

Solubility, liquid-liquid equilibrium and critical states for quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water at 303.15 K and atmospheric pressure



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ABSTRACT

The object of this study is multicomponent heterogeneous liquid-liquid system with *n*-amyl acetate synthesis reaction. New experimental data on solubility, liquid-liquid equilibrium (LLE) and critical compositions for acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water at 303.15 K and atmospheric pressure are presented. Solubility and critical states were investigated by “cloud-point technique” and pale opalescence blue methods accordingly. LLE compositions were determined by gas chromatography and correlated by NRTL model. Results calculated using NRTL modeling are in sufficient agreement with experimental data. Standard deviations for binary, ternary subsystems do not exceed 0.45% and for quaternary system investigated – 0.53%.

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1. Introduction

Experimental study of solubility, liquid-liquid equilibrium (LLE) and compositions of the critical phases is important both for applied tasks of chemical engineering processes, as well as for the development of basic thermodynamic theory. A significant obstacle to the development of theory of chemical processes in heterogeneous (liquid-liquid) systems is both the complexity of the solution of experimental problems and the direct lack of a sufficient base of experimental data. Especially it concerns to the immediate vicinity of critical states and, in the case of systems containing a large number of components, the areas of liquid phase splitting. At the same time the practical importance of the problem of delamination of reaction mixtures is fundamentally changes the technology and design of the processes of chemical synthesis, reactive distillation and extraction. Because of great importance for novel effective and energy saving industrial processes the phase equilibria in reactive systems were the subject matters of many recent researches [1,2]. The object of our study is a multicomponent liquid-phase system

with amyl acetate synthesis which is used in the production of lacquers as a solvent for cellulose, nitrocellulose and cellulose acetate (a widely spread lacquer of this type is zapon lacquer, namely a solution of nitrocellulose in amyl acetate) [3,4]. In addition, amyl acetate is often used as a solvent for lacquers for coating of metal products, wire, optical devices, leather, in the production of pencils, glues and etc. Amyl acetate is also applies as an adhesive in the brushes production and products of celluloid, plastics, rayon (acetate silk), as a solvent for film and camera roll, in the manufacture of accumulators and tapes.

There are some literature LLE data on systems containing acetic acid, *n*-amyl alcohol, *n*-amyl acetate and water. LLE data for binary *n*-amyl alcohol – water [5–12] and *n*-amyl acetate – water [13–15] systems are presented in a number of works at different temperatures and atmospheric pressure. Wang et al. [16] were carried out LLE for acetic acid – *n*-amyl acetate – water ternary system at 304.15, 332.15 and 366.15 K (atmospheric pressure). The experimental data were correlated with the NRTL model. Data on solubility and LLE for ternary acetic acid – *n*-amyl alcohol – water system were obtained by Ref. [17] at 303.15, 323.15 K and atmospheric pressure. The same system had been studied in Ref. [18] at 288.15, 298.15, 303.15, 308.15, 318.15, 323.15 K and atmospheric pressure. There are no LLE data for ternary *n*-amyl alcohol – *n*-amyl

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acetate – water and quaternary acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water systems in literature at all.

Our work presents new experimental data on solubility, LLE and critical phases for quaternary acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water system at 303.15 K and atmospheric pressure.

2. Experimental

2.1. Materials

Acetic acid (>0.99, Vekton company, Russia), *n*-amyl alcohol (>0.99, Vekton company, Russia) and *n*-amyl acetate (>0.99, Vekton company, Russia) were purified using laboratory distillation columns of high performance; water was distilled twice. The purities of reagents were determined and checked by gas chromatography method (Table 1). Physical and chemical properties and constants of compounds after thorough purification were in good concordance with the literature data [19].

