

PHASE TRANSITIONS IN QUATERNARY REACTING SYSTEMS WITH ESTERIFICATION REACTION

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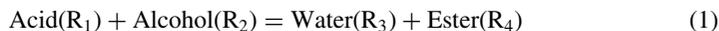
The main goal of this work is to discuss some peculiarities of quaternary systems with ester synthesis reaction. For this purpose the brief review of existing data on VLE and LLE in some quaternary reacting systems with an esterification reaction is presented. The azeotropic properties and the topological structure of phase diagrams are discussed. Some VLE data are considered for the systems with *n*-propyl acetate, ethyl acetate and methyl formate synthesis reactions. A new set of LLE data for the system acetic acid (1)–*n*-propanol (2)–water (3)–*n*-propyl acetate (4) at 313.15 K are presented.

KEYWORDS: reacting systems, phase transitions, simple distillation, chemical equilibrium, nonequilibrium chemical reaction

INTRODUCTION

Phase separation processes accompanied by chemical reactions are of the great importance as a novel effective and energy saving industrial methods. The reactive distillation can be used both for reaction engineering and separation technology purposes. Accordingly phase equilibria and phase transitions in systems with chemical reactions are a subject of interest from practical and theoretical point of view. In spite of the importance of these results only a small number of experimental data include a full description of the thermodynamic properties of such multicomponent systems. Most of modern works concerned different aspects of the problem of simultaneous phase and chemical equilibrium but the systems in chemically nonequilibrium states usually are not considered. In presented paper we consider the thermodynamics of simple distillation in reacting systems both for equilibrium and nonequilibrium chemical reactions.

Among works on vapour–liquid equilibrium (VLE) in reactive systems the esterification reaction is most studied. A majority of experimental data were obtained for chemically equilibrium states only. According to the equation of the reaction:



all four ternary sub-systems of such quaternary system are in chemically nonequilibrium states. Two binary systems ($R_1 - R_2$ and $R_3 - R_4$) are also chemically nonequilibrium, the rest four binary sub-systems ($R_1 - R_3$, $R_1 - R_4$, $R_2 - R_3$, $R_2 - R_4$) are without reactions and should be considered as systems belong to borders of the surface of chemical equilibrium. Due to the usual immiscibility of water and esters phase diagrams for considered

systems have an area of limited miscibility but the data on liquid–liquid equilibrium (LLE) in reacting systems are much seldom than VLE data.

DISCUSSION

Compositions of considering reacting systems should be represented in concentration tetrahedron as usual. For a graphical representation of compositions that belongs to chemical equilibrium manifold the number of variables can be reduced. We use transformed composition variables that were introduced by Zharov [1, 2] on the base of the properties of thermodynamic fundamental equations for the case of equilibrium chemical reaction. In the case of reaction (1) these composition variables comply with transformed composition coordinates that were introduced by Barbosa and Doherty [3]. Due to the values of stoichiometric numbers in esterification reaction ($-1, -1, +1, +1$) the concentration complex is a square of transformed composition variables (α_i):

$$\begin{aligned}\alpha_1 &= x_1 + x_4 \\ \alpha_2 &= x_2 + x_4 \\ \alpha_3 &= x_3 - x_4\end{aligned}\tag{2}$$

those are related by the equation

$$\alpha_1 + \alpha_2 + \alpha_3 = 1.$$

Recently the reactive system with the propyl acetate synthesis reaction has been discussed in a several papers (e.g. [4–6]). Experimental data on the VLE for chemical equilibrium compositions for the system acetic acid–*n*-propanol–water–*n*-propyl acetate were firstly obtained in work [7]. To the our knowledge this is the only reacting system with almost full set of experimental data on binary and ternary subsystems [8–10] under the isothermal conditions, 313.15 K. VLE data for some chemically nonequilibrium compositions are presented in works [10, 11]. This system was also studied in the work [6] but VLE data were calculated only; the residue curve map for 378.15 K was investigated experimentally. The azeotropic data for 313.15 K those are necessary for the quality description of the topological structure of residue curve map or VLE diagram are listed in Table 1.

