



Liquid-liquid equilibrium for the quaternary system propionic acid + *n*-propanol + *n*-propyl propionate + water at 293.15, 313.15 and 333.15 K



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ABSTRACT

Liquid-liquid equilibrium (LLE) for the quaternary system propionic acid + *n*-propanol + *n*-propyl propionate + water and for the ternary sub-systems propionic acid + *n*-propyl propionate + water and *n*-propanol + *n*-propyl propionate + water were studied at 293.15, 313.15 and 333.15 K and atmospheric pressure. Binodal surface in quaternary system and binodal curves in ternary systems were determined. 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 diagrams of heterogeneous systems are of well-known importance for the design of modern industrial processes. *n*-Propyl propionate is one of commonly used solvents having a lot of practical applications. This ester is used in many different fields, for example, as a constituent part of coatings, printing inks, air freshener, confecting essence, detergent and other industrial products. *n*-Propyl propionate is readily biodegradable and it is expected to be rapidly degraded in wastewater treatment plants or in the environment [1]. *n*-Propyl propionate is generally synthesized by the esterification reaction of propionic acid with *n*-propanol. The complex process of its production involves reaction and separation operations. One of the best and well-known chemical engineering processes which combines chemical reaction and separation into a multifunctional reactor is a reactive distillation [2] and [3]. The limited mutual solubility of components of *n*-propyl propionate synthesis reaction should be taken into account in reactive distillation design. For example, one can use the advantage of the phase splitting by coupling the distillation column with a liquid-liquid separator [4]. For this reason the majority of

recent papers on *n*-propyl propionate production include the discussion of the splitting in propionic acid + *n*-propanol + *n*-propyl propionate + water system [1,4–10]. Nevertheless the available experimental data sets on LLE were presented for binary sub-systems and for ternary *n*-propanol + water + *n*-propyl propionate system only [11]. The LLE in this ternary system was studied by Altman et al. at 288.15 K [5] and by Mozzhukhin et al. at 293.15 K [12]. The aim of our work was to study LLE for quaternary system propionic acid + *n*-propanol + *n*-propyl propionate + water and for both ternary sub-system propionic acid + *n*-propyl propionate + water and *n*-propanol + *n*-propyl propionate + water with miscibility gap at three temperatures, 293.15, 313.15 and 333.15 K. The sets of obtained experimental data gave us the opportunity to present in more details the binodal surface and tie-lines position of the system with *n*-propyl propionate synthesis reaction in composition triangle and composition tetrahedron. It should be noted that there is a lack of the data on LLE in propionic acid + *n*-propanol + *n*-propyl propionate + water system in modern literature. The set of the data on LLE in quaternary system should give the additional opportunities for the optimization of the processes of *n*-propyl propionate synthesis and for the design of coupled processes, e.g. reactive distillation.

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2. Experimental

2.1. Materials

Propionic acid (>0.99 mole fraction, Vekton, Russia), *n*-propanol (>0.99 mole fraction, Vekton, Russia) and *n*-propyl propionate (>0.98 mole fraction, Sigma Aldrich) 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 [13].

2.2. LLE determination

The study of the phase equilibria was carried out by method described in Ref. [14] using GC analysis for analytical determination of phase compositions. Firstly, binary, ternary and quaternary mixtures of known overall composition within the heterogeneous region were prepared in glass vials (5 ml) by gravimetric method using analytical balance Shinko VIBRA HT-120CE (Japan). Heterogeneous mixtures were stirred in sealed vials. Then vials were placed in the liquid thermostat (293.15, 313.15 and 333.15 K). We consider that the equilibrium is reached when there is a full separation of the phases: phases become completely transparent and there is no variation of compositions with a time. After reaching of phase equilibrium, samples were taken from both phases with chromatographic syringe (“Hamilton”, USA) and analyzed by GC. To avoid the splitting of samples directly into the needle the chromatographic syringe was preliminary heated. Gas chromatograph “Chromatec Crystal 5000.2” (Russia) with thermal conductivity detector (TCD) and packed column Porapak R (1 m* 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 were 483 K, 503.15 K and 513 K, respectively. The methods of internal standard and relative calibration were used to calculate compositions of equilibrium liquid phases. Propionic acid was accepted as linking component. Uncertainty of GC analysis averaged ± 0.005 mole fraction. Accuracy of initial solutions preparing is 0.001 g. The temperature uncertainty of the liquid thermostat was ± 0.05 K. The reproducibility of the experimental data was confirmed by the repeated analysis of samples. All equilibrium liquid phases were analyzed 3–5 times and the deviations of the results were in the frame of GC analysis uncertainties.

