

EVAPORATION IN REACTING SYSTEMS WITH LIQUID PHASE SPLITTING

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Abstract

Some theoretical and experimental results on the peculiarities of reacting systems with liquid phase splitting are considered. The evaporation in these systems is a complex process that combines three stages: liquid-vapor phase transition, liquid-liquid phase transition and chemical reaction. Both the simultaneous vapor-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE) and chemical equilibrium (CE) and non-equilibrium cases are of important practical interest, e.g. for reactive distillation. The properties of two-phase liquid solutions with chemical interaction are the main elements that determine the behavior of the system in evaporation process. The main experimental example is a quaternary system with *n*-propyl acetate synthesis reaction.

Keywords: reactions, liquid-liquid equilibrium, evaporation

1. Introduction

The aim of the paper is to present some theoretical and experimental results on the thermodynamic peculiarities of evaporation processes in reacting systems in the cases of the liquid phase splitting. The evaporation in these systems is a complex process that combines three stages: liquid-vapor phase transition, liquid-liquid phase transition and chemical reaction. Both the simultaneous vapor-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE) and chemical equilibrium (CE) and non-equilibrium cases are of important practical interest, e.g. for reactive distillation¹. In general such complex systems (with three types of coupled processes) need the non-equilibrium approach. For example in the case of liquid phase splitting the hydrodynamic conditions may be taken into account. Nevertheless the equilibrium approach should be the first step in the consideration of the complex of phase and chemical processes. In this paper we consider the evaporation process as a simple distillation, i.e. the diagram of the process could be presented as a residue curve map. We also confine ourselves to the systems with chemical interaction in liquid phases only. Chemical reactions in the vapor and reactions at the phase boundaries are not considered.

The VLE in the system with miscibility gap, i.e. the case of the existing of vapor-liquid-liquid equilibrium (VLLE), is a developed area of thermodynamics of phase equilibria^{2,3}. The problems of thermodynamics of phase equilibria in reacting systems had been the object of both basic and applied research. First significant works in this area belong to Zharov, Serafimov, Doherty and co-workers⁴⁻⁹. Most of these research deal with simultaneous phase and chemical equilibrium in the systems with homogeneous liquid solution. The miscibility gap adds extra elements to the topological structure of phase diagrams of reacting systems. The study of phase processes in such systems had been carried out in some recent works¹⁰⁻¹⁴. For example Ung and Doherty¹⁰ had proposed the term "unique reactive liquid-liquid tie-line" that corresponds to the intersection of liquid-liquid envelope with chemical equilibrium curve. The significance of the study of phase equilibria in the reacting systems with miscibility gap is connected with some industrial application, e.g. ester production. Due to limited mutual miscibility of water and ester the miscibility gap is a common phenomenon in the systems with ester synthesis reaction. In spite of the progress in the research of reacting systems with liquid phase splitting many problems needs further development. One of the problems is a lack of experimental information on these systems (e.g. see review article¹⁵).

2. Thermodynamic and Topological Peculiarities of Liquid-Liquid Reacting Systems

The complex structure of the solution with miscibility gap and chemical interaction (chemical equilibrium) is a main factor that determines the peculiarities of the evaporation process. Let us consider the cases of ternary and quaternary liquid-liquid systems with equilibrium chemical reaction

(i.e. systems in chemical equilibrium). According to the phase rule^{2, 16-18}

$$f = n + 2 - r - k \quad (1)$$

(where f , n , and r are numbers of degrees of freedom, numbers of components (chemically distinct species) and phases accordingly, k is the number of equilibrium chemical reactions) for n -component system with two liquid phases and one equilibrium chemical reaction the following equality holds:

$$f = n + 2 - r - k = n + 2 - 2 - 1 = n - 1. \quad (2)$$

For varying pressure and temperature the ternary systems in the states of simultaneous LLE and CE have two degrees of freedom (bivariant equilibrium), quaternary systems – three degrees of freedom (polyvariant equilibrium). For $P = const$ (or $T = const$) ternary systems is in a monovariant equilibrium. Invariant states in ternary systems exist at $T, P = const$. Simultaneous phase and chemical equilibrium in quaternary systems at isothermal-isobaric conditions would be a monovariant state. Therefore at isothermal-isobaric conditions the simultaneous phase and chemical equilibrium in quaternary liquid-liquid systems is presented as a curve in the composition tetrahedron. The same curve (in appropriate thermodynamic space) may be in the case of ternary simultaneous phase and chemical equilibrium but at variable temperature or pressure. It should be noted that these results concern the chemical equilibrium systems. If systems are in chemically nonequilibrium states the phase rule should be considered as in the case of non-reactive systems.

