



Liquid–liquid equilibrium and critical states for the system acetic acid + *n*-butanol + *n*-butyl acetate + water at 308.15 K



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ABSTRACT

Liquid–liquid equilibrium (LLE) for the quaternary system acetic acid–*n*-butanol–*n*-butyl acetate–water and for the ternary sub-systems acetic acid–*n*-butyl acetate–water, *n*-butanol–*n*-butyl acetate–water and acetic acid–*n*-butanol–water were studied at 308.15 K and atmospheric pressure. Binodal surface and curves, tie-lines and compositions of critical points of LLE were determined. Experimental LLE data were correlated by NRTL model. Experimental LLE data were compared with the values calculated by NRTL models, these data are in good agreement.

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1. Introduction

The data on phase equilibrium and the structure of diagram of multicomponent systems is of well-known importance for the design of industrial separation processes. *n*-Butyl acetate is one of the most abundant chemical solvents because of a low environment impact in comparison with other solvents. *n*-Butyl acetate is generally synthesized by the esterification reaction of acetic acid with *n*-butanol. The knowledge of phase diagram of reacting mixture could be useful for the design of coupled process that includes the simultaneous separation of reaction products. Both for synthesis and distillation processes the opportunity of the splitting of reaction mixture should be taken into account. The coupled processes, primary reactive distillation allows to get a significant improvement the degree of conversion of the reactants, the lowering of energy costs and environmental risks. Consequently the phase transitions and other thermodynamic and kinetic properties of the acetic acid–*n*-butanol–*n*-butyl acetate–water systems have been studied in recent years both for basic and applied purposes (see e.g., [1–4]).

In this paper we present the results of experimental study and modeling of the LLE in the acetic acid–*n*-butanol–*n*-butyl acetate–water system at 308.15 K and atmospheric pressure. Due to the limited miscibility of water and ester the liquid phase splitting also occurs in quaternary system.

The paper [5] of Campanella and Mandagaran describes the influence of the simultaneous chemical and phase equilibrium on the conceptual design of reactive distillation processes in the esterification of acetic acid with methanol, ethanol and butanol. The LLE (solubility and tie-line data) was experimentally investigated in ternary system acetic acid–*n*-butyl acetate–water at 298.15, 303.15 and 308.15 K by İnce and İsmail Kõrbařlar [6]. The UNIFAC method was used to predict the LLE and it was found that the used parameters do not give a good agreement.

The correlation of the data for phase and chemical equilibrium (CE) in acetic acid–*n*-butanol–*n*-butyl acetate–water is presented by Mandagaran and Campanella in [3]. The azeotropic properties, the topological structure and the existence of a reactive azeotrope are discussed. The data are correlated by Hayden–O'Connell second virial coefficients and NRTL model. CE constant has a strong influence on the reactive azeotrope.

LLE of the binary 1-butyl acetate–water system and ternary acetic acid–1-butanol–water, acetic acid–1-butyl acetate–water, 1-butanol–1-butyl acetate–water systems at temperatures between 348.15 K and 393.15 K were studied by Grob and Hasse [7]. Chemical equilibrium data for quaternary system in liquid–liquid equilibria were obtained at temperatures between 353.15 K and 393.15 K. There was the comparison between the modeling approaches: the Gibbs energy (GE) models NRTL and UNIQUAC as well as the PC-SAFT equation of state and the COSMO-RS model. These models were used successfully, but the COSMO-RS model, however, has the highest predictive power.

LLE in the ternary system acetic acid–1-butanol–water was investigated in [8] by Esquivel and Bernardo-Gil [8]. The titration

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method was used to determine the binodal curves; the tie-lines data were obtained using GC by analyzing the compositions of the organic phase. A Nelder–Mead technique was used to calculate NRTL and UNIQUAC parameters [8].

The ternary acetic acid–water–butyl acetate and acetic acid–water–2-methyl propyl acetate systems were investigated at 304.15 K, 332.15 K and 366.15 K under atmospheric pressure in the work of Wang et al. [9]. The LLE experimental data were used in the NRTL model to estimate the LLE interaction parameters.

In comparison with ternary and binary subsystems there are moderate data sets on LLE in quaternary systems with butyl acetate synthesis reaction. The paper by Bevia et al. [10] contains the experimental data of mutual solubility and tie-lines at 298 K and atmospheric pressure which were obtained for the quaternary system acetic acid–*n*-butanol–*n*-butyl acetate–water. To correlate the LLE data the UNIQUAC equation was used.

The aim of our work was the study of LLE in water–acetic acid–1-butanol–*n*-butyl acetate system at 308.15 K. Additionally we obtained the data on critical states of LLE and determined the disposition of critical curve in composition tetrahedron.

