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Experimental Data on Chemical Equilibrium in the System with Ethyl Formate Synthesis Reaction at 298.15 K

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



ABSTRACT: Chemical equilibrium (CE) in the quaternary reacting system formic acid-ethanol-ethyl formate-water was experimentally studied at 298.15 K and atmospheric pressure. The CE compositions were determined by gas chromatography analysis. The obtained data gave an opportunity to present the disposition of the surface of CE in a composition tetrahedron. The constants of CE ("concentration" and thermodynamic) were determined on the base of acid experimental data and UNIFAC model.

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1. INTRODUCTION

Ethyl formate (CAS Number 109-94-4) one of the esters of carbon acids that have various practical applications, for example, in food, agricultural, pulp industry, manufacturing of paintwork materials, pharmaceutics (vitamin B production, etc.). A common method of ethyl formate synthesis is the use of formic acid and ethanol as a raw material and sulfuric acid as a catalyst. However, the industrial production of ethyl formate is quite a power-consuming one. The synthesis requires significant energy inputs; for example, the processes of esterification of formic acid with ethanol and carbonylation of ethanol are carried out at temperatures about 420 K.¹ The development of an energy- and resource-saving technology of ethyl formate synthesis requires data on phase and chemical equilibria that would help the choice of optimal process conditions, also according to the principles of green chemistry. Despite the importance of these data for process design an analysis of scientific literature revealed the absence of reliable experimental data on chemical equilibrium and kinetics of the reaction of ethyl formate synthesis, except as described in refs 2 and 3. Konaka et al.² studied kinetics of esterification of formic acid with ethanol within the temperature range 273.15-309.15 K, for which the mole ratios of reagents ranged from 1 to 35 and sulfuric acid was used as catalyst. Experimental values of the reaction rate constant were additionally compared with calculated values, and the results showed agreement between observation and calculation within allowable error. Lisnyanskii et al.³ proposed the method of ethyl formate synthesis using silica gel as a catalyst with a formic acid and ethyl alcohol ratio

of 1:1.48 at a temperature of 341.15-343.15 K. However, the duration of the synthesis performed was not mentioned.

The data on phase equilibria in formic acid-ethanol-ethyl formate—water system are also limited.⁴ The vapor—liquid equilibrium (VLE) in the temperature range of 313-333 K in this system was studied by Tischmeyer and Arlt.⁵ The changes of temperature, pressure, and composition along some stoichiometric lines beginning the binary acid-alcohol mixture were determined. One of the aims of this study was, first of all, to estimate the change of VLE parameters in the run of the reaction. With regard to the studies of solubility and liquidliquid equilibrium in formic acid-ethanol-ethyl formatewater quaternary system, detailed experimental data and binodal surfaces in the composition tetrahedron at 298.15 and 308.15 K were published in a recent paper.⁶

The present work is dedicated to the experimental study of CE in formic acid-ethanol-ethyl formate-water system at 298.15 K.

2. EXPERIMENTAL SECTION

2.1. Materials. Formic acid (for analysis, ACS grade, PanReac AppliChem) and ethyl formate (reagent grade, Sigma-Aldrich) were used without additional purification.

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Table 1. CAS Registry Number, Boiling Temperatures, and Purity^a of the Chemicals

substance	CASRN	supplier	purity, mole fraction	boiling temp $^{\boldsymbol{c}}$ this work	<i>T,</i> K (at101.3 kPa) literature data ⁷
ethyl formate	109-94-4	Sigma-Aldrich	0.994 ^b	327.40	327. ± 1
formic acid	64-18-6	PanReac AppliChem	0.996 ^b	373.80	373.9 ± 0.5
ethanol	64-17-5	Vekton	0.995	351.50	351.5 ± 0.2
water	7732-18-5		0.995	373.15	373.17 ± 0.04

^{*a*}Gas chromatograph. ^{*b*}As reported by the suppliers in accordance with certificate of analysis. ^{*c*}Standard uncertainties of boiling temperatures u(T) = 0.05, u(P) = 0.5 kPa.

