Separation of a Multicomponent System Formed in the Production of Epichlorohydrin*

E.A. Okhlopkova@, L.A. Serafimov, A.V. Frolkova, P.P. Tsekin

Moscow Technological University (Institute of Fine Chemical Technologies), Moscow, 119571 Russia
@*Corresponding author e-mail:* ea.okhl@ya.ru

Epichlorohydrin is an important product of the basic organic synthesis. One promising direction of epichlorohydrin manufacturing is the liquid-phase epoxidation of allyl chloride with an aqueous solution of hydrogen peroxide in an organic solvent, methanol, in the presence of a heterogeneous catalyst, a titanium-containing zeolite. The multicomponent system of epichlorohydrin production according to this method contains allyl chloride, methanol, water, epichlorohydrin, 3-chloro-1,2-propanediol, 3-chloro-1-methoxypropanol-2 and hydrogen peroxide. In this work the thermodynamic topological analysis of the phase diagram of this multicomponent system of epichlorohydrin production was performed. On the basis of this study a principal technological scheme of separation of the studied system containing five distillation columns and a Florentine vessel was proposed.

Keywords: *epichlorohydrin, phase equilibrium, mathematical simulation, separation complex.*

Introduction

Epichlorohydrin is an important product of the basic organic synthesis. It is used for producing a number of products that are applied in different industries. Epichlorohydrin contains an active epoxy group and a labile chlorine atom. Due to this it easily enters various reactions of electrophilic and nucleophilic addition and substitution. Paints, glues, ion exchange resins, synthetic fibers and rubbers characterized by high thermal stability and gas-tightness [1] are produced on its basis. About 80% of products based on epichlorohydrin are used for obtaining epoxy resins [2].

The estimated world production of epichlorohydrin is more than 1.8 million tons a year [3]. In Russia, two plants for obtaining epichlorohydrin with total capacity not higher than 66,000 tons a year functioned, which made about 3.8% of the world production. However, they were taken out of service in 2010. Thus, the problem of creating epichlorohydrin production based on perspective methods is an urgent task.

Nowadays, there are several industrially significant technologies for obtaining epichlorohydrin. One of perspective methods is liquid-phase epoxidation of allyl chloride with an aqueous solution of hydrogen peroxide [4, 5] in methanol in the presence of a heterogeneous catalyst [6] – titanium-containing zeolite [7], which results in the formation of a multi-component mixture.

* *Original Russian Text © E.A. Okhlopkova, L.A. Serafimov, A.V. Frolkova, P.P. Tsekin, 2016, published in Tonkie Khimicheskie Tekhnologii /Fine Chemical Technologies, 2016, Vol. 11, No. 6, pp. 36–42.*

In this work the phase equilibrium of a multi-component mixture of products of the synthesis of epichlorohydrin obtained by this method was studied. On the basis of thermodynamic topological analysis of the phase diagram a scheme for separating the reaction mixture and obtaining epichlorohydrin of the required purity is offered.

Theoretical Part

Liquid-phase epoxidation of allyl chloride with an aqueous solution of hydrogen peroxide occurs in an organic solvent, methanol [7]. The solvent in this process plays the role of a homogenizer for allyl chloride and hydrogen peroxide. Its concentration exercises a significant influence on the epoxidation. The three-component system allyl chloride-methanol-water is characterized by the existence of a phase separation region. Therefore, the choice of the solvent concentration is limited, on one hand, to the possibility of obtaining a homogeneous reaction mixture, and, on the other hand, by the inexpediency of its considerable dilution, because this will complicate the subsequent isolation of epichlorohydrin.

In order to study the influence of methanol concentration on the epoxidation process the author of [7] carried out a series of experiments at various solvent concentrations and constant amounts of the reagents and catalyst. The study showed that it is expedient to carry out the epoxidation at the solvent content about 55–60% (mass), which corresponds to methanol-allyl chloride molar ratio (4.2–5.3):1. When the content of methanol is less than 55% mass, the probability of transition from the homophase state to the heterophase one increases. The solvent content more than 60% mass leads to a reduction in the process rate and complicates the subsequent stage of epichlorohydrin isolation because of high dilution of the reaction mass. The solvent content of 55–60% mass provides a rather high epoxidation rate and main product yield.