2. Experimental

2.1. Materials

Acetic acid (>0.99 mol fraction, Vekton, Russia) was additionally purified by distillation, with the presence of 98% sulfuric acid. *n*-Butanol (>0.99 mol fraction, Vekton, Russia) and *n*-butyl acetate (>0.99 mol fraction, Vekton, Russia) were purified by distillation, water was bidistilled. Purity was determined by gas chromatography (GC) and is given in Table 1. All physical–chemical constants of pure substances are in agreement with the literature data [11].

2.2. Critical states and LLE determination

Cloud-point technique was used to study the compositions of critical states of LLE. Binary and ternary mixtures of known overall composition within the homogeneous region were prepared by gravimetric method using analytical balance Shinko VIBRA HT-120CE (Japan) with an accuracy of 0.001 g. Titration was performed in round-bottomed flask (10 ml) in a liquid thermostat (308.15 K) at the constant stirring with a magnetic stir bar. The temperature uncertainty was ± 0.05 K. Water as a titrant was added to initial mixtures using a 2 ml micro burette. The accuracy of the titrant volume measurement was estimated to be 0.005 ml. Turbidity of the solution to be titrated persisting for at least 2 min was considered to be a final point of titration. Taking into account the volume of mixtures (10–30 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 ± 0.002 mol fraction of the component.

The studying LLE was carried out using GC analysis. Initial binary, ternary and quaternary mixtures of known overall composition within the heterogeneous region were prepared in

glass vessels (5 ml) by gravimetric method. Stirred up sealed vessels were placed in the liquid thermostat (308.15 K). The temperature uncertainty was ± 0.05 K. It was considered that the phase equilibrium is achieved after full separation of phases and the phases became quite transparent. Then samples were taken separately from water and organic phases with 10 μ l chromatographic syringe (“Hamilton”, USA) and analyzed by GC. The chromatographic syringe was preliminary heated to avoid the splitting of samples directly into the needle. Gas chromatograph “Chromatec Crystal 5000.2” (Russia) with thermal conductivity detector (TCD) and packed column Porapak R (1 m \times 3 mm i.d.) was used. The TCD was chosen because of the presence of water. Helium with the flow rate of 60 ml/min was used as a carrier gas. Operating temperature of column, vaporizing injector and TCD temperature were 483 K, 503 K and 513 K, respectively. The method of internal standard and relative calibration were used to calculate compositions of equilibrium liquid phases. Acetic acid was accepted as an internal standard. The time required to establish equilibrium determined the additional experiments of various time length. During these experiments it was found that an hour is sufficient for equilibrium approach. All the components of the system have been analyzed in both equilibrium phases by GC analysis. Uncertainty of GC analysis averaged ± 0.005 mol fraction.

3. Results and discussions

3.1. Experimental data

The determination of the LLE of the ternary subsystems acetic acid–*n*-butyl acetate–water, *n*-butanol–acetic acid–water, *n*-butanol–*n*-butyl acetate–water at 308.15 K and atmospheric pressure are presented in Tables 2–4, respectively (mole fractions).

Fig. 1 shows LLE of the ternary subsystem acetic acid–*n*-butyl acetate–water at 308.15 K (Ince et al. and this work) and 298.15 K (Bevia et al.). As usual the solubility increases with temperature and the area of immiscibility at 298.15 K [10] covers a larger area in comparison with 308.15 K (our data). There are some difference of our results and the data [6] at 308.15 K. As a whole the solubility in this ternary system slightly depends on temperature, including a critical region.

Fig. 2 shows LLE of the ternary system *n*-butanol–acetic acid–water at 298.15 K [10], 303.15 K [8] and 308.15 K (our work). The Fig. 3 shows LLE of the ternary system *n*-butanol–*n*-butyl acetate–water at 298.15 K [10], 303.15 K [12] and 308.15 K (our work). In both system the immiscibility area also slightly depends on temperature (decrease with the temperature rising).

The LLE data for the quaternary system acetic acid–*n*-butanol–*n*-butyl acetate–water at 308.15 K at atmospheric pressure are presented in Table 5.

Table 2

The experimental LLE data for the ternary system acetic acid (1)–*n*-butanol (2)–water (3) for mole fractions x at 308.15 and atmospheric pressure.^a

Water phase		Organic phase	
x_1	x_2	x_1	x_2
0.000	0.017	0.000	0.476
0.009	0.017	0.017	0.414
0.019	0.023	0.043	0.356
0.029	0.029	0.064	0.294
0.032	0.037	0.070	0.273
0.040	0.046	0.078	0.225
0.048	0.060	0.079	0.181
$\sigma(\text{NRTL}) = 1.33\%$			

^a Standard uncertainties $u(x) = 0.005$, $u(T) = 0.05$.

Table 1
The purities of the chemicals.

Substance	Purity, mole fraction ^a
Acetic acid	0.998
<i>n</i> -Butanol	0.995
<i>n</i> -Butyl acetate	0.998
Water	0.999

^a The uncertainty is estimated to be ± 0.002 mol fraction.

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