

# Solubility, liquid–liquid equilibrium and critical states for the quaternary system acetic acid–ethanol–ethyl acetate–water at 293.15 K

Maya Trofimova, Maria Toikka, Alexander Toikka\*

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

## ARTICLE INFO

### Article history:

Received 6 July 2011

Received in revised form

25 September 2011

Accepted 27 September 2011

Available online 5 October 2011

### Keywords:

Liquid–liquid equilibria

Quaternary reacting systems

Critical states

## ABSTRACT

Solubility, critical states and liquid–liquid equilibrium (LLE) data for the quaternary system acetic acid–ethanol–ethyl acetate–water and for the ternary sub-systems acetic acid–ethyl acetate–water and ethanol–ethyl acetate–water were obtained at 293.15 K and atmospheric pressure. Binodal curves, tie-lines and compositions of critical points were determined. In order to construct the binodal surface and critical curve of the quaternary system, three quaternary sectional planes with several ratios of acetic acid and ethanol were studied. Experimental LLE data were compared with the values calculated by UNIFAC model and it was found that the experimental and calculated data are in a good agreement.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The investigation of phase transitions accompanied by chemical reaction is of importance for design of energy- and resource-saving chemical engineering processes. The completion of chemical reaction is limited by chemical equilibrium between reactants and products, so industrially important chemical processes must include following separation of equilibrium mixture and recycling of the reactants. Also the limited miscibility in reacting mixture may substantially influence on the run of chemical reaction and complicate industrial processes. Thereby coupled processes combining phase transition and chemical reaction has been intensively studied in recent decades. These researches mostly concerned with reactive distillation combining chemical reaction and vapor–liquid phase transition (see, e.g. [1–7]).

Except for practical application the study of the phase equilibria in chemical reactive systems makes a contribution to the development of fundamental thermodynamic theory, it gives, for example, new data on structure and peculiarities of phase diagrams and on critical states in multicomponent reacting systems. However in spite of applied and fundamental significance of the systems combining phase transition and chemical reaction experimental data sets on these systems are relatively scarce. The most investigated now are systems with ester synthesis reaction [8]. Because of limited solubility of ester and water the phase diagrams of these

systems usually has a miscibility gap. Liquid–liquid envelop should significantly influence on the chemical reaction run and the study of solubility is a necessary both for process design and basic consideration. The description of phase diagrams should also include the data on liquid–liquid equilibrium (LLE) and critical states: some new experimental results for the system with *n*-propyl acetate synthesis reaction and thermodynamic consideration of critical states of LLE in reacting systems had been recently presented in our papers [9,10]. Calculation of the disposition of critical points is discussed in [11–14]; new experimental data on critical states in multicomponent systems are reported in [15].

In presented work the system acetic acid–ethanol–ethyl acetate–water, which is industrially important system (i.e. for ethyl acetate synthesis), was chosen as an object of investigation of miscibility gap and critical states of LLE. There are a number of theoretical and experimental researches that present detailed data on vapor–liquid equilibrium in this system. Theoretical analysis of thermodynamic properties and description of topological structure of the system are presented in [16], calculation was carried out using UNIQUAC model (343–352 K, 101.3 kPa). Vapor–liquid equilibrium was experimentally investigated at isobaric conditions (101.3 kPa) in [17]. In this work except for the quaternary system in a state of chemical equilibrium (352–357 K), vapor–liquid equilibrium was studied in non-reactive binary systems ethyl acetate–ethanol (347–351 K), ethyl acetate–acetic acid (351–389 K), water–acetic acid (373–387 K), data from [18–20] were used for system ethanol–water. The correlation of binary data was carried out on the base of the equations of Wilson, NRTL and UNIQUAC. Experimental results are in a good agreement with other data [21,22]. System with ethyl acetate synthesis

\* Corresponding author. Tel.: +7 812 4284052.

E-mail addresses: [toikka@yandex.ru](mailto:toikka@yandex.ru), [alexander.toikka@chem.spbu.ru](mailto:alexander.toikka@chem.spbu.ru) (A. Toikka).