For the further thermodynamic analysis it is necessary to consider possible geometry of chemical equilibrium manifolds. In the case of one reaction in the homogeneous solution the phase rule leads to the following:

$$f = n + 2 - r - k = n + 2 - 1 - 1 = n. \quad (3)$$

Therefore, at isothermal-isobaric conditions the manifold of chemical equilibrium in ternary system would be a curve, in quaternary system – a surface in the composition simplex (triangle or tetrahedron). The typical form and disposition of the surface of chemical equilibrium is presented at Figure 1 (system with n -propyl acetate synthesis reaction). The experimental research of CE in the system acetic acid – n -propanol – n -propyl acetate – water firstly had been done in the work¹⁹ at $T = 313.15$ K. The disposition of CE surface constructed on the base of these data had been presented in the work²⁰. According to our further research of this system^{21, 22} and new experimental data²³ for $T = 293.15$ K and 303.15 K the form and disposition of CE surface in the composition tetrahedron is approximately the same for different temperature conditions.

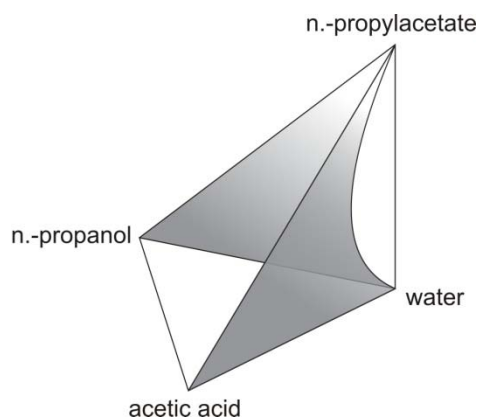


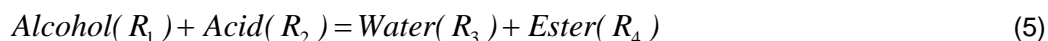
Figure 1. The typical form and disposition of the surface of CE in composition tetrahedron (the system with n -propyl acetate synthesis reaction)

The case of ternary system had been considered in detail in paper²⁴. In this work some variants of the topology of reactive systems diagrams had been discussed: the mutual arrangement of the binodal curve and the curve of CE. Also the opportunity and conditions of the simultaneous existing of CE and critical points of LLE had been considered. This work²⁴ had been performed in the frame of our study of critical phenomena on the base of stability conditions and transformed form of stability matrix.

In the case of the critical state of LLE the number of degrees of freedom will be reduced by unity. It follows from the rule that for the determination of the variance the critical phase should be taken into account thrice^{17, 25, 26}: the value $r = 3$ must be substituted in the phase rule and the variance of the critical phase with one equilibrium chemical reactions is

$$f = n + 2 - r - k = n + 2 - 3 - 1 = n - 2 . \quad (4)$$

Hence in quaternary reactive system at $T, P = const$ the critical phase of LLE in chemical equilibrium is in the invariant state. The example of diagram of quaternary reacting system with critical states of LLE is presented on Figure 2. This Figure illustrates the mutual arrangement of the binodal surface and CE surface. The diagram is constructed with the use of transformed composition variables^{4, 7} (α_i) that give opportunity to present the quaternary data on CE as a 2D diagram. In the case of ester synthesis reaction



all stoichiometric numbers are unit (+1 and -1) and transformed composition variables are:

$$\alpha_1 = x_1 + x_4 \quad (6)$$

$$\alpha_2 = x_2 + x_4 \quad (7)$$

$$\alpha_3 = x_3 - x_4 \quad (8)$$

where x_i is the molar fraction of specie i . For the sum of variables these equations yield:

$$\alpha_1 + \alpha_2 + \alpha_3 = 1 . \quad (9)$$

Hence the composition space for α_i -variables in the case of reaction (5) would be a square. The border of the area of simultaneous chemical equilibrium and LLE (closed line on Figure 2) is a binodal curve that belongs to both binodal and chemical equilibrium surfaces in the composition tetrahedron. Two critical points on this curve also correspond to the critical curve in the composition tetrahedron. The area of simultaneous LLE and CE represents a continuous set of tie-lines and may be considered as analogous to unique reactive tie-lines¹⁰ in ternary systems.

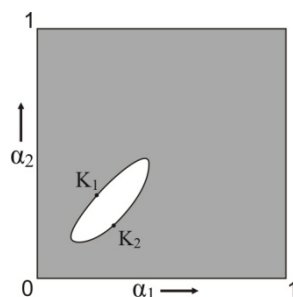


Figure 2. The area of simultaneous LLE and CE and critical points in the square of α_i -variables (white region) in the system with *n*-propyl acetate synthesis reaction (experimental data²³ for $T = 303.15$ K). Two critical points K_1 and K_2 also correspond to the critical line in composition tetrahedron

