J. Chem. Eng. Data **2007,** *52,* 20−23

Articles

Vapor−Liquid and Chemical Equilibria in the Ethanol + Ethanoic Acid System at 348.15 K

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Phase and chemical equilibria in the quaternary water + ethanol + ethanoic acid + ethyl ethanoate system was measured in a modified Dvorak and Boublík still. In total, 39 experimental points at 348.15 K were determined. The experimental data were correlated by means of the maximum likelihood procedure by using the NRTL model. Binary model parameters for the four nonreacting binary subsystems were obtained from available experimental vapor−liquid equilibrium data by using either the Hayden−O'Connell or Marek−Standart correction to account for the nonideality of vapor phase. NRTL parameters for the water + ethyl ethanoate and ethanol + ethanoic acid systems were estimated from the global optimization based on the quaternary data. The results obtained from the correlation show a good agreement of calculated and experimental data. The three-dimensional phase diagrams for the quaternary system have been constructed with use of transformed compositions.

Introduction

This paper is the second one in the series dealing with phase equilibrium accompanied with chemical reaction. In the first paper,[1] the vapor−liquid equilibrium (VLE) in the esterification reaction isopropanol + ethanoic acid ⇔ isopropyl ethanoate + water was investigated. The knowledge of phase equilibria in such systems is rather important, especially in connection with industrially interesting "reactive distillations", which are in fact coupling reactor with separation unit.

The quaternary water + ethanol + ethanoic acid + ethyl ethanoate system was chosen as a second model system. The 88 isobaric data points at atmospheric pressure have been measured by Kang at al.[2] The system was also investigated at atmospheric pressure by Hirata and Komatsu;[3] however, the data cannot be directly used for comparison. Since there are azeotropes present in the three binaries consisting of ethanol, water, and ethyl ethanoate (see ref 4), the occurrence of a reactive azeotrope in the studied quaternary system seems to be most likely.

Experimental Section

Phase equilibrium in the title quaternary system is rather complex since the chemical equilibrium is superimposed on it. Before the start of VLE measurements on the reactive system, we had to determine how the two types of equilibria affect each other. Preliminary investigation of esterification dynamics was necessary. The experiments were conducted by using the modified Dvorak and Boublik recirculating still (see ref 5) with liquid-phase total volume of 150 mL.

Materials. The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) with respective purity specifications as follows: ethanol absolute, analytical reagent ≥ 99.8%; ethanoic acid, puriss p.a., > 99.8%; ethyl ethanoate, puriss p.a., ≥ 99.9%; all of them were used as received. *p*-Toluenesulfonic acid p.a. was purchased from Lachema (Brno, Czech Republic). The water sample was twice distilled.

Kinetics of Chemical Reaction. An equimolar mixture of ethanol + ethanoic acid was charged into the still and boiled at a constant temperature of 348.15 K for 12 h. Samples of both the vapor and liquid phases were collected every 2 h. It was found that the rate of esterification was rather slow; about 6 mol % of ethyl ethanoate was formed during the whole period. In order to accelerate the reaction rate, 1.5 wt % of *p*-toluenesulfonic acid as catalyst was added to the liquid equimolar mixture. After that, the boiling point of the mixture was measured continuously for 8 h at 348.15 K. It was observed that after 5 h, the boiling point of the mixture attained a constant value, indicating that the state of both chemical and phase equilibrium was reached. A maximum amount of 36 mol % of ethyl ethanoate was formed. It was found that the time required to achieve both chemical and phase equilibria is dependent on the initial ratio of ethanol/ethanoic acid/water/ethyl ethanoate in the investigated mixture. Within the range of compositions explored in this study, the time required to reach the equilibrium was (3 to 8) h.