Besides, it was shown in [7] that it is expedient to carry out allyl chloride epoxidation by hydrogen peroxide at excess of allyl chloride. The influence of allyl chloride-hydrogen peroxide initial ratio on the main regularities of the epoxidation was estimated. The study showed that it is expedient to maintain the initial allyl chloride-hydrogen peroxide ratio in the range of 3–4 (mol/mol) for ensuring a high yield of the main product at high degrees of hydrogen peroxide transformation.

Therefore, it can be concluded that allyl chloride and methanol flows should be recycled to maintain the recommended conditions.

As a result of the reaction a multicomponent mixture is formed. It contains allyl chloride (AC), methanol (M), water (W), epichlorohydrin (ECH), 3-chloro-1,2-propanediol (CPD), 3-chloro-1-methoxypropanol-2 (CMP) and hydrogen peroxide (HP). The composition of the multicomponent mixture formed when obtaining 50000 tons of epichlorohydrin per year was obtained on the basis of sources [8, 9], and it is presented in Table 1.

Table 1. Boiling points, quantities and concentrations of the components of the seven-component mixture formed in the production of epichlorohydrin

Mixture component	Boiling point, °C	Component quantity, kg/h	Component concentration, % mass	Component concentration, mole fraction
Allyl chloride	45.0	10,490.00	16.66	0.0761
Methanol	64.5	38,800.00	61.61	0.6723
Water	100.0	6,848.50	10.88	0.2111
Epichlorohydrin	116.1	6,390.00	10.15	0.0384
Hydrogen peroxide	150.0	7.50	0.01	0.0001
3-Chloro-1-methoxypropanol-2	171.0	189.00	0.30	0.0008
3-Chloro-1,2-propanediol	213.0	248.00	0.39	0.0012
Total		62,973.00	100	1

According to [7] data, HP, CMP and CPD do not form azeotropes with the other components. Therefore, they can be combined in a fraction of high boiling components (HBC). In further analysis of the phase diagram we will consider a five-component system: AC – M – W – ECH – HBC.

Calculation Part

Previously [10] the parameters of binary interaction allowing to describe adequately the phase equilibrium in the quaternary system AC – M – W – ECH were found. It was shown that the system has three binary azeotropes. Information on them is shown in Table 2.

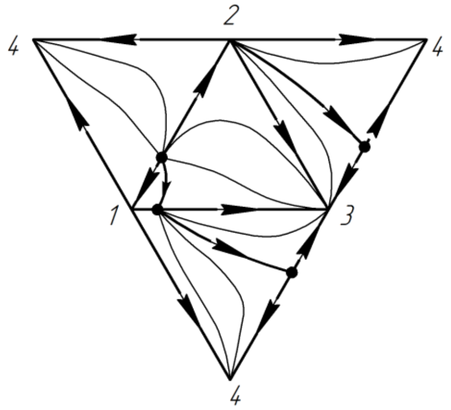
Table 2. Azeotropy in allyl chloride – methanol – water – epichlorohydrin system

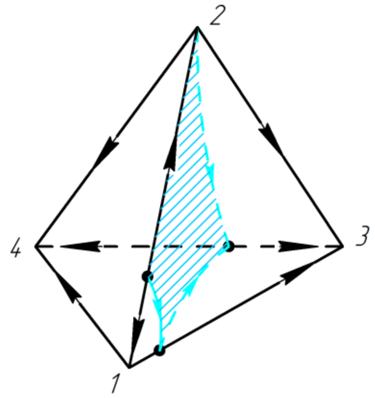
Binary system 1 – 2	bp^{az}, °C	x_1^{az}, mole fraction	Relative error	
			by bp^{az}	by x_1^{az}
M – AC	40.12	0.244	0.68	5.058
W – AC	43.4	0.086	0.93	1.149
W – ECH	89.68	0.664	1.91	5.230

Knowing the boiling points of the components and azeotrope it is possible to carry out the thermodynamic topological analysis of the vapor-liquid phase diagram.