Table 2. Experimental Data on Chemical Equilibrium in the System Formic Acid (1)–Ethanol (2)–Ethyl Formate (3)–Water (4) at 298.15 K and 101 kPa^{*a*}, the Values of "Concentration Constant" of CE (K_c), Thermodynamic Constant (K_a) and Deviations of K_a from Average Magnitude (σ); x_i , Mole Fraction of Substance *i*

initial compositions				equilibrium compositions					
x_1	<i>x</i> ₂	<i>x</i> ₃	x_4	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	$K_{\rm c}$	K_{a}	σ
0.901	0.099	0.000	0.000	0.784	0.001	0.097	15.7	3.5	0.17
0.799	0.201	0.000	0.000	0.592	0.005	0.195	12.6	4.3	0.00
0.700	0.300	0.000	0.000	0.413	0.020	0.279	9.5	4.5	0.05
0.600	0.400	0.000	0.000	0.261	0.068	0.335	6.3	4.1	0.04
0.499	0.501	0.000	0.000	0.160	0.168	0.331	4.2	3.8	0.11
0.400	0.600	0.000	0.000	0.097	0.309	0.292	2.9	3.9	0.09
0.299	0.701	0.000	0.000	0.057	0.461	0.238	2.2	4.3	0.01
0.200	0.800	0.000	0.000	0.027	0.629	0.169	1.7	5.1	0.19
0.101	0.899	0.000	0.000	0.013	0.808	0.086	0.8	3.7	0.13
0.698	0.100	0.202	0.000	0.583	0.005	0.295	12.6	4.4	0.03
0.599	0.199	0.201	0.000	0.405	0.019	0.383	9.8	4.8	0.13
0.500	0.300	0.200	0.000	0.251	0.062	0.439	7.0	4.7	0.10
0.400	0.400	0.200	0.000	0.147	0.159	0.444	4.8	4.5	0.06
0.303	0.497	0.200	0.000	0.085	0.293	0.407	3.5	4.8	0.11
0.200	0.599	0.201	0.000	0.046	0.452	0.349	2.6	5.3	0.23
0.097	0.677	0.226	0.000	0.024	0.609	0.292	1.5	4.5	0.05
0.501	0.099	0.400	0.000	0.396	0.011	0.489	12.0	6.0	0.41
0.400	0.200	0.401	0.000	0.232	0.047	0.557	8.4	5.8	0.35
0.299	0.301	0.399	0.000	0.124	0.141	0.563	5.6	5.4	0.26
0.200	0.400	0.400	0.000	0.064	0.276	0.528	4.0	5.5	0.28
0.102	0.499	0.399	0.000	0.031	0.435	0.463	2.5	5.0	0.16
0.300	0.100	0.600	0.000	0.207	0.027	0.678	10.7	$(7.6)^{b}$	$(0.76)^{b}$
0.200	0.204	0.596	0.000	0.091	0.112	0.692	7.1	$(6.9)^{b}$	$(0.62)^{b}$
0.100	0.300	0.599	0.000	0.038	0.254	0.642	4.5	$(6.2)^{b}$	0.44) ^b
0.100	0.102	0.799	0.000	0.051	0.070	0.831	11.0	$(10.5)^{b}$	$(1.45)^{b}$
0.688	0.117	0.000	0.195	0.572	0.005	0.112	11.9	4.2	0.03
0.601	0.201	0.000	0.198	0.413	0.019	0.184	9.2	4.2	0.02
0.495	0.297	0.000	0.207	0.259	0.067	0.231	5.9	3.6	0.15
0.404	0.403	0.000	0.193	0.159	0.164	0.241	4.0	3.5	0.19
0.305	0.494	0.000	0.202	0.099	0.292	0.202	2.8	3.4	0.20
0.199	0.596	0.000	0.205	0.053	0.452	0.143	2.1	3.8	0.11
0.100	0.697	0.000	0.203	0.021	0.619	0.077	1.6	4.4	0.04
0.500	0.100	0.000	0.400	0.412	0.012	0.088	8.6	3.8	0.12
0.398	0.200	0.000	0.402	0.252	0.055	0.145	5.7	3.3	0.23
0.299	0.301	0.000	0.400	0.149	0.151	0.147	3.6	2.9	0.33
0.200	0.396	0.000	0.404	0.080	0.280	0.116	2.7	3.0	0.30
0.098	0.496	0.000	0.405	0.033	0.433	0.063	2.1	3.3	0.22
0.299	0.099	0.000	0.602	0.250	0.038	0.074	4.9	$(2.6)^{b}$	$(0.38)^{b}$
0.200	0.200	0.000	0.601	0.118	0.122	0.078	3.7	$(2.7)^{b}$	$(0.38)^{b}$
0.099	0.298	0.000	0.603	0.049	0.250	0.048	2.6	$(2.6)^{b}$	$(0.40)^{b}$
0.100	0.100	0.000	0.800	0.073	0.077	0.023	3.4	$(2.2)^{b}$	$(0.50)^{b}$
^a Standard un	cortainties u(m)	-0.005 u(T)	-0.05 ^b Valu	$\alpha \in \sigma$ for the co	mpositions cla	sea ta tha adaa	s of the conce	ntration totraho	dran (had haa

