

Solubility, liquid–liquid equilibrium and critical states for the quaternary system acetic acid–ethanol–ethyl acetate–water at 303.15 K and 313.15 K



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ABSTRACT

Solubility, critical states and liquid–liquid equilibrium (LLE) data for the quaternary system acetic acid–ethanol–ethyl acetate–water and for the ternary subsystems acetic acid–ethyl acetate–water and ethanol–ethyl acetate–water were studied at 303.15 K and 313.15 K and atmospheric pressure. Binodal surfaces, binodal curves, tie-lines and compositions of critical points were determined. In order to construct the binodal surfaces and critical curves of the quaternary system, five quaternary sectional planes with several different ratios of concentration of acetic acid to ethanol were studied. Experimental LLE data were compared with the values calculated by UNIFAC and NRTL models, and it was found that the experimental and calculated data are in good agreement.

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1. Introduction

During the past few decades, interest in coupled processes (e.g., phase transitions accompanied by chemical reaction) has grown because of their significance for the development of energy- and resource-saving chemical engineering processes. Sometimes it is necessary to include the stages of separation or recycling of the components in the industrial chemical processes if the completion of chemical reaction is limited by chemical equilibrium between reactants and products. In addition, the run of chemical reaction depends on the limited miscibility of the reacting mixture, and therefore, industrial processes can be significantly complicated. It should be noted that the overwhelming majority of experimental and theoretical works in the field of coupled processes is devoted to the investigation of esterification reaction [1]. This interest in studying esterification stems from the fact that the ideas of green chemistry, environmental management and the development of

renewable energy sources now dominate in both fundamental as well as applied chemistry.

With respect to environmental management in the field of organic synthesis and separation processes, we should mention reactive distillation (RD) [2]. This process conjoins reaction and separation stages, provides a significant increase in the conversion of reactants, and decreases the environmental risks. Some recent papers [3,4] present the experimental kinetic data of heterogeneous esterification of acetic and glutaric acid with methanol and show that RD technology is a feasible method to convert carboxylic acids to esters and to recover them from aqueous solutions. Article [5] by Yagyu et al. is devoted to the ecological problem of ethyl acetate production, the improvement of esterification yield and wastewater treatment. The authors studied the esterification of acetic acid with ethanol in aqueous media at 313.15 K using various catalysts to intensify the recovery. Hu and colleagues [6] report the design of RD process for the production of ethyl acetate. Data on vapor–liquid equilibrium and vapor–liquid–liquid equilibrium at the temperature range 343.15–393.15 K are simulated by NRTL model (including several phase diagrams). Besides the papers mentioned above, there are some other works on RD and vapor–liquid equilibrium in systems with an esterification reaction [7–11].

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Furthermore, research in the field of biodiesel production has developed in recent years. The data of works [12,13] can be used for the development of biodiesel production processes via fatty acids esterification (e.g., lauric acid with ethanol). Such works are mainly related to the study of kinetics of catalyzed esterification, especially in using those kinds of catalysts as different types of ion-exchange resins [14–17].

In addition to the practical importance of investigating phase equilibria in reactive systems, they are also of interest in the development of basic thermodynamic theory. It gives, for example, new data on the structure and features of phase diagrams, such as critical states [18–25].

However, despite the potential applied and basic significance of systems with coupled processes, experimental data on these systems are relatively rare in comparison with non-reactive systems. We presented experimental results for a system with *n*-propyl acetate synthesis reaction in recent papers [26–28].

The present work continues the investigation of the system acetic acid–ethanol–ethyl acetate–water, which has before been intensively studied by many authors, including our scientific group. Previously, we presented experimental data on solubility, critical states, LLE and chemical equilibrium of esterification in this system at 293.15 K and atmospheric pressure; LLE data calculated by UNIFAC model were also reported in papers [29,30]. Our research concerns mostly solubility and LLE determination because the data sets on these properties are limited in comparison with VLE. VLE was experimentally studied by Calvar et al. [31]. Experimental results of [31] are in agreement with the data of other authors [32,33]. Some works are only devoted to investigation of ethyl acetate synthesis reaction: e.g., Venkateswarlu et al. [34] studied this reaction in vapor phase at 519–559 K and atmospheric pressure. System with ethyl acetate synthesis reaction was considered by Reichl et al. [35], but the paper's experimental data sets include only data for binary sub-systems ethanol–acetic acid, ethyl acetate–water and ethanol–water (at 50 kPa and atmospheric pressure). Theoretical consideration of thermodynamic properties and description of the topological structure of the quaternary system are reported in Ref. [36]. The description of LLE in acetic acid–ethanol–ethyl acetate–water system (at 101.3 and 200 kPa) with the help of UNIFAC model; calculated LLE diagrams for these pressures are presented in Ref. [37]. The chemical equilibrium surface of the system acetic acid–ethanol–ethyl acetate–water is presented in Ref. [7].