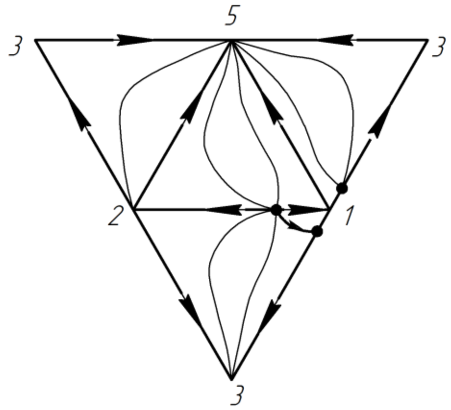
Figure 1 shows the 2D nets and the full structures of the vapor-liquid phase diagrams of the five four-component constituents of the studied system.

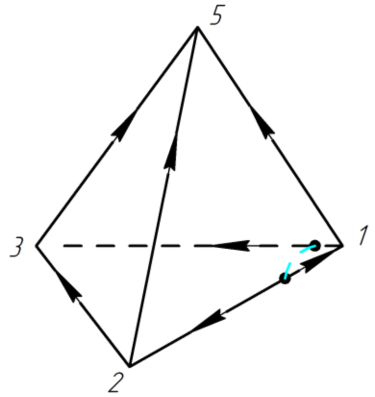
Analysis of the types and indexes of singular points is given in Table 3.