2.2. Solubility and critical states determination

The solubility data and compositions corresponding to critical states were determined by well-known method of cloud-point technique. The methodology of the experiment was tested in our previous studies concerning the reactive mixtures with limited solubility [20–22]. Initial homogeneous binary and ternary mixtures of known compositions were prepared in round-bottomed flask (8 ml) using an analytical balance Pioneer OHAUS PA224 (USA). The sample compositions correspond to the points in concentration tetrahedron which are evenly distributed on liquid-liquid envelope. Mixtures were titrated on turbidity with constant stirring with a magnetic stir bar (IKA C-Mag HS 7) at constant temperature (303.15 K) and atmospheric pressure in a liquid ultra-

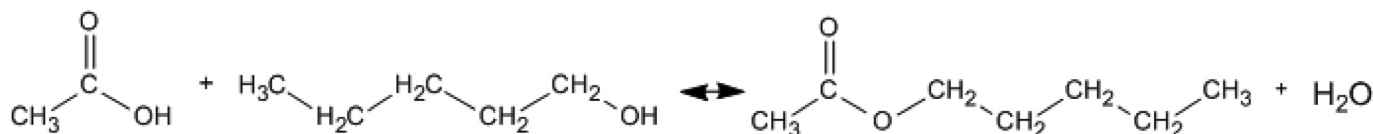
2.3. LLE determination

LLE compositions (tie-lines disposition) were determined by GC analysis using gas chromatograph “Crystal 5000.2” (Russia) with thermal conductivity detector (TCD) and packed column Porapak R (1 m × 3 mm i.d.). We used TCD by necessity of water composition determination. The flow rate of carrier gas (helium) was 60 ml/min; the temperatures of GC column, injector and detector were 503.15 K, 503.15 K and 513.15 K correspondingly. GC results processing was performed by the methods of internal standard and relative calibration; acetic acid was a linking component. Initial samples of solutions (binary, ternary and quaternary mixtures) were prepared using an analytical balance Pioneer OHAUS PA224 (USA) in small glass bottle (volume of 4 ml). Stirred up sealed bottles were kept in the thermostat at 303.15 K during 2 h. According to our previous works [23–25] and additional checking in this study this time is sufficient for the establishing of the equilibrium. Each water and organic phase was taken directly with syringe (1 μl “Hamilton”, USA) and analyzed by GC. The analysis of each samples of phases was repeated 2–3 times. Uncertainty of LLE determination by GC analysis averaged 0.005 mol fraction.

3. Results and discussion

3.1. Experimental data

The obtained solubility data for ternary systems acetic acid – *n*-amyl acetate – water, acetic acid – *n*-amyl alcohol – water, *n*-amyl alcohol – *n*-amyl acetate – water systems at 303.15 K are listed in Table 2. The disposition of solubility curves in composition triangles is presented in Figs. 1–3. Because of chemical reactions (esterification and hydrolysis of the ester).



thermostat (LOIP LT-100). The uncertainty of temperature support was 0.05 K. Titrant (water) was added dropwise to every initial solutions using a 2 ml micro burette. The accuracy of the titrant volume measurement was not less than 0.005 ml. Turbidity of the mixtures to be titrated persisting during at least 2 min was considered as a final point of composition determinations. The accuracy of composition determination was estimated to be 0.005 mol fractions with considering the volumes of mixtures (2–6 ml) and of titrant (0.02 ml). The maximum error of an experimental data was appreciable to be ±0.01 mol fraction.

Table 1
The purities of the compounds.

Compounds	Purity, mole fraction ^a
acetic acid	0.997
<i>n</i> -amyl alcohol	0.997
<i>n</i> -amyl acetate	0.998
water	0.999

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

there are chemical interactions in the systems investigated, however it does not influence on the composition at the experimental conditions: according to our study the rates of reactions are very slow without catalyst. We checked it by special additional experiments: the concentrations of acid, alcohol, ester and water after few hours were changed less than 0.001 mol fraction.

The determination of the compositions of critical states for quaternary system was carried out jointly with the study of solubility at 303.15 K and atmospheric pressure. The initial mixtures acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water of known concentrations were prepared with the constant ratios of alcohol and ester: 1:5, 1:2, 1:1, 2:1 and 5:1 (Fig. 4). Such choice of compositions gives the opportunity to obtain the correct disposition of solubility surface in composition tetrahedron [20–25].

The obtained solubility data for quaternary system are listed in Table 3. The solubility surface in quaternary system is presented in Fig. 5 in composition tetrahedron.

In the study of critical states the blue opalescence was observed in close vicinity of critical points of LLE [20–24]. Previously we calculated the critical states compositions on the base of LLE data using Coollodge method [26]. Additionally we used opalescence

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