Using various models, Kang et al. [38] proposed new algorithms for calculating simultaneous chemical and phase equilibrium for reactive systems. The calculation results for the acetic acid–ethanol–ethyl acetate–water system were compared with calculations made by Peres-Cisneros et al. [39]. The thermodynamic coherence of experimental data for the quaternary system with ethyl acetate synthesis reaction is discussed in Ref. [40]. Paper [41] considers the results of modeling equilibria in this system using Margules and Wilson equations. Simulation on the base of a group model (ASOG, Analytical Solutions of Groups) is described in Ref. [42].

Analysis of literature data shows that there are numerous papers on the experimental study of VLE and modeling of VLE and chemical equilibrium in acetic acid–ethanol–water–ethyl acetate system. In contrast, the data sets on LLE are limited and mostly related to isobaric conditions (e.g., atmospheric pressure). Accordingly, the aim of our work was the experimental study of solubility and LLE in this system under isothermal conditions (303.15 and 313.15 K). Our experimental task included the determination of critical states of LLE in this system. The calculations were carried out using UNIFAC and NRTL models.

Table 1
The purities of the chemicals.

Substance	Purity (mole fraction) ^a
Acetic acid	0.998
Ethanol	0.995
Ethyl acetate	0.998
Water	0.999

^a Uncertainty is estimated to be ± 0.002 mole fraction.

2. Experimental

2.1. Materials

Ethanol (“reagent” grade, Vekton, Russia) and ethyl acetate (“purified” grade, Vekton, Russia) were purified by distillation. Water was bidistilled. Acetic acid (“purified” grade, Vekton, Russia) was purified by two times rectification, with the presence of 98% sulphuric acid. The purity of chemicals (see Table 1) was verified chromatographically and in terms of refraction indexes and boiling points. All physico-chemical constants of pure substances were found to be in agreement with NIST Standard Reference Database [43].

2.2. Methods

Cloud-point technique was used to study solubility and critical phenomena. The operating procedure was the same as in our previous work. Details of the method had been published in paper [29]. Titration was performed in a liquid thermostat (303.15 and 313.15 K). Accuracy of the determination of concentration was estimated to be 0.001 mole fraction. In consideration of other possible factors affecting accuracy (such as purity of chemicals, thermostatic control uncertainty and others), maximum error of experimental data was appreciable to ± 0.002 mole fraction of the component.

LLE was studied using gas chromatography (GC). Firstly, binary, ternary and quaternary mixtures of known overall composition within the heterogeneous region were prepared in glass vessels (5 ml) by gravimetric method. Heterogeneous mixtures were stirred in sealed vessels. Then vessels were placed in the liquid thermostat (303.15 K). We considered the phase equilibrium reached when there was a full separation of the phases and they became quite transparent. After reaching phase equilibrium, samples were taken from both phases with 1 μ l chromatographic syringe (“Hamilton”, USA) and analyzed by GC. We used a gas chromatograph “Chromatec Crystal 5000.2” (Russia) with thermal conductivity detector (TCD) and packed column Porapak R (1 m long and 0.003 m i.d.). Helium with a flow rate of 60 ml/min was used as a carrier gas. The operating temperature of a column was 468 K, vaporizing injector was maintained at 503 K, and TCD temperature was 513 K. Method of internal standard and relative calibration were used to calculate compositions of equilibrium liquid phases. Ethanol was used as an internal standard and accepted as a linking component. Uncertainty of GC analysis averaged ± 0.005 mole fraction.