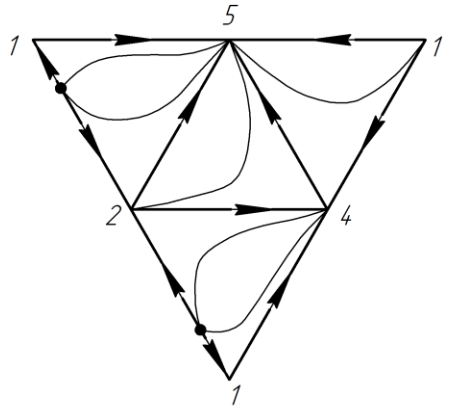


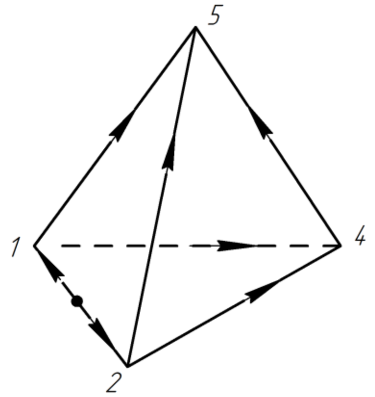
а



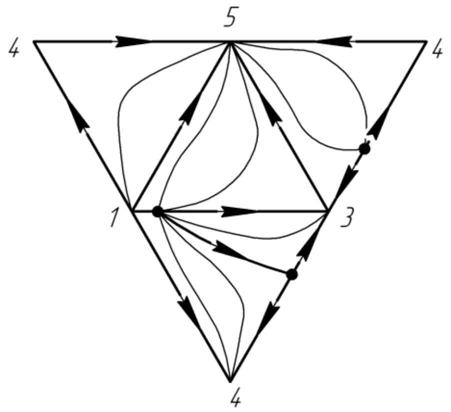


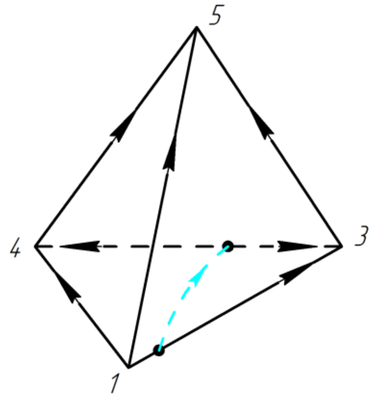
б





в





г

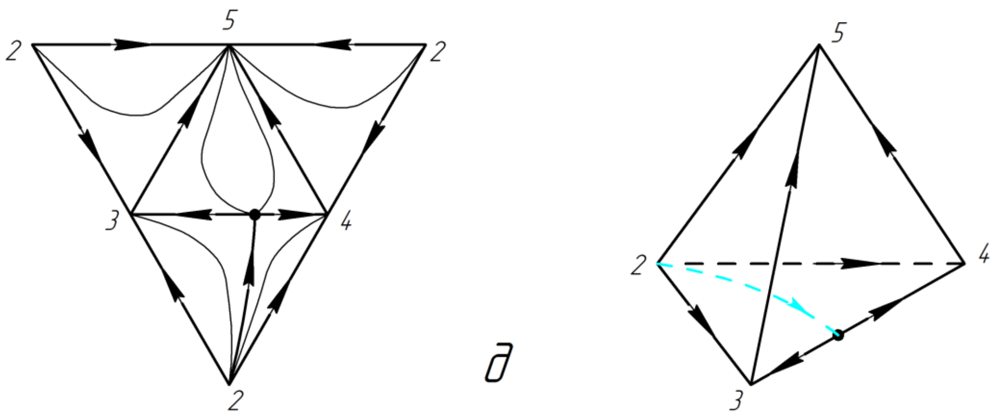


Figure 1. The 2D net and the full structures of the vapor-liquid phase diagrams of quaternary constituents of the system AC (1) – M (2) – W (3) – ECH (4) – HBC (5):

a) 1 – 2 – 3 – 4, b) 1 – 2 – 3 – 5, c) 1 – 2 – 4 – 5, d) 1 – 3 – 4 – 5, e) 2 – 3 – 4 – 5.

[а means a; б means b; в means c; г means d; д means e]

Table 3. Types and indexes of singular points of quaternary constituents of the studied system AC – M – W – ECH – HBC

With respect to the 2D net of the concentration tetrahedron										
System	AC-M-W-ECH		AC-M-W-HBC		AC-M-ECH-HBC		AC-W-ECH-HBC		M-W-ECH-HBC	
Singular point	Type	*i*	Type	*i*	Type	*i*	Type	*i*	Type	*i*
AC	*CN*	0	*CN*	0	*CN*	0	*CN*	0	–	–
M	*CN*	0	*CN*	0	*CN*	0	–	–	N^{unstab}	+1
W	N^{stab}	+1	*CN*	0	–	–	*CN*	0	*CN*	0
ECH	N^{stab}	+1	–	–	*CN*	0	*CN*	0	*CN*	0
HBC	–	–	N^{stab}	+1	N^{stab}	+1	N^{stab}	+1	N^{stab}	+1
AC-M	N^{unstab}	+1	N^{unstab}	+1	N^{unstab}	+1	–	–	–	–
AC-W	*CN*	0	*CN*	0	–	–	N^{unstab}	+1	–	–
W-ECH	*C*	–1	–	–	–	–	*CN*	**0**		
Σ	–	**2**	–	**2**	–	**2**	–	**2**	–	**2**
With respect to the complete structure of the concentration tetrahedron										
System	AC-M-W-ECH		AC-M-W-HBC		AC-M-ECH-HBC		AC-W-ECH-HBC		M-W-ECH-HBC	
Singular point	Type	*i*	Type	*i*	Type	*i*	Type	*i*	Type	*i*
AC	*CN*	0	*CN*	0	*CN*	0	*CN*	0	–	–
M	*CN*	0	*CN*	0	*CN*	0	–	--	N^{-}	–1
W	N^{+}	+1	*CN*	0	–	–	*CN*	0	*CN*	0
ECH	N^{+}	+1	–	–	*CN*	0	*CN*	0	*CN*	0
HBC	–	–	N^{+}	+1	N^{+}	+1	N^{+}	+1	N^{+}	+1
AC-M	N^{-}	–1	N^{-}	–1	N^{-}	–1	–	–	–	–
AC-W	*CN*	0	*CN*	0	–	–	N^{-}	–1	–	–
W-ECH	*C*	–1	–	–	–	–	*CN*	**0**		
Σ	–	**0**	–	**0**	–	**0**	–	**0**	–	**0**

The obtained data suggest the following:

- The quaternary system AC-M-W-ECH has three binary azeotropes of unstable node type, a saddle-node and a saddle. The latter generates a two-dimensional separatrix manifold in the concentration tetrahedron, the borders of which are one-dimensional separatrixes. This manifold divides the simplex into two distillation regions.
- In other systems the binary azeotropes are represented by unstable nodes and/or a saddle-node. AC-M-W-HBC, AC-W-ECH-HBC and M-W-ECH-HBC systems have a one-dimensional separatrix and no two-dimensional separatrix manifolds. This is because these systems have no special point of the saddle type. AC-W-ECH-HBC system has no one-dimensional separatrix. All the systems have one distillation region.