Vapor−Liquid Equilibrium Measurements. For the title system, 39 experimental points at isothermal (348.15 K) conditions were determined. In order to cover a meaningful composition range for the quaternary reactive mixture, a set of experimental runs has been carried out, with each starting with different ratios of reactants to products and then adding successively one of the reactants. The VLE variables were determined after chemical equilibrium was reached and after temperature and pressure reached constant values. Temperature was measured by using the F250 precision thermometer (ΑΣΛ

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10.1021/je060143m CCC: $37.00

Table 1. NRTL Parameters for Binary Subsystems of the Water (1) + Ethanol (2) + Ethanoic Acid (3) + Ethyl Ethanoate (4) System

subsystem	$G_{ij}-G_{jj}$ $\text{J}\cdot\text{mol}^{-1}$	$G_{ji}-G_{ii}$ $\text{J}\cdot\text{mol}^{-1}$	α	reference
(i) + (j)				
(1) + (2)	648.139	1986.89	−1.3544	11
(1) + (3)	594.750	814.990	−5.2505	12
(1) + (4)	1035.620	486.390	0.8652	optimized in this work
(2) + (3)	−769.423	856.328	−1.4283	optimized in this work
(2) + (4)	993.014	1281.82	−0.5876	11
(3) + (4)	−6522.74	9952.13	0.1045	13

Automatic Systems Laboratories) calibrated against a platinum resistance thermometer with accuracy better than ± 0.02 K on ITS-90. Pressure was controlled by the precision pressure controller PPC 159 (Texas Instruments) and determined indirectly from the boiling point of water in an ebulliometer connected in parallel to the equilibrium still with overall accuracy of 0.1% of the measured value. Compositions of the quaternary mixture were determined by gas chromatograph HP5890 (Hewlett−Packard) with a thermal conductivity detector calibrated by three binary subsystems of ethanol with ethanoic acid, water, or ethyl ethanoate. Calibration curves were obtained by producing chromatograms for a set of solutions of known composition; then the peak area of each component was correlated with the corresponding mass. The stainless steel column was 4 m long, 3 mm o.d., and filled with 80/100 Porapak Q. The optimum operational conditions were as follows: injector temperature 200 °C; oven temperature 180 °C; detector temperature 200 °C; helium was used as carrier gas with a flow rate of 30 $\text{mL}\cdot\text{min}^{-1}$. Estimated uncertainty in phase compositions so determined was 0.005 and 0.01 in mole fraction of the liquid and vapor phase, respectively.

Phase Equilibrium with Chemical Reaction Equilibrium Computation

The theoretical principles of the computations were presented in the first paper[1] of the series. However, it is worth mentioning that for systems containing polar compounds with strong molecular association in the vapor phase such as ethanoic acid, the association effect must not be neglected in a VLE computation. In a general method for prediction of the second virial coefficients, Hayden and O'Connell[6] (H−C) took into account these effects by using a chemical theory. Marek and Standart[7,8] (M−S) handled the problem by treating the association of molecules as a chemical reaction. Both the corrections were taken into the account (see ref 1 for details).

Results and Discussion

All 39 experimental points P, T, x, and y were correlated by using the NRTL model. For this purpose, first the binary model parameters for the four nonreacting subsystems have been obtained from correlation of literature data. To take into account the nonideal behavior of the vapor phase, the M−S theory was used for binary mixtures containing ethanoic acid while the H−C method was used in all other cases. The regression was performed by means of the maximum likelihood method with use of the program described by Hála et al.,[9] which was further modified to incorporate the M−S theory for mixtures containing ethanoic acid. This type of correlation has been carried out for all binary subsystems except for the two mutually reacting mixtures. The obtained NRTL parameters are listed in Table 1 along with the references to binary data literature sources.

The remaining two triads of parameters for the water + ethyl ethanoate and ethanol + ethanoic acid binaries were then estimated by means of global optimization based on the complete set of experimental points consisting of the isothermal and isobaric quaternary data. A simplified maximum likelihood procedure based on minimizing the objective function:

$$S = \sum_j \Big[\sum_i [(x_i^{\text{exp}} - x_i^{\text{cal}})^2/\sigma_{xi}^2 + (y_i^{\text{exp}} - y_i^{\text{cal}})^2/\sigma_{yi}^2] + (T^{\text{exp}} - T^{\text{cal}})^2/{\sigma_T}^2 + (P^{\text{exp}} - P^{\text{cal}})^2/{\sigma_p}^2\Big] \quad (1)$$

