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Chemical equilibrium for the reactive system propionic acid + ethanol + ethyl propionate + water at 303.15 and 313.15 K

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A B S T R A C T

Chemical equilibrium for the quaternary system propionic acid + ethanol + ethyl propionate + water was experimentally studied at 303.15 and 313.15 K and atmospheric pressure. The chemically equilibrium compositions were determined by gas chromatography and nuclear magnetic resonance analytical methods. It is shown that chemical equilibrium is reached both in homogeneous and heterogeneous area of composition of reactive mixture. The liquid – liquid equilibrium data for the surface of chemical equilibrium were obtained. The thermodynamic constants of chemical equilibrium at 303.15 and 313.15 K were determined.

Keywords:

Chemical equilibrium
Ethyl propionate
Phase equilibrium
Reactive system

1. Introduction

Heterogeneous systems with chemical reactions are complex objects and their study gives new thermodynamic information, allows establishing new physical and chemical regularities. At the same time it is obvious not only fundamental, but also the practical importance of the problem of the splitting of liquid reaction mixtures. Such effect fundamentally changes the technological process of chemical synthesis. The object of our study is a quaternary reacting system with ethyl propionate synthesis reaction. Ethyl propionate is widely used in the food processing, flavor industry and biofuel production [1,2]. This ester is an important reagent in pharmaceutical industries, e.g. for the production of some anti-malarial drugs including pyrimethamine. Ethyl propionate has also other promising areas of application, for example, in the manufacture of lithium batteries [3]. The esterification is one of the main industrial methods of ester synthesis and the data on phase and chemical equilibria are necessary for the process design. Unfortunately despite a practical importance of ethyl propionate the data sets on equilibrium properties of system propionic

acid + ethanol + ethyl propionate + water are very limited.

The only experimental data related to the properties of propionic acid + ethanol + ethyl propionate + water system were presented by Macedo and Rasmussen in 1982 [4]. The vapor – liquid equilibrium (VLE) was determined for the ethyl propionate – propionic acid mixture at 358 and 368 K and pressure 134.28–573.05 mm Hg for 20 compositions of binary mixtures. The VLE data have been correlated by UNIFAC model.

The aim of our work is the study of CE in propionic acid + ethanol + ethyl propionate + water system at 303.15 and 313.15 K and atmospheric pressure in a wide range of compositions including homogeneous and heterogeneous areas of reactive solutions. Accordingly we determined the liquid – liquid equilibrium (LLE) for chemically equilibrium states, i.e. simultaneous LLE and CE. The experimental data allow expanding the database on the phase and chemical equilibria in reacting systems and give the additional opportunities for the design of the process of ethyl propionate synthesis.

2. Experimental

2.1. Materials

Propionic acid (>0.98 mol fraction, BASF, Germany), ethanol

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Table 1
The purities of the chemicals.

Substance	Purity, initial mole fraction	Purity, final mole fraction ^a
Propionic acid	0.980	0.990
Ethanol	0.960	0.960 ^b
Ethyl propionate	0.980	0.997
Water	0.999	0.999

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

^b Ethanol sample contains 0.040 mol fraction of water.

(>0.96 mol fraction, Vekton, Russia) and ethyl propionate (>0.98 mol fraction, Vekton, Russia) were purified by distillation, water was bidistilled. Purity was determined by gas chromatography (GC) and is given in Table 1. All physical-chemical constants of pure substances are in agreement with the NIST data [5]. The fact that water is one of the components of the system under the study, gives the ability to use ethanol containing a known amount of water instead of absolute alcohol: this facilitated the experimental procedure. The amount of water remaining in ethanol after distillation was taken into account in preparation of initial mixtures.

2.2. CE determination

The study of the CE at 303.15 and 313.15 K was carried out using ¹H NMR spectroscopy (for homogeneous solutions) and GC analysis (for heterogeneous area) by methods describing in Refs. [6,7].