3. Results and discussion

Binary mixtures ethanol–ethyl acetate and acetic acid–ethyl acetate were chosen as initial solutions for the study of solubility in ternary subsystems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water, respectively, and were titrated with bidistilled water. All these binary systems were homogeneous before titration. At the moment when the solution became cloudy, i.e., when the second phase began, compositions belonging to the solubility curve were fixed. It should be noted that the

Table 2
The experimental data on solubility (mole fractions, x) for the ternary system ethanol (1)–ethyl acetate (2)–water (3) at 303.15 K, 313.15 K and atmospheric pressure.^a

X_1	X_2	X_1	X_2
303.15 K		313.15 K	
0.102	0.053	0.132	0.130
0.117	0.073	0.144	0.163
0.132	0.103	0.155	0.204
0.135	0.112	0.165	0.258
0.138	0.123	0.164	0.259
0.143	0.134	0.166	0.279
0.147	0.146	0.168	0.312
0.150	0.156	0.166	0.339
0.166	0.217	0.158	0.402
0.176	0.322	0.124	0.541
0.176	0.369	0.134	0.515
0.175	0.411	0.109	0.588
–	–	0.094	0.621
–	–	0.079	0.662
–	–	0.107	0.081
–	–	0.130	0.116
–	–	0.134	0.124
–	–	0.138	0.137
–	–	0.145	0.150
–	–	0.147	0.161
–	–	0.158	0.206

^a Standard uncertainties $u(x)=0.002$ and $u(T)=0.05$.

Table 3
The experimental data on solubility (mole fractions, x) for the ternary system acetic acid (1)–ethyl acetate (2)–water (3) at 303.15 K, 313.15 K and atmospheric pressure.^a

X_1	X_2	X_1	X_2
303.15 K		313.15 K	
0.077	0.050	0.121	0.163
0.093	0.074	0.130	0.215
0.105	0.100	0.139	0.321
0.108	0.110	0.129	0.413
0.111	0.119	0.121	0.448
0.117	0.136	0.095	0.544
0.121	0.148	0.074	0.615
0.125	0.162	0.054	0.683
0.128	0.173	0.092	0.097
0.141	0.240	0.107	0.118
0.144	0.294	0.110	0.127
0.144	0.337	0.114	0.139
0.140	0.377	0.119	0.155
0.131	0.447	0.123	0.166
		0.126	0.184
		0.138	0.259

^a Standard uncertainties $u(x)=0.002$ and $u(T)=0.05$.

possible run of ethyl acetate hydrolysis reaction in ternary subsystems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water did not affect the composition of solutions [29]. Experimental data on the solubility of ternary subsystems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water at 303.15 K and 313.15 K are presented in Tables 2 and 3.

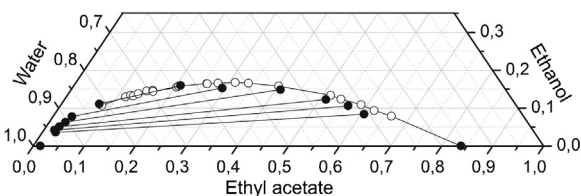


Fig. 1. The diagram of solubility and LLE in ternary system ethanol–ethyl acetate–water at 313.15 K: (○) solubility data, (●-●) tie-lines. Compositions are given in molar fractions.

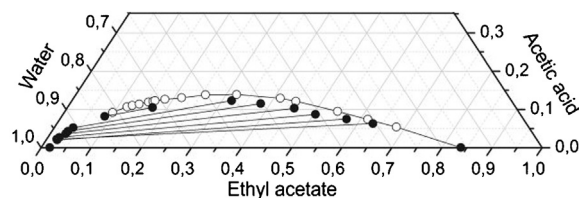


Fig. 2. The diagram of solubility in ternary system acetic acid–ethyl acetate–water at 313.15 K: (○) solubility data, (●-●) tie-lines. Compositions are given in molar fractions.

Figs. 1 and 2 present the run of binodal curves for 313.15 K. In order to construct the binodal surface in the composition tetrahedron, the solubility for quaternary system acetic acid–ethanol–ethyl acetate–water was studied for the initial solutions of constant ratios concentrations of acetic acid and ethanol (3:1, 5:3, 1:1, 3:5 and 1:3).

The investigation of solubility was carried out for compositions belonging to chosen ratios, i.e., for sections of the concentration tetrahedron (see Fig. 3).

The choice of sections gave the opportunity to present the form of the binodal surface clearly and as a whole. Experimental data on solubility in the system acetic acid–ethanol–ethyl acetate–water at 303.15 K and 313.15 K are listed in Tables 4 and 5, and diagrams of solubility constructed in concentration tetrahedron for several sections at 313.15 K are shown in Fig. 4.