If one considers the two-dimensional net of the pentatope (Figure 2), it can be seen that when the borders in the concentration pentatope are joined, there is no three-dimensional separatrix manifold. This indicates that there is only one distillation region, in which the unstable node is azeotrope AC-M, and the stable one is HBC.

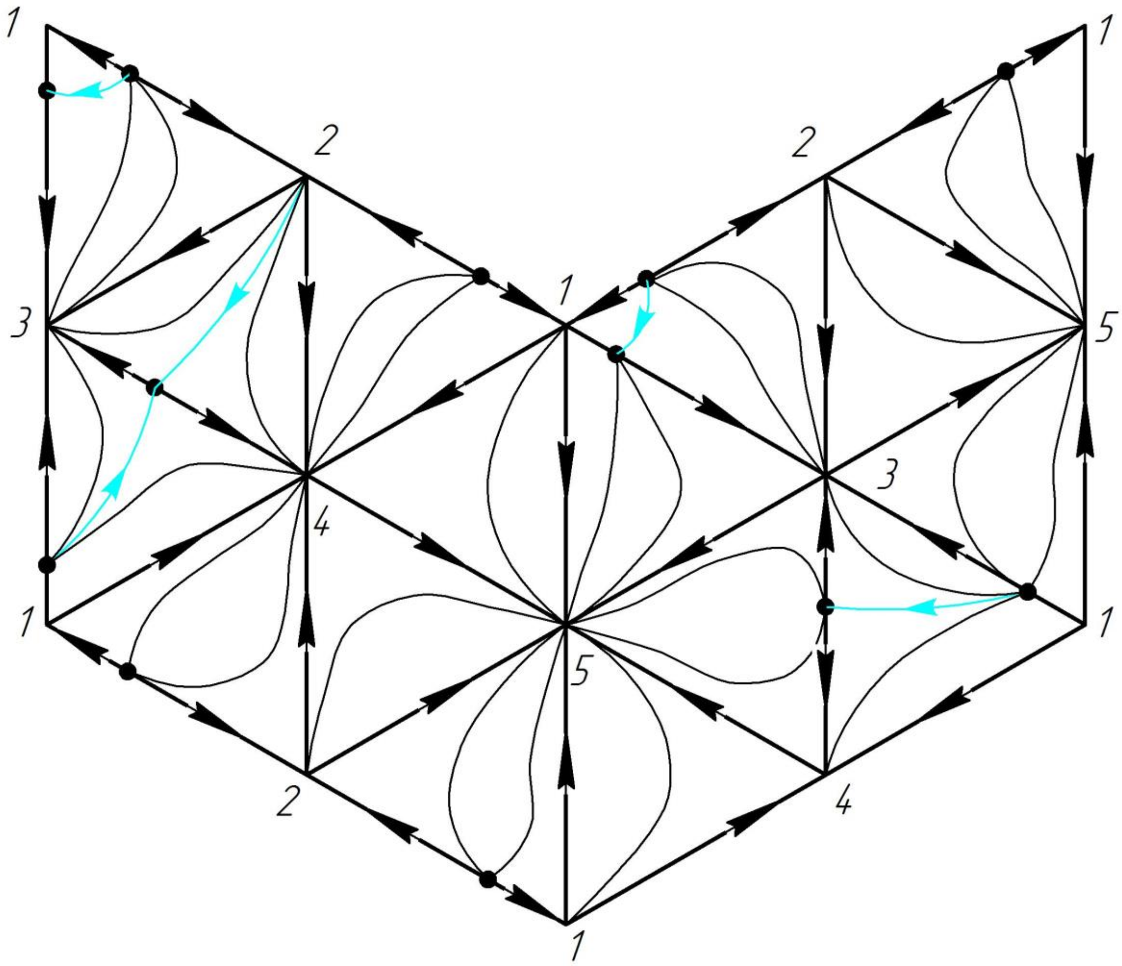


Figure 2. A two-dimensional net of the pentatope of AC (1) – M (2) – W (3) – ECH (4) – HBC (5) system.

Thus, at the first stage of separation it is possible to separate the high boiling components fraction from AC-M-W-ECH mixture in an ordinary rectification column (K1, Figure 3).

