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

Artemiy Samarov, Maria Toikka, Maya Trofimova, Alexander Toikka*

Department of Chemical Thermodynamics and Kinetics, Saint Petersburg State University, Universitetskiy prospect 26, Peterhof, St. Petersburg 198504, Russia

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.

Keywords: Liquid-liquid equilibria, *n*-propyl propionate, NRTL model

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.

2. Experimental

* Corresponding author: a.toikka@spbu.ru

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].

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

^aThe uncertainty is estimated to be ± 0.002 mole fraction.

2.2 LLE determination

The study of the phase equilibria was carried out by method described in [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 vessels 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 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.

Fig. 1. The diagram of the LLE in ternary system propionic acid + *n*-propyl propionate + water: ●---● – tie-lines at 293.15 K, ■---■ – tie-lines at 313.15 K, ▲---▲ – tie-lines at 333.15 K.

Fig. 2. The solubility in ternary system *n*-propanol + *n*-propyl propionate + water: ○ – 288.15 K [5], ● – 293.15 K, ■ – 313.15 K, ▲ – 333.15 K, ▲---▲ – tie-lines at 333.15 K.

Fig 3. The qualitative view of the binodal surface of quaternary system propionic acid + *n*-propanol + *n*-propyl propionate – water at 333.15 K.

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
σ (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
σ (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
σ (NRTL) = 3.1%			

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

Table 3

The experimental LLE data for the ternary system *n*-propanol (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
0.013	0.011	0.073	0.842
0.022	0.008	0.154	0.720
0.031	0.007	0.214	0.625
0.035	0.005	0.268	0.521
0.038	0.003	0.305	0.447
0.041	0.003	0.332	0.395
0.044	0.004	0.353	0.346
0.046	0.004	0.366	0.299
0.052	0.004	0.381	0.219
0.053	0.003	0.378	0.195
0.056	0.003	0.376	0.164
0.068	0.003	0.330	0.085
$\sigma(\text{NRTL}) = 2.9\%$			
313.15 K			
0.000	0.009	0.000	0.881
0.010	0.015	0.084	0.790
0.017	0.006	0.165	0.671
0.027	0.007	0.226	0.569
0.029	0.004	0.271	0.481
0.033	0.002	0.303	0.421
0.036	0.005	0.329	0.363
0.038	0.003	0.348	0.323
0.041	0.004	0.362	0.284
0.045	0.003	0.372	0.206
0.051	0.004	0.363	0.154
0.065	0.003	0.318	0.078
0.088	0.006	0.244	0.040
$\sigma(\text{NRTL}) = 2.2\%$			
333.15 K			
0.000	0.013	0.000	0.828
0.009	0.012	0.092	0.745
0.015	0.007	0.170	0.639
0.020	0.008	0.226	0.533
0.027	0.005	0.273	0.460
0.030	0.004	0.305	0.400
0.033	0.005	0.325	0.354
0.037	0.007	0.343	0.310
0.040	0.006	0.354	0.270
0.044	0.004	0.356	0.193
0.048	0.003	0.349	0.145
0.065	0.004	0.295	0.072
0.094	0.007	0.213	0.032
$\sigma(\text{NRTL}) = 3.2\%$			

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

Table 4

The experimental LLE data for the quaternary system propionic acid (1) + *n*-propanol (2) + *n*-propyl propionate (3) + water (4) (mole fractions x , atmospheric pressure ^a)

Water phase			Organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
293.15 K					
0.022	0.016	0.006	0.098	0.145	0.481
0.029	0.022	0.012	0.119	0.168	0.393
0.032	0.022	0.006	0.132	0.173	0.330
0.037	0.025	0.007	0.146	0.182	0.260
0.045	0.030	0.007	0.164	0.180	0.181
0.048	0.034	0.006	0.162	0.167	0.122
0.060	0.042	0.007	0.143	0.140	0.071
313.15 K					
0.023	0.017	0.016	0.091	0.146	0.459
0.031	0.018	0.008	0.107	0.168	0.376
0.033	0.020	0.007	0.125	0.171	0.312
0.033	0.022	0.005	0.140	0.176	0.245
0.042	0.027	0.006	0.155	0.172	0.171
0.049	0.032	0.006	0.147	0.159	0.114
0.061	0.045	0.009	0.131	0.125	0.061
333.15 K					
0.025	0.009	0.008	0.047	0.106	0.589
0.028	0.014	0.009	0.079	0.148	0.446
0.033	0.018	0.012	0.103	0.166	0.363
0.036	0.019	0.009	0.117	0.171	0.302
0.038	0.022	0.008	0.135	0.170	0.232
0.044	0.027	0.007	0.151	0.166	0.160
0.052	0.034	0.007	0.147	0.151	0.107

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

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]:

$$W_3^O = a + b \left(\frac{W_3^O}{W_4^A} \right) \quad (2)$$

where W_1^A is the mass fraction of propionic acid (or *n*-propanol) in the water-rich phase, W_4^A is the mass fraction of water in the water-rich phase, W_1^O is the mass fraction of propionic acid (or *n*-propanol) in the organic phase, W_3^O is the mass fraction of *n*-propyl acetate in the organic phase, a and b are adjustable parameters. Correlations with the use of Bachman and Hand equation are shown in Fig. 4 and Fig. 5, respectively.

