



Solubility in the system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – Water at 293.15 K, 303.15 K, 313.15 K and 323.15 K and atmospheric pressure



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ABSTRACT

Solubility of the quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water was investigated at 293.15 K, 303.15 K, 313.15 K, 323.15 K and atmospheric pressure. Binodal curves and binodal surfaces were determined using isothermal titration (cloud-point technique) and presented in composition simplices including 3D phase diagrams in composition tetrahedron. Binary mixtures were carried out by the gas chromatography method. Experimental data were predicted using UNIFAC model, and it was found that the calculating results of liquid–liquid equilibria (LLE) are in inconsistent agreement with the experimental data on solubility at all temperatures.

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1. Introduction

In recent years the system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water has been extensively studying due to its industrial significance for *n*-amyl acetate production. This ester is widely utilized as a solvent for many organic compounds, primarily for nitrocellulose. It is used in the production of high quality varnishes and paints. It is a component of multipurpose fuel additives. Highly purified *n*-amyl acetate is used as a food additive, i. e. pear essence [1,2]. One of the most important areas of research of the system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water is the study of solubility and phase equilibria for organizing an industrial process of reactive distillation of *n*-amyl acetate [3–5] which is a coupled process combining reaction and separation stages that increasingly employed in fuel synthesis, including biodiesel. The system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water can also be of interest as a model system for production of biodiesel from coconut oil [6].

As for the analysis of literature data on the solubility in the system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water, over the past eighty years a significant array of experimental data has been accumulated. It should be noted that overwhelming majority of the data on solubility refers to the binary subsystems. Due to their numerousness, we limit ourselves to report these works summar-

ily without focusing on the used experimental methods, research context and other details. The data on solubility in the system *n*-amyl acetate – water covering temperature range 273.15–363.65 K presented in papers [7–12]. The data on solubility in the system *n*-amyl alcohol – water within temperature range 273.15–453.15 K reported in papers [13–41].

Found in the literature, the data on solubility and LLE in the ternary subsystems acetic acid – *n*-amyl alcohol – water and acetic acid – *n*-amyl acetate – water are scarce and fragmented [42–44]. The data on solubility and LLE for the ternary subsystem *n*-amyl alcohol – *n*-amyl acetate – water are not available in the literature. There is the only paper containing the data for quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water [45].

Wang et al. [42] studied experimentally LLE for the ternary subsystem acetic acid – *n*-amyl acetate – water at 304.15, 332.15 and 366.15 K and atmospheric pressure. To analyze the composition of equilibrium liquid phases, a gas chromatography (GC) and titration by a Karl Fischer titrator were used. The NRTL model was used to correlate the experimental data. The average absolute deviations between calculated results and experimental results were found to be small and fell within the range 0.0035–0.0099.

Esquivel et al. [43] obtained a new experimental data on LLE for the system acetic acid – *n*-amyl alcohol – water at 303.15 and 323.15 K. The binodal curves were determined using the titration method and the tie-lines were found using an analytical method with sampling and the composition of the samples were determined with GC. The NRTL and UNIQUAC equations were used to

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correlate the experimental phase equilibrium data. It was found that both models represented the binodal curves and the tie-lines correctly at 323.15 K. The results are not so satisfactory using the UNIQUAC equation at 303.15 K: heterogeneous region is smaller than the experimental one and the tie-lines have a different inclination. RMSD values do not exceed 2.4% at 303.15 for both models, 1.6% at 323.15 K for UNIQUAC model and 0.7% at 323.15 K for NRTL model.

LLE for the ternary subsystem acetic acid – *n*-amyl alcohol – water was measured experimentally for the temperatures 288.15, 298.15, 303.15, 308.15, 318.15, and 323.15 K by Fahim et al. [44] using analytical method with sampling and the composition of the samples were determined by GC. The experimental equilibrium compositions of the studied system were successfully correlated by the models NRTL, UNIQUAC, and UNIFAC. The NRTL and UNIQUAC models were almost equally good with RMSD values of 2.2% and 2.3%, respectively. They were better than the UNIFAC model (with an RMSD value of 2.9%) in predicting the overall equilibrium composition. The distribution coefficients were also calculated and compared with the experimental values: the NRTL and UNIFAC predictions of the distribution coefficients were equal, and they were the nearest to the experimental data, while UNIQUAC predictions of the distribution coefficients were less accurate.

Paper [45] presents the experimental data on solubility, LLE and critical compositions for the quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water at 303.15 K and atmospheric pressure. The study [45] was carried out by our research team in 2018, and current work continues our investigation of phase behavior in the system with reaction of *n*-amyl acetate synthesis. It should be noted that, in the scope of current work, we re-studied the solubility in the system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water at 303.15 K. The previously chosen method of titration with small volumes (2–6 ml) of binary and ternary mixtures with water led to large inaccuracies and, accordingly, possible distortion of research results. To avoid gross inaccuracies and to ensure that the previously obtained data is correct, this time we have chosen the high volume titration method (see Section 2.2).

2. Experimental

2.1. Materials

Acetic acid («chemically pure» grade, Vekton, Russia), *n*-amyl alcohol («chemically pure» grade, Vekton, Russia) and *n*-amyl acetate («chemically pure» grade, Vekton, Russia) were previously purified using laboratory distillation columns of high performance. Water was distilled twice. Purity of all reactants was tested by GC method (see Section 2.2). Physical characteristics of pure substances (boiling points and refraction indices) showed close agreement with the data reported by National Institute of Standards and Technology (NIST) [46]. The mole fraction purity of all reagents used in this work are listed in Table 1.

Table 1
Purities of the reagents.

