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Heterogeneous fluids in supercritical binary and ternary water–salt systems☆

V.M. Valyashko*

Kurnakov Institute of General and Inorganic Chemistry RAS, Leninsky av. 31, IONCh RAN, Moscow RU-119991, Russia

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ABSTRACT

The systematic classification of complete phase diagrams for binary systems and theoretical derivation of ternary phase diagrams with one volatile component, based on the method of continuous topological transformation, are briefly discussed. Review of high-temperature experimental data for ternary water–salt systems permits to establish both the main directions of phase transformations at sub- and supercritical conditions and some details of phase behavior in stable and metastable equilibria. The greater attention is paid to the ternary systems with binary water–salt subsystems of different types, where the heterogenization of homogeneous supercritical fluid takes place. The topological schemes of ternary phase diagrams are used for interpretation of available experimental data both for critical and non-critical phase behavior in stable and metastable conditions.

1. Introduction

Fluid equilibria include such phases as gas (vapor), liquid and supercritical fluid (SCF). Transition from gas to liquid and back usually undergoes through two-phase liquid–gas equilibria, whereas a transition between SCF and gas or liquid as well as the property variations of SCF (from gas-like to liquid-like fluid) with density take place continuously without an appearance of heterogeneous equilibria. SCF equilibria (where the fluid is homogeneous at any pressure) in some binary systems with components of different volatility take place not only at temperatures above the critical points of both components but also at lower temperatures, near the critical point of volatile substance. Such "low-temperature" SCF equilibria are the result of critical phenomena in solid-saturated solutions (critical end-points ***p*** and ***Q***) in the binary systems of type **2**, where the melting temperature of nonvolatile component (salt component in water–salt system) is above the critical temperature of volatile one (water in water–salt system), and take place in the temperature range between points ***p*** and ***Q***. In the case of binary systems of type **1**, where the melting temperature of nonvolatile component can be above or below the critical temperature of volatile one, the "low-temperature" SCF equilibria are absent.

These two types of phase behavior observed in the binary mixtures were used for classification of binary systems from the time of Van der Waals and Konstamm [1] and it is one of the milestones in the systematic classification of complete phase diagrams developed by the method of continuous topological transformations [2–4].

The method of continuous topological transformation of phase diagrams is based on the premise that each type (or topological scheme) of phase diagram can be continuously transformed into another type through the boundary version of phase diagram, which has the properties of both neighboring types and contains the equilibria possible only in the systems with the higher numbers of components. It was established for the binary fluid phase diagrams as the result of calculations of various equations of state that boundary versions with ternary nonvariant points appear during the transitions of one type of binary fluid phase diagram into another [5,6]. Originally, the concept of a continuity of all types of fluid phase equilibria in binary mixtures was formulated by Schneider in 1960s on the basis of systematic measurements of so-called "families" of binary systems (one component is constant, the second component is varied) [7,8].

Another milestone of the method of continuous topological transformation and the classification of complete phase diagrams is the statement that the modifications of fluid equilibria, hidden by occurrence of a solid, do not change the type and topological scheme of fluid phase behavior. As a result of such modifications, a part of fluid equilibria (for instance, a part of immiscibility regions and/or critical curves) is suppressed by solidification of the nonvolatile component and transforms into the metastable equilibria. Such metastable equilibria have an effect on a form of adjacent stable part of the phase diagram, could be observed at nonequilibrium

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* Fax: +7 495 952 1801.
E-mail address: Valyashko@igic.ras.ru.

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conditions or may emerge in stable equilibria with increasing the number of components in the system.

The phase diagrams that describe not only fluid but also any equilibria between liquid, gas and/or solid phases in a wide range of temperatures and pressures are referred to as complete phase diagrams.

The systematic classification of complete phase diagrams for binary systems (Fig. 1), consisted of four horizontal rows (**a**–**d**) and three vertical columns (**1**, **1**′(**1**″), **2**). It is a complete and exhaustive system within the framework of the definite limitations [3,4]. Four rows correspond to four main types of fluid phase behavior possible in binary mixtures, where only type **a** shows the fluid phase behavior without liquid–liquid immiscibility phenomena. Limited, so-called "closed-loop", immiscibility region is a permanent element of phase diagrams in the row **b**. Two three-phase immiscibility regions L_1–L_2–G of different nature are the constituents of complete phase diagrams in the row **c**. Three-phase immiscibility region with two critical end-points ***N*** ($L_1 = L_2$–G) and ***R*** (L_1 = G–L_2) of different nature can be found in any complete phase diagrams of the row **d**.

Three vertical columns (left (**1**), central (**1**′(**1**″)), and right (**2**)) of complete phase diagrams reflect the various features of solid–fluid equilibria. The complete phase diagrams, which show four main types of fluid phase behavior without critical or immiscibility phenomena in solid-saturated solutions, are found in the left column (**1**) and correspond to types I, V, VI and VII in the classification of Scott and Van Konynenburg [5] and Boshkov [11]. The central (**1**′(**1**″)) and right (**2**) columns contain diagrams with nonvariant points where critical phenomena occur in equilibrium with a solid phase. "Low-temperature" supercritical fluid and supercritical fluid–solid equilibria are absent on the diagrams from central column, but they appear on the diagrams of type **2** from the right column. The boundary versions of binary phase diagrams, shown in frames, separate and show a continuous transformation the neighboring types of complete phase diagrams.