These azeotropic data gives significantly different topological structure of residue curve map In comparison with results of works [4, 6]. Of course it can be explained by different conditions (pressure and temperature) for the considered system in our work and papers [4, 6]. For example the reactive azeotrope belongs to the homogeneous region of concentration tetrahedron at 313.15 K. On the other side the existence of heterogeneous reactive azeotrope was predicted in the work [4] on the base of theoretical considerations and calculations at atmospheric pressure and 357.35 K. The residue curve maps that were obtained in work [6] for non-reactive and kinetically controlled (also chemically equilibrium) cases include only quaternary and binaries azeotropes and pure substances as singular points. Accordingly the residue curve map for non-reactive

Table I. Azeotropic data for the system acetic acid (1)-*n*-propanol (2)-water (3)-*n*-propyl acetate (4), 313.15 K

System	Azeotropic point						
	Type	x_1	x_2	x_3	x_4	P, kPa	References
acetic acid (1)- <i>n</i> -propanol (2)	min P	0.77 ± 0.02	0.23 ± 0.02	-	-	4.63 ± 0.05	[9]
acetic acid (1)-water (3)	non- azeotropic	-	-	-	-	-	[7]
acetic acid (1)- <i>n</i> -propyl acetate (4)	non- azeotropic	-	-	-	-	-	[7]
<i>n</i> -propanol (2)-water (3)	max P	-	0.407	0.593	-	11.44	[7]
<i>n</i> -propanol (2)- <i>n</i> -propylacetate (4)	max P	-	0.342	-	0.658	10.88	[7]
water (3)- <i>n</i> -propyl acetate (4)	max P	-	-	0.444	0.556	16.39	calculated from data [12]
acetic acid (1)- <i>n</i> -propanol (2)-water (3)	non- azeotropic	-	-	-	-	-	[9]
acetic acid (1)- <i>n</i> -propanol (2)- <i>n</i> -propyl acetate (4)	non- azeotropic	-	-	-	-	-	[10], calculation
acetic acid (1)-water (3)- <i>n</i> -propyl acetate (4)	non- azeotropic	-	-	-	-	-	[8]
<i>n</i> -propanol (2)-water (3)- <i>n</i> -propyl acetate (4)	max P	-	0.437	0.044	0.519	16.53	calculated from data [13]
acetic acid (1)- <i>n</i> -propanol (2)-water (3)- <i>n</i> -propyl acetate (4)	reactive azeotrope	$x_1^V =$ 0.005; $\alpha_1 = 0.365$	$x_2^V = 0.162$; $\alpha_2 = 0.522$	$x_3^V = 0.473$; $\alpha_3 = 0.113$	$x_4^V =$ 0.360	13.89	[7]

simple distillation has no ternary azeotropic points at 378.15 K [6]. There are a numerous experimental data on the existing of ternary heterogeneous azeotrope *n*-propanol–water–*n*-propyl acetate in the wide temperature interval (e.g. ~323 K–353 K [13]) but these temperature and pressure conditions differ from conditions of the experiment in the work [6], 378.15 K.

According to the works [10, 11] the ordinary quaternary azeotropic point for the non-reactive system was not detected, i.e. there was no absolute extremum of the pressure for all set of chemically non-equilibrium and equilibrium compositions of quaternary liquid mixture at 313.15 K. On the other side this conclusion was made on the base of limited experimental data and should be checked additionally. The diagrams for chemically equilibrium states include point of quaternary reactive azeotrope. Isotherms of dew point, bubble point surfaces and residue curve map (qualitative) are presented on Figure 1, Figure 2 and Figure 3.

The topological analysis of such complex systems as reactive mixtures can be based not only on the information on singular points and residue curve map (or bubble and dew point surfaces). The location of reaction (stoichiometric) lines and surfaces of constant affinity (including chemical equilibrium surface) should be also taken into account. For example conditions of the stationary point of the pressure on the reaction lines can be derived on the base of the analysis of the isoaffinity surfaces location relative to tie-lines (e.g. see [14, 15]). The mutual consideration of equations of reaction lines and mass balance gives a necessary condition of kinetic azeotrope that in the case of reaction (1) can be presented in a simple form:

$$\frac{x_1^V - x_1^L}{x_2^V - x_2^L} = 1 \quad \text{or} \quad \frac{x_1^V - x_1^L}{x_3^V - x_3^L} = -1.$$

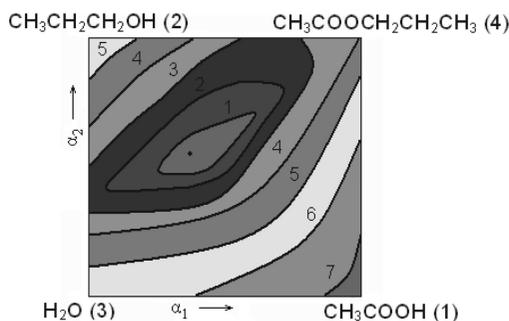


Figure 1. Isotherms of dew point surface at 313.15 K (projection on the complex of composition variables α_i): (1) 13.33, (2) 12.00, (3) 10.67, (4) 9.33, (5) 8.00, (6) 6.67, (7) 5.33 kPa. •—location of reactive azeotrope, 13.89 kPa