reaction had been also considered in [23], but this work does not give a complete thermodynamics description, only binary systems ethanol–acetic acid and ethyl acetate–water were investigated (50 kPa and 101.3 kPa). Authors of [24] measured the chemical equilibrium constant (348–373 K), the experimental data on vapor–liquid equilibria were correlated using UNIQUAC model, calculations were found to be in a good agreement with the experimental data (343 K, 101.3 kPa). Another research of vapor–liquid equilibria (519–559 K, 101.3 kPa) is presented in [25]. Chemical equilibrium surface in the system with ethyl acetate synthesis reaction is presented in paper [1]. The study of liquid–liquid equilibria in system acetic acid–ethanol–ethyl acetate–water (342 and 363 K; 101 kPa and 200 kPa, respectively) is reported at [26], calculation of liquid–liquid equilibria was carried out by UNIFAC model; diagrams of liquid–liquid equilibria are shown for 101.3 kPa and 200 kPa, data on vapor–liquid equilibria are presented for 101.3 kPa. Paper [27] represents new algorithms for calculation of simultaneous chemical and phase equilibrium and phase diagrams for system under study; calculation was made on the base of UNIQUAC model; authors make reference to results of calculations in [28]. The thermodynamic consistency of experimental data for the system acetic acid–ethanol–ethyl acetate–water is also discussed in [29], parameters of Wilson equation are calculated using different sets of experimental data. In paper [30] the results of the modeling of equilibria in system acetic acid–ethanol–water–ethyl acetate using the equations of Margules and Wilson is discussed. Modeling on the base of a group model is described in [31].

Literature data analysis shows that there are no experimental sets of the data on liquid–liquid critical states in considered system. Accordingly the problem of experimental determination or calculation of critical points in the system acetic acid–ethanol–ethyl acetate–water has not been set up to the present day. This work presents the results of our experimental study of solubility, LLE and critical states in system acetic acid–ethanol–ethyl acetate–water at 293.15 K.

## 2. Experimental

### 2.1. Materials

Acetic acid (“purified” grade) was purified by two times rectification, with the presence of 98% sulphuric acid. Ethanol (“reagent” grade) and ethyl acetate (“purified” grade) were purified by distillation, water was bidistilled. 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 the literature data [32].

### 2.2. Methods

The solubility and critical phenomena were studied by cloud-point technique method. Binary or ternary mixtures of known overall composition within the homogeneous region were prepared by gravimetric method in round-bottomed flask (100 ml) using analytical balance Shinko VIBRA HT-120CE (Japan) with an accuracy of 0.001 g. Initial compositions were chosen so that experimental

points were placed on the same distance on the bimodal surface. Titration was performed in liquid thermostat (293.15 K) at continuous stirring by magnetic stir bar. Bidistilled water as a titrant was added to initial mixtures using 2 ml microburette. Accuracy of titrant volume measurement was estimated to be 0.05 ml. Turbidity of the solution to be titrated persisting during at least 2 min was considered to be a final point of titration. Taking into account a volume of mixtures (20–50 ml) and volume of titrant drop (0.02 ml) accuracy of concentration determination was estimated to be 0.001 mole percent. Taking into consideration another possible factors affecting on accuracy (such as purity of chemicals, thermostatic control uncertainty and others) maximum error of an experimental data was appreciable to be  $\pm 0.002$  mole fraction of the component.

LLE was investigated using gas chromatography. At first binary, ternary and quaternary mixtures of known overall composition within the heterogeneous region were prepared in glass vessels (2–3 ml) by gravimetric method. Stirred up sealed vessels were placed in the liquid thermostat (293.15 K). It was considered that the phase equilibrium is reached when there was a full distribution of the phases among themselves. After reaching of phase equilibrium samples were taken from both phases with 1  $\mu$ l chromatographic syringe (“Hamilton”, USA) and analyze by gas chromatography. Gas chromatograph “Chromatec Crystal 5000.2” (Russia) with packed column Porapak R 1 m long and 3 mm i.d. was used. Helium with flow rate equal to 30 ml/min was used as a carrier gas. Operating temperature of column measured up to 453 K. Vaporizing injector was maintained at 503 K. Detection was carried out by a thermal conductivity detector at 513 K. Method of internal normalization and relative calibration were used to calculate compositions of equilibrium liquid phases. Ethanol was accepted as linking component. Uncertainty of gas chromatographic analysis averaged 0.005 mole fraction.

## 3. Results and discussion

In studies of solubility in ternary systems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water mixtures of ethanol + ethyl acetate and acetic acid + ethyl acetate were chosen as initial solutions, respectively, and were titrated with bidistilled water. Such binary systems are homogeneous (transparent solutions) and its turbidity takes place during titration. Compositions belonging to the solubility curve were fixed at a moment when the solution became “cloudy”, i.e. genesis of the second phase took place. There is a chemical reaction (reaction of ethyl acetate hydrolysis) in ternary systems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water, however it does not influence on the composition of the experimental solutions because of ethanol (in the first case) and acetic acid (in the second case), products of ethyl acetate hydrolysis, are the components of systems under study and the rate of reaction is very small, so concentration of ethanol (in the first case) and acetic acid (in the second case) obtained in the course of the reaction are less than 0.001 mole fraction. Thus data presented in this paper refer to the state of partial equilibrium: i.e. phase equilibrium, but not chemical equilibrium. Experimental data on solubility of ternary systems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water are listed in Tables 2 and 3 and its binodals are shown in Figs. 1 and 2. Solubility of quaternary system acetic acid–ethanol–ethyl acetate–water was investigated with account of further construction of binodal surface in the composition tetrahedron on the base of experimental data. Series of solutions under study were prepared with keeping of certain constant ratios of acetic acid and ethanol in mixture investigated (3:1, 1:1 and 1:3). The disposition of sections in concentration tetrahedron is shown in Fig. 3. Such a choice of sections can clearly and convenient present the form of binodal surface. Investigation of solubility was carried out for points of composition belonging