Substance	Supplier	CAS	Purification method	The purity analysis method	Purity, mole fraction ^a	
					initial	final
acetic acid	Vekton	64-19-7	rectification	GC	0.980	0.990
<i>n</i> -amyl alcohol	Vekton	71-41-0	rectification	GC	0.980	0.991
<i>n</i> -amyl acetate	Vekton	628-63-7	rectification	GC	0.993	0.997
water	–	7732-18-5	double distillation	GC	0.999	0.999

^a Standard uncertainties u (mole fraction) = 0.001.

2.2. Solubility determination

A cloud-point technique was applied to study the solubility of the ternary subsystems acetic acid – *n*-amyl alcohol – water, acetic acid – *n*-amyl acetate – water and *n*-amyl alcohol – *n*-amyl acetate – water and the quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water. Titration was carried out in a thermostated glass vial of 25 ml at 293.15 K, 303.15 K, 313.15 K, 323.15 K and atmospheric pressure. Titration end point was fixed visually by homogenizing at first and by heterogenizing hereafter of initial solutions, this suggested approach to the determination of solubility of mentioned systems led to the smallest titration error compared with previously used method [45]. The sequence of experimental stages for investigation of the ternary subsystems was as follows:

- 1) initial heterogeneous binary mixtures of *n*-amyl acetate and water of known compositions were prepared at room temperature by gravimetric method with accuracy of 0.0001 g using an analytical balance Ohaus Pioneer PA214; a volume of each initial solution was averaged 10 ml;
- 2) prepared binary mixtures of ester and water were heated up to 343.15 K using a liquid thermostat LOIP LT-105 and then were homogenized by adding of titrant (*n*-amyl alcohol or acetic acid) using 2 ml microburette while stirring with a magnetic stir bar;
- 3) obtained ternary mixtures (acetic acid – *n*-amyl acetate – water and *n*-amyl alcohol – *n*-amyl acetate – water) were cooled up to 323.15 K, as a result, second phase appeared, its appearance was fixed visually by the presence of turbidity keeping during at least two minutes;
- 4) after that, heterogeneous ternary mixtures were homogenized again by adding of titrant (*n*-amyl alcohol or acetic acid) and composition of the solution belonging to the solubility curve at 323.15 K was fixed;
- 5) finally, the temperature of studied solution was lowered again by 10 degrees and the same procedure was repeated several times for 313.15 K, 303.15 K and 293.15 K.

A similar procedure was carried out in the study of quaternary acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water system (see Section 3). The experiment to determine each composition belonging to the solubility border was carried out 2–3 times. The standard uncertainty was estimated as 0.002 mol fraction.

Due to the complexity of visual determination of solubility in binary systems these mixtures were analyzed by GC analysis described below.

In order to verify the correctness of the results obtained by the titration method the additional experiments were carried out using the method of GC according to the procedure described earlier in our works [47,48]. All binary mixtures and some compositions of ternary and quaternary samples were analyzed 2–3 times with the use of GC “Crystal 5000.2” (Russia) with packed column Porapak R (1 m × 3 mm i.d.). A thermal conductivity detector

(TCD) was used due to the presence of water in samples. The carrier gas was helium (grade A) with the flow rate of 60 ml/min. Operating temperatures of vaporizing injector and TCD were 503.15 K and 513.15 K respectively. For the column temperature, the following mode was applied: heating from 373.15 to 473.15 K with a step of 10 K/min. The methods of internal standard (propyl acetate) and relative calibration were used. Ethyl alcohol was taken as a solvent. Uncertainty of GC analysis averaged 0.001 mol fraction.

One more important aspect that should be mentioned consists in occurrence of chemical reactions in the investigated system: esterification of acetic acid with *n*-amyl alcohol and hydrolysis of *n*-amyl acetate. However, it has to be said that these reactions do not influence on the compositions of studied solutions at selected temperatures as under these conditions the rates of both uncatalyzed reactions are zero and the concentrations of acid, alcohol, ester and water do not change for several hours. Thus, to carry out these chemical reactions under the conditions of the present experiment, i.e. in order for the concentrations of the components of the mixture to change as a result of chemical interaction, it is necessary to add a catalyst (strong acid).

3. Results and discussion

Data for binary *n*-amyl alcohol – water and *n*-amyl acetate – water systems obtained by GC method under polythermal conditions (293.15–323.15 K) and 101 kPa are shown in Table 2. The results of experimental investigation of solubility in the quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water and in its ternary subsystems acetic acid – *n*-amyl alcohol – water, acetic acid – *n*-amyl acetate – water and *n*-amyl alcohol – *n*-amyl acetate – water within temperature range 293.15–323.15 K by cloud-point technique are presented in Tables 3–6.

Experimentally determined binodal curves for ternary systems acetic acid – *n*-amyl alcohol – water, acetic acid – *n*-amyl acetate – water and *n*-amyl alcohol – *n*-amyl acetate – water are given in Figs. 1–3. The last figure contains an additional phase diagram, since the system *n*-amyl alcohol – *n*-amyl acetate – water belongs to 2 homogeneous regions, one of which is relatively small in size, as a result of which there was a need for an enlarged fragment of the diagram for this system (Fig. 3). It should be noted that the presence of two homogeneous and one heterogeneous areas occurs only at two temperatures (293.15 K and 303.15 K). In the case when the temperature rises to 313.15 K and 323.15 K, GC analysis does not make it possible to accurately recognize the presence of a homogeneous phase enriched with water.