Initial quaternary mixtures of known overall compositions were prepared by gravimetric method in NMR-tubes (178 mm \times 4.2 mm i.d.) using an analytical balance Shinko VIBRA HT-120CE (Japan) with the accuracy of 0.001 g. Hydrochloric acid was used as a catalyst in amount of 0.003 mol fraction. NMR-tubes were placed in the liquid thermostat (303.15 and 313.15 K). The temperature uncertainty was ± 0.05 K. The CE was reached in no longer than 4 days (303.15 and 313.15 K). All samples were analyzed using a 500 MHz Bruker AVANCE III NMR spectrometer, equipped with a BBI probe head with inner coil for ¹H nuclei. The spectra were acquired with an acquisition time of 3 s, a relaxation delay of 1 s, and a pulse with 30° flip angle. The 16 scans were accumulated. The spin-lattice NMR relaxation times T_1 for all molecular groups of all compounds were measured. Observed T_1 values are in range from 3 to 5 s. The relaxation delay was high enough for quantitative analysis of peak integrals since the relaxation times had close values and the flip angle of pulse was relatively small. The error introduced by saturation was below 1%. The processing of the acquired spectra was carried out using Bruker TopSpin software. The phase correction was done manually. Polynomial baseline correction was done automatically. The integration region of 250–500 Hz which was over 20 times wider than the linewidth of analyzed peak was chosen. The constancy of composition confirmed the achievement of CE. The uncertainty of the determination of the peak areas introduced by the processing is estimated to be 3%.

In the case of the splitting of chemically equilibrium mixtures the compositions were determined using GC analysis. Gas chromatograph “Chromatec Crystal 5000.2” (Russia) with thermal conductivity detector (TCD) and packed column Porapak R

(1 m \times 3 mm i.d.) was used. The TCD was chosen because of the presence of water. Helium with the flow rate of 60 ml/min was used as a carrier gas. Operating temperature of column, vaporizing injector and TCD were 483 K, 503.15 K and 513 K, respectively. Initial quaternary mixtures were prepared by gravimetric method in glass vessels (5 ml) using an analytical balance Shinko VIBRA HT-120CE (Japan) with the accuracy of 0.001 g. The CE was reached in no longer than 4 days (303.15 and 313.15 K). After reaching of CE and phase equilibrium heterogeneous samples were taken from both phases with chromatographic syringe (“Hamilton”, USA) and analyzed by GC. To avoid the splitting of samples directly into the needle the chromatographic syringe was preliminary heated. The methods of internal standard and relative calibration were used to determine the compositions of CE. Propionic acid was accepted as linking component. Uncertainty of GC analysis averaged ± 0.005 mol fraction. Accuracy of initial solutions preparing was 0.001 g. The temperature uncertainty of the liquid thermostat was ± 0.05 K. The reproducibility of the experimental data was confirmed by the repeated analysis of samples. All chemically equilibrium mixtures were analyzed 3–5 times and the deviations of the results were in the frame of GC analysis uncertainties.

To check the consistency between two analytical methods (GC and NMR), we also determined few compositions in homogeneous area by GC analysis. The discrepancy does not exceed 0.005 mol fractions. In general both of methods enable to accurately determine the compositions of mixtures, but NMR method takes less time in comparison with GC analysis [6].

3. Results and discussions

3.1. Experimental data

The data on CE in homogeneous area of composition in propionic acid + ethanol + ethyl propionate + water system at 303.15 and 313.15 K and atmospheric pressure (NMR method) are presented in Table 2.

The data of Table 2 gives the opportunity to calculate the values of so-called concentration constants (pseudoreaction equilibrium constants)

$$K_x = \frac{x_{\text{ethyl propionate}} x_{\text{water}}}{x_{\text{propionic acid}} x_{\text{ethanol}}}$$

which depends on the composition and should be not considered as real thermodynamic constant of CE. On the other hand the relative constancy of K_x can be used to check the consistency of the data. The average K_x values for homogeneous area of CE are 5.5 ± 1.0 at 303.15 K and 5.0 ± 0.9 at 313.15 K.

The consistency of the CE data is also confirmed by the fact that in all cases the initial and final (CE) compositions belong to the same stoichiometric line (within standard uncertainties $u(x)$).

The data on CE and LLE for the heterogeneous region at 303.15 and 313.15 K and atmospheric pressure (GC analysis) are presented in Table 3.