The main part of this paper deals with heterogeneous high-temperature equilibria in ternary mixtures both derived by the method of continuous topological transformation and obtained as a result of experimental hydrothermal studies.

2. Derivation of ternary phase diagrams

If the phase behavior of the constituent binary subsystems is known the task of constructing a topological scheme for a ternary system translates into finding of the new nonvariant equilibria. These new equilibria result from the intersections of monovariant curves originated at nonvariant points of the constituent binary subsystems. In transition from one subsystem to another, the phase diagrams of the binary subsystems must undergo continuous topological transformations in the three-component region of composition.

2.1. Quasi-binary approach

So-called "quasi-binary approach", which is used often in modern literature [8,12,13], permits to represent the ternary system as a set of quasi-binary cross-sections. In the case of ternary systems with one volatile (A) and two nonvolatile components (B, C), the quasi-binary sections consist of one constant volatile component (A) and second continuously changing component which is the mixture of two nonvolatile components (B + C) of ternary system. Such representation is not quite rigorous for the most real ternary mixtures because a ratio of nonvolatile components (B/C) in equilibrium phases is not usually constant. However, if we intend to study the phase behavior from topological schemes point of view, the sequence of binary phase diagrams for quasi-binary sections (including the sections through the ternary nonvariant points) give an exhaustive description of possible phase equilibria and phase transformations in ternary systems.

If the phase diagrams of the binary subsystems are present in the scheme of classification Fig. 1, then all the steps of the topological transformation between these diagrams are also shown on the same figure as a set of complete phase diagrams corresponding to the quasi-binary sections [3,4,9]. Such sets include the boundary versions of phase diagrams, which show ternary nonvariant points that should appear in the studied three-component systems. For example, the sequence of quasi-binary sections of ternary phase diagram for the systems with binary subsystems of types **1a** and **1b**′ should be the following: **1a** ⇔ **1ab**′ ⇔ **1b**′ or **1a** ⇔ **1ab** ⇔ **1b** ⇔ **1bb**′ ⇔ **1b**′.

The variety of ternary phase diagrams derived by this method is the result not only the various combinations of corresponding binary subsystems but also by the ways of continuous transformation between them.

Usually this approach for ternary phase diagram derivation gives several versions of ternary diagrams for each combination of binary subsystems because there are several ways for continuous transformation between them. For instance, the immiscibility regions spreading from two binary subsystems of type **1** can either merge or be separated by a miscibility region. Hence, if two binary subsystems belong to types **1b** and **1d**, the set of quasi-binary sections should be **1b** ⇔ **1bc** ⇔ **1c** ⇔ **1cd** ⇔ **1d** or **1b** ⇔ **1bc** ⇔ **1c** ⇔ **1CD** ⇔ **1d** when spreading immiscibility regions are joined, or **1b** ⇔ **1ab** ⇔ **1a** ⇔ **1ad** ⇔ **1d** when a miscibility region separates the immiscibility regions. When two binary subsystems belong to types **1b**′ and **1d**′ even in the case of two immiscibility regions separated by a miscibility one, the following sequences of phase transformations are possible in the ternary systems: **1b**′ ⇔ **1ab**′ ⇔ **1a** ⇔ **1ad** ⇔ **1d** ⇔ **1dd**′ ⇔ **1d**′ or **1b**′ ⇔ **1b**′**b** ⇔ **1b** ⇔ **1ab** ⇔ **1a** ⇔ **1ad** ⇔ **1d** ⇔ **1dd**′ ⇔ **1d**.

2.2. Systematic approach

The systematic approach starts with a derivation of the main types of ternary fluid phase diagrams which further are modified by presence of solid phase of the nonvolatile components [4,9,10].

2.2.1. Fluid phase diagrams

As in binary systems, the main types of fluid phase diagram of ternary mixtures should not have an intersection of critical curves and immiscibility regions with a crystallization surface. Combination of four main types of binary fluid phase behavior **1a**, **1b**, **1c** and **1d** for constituting binary subsystems gives six major types of ternary fluid mixtures with one volatile component, two binary subsystems (with volatile component) complicated by the immiscibility phenomena and the third binary subsystem (consisted from two nonvolatile components) of type **1a**. These six ternary types can be referred as ternary type **1b**–**1b**–**1a** (designated by types of three binary subsystems), ternary type **1c**–**1c**–**1a**, ternary type **1d**–**1d**–**1a**, ternary type **1b**–**1d**–**1a**, ternary type **1b**–**1c**–**1a** and ternary type **1c**–**1d**–**1a** [4,9]. As it was mentioned above, the immiscibility regions spreading from two binary subsystems can either merge or be separated by a field of liquid phase miscibility. The latter case is especially important since it illustrates the phase transformations where only one of the binary subsystems with volatile component is complicated by liquid–liquid immiscibility therefore generating new ternary types: **1a**–**1b**–**1a**, **1a**–**1c**–**1a** and **1a**–**1d**–**1a**.