^aStandard uncertainties u(x) = 0.005, u(T) = 0.05. ^bValues σ for the compositions, close to the edges of the concentration tetrahedron (had been excluded in calculation of average K_{3a}).

Ethanol (reagent grade, Vekton) was previously dried using molecular sieves (synthetic zeolite), Water was distilled twice. The purity was controlled by gas chromatography (GC) method. Values of boiling point temperatures were in good agreement with the data reported by National Institute of Standards and Technology (NIST).⁷ The temperatures of

boiling points of substances at 101.3 kPa (± 1 kPa) were determined by ebulliometer with an accuracy of ± 0.05 K. All suppliers, CAS Registry number, and the mole fraction purity of substances used in the experiments are listed in Table 1.

2.2. CE Determination. The compositions of reacting mixtures corresponding to CE in the system formic acidethanol-ethyl formate-water were determined by GC analysis. The experimental procedure was similar to the studies described in refs 8 and 9. Original quaternary solutions with known mole fractions of each component were prepared in vials (5 mL) by a gravimetric method with an accuracy of 0.001 g. Then sealed vials were held in liquid thermostat at a given temperature (298.15 K) for at least 72 h. Because of the presence of formic acid in all solutions, it was not necessary to use additional catalyst in this case: the catalytic properties of formic acid were sufficient for the run of the reaction. It was considered that chemical equilibrium was reached when the concentration of each component was constant for several hours. It should be noted that during the experiment all samples remained homogeneous at 298.15 K.

The samples of equilibrium and nonequilibrium (also during reaction) solutions were analyzed by the GC method. The chromatographic syringe ("Hamilton", USA, 10 μ L) was preliminary heated to avoid the splitting of samples. A gas chromatograph "Chromatec Crystal 5000.2" (Russia) with thermal conductivity detector (TCD) and packed column Porapak QS $(1 \text{ m} \times 3 \text{ mm i.d.})$ was used. The choice of the TCD is connected with the presence of water in the system and, accordingly, in samples. The carrier gas was helium with the flow rate of 60 mL/min. Operating temperatures of the vaporizing injector and TCD were 513 K. For the chromatographic column, a variable temperature regime was applied: 2 min at 453 K, then heating to 483 K at a rate of 20 K/min. The method of external standard and relative calibration were used to determine CE compositions. Propyl acetate was accepted as a linking component. The average uncertainty of GC analysis was ± 0.005 mole fraction.

