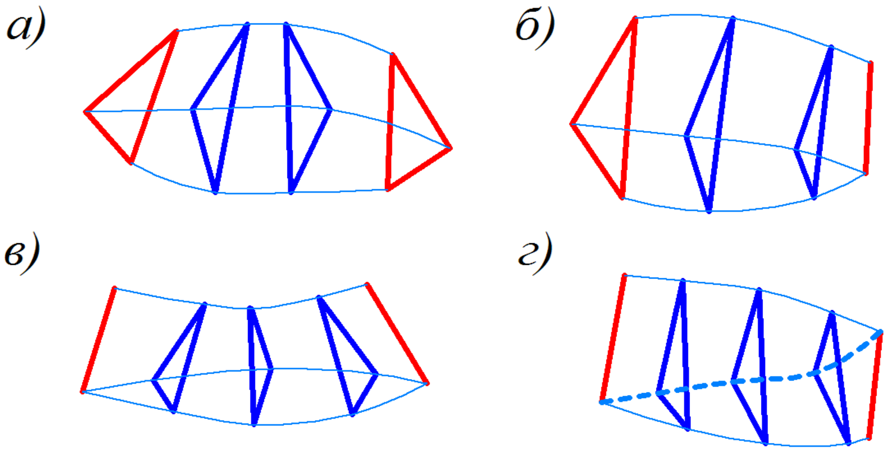

**Figure 2.** Evolution of the three-phase separation region in the concentration simplex of quaternary systems.
[а means a; б means b; в means c; г means d]

Cases (c) and (d) of Figure 2 differ in that the evolution is accompanied by disintegration of one of the equilibrium liquid layers into two layers followed by their merge in one layer (c) or by the merge of one of the new layers with another layer. Some of the presented types of evolution were experimentally confirmed. Thus, for example, case (a) of Figure 2 is related to water – aniline – hexane – heptane and nitromethane – ethylene glycol – dodecanol – heptane systems [6]; case (b) of Figure 2, to water – acetonitrile – cyclohexene – cyclohexanone [20], aniline – hexane – water – benzene and nitromethane – nonanol – water – propanol [6] systems; case (d) of Figure 2, to ethylene glycol – nitromethane – tetrachloroethylene – heptane [6] and water – benzene – ethanol – ammonium sulfate [20] systems.

From the geometrical point of view, the structure of a separation diagram is a set of certain geometrical elements filling the interior of the concentration simplex. These elements are phase simplexes with edges of various length. Their tops correspond to equilibrium compositions, into which the liquid is separated. Phase simplexes are: a line segment (a liquid–liquid node, along which two-phase separation occurs); a phase triangle (three equilibrium liquid phases correspond to the tops of the phase triangle); a separation tetrahedron; a separation pentatope, etc. The point as a phase simplex formally corresponds to a homogeneous solution. Phase simplexes form a series similar to the series of concentration simplexes.

All the elements of a separation diagram are interrelated in a certain way and form the thermodynamic-geometrical structure of the diagram. Let us consider a number of topological characteristics inherent in separation diagrams, and also approaches to studying them.

It is known that the study of heterogeneous systems is based on an equation determining the interrelation of the number of independent variables (the number of degrees of freedom) describing the object and determining the dimension of the state diagram of the multiphase system. In case of open $n$-component $\varphi$-phase chemically inert systems this dependence is determined by the Gibbs phase rule [21]:

$$f = n - \varphi + 2 \tag{1}$$

This equation was derived by Gibbs on the basis of zero potential. Work [18] considers another approach to deriving the phase rule. According to this approach the system is considered as a complex of liquid phases and a vapor phase. In this case the number of degrees of freedom of the system is equal to $F = n + 2$.

In case of systems with low variance we deal with real (net) concentrations of components in the liquid phase; in case of systems with a large number of variables – with gross concentrations, the interrelation of which is determined by the following equation:

$$X_i = \frac{\Sigma(m^k x_i^k)}{\Sigma m^k} \ , \tag{2}$$

where $X_i$ is the gross concentration of component *i*, $x_i^k$ is the net concentration of component *i* in liquid phase *k*, $m^k$ is the mass of liquid phase *k*.