The solubility curves and experimental tie-lines qualitatively present the disposition of the binodal surface (Fig. 4). The liquid splitting region occupies a small area of the concentration tetrahedron. On the binodal surface, the maximum overall concentration of acetic acid and ethanol is 0.2 mole fraction. As to be expected, the area of immiscibility in both ternary and quaternary systems increases in size with a decrease in temperature. These data can be compared with recent data on 293.15 K [29], when the immiscibility gap became even greater.

Compositions of initial solutions for the experimental study of LLE in ternary subsystems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water were chosen so that compositions of coexisting phases (tie-lines) could be ordered uniformly on a binodal curve. Experimental data on LLE for these systems are listed in Tables 6 and 7 and tie-lines are presented in Figs. 1 and 2. There is a small difference between LLE data (tie-lines) and solubility curves that is explained by method's features.

The choice of compositions of initial solutions in the study of the binodal surface of quaternary system acetic acid–ethanol–ethyl acetate–water was performed under the same guidelines as in the investigation of solubility (constant ratios of ethanol and acetic acid

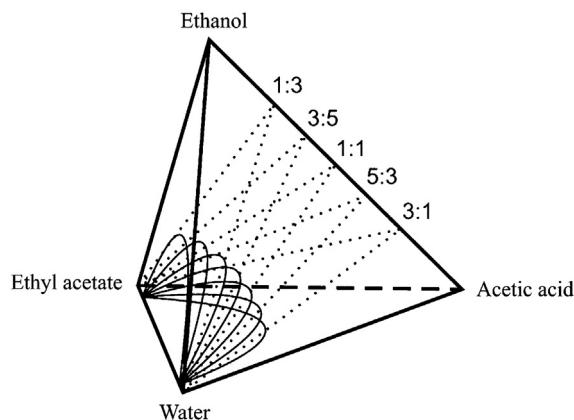


Fig. 3. Planes of composition tetrahedron studied.

Table 4

The experimental data on solubility (mole fractions, x) for the quaternary system acetic acid (1)–ethanol (2)–ethyl acetate (3)–water (4) at 303.15 K and atmospheric pressure.^a

The ratio of acetic acid and ethanol molar fractions	X_1	X_2	X_3
3:1	0.081	0.027	0.092
	0.089	0.029	0.115
	0.093	0.031	0.136
	0.097	0.032	0.145
	0.101	0.034	0.162
	0.104	0.034	0.175
	0.108	0.036	0.194
	0.110	0.036	0.208
	0.116	0.039	0.275
	0.117	0.038	0.331
	0.115	0.038	0.377
5:3	0.063	0.037	0.071
	0.071	0.042	0.097
	0.078	0.045	0.117
	0.082	0.048	0.136
	0.085	0.051	0.154
	0.088	0.053	0.169
	0.091	0.055	0.185
	0.094	0.056	0.203
	0.096	0.057	0.218
	0.101	0.060	0.289
	0.100	0.059	0.342
0.098	0.058	0.385	
0.095	0.056	0.417	
1:1	0.052	0.051	0.069
	0.060	0.060	0.102
	0.062	0.062	0.114
	0.065	0.063	0.122
	0.067	0.067	0.137
	0.070	0.069	0.150
	0.072	0.072	0.163
	0.081	0.077	0.219
	0.083	0.084	0.283
	0.083	0.084	0.329
	0.082	0.081	0.367
0.080	0.079	0.404	
3:5	0.035	0.058	0.053
	0.041	0.068	0.074
	0.047	0.079	0.107
	0.049	0.081	0.118
	0.051	0.085	0.136
	0.053	0.086	0.141
	0.054	0.091	0.156
	0.057	0.093	0.172
	0.063	0.104	0.237
	0.064	0.107	0.291
	0.064	0.106	0.337
0.063	0.103	0.378	
1:3	0.029	0.087	0.079
	0.033	0.098	0.110
	0.034	0.103	0.124
	0.035	0.106	0.137
	0.037	0.110	0.150
	0.038	0.113	0.161
	0.039	0.117	0.176
	0.044	0.125	0.236
	0.044	0.131	0.295
	0.045	0.129	0.341
	0.043	0.126	0.382
0.041	0.123	0.419	

^a Standard uncertainties $u(x)=0.002$ and $u(T)=0.05$.

in mixture were 3:1, 5:3, 1:1, 3:5 and 1:3). Compositions of initial solutions belonged to the region of splitting (heterogeneous region). Experimental data on LLE for the quaternary system are listed in Tables 8 and 9.