3. RESULTS AND DISCUSSION

3.1. Experimental Data. Experimentally obtained compositions of chemically equilibrium solutions for the system with ethyl formate synthesis reaction (formic acid–ethanol–ethyl formate–water)



at 298.15 and 308.15 K and atmospheric pressure are tabulated in Table 2. The surface of chemical equilibrium at 298.15 K constructed on the basis of obtained experimental data is presented in Figure 1. This surface is located inside the concentration 3D space (composition tetrahedron) in a certain way: its lean on four edges corresponding to the binary subsystems without chemical interaction (ethanol-water, ethanol-ethyl formate, formic acid-water, and formic acidethyl formate) and passes near the edge corresponding to the only binary subsystem with limited solubility (ethyl formatewater) and homogeneous binary system formic acid-ethanol. The appearance of the chemical equilibrium surface coincides with the overall view of chemical equilibrium surfaces of other systems of carboxylic acid-monohydric alcohol-ester-water (e.g., presented in refs 8 and 9). The diagram in Figure 1 also



Figure 1. Comparison of mutual position of the binodal and the surface of chemical equilibrium in the system formic acid—ethanol—ethyl formate—water at 298.15 K. Red color, surface of CE and compositions belonging to this surface (experimental results of this work); blue color, binodal surface, according to ref 6.

contains a binodal surface that was presented in our previous work at 298.15 $\mathrm{K.}^6$

As it was noted before, during the experimental investigation of chemical equilibrium in the system formic acid–ethanol– ethyl formate–water, the splitting of samples was not detected, that is, all chemically equilibrium samples remained homogeneous. To verify the fact that in the system formic acid– ethanol–ethyl formate–water only homogeneous solutions correspond to chemical equilibrium, the obtained data were compared with solubility data of work.⁶ Surfaces of CE and solubility are presented in Figure 1.

It is evident that the surface of chemical equilibrium and the surface of solubility do not intersect, which confirms the experimentally observed fact: the CE of the ethyl formate synthesis reaction at 298.15 K is achieved only in the homogeneous region of compositions. It should be noted that some systems carboxylic acid—monohydric alcohol—ester—water show similar phase behavior (for example, acetic acid—ethanol—ethyl acetate—water, refs 8 and 10), while in others there are both areas of homogeneous and splitting chemically equilibrium solutions (for example, acetic acid—npropanol—n-propyl acetate—water and propionic acid—ethanol—ethyl propionate—water, refs 9 and 11).

The obtained data gave opportunity for the calculation of the so-called "concentration constant" of CE (K_c). Opposite to the thermodynamic constant of CE that is constant at given temperature and pressure, the values K_c depend on composition. Nevertheless this parameter reflects the shifting of compositions corresponding to chemical equilibrium and is useful for the presentation of the data. The K_c values are also presented in Table 2. According to these data we calculated and plotted isolines of K_c using transformed composition variables, α_i .^{12,13} In the case of the considered reaction these variables are

$$\alpha_1 = x_1 + x_3$$
$$\alpha_2 = x_2 + x_3$$
$$\alpha_4 = x_4 - x_3$$



Figure 2. Dependence of K_c on composition in the system formic acid (1)–ethanol (2)–ethyl formate (3)–water (4) at 298.15 K. (a) Diagram in coordinates "transformed composition variables $\alpha_i - K_c$ " ($\alpha_1 = x_1 + x_3$, $\alpha_2 = x_2 + x_3$): red points, values of K_c calculated from obtained experimental data; (b) surface K_c ; (c) projections of isolines of K_c on the square of α -variables (values of K_c are indicated near every isoline).

where x_i is a molar fraction of specie *i*. As a result the composition space is a square of α -variables (Figure 2). In Figure 2a we presented the dependence of K_c on composition using α -variables. The resulting surface K_c is given in Figure 2b. The disposition of isolines of K_c ($K_c = \text{const}$) at the surface of CE is presented in Figure 2c as projections of these isolines on the square of α -variables. The construction of isolines had been performed using spline interpolation. These diagrams give a clear presentation of concentration dependence of K_c for the surface of CE, in other words, the relative concentrations of reagents. Such dependence could be useful for the design of ethyl formate synthesis.