The correlation factor R^2 values were determined by a partial least-squares regression. The correlation factor for Bachman and Hand test in the case of propionic acid + *n*-propyl propionate + water system indicates the consistency of the LLE data: $R^2 > 0.95$. The same result of Bachman

correlation ($R^2 > 0.95$) is for *n*-propanol + *n*-propyl propionate + water system. The Hand plot in the case of *n*-propanol + *n*-propyl propionate + water system has not linear form: there are inflection points on the graphs (Fig. 5). Such behavior could be explained by the tie-line disposition and peculiarity of changes of organic phase composition. First, the concentration of *n*-propanol in the organic phase increases, but then, closer to the critical point, begins to diminish. It also follows from the critical point disposition and, respectively, from the asymmetric shape of binodal curve. In this case, additionally to Bachman equation, we correlated LLE data with the use of polynomial dependence:

$$W_3^O = a + b \left(\frac{W_3^O}{W_4^A} \right) + c \left(\frac{W_3^O}{W_4^A} \right)^2 + d \left(\frac{W_3^O}{W_4^A} \right)^3 \quad (3)$$

The correlation factor calculated for equation (3), $R^2 > 0.95$, along with Bachman correlation, indicates the consistency of the measured LLE data.

Fig. 4. Bachman plot for the ternary system *n*-propanol + *n*-propyl propionate + water: ○ – 293.15 K, □ – 313.15 K, Δ – 333.15 K; and ternary system propionic acid + *n*-propyl propionate + water: ● – 293.15 K, ■ – 313.15 K, ▲ – 333.15 K.

Fig. 5. Hand plot for the ternary system *n*-propanol + *n*-propyl propionate + water: ○ – 293.15 K, □ – 313.15 K, Δ – 333.15 K; and ternary system propionic acid + *n*-propyl propionate + water: ● – 293.15 K, ■ – 313.15 K, ▲ – 333.15 K.

4. Modeling of LLE

The experimental data on ternary and quaternary systems were correlated by NRTL model [17]. The NRTL equation for the activity coefficients in the solution of n components was used in the following form:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^m x_j \tau_{ji} G_{ji}}{\sum_{l=1}^m x_l G_{li}} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m x_l G_{lj}} \left(\tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m x_l G_{lj}} \right)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji})$$

$$(\alpha_{ji} = \alpha_{ij})$$

where g_{ji} is energy parameter that characterizes the interaction of components j and i ; parameter α_{ji} is responsible for the nonrandomness in the systems. Optimization of NRTL parameters was carried out by minimization of objective function (OF):

$$OF = \sum_{k=1}^n \sum_{i=1}^n \left[(x_{ik}^{exp} - x_{ik}^{cal})_{or}^2 + (x_{ik}^{exp} - x_{ik}^{cal})_w^2 \right]$$

The parameters estimated by this procedure are presented in Table 5. These parameters were obtained by correlation of the quaternary and the ternary systems.

Table 5

Binary parameters for NRTL simulation

	propionic acid – <i>n</i> - propanol	propionic acid – water	propionic acid – <i>n</i> - propyl propionate	<i>n</i> - propanol – water	<i>n</i> - propanol – <i>n</i> - propyl propionate	<i>n</i> - propyl propionate – water
$\Delta g_{ji} / \text{J mol}^{-1}$	1120.8	1631.9	590.0	1744.7	566.0	3505.0
$\Delta g_{ij} / \text{J mol}^{-1}$	1754.0	-182.3	32.1	-93.5	236.9	1142.5
α_{ji}	0.3	0.3	0.3	0.3	0.3	0.3

Standard deviation, σ was determined:

$$\sigma(\%) = 100 \sqrt{\frac{\sum_{k=1}^n \sum_{i=1}^4 (x_{ik}^{exp} - x_{ik}^{cal})_{or}^2 + (x_{ik}^{exp} - x_{ik}^{cal})_w^2}{2mn}}$$

where n is a number of tie-lines, m is a number of components. Subscripts i, k indicate components and tie-lines respectively; *or*, *w* – organic and water phases.

The results of NRTL modeling both for quaternary and ternary systems are in good agreement with experimental data. Accordingly, these parameters are suitable for data correlation for the whole composition range of quaternary system. Standard deviation for subsystems propionic acid + *n*-propyl propionate + water and *n*-propanol + *n*-propyl propionate + water and quaternary system propionic acid + *n*-propanol + *n*-propyl propionate + water does not exceed 4.1%.

5. Conclusions

LLE data for the quaternary system propionic acid + *n*-propanol + *n*-propyl propionate + water and for the ternary subsystems propionic acid + *n*-propyl propionate + water and *n*-propanol + *n*-propyl propionate + water were obtained at 293.15, 313.15 and 333.15 K and atmospheric pressure. These set of new experimental data allow presenting the binodal surface in composition tetrahedron. Verification the reliability of the experimental data on LLE was carried out using Bachman and Hand equations. The comparison of experimental LLE data with the values which were calculated using NRTL model indicates that the experimental and calculated data are in sufficient agreement. Obtained NRTL parameters may be used for the data correlation in the whole composition range of quaternary system.

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