The determination of critical compositions in ternary and quaternary systems was carried out with cloud-point technique and

Table 5

The experimental data on solubility (mole fractions, x) for the quaternary system acetic acid (1)–ethanol (2)–ethyl acetate (3)–water (4) at 313.15 K and atmospheric pressure.^a

The ratio of acetic acid and ethanol molar fractions	X_1	X_2	X_3	
3:1	0.081	0.027	0.107	
	0.087	0.029	0.123	
	0.091	0.030	0.138	
	0.092	0.031	0.146	
	0.093	0.030	0.152	
	0.099	0.032	0.165	
	0.101	0.034	0.180	
	0.103	0.034	0.189	
	0.109	0.037	0.243	
	0.108	0.041	0.251	
	0.111	0.037	0.342	
	0.101	0.034	0.432	
	0.096	0.032	0.471	
	0.073	0.024	0.557	
	0.056	0.019	0.621	
	0.040	0.013	0.682	
	5:3	0.069	0.041	0.113
0.075		0.046	0.135	
0.080		0.05	0.152	
0.082		0.051	0.169	
0.088		0.053	0.188	
0.086		0.052	0.190	
0.087		0.054	0.211	
0.094		0.057	0.252	
0.090		0.057	0.256	
0.095		0.057	0.350	
0.089		0.051	0.432	
0.081		0.049	0.482	
0.063		0.037	0.570	
0.047		0.028	0.622	
1:1		0.057	0.057	0.099
		0.060	0.060	0.116
		0.063	0.062	0.131
	0.067	0.067	0.152	
	0.072	0.061	0.156	
	0.069	0.069	0.165	
	0.071	0.069	0.179	
	0.073	0.071	0.188	
	0.077	0.073	0.212	
	0.077	0.077	0.241	
	0.079	0.078	0.319	
	0.076	0.076	0.386	
	0.072	0.072	0.428	
	0.053	0.053	0.561	
	0.039	0.038	0.640	
	3:5	0.043	0.068	0.104
		0.048	0.078	0.132
0.051		0.085	0.151	
0.053		0.088	0.167	
0.055		0.089	0.177	
0.057		0.091	0.193	
0.057		0.095	0.203	
0.058		0.096	0.220	
0.060		0.097	0.251	
0.061		0.100	0.267	
0.060		0.100	0.369	
0.053		0.088	0.451	
0.037		0.063	0.572	
0.029		0.048	0.633	
0.020		0.033	0.658	
1:3		0.03	0.087	0.113
		0.033	0.097	0.126
	0.034	0.101	0.137	
	0.031	0.104	0.146	
	0.035	0.105	0.151	
	0.037	0.107	0.162	
	0.039	0.109	0.185	
	0.038	0.114	0.204	
	0.042	0.112	0.210	
	0.041	0.122	0.272	

^a Standard uncertainties $u(x)=0.002$ and $u(T)=0.05$.

Table 5 (Continued)

The ratio of acetic acid and ethanol molar fractions	X_1	X_2	X_3
	0.041	0.121	0.372
	0.033	0.101	0.493
	0.026	0.077	0.585
	0.020	0.059	0.652
	0.014	0.041	0.703

^a Standard uncertainties $u(x)=0.002$ and $u(T)=0.05$.