On the basis of the approach related to the gross concentrations of components a topological invariant of the separation region as the direct sum of two manifolds was suggested: nonlinear manifold *f* equal to the number of degrees of freedom of the region and linear manifold *R* equal to the phase simplex dimension [13, 22]:

$$f + R = n - 1 = const \tag{3}$$

Equation (3) determines the interrelation of the dimension of a concentration simplex and a separation (two-, three- or *n*-phase) simplex. The rule of separation regions contact is a consequence of analyzing equation (3) [13]: the number of phases changing upon transition from one region of the diagram to another is equal to the phase diagram dimension minus the dimension of the boundary between the regions.

Work [23] describes the invariant of the separation diagram related to the Euler characteristic. The essence of this approach is that the concentration simplex of the separation diagram is imaged into the sphere of the dimension, the Euler characteristic (Э) of which will depend on the dimension of the sphere itself

$$Э = 1 + (-1)^r, \tag{4}$$

where *r* is the sphere dimension.

On the other hand, the separation diagram can be considered as a manifold with an edge, and in this case Euler's characteristic is determined as the alternative sum of elements of different dimension

$$Э = \alpha_0 - \alpha_1 + \alpha_2 - \ldots, \tag{5}$$

where $\alpha_i$ is the number of elements of *i*-th dimension.

The existence of separation regions of various type (two-phase opened-type or closed-type, three-phase) will result in the formation of "holes" on the sphere, and, therefore, to the reduction of the Euler characteristic (by the number of the "holes") [23].

The regularities of phase equilibrium of multiphase systems are reflected in the van der Waals–Storonkin equation [24, 25]. This equation describes the equilibrium distribution of all components between phases and establishes correspondence between the phase transformation parameters, i.e., it reflects the regularities of the system behavior upon transition of an infinitely small quantity of one phase to a finite quantity of another phase. For multi-component systems the author of [26] suggested a vector form of this equation. On the basis of the obtained equation the local and non-local regularities of the structures of phase diagrams of multiphase systems [13] were studied.

Work [27] describes isothermo-isobaric manifolds in multiphase systems. The obtained general formula of the isothermo-isobaric manifold invariant is given by:

$$R_\sigma \times f_\sigma = n - 1 - \frac{1 + (-1)^k}{2}, \qquad (6)$$

where $R_\sigma$ is the dimension of linear elements of the manifold, $f_\sigma$ is the dimension of nonlinear elements of the manifold, $k$ is the number of subregions, into which the separation region divides the isothermo-isobaric manifold, and $n$ is the number of components in the system. On the basis of analyzing this equation, types of configurations of isothermo-isobaric manifolds are described. Thus, for example, isothermo-isobaric manifolds in the separation region with the maximum number of liquid phases are characterized by the linear component $(R_\sigma)$, while the nonlinear one $(f_\sigma)$ is equal to zero. (This part of the isothermo-isobaric manifold will coincide with the structure of the separation simplex.) Other manifolds including linear and nonlinear components will be characterized by a more complex structure. For each type of isothermo-isobars the conditions of implementation were formulated [28]. In general, analyzing the isothermo-isobars of systems with separation regions, the number of which is equal to the number of components, it can be said that the isothermo-isobars in this case are piecewise type manifolds and are characterized by a nontrivial geometrical structure.

The above invariants of equations (3)–(6) are related to the topological structure of the separation diagram, i.e., in fact, they are its topological characteristics.

In order to study the evolution of the three-phase separation region in the concentration tetrahedron (the types of evolution were described above) two approaches were suggested [19, 28]. The first one is based on adding a conjugate composition to the original mixture (of gross concentration) and studying the changes in the composition of the equilibrium liquid layers (of net concentration) that correspond to the three-phase separation region [19]. A composition, in which the gross concentration of one or several components that are in a certain ratio changes, can be chosen as a conjugate composition. This approach can be developed both on the basis of a natural experiment and on the basis of mathematical modeling of phase equilibrium. It has a predictive potential and allows studying the specific features of the three-phase separation region inclusion in the concentration tetrahedron under the conditions of limited experimental information. The authors of [19] illustrated the possibilities of the suggested method with water – acetonitrile – cyclohexene – cyclohexanone system as an example.

A second approach is based on solving equation (3) and using the mathematical concept of a centroid [28, 29].

The described approaches are the mathematics for studying the phase equilibrium of quaternary systems containing three-phase separation regions.

