

THE SIMULATION OF VAPOR-LIQUID EQUILIBRIUM IN TERNARY SYSTEMS WITH TWO TERNARY AZEOTROPES

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Abstract

Theoretical substantiation of biazeotropy phenomenon in ternary systems is presented. The mathematical models of vapor-liquid equilibrium in benzene–perfluorobenzene–methyl propionate and benzene–perfluorobenzene–tert-amyl alcohol systems at various pressures had been developed.

Key words: simulation, vapor-liquid equilibrium, azeotrope, biazeotropy

1. Introduction

The possibilities of distillation separation of liquid multicomponent mixture are limited by azeotropy. Recently the attention of researchers attracts the phenomenon of biazeotropy, i.e. the existing of two azeotropic points on the one and the same element of composition simplex. The sets of data on 12 biazeotropic binary systems are presented in the literature. The search of biazeotropic ternary systems had been carried out in the work¹. The complex topological structure of such biazeotropic systems needs new approaches for calculations and approximations of vapor-liquid equilibrium (VLE). One of the problems is the simulation of VLE in such systems with the use of known mathematical models.

2. Theoretical substantiation of biazeotropy phenomenon

The azeotropy existence in binary systems is defined by some properties of components: boiling temperatures (T), partial molar heats of evaporation, the existing of Bancroft point (for temperature dependence of vapor pressure P). The sufficient condition of the existence of ternary azeotrope² is connected with inversion of boiling temperatures of components and binary azeotrope (the Bancroft point of the second type) or two binary azeotropes (Bancroft point of the third type). It is evident, the more singular points in the boundary constituents of concentration simplex, the more phenomenon of biazeotropy is probable. Accordingly the system with biazeotropic binary constituent sub-system had been chosen for the search of ternary biazeotropic systems. In papers^{3,4} the dependences of temperature on vapor pressure for singular points in ternary systems (pure components and binary azeotropes) had been analyzed for the cases of various correlations of boiling temperatures. Variants of the sufficient conditions of the existing of two ternary azeotropes had been determined and considered.

3. The choice of research objects and the model of phase equilibrium

Benzene (B) – perfluorobenzene (PFB) – methyl propionate (MP) and benzene–perfluorobenzene–tert-amyl alcohol (TAA) systems include the binary biazeotropic constituent sub-system benzene–perfluorobenzene. Both ternary systems satisfy to conditions formulated in the work¹ for ternary biazeotropy and had been the objects of mathematical simulation of VLE in our study. Some difficulties in the study of phase equilibrium are connected with the closeness of boiling temperatures for practically all compositions of ternary systems. These difficulties are also determined by small difference in the compositions of equilibrium phases and the values of relative volatility (which is closed to unit). The simulation of VLE had been carried out with the use of the Wilson equation. Available sets of experimental data were not sufficient for the calculation of reliable parameters of the Wilson equation for all binary systems. Due to it VLE in binary constituent sub-systems had been firstly calculated on the base of UNIFAC model. Then parameters of Wilson model had been estimated with the use of these pseudo-experimental data on VLE. As a result VLE in ternary systems had been simulated with the use of these parameters. The choice of initial liquid phase compositions for VLE calculation was based on the method of “secants and sections”. The features of the formation of some phase iso-manifolds had been studied by the extensive computation experiments on VLE

simulation. The VLE simulation was carried out for the system B–PFB–MP at 500 and 760 mm Hg, and for the system B–PFB–TAA at 300 (biazeotropy), 500 (internal tangential azeotrope⁵), 760 (zeotropic system) mm Hg.

4. The results of mathematical simulation

The obtained VLE data sets were treated for the construction of unit K-lines (K – partition coefficient of component between liquid and vapor) and unit α -lines (α – relative volatility). These lines were used for the establishment of ternary azeotropes existence and determination of azeotrope compositions. This information is necessary for the construction of residue curve maps. The results of mathematical simulation for ternary systems are listed in Tables 1 and 2: properties of pure components, binary and ternary azeotropes. The course of unit K-lines and α -lines, also residue curve maps are presented by Figure 1. We had studied the evolution of ternary phase diagrams structures at pressure variation. The structure of the phase diagram of B–PFB–MP system remains the same at both pressures (500 and 760 mm Hg). The system B–PFB–TAA undergoes essential changes at pressure variation. The evolution of the structures of residue curve maps with pressure changes is illustrated by Figure 2. It is evident that at 100 mm Hg only one ternary azeotrope exists. At the pressure of 300 mm Hg there are two ternary azeotropes, and at 500 mm Hg the appearance of the internal tangential azeotrope is fixed. At atmospheric pressure ternary azeotropes does not exist.

