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Liquid-liquid equilibrium and critical states for the quaternary system propionic acid–*n*-butanol–*n*-butyl propionate–water at 303.15 K

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ABSTRACT

New experimental data on liquid-liquid equilibrium (LLE) and critical phases for the propionic acid – *n*-butanol – *n*-butyl propionate – water system at 303.15 K and atmospheric pressure are presented. The LLE compositions were determined by gas chromatography, correlated and predicted by NRTL and UNIFAC models respectively. The results of NRTL and UNIFAC modelling are in sufficient agreement with experimental data. Standard deviations for binary and ternary subsystems do not exceed 0.79% (NRTL) and 5.1% (UNIFAC). In case of quaternary system investigated $\sigma(\mathrm{NRTL}) = 0.56\%$ and $\sigma(\mathrm{UNIFAC}) = 2.2\%$. The study of critical states was carried out by "cloud-point technique" method. The run of critical curve in quaternary system was studied.

1. Introduction

The study of phase transitions and phase diagrams of multicomponent systems is of well-known importance for the design of modern industrial processes, in particular an ester production. *N*-butyl propionate is widely used as a solvent in various industries due to the high boiling temperature and, accordingly, low volatility [1]. For example, *n*-butyl propionate was used as a flavoring in a food products and as well as in a paint industry [2]. In fuel industry *n*-butyl propionate and other butyl carboxylate esters are considered as a promising fuel products and components of biodiesel and bio-oil (e.g. see Refs. [3–7]). Accordingly the studies of butyl carboxylate esters and systems containing these esters are necessary elements for the development of data base for modern fuel technology.

The direct synthesis of *n*-butyl propionate is based on acid-catalyzed esterification of propionic acid with *n*-butanol. The coupled processes, primary reactive distillation, provide energy-saving ester production with significantly improvement the degree of conversion of reactants [8,9]. Consequently the phase equilibria data give important thermodynamic information which is necessary for the process design and for the development of the data base on physico-chemical properties of multicomponent reactive systems.

There are a number of the works on the kinetics of *n*-butyl propionate synthesis. Formerly the reaction kinetics using gel-type Dowex 50W-X8 as solid catalyst was studied by Sharma et al. [10]. The comparison of the kinetics results using several cation exchange resins was carried out by Liu and Tan [11]. Lee et al. presented kinetic model of *n*-butyl propionate synthesis using Amberlyst 35 as catalyst [12]. Other study of the synthesis of this ester was carried out by Zhao [13] in the presence of novel aluminophosphate molecular sieve. Recently the synthesis of *n*-butyl propionate using the catalyst SBA-8-SO_3H was studied by Xi and Cao [14].

Other data sets on the propionic acid – *n*-butanol – *n*-butyl propionate – water system are related to vapor-liquid equilibrium (VLE). The experimental data on VLE for binary subsystems are presented in Ref. [15]. VLE data for propionic acid – *n*-butyl propionate system were obtained by Liu and Tan [11] using the NRTL model and Hayden-O'Connell equation. Gonzales and Ortega presented VLE data for binary mixture *n*-butanol – *n*-butyl propionate in temperature range 390.78–395.26 K [16]. VLE for propionic acid – *n*-butyl propionate system at 373.15 and 393.15 K, and vapor–liquid–liquid equilibrium (VLLE) for the systems *n*-butanol – water, *n*-butyl propionate – water and water – *n*-butanol – *n*-butyl propionate at 323.15–393.15 K were measured by Lee et al. [17]. Due to the association of propionic acid in vapor phase the fugacity

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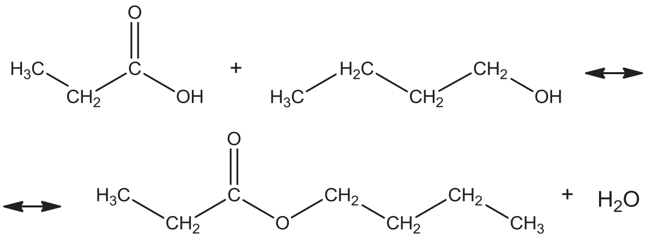
coefficients were calculated by employing the Hayden and O'Connell model [18]. The results of calculation of VLE on the base of NRTL model for binary subsystems propionic acid – *n*-butanol, propionic acid – *n*-butyl propionate, propionic acid – water, *n*-butanol – *n*-butyl propionate, *n*-butanol – water and *n*-butyl propionate – water at 363.15–423.15 K were presented by Lee et al. [8]. Liu and Tan presented experimental data on VLE for binary system propionic acid – *n*-butyl propionate at 60, 80 and 101.3 kPa by using a dual circulation technique [19]. The experimental data were fitted with the NRTL, Wilson, and UNIQUAC models. For the system propionic acid – *n*-butyl propionate Kushner et al. [20] observed the existence of an unusual biazeotrope (double azeotrope) at a pressure below 17.4 kPa.