was used, where index j runs over all 39 experimental observations (and is skipped in designating the individual variables within summation over j) and index i runs over 3 components (whose molar fractions are independent in a quaternary system). On the basis of the measurement procedure and equipment, the standard deviation estimates were adopted (for all observations and components) as follows: $\sigma_{x_i} = 0.005$, $\sigma_{y_i} = 0.01$, $\sigma_T = 0.05$ K, and $\sigma_P = 0.001$ P. Vapor-phase imperfection and association of ethanoic acid were both again taken into account during this evaluation by employing the H−C and M−S methods, respectively. The six resulting NRTL parameters optimized in this work for the two reacting binaries are also listed in Table 1. All the experimental values and calculated deviations in liquid and vapor compositions, temperature, and pressure together with chemical equilibrium constant calculated from

$$\ln \gamma_i = \frac{\sum_{r=1}^{k} \tau_{ri} G_{ri} x_r}{\sum_{s=1}^{k} G_{si} x_s} + \sum_{r=1}^{k} \frac{x_r G_{ir}}{\sum_{s=1}^{k} G_{sr} x_s} \left(\tau_{ir} - \frac{\sum_{t=1}^{k} \tau_{tr} G_{tr} x_t}{\sum_{s=1}^{k} G_{sr} x_s} \right) \quad (2)$$

where $G_{ij} = \exp[-\alpha_{ij}\tau_{ij}]$; $\tau_{ij} = (g_{ij} - g_{jj})/RT$; $\tau_{ii} = 0$; $\alpha_{ij} = \alpha_{ji}$; $G_{ii} = 1$, and k in number of components in a mixture.

All the experimental quaternary values and calculated deviations in liquid and vapor compositions, temperature, and pressure together with chemical equilibrium constant are summarized in Table 2 where also the mean absolute deviations in the single variables are reported. The average value of the chemical equilibrium constant is $K_r = 5.5$; however, the values calculated for single observations are largely scattered. Clearly, since the chemical equilibrium constant is not an explicit parameter of the thermodynamic model used, it cannot be adjusted (i.e., optimized) to obtain a better fit of data. Actually it is calculated "as a byproduct" only.

The VLE in binary and ternary mixtures can be explicitly described by a two- or three-dimensional phase diagram. For a graphical representation of a quaternary mixture, the number of variables must be reduced. Therefore, Barbosa and Doherty[10] introduced transformed composition variables for reactive systems as follows:

$$\begin{cases} X_1 = x_1 - x_4;\ X_2 = x_2 + x_4;\ X_3 = x_3 + x_4;\ X_4 = x_4 - x_4 = 0 \\ Y_1 = y_1 - y_4;\ Y_2 = y_2 + y_4;\ Y_3 = y_3 + y_4;\ Y_4 = y_4 - y_4 = 0 \end{cases} \quad (3)$$

which fulfills the conditions $X_1 + X_2 + X_3 = 1$ and $Y_1 + Y_2 + Y_3 = 1$. This transformation is very useful for graphical representation; however, some information is lost (e.g., some nonreactive azeotropes may not be visible). In general, it can be stated that this is a purely mathematical re-formulation of the concentrations, providing a tool that describes reactive distillation in a way that is analogous to conventional distillation.

Table 2. Experimental Vapor−Liquid Equilibrium Data for the Water (1) + Ethanol (2) + Ethanoic Acid (3) + Ethyl Ethanoate (4) System at 348.15 K and Deviation from Model