The compositions of chemically equilibrium mixtures in the case of ester synthesis reaction

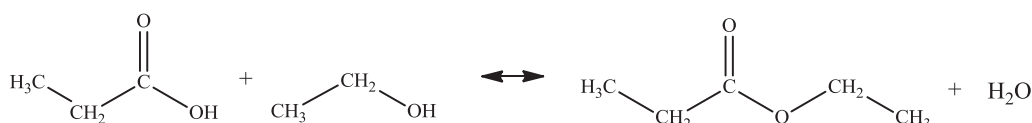


Table 2

The experimental CE data for the quaternary system propionic acid (1) + ethanol (2) + ethyl propionate (3) + water (4) at 303.15 and 313.15 K in the homogeneous region of compositions analyzed by ¹H NMR spectroscopy (mole fractions x_i , at atmospheric pressure^a).

x_1	x_2	x_3	x_1	x_2	x_3
303.15 K					
0.165	0.131	0.475	0.064	0.299	0.156
0.151	0.127	0.548	0.071	0.303	0.197
0.121	0.181	0.244	0.067	0.276	0.259
0.096	0.182	0.158	0.081	0.295	0.318
0.224	0.028	0.064	0.056	0.294	0.390
0.253	0.061	0.191	0.071	0.282	0.394
0.270	0.064	0.249	0.066	0.281	0.453
0.276	0.061	0.267	0.416	0.007	0.039
0.310	0.064	0.304	0.445	0.013	0.075
0.286	0.063	0.356	0.465	0.015	0.103
0.281	0.057	0.430	0.447	0.021	0.151
0.250	0.063	0.466	0.473	0.020	0.184
0.036	0.172	0.044	0.424	0.026	0.230
0.055	0.205	0.085	0.466	0.022	0.271
0.066	0.209	0.113	0.447	0.023	0.367
0.074	0.223	0.152	0.436	0.023	0.392
0.081	0.234	0.191	0.011	0.367	0.035
0.101	0.220	0.234	0.025	0.372	0.066
0.101	0.221	0.254	0.034	0.376	0.097
0.095	0.238	0.310	0.049	0.333	0.124
0.103	0.232	0.356	0.046	0.387	0.168
0.098	0.221	0.388	0.053	0.379	0.209
0.090	0.200	0.489	0.053	0.382	0.301
0.324	0.023	0.096	0.055	0.368	0.336
0.332	0.032	0.144	0.058	0.348	0.361
0.337	0.034	0.170	0.516	0.005	0.037
0.339	0.041	0.217	0.526	0.009	0.070
0.353	0.039	0.238	0.520	0.012	0.100
0.337	0.045	0.319	0.526	0.013	0.134
0.331	0.043	0.362	0.518	0.016	0.188
0.342	0.042	0.391	0.527	0.016	0.226
0.333	0.041	0.451	0.509	0.017	0.243
0.044	0.283	0.089	0.516	0.016	0.301
0.038	0.444	0.272	0.520	0.015	0.336
0.010	0.449	0.037	—	—	—
313.15 K					
0.156	0.126	0.496	0.330	0.044	0.410
0.142	0.118	0.577	0.320	0.042	0.459
0.176	0.107	0.501	0.045	0.277	0.089
0.048	0.128	0.042	0.058	0.270	0.119
0.036	0.187	0.048	0.066	0.276	0.160
0.052	0.209	0.088	0.074	0.293	0.201
0.064	0.214	0.113	0.086	0.263	0.232
0.075	0.225	0.149	0.078	0.301	0.270
0.084	0.237	0.186	0.082	0.281	0.316
0.098	0.224	0.228	0.088	0.256	0.356
0.100	0.228	0.246	0.080	0.261	0.373
0.100	0.246	0.295	0.073	0.275	0.438
0.103	0.236	0.347	0.443	0.020	0.143
0.103	0.223	0.379	0.458	0.021	0.169
0.100	0.214	0.464	0.417	0.028	0.221
0.325	0.034	0.143	0.461	0.024	0.248
0.331	0.042	0.215	0.420	0.029	0.272
0.338	0.043	0.243	0.432	0.031	0.306
0.334	0.047	0.297	0.428	0.029	0.375
0.330	0.049	0.321	0.014	0.373	0.033
0.327	0.046	0.362	0.024	0.372	0.067
0.525	0.014	0.130	0.026	0.375	0.099
0.521	0.016	0.148	0.037	0.349	0.131
0.521	0.016	0.182	0.043	0.391	0.167
0.524	0.017	0.203	0.051	0.386	0.205
0.506	0.019	0.239	0.051	0.392	0.249
0.500	0.020	0.285	0.051	0.392	0.293
0.506	0.020	0.317	0.050	0.377	0.335
0.011	0.448	0.036	0.050	0.365	0.360
0.015	0.454	0.061	0.516	0.005	0.034
0.023	0.453	0.086	0.529	0.009	0.070
0.035	0.454	0.169	0.519	0.012	0.103
0.041	0.430	0.192	0.037	0.444	0.273
0.040	0.433	0.233	—	—	—