A general view, form and spatial arrangement of the binodal surface of the quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water with mole fractions ratio of *n*-amyl alcohol

and *n*-amyl acetate = 1:1 under mentioned above polythermal conditions are pictured in 3D composition space (quadrangular tetrahedron) in Fig. 4.

Fig. 4 shows clearly that the binodal surface of studied system, limiting the region of solution splitting, is located inside the composition tetrahedron in the following way: it is rest on the edges «*n*-amyl acetate – water» and «*n*-amyl alcohol – water» corresponding to the binary subsystems with limited miscibility, and it is end up on three faces of tetrahedron corresponding to the ternary subsystems acetic acid – *n*-amyl alcohol – water, acetic acid – *n*-amyl acetate – water and *n*-amyl alcohol – *n*-amyl acetate – water. Heterogeneous area occupies appreciable volume of the composition tetrahedron reaching nearly 40% of its total volume. According to our experimental results total content of acetic acid and *n*-amyl alcohol on the binodal surface is within 0.41 mol fraction at 293.15 K and 0.39 mol fraction at 323.15 K. General view of the binodal surface of the system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water keeps visually almost unchanged within selected temperature range. Therefore, in the Fig. 4, we show the phase diagram only at one temperature (293.15 K), so as not to clutter the graph with compositions. It is noteworthy that a form of heterogeneous region of the system under study is typical for some other systems carboxylic acid – monohydric alcohol – ester – water, for example, the systems propionic acid – *n*-butanol – *n*-butyl propionate – water [47] and acetic acid – *n*-butanol – *n*-butyl acetate – water [49].

Fig. 5 shows comparative information on our experimental solubility data and literature LLE data [13,14,16,20,22,25,34–38,41,45] for the binary *n*-amyl alcohol – water system at 293.15 K, 303.15 K, 313.15 K, 323.15 K and atmospheric pressure. It can be concluded from this graph that variability of data for the aqueous phase is minimal and does not exceed 0.005 mol fractions. On the other hand, variability of data for the organic phase is more significant. In addition, based on the analysis of Fig. 5, it should be noted that our data on the solubility in the binary system *n*-amyl alcohol – water are in agreement with the data of works [16,25,38,41,45].

A comparative analysis of the literature data and the results obtained in this work was also carried out for the system *n*-amyl acetate – water system at 293.15 K, 303.15 K, 313.15 K, 323.15 K and atmospheric pressure (Fig. 6). For the ester – water system, for both phases, there is an inconsistency between the literature data as a whole. In the case of the aqueous phase, the scatter of the ester composition values does not exceed 0.005 mol fractions from the data obtained in this work. As for the organic phase, the results vary on average from 0.89 to 0.98 mol fractions, i.e. almost 0.1 mol fraction, in particular, for 303.15 K. Our data are in sufficient agreement with the compositions obtained in [7,9,10,45].

Obtained polythermal data on solubility give opportunity to analyze temperature evolution of phase behavior of the system

Table 2

Experimental data (mole fractions) obtained by GC for the binary systems *n*-amyl alcohol (1) – water (3) and *n*-amyl acetate (2) – water (3) at 293.15 K, 303.15 K, 313.15 K and 323.15 K, $p = 101 \text{ kPa}^a$.

293.15 K		303.15 K		313.15 K		323.15 K	
<i>n</i> -amyl alcohol (1) – water (3)							
x_1	x_3	x_1	x_3	x_1	x_3	x_1	x_3
0.663	0.337	0.656	0.344	0.638	0.362	0.620	0.380
0.005	0.995	0.005	0.995	0.004	0.996	0.004	0.996
<i>n</i> -amyl acetate (2) – water (3)							
x_2	x_3	x_2	x_3	x_2	x_3	x_2	x_3
0.938	0.062	0.927	0.073	0.917	0.083	0.908	0.092
0.001	0.999	0.001	0.999	0.000	1.000	0.000	1.000

^a Standard uncertainties $u(x) = 0.001$, $u(P) = 1.5 \text{ kPa}$, $u(T) = 0.05 \text{ K}$.

Table 3Experimental data on solubility (mole fractions) in the system acetic acid (1) – *n*-amyl alcohol (2) – water (3) at 293.15 K, 303.15 K, 313.15 K and 323.15 K, $p = 101 \text{ kPa}^a$.

293.15 K		303.15 K		313.15 K		323.15 K	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.112	0.468	0.104	0.472	0.101	0.459	0.089	0.466
0.161	0.351	0.152	0.355	0.146	0.357	0.133	0.363
0.172	0.309	0.164	0.312	0.155	0.316	0.145	0.319
0.181	0.188	0.175	0.190	0.167	0.192	0.159	0.193
0.166	0.122	0.160	0.123	0.154	0.124	0.147	0.125
0.119	0.043	0.113	0.043	0.107	0.044	0.101	0.044

^a Standard uncertainties $u(x) = 0.002$, $u(P) = 1.5 \text{ kPa}$, $u(T) = 0.05 \text{ K}$.**Table 4**Experimental data on solubility (mole fractions) in the system acetic acid (1) – *n*-amyl acetate (2) – water (3) at 293.15 K, 303.15 K, 313.15 K and 323.15 K, $p = 101 \text{ kPa}^a$.