Of special interest are homologous systems containing three-phase separation regions. In works [30–33] the specific features of solubility change in binary and ternary systems in a series of systems were studied. One of the components of these systems is the member of a homologous series: water – benzyl alcohol – saturated hydrocarbons ($C_6$–$C_{10}$) [31], water – furfural – saturated hydrocarbons ($C_6$–$C_{10}$) [32], water – aniline - saturated hydrocarbons ($C_6$–$C_{10}$) [30, 32]. The authors note that in all the cases increasing the number of carbon atoms in the saturated hydrocarbons results in increasing the components mutual solubility, which, respectively, reduces the three-phase separation region. In water systems with furfural the author of [32] predicts on the basis of analyzing the experimental data that degeneration of the three-phase separation region will occur in the system with $C_{20}H_{42}$.

The revealed regularities are of practical interest, because: 1) they allow predicting the structures of the phase equilibrium diagrams of systems, which were not studied experimentally, but which relate to the considered homologous series; 2) they can serve to check the adequacy of mathematical modeling (in case of using of the UNIFAC group model); 3) they can be useful when planning a natural experiment.

A list of systems with three-phase separation and the corresponding references to the literature are presented in Table 1, and a list of systems with four-phase separation, in Table 2. The total of the considered systems is 160; 55 of them are water-organic systems, 89 are organic, and 9 are systems with electrolytes. Besides, 7 systems with four-component separation are considered. The systems noted with * were obtained by the author of [32] by means of a nomogram.

**Table 1.** Systems with three-phase separation

| System | Literature |
|---|---|
| ***Water-organic systems*** | |
| Water – aniline – hexane (heptane, octane, nonane, decane, tetradecane*) | [2, [32, [36–38] |
| Water – benzyl alcohol – hexane (heptane, decane, tetradecane)* | [32] |
| Water – dodecyl alcohol – nitromethane (nitroethane, adiponitrile) | [32] |
| Water – nitromethane – hexane (decane, tetradecane, tetrachloroethylene, carbon disulphide, isoamyl alcohol, cyclohexanol, hexanol, octanol, nonanol) | [2], [32], [39–42] |
| Water – nitroethane (nitrobenzene, ethyl cyanide, benzonitrile) – hexane (decane, tetradecane) | [2], [32] |
| Water – adiponitrile (methylethylketone)* – tetrachloromethane (diethyl ether, methylethylketone, carbon disulphide, cyclohexanol, amyl alcohol)* | [32] |
| Water – furfural (phenol, succinonitrile) – hexane (heptane, octane, nonane, decane, tetradecane, cyclohexane, $CO_2$) | [32], [37], [38], [43–46] |
| Water – dimethylpyridine – *n*-butyric acid | [45] |
| Water – ethanol – ethyl isovaleriate | [46] |
| Water – salicylic acid – benzene | [47] |

| | |
|---|---|
| Water – acetonitrile (sulpholane) – benzene – heptane | [4] |
| Water – cyclohexane – diethylene glycol monobutyrate – formamide | [50], [57] |
| *Organic systems* | |
| Glycol – nitromethane (glycerine) – tetrachloroethylene (*n*-dodecyl alcohol, heptyl alcohol, caprylic acid) | [51–55] |
| Nitrobenzene – ethanol – trimethylpentane | [56] |
| Formamide – methylformamide – $CO_2$ | [46] |
| Nitromethane – hexanol-1 – octanoic acid – 1,2,3-propanetriol | [58] |
| Ethanol (propanol) – ethylene glycol – methylene iodide (tetradecane)* | [32] |
| Amyl alcohol (carbon tetrachloride, cyclohexane, diethyl ether, methylethylkenone, amyl acetate, carbon disulphide) – ethylene glycol (glycerine) – nitromethane (adiponitrtile, methylethylketone)* | [32] |
| Octanol – ethylene glycol (glycerine) – nitromethane* | [32] |
| Dodecyl alcohol (tetrachloroethylene) – ethylene glycol (glycerine) – nitromethane (nitroethane, adiponitrile, acetonitile)* | [32] |
| Ethylene glycol – nitromethane (nitroethane, nitrobenzene) – hexane (decane, tetradecane, amyl acetate, tetrachloroethylene, carbon disulphide, lauryl alcohol)* | [32], [50], [51] |
| Ethylene glycol – methylene iodide – hexane (decane, tetradecane, cyclohexane)* | [32] |
| Glycerine (carbon tetrachloride, diethanolamine) – nitromethane (nitroethane, nitrobenzene, acetonitile, propionitrile, benzonitrile, adiponitrile) – cyclohexanone (hexane, cyclohexane, decane, tetradecane, amyl acetate, carbon disulphide, isoamyl alcohol, carbon tetrachloride, diethyl ether, methylethylketone, amyl acetate)* | [32] |
| Diethanolamine – nitromethane – amyl acetate (carbon disulphide) | [32] |
| Benzonitrile – cyclohexanone – formamide | [32] |
| Acetic acid (formic acid) – methylene iodide – hexane (decane, tetradecane)* | [32] |
| ***Systems with electrolytes*** | |
| Water – *n*-octane (*n*-butanol, acetonitrile) – propanol-1 (hexane, tetradecane) – sodium chloride | [59], [60], [66] |
| Water – benzene (heptane, heptanol-1) – caprolactam (ethanol) – ammonium sulphate | [20], [61–63], [65] |
| Water – hydrocarbons – alcohols – salt systems | [63], [64] |

