



# Solubility, liquid–liquid equilibrium and critical states for the system acetic acid + *n*-propanol + *n*-propyl acetate + water at 293.15 K and 303.15 K



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## ABSTRACT

Solubility and liquid–liquid equilibrium (LLE) for the quaternary system acetic acid–*n*-propanol–*n*-propyl acetate–water and for the ternary sub-systems acetic acid–*n*-propyl acetate–water and *n*-propanol–*n*-propyl acetate–water were studied at 293.15 K and 303.15 K and atmospheric pressure. Binodal surfaces and curves, tie-lines, and compositions of critical LLE points were determined. Experimental LLE data were correlated by UNIFAC and NRTL models.

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## 1. Introduction

The data on phase structure of multicomponent systems is of well-known importance for the design of modern industrial processes. *n*-Propyl acetate is one of commonly used chemical reagents having a lot of practical applications as a solvent. It has also various application areas such as pharmaceutical industry or printing industry. *n*-Propyl acetate is generally synthesized by esterification of acetic acid with *n*-propanol. Accordingly, the reactive mixture of *n*-propyl acetate synthesis reaction includes these reagents (acid + alcohol) together with ester and water. Usually, the industrial synthesis is combined with the separation. In the coupled processes, primary reactive distillation allows one to get a significant improvement of the degree of reactant conversion, together with the lowering of energy costs and environmental risks. Thereby the phase transition and important thermodynamic and kinetic properties of the system acetic acid–*n*-propanol–*n*-propyl acetate–water and constituent sub-systems have been intensely studied in recent years (see, e.g. [1–6]).

In this work we present the results of experimental investigation and modeling of LLE in the system acetic acid–*n*-propanol–*n*-propyl

acetate–water at 293.15 K and 303.15 K. Due to the limited miscibility of water and ester, the liquid phase splitting in the quaternary system also occurs. It is a common phenomenon in systems with the esterification reaction.

The brief review of phase transitions (vapor–liquid, LLE) and azeotropic properties in this system is presented in [7]. Accordingly, in this paper we only give some additional references to recent papers. Data on the solubility of the quaternary system acetic acid–*n*-propanol–*n*-propyl acetate–water and ternary subsystem *n*-propanol–*n*-propyl acetate–water were studied at 313.15 K in [8]. In this paper, we also consider the critical curves of LLE. Experimental data on solubility and LLE together with NRTL and UNIFAC modeling for the ternary system acetic acid–*n*-propyl acetate–water at 293.15, 303.15, and 313.15 K including critical states are presented in [9]. The study of solubility, LLE, and UNIFAC modeling were carried out for the ternary subsystem *n*-propanol–*n*-propyl acetate–water at 293.15, 303.15, and 313.15 K in [10]. Experimental data on LLE of the ternary sub-system acetic acid–*n*-propyl acetate–water at 298.15 K, 313.15 K, and 363.65 K together with UNIQUAC modeling are presented in [11]. Theoretical and experimental study on residue curve maps in the quaternary system was carried out in [4]. The development of a catalytic reactive distillation process for the production of *n*-propyl acetate based on experiment and simulation is proposed in [12]. The kinetic study of *n*-propyl acetate synthesis reaction was also examined in work [13].

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**Table 1**  
The purities of the chemicals.

Substance	Purity, mole fraction <sup>a</sup>
Acetic acid	0.998
<i>n</i> -Propanol	0.995
<i>n</i> -Propyl acetate	0.998
Water	0.999

<sup>a</sup> The uncertainty is estimated to be  $\pm 0.002$  mole fraction.

In spite of a lot of data on ternary sub-systems and some data on *n*-propyl acetate synthesis, the study of solubility and LLE in the quaternary system acetic acid–*n*-propanol–*n*-propyl acetate–water had been carried out in a limited number of works, e.g. [8]. The aim of our work was to study solubility and LLE at two temperatures. The sets of obtained experimental data should give the opportunity to present in more detail the binodal surface, tie-lines position, and critical LLE curves.

## 2. Experimental

### 2.1. Materials

Acetic acid (>0.99, Vekton, Russia) was additionally purified by distillation in the presence of 98% sulfuric acid. *n*-Propanol (>0.99, Vekton, Russia) and *n*-propyl acetate (>0.99, Vekton, Russia) were purified by distillation; water was bidistilled. Purity was determined by gas chromatography (GC) and is presented in Table 1. All physical and chemical constants of pure substances are in agreement with the literature data [14].