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

Substance	Purity, mole fraction <sup>a</sup>
Acetic acid	0.998
Ethanol	0.995
Ethyl acetate	0.998
Water	0.999

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

**Table 2**  
The experimental data on solubility of ternary system ethanol–ethyl acetate–water at 293.15 K.

Composition, mole fraction <sup>a</sup>		
Ethanol	Ethyl acetate	Water
0.120	0.063	0.817
0.131	0.083	0.786
0.141	0.102	0.757
0.149	0.123	0.728
0.153	0.137	0.710
0.157	0.147	0.696
0.164	0.170	0.666
0.172	0.198	0.630
0.178	0.222	0.600
0.182	0.247	0.571
0.185	0.291	0.524
0.182	0.380	0.438

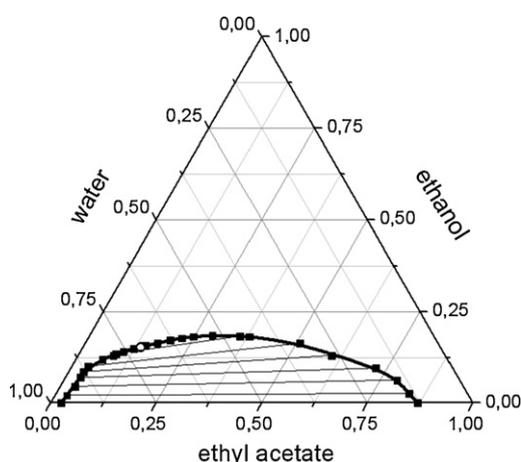
<sup>a</sup> The uncertainty is estimated to be  $\pm 0.002$  mole fraction.

**Table 3**  
The experimental data on solubility of ternary system acetic acid–ethyl acetate–water at 293.15 K.

Composition, mole fraction <sup>a</sup>		
Acetic acid	Ethyl acetate	Water
0.081	0.055	0.864
0.107	0.102	0.791
0.111	0.113	0.776
0.115	0.126	0.759
0.120	0.138	0.742
0.124	0.153	0.723
0.132	0.179	0.689
0.139	0.208	0.653
0.143	0.232	0.625
0.146	0.259	0.595
0.147	0.297	0.556

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

to the chosen sections. Results of experimental determination of solubility in system acetic acid–ethanol–ethyl acetate–water are presented in Table 4. Diagram of solubility constructed in concentration triangle for several sections of composition tetrahedron are shown in Fig. 4. Disposition of binodals completely features the binodal surface shape of quaternary system as a whole. Binodal surface constructed on the basis of experimental data of this work is presented in Fig. 5. Region of splitting is a relatively small area of the concentration tetrahedron, the overall concentration of acetic



**Fig. 1.** The diagram of solubility in ternary system ethanol–ethyl acetate–water at 293.15 K (○ – critical point).

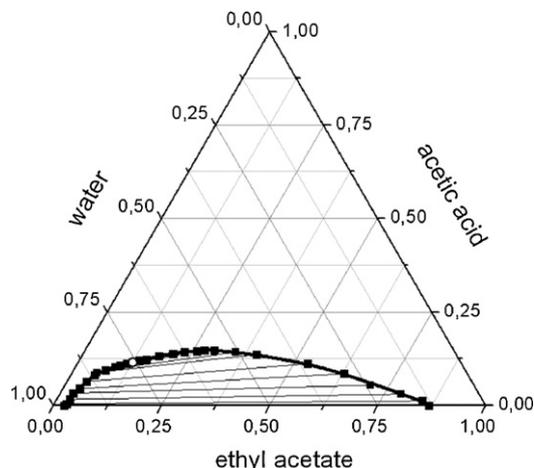
**Table 4**  
The experimental data on solubility of quaternary system acetic acid–ethanol–ethyl acetate–water at 293.15 K.