Table 1. The properties of components and binary azeotropes in B–PFB–MP and B–PFB–TAA systems

System 1-2	Pressure, mm Hg	$T_1, ^\circ\text{C}$	$T_2, ^\circ\text{C}$	Azeotropic properties			
				$T_{\text{calc}}, ^\circ\text{C}$	$x_{1\text{calc}},$ mole fraction	$T_{\text{exp}}, ^\circ\text{C}$	$x_{1\text{exp}},$ mole fraction
B-PFB	760	80,13	80,24	80,34	0,21	80,45	0,24
				79,20	0,83	79,35	0,82
B-PFB	500	67,13	67,85	67,91	0,16	67,96*	0,2*
				66,39	0,85	66,59*	0,85*
B-PFB	300	52,73	54,08	54,17	0,15	54,2*	0,2*
				52,39	0,91	52,44*	0,9*
B-MP	760	80,13	79,46	78,71	0,45	79,45	0,49
	500	67,13	67,18	66,19	0,53	66,18	0,53
PFB-MP	760	80,24	79,46	80,39	0,70	80,39*	0,65*
	500	67,85	67,18	68,07	0,65	68,05*	0,65*
B-TAA	760	80,13	101,84	78,89	0,88	80,00	0,865
	500	67,13	90,62	66,35	0,90	66,47*	0,9*
	300	52,73	78,16	52,35	0,95	52,41*	0,95*
PFB-TAA	760	80,24	101,84	76,69	0,79	76,98*	0,79*
	500	67,85	90,62	65,11	0,82	65,29*	0,80*
	300	54,08	78,16	52,11	0,85	52,25*	0,84*

* - pseudo-experimental data (UNIFAC)

Table 2. The properties of ternary azeotropes in B–PFB–MP and B–PFB–TAA systems

System 1-2-3	Pressure, mm Hg	Azeotropic properties					
		saddle			node		
		$x_{1\text{calc}},$ mole fraction	$x_{2\text{calc}},$ mole fraction	$T_{0\text{calc}},$ $^\circ\text{C}$	$x_{1\text{calc}},$ mole fraction	$x_{2\text{calc}},$ mole fraction	$T_{0\text{calc}},$ $^\circ\text{C}$
B-PFB-MP	760	0,81	0,09	79,36	0,08	0,72	80,41
B-PFB-TAA	300	0,29	0,56	52,5	0,85	0,09	52,05