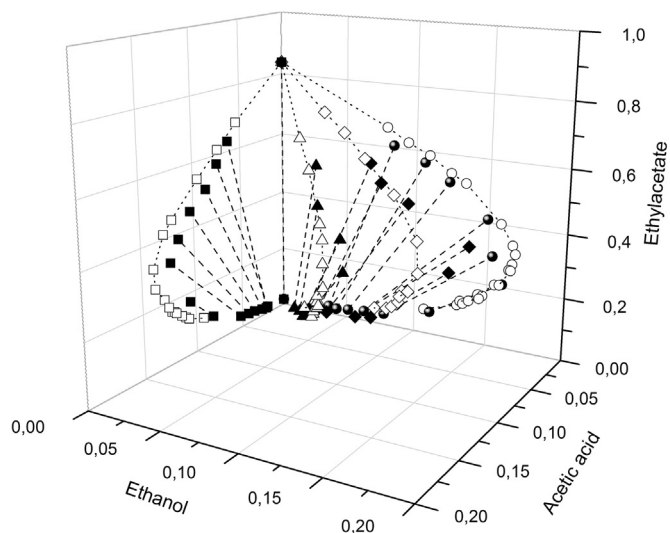


Fig. 4. Qualitative view of the binodal surface of acetic acid–ethanol–ethyl acetate–water system at 313.15 K. Tie-lines in ternary systems: acetic acid–ethyl acetate–water (■–■) and ethanol–ethyl acetate–water (●–●); (▲–▲) and (◆–◆) selected tie-lines in quaternary system; solubility curves in ternary systems: acetic acid–ethyl acetate–water (□) and ethanol–ethyl acetate–water (○). Points (◇) and (△) represent selected solubility data for quaternary solutions with constant ratios of concentrations of acetic acid and ethanol: 3:1 (◇) and 1:1 (△). Compositions are given in molar fractions.

visual control: transfer to a critical state was accompanied by opalescence [25]. Experimental data on the critical states of ternary subsystems and the quaternary system at 303.15 K and 313.15 K are listed in Table 10. The set of critical points in the quaternary

Table 6

The experimental LLE data for the ternary system ethanol (1)–ethyl acetate (2)–water (3) for mole fractions x at 303.15 K, 313.15 K and atmospheric pressure.^a

Water phase		Organic phase	
X_1	X_2	X_1	X_2
303.15 K			
0.032	0.000	0.858	0.000
0.027	0.010	0.825	0.018
0.029	0.026	0.788	0.042
0.033	0.040	0.736	0.068
0.033	0.061	0.667	0.102
0.044	0.080	0.570	0.135
0.053	0.095	0.496	0.159
0.060	0.107	0.419	0.174
$\sigma(\text{NRTL})=5.4\%$, $\sigma(\text{UNIFAC})=2.8\%$			
313.15 K			
0.017	0.000	0.838	0.000
0.026	0.036	0.606	0.084
0.021	0.042	0.564	0.106
0.026	0.051	0.512	0.123
0.032	0.063	0.410	0.149
0.037	0.078	0.294	0.153
0.074	0.111	0.209	0.160
$\sigma(\text{NRTL})=3.3\%$, $\sigma(\text{UNIFAC})=5.4\%$			

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

Table 7

The experimental LLE data for the ternary system acetic acid (1)–ethyl acetate (2)–water (3) for mole fractions x at 303.15 K, 313.15 K and atmospheric pressure.^a

Water phase		Organic phase	
X_1	X_2	X_1	X_2
303.15 K			
0.032	0.000	0.858	0.000
0.029	0.014	0.815	0.016
0.032	0.025	0.769	0.039
0.035	0.037	0.697	0.066
0.043	0.057	0.592	0.099
0.049	0.069	0.470	0.129
$\sigma(\text{NRTL})=3.6\%$, $\sigma(\text{UNIFAC})=2.7\%$			
313.15 K			
0.017	0.000	0.838	0.000
0.020	0.022	0.631	0.063
0.022	0.020	0.572	0.075
0.023	0.027	0.504	0.087
0.031	0.036	0.454	0.103
0.032	0.043	0.381	0.115
0.038	0.052	0.319	0.123
0.086	0.082	0.170	0.105
$\sigma(\text{NRTL})=2.0\%$, $\sigma(\text{UNIFAC})=7.6\%$			

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

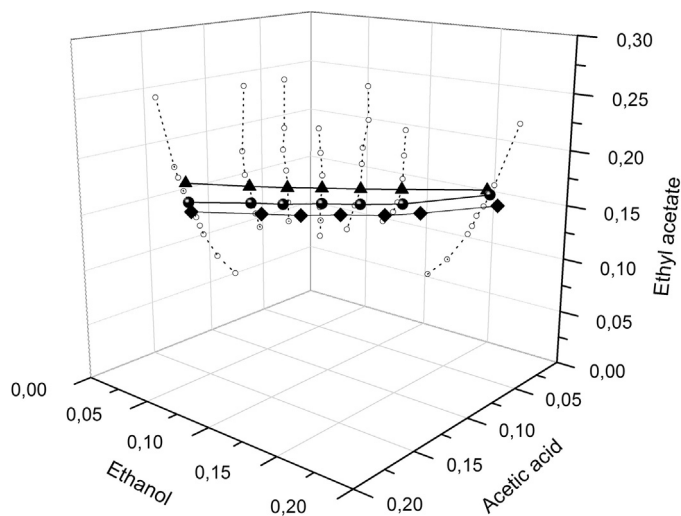


Fig. 5. The critical curves of acetic acid–ethanol–ethyl acetate–water system at polythermal conditions, where (◆) is 293.15 K [29], (●) is 303.15 K, and (▲) is 313.15 K. Compositions are given in molar fractions.

system forms a critical curve in the composition tetrahedron. The final points of this curve correspond to critical states of ternary systems. The run of critical curves is presented in Fig. 5 for 303.15 K and 313.15 K.