The ratio of acetic acid and ethanol molar fractions	Composition, mole fraction <sup>a</sup>				
	Ethanol	Acetic acid	Ethyl acetate	Water	
3:1	0.028	0.064	0.058	0.850	
	0.036	0.081	0.103	0.780	
	0.039	0.089	0.130	0.742	
	0.042	0.096	0.156	0.706	
	0.044	0.102	0.185	0.669	
	0.048	0.112	0.251	0.589	
	0.050	0.113	0.309	0.528	
	0.049	0.111	0.353	0.487	
	0.047	0.108	0.393	0.452	
	0.046	0.104	0.424	0.426	
	0.057	0.044	0.059	0.840	
	0.073	0.055	0.105	0.767	
1:1	0.079	0.060	0.131	0.730	
	0.085	0.065	0.159	0.691	
	0.090	0.069	0.188	0.653	
	0.097	0.075	0.253	0.575	
	0.099	0.076	0.310	0.515	
	0.094	0.073	0.390	0.443	
	0.091	0.070	0.423	0.416	
	1:3	0.089	0.023	0.062	0.826
		0.108	0.028	0.105	0.759
		0.116	0.030	0.129	0.725
		0.119	0.031	0.140	0.710
		0.132	0.034	0.184	0.650
0.143		0.037	0.248	0.572	
0.145		0.038	0.302	0.515	
0.145		0.038	0.331	0.486	
0.140		0.036	0.389	0.435	
0.135		0.037	0.422	0.406	

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

acid and ethanol on the binodal surface does not exceed 0.2 mole fraction.

In studies of LLE in ternary systems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water compositions of initial solutions were chosen so that experimental compositions of coexisting phases (tie-lines) were ordered uniformly on binodal curve. Experimental data on LLE for two above mentioned systems are listed in Tables 5 and 6. Binodal curves constructed on the base of experimental data are presented in Figs. 1 and 2. Experimental investigation of binodal surface of quaternary system acetic acid–ethanol–ethyl acetate–water was carried out with account of requirements for the choice of compositions of initial solutions.



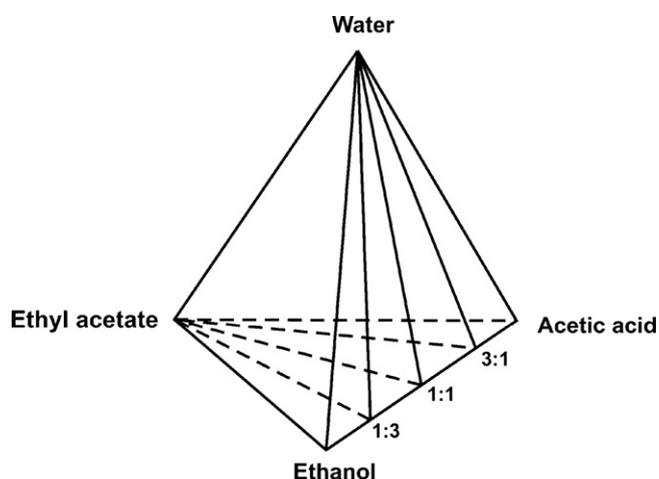
**Fig. 2.** The diagram of solubility in ternary system acetic acid–ethyl acetate–water at 293.15 K (○ – critical point).

**Table 5**

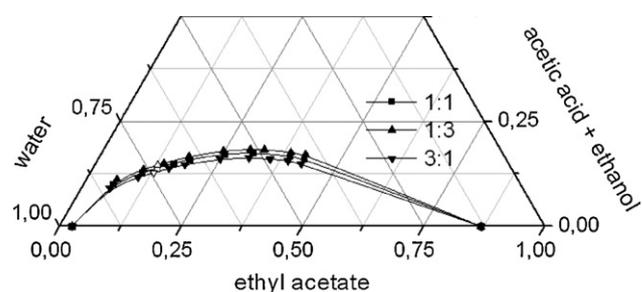
The experimental and calculated data values on LLE of ternary system ethanol–ethyl acetate–water at 293.15 K.

Compositions of coexisting phases, mole fraction				UNIFAC			
Experimental <sup>a</sup>		UNIFAC		Experimental <sup>a</sup>		UNIFAC	
Water phase		Organic phase		Water phase		Organic phase	
Ethyl acetate	Ethanol	Ethyl acetate	Ethanol	Ethyl acetate	Ethanol	Ethyl acetate	Ethanol
0.028	0.021	0.836	0.027	0.015	0.011	0.780	0.035
0.035	0.046	0.789	0.063	0.018	0.025	0.705	0.076
0.035	0.070	0.722	0.096	0.021	0.039	0.633	0.114
0.035	0.086	0.599	0.131	0.025	0.055	0.552	0.152
0.039	0.101	0.508	0.164	0.030	0.071	0.475	0.183
0.088	0.135	0.357	0.184	0.039	0.093	0.376	0.215