**Table 2.** Systems with four-phase separation

| System | Literature |
|---|---|
| Ethylene glycol (glycerin, diethanolamine, water) – nitromethane – benzene – carbon disulphide | [32] |
| Water (glycerin) – adiponitrile – carbon tetrachloride – methylethylketone | [32] |
| Methyl iodide – cyclohexane – nitromethane – ethylene glycol | [6] |

## Modeling of phase equilibrium of systems with three liquid phases

The existence of three-phase separation in a system considerably complicates the mathematical modeling and correlation of experimental data on phase equilibrium. The most often used commercial software products for these purposes are AspenTech and CosmoRS. For the description of phase equilibrium and correlation of experimental data the equations of local structures NRTL [19, 43], UNIQUAC [49, 57, 58], and also UNIFAC [65–67] group model are used. The results of work [65] showed that the use of the group model is limited because of considerable errors in the description of liquid-liquid-liquid equilibrium.

Correlation of experimental data for systems containing electrolytes depends on the ability of the model to describe the influence of ions on phase behavior. For the description of such systems the authors of [68, 69] use the expanded NRTL model that includes Debye–Hückel and Bourne equations for the description of electrostatic effects.

The specific features of applying various models and the procedure of describing and correlating phase equilibrium data of systems with three-phase separation containing electrolytes are submitted in most detail in [69].

The authors of [49] suggested a method allowing to describe the equilibrium of three liquid phases. However, it does not allow carrying out correlation of results obtained in a natural experiment. A method for correlating experimental equilibrium data of ternary systems with three-phase separation is presented in [38]. It is based on estimating the geometrical features of the surface of Gibbs energy of mixing (the existence of a local and a global minimum). Similar studies were carried out by the authors of [70].

In general, it can be noted that there is no consensus today as for the advantages of any models for studying phase equilibrium of multiphase systems. Besides, there is no exact method allowing to predict the existence of a three-phase separation region in a system. It can be recommended to use the models of local compositions (NRTL, UNIQUAC) or their modifications, because they are well-proven for the description of multiphase systems. But studying mixtures by means of UNIFAC model does not always allow obtaining adequate results [65]. The only criterion of mathematical modeling adequacy is still the comparison of experimental and calculated data on phase equilibrium. But, at the same time, information on liquid–liquid–liquid phase equilibrium is extremely limited. Modern databases contain, as a rule, information on equilibrium of two liquid phases in binary and ternary mixtures. The available results of a natural experiment on the equilibrium of three liquid phases cannot always be used for obtaining the parameters of a model. In this case the approaches developed on the basis of the method suggested in [49] can be used for data correlation.

Therefore, studying and predicting the properties of systems where one or several components belong to the same homologous series can be considered as promising.

**Using the effect of three-phase separation in separation processes**

Processes proceeding with the participation of three-phase systems are used in the production of cosmetics, drugs, paints, lubricants, fats processing etc. [49, 71]. They play a special role in the petrochemical industry [59, 72, 73].

Let us consider several separation processes based on the ability of a system to form three liquid phases.

One of such methods is extraction. It is used in oil and gas processing for aromatic hydrocarbons and paraffins separation [74, 75], as well as for alkanes and alkenes separation [76]. Studying phase equilibrium in nitromethane – hexyl alcohol – water system the authors of [39] point to the possibility of separating aliphatic alcohols with the use of water and nitromethane by extraction methods. (Nitromethane and water are miscible in all proportions with lower aliphatic alcohols and partially miscible with higher alcohols.) Three-liquid extraction is used for the recovery of target metals from complex ores and industrial waste [77].