293.15 K		303.15 K		313.15 K		323.15 K	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.295	0.070	0.290	0.071	0.286	0.071	0.280	0.072
0.324	0.130	0.318	0.131	0.313	0.132	0.307	0.133
0.340	0.206	0.334	0.208	0.327	0.210	0.320	0.212
0.340	0.243	0.333	0.245	0.326	0.248	0.318	0.251
0.322	0.343	0.314	0.347	0.305	0.352	0.297	0.356
0.300	0.409	0.287	0.416	0.277	0.422	0.269	0.427
0.235	0.534	0.226	0.541	0.216	0.548	0.205	0.556
0.019	0.887	0.013	0.892	0.007	0.897	0.001	0.903

^a Standard uncertainties $u(x) = 0.002$, $u(P) = 1.5 \text{ kPa}$, $u(T) = 0.05 \text{ K}$.**Table 5**Experimental data on solubility (mole fractions) in the system *n*-amyl alcohol (1) – *n*-amyl acetate (2) – water (3) at 293.15 K, 303.15 K, 313.15 K and 323.15 K, $p = 101 \text{ kPa}^a$.

293.15 K		303.15 K		313.15 K		323.15 K	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.615	0.069	0.600	0.073	0.577	0.078	0.563	0.081
0.583	0.111	0.569	0.116	0.548	0.123	0.530	0.126
0.508	0.220	0.493	0.227	0.478	0.236	0.445	0.250
0.369	0.411	0.349	0.426	0.331	0.439	0.309	0.455
0.272	0.553	0.264	0.560	0.240	0.580	0.211	0.604
0.197	0.656	0.189	0.663	0.163	0.687	0.123	0.722
0.091	0.810	0.067	0.832	0.043	0.856	0.014	0.883

^a Standard uncertainties $u(x) = 0.002$, $u(P) = 1.5 \text{ kPa}$, $u(T) = 0.05 \text{ K}$.**Table 6**Experimental data on solubility (mole fractions) in the system acetic acid (1) – *n*-amyl alcohol (2) – *n*-amyl acetate (3) – water (4) with mole fractions ratio of *n*-amyl alcohol and *n*-amyl acetate = 1:1 at 293.15 K, 303.15 K, 313.15 K and 323.15 K, $p = 101 \text{ kPa}^a$.

293.15 K			303.15 K			313.15 K			323.15 K		
x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
0.044	0.343	0.351	0.031	0.347	0.356	0.018	0.352	0.361	0.011	0.355	0.364
0.082	0.315	0.323	0.072	0.318	0.327	0.062	0.322	0.330	0.065	0.311	0.319
0.193	0.222	0.227	0.188	0.223	0.229	0.175	0.227	0.232	0.161	0.230	0.236
0.223	0.188	0.193	0.215	0.190	0.195	0.206	0.192	0.197	0.197	0.194	0.199
0.251	0.145	0.149	0.244	0.146	0.150	0.236	0.148	0.152	0.231	0.149	0.153
0.260	0.104	0.107	0.254	0.105	0.108	0.247	0.106	0.109	0.239	0.107	0.110
0.253	0.074	0.076	0.246	0.075	0.077	0.239	0.075	0.077	0.233	0.076	0.078
0.224	0.038	0.039	0.219	0.038	0.039	0.213	0.039	0.040	0.207	0.039	0.040

^a Standard uncertainties $u(x) = 0.002$, $u(P) = 1.5 \text{ kPa}$, $u(T) = 0.05 \text{ K}$.

acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water and in its ternary subsystems. In correspondence with our experimental data we can suggest that the solubility of the system under study increases slightly with temperature increasing, there is a small temperature shift of the binodal surface (it is average no more than 5%) with rise of temperature from 293.15 K up to 323.15 K. Figs. 7–9 show comparison diagrams for all ternary subsystems with liquid phase splitting. These diagrams are shown separately from Figs. 1–3, since the literature data are superimposed on the results of this work.

Fig. 7 contains results from this work and literature data [43–45]. A comparative analysis shows that all compositions are in good agreement except data from [44]. These results [44] are located much higher (in this case, relative to the apex of the triangle corresponding to acetic acid) for both 303.15 K and 323.15 K compared to other literary compositions [43,45], including the data of this work.

The compositions shown in Fig. 8, obtained at different temperatures by us (including [45]) and in the works of other authors, are in sufficient agreement with each other. In general, the solubility in

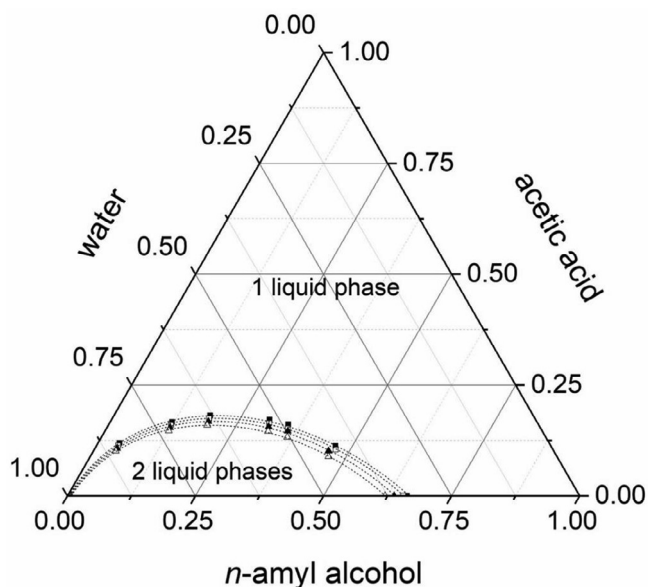


Fig. 1. Solubility data of the system acetic acid – *n*-amyl alcohol – water (mole fractions, atmospheric pressure): ■ – at 293.15 K, □ – at 303.15 K, ▲ – at 313.15 K, Δ – at 323.15 K.