RMSD = 3.59%

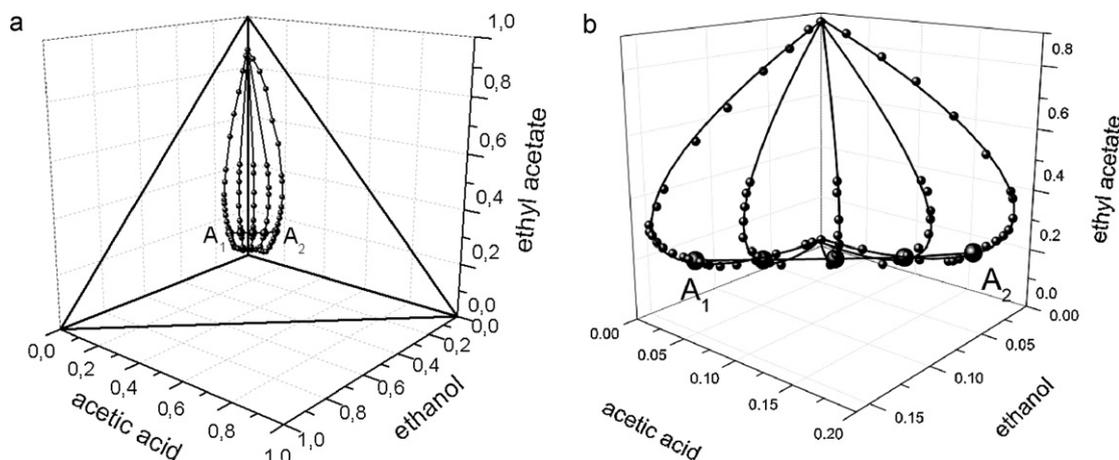
<sup>a</sup> The uncertainty is estimated to be  $\pm 0.005$  mole fraction.**Fig. 3.** Planes of composition tetrahedron for the study of solubility.

Series of quaternary solutions under study were prepared with keeping of certain constant ratios of ethanol and acetic acid in mixture for ordered and uniform disposition of experimental points on binodal surface; compositions of initial solutions were belonged to region of splitting (heterogeneous region). Experimental data on LLE for quaternary system acetic acid–ethanol–ethyl acetate–water are listed in Table 7. Analysis of the experimental data shows that tie-lines (compositions of coexisting phases) do not belong to the planes of sections of the concentration tetrahedron but intersect them. Thus the presentation of the experimental tie-lines on planes

**Fig. 4.** The diagram of solubility in quaternary system acetic acid–ethanol–ethyl acetate–water at 293.15 K for several ratios of acetic acid and ethanol in mixture (—■— 1:1; —▲— 1:3; —▼— 3:1; □ – critical point for 1:1; △ – critical point for 1:3; ▽ – critical point for 3:1).

of sections is incorrectly; these data should be presented in the space of concentration tetrahedron as in Fig. 6.

Analysis of disposition of critical points on the binodal curve (in the case of ternary systems) and critical curve on the binodal surface (in the case of quaternary system) is another object of the experiment. The critical points composition for such system could be also found by cloud-point technique method i.e. by observation of blue opalescence at the moment of phase transition [15]. Ternary systems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water have the only critical point. Quaternary system acetic acid–ethanol–ethyl acetate–water has a critical curve, its run is presented in 3D concentration space (concentration tetrahedron) in Fig. 5 in a quality manner. Compositions of critical points of ternary sub-systems and quaternary system are

**Fig. 5.** The binodal surface of the system acetic acid–ethanol–ethyl acetate–water at 293.15 K: (a) the binodal surface in the concentration tetrahedron, (b) enlarged image of the binodal surface ( $A_1A_2$  – critical curve of LLE).

**Table 6**  
The experimental and calculated data values on LLE of ternary system acetic acid–ethyl acetate–water at 293.15 K.

Compositions of coexisting phases, mole fraction							
Experimental <sup>a</sup>				UNIFAC			
Water phase		Organic phase		Water phase		Organic phase	
Ethyl acetate	Acetic acid	Ethyl acetate	Acetic acid	Ethyl acetate	Acetic acid	Ethyl acetate	Acetic acid
0.028	0.004	0.847	0.012	0.014	0.004	0.817	0.011
0.030	0.016	0.788	0.030	0.015	0.012	0.773	0.033
0.030	0.033	0.706	0.054	0.017	0.022	0.710	0.065
0.039	0.045	0.629	0.085	0.019	0.032	0.642	0.097
0.045	0.064	0.533	0.111	0.022	0.045	0.563	0.132
0.057	0.088	0.401	0.136	0.027	0.062	0.466	0.171
0.073	0.095	0.351	0.142	0.028	0.068	0.438	0.181
0.092	0.104	0.275	0.148	0.031	0.077	0.396	0.194

RMSD = 3.07%

<sup>a</sup> The uncertainty is estimated to be  $\pm 0.005$  mole fraction.