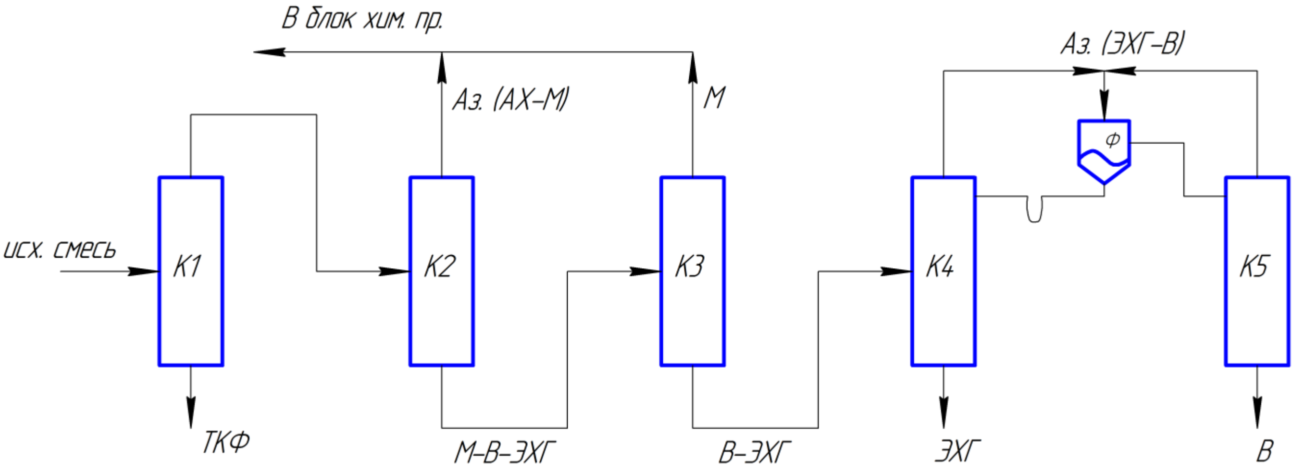


Figure 3. A principle diagram of separating the products of a mixture formed in the production of epichlorohydrin.

[исх. смесь means; К1 means C1; К2 means C2; К3 means C3; К4 means C4; К5 means C5; В блок хим. пр. means to chem. transf. block; Аз. (АХ-М) means Az. (AC-M); М means M; Аз. (ЭХГ-В) means Az. (ECH-W); ТКФ means HBC; М-В-ЭХГ means M-W-ECH; В-ЭХГ means W-ECH; ЭХГ means ECH; В means W; Ф means F]

This column (C1) should operate at low pressure because of the thermal lability of the substances in it. The remaining mixture [AC (mol fraction 0.0761) – M (mol fraction 0.6723) – W (mol fraction 0.2111) – EHG (mol fraction 0.0405)] contains azeotropes and a separatrix manifold. Therefore, it is impossible to separate it by the usual rectification. At the same time it has components with limited mutual solubility [7, 10], namely: W-ECH, AC-W and AC-M. Figure 4 shows features of the relative positioning of the separatrix and binodal manifolds.

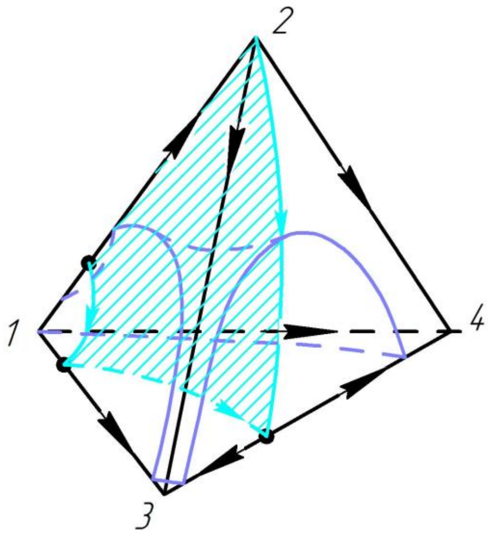


Figure 4. Relative positioning of the separatrix surface and separation regions in AC (1) – M (2) – W (3) – ECH (4) system.