Recently, there is increasing interest in using ionic liquids as solvents for three-liquid extraction [78–83]. They have a number of advantages as compared to the classical solvents: they are not combustible, they have low vapor pressure, they are thermally stable and non-toxic. The possibility of using an ionic liquid for the separation of aliphatic and aromatic hydrocarbons is considered in [79]. In [81], the properties of an ionic liquid in the process of penicillin extraction were studied. In fact, an ionic liquid acts as a liquid membrane. The studies of the authors of [83] showed the opportunity and restrictions of using an ionic liquid, 1-butyl-trimethylimidazolium hexafluorophosphate, for extraction.

The effect of three-phase separation is used for the separation of mixtures of complex physical and chemical nature by rectification. Phase separation is a natural process. Therefore, it allows in some cases reducing energy consumption for the separation. Besides, one or several equilibrium layers may contain an almost pure component or contain trace amounts of one of the components. This also facilitates the separation task, because this allows to avoid using additional apparatuses in the separation scheme, in particular, using rectification columns. A number of works are devoted to three-component mixtures separation in schemes based on the combination of rectification and three-phase separation [19, 29, 32, 84–86]. By now, schematic diagrams of separating the following mixtures have been suggested: acetonitrile – trimethylethylene – water [32], acetonitrile – trimethylethylene – water – isoprene [29], water – acetonitrile – cyclohexene – cyclohexanone [19], nitromethane – hexane – water [86] and 2-methyl-1,3-butadiene – 2-methyl-2-butene –acetonitrile – water [29].

The presence of a third liquid phase in a system results in the emergence of additional flows in the process design and complicates the calculation of the scheme material balance as compared to mixtures with two-phase separation. Work [87] discusses the calculation of the material balance of such systems and specific features of assigning free variables required to solve the balance problem. At the same time, as shown in [29], when one or two components are practically absent in the equilibrium liquid phases (2-methyl-1,3-butadiene – 2-methyl-2-butene – acetonitrile – water), the schematic diagram can be simplified, i.e., some thermodynamic restrictions can be removed.

When separating mixtures with the use of three-phase separation, a key role is played by the specific features of the relative positioning of the simplex corresponding to three-phase separation and by the specific features of separatrix manifolds. At present such studies are performed at the department of chemistry and technology of basic organic synthesis of the Institute of Fine Chemical Technologies of the Moscow Technological University.

Analyzing scientific publications of the recent years it is possible to note that studying the local and non-local regularities of the diagrams of multiphase systems, obtaining new experimental data about phase equilibrium in multiphase systems, studying the nature of three-phase separation and the general regularities of the formation of phase diagrams of such systems remains an urgent problem. Solving the complex of these problems forms a basis of synthesizing process designs for separating multi-component mixtures based on a combination of rectification and phase separation.

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**References:**

1. Parmentier F. Ac. Sci. C.R. 1887. № 104. P. 686–688.
2. Mertclin R.V. Zhurnal fizicheskoi khimii (Russian Journal of Physical Chemistry A). 1938. V. 8. № 17. P . 1742–1755. (in Russ.).
3. Shapiro Yu.M., Nichepurenko V.I. Izv. vuzov. Pischevaya technologia (News of Institutes of Higher Education. Food Technology). 2005. № 5. P. 53–54 (in Russ.).
4. Dahyabhai J Shah, Krishna K. Tiwari. J. Chem. Eng. Data. 1981. V. 26. № 4. P . 375–378.
5. Schreinemakers F.A.N. Z. Furphys. Chem. 1901. V. 37. №. 2. P. 129–156.
6. Sazonov V.P. Thermodynamics and topology of two, three and four phase equilibrium of three- and four component systems): PhD dissertation. Samara, 1997 (in Russ.).
7. Roozeboom H.V.B., Screinemakers F.A.N. Die Hetetrogenen Gleichgewichte vom Standpunkte der Phasenlehre. Braunschweig. 1913. Heft 3. Teil 2. 348 s.
8. Alfred W. Francis. Liquid-liquid equilibrium. Interscience, 1963. 288 p.
9. Vogel R. Die Heterogenen Gleichgewichte. Leipzig: Academische Verlagsgesselschaft, 1959. 728 s.
10. Alders L. Liquid-liquid extraction. Amsterdam: Elsevier Publishing Company, 1959. 209 p.
11. Treybal R.E. Liquid extraction. McGraw-Hill Book Company, 1963. 640 p.
12. Beregovykh V.V. Research in the field of physical-chemical foundations of rectification of three component splitting mixtures. : D.Sc. dissertation M.: MITHT, 1971. (in Russ.).
13. Frolkova A.K. Theoretical basis of rectification of multicomponent multiphase systems using functional complex: PhD dissertation. M.: MITHT, 2000 (in Russ.).
14. Illarionov V.V. Investigation of properties of multiphase systems to creature effective technological flowsheets: PhD dissertation. M.: MITHT, 2011 (in Russ.).
15. Serafimov L.A., Frolkova A.V., Illarionov V.V. Vestnik MITHT (Fine Chemical Technologies). 2011. V. 2. № 2. P . 98–103 (in Russ.).
16. Frolkova A.K., Speranskii A.V., Serafimov L.A. Theoret. Found. Chem. Eng. 2002. V. 36. № 2. P. 128–135.
17. Serafimov L.A., Frolkova A.V., Illarionov V.V. Classification of splitting diagrams of three component systems. Moscow: MITHT, 2013. 28 p. (in Russ.).
18. Palatnik L.S., Landau A.I. Phase equilibria in multicomponent systems. Kharkov: Kharkov University, 1961. 406 p. (in Russ.).
19. Frolkova A.V., Balbenov S.A., Frolkova A.K., Akishina A.A. Russ. Chem. Bull. 2015. V. 64. № 10. P. 2330–2336.