### 2.2. Solubility and liquid–liquid equilibrium measurements

Cloud-point technique was used to study solubility and critical states. Binary or ternary mixtures of known overall composition within the homogeneous region were prepared by the gravimetric method in a round-bottomed flask (50 ml) using the Shinko VIBRA HT-120CE analytical balance (Japan) with an accuracy of 0.001 g. For the best presentation of the solubility surface, the initial compositions were chosen so that experimental points were regularly placed on the binodal surface. Titration was performed in

**Table 2**  
The experimental data on solubility (mole fractions,  $x$ ) for the ternary system *n*-propanol (1)–*n*-propyl acetate (2)–water (3) at 293.15 K, 303.15 K and atmospheric pressure.<sup>a</sup>

$X_1$	$X_2$	$X_1$	$X_2$
293.15 K		303.15 K	
0.000	0.003	0.000	0.004
0.063	0.007	0.064	0.008
0.101	0.018	0.095	0.017
0.143	0.033	0.144	0.034
0.129	0.028	0.171	0.046
0.154	0.038	0.183	0.051
0.142	0.033	0.156	0.039
0.138	0.031	0.135	0.031
0.151	0.037	0.205	0.063
0.185	0.051	0.231	0.081
0.226	0.076	0.259	0.116
0.262	0.116	0.279	0.162
0.284	0.166	0.285	0.216
0.288	0.250	0.286	0.298
0.272	0.343	0.267	0.372
0.246	0.427	0.243	0.423
0.182	0.585	0.222	0.490
0.124	0.713	0.205	0.534
0.000	0.948	0.172	0.627
–	–	0.000	0.890

<sup>a</sup> Standard uncertainties  $u(x)=0.002$ ,  $u(T)=0.05$ .

**Table 3**  
The experimental data on solubility (mole fractions,  $x$ ) for the ternary system acetic acid (1), *n*-propyl acetate (2), water (3) at 293.15 K, 303.15 K and atmospheric pressure.<sup>a</sup>

$X_1$	$X_2$	$X_1$	$X_2$
293.15 K		303.15 K	
0.000	0.003	0.000	0.004
0.113	0.019	0.122	0.023
0.132	0.028	0.128	0.027
0.141	0.033	0.138	0.033
0.155	0.045	0.144	0.038
0.166	0.059	0.151	0.044
0.169	0.065	0.156	0.051
0.178	0.079	0.162	0.057
0.180	0.082	0.165	0.063
0.184	0.090	0.167	0.065
0.185	0.092	0.167	0.066
0.187	0.097	0.170	0.069
0.188	0.099	0.171	0.071
0.190	0.103	0.172	0.073
0.193	0.108	0.172	0.074
0.196	0.115	0.173	0.075
0.215	0.162	0.175	0.079
0.224	0.198	0.178	0.084
0.231	0.257	0.179	0.087
0.228	0.314	0.180	0.089
0.220	0.370	0.181	0.091
0.206	0.431	0.183	0.094
0.179	0.520	0.184	0.097
0.000	0.948	0.186	0.100
–	–	0.187	0.104
–	–	0.189	0.107
–	–	0.189	0.109
–	–	0.189	0.110
–	–	0.191	0.112
–	–	0.192	0.115
–	–	0.204	0.143
–	–	0.219	0.193
–	–	0.226	0.265
–	–	0.222	0.323
–	–	0.214	0.375
–	–	0.194	0.449
–	–	0.186	0.480
–	–	0.158	0.551
–	–	0.127	0.626
–	–	0.000	0.890

<sup>a</sup> Standard uncertainties  $u(x)=0.002$ ,  $u(T)=0.05$ .

a liquid thermostat (293.15 and 303.15 K) with continuous stirring by a magnetic stir bar. The temperature uncertainty was  $\pm 0.05$  K. Water as a titrant was added to initial mixtures using a 2 ml micro burette. Accuracy of titrant volume measurement was estimated to be 0.005 ml. Turbidity of the titrated solution persisting during at least 2 min was considered to be the final point of titration. Taking into account a volume of mixtures (10–30 ml) and titrant drop (0.02 ml), the accuracy of concentration determination was estimated to be 0.001 mole fraction. Taking into consideration other possible factors affecting the accuracy (such as the purity of chemicals, thermostatic control uncertainty, and others) the maximum error of experimental data was estimated to be  $\pm 0.002$  mole fraction of the component.

LLE studies were carried out using the GC analysis. Initially, binary, ternary, and quaternary mixtures of known overall composition within the heterogeneous region were prepared in glass vessels (5 ml) by the gravimetric method. Stirred up sealed vessels were placed in the liquid thermostat (293.15 K and 303.15 K). The temperature uncertainty was  $\pm 0.05$  K. It was considered that the phase equilibrium is achieved when there is a full separation of phases and phases are quite transparent. After reaching the phase equilibrium, samples were taken separately from water and organic phases with 1  $\mu$ l chromatographic syringe (“Hamilton”, USA) and analyzed by GC. The chromatographic syringe was

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