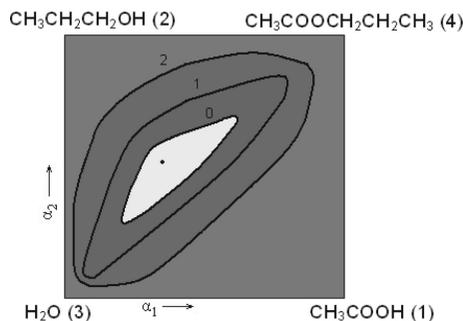


Figure 2. Isotherms of bubble point surface at 313.15K (projection on the complex of composition variables α_i): (0) 13.5, (1) 13.33, (2) 12.00 kPa. •—location of reactive azeotrope, 13.89 kPa

The additional complication of the structure of phase diagram with esterification reaction is an area of immiscibility that can exist due to the limited miscibility in water–ester subsystem. Accordingly the study of liquid–liquid phase transitions is of significance value for the topological analysis of such system. In particular the crossing of binodal and chemical equilibrium surfaces is a necessary condition for the existing of heterogeneous reactive azeotrope. The experimental data on LLE in acetic acid–*n*-propanol–water–*n*-propyl acetate system at 313.15 K were obtained in [11]. The crossing of bimodal and chemical equilibrium surfaces was not determined. According to the work [4] the heterogeneous minimum-boiling reactive azeotrope should exist at normal boiling

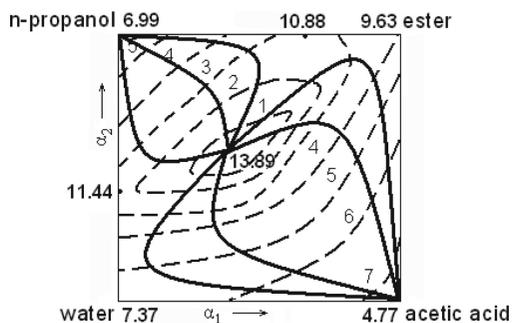


Figure 3. Residue curve map and pressure in singular points (kPa) for the chemical equilibrium surface in the system acetic acid–*n*-propanol (2)–water (3)–*n*-propyl acetate (4) at 313.15 K. •—location of reactive azeotrope (13.89 kPa), binary azeotrope *n*-propanol–water (11.44 kPa), binary azeotrope *n*-propanol–*n*-propyl acetate (10.88 kPa)

temperature 357.35 K. To check additionally the possibility of the crossing of binodal and chemical equilibrium surfaces at 313.15 K we had carried out the new experimental study of LLE (Table 2). The compositions of coexisting liquid phases were determined with the use of titration method and gas chromatograph analysis. The data of Table 2 were considered together with the data [11]. The crossing of two surfaces was not fixed but for some composition areas surfaces are very close to one another.

The particularities of phase transitions and diagrams are similar for most of the systems with esterification reaction. Now we will consider two other reacting systems that include ethyl acetate or methyl formate as components. The acetic acid–ethanol–ethyl acetate–water system is of significant importance due to the reaction of ethyl acetate synthesis. There are a number of researches of this process connected with different aspects of reactive distillation, e.g. [16–19]. Most of the data were obtained under isobaric conditions (atmospheric pressure) that is also should be explained by industrial significance of this system. The most complete data sets on simultaneous phase and chemical equilibrium were obtained in [18, 19]. Unfortunately both in the paper [18] and [19] diagrams of bubble and dew point or residue curve map are not presented. Also there is no any discussion on the existing of quaternary reactive azeotrope in [18]; the similar results of paper [19] are not clear enough. One of the last considerations of the topological structure of the diagrams of acetic acid–ethanol–ethyl acetate–water systems that include quaternary reactive azeotrope was carried out in the work [16].

The methyl formate is a first member of a homologous raw of esters. The location of the surface of chemical equilibrium of the reacting system formic acid–methanol–methyl formate–water in composition tetrahedron at 318.15 K is presented in Figure 4. The bubble point surface and residue curve map [20] for simultaneous phase and chemical equilibrium has a simple form (Figure 5): there is no reactive azeotrope, the only binary azeotrope formic acid–water (minimum pressure value) exists.

In the case of chemical equilibrium both isotherms of bubble point surface and residue curve map reflect the topological structure of diagrams for reacting systems. In the case of nonequilibrium chemical reaction there is no simple correlations between residue curve map and isotherms–isobars. One should take into account the shifting of composition that depends on both evaporation rate and reaction kinetics. As a result some particularities of residue curve map are not always valid, e.g. Schreinemakers rule for the rising of the temperature. On the other side in the frame of the conception of partly equilibrium (i.e. phase equilibrium saving in nonequilibrium chemical reaction) the general thermodynamic relationships can be used. For the analysis of the shifting of thermodynamic parameters and phase equilibrium in chemically nonequilibrium system we use the modified form of generalized Storonkin–Van der Waals differential equation (see e.g. [14, 15]). In such way some new form of particularities for reacting system were derived, e.g. conditions of the extremum of vapour pressure on reaction lines or modified form of the condition of reactive azeotrope [14, 15].