20. Lang J. C., Widom B. Physica A: Statistical Mechanics and its Applications. 1975. V. 81. № 2. P. 190–213.

21. Gibbs G.W. Thermodynamic. Statistical Mechanics. Moscow: Nauka Publ., 1982. 584 p. (in Russ.).

22. Serafimov L.A., Frolkova A.K. Theoret. Found. Chem. Eng. 1998. V. 32. № 4. P . 347–356.

23. Frolkova A.V., Serafimov L.A., Semin G.A. Theoret. Found. Chem. Eng. 2014. V. 48. № 2. P. 158–166.

24. van der Waals I.D. Course of Thermostatic. Thermal Equilibrium of Material Systems. Moscow: ONTI, 1936. (in Russ.).

25. Storonkin A.V. Thermodynamic of heterogenic systems. Part III. Leningrad: LGU Publ., 1969. 190 p. (in Russ.)

26. Serafimov L.A. Theoret. Found. Chem. Eng. 1987. V. 21. № 1. P . 74–85. (in Russ.).

27. Frolkova A.K., Serafimov L.A. Theoret. Found. Chem. Eng. 2000. V. 34. № 3. P . 286–291.

28. Sebyakin A.Yu., Frolkova A.K. Theoret. Found. Chem. Eng. 2016. V. 50. № 2. P. 207–214. (in Russ.).

29. Sebyakin A.Yu., Frolkova A.K. Tonkie khimicheskie tekhnologii (Fine Chemical Technologies). 2016. V. 11. № 5. P. 65–69. (in Russ.)

30. Akishina A.A., Frolkova A.V., Illarionova Ye., Frolkova A.K. Diagrams of phase equilibria of ternary systems containing aniline, water and saturated hydrocarbons. XIX International conference of chemical thermodynamics in Russia (RCCT-2015), 2015. Nizhniy Novgorod. Book of Abstracts. P. 230.

31. Ivanova G.G., Telichko T.N., Timofeev V.S., Serafimov L.A. // Sbornik trudov instituta (Book of articles). 1974. V. 4. № 1. P. 101–106. (in Russ.).

32. Koliuchkina G.Ya. Investigation of rectification of heteroazeotropic mixtures: PhD dissertation. M.: MITHT, 1972. (in Russ).

33. Frolkova A.V., Afanas’eva I.V. Investigation of physic-chemical properties of ternary homologic systems / XXVIII Int. Conf. “Modern problems of humanitarian and natural sciences”. Moscow, 2016. P. 13–16.

34. Nikurashina N.I., Mertclin R.V., Timofeeva V.B. Uchenye zapiski Saratovskogo universiteta (Journal of Saratov’s university). 1959. V. 71. P. 89. (in Russ.).

35. Sazonov V.P., Sarkisov A.G. Zhurnal fizicheskoi khimii (Russian Journal of Physical Chemistry A). 1968. V. 42. № 8. P. 2066–2068. (in Russ.).

36. Shapiro Yu.M. Three phase liquid systems. Review. Cherkassy, 1986. Dep. ONIITEKHim 16.03.86. № 382khp-86Dp. – RZHKHim – 17B3079. 37. Denes F., Lang P., Lang-Lazi M. IChemE Symposium Series. 2006. № 152. P . 877–890.