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

Table 3

The experimental CE and LLE data for the quaternary system propionic acid (1) + ethanol (2) + ethyl propionate (3) + water (4) in the heterogeneous region of compositions at 303.15 and 313.15 K (mole fractions x_i , atmospheric pressure^a).

Aqueous phase			Organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
303.15 K					
0.081	0.148	0.059	0.165	0.154	0.440
0.081	0.122	0.055	0.197	0.130	0.449
0.097	0.098	0.046	0.211	0.105	0.451
0.111	0.080	0.042	0.236	0.090	0.430
0.134	0.068	0.044	0.263	0.074	0.412
313.15 K					
0.081	0.154	0.069	0.162	0.161	0.424
0.086	0.129	0.057	0.191	0.137	0.427
0.098	0.103	0.051	0.210	0.111	0.430
0.112	0.089	0.049	0.241	0.094	0.412
0.127	0.071	0.047	0.256	0.080	0.393

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

belong to the surface in composition tetrahedron. Four binary subsystems (propionic acid + ethyl propionate, propionic acid + water, ethanol + ethyl propionate, ethanol + water) are nonreactive and should be considered as borders of the surface of CE (edges of tetrahedron). Two reacting binary systems (propionic acid + ethanol and ethyl propionate + water) and all four ternary subsystems are in chemically nonequilibrium states and do not belong to this surface. Fig. 1 presents the CE surface of the quaternary propionic acid + ethanol + ethyl propionate + water system at 313.15 K (the CE surface for 303.15 K has approximately the same view). The LLE tie-lines in Fig. 1 give only a schematic representation of liquid-liquid envelope on this surface. It should be noted that LLE tie-lines on the surface of CE are analogous to unique reactive tie-lines which were introduced by Ung and Doherty for heterogeneous CE in ternary mixtures [8]. In quaternary system the set of unique reactive tie-lines forms the linear surface in composition tetrahedron [7,9].

The square of transformed composition variables α_i [10,11] gives more visual representation of liquid-liquid envelope at CE surface. In the case of quaternary CE these variables α_i are determined as following:

$$\alpha_1 = x_1 + x_4$$

$$\alpha_2 = x_2 + x_4$$

$$\alpha_3 = x_3 - x_4$$

The LLE tie-lines on the surface of CE 313.15 K, area of immiscibility and experimental homogeneous CE composition at 313.15 K

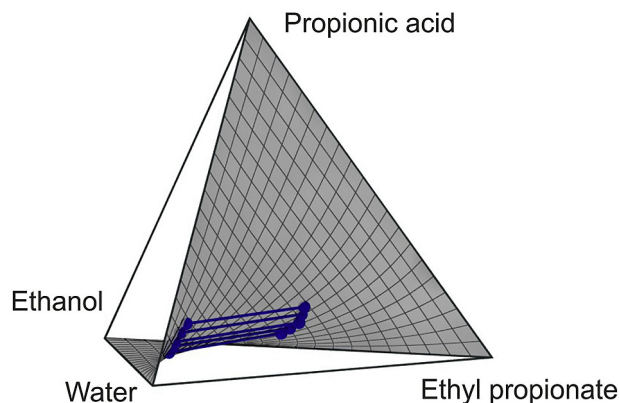


Fig. 1. The CE surface of propionic acid + ethanol + ethyl propionate + water system at 313.15 K ■■■ — surface of CE; ●—● — experimental liquid-liquid tie-lines on the surface of CE.