4. CALCULATION OF THERMODYNAMIC CONSTANT OF CE

The thermodynamic constant of CE, K_a

$$K_{a} = \prod a_{i}^{\nu_{i}}$$

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where a_i is an activity of component *i*, and ν_i a stoichiometric number of reactants and products that are negative and positive, respectively, was calculated using the modified UNIFAC model.¹⁴ The authors of ref 14 developed and supplemented the original UNIFAC model proposed earlier in work 15. This new approach, according to ref 14 can be applied more reliably for systems involving molecules that are very different in size. According to the UNIFAC model the activity coefficients γ_i is determined by the equation

$$\ln \gamma_i = \ln \gamma_i^{\rm C} + \ln \gamma_i^{\rm I}$$

where γ_i^{C} is a combinatorial part and γ_i^{R} is a residual part.¹⁴ All parameters that are necessary for the calculations have been also taken from ref 14.

The value of thermodynamic constant K_a is the only one for the given temperature and pressure and, as it is well-known, does not depend on composition. Nevertheless the results of the calculation of K_a on the base of experimental data often lead to the large scatter of the data. This is due to the choice of models for calculations (see e.g., ref 16) or other reasons. It can be also explained by high sensitivity of the results even to minor data errors for small values of compositions, that is, for areas of the surface CE close to the edges of the composition tetrahedron. Because of it, the values of K_a were calculated on the base of experimental data for the middle area of composition: eight compositions for the vicinities of tetrahedron tops (corresponding to ethanol and ethyl formate) had not been considered. The calculated K_a have the value 4.3 \pm 0.8. The relative deviation (σ) was calculated using the following equation:

$$\sigma = \frac{|x_i - \overline{x}|}{\overline{x}}$$

Despite the relatively large spread of this value the averaged magnitudes should satisfactorily characterize the chemical equilibrium.

5. CONCLUSIONS

New experimental data on CE for the system formic acidethanol-ethyl formate-water at 298.15 K and atmospheric pressure (101 kPa) were obtained. The surface of CE was constructed in a 3D concentration space of a composition tetrahedron. The mutual position of the chemical equilibrium surface and the binodal surface was additionally analyzed: the absence of the intersection of these surfaces was revealed. It was shown that the CE of esterification of formic acid with ethanol at 298.15 K is achieved only in the homogeneous area, which is a positive trend for the industrial process of synthesis of ethyl formate. The data on the so-called "concentration constant" of CE (K_a) are also presented as isolines K_a in the square of transformed composition variables. The value of the thermodynamic constant of CE for 298.15 K was estimated on the basis of experimental data and the UNIFAC model: $K_a =$ 4.3 ± 0.8 .

AUTHOR INFORMATION

Corresponding Author

Alexander Toikka – Saint Petersburg State University, Department of Chemical Thermodynamics and Kinetics, Peterhof, St. Petersburg 198504, Russia; orcid.org/0000-0002-1863-5528; Email: a.toikka@spbu.ru

Authors

Artemiy Samarov – Saint Petersburg State University, Department of Chemical Thermodynamics and Kinetics, Peterhof, St. Petersburg 198504, Russia; orcid.org/0000-0002-9385-1335

Maya Trofimova – Saint Petersburg State University, Department of Chemical Thermodynamics and Kinetics, Peterhof, St. Petersburg 198504, Russia

Maria Toikka – Saint Petersburg State University, Department of Chemical Thermodynamics and Kinetics, Peterhof, St. Petersburg 198504, Russia

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jced.9b01205

Notes

The authors declare no competing financial interest.

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