37. Marcilla A., Olaya M.M., Serrano M.D., Velasco R., Reyes-Labarta J.A. Fluid Phase Equilibria. 2009. V. 281. № 1. P . 87–95.

38. Sazonov V.P., Markuzin N.P., Filippov V.V. Zhurnal prikladnoi khimii (Russian Journal of Applied Chemistry). 1976. V. 49. № 4. P. 784–788. (in Russ.).

39. Sazonov V.P. Zhurnal obshcgei khimii (Russian Journal of General Chemistry). 1982. V. 52. № 8. P. 1697–1703. (in Russ.).

40. Sazonov V.P., Sarkisov A.G. Zhurnal fizicheskoi khimii (Russian Journal of Physical Chemistry A). 1966. V. 40. № 2. P. 2719–2725. (in Russ.).

41. Nikurashina N.I., Mertclin R.V., Goskova I.D. Zhurnal organicheskoi khimii (Russian Journal of Organic Chemistry). 1959. V. 29. № 10. P. 3161–3166. (in Russ.).

42. Heidemann R.A., Abdel-Ghani R.M. Chemical Engineering Science. 2001. V. 56. № 24. P. 6873–6881.

43. Francis A.W. J. Phys. Chem. 1954. V. 58. № 12. P. 1099–1114.

44. Sergeeva V.F., Zakumbaeva Z.A. Zhurnal obshcgei khimii (Russian Journal of General Chemistry). 1982. V. 52. № 8. P. 1704–1706. (in Russ.).

45. Charg Y.C., Moulton R. W. Ind. Eng. Chem., 1953. V. 45. № 10. P . 2350–2361.

46. Krupatkin I.L. Zhurnal obschei khimii (Russian Journal of General Chemistry). 1956. V. 26. № 12. P. 3240–3246. (in Russ.)

47. Garcia-Sanchez F., Schwartzentruber J., Ammar M. N., Renon H. Fluid Phase Equilibria. 1996. V. 121. № 1-2. P . 207–225.

48. Stateva R.P., Cholakov G.S., Galushko A.A., Wakeham W. A. Chem. Eng. Sci. 2000. V. 55. № 11. P. 2121–2129.

49. Hou Hai-Yun, Liu Song-Tao, Geng Xin-Peng Chemical Journal of Chinese Universities. 2008. V. 29. № 1 1. P. 2249–2253.

50. Sazonov V.P., Zhilyaeva I.N. Three liquid phase equilibrium of three-component systems. VII. System of nitromethane – tetrachloroethylene – ethylene glycol. Moscow, 1972. – Dep. VINITI № 5005-72; RZHKHim – 9B905 (in Russ.).

51. Francis A.W. J. Phys. Chem. 1956. V. 60. № 1. P. 20–27.

52. Sazonov V.P., Zhilyaeva I.N. Three liquid phase equilibrium of threecomponent systems. V. System of nitromethane – hexyl acetic acid – glycerol and nitromethane – heptyl alcohol – glycerol. Moscow, 1970. – Dep. VINITI № 2410- 70; RZHKHim – 1 1B821 (in Russ.).

53. Francis A.W. J. Am. Chem. Soc. 1954. V. 76. № 2. P. 393–395.

54. Haiyun Hou Xueqin An Weiguo Shen. J. Chem. Eng. Data. V. 50. № 4. P . 1308–1312.

55. Sazonov V.P., Sazonov N.V., Lisov N.I. J. Chem. Eng. Data. V. 47. № 6. P . 1462–1465.

56. Negahban S., Willhite G.P., Walas S.M., Michnick M.J. Fluid Phase Equilibria. 1986. V. 32. № 1. P. 49–61.

57. Negahban S., Willhite G.P., Walas S.M. SPE Reservoir Engineers. 1988. V. 3. № 3. P. 1017–1024.

58. Huan Z., Van Bochove G.H., De Loos T.W. AIChE Journal. 2003. V. 49. № 3. P . 745–752.

59. Van Bochove G.H., Krooshof G.J.P, De Loos Th.W. Fluid Phase Equilibria. 2002. V. 194-197. P. 1029–1044.

60. Knickerbocker B.M., Pesheck C.V., Davis H.T., Scriven L.E. J. Phys. Chem. 1982. V. 86. № 3. P 393-400.

61. Knickerbocker B.M., Pesheck C.V., Scriven L.E., Davis H.T. J. Phys. Chem. 1979. V. 83. № 15. P. 1984–1990.

62. Wijtkamp M., van Bochove G. H., de Loos Th. W., Niemann S.H. Fluid Phase Equilibria. 1999. V. 158-160. P. 939–947.

63. Frankovskii V.A., Piatnitskii I.V., Tarasevich V.Yu. Zhurnal analiticheskoi khimii (Journal of Analytical Chemistry). 1988. V. 43. № 12. P. 2151–2156. (in Russ.).