**Table 7**  
The experimental and calculated data values on LLE of quaternary system acetic acid–ethanol–ethyl acetate–water at 293.15 K.

Ratio of acetic acid and ethanol molar fractions	Compositions of coexisting phases, mole fraction											
	Experimental <sup>a</sup>						UNIFAC					
	Water phase			Organic phase			Water phase			Organic phase		
	Acetic acid	Ethanol	Ethyl acetate	Acetic acid	Ethanol	Ethyl acetate	Acetic acid	Ethanol	Ethyl acetate	Acetic acid	Ethanol	Ethyl acetate
3:1	0.006	0.005	0.026	0.009	0.007	0.767	0.004	0.003	0.014	0.011	0.009	0.800
	0.012	0.011	0.031	0.027	0.017	0.679	0.010	0.007	0.016	0.030	0.022	0.740
	0.025	0.015	0.032	0.031	0.025	0.657	0.014	0.010	0.018	0.043	0.031	0.696
	0.026	0.020	0.033	0.058	0.035	0.519	0.022	0.014	0.020	0.068	0.045	0.611
	0.038	0.029	0.047	0.088	0.045	0.428	0.034	0.020	0.025	0.100	0.059	0.508
1:1	0.053	0.033	0.069	0.101	0.053	0.375	0.042	0.023	0.028	0.117	0.066	0.446
	0.004	0.009	0.028	0.002	0.013	0.756	0.002	0.005	0.014	0.004	0.017	0.800
	0.007	0.025	0.029	0.009	0.037	0.658	0.004	0.015	0.017	0.012	0.049	0.726
	0.026	0.034	0.037	0.029	0.057	0.554	0.014	0.023	0.021	0.043	0.072	0.618
	0.022	0.051	0.042	0.035	0.080	0.495	0.015	0.034	0.024	0.044	0.102	0.551
1:3	0.032	0.058	0.046	0.050	0.094	0.433	0.022	0.041	0.027	0.062	0.115	0.473
	0.037	0.064	0.053	0.059	0.109	0.369	0.027	0.049	0.031	0.071	0.128	0.409
	0.046	0.078	0.076	0.064	0.115	0.318	0.032	0.056	0.035	0.078	0.137	0.356
	0.011	0.019	0.032	0.001	0.023	0.762	0.003	0.010	0.015	0.009	0.032	0.768
	0.008	0.032	0.036	0.004	0.042	0.716	0.003	0.018	0.017	0.009	0.056	0.725
	0.011	0.048	0.037	0.005	0.067	0.670	0.004	0.028	0.020	0.012	0.085	0.664
	0.009	0.065	0.037	0.014	0.097	0.580	0.006	0.041	0.023	0.017	0.119	0.581
0.015	0.078	0.045	0.022	0.125	0.481	0.010	0.054	0.028	0.027	0.147	0.490	
	0.016	0.096	0.055	0.028	0.153	0.404	0.012	0.069	0.034	0.031	0.174	0.403

RMSD = 2.24%

<sup>a</sup> The uncertainty is estimated to be  $\pm 0.005$  mole fraction.

listed in Table 8. Figs. 1 and 2 show the disposition of the critical points of ternary sub-systems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water.

The experimental data sets on both ternary and quaternary systems had been compared with the data calculated with the use of UNIFAC model. The calculation procedure was based on approach

**Table 8**  
The compositions of critical points belonging to critical curve in composition tetrahedron of quaternary system at 293.15 K.

Composition, mole fraction <sup>a</sup>			
Ethanol	Acetic acid	Ethyl acetate	Water
0.000	0.115	0.126	0.759
0.153	0.000	0.137	0.710
0.039	0.089	0.130	0.742
0.079	0.060	0.131	0.730
0.116	0.030	0.129	0.725