For the analysis of diagrams of reacting systems both in chemical equilibrium and chemically nonequilibrium states the stability test can be also applied. One of such tests based on the thermodynamic inequalities was previously used for the analysis of the

Table 2. LLE data for the system acetic acid (1)–*n*-propanol (2)–water (3)–*n*-propyl acetate (4), 313.15 K

	Organic-rich phase, mole fractions			Aqueous-rich phase, mole fractions			
	<i>n</i> -propanol	water	<i>n</i> -propyl acetate	acetic acid	<i>n</i> -propanol	water	<i>n</i> -propyl acetate
0.071	0.075	0.249	0.605	0.016	0.028	0.950	0.006
0.062	0.131	0.319	0.488	0.024	0.012	0.959	0.005
0.147	0.121	0.324	0.408	0.035	0.015	0.944	0.006
0.053	0.235	0.529	0.183	0.019	0.039	0.935	0.007
0.096	0.256	0.430	0.218	0.032	0.026	0.935	0.007
0.032	0.116	0.278	0.574	0.013	0.011	0.973	0.004
0.044	0.060	0.168	0.728	0.007	0.008	0.981	0.004
0.093	0.162	0.366	0.380	0.023	0.020	0.952	0.005

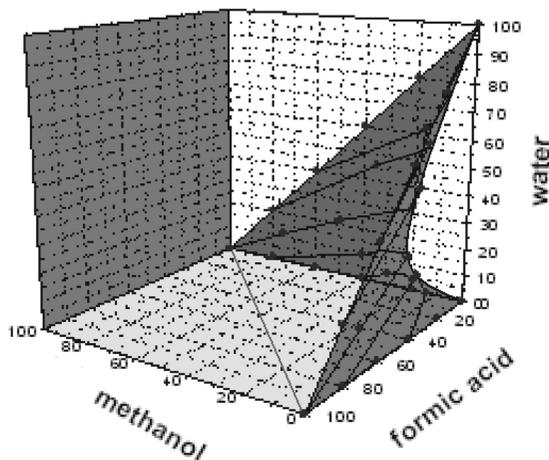


Figure 4. Chemical equilibrium surface of formic acid–methanol–methyl formate–water system at 318.15 K (composition variables are indicated as molar %)

properties of acetic acid–*n*-propanol–water–*n*-propyl acetate system [21]. The method (see e.g. [22]) allow to check thermodynamic properties of multicomponent system on the base of constituent mixtures data, agreement between parameters of multicomponent system and subsystems or to define restrictions on thermodynamic parameters of systems

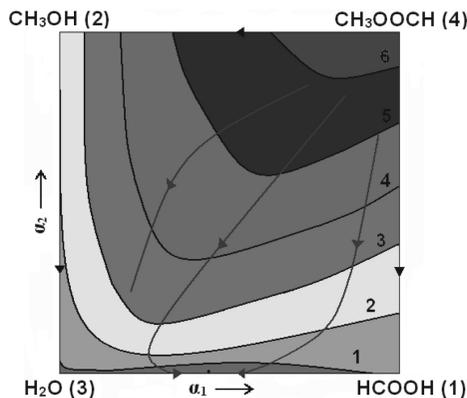


Figure 5. Residue curve map (arrows on curves – directions of simple distillation lines) and isotherms of bubble point surface of formic acid–methanol–methyl formate–water system at 318.15 K (projection on the complex of α_1 -variables): (1) 13.33, (2) 40.00, (3) 66.66, (4) 93.33, (5) 120.00, (6) 146.65 kPa

calculated from subsystems data. On the base of this approach we considered the location of isotherms of bubble point surface of formic acid–methanol–methyl formate–water system. The test showed good agreement between quaternary and binary subsystem data for system considered.

CONCLUSIONS

Particularities of reacting systems with phase transitions are considered on the example of some mixtures with esterification reaction. Opportunities of thermodynamic methods for the analysis of these systems are discussed. Some examples of phase diagrams (dew and bubble point surfaces, residue curve map) are presented.

ACKNOWLEDGEMENTS

This research was supported by Russian Foundation for Basic Research (grant 06-03-32698). Author is grateful to D. Ruksha for the help in the experimental work.

NOMENCLATURE

P	pressure, kPa
R _i	symbol of reacting species
X _i	molar fraction of component I

GREEK SYMBOLS

α_i	transformed concentration variables, equation (2)
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SUBSCRIPTS

1, 2, i	indexes components or transformed concentration variables
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SUPERSCRIPTS

L	liquid phase (phases)
V	vapour phase

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