64. Frolkova A.V., Zakharova D.S., Frolkova A.K., Balbenov S.A. Fluid Phase Equilibria. 2016. V. 408. P. 10–14.

65. McDonald C.M., Floudas C.A. AIChE Journal. 1995. V. 41. № 7. P. 1798–1814.

66. McDonald C.M., Floudas C.A. Computers & Chemical Engineering. 1997. V. 21. № 7. P. 821–822.

67. Chen C.C., Evans L.B. AIChE Journal. 1986. V. 32. № 3. P. 444–454.

68. Van Bochove G.H. Two- and Three-Liquid Phase Equilibria in Industrial Mixed Solvent Electrolyte Solutions: Experiments and Modeling of Systems of Importance for the Extraction of Caprolactam. IOS Press, Inc., 2003. 192 p.

69. Lucia A., Dimaggio P.A., Depa P. Journal of Global Optimization. 2004. V. 29. № 3. P. 297–314.

70. Arutyunian N.S., Arisheva E.A., Yanova L.I. Fat processing technology. Moscow: Agropromizdat, 1985. 368 p. (in Russ.).

71. Kalhweit M., Strey R., Busse G. J. Phys. Chem. 1990. V. 94. № 10. P. 3881–3894.

72. Andersen J.G., Koak N., de Loos T.W. Fluid Phase Equilibria. 1999. V. 163. № 2. P. 259–273.

73. Griswold J., Chew J.N., Klecka M.E. Ind. Eng. Chem. 1950. V. 42. № 6. P. 1246–1251.

74. Hartwig G.M., Hood G.C., Maycock R.L. J. Phys. Chem. 1955. V. 59. № 1. P. 52–54.

75. Griswold J., Klecka M.E., West R.V. Chem. Eng. Progr. 1948. V. 44. P. 839.

76. Huang K., Liu H. Liquid-liquid-liquid three phase extraction: A promising strategy for multi-metal separation from complex systems. // The 51 Annual Conference of Metallurgists of CIM (COM – 2012). Niagara, ON, Canada.

77. Pletnev I.V., Smirnova S.V., Khachatrian K.S., Zernov V.V. Russian Journal of General Chemistry. 2004. V. 48. № 6. P. 51–58. (in Russ.).

78. Basheer C., Alnedhary A.A., Madhavarao B.S., Balasubramanian R., Lee H.K. J. Chromatography A. 2008. V. 1210. № 1. P. 19–24.

79. Boiadzhiev L. Theoret. Found. Chem. Eng. 1984. V. 18. № 6. P. 735-743. (in Russ.).

80. Tan Xian-Dong, Ji Qing-Rong, Chang Zhi-Dong The Chinese Journal of Process Engineering. 2006. V. 6. № 3. P. 363–368.

81. Guo L., Lee H.K. J. Chromatography A. 2011. V. 1218. № 28. P. 4299–4306.

82. Carda-Broch S., Berthod A., Armstrong D.W. Anal. Bioanal. Chem. 2003. V. 375. № 2. P. 191–199.

83. Timofeev V.S. Physico-chemical basics of technology of rectification of heteroazeotropic multicomponent mixtures: PhD dissertation. M.: MITHT, 1974. (in Russ.).

84. Timofeev V.S., Serafimov L.A., Timoshenko A.V. Principles of technology of basic organic and petrochemical synthesis. M.: Vysshaya Shkola Publ., 2010. 408 p. (in Russ.).

85. Frolkova A.V., Ablizin M.A., Maevskii M.A., Frolkova A.K. Tonkie Khimicheskie Tekhnologii (Fine Chemical Technologies). 2016. V. 11 № 3. P. 44–47. (in Russ.).

86. Frolkova A.V., Akishina A.A., Ablizin M.A., Mayevskiy M.A. Feathers of calculation of material balance of quaternary splitting system separation flowsheet // High-Tech in Chemical Engineering – 2016 : Abstracts of XVI Int. Scientific Conf. (October 10–15, 2016, Moscow). Moscow: Moscow Technological University, 2016. P. 32.