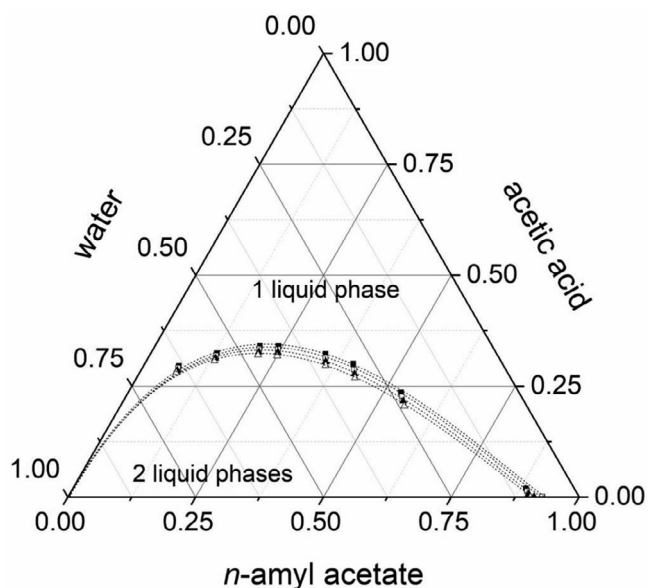


Fig. 2. Solubility data of the system acetic acid – *n*-amyl acetate – water (mole fractions, atmospheric pressure): ■ – at 293.15 K, □ – at 303.15 K, ▲ – at 313.15 K, Δ – at 323.15 K.

acetic acid – *n*-amyl acetate – water system (Fig. 8) corresponds to the well-known rule of decreasing the heterogeneous region with increasing temperature.

Fig. 9 shows that the data of [45] are in satisfactory agreement with the experimental results of this work. In the case of a comparative analysis of the results obtained by us earlier in [45], shown in the last three phase diagrams (Figs. 7–9), it is necessary to give some explanations: due to the titration method with smaller samples (8 ml) the larger uncertainties were estimated in [45] relative to the current work, which resulted in some deviations observed in Figs. 7–9 between data from [45] and this work.

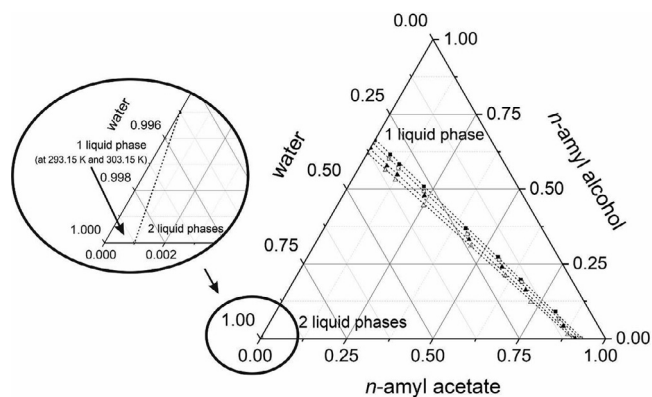


Fig. 3. Solubility data of the system *n*-amyl alcohol – *n*-amyl acetate – water (mole fractions, atmospheric pressure): ■ – at 293.15 K, □ – at 303.15 K, ▲ – at 313.15 K, Δ – at 323.15 K.

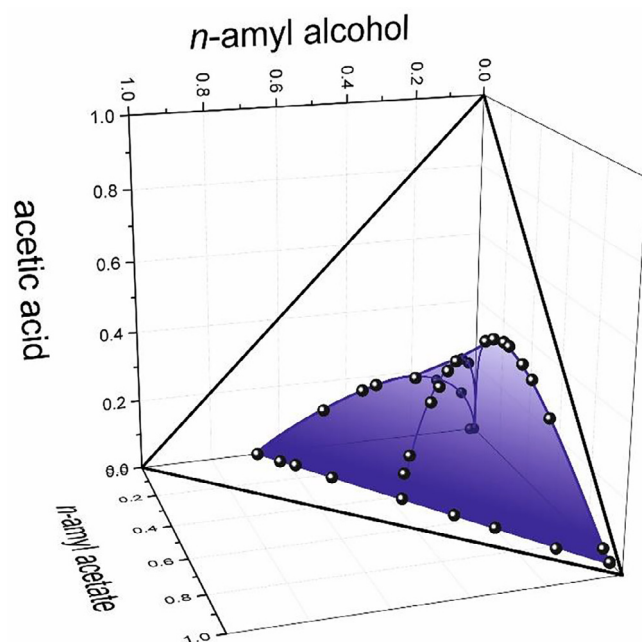


Fig. 4. General view of the binodal surface of the system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water at 293.15 K and atmospheric pressure (mole fraction).

4. LLE modelling

The calculation algorithm for predicting the compositions of coexisting phases using the UNIFAC model was based on the approach described in [50]. This model was chosen due to the lack of experimental data on LLE. The parameters of UNIFAC were taken from [51]. The activity coefficients of component *i* in the multicomponent mixture were calculated according to the equation:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

where γ_i^C and γ_i^R are combinatorial segment and residual segment of an activity coefficient, respectively.