The data on LLE are more limited in comparison with VLE and kinetic data. The data on LLE in two binary systems *n*-butanol – water and *n*-butyl propionate – water data can be found in Ref. [21]. The NRTL model was used to correlate the mutual solubility data of the binary aqueous systems, *n*-butanol – water, *n*-butyl propionate – water in a work of Lee et al. [17]. In this work the results on LLE calculation for *n*-butanol – *n*-butyl propionate – water ternary system using NRTL model are also presented [8].

In our work we obtained the new experimental data on LLE in quaternary system propionic acid – *n*-butanol – *n*-butyl propionate – water system at 303.15 K and atmospheric pressure. The liquid-liquid envelope in quaternary mixtures is caused by limited miscibility in two binary sub-systems alcohol – water and ester – water. The components of this system are the reactants of *n*-butyl propionate synthesis reaction:



but the reaction rate is very low in the absence of catalyst [10,11]. We additionally checked this conclusion during LLE experiments at 303.15 K. Accordingly there was an opportunity for the study of phase equilibria neglecting the chemical reaction. The compositions of critical points are also carried out at the same temperature and pressure.

2. Experimental

2.1. Materials

Propionic acid (>0.99, Vekton, Russia), *n*-butanol (>0.99, Vekton, Russia) and *n*-butyl propionate (>0.99, Vekton, Russia) were purified by distillation; water was bidistilled. The purities were determined by gas chromatography (GC) (Table 1). All physical and chemical constants of pure substances are in agreement with the literature data [22].

Table 1
The purities of the chemicals.

Substance	Purity, mole fraction[a]
Propionic acid	0.997
n-Butanol	0.997
n-Butyl propionate	0.998
Water	0.999

[a] The uncertainty is estimated to be ±0.005 mol fraction.

2.2. LLE and critical states determination

The data on LLE were obtained by GC analysis. Initial binary, ternary and quaternary mixtures were prepared in glass vessels (5 ml) using an analytical balance Shinko VIBRA HT-120CE (Japan) with the accuracy of 0.001 g. Stirred up sealed vessels were placed in the liquid thermostat (303.15 K). The temperature uncertainty was 0.05 K. Samples were kept in a thermostat during 2 h. This time is enough to establish the phase equilibrium. After full separation of phases in vessels (phases became quite transparent) it was considered that the phase equilibrium is achieved. Further samples from water and organic phases were separately taken with 1 μl chromatographic syringe ("Hamilton", USA) and analyzed by GC method. Gas chromatograph "Crystal 5000.2" (Russia) with thermal conductivity detector (TCD) and packed column Porapak R (1 m × 3 mm i.d.) was used. The analysis of each sample was repeated 2–3 times. The TCD was chosen because of the presence of water in mixtures investigated. The carrier gas was helium with the flow rate of 60 ml/min. Operating temperatures of column, vaporizing injector and TCD were 463.15 K, 503.15 K and 513.15 K respectively. The method of internal standard and relative calibration were used to determine LLE compositions. Propionic acid was accepted as a linking component. Uncertainty of GC analysis averaged 0.005 mol fraction.

The compositions of critical points were obtained with the use of cloud-point technique method. Initial homogeneous binary and ternary mixtures were prepared using an analytical balance Shinko VIBRA HT-120CE (Japan) with the accuracy of 0.001 g. Titration on turbidity was carried out with the use of round-bottomed flask (8 ml) in a liquid thermostat (303.15 K) at the constant stirring with a magnetic stir bar. The temperature uncertainty was 0.05 K. Titrant (water) was added dropwise to initial mixtures using a 2 ml micro burette. The accuracy of the titrant volume measurement was estimated to be 0.005 ml. For the final titration point the composition of heterogeneous mixture, which remained cloudy during 2 min, was considered. Taking into account the volume of mixtures (4–8 ml) and volume of titrant (0.02 ml) the accuracy of composition determination was estimated to be 0.001 mol fractions. In consideration of other factors affecting accuracy (purity of chemicals, thermostatic control uncertainty and others) the maximum error of an experimental data was appreciable to be 0.005 mol fraction of the component. All experiments were carried out at atmospheric pressure.

3. Results and discussion

3.1. Experimental data

LLE for the quaternary system propionic acid (1) – *n*-butanol (2) – *n*-butyl propionate (3) – water (4) system was measured in all concentration range at 303.15 K and atmospheric pressure. The experimental data on LLE for binary *n*-butanol – water, *n*-butyl propionate – water subsystems and ternary *n*-butanol – *n*-butyl propionate – water, propionic acid – *n*-butanol – water and propionic acid – *n*-butyl propionate – water are presented in Table 2 (mole fractions).

The Fig. 1 presents LLE of binary *n*-butanol – water and *n*-butyl propionate – water and ternary *n*-butanol – *n*-butyl propionate – water systems at 303.15 K and its heterogeneous region occupies almost half of the concentration region of the diagram (the concentration of *n*-butanol does not exceed 0.5 mol fractions). A comparative analysis of experimental results on binary subsystems with literature data [22] indicates a good agreement. An absolute deviations for *n*-butanol – water system do not exceed 0.005 mol fractions (organic phase) and 0.001 mol fractions (water phase) and