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Solubility, liquid–liquid equilibrium and critical states for the quaternary system acetic acid–ethanol–ethyl acetate–water at 303.15 K and 313.15 K

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ABSTRACT

Solubility, critical states and liquid–liquid equilibrium (LLE) data for the quaternary system acetic acid–ethanol–ethyl acetate–water and for the ternary subsystems acetic acid–ethyl acetate–water and ethanol–ethyl acetate–water were studied at 303.15 K and 313.15 K and atmospheric pressure. Binodal surfaces, binodal curves, tie-lines and compositions of critical points were determined. In order to construct the binodal surfaces and critical curves of the quaternary system, five quaternary sectional planes with several different ratios of concentration of acetic acid to ethanol were studied. Experimental LLE data were compared with the values calculated by UNIFAC and NRTL models, and it was found that the experimental and calculated data are in good agreement.

1. Introduction

During the past few decades, interest in coupled processes (e.g., phase transitions accompanied by chemical reaction) has grown because of their significance for the development of energy- and resource-saving chemical engineering processes. Sometimes it is necessary to include the stages of separation or recycling of the components in the industrial chemical processes if the completion of chemical reaction is limited by chemical equilibrium between reactants and products. In addition, the run of chemical reaction depends on the limited miscibility of the reacting mixture, and therefore, industrial processes can be significantly complicated. It should be noted that the overwhelming majority of experimental and theoretical works in the field of coupled processes is devoted to the investigation of esterification reaction [1]. This interest in studying esterification stems from the fact that the ideas of green chemistry, environmental management and the development of renewable energy sources now dominate in both fundamental as well as applied chemistry.

With respect to environmental management in the field of organic synthesis and separation processes, we should mention reactive distillation (RD) [2]. This process conjoins reaction and separation stages, provides a significant increase in the conversion of reactants, and decreases the environmental risks. Some recent papers [3,4] present the experimental kinetic data of heterogeneous esterification of acetic and glutaric acid with methanol and show that RD technology is a feasible method to convert carboxylic acids to esters and to recover them from aqueous solutions. Article [5] by Yagyu et al. is devoted to the ecological problem of ethyl acetate production, the improvement of esterification yield and wastewater treatment. The authors studied the esterification of acetic acid with ethanol in aqueous media at 313.15 K using various catalysts to intensify the recovery. Hu and colleagues [6] report the design of RD process for the production of ethyl acetate. Data on vapor–liquid equilibrium and vapor–liquid–liquid equilibrium at the temperature range 343.15–393.15 K are simulated by NRTL model (including several phase diagrams). Besides the papers mentioned above, there are some other works on RD and vapor–liquid equilibrium in systems with an esterification reaction [7–11].

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Furthermore, research in the field of biodiesel production has developed in recent years. The data of works [12,13] can be used for the development of biodiesel production processes via fatty acids esterification (e.g., lauric acid with ethanol). Such works are mainly related to the study of kinetics of catalyzed esterification, especially in using those kinds of catalysts as different types of ion-exchange resins [14–17].

In addition to the practical importance of investigating phase equilibria in reactive systems, they are also of interest in the development of basic thermodynamic theory. It gives, for example, new data on the structure and features of phase diagrams, such as critical states [18–25].

However, despite the potential applied and basic significance of systems with coupled processes, experimental data on these systems are relatively rare in comparison with non-reactive systems. We presented experimental results for a system with n-propyl acetate synthesis reaction in recent papers [26–28].

The present work continues the investigation of the system acetic acid–ethanol–ethyl acetate–water, which has before been intensively studied by many authors, including our scientific group. Previously, we presented experimental data on solubility, critical states, LLE and chemical equilibrium of esterification in this system at 293.15 K and atmospheric pressure; LLE data calculated by UNIFAC model were also reported in papers [29,30]. Our research concerns mostly solubility and LLE determination because the data sets on these properties are limited in comparison with VLE. VLE was experimentally studied by Calvar et al. [31]. Experimental results of [31] are in agreement with the data of other authors [32,33]. Some works are only devoted to investigation of ethyl acetate synthesis reaction: e.g., Venkateswarlu et al. [34] studied this reaction in vapor phase at 519–559 K and atmospheric pressure. System with ethyl acetate synthesis reaction was considered by Reichl et al. [35], but the paper's experimental data sets include only data for binary sub-systems ethanol–acetic acid, ethyl acetate–water and ethanol–water (at 50 kPa and atmospheric pressure). Theoretical consideration of thermodynamic properties and description of the topological structure of the quaternary system are reported in Ref. [36]. The description of LLE in acetic acid–ethanol–ethyl acetate–water system (at 101.3 and 200 kPa) with the help of UNIFAC model; calculated LLE diagrams for these pressures are presented in Ref. [37]. The chemical equilibrium surface of the system acetic acid–ethanol–ethyl acetate–water is presented in Ref. [7].