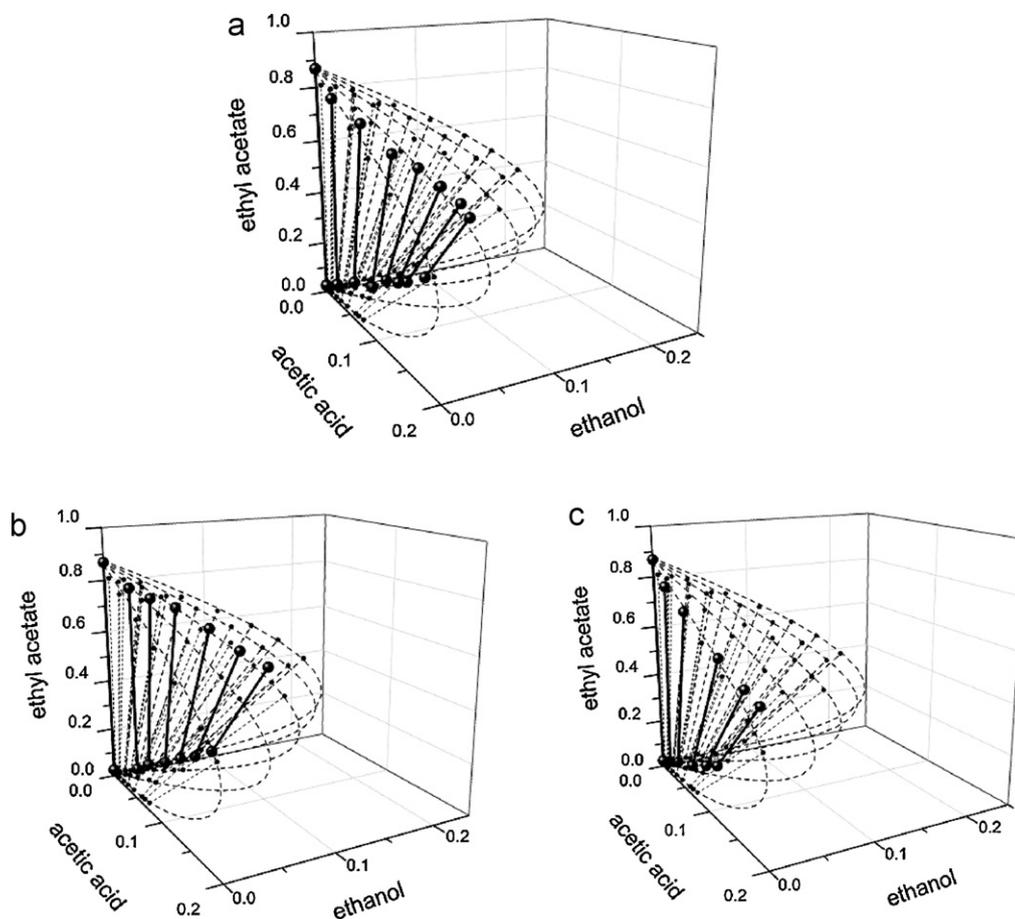
<sup>a</sup> The uncertainty is estimated to be  $\pm 0.002$  mole fraction.

developed in work [33]. UNIFAC parameters presented in book [34] had been used for the modeling.

The root-mean-square deviation (RMSD) was a measure of the agreement between the calculated values and experimental data:

$$\text{RMSD} (\%) = \frac{100}{N} \sum_{l=1}^N \left( \frac{\sum_{k=1}^r \sum_{i=1}^{n-1} (x_{ikl}^{\text{exp}} - x_{ikl}^{\text{calc}})^2}{r(n-1)} \right)^{1/2},$$

where  $x_{ikl}^{\text{exp}}$  and  $x_{ikl}^{\text{calc}}$  are experimental and calculated molar fractions of component  $i$  in phase  $k$  on tie-line  $l$ ;  $N$  is a number of tie-lines. The calculated values and average RMSD are presented in Tables 5–7 in comparison with experimental data. In general the simulation on the base of UNIFAC model leads to results which are in good agreement with experimental data. For quaternary system and both ternary systems the RMSD does not exceed 3.6%. For quaternary system the average RMSD value is smaller that indicate the possibility of simulation of LLE in acetic acid–ethanol–ethyl acetate–water system on the base of UNIFAC model.



**Fig. 6.** The composition points of coexisting phases of quaternary system acetic acid–ethanol–ethyl acetate–water at 293.15 K for several ratios of acetic acid and ethanol in mixture: (a) 1:1; (b) 1:3; (c) 3:1 (●—●— experimental composition points of coexisting phases, ●—●— binodal surface calculated by UNIFAC).

#### 4. Conclusion

Detailed experimental data on solubility and LLE were obtained for ternary systems ethanol–ethyl acetate–water and acetic acid–ethyl acetate–water and quaternary system acetic acid–ethanol–ethyl acetate–water at 293.15 K. Compositions of critical points of LLE were determined for systems investigating. The set of new experimental data on solubility and LLE for quaternary system acetic acid–ethanol–ethyl acetate–water and ternary sub-systems enables to present the binodal surface and run of the critical curve in concentration tetrahedron. The comparison of LLE data with the values calculated from UNIFAC model indicates that the experimental and calculated data are in sufficient agreement.

#### Acknowledgments

This work was supported by Russian Foundation for Basic Research (RFBR project 09-03-00812a). Authors are grateful to TDE group (NIST) for the data on the property of considered system. We also wish to thank Nikita Tsvetov for the help in the model calculation.