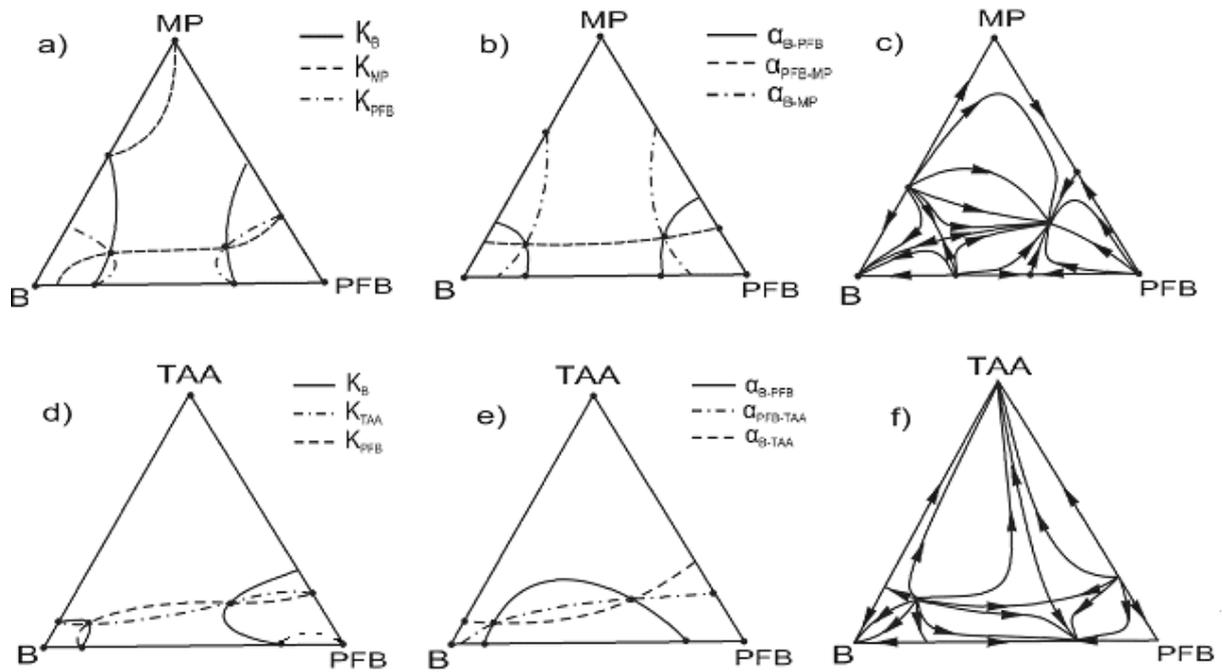


Figure 1. The diagrams of the course of unit K-lines (a, d), α -lines (b, e) and residue curve maps (c, f) in the systems B-PFB-MP (P=760 mm Hg) and B-PFB-TAA (P=300 mm Hg)

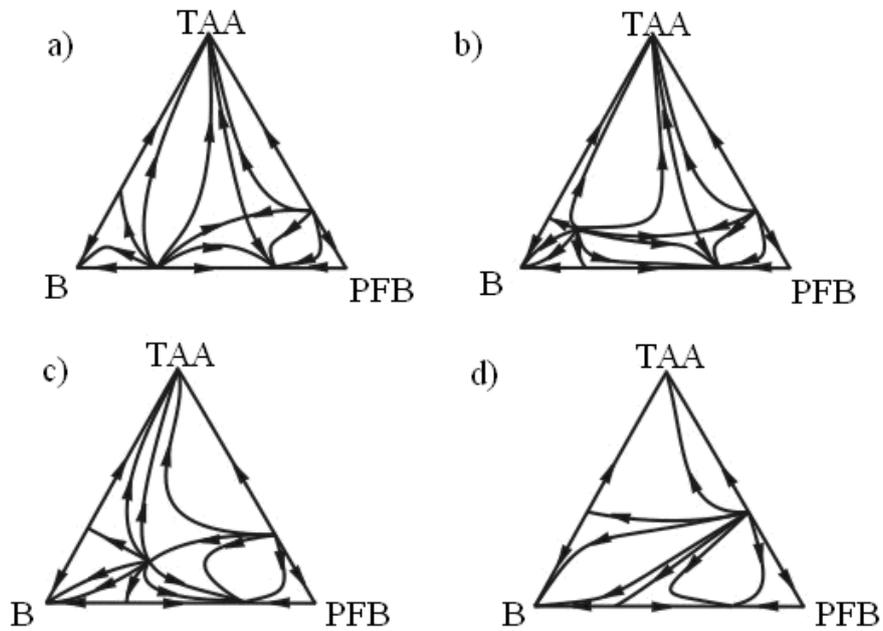


Figure 2. Evolution of the structure of phase diagram (residue curve maps) of system B-PFB-TAA at pressure variation a) 100; b) 300; c) 500; d) 760 mm Hg

5. Conclusions

It is established that the system B–PFB–MP contains stable node and saddle ternary azeotropes at 500 and 760 mm Hg, and the system B–PFB–TAA contains unstable node and saddle ternary azeotropes at 300 mm Hg. The topological structures of diagrams of both systems include 5 areas of distillation. According to classification¹ the system B–PFB–MP belongs to the class 3.4.2-3c and the system B–PFB–TAA is of class 3.4.2-3a. The proposed mathematical model describes thermodynamically correctly the evolution of VLE diagrams structures of biazeotropic ternary system B–PFB–TAA at pressure variation.

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