3. Results and discussions

3.1. Experimental data

The LLE data for the ternary sub-systems propionic acid + *n*-propyl propionate + water and *n*-propanol + *n*-propyl propionate + water at 293.15, 313.15 and 333.15 K and atmospheric pressure are presented in Tables 2 and 3, respectively (mole fractions).

The Fig. 1 shows binodal curves and tie-lines of LLE of the ternary sub-system propionic acid + *n*-propyl propionate + water

Table 1
The purities of the chemicals.

Substance	Purity, mole fraction ^a
Propionic acid	0.998
<i>n</i> -propanol	0.995
<i>n</i> -propyl propionate	0.980
Water	0.999

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

Table 2

The experimental LLE data for the ternary system propionic acid (1) – *n*-propyl propionate (2) – water (3) (mole fractions x , atmospheric pressure^a).

Water phase		Organic phase	
x_1	x_2	x_1	x_2
293.15 K			
0.000	0.006	0.000	0.926
0.038	0.004	0.143	0.610
0.035	0.008	0.189	0.526
0.044	0.010	0.246	0.416
0.064	0.009	0.272	0.340
0.093	0.009	0.288	0.227
0.107	0.011	0.284	0.162
0.124	0.015	0.275	0.118
$\sigma(\text{NRTL}) = 4.1\%$			
313.15 K			
0.000	0.009	0.000	0.881
0.029	0.007	0.137	0.581
0.053	0.007	0.178	0.501
0.057	0.006	0.213	0.421
0.069	0.008	0.260	0.317
0.092	0.010	0.277	0.210
0.122	0.015	0.270	0.138
0.129	0.020	0.263	0.106
$\sigma(\text{NRTL}) = 3.2\%$			
333.15 K			
0.000	0.013	0.000	0.828
0.037	0.004	0.133	0.560
0.044	0.012	0.176	0.473
0.051	0.011	0.204	0.391
0.072	0.007	0.253	0.300
0.103	0.014	0.265	0.195
0.122	0.021	0.252	0.133
$\sigma(\text{NRTL}) = 3.1\%$			

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

at 293.15, 313.15 and 333.15 K.

The solubility in the ternary system *n*-propanol + *n*-propyl propionate + water at 293.15, 313.15 and 333.15 K is presented on Fig. 2. The data of Altman et al. at 288.15 K [5] are also presented for comparison. As usual the solubility increases with temperature and the area of immiscibility at 288.15 K covers a larger area in comparison with 308.15 K and 333.15 K. In both systems the immiscibility area slightly depends on temperature (decrease with the temperature rising). The LLE tie-lines are presented for 333.15 K only. For other temperatures the general disposition of tie-lines is approximately the same.

The LLE data for the quaternary system propionic acid + *n*-propanol + *n*-propyl propionate + water at 293.15, 313.15 and 333.15 K and atmospheric pressure are presented in Table 4 (mole fractions). The initial series of quaternary solutions were prepared with keeping of constant ratio of propionic acid and *n*-propanol that is 1:1. These compositions conveniently display the form of binodal surfaces in composition tetrahedron. The view of the surface for 293.15 K is presented on Fig. 3.

3.2. Reliability of tie-line data

To check the reliability of the experimental data on LLE we used the Bachman equation [15]:

$$\ln\left(\frac{W_1^A}{W_4^A}\right) = a + b \ln\left(\frac{W_1^O}{W_3^O}\right) \quad (1)$$

and Hand equation [16]:

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