#### References

- [1] E.Y. Kenig, H. Bäder, A. Górak, B. Beßling, T. Adrian, H. Schoenmakers, *Chem. Eng. Sci.* 56 (2001) 6185–6193.
- [2] N. Vora, P. Daoutidis, *Ind. Eng. Chem. Res.* 40 (2001) 833–849.
- [3] K. Sundmacher, A. Kienle (Eds.), *Reactive Distillation – Status and Future Directions*, Wiley-VCH, Weinheim, 2003.
- [4] L.A. Serafimov, Yu.A. Pisarenko, N.N. Kulov, *Chem. Eng. Sci.* 54 (1999) 1383–1388.
- [5] M.F. Malone, R.S. Huss, M.F. Doherty, *Environ. Sci. Technol.* 37 (2003) 5325–5329.
- [6] S. Ung, M. Doherty, *Chem. Eng. Sci.* 50 (1995) 23–48.
- [7] A. Heintz, S.P. Verevkin, *Fluid Phase Equilib.* 179 (2001) 85–100.
- [8] A.M. Toikka, M.A. Toikka, Yu.A. Pisarenko, L.A. Serafimov, *Theor. Found. Chem. Eng.* 43 (2009) 129–142.
- [9] M.A. Toikka, B.I. Gorovits, A.M. Toikka, *Russ. J. Appl. Chem.* 81 (2008) 223–230.
- [10] A.M. Toikka, M.A. Toikka, *Pure Appl. Chem.* 81 (2009) 1591–1602.
- [11] J. Novák, K. Řehák, P. Voňka, J. Matouš, *Fluid Phase Equilib.* 208 (2003) 199–221.
- [12] M.L. Michelsen, *Fluid Phase Equilib.* 16 (1984) 57–76.
- [13] M. Cismondi, M.L. Michelsen, *J. Supercrit. Fluids* 39 (2007) 287–295.
- [14] D.N. Justo-García, F. García-Sánchez, J. Águila-Hernández, R. Eustaquio-Rincón, *Fluid Phase Equilib.* 264 (2008) 164–173.
- [15] D.G. Cherkasov, K.K. Ilin, *J. Chem. Eng. Data* 47 (2002) 1303–1306.
- [16] E.A. Campanella, B.A. Mandagaran, *Lat. Am. Appl. Res.* 33 (2003) 223–231.
- [17] N. Calvar, A. Dominguez, J. Tojo, *Fluid Phase Equilib.* 235 (2005) 215–222.
- [18] A. Arce, J. Martínez-Ageitos, A. Soto, *Fluid Phase Equilib.* 122 (1996) 117–129.
- [19] K. Kurihara, M. Nakamichi, K. Kojima, *J. Chem. Eng. Data* 38 (1993) 446–449.
- [20] B. Yang, H. Wan, *J. Chem. Eng. Data* 47 (2002) 1324–1329.
- [21] C.H. Tu, T.S. Wu, F.C. Ou, *Fluid Phase Equilib.* 130 (1997) 243–252.
- [22] F. Mato, E. Cepeda, *An. Quim. Ser. A* 80 (1984) 338–342.
- [23] A. Reichl, U. Daiminger, A. Schmidt, M. Davies, U. Hoffmann, C. Brinkmeier, C. Reder, W. Marquardt, *Fluid Phase Equilib.* 153 (1998) 113–134.
- [24] Y.W. Kang, Y.Y. Lee, W.K. Lee, *J. Chem. Eng. Jpn.* 25 (1992) 649–655.
- [25] C. Venkateswarlu, M. Satyanarayana, M. Narasinga, *Ind. Eng. Chem.* 50 (1958) 973–978.
- [26] I.A. Furzer, *Chem. Eng. Sci.* 49 (1994) 2544–2548.
- [27] E.S. Peres-Cisneros, R. Gani, M.L. Michelsen, *Chem. Eng. Sci.* 52 (1997) 527–543.
- [28] C.M. McDonald, C.A. Floudas, *Comput. Chem. Eng.* 19 (1995) 1111–1141.
- [29] D. Haberland, J. Mentel, *Z. Chem.* 19 (1979) 68–69.
- [30] I. Suzuki, H. Komatsu, M. Hirata, *J. Chem. Eng. Jpn.* 3 (1970) 152–157.
- [31] K. Toshigi, S. Minami, K. Kojima, *J. Chem. Eng. Jpn.* 10 (1977) 349–354.
- [32] M. Frenkel, R.D. Chirico, V. Diky, A.F. Kazakov, C.D. Muzny, J.W. Magee, I. Abdulagatov, K. Kroenlein, J.W. Kang, NIST ThermoData Engine, NIST Standard Reference Database 103b-Pure Compounds, Binary Mixtures, and Chemical Reactions, Version 5.0; Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg, MD, 2010.
- [33] M.L. Michelsen, *Fluid Phase Equilib.* 9 (1982) 21–40.
- [34] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, *The Properties of Gases and Liquids*, fifth ed., The McGraw-Hill Companies, NY, 2004.