The combinatorial segment was calculated based on the following expression:

$$\ln \gamma_i^C = \ln \left(\frac{\phi_i}{x_i} \right) + \frac{z}{2} q_i \ln \left(\frac{\theta_i}{\phi_i} \right) + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j$$

wherein:

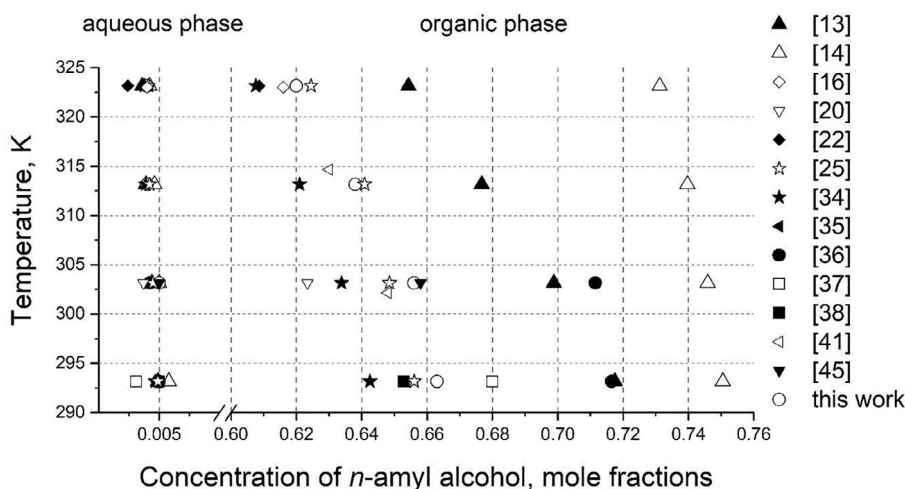


Fig. 5. The comparison of experimental solubility data with literature LLE data for the binary *n*-amyl alcohol – water system at the temperature range 293.15–323.15 K and atmospheric pressure.

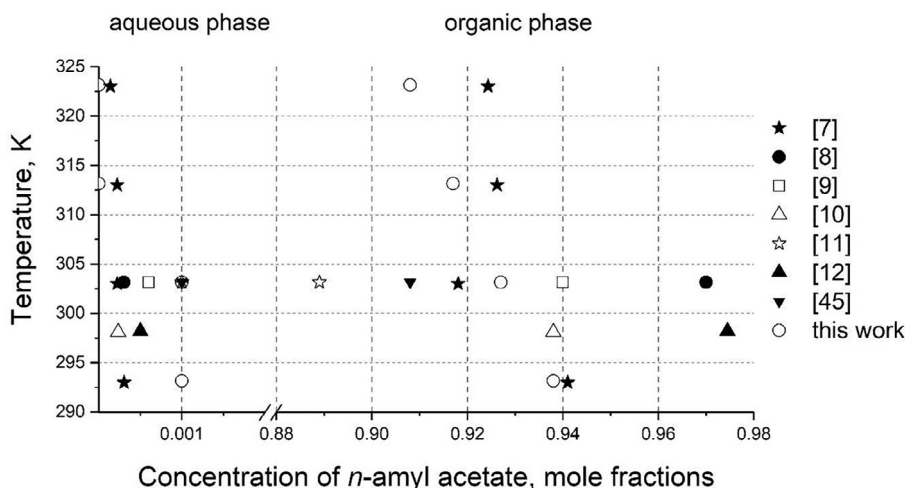


Fig. 6. The comparison of experimental solubility data with literature LLE data for the binary *n*-amyl acetate – water system at the temperature range 293.15–323.15 K and atmospheric pressure.

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1)$$

The coordination number of lattice z equals 10. The calculation of the parameters q_i and r_i is carried out as a sum of the group volume and the parameters of the domains Q_k and R_k :

$$q_i = \sum_k v_k^{(i)} Q_k$$

$$r_i = \sum_k v_k^{(i)} R_k$$

where $v_k^{(i)}$ shows the number of times that group k appears in molecule i , therefore $v_k^{(i)}$ is an integer. Due to adaptability of surface region and group volume parameters Q_k and R_k for LLE modeling we used the method of Magnussen et al. [51].

The residual segment of the activity coefficient corresponds to an equality such as:

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)})$$

where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a control solution containing only type i molecules.

$$\ln \Gamma_k = M_k Q_k \left[1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \left(\frac{\Theta_m \Psi_{mk}}{\sum_m \Theta_m \Psi_{mk}} \right) \right]$$

where Θ_m is calculated by the same algorithm as for θ_i ; Ψ_m is the group-interaction parameter. Their calculation is carried out according to the equation:

$$\Theta_m = \frac{\Theta_m X_m}{\sum_n \Theta_n X_n}$$

$$\Psi_{mn} = \exp \left(-\frac{U_{mn} - U_{nn}}{RT} \right) = \exp \left(-\frac{a_{mn}}{T} \right)$$

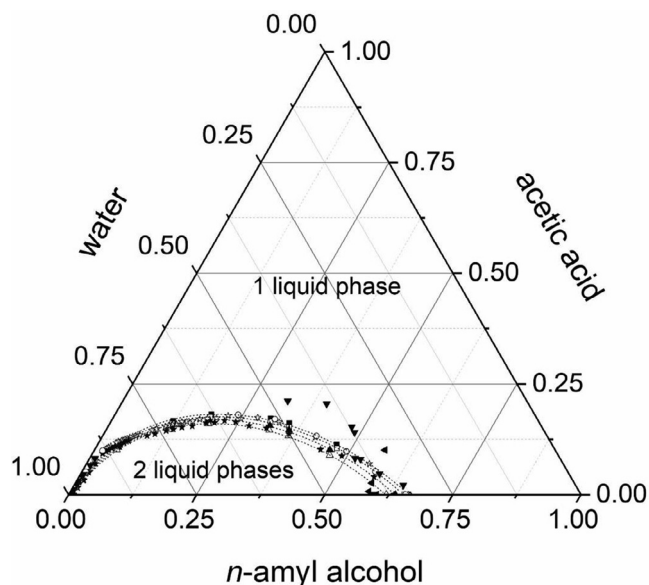


Fig. 7. The comparison of experimental solubility data with literature results for the system acetic acid – *n*-amyl alcohol – water (mole fractions, atmospheric pressure): ■ – at 293.15 K (this work), □ – at 303.15 K (this work), white star – at 303.15 K [43], ◀ – at 303.15 K [44], ○ – at 303.15 K [45], ▲ – at 313.15 K (this work), Δ – at 323.15 K (this work), black star – at 323.15 K [43], ▼ – at 323.15 K [44].