Using various models, Kang et al. [38] proposed new algorithms for calculating simultaneous chemical and phase equilibrium for reactive systems. The calculation results for the acetic acid–ethanol–ethyl acetate–water system were compared with calculations made by Peres-Cisneros et al. [39]. The thermodynamic coherence of experimental data for the quaternary system with ethyl acetate synthesis reaction is discussed in Ref. [40]. Paper [41] considers the results of modeling equilibria in this system using Margules and Wilson equations. Simulation on the base of a group model (ASOG, Analytical Solutions of Groups) is described in Ref. [42].

Analysis of literature data shows that there are numerous papers on the experimental study of VLE and modeling of VLE and chemical equilibrium in acetic acid–ethanol–water–ethyl acetate system. In contrast, the data sets on LLE are limited and mostly related to isobaric conditions (e.g., atmospheric pressure). Accordingly, the aim of our work was the experimental study of solubility and LLE in this system under isothermal conditions (303.15 and 313.15 K). Our experimental task included the determination of critical states of LLE in this system. The calculations were carried out using UNIFAC and NRTL models.

Table 1
The purities of the chemicals.

Substance	Purity (mole fraction)[a]
Acetic acid	0.998
Ethanol	0.995
Ethyl acetate	0.998
Water	0.999

[a] Uncertainty is estimated to be ±0.002 mole fraction.

2. Experimental

2.1. Materials

Ethanol ("reagent" grade, Vekton, Russia) and ethyl acetate ("purified" grade, Vekton, Russia) were purified by distillation. Water was bidistilled. Acetic acid ("purified" grade, Vekton, Russia) was purified by two times rectification, with the presence of 98% sulphuric acid. The purity of chemicals (see Table 1) was verified chromatographically and in terms of refraction indexes and boiling points. All physico-chemical constants of pure substances were found to be in agreement with NIST Standard Reference Database [43].

2.2. Methods

Cloud-point technique was used to study solubility and critical phenomena. The operating procedure was the same as in our previous work. Details of the method had been published in paper [29]. Titration was performed in a liquid thermostat (303.15 and 313.15 K). Accuracy of the determination of concentration was estimated to be 0.001 mole fraction. In consideration of other possible factors affecting accuracy (such as purity of chemicals, thermostatic control uncertainty and others), maximum error of experimental data was appreciable to ±0.002 mole fraction of the component.

LLE was studied using gas chromatography (GC). Firstly, binary, ternary and quaternary mixtures of known overall composition within the heterogeneous region were prepared in glass vessels (5 ml) by gravimetric method. Heterogeneous mixtures were stirred in sealed vessels. Then vessels were placed in the liquid thermostat (303.15 K). We considered the phase equilibrium reached when there was a full separation of the phases and they became quite transparent. After reaching phase equilibrium, samples were taken from both phases with 1 μl chromatographic syringe ("Hamilton", USA) and analyzed by GC. We used a gas chromatograph "Chromatec Crystal 5000.2" (Russia) with thermal conductivity detector (TCD) and packed column Porapak R (1 m long and 0.003 m i.d.). Helium with a flow rate of 60 ml/min was used as a carrier gas. The operating temperature of a column was 468 K, vaporizing injector was maintained at 503 K, and TCD temperature was 513 K. Method of internal standard and relative calibration were used to calculate compositions of equilibrium liquid phases. Ethanol was used as an internal standard and accepted as a linking component. Uncertainty of GC analysis averaged ±0.005 mole fraction.

3. Results and discussion

Binary mixtures ethanol–ethyl acetate and acetic acid–ethyl acetate were chosen as initial solutions for the study of solubility in ternary subsystems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water, respectively, and were titrated with bidistilled water. All these binary systems were homogeneous before titration. At the moment when the solution became cloudy, i.e., when the second phase began, compositions belonging to the solubility curve were fixed. It should be noted that the