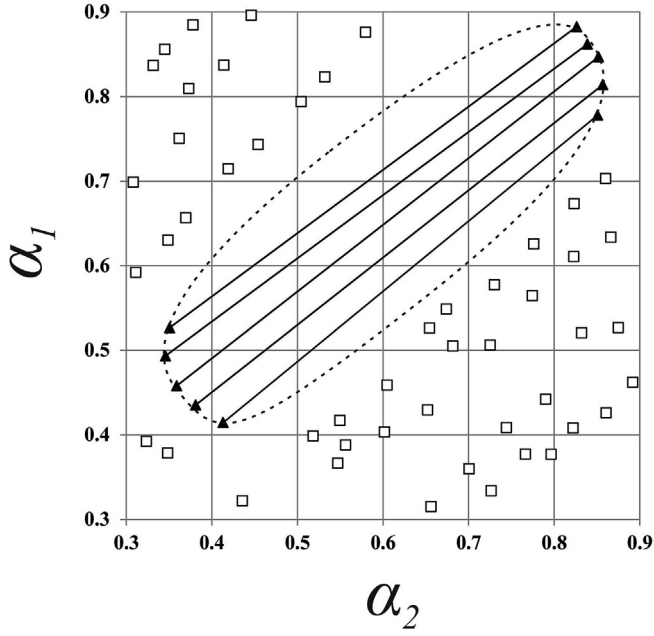


Fig. 2. The area of immiscibility at the surface of CE in propionic acid + ethanol + ethyl propionate + water system at 313.15 K: \blacktriangle — \blacktriangle – liquid-liquid tie-lines at 313.15 K; ---- – the area of intersection of CE and LLE surfaces; \square – composition points corresponding to CE in the homogeneous area (experimental results).

are presented in Fig. 2. Figs. 1 and 2 also display the mutual disposition of CE and binodal surfaces. The area of intersection of these surfaces in the composition tetrahedron corresponds to simultaneous CE and LLE.

4. Calculation of thermodynamic constant of CE

In this work, the original UNIFAC model [12] was used for the prediction of the activity coefficients. The activity coefficient of component i in a multicomponent mixture according to UNIFAC model determines by the following equation:

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

where an activity coefficient consists of two parts, a combinatorial part γ_i^C and a residual part γ_i^R .

The combinatorial part can be expressed as:

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

wherein:

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

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

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

where z is the lattice coordination number which is equal to 10. Parameters q_i and r_i are calculated as the sum of the group volume and region parameters Q_k and R_k :

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

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

where $\nu_k^{(i)}$ is an integer that indicates the number of times that group k appears in molecule i ; surface region and group volume parameters Q_k and R_k were taken from Ref. [13] due to their applicability for LLE calculation.

Following expression describes another part of the activity coefficient:

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

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

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

where Θ_m is calculated in the same way as for θ_i ; Ψ_m is the group-interaction parameter. They are calculated according to the equation:

$$\Theta_m = \frac{\Theta_m X_m}{\sum_G^n \Theta_n X_n}$$

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

where X_m is the mole fraction of group m in the solution; U_{mn} is the energy of interaction between groups m and n . The group interaction parameters a_{mn} were taken from the literature [13].

The UNIFAC model was used for calculations of activities and thermodynamic constant of CE, K_a . The value of K_a could be expressed in terms of activities of species:

$$K_a = \prod_i a_i^{\nu_i},$$

where α_i – activity, ν_i – stoichiometric coefficients of reactants and products that are negative and positive, respectively. The values of K_a were calculated on the basis of the experimental data for homogeneous area of composition. The obtained constants of CE have the value 18.4 ± 2.7 at 303.15 K and 17.2 ± 2.3 at 313.15 K.

5. Conclusions

Chemical equilibrium data for the quaternary reacting system propionic acid + ethanol + ethyl propionate + water were obtained at 303.15 and 313.15 K and atmospheric pressure. The existence of liquid-liquid envelope on the surface of CE is experimentally proved. The set of new experimental data enables to present surface of CE with the area of its intersection with LLE surface in composition tetrahedron. Using experimental data and UNIFAC model the values of thermodynamic constants of CE at 303.15 and 313.15K were determined as 18.4 ± 2.7 and 17.2 ± 2.3 respectively.

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