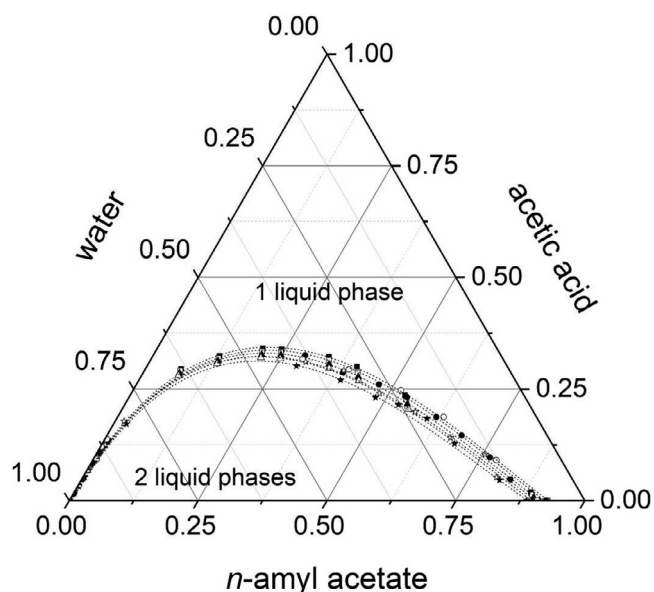


Fig. 8. The comparison of experimental solubility data with literature results for the system acetic acid – *n*-amyl acetate – water (mole fractions, atmospheric pressure): ■ – at 293.15 K (this work), □ – at 303.15 K (this work), ○ – at 303.15 K [45], ● – at 304.15 K [42], ▲ – at 313.15 K (this work), Δ – at 323.15 K (this work), white star – at 332.15 K [42], black star – at 366.15 K [42].

where X_m is the mole fraction of group m in the mixture; U_{mn} is the interaction energy between groups m and n . The values of group interaction parameters a_{mn} are given in [51].

The calculated compositions of coexisting phases (LLE) for the systems acetic acid – *n*-amyl alcohol – water, acetic acid – *n*-amyl acetate – water and *n*-amyl alcohol – *n*-amyl acetate – water including binary subsystems *n*-amyl alcohol – water and *n*-amyl

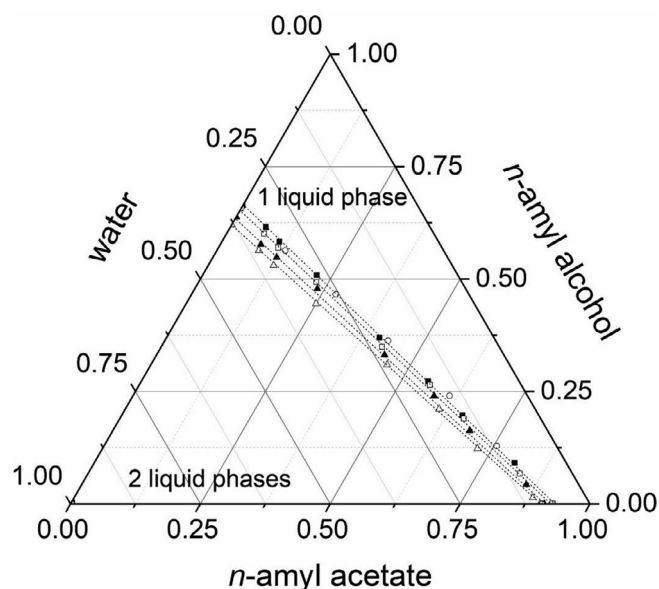


Fig. 9. Solubility data of the system *n*-amyl alcohol – *n*-amyl acetate – water (mole fractions, atmospheric pressure): ■ – at 293.15 K (this work), □ – at 303.15 K, ○ – at 303.15 K [45], ▲ – at 313.15 K (this work), Δ – at 323.15 K (this work).

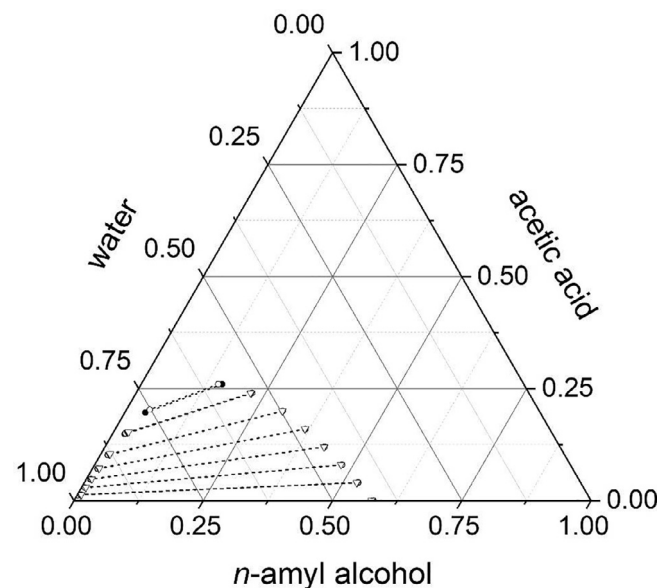


Fig. 10. Tie-lines of the system acetic acid – *n*-amyl alcohol – water calculated by UNIFAC method (mole fractions, atmospheric pressure): ● – at 293.15 K, ○ – at 303.15 K, ▼ – at 313.15 K, ▽ – at 323.15 K.

acetate – water for several temperatures are presented in Figs. 10–12. Visualization of the calculated data is given for the ternary subsystems only, since they are much easier for visual perception than spatial phase diagrams representing calculated LLE for the quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water.