As mentioned above, allyl chloride and methanol should be directed to the chemical transformation block. Therefore, it is expedient to isolate AC-M azeotrope (an unstable node) in column C2 distillate (Figure 3) and to recycle it to the chemical stage. In the bottom of column C2, three-component mixture M-W-ECH is formed. After separating the rest of methanol (column C3, Figure 3) W-EHG binary azeotrope mixture can be separated in the heteroazeotropic rectification complex (C4-F-C5).

The carried-out analysis shows that it is impossible to isolate allyl chloride from the original mixture at the first stage, as shown in [7], because this special point is a saddle-node with respect to the concentration space.

The suggested principle diagram has a number of advantages as compared to the scheme presented in [7]: it contains a smaller number of apparatuses (5 columns and a Florentine vessel); it allows isolating the high-boiling fraction at the first stage of separation.

Conclusion

Thus, this work presents a thermodynamic topological analysis of the phase diagram of the multi-component system formed in the production of epichlorohydrin obtained by one of perspective industrial methods, namely, by allyl chloride epoxidation with hydrogen peroxide in an organic solvent – methanol –in the presence of a heterogeneous catalyst – titanium-containing zeolite. A principle diagram of the separation of the studied mixture containing five rectification columns and a Florentine vessel is suggested.

The authors are grateful to Doctor of Engineering Mark Rafailovich Flid for consultations on specific matters of the article.

References:

1. Rakhmankulov D.L., Kimsanov B.K., Loktionov N.A., Dmitriev Yu.K., Chanishev R.R. Epichlorohydrin. Methods of preparation, physical and chemical properties, technology of production. Moscow: Khimiya Publ., 2003. 244 p (in Russ.).
2. Epicerol Process. Growing Green. Solvay Chemicals, INC., February 2008.
3. Epichlorohydrin: review of world production and market. Evrazi'skiy chimicheskiy rinok. 2010. № 3. P. 2–7 (in Russ.).
4. Gao H., Lu G., Suo J., Li S. Applied Catalysis A: General. 1996. V. 138(1). P. 27–38.
5. Kumar R.P., Kumar R. Eco-friendly synthesis of epichlorohydrin catalyzed by titanium silicate (TS-1) molecular sieve and hydrogen peroxide. Catalysis Commun. 2007. V. 8. P. 379–382.
6. Sulimov A.V., Danov S.M., Ovcharova A.V., Obrivalina A.V., Telyashev R.G., Ovcharov A.A., Balashov A.L. Neftegazochimiya (Oil-Gas Chemistry). 2013. № 1. P. 32–37 (in Russ.).
7. Ovcharova A.V. Development of technology for the production of epichlorohydrin: PhD dissertation. Moscow, 2012. (in Russ.).
8. Sulimov A.V. Development of scientific bases and technologies for the production of heterocyclic oxygen-containing compounds: D.Sc. thesis. Moscow, 2013. 330 p. (in Russ.).
9. Sulimov A.V., Danov S.M., Ovcharova A.V., Ovcharov A.A., Flid V.R., Leont'eva S.V., Flid M.R., Trushechkina M.A. Izvestiya Akademii nauk. Seriya chimicheskaya (Proceedings of the Academy of Sciences. The Chemical series). 2016. № 2. P. 469–472 (in Russ.).
10. Okhlopkova E.A., Serafimov L.A., Frolkova A.V. The study of the structure of phase equilibrium diagrams of four-component mixture of epichlorohydrin production products / Problemy idostizheniya v nauke i tekhnike (Problems and Advances in Science and Technology) / Collection of scientific papers according to the results of the international scientific-practical conference № 3. ICRON, Omsk, 2016. P. 152–158 (in Russ.).
11. Garov V.T., Serafimov L.A. Physical and chemical basis of distillation and rectification. Leningrad: Khimiya Publ., 1975. 240 p. (in Russ.).
12. Medvedev D.V., Frolkova A.V., Serafimov L.A. Determination of the structure of the diagram of distillation lines of quaternary system based on its sweep. Moscow: MITHT, 2011. 46 p (in Russ.).
13. Serafimov L.A., Frolkova A.K. Thermodynamic topological analysis of the phase diagram as base of synthesis of separation schemes. Moscow: MITHT, 2004. 90 p (in Russ.).