4. Modeling of LLE

The experimental data sets on both ternary and quaternary systems have been compared with data calculated using UNIFAC and NRTL models.

4.1. UNIFAC model

The approach developed in Ref. [44] was used for calculation. Modeling was based on UNIFAC parameters presented in Ref. [45].

Table 8The experimental LLE data for the quaternary system acetic acid (1)–ethanol (2)–ethyl acetate (3)–water (4) for mole fractions x at 303.15 K and atmospheric pressure.^a

Ratio of acetic acid to ethanol mol. fractions in the initial heterogeneous mixture	Water phase			Organic phase		
	X_1	X_2	X_3	X_1	X_2	X_3
3:1	0.010	0.005	0.025	0.015	0.011	0.753
	0.020	0.010	0.036	0.026	0.023	0.664
	0.032	0.017	0.048	0.049	0.028	0.589
5:3	0.036	0.020	0.060	0.086	0.035	0.438
	0.007	0.005	0.023	0.003	0.008	0.794
	0.010	0.009	0.026	0.005	0.016	0.744
	0.013	0.015	0.031	0.014	0.025	0.667
1:1	0.018	0.019	0.033	0.030	0.036	0.568
	0.027	0.032	0.057	0.053	0.055	0.420
	0.014	0.006	0.050	0.017	0.013	0.750
	0.017	0.019	0.050	0.025	0.031	0.630
	0.021	0.036	0.044	0.033	0.064	0.477
3:5	0.035	0.052	0.072	0.058	0.082	0.376
	0.005	0.007	0.023	0.008	0.012	0.787
	0.007	0.015	0.026	0.009	0.025	0.727
	0.010	0.023	0.028	0.012	0.040	0.616
	0.014	0.035	0.034	0.015	0.057	0.568
1:3	0.014	0.047	0.043	0.025	0.078	0.458
	0.006	0.009	0.024	0.007	0.016	0.796
	0.008	0.027	0.028	0.012	0.050	0.672
	0.009	0.043	0.033	0.018	0.070	0.613
	0.010	0.056	0.046	0.027	0.099	0.542
	0.011	0.065	0.050	0.012	0.120	0.491

 $\sigma(\text{NRTL}) = 3.2\%$, $\sigma(\text{UNIFAC}) = 3.1\%$ ^a Standard uncertainties $u(x) = 0.005$ and $u(T) = 0.05$.**Table 9**The experimental LLE data for the quaternary system acetic acid (1)–ethanol (2)–ethyl acetate (3)–water (4) for mole fractions x at 313.15 K and atmospheric pressure.^a

Ratio of acetic acid to ethanol mol. fractions in the initial heterogeneous mixture	Water phase			Organic phase		
	X_1	X_2	X_3	X_1	X_2	X_3
3:1	0.018	0.003	0.017	0.049	0.020	0.618
	0.020	0.007	0.027	0.065	0.024	0.544
	0.024	0.010	0.027	0.077	0.026	0.501
	0.045	0.016	0.033	0.090	0.039	0.403
5:3	0.055	0.022	0.049	0.093	0.041	0.295
	0.016	0.009	0.019	0.037	0.030	0.678
	0.028	0.017	0.024	0.067	0.046	0.539
	0.032	0.020	0.030	0.073	0.052	0.514
	0.038	0.025	0.037	0.082	0.057	0.440
1:1	0.045	0.029	0.047	0.086	0.058	0.326
	0.015	0.018	0.025	0.043	0.052	0.565
	0.018	0.024	0.024	0.053	0.059	0.453
	0.030	0.034	0.035	0.060	0.079	0.370
3:5	0.034	0.039	0.046	0.053	0.077	0.253
	0.009	0.017	0.019	0.023	0.044	0.632
	0.016	0.021	0.021	0.034	0.053	0.560
	0.019	0.027	0.026	0.039	0.076	0.509
	0.030	0.034	0.030	0.037	0.078	0.447
1:3	0.031	0.041	0.034	0.063	0.082	0.396
	0.028	0.056	0.044	0.039	0.104	0.264
	0.011	0.027	0.023	0.022	0.079	0.568
	0.008	0.033	0.028	0.023	0.087	0.511
	0.013	0.042	0.030	0.017	0.103	0.449
	0.017	0.066	0.043	0.018	0.145	0.343
	0.020	0.079	0.057	0.025	0.135	0.262