run	x_{1exp}	x_{2exp}	x_{3exp}	y_{1exp}	y_{2exp}	y_{3exp}	P_{exp} / kPa	Δx_1	Δx_2	Δx_3	Δy_1	Δy_2	Δy_3	ΔP / kPa	ΔT / K	K_r
1	0.3661	0.1510	0.1822	0.3069	0.1612	0.0177	92.61	0.0042	0.0054	0.0003	−0.0238	−0.0253	−0.0013	−0.01	0.01	5.7
2	0.3688	0.1505	0.1899	0.3168	0.1586	0.0190	92.26	0.0050	0.0044	−0.0023	−0.0270	−0.0236	−0.0021	−0.02	0.02	6.2
3	0.3820	0.0917	0.2604	0.3334	0.1098	0.0325	86.76	0.0045	0.0027	−0.0014	−0.0232	−0.0151	−0.0005	−0.01	0.01	6.1
4	0.3715	0.0584	0.3231	0.3544	0.0730	0.0558	76.88	−0.0105	0.0014	0.0488	0.0075	−0.0368	−0.0422	0.13	−0.16	3.4
5	0.3540	0.0343	0.4150	0.3486	0.0504	0.0979	68.39	−0.0123	−0.0011	0.0531	−0.0045	−0.0355	−0.0267	0.18	−0.20	3.7
6	0.3050	0.0193	0.4516	0.2835	0.0275	0.1305	60.30	0.0031	0.0099	−0.0007	−0.0151	−0.0362	−0.0150	−0.01	0.02	4.4
7	0.2831	0.0095	0.5432	0.2923	0.0181	0.2027	52.95	0.0014	0.0078	0.0081	−0.0180	−0.0362	−0.0115	0.02	−0.02	4.7
8	0.2353	0.0047	0.6339	0.3072	0.0109	0.2822	39.00	0.0047	0.0098	−0.0059	−0.0181	−0.0406	0.0042	−0.03	0.03	5.3
9	0.1821	0.0022	0.7276	0.2449	0.0056	0.4491	39.98	0.0020	0.0079	0.0018	−0.0133	−0.0358	0.0007	−0.00	0.00	5.8
10	0.1371	0.0015	0.7998	0.2204	0.0033	0.5595	34.54	−0.0002	0.0066	0.0093	−0.0097	−0.0314	−0.0052	0.03	−0.03	6.1
11	0.1294	0.0010	0.8142	0.2043	0.0020	0.6190	33.31	0.0051	0.0059	−0.0062	−0.0220	−0.0298	−0.0016	−0.04	0.04	6.4
12	0.2594	0.4103	0.0358	0.2087	0.3557	0.0014	105.56	0.0036	0.0046	−0.0002	−0.0183	−0.0233	0.0006	−0.01	0.01	6.9
13	0.2930	0.3342	0.0570	0.2180	0.3000	0.0025	104.57	0.0031	0.0032	−0.0009	−0.0151	−0.0169	−0.0033	−0.01	0.01	7.4
14	0.3068	0.2720	0.0829	0.2346	0.2478	0.0046	101.86	0.0040	0.0021	−0.0003	−0.0194	−0.0115	−0.0027	−0.01	0.01	7.9
15	0.3252	0.2102	0.1184	0.2472	0.1921	0.0084	97.48	−0.0092	−0.0026	−0.0018	−0.0201	−0.0140	−0.0006	−0.13	0.13	6.0
16	0.3712	0.1281	0.1642	0.2675	0.1342	0.0144	91.73	−0.0028	−0.0009	−0.0119	−0.0185	−0.0177	−0.0023	−0.04	0.04	2.2
17	0.3573	0.0848	0.2288	0.2768	0.0907	0.0266	84.14	−0.0022	−0.0009	−0.0118	−0.0233	−0.0170	−0.0017	−0.03	0.04	3.8
18	0.3499	0.0482	0.3188	0.2850	0.0584	0.0521	75.37	−0.0013	0.0022	−0.0167	−0.0298	−0.0298	−0.0029	−0.05	0.05	4.3
19	0.3322	0.0246	0.4190	0.2931	0.0336	0.1029	63.45	0.0008	−0.0010	−0.0070	−0.0115	−0.0045	−0.0016	−0.03	0.03	3.4