In general, the calculated values of the LLE prediction using UNIFAC are in insufficient agreement with the experimental data. Thus, we propose to use an activity coefficient model like NRTL for correlating the data basis on experimental LLE compositions.

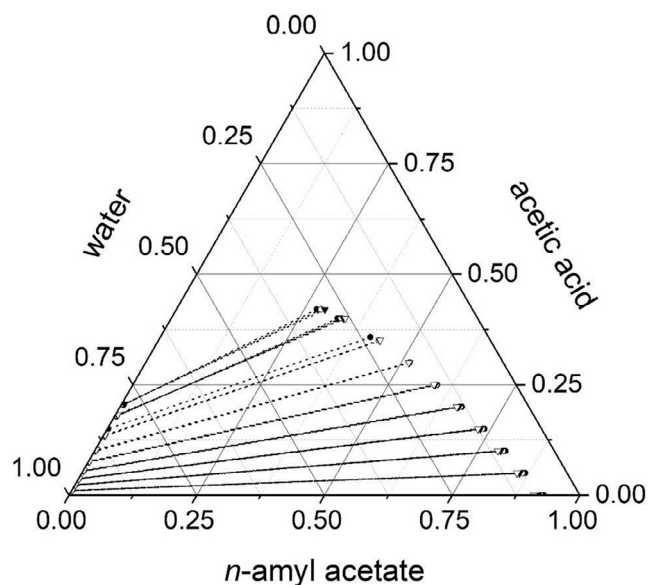


Fig. 11. Tie-lines of the system acetic acid – *n*-amyl acetate – water calculated by UNIFAC method (mole fractions, atmospheric pressure): ● – at 293.15 K, ○ – at 303.15 K, ▼ – at 313.15 K, ▽ – at 323.15 K.

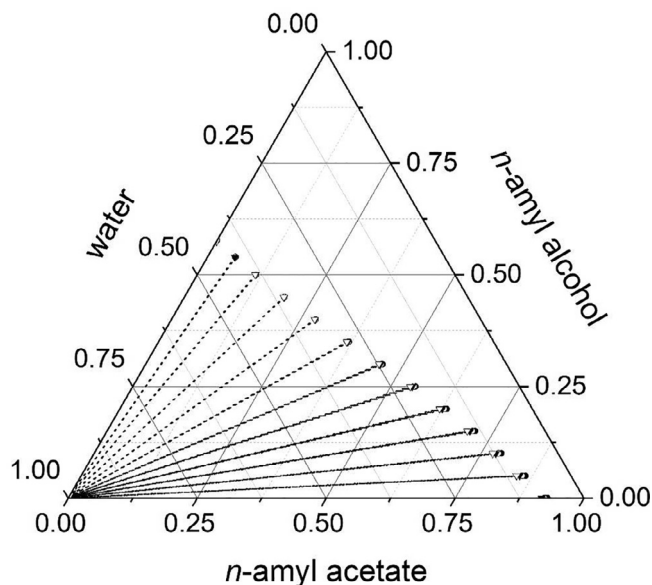


Fig. 12. Tie-lines of the system *n*-amyl alcohol – *n*-amyl acetate – water calculated by UNIFAC method (mole fractions, atmospheric pressure): ● – at 293.15 K, ○ – at 303.15 K, ▼ – at 313.15 K, ▽ – at 323.15 K.

5. Conclusions

Our research presents new experimental data on solubility in the quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water and its ternary subsystems acetic acid – *n*-amyl alcohol – water, acetic acid – *n*-amyl acetate – water and *n*-amyl alcohol – *n*-amyl acetate – water including binary mixtures (*n*-amyl alcohol – water and *n*-amyl acetate – water) at 293.15 K, 303.15 K, 313.15 K, 323.15 K and atmospheric pressure. Investigation of solubility was carried out by cloud-point technique for ternary and quaternary mixtures and by GC for binary subsystems. Experimental results comprise binodal curves and surfaces constructed in composition spaces including 3D phase diagrams in composition

tetrahedron. It was found that the miscibility gap in the quaternary system acetic acid – *n*-amyl alcohol – *n*-amyl acetate – water occupies significant part of the composition tetrahedron (about 40% of its total volume). A comparative analysis shows that there are a lot of inconsistencies between available literature data, especially for binary subsystems. However, there is a general tendency for the quaternary system as a whole to decrease solubility with decreasing temperature. Thus there is a small temperature shift of the binodal surface (it is average no more than 5%) with rise of temperature from 293.15 K up to 323.15 K. Prediction of LLE was carried out using UNIFAC method. It was found that in general calculated results are in insufficient agreement with the experimental data on solubility within entire temperature range. Obtained solubility results could be helpful for organizing an industrial process of reactive distillation of *n*-amyl acetate. Also this system can be of interest as a model system for production of biodiesel, for example, from coconut oil.

CRedit authorship contribution statement

Maya Trofimova: Writing – original draft, Formal analysis. **Georgii Misikov:** Conceptualization, Methodology, Formal analysis. **Artemiy Samarov:** Conceptualization, Methodology, Writing – review & editing. **Igor Prikhodko:** Modelling, Writing – original draft. **Maria Toikka:** Project administration, Supervision, Conceptualization, Writing – original draft, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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