3. Evaporation in Reacting Systems

The theory of VLE in reactive system (CE case) is an important direction of thermodynamics of phase equilibrium and is a base of chemical engineering process design, generally, reactive distillation¹. Therefore in this chapter we will briefly describe some problems which should be significant for the development of the methods of the study of evaporation in reacting systems with liquid phase splitting. The most important aspects concern the non-equilibrium effects and some additional singularities. First of all the influence of chemical reaction kinetics should be taken into account. The values of relative rates of chemical reaction (i.e. reaction kinetics) and phase process (evaporation) may to cause new singularities such as kinetic azeotrope. The term “kinetic azeotrope” had been proposed in the work²⁷ for the case of equal mass balance and opposite direction of evaporation and chemical processes. As a result the composition of liquid phase would be constant in the point of kinetic azeotrope. The necessary condition demands the coincidence of the directions of chemical reaction (stoichiometric line) and VLE tie-line in composition space. The mathematical form of necessary condition of kinetic azeotrope is following²⁸:

$$\frac{x_k^{(2)} - x_k^{(1)}}{V_k - x_k \sum_{j=1}^n V_j} = \frac{x_i^{(2)} - x_i^{(1)}}{V_i - x_i \sum_{j=1}^n V_j} \quad (10)$$

where $x_s^{(1)}$ and $x_s^{(2)}$ molar fractions of species s in liquid and vapor of n -component system with chemical reaction

$$\sum_{i=1}^n \nu_s R_s = 0 \quad (11)$$

(R_s – symbols of species, ν_s – stoichiometric numbers for reaction products are defined as positive numbers and, for reactants, negative numbers). The condition of kinetic azeotrope does not require the simultaneous existing of the stationary point of temperature or pressure as opposite to the case of the conditions of reactive azeotrope^{4, 7, 29} (system in CE). For ternary vapor-liquid system the condition of reactive azeotrope can be presented in following matrix form^{15, 30}:

$$\begin{vmatrix} x_1^{(1)} & x_2^{(1)} & x_3^{(1)} \\ x_1^{(2)} & x_2^{(2)} & x_3^{(2)} \\ \nu_1 & \nu_2 & \nu_3 \end{vmatrix} = 0. \quad (12)$$

In spite of a numerous thermodynamic approach to the study of evaporation processes in reacting systems the most widespread method in chemical engineering is based on the well-known conception of Damköhler numbers.

4. Liquid Phase Splitting and Evaporation in Reacting Systems

It was mentioned above that the liquid phase splitting adds extra elements to the topological structure of diagrams of reacting systems. Most of them are connected with peculiarities of the realizing of simultaneous LLE and CE; some of them had been characterized in Chapter 2. Another type of problems is connected with the effect of the reaction kinetics on the behaviour of the system with miscibility gap. In the case of two liquid phases the reaction rates in coexisting phases could significantly differ. For example the system with ester synthesis reaction and liquid splitting consists of “water” and “organic” phases with a large difference in the compositions. The mass balance of the coupled reactive–evaporation process can be also described with the use of the Damköhler number that helps to take into account the value of the reaction rate. Therefore different Damköhler numbers for every liquid phase should be taken into consideration. The problems of reactive distillation in the systems with limited miscibility are discussed in recent works, e.g. papers^{11, 13, 14}. In work¹³ the existing of *heterogeneous reactive azeotrope* in the n -propanol(1) – acetic acid(2) – water(3) – n -propyl acetate(4) system had been predicted. The estimated azeotropic parameters are following: normal

boiling temperature 357.35 K; $x_1= 0.2527$, $x_2= 0.0752$, $x_3= 0.4001$, $x_4= 0.2720$ ("organic-rich phase", liquid phase fraction = 0.88); $x_1= 0.0565$, $x_2= 0.0289$, $x_3= 0.9023$, $x_4= 0.0123$ ("aqueous-rich phase", liquid phase fraction = 0.12). From our point of view and according to existing experimental data sets on thermodynamic properties of this system²¹ the realizing of the heterogeneous reactive azeotrope in this system at mentioned conditions is hardly probable. The most recent experimental data for various temperature conditions²³ also had confirmed this statement.

The conditions of *kinetic heterogeneous azeotrope* can be also deduced. The necessary condition of such phenomena demands the coincidence of the directions of stoichiometric line, LLE tie-line and VLE tie-line in composition space. It should be noted that the coincidence of LLE tie-line and VLE tie-line is a condition of ordinary heterogeneous azeotrope³.

5. Conclusions

Some aspects of thermodynamic approach for the study of evaporation processes in reacting systems with liquid phase splitting had been discussed. The complex structure of solution in the case of the splitting and the chemical reaction is a main factor that should be taken into account in the evaporation process design. There are a number of variant of the mutual arrangement of miscibility gap and the area of chemical equilibrium. The mutual crossing of the chemical equilibrium surface and binodal in the composition tetrahedron leads to the origin of the area of simultaneous chemical and liquid-liquid equilibrium with two critical points (reactive critical phases). The experimental data on the system with propyl acetate synthesis reaction gives the example of such phenomena. There are specific singularities of the evaporation in reacting systems with liquid splitting that are similar to reacting systems with homogeneous solution: e.g. the phenomena of heterogeneous reactive azeotrope. Unfortunately the existing experimental data base on reacting systems is very limited still: therefore most predicted peculiarities had only theoretical conformation.

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