20	0.0587	0.8954	0.0000	0.0523	0.8482	0.0000	92.89	0.0026	−0.0007	−0.0024	−0.0192	−0.0006	−0.0010	−0.01	0.01	5.1
21	0.1324	0.7442	0.0032	0.1118	0.6608	0.0000	98.99	0.0031	0.0031	0.0005	−0.0167	−0.0143	−0.0007	−0.01	0.01	5.9
22	0.2102	0.5906	0.0115	0.1654	0.5118	0.0004	103.02	0.0040	0.0033	0.0013	−0.0217	−0.0172	−0.0043	−0.00	0.00	6.6
23	0.2502	0.4828	0.0241	0.2011	0.4147	0.0009	104.75	0.0042	0.0012	0.0021	−0.0213	−0.0056	−0.0027	0.01	−0.01	6.5
24	0.2922	0.3757	0.0443	0.2197	0.3269	0.0025	104.46	0.0050	−0.0016	−0.0086	−0.0222	−0.0002	−0.0018	−0.03	0.03	4.3
25	0.2418	0.0119	0.5438	0.2632	0.0189	0.1898	55.06	0.0111	0.0160	−0.0252	−0.0039	−0.0277	−0.0283	−0.12	0.13	5.0
26	0.2409	0.0115	0.5511	0.2706	0.0180	0.1913	54.37	0.0113	0.0154	−0.0274	−0.0047	−0.0362	−0.0154	−0.13	0.13	4.9
27	0.2863	0.0231	0.4366	0.2750	0.0315	0.1084	63.70	0.0099	0.0135	−0.0250	−0.0073	−0.0399	−0.0080	−0.12	0.12	5.4
28	0.3311	0.0457	0.3155	0.2765	0.0545	0.0523	74.73	0.0062	0.0095	−0.0121	−0.0119	−0.0359	−0.0055	−0.06	0.06	5.9
29	0.3317	0.0854	0.2415	0.2749	0.0890	0.0280	84.73	0.0058	0.0075	−0.0087	−0.0174	−0.0330	−0.0047	−0.05	0.05	6.3
30	0.3024	0.2814	0.0764	0.2291	0.2593	0.0039	103.20	0.0091	0.0008	−0.0124	−0.0305	−0.0098	−0.0031	−0.06	0.05	5.8
31	0.3132	0.2203	0.1079	0.2389	0.2050	0.0071	99.53	0.0069	0.0034	−0.0077	−0.0253	−0.0193	−0.0037	−0.04	0.04	6.5
32	0.3235	0.1586	0.1495	0.2510	0.1497	0.0119	94.83	0.0417	0.0352	−0.0363	0.0277	0.0081	−0.0106	−0.19	0.20	7.4
33	0.3164	0.1081	0.2054	0.2576	0.1098	0.0208	89.40	0.0423	0.0456	−0.0428	0.0448	0.0282	−0.0150	−0.22	0.26	9.0
34	0.3293	0.0675	0.2665	0.2727	0.0742	0.0339	81.44	0.0325	0.0458	−0.0386	0.0406	0.0452	−0.0408	−0.19	0.24	3.8
35	0.3136	0.0420	0.3439	0.2760	0.0514	0.0575	73.31	0.0363	0.0486	−0.0393	0.0206	0.0584	−0.0510	−0.17	0.23	6.5
36	0.2766	0.0223	0.4675	0.2883	0.0312	0.1124	62.75	0.0063	0.0189	−0.0057	0.0046	0.0143	−0.0656	−0.06	0.08	8.0
37	0.2645	0.0114	0.5459	0.2797	0.0188	0.2008	53.25	0.0004	0.0095	0.0123	−0.0029	−0.0005	−0.1052	−0.03	0.04	5.7
38	0.2232	0.0027	0.6504	0.2843	0.0102	0.3183	45.06	0.0048	0.0076	0.0073	−0.0148	−0.0042	−0.0625	−0.02	0.03	5.0
39	0.1647	0.0019	0.7554	0.2613	0.0048	0.4612	38.08	−0.0004	−0.0178	0.0492	−0.0018	−0.0635	−0.0105	0.08	−0.14	1.0
mean								0.0083	0.0099	0.0142	0.0179	0.0242	0.0145	0.06	0.07	5.5

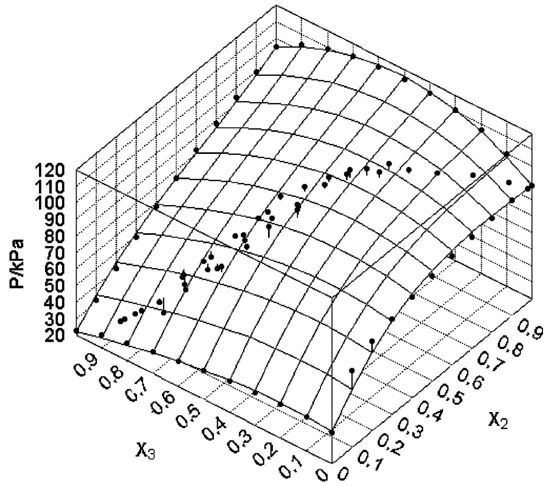

Figure 1