 $\sigma(\text{NRTL}) = 2.6\%$, $\sigma(\text{UNIFAC}) = 5.1\%$ ^a Standard uncertainties $u(x) = 0.005$ and $u(T) = 0.05$.Standard deviation, σ was determined using the following equation:

$$\sigma = 100 \times \sqrt{\frac{\sum_{i=1}^n \sum_{j=1}^m (x_{\text{exp}}^{ik} - x_{\text{cal}}^{ik})^{\text{or}} + (x_{\text{exp}}^{ik} - x_{\text{cal}}^{ik})^{\text{aq}}}{2 \times m \times n}} \quad (1)$$

where n is a number of datasets and m is a number of components.

Generally UNIFAC model simulation leads to results that are in good agreement with experimental data. For the quaternary systems and both ternary subsystems, the standard deviation does not exceed 3.0% at 303.15 K and 5.5% at 313.15 K. These standard deviations are approximately the same as in our previous work on this system at 293.15 K (<3.1%) [29].

Table 10

The experimental data on compositions of critical states (mole fractions, x) for the system acetic acid (1)–ethanol (2)–ethyl acetate (3)–water (4) at 303.15 K and 313.15 K and atmospheric pressure.^a

Temperature (K)	X_1	X_2	X_3
303.15	–	0.147	0.146
	0.035	0.106	0.137
	0.051	0.085	0.136
	0.067	0.067	0.137
	0.082	0.048	0.136
	0.093	0.031	0.136
	0.117	–	0.136
313.15	–	0.145	0.150
	0.035	0.105	0.151
	0.051	0.085	0.151
	0.067	0.067	0.152
	0.080	0.050	0.152
	0.093	0.030	0.152
	0.119	–	0.155

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

Table 11

Binary parameters for NRTL simulation.

	Acetic acid–ethanol	Acetic acid–water	Acetic acid–ethyl acetate	Ethanol–water	Ethanol–ethyl acetate	Water–ethyl acetate
Δg_{ji}	76	1949	1128	1724	186	1001
Δg_{ij}	–719	–636	–371	–515	391	2321
α_{ji}	0.3	0.2	0.2	0.3	0.4	0.35

4.2. NRTL model

The NRTL model, developed by Renon and Prausnitz [46], was chosen to correlate the experimental results. NRTL equation for the activity coefficients in the solution of n components is the following:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^m x_j \tau_{ji} G_{ji}}{\sum_{i=1}^m x_i G_{ji}} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{i=1}^m x_i G_{ij}} \left(\tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{i=1}^m x_i G_{ij}} \right),$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT}, \quad G_{ji} = \exp(-\alpha_{ji} \tau_{ji}), \quad (\alpha_{ji} = \alpha_{ij}),$$

where g_{ji} is energy parameter of the interaction of components j and i ; parameter α_{ji} characterizes nonrandomness in the systems. The optimization tool for the calculation of NRTL parameters, which minimizes the composition objective function (OF), is:

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

Parameters presented in Table 11 were used for the simulations. The NRTL parameters were adjusted to the data for the quaternary mixtures. Generally NRTL model simulation also leads to results that are in good agreement with experimental data. Standard deviation for system acetic acid–ethanol–ethyl acetate–water does not exceed 3.7% at 303.15 K and 2.8% at 313.15 K. Both models show a low standard deviation that indicates the possibility of simulation of LLE in acetic acid–ethanol–ethyl acetate–water system on the base of UNIFAC and NRTL models.

5. Conclusions

The new detailed experimental data on the solubility and LLE for quaternary system acetic acid–ethanol–ethyl acetate–water and two ternary systems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water at 303.15 K and 313.15 K were obtained. The experimental study was carried out with the use of GC analysis and cloud-point technique. The run of critical curves in the composition tetrahedron was determined at both temperatures. A comparison of LLE data with the values calculated by UNIFAC and

NRTL models indicates the experimental and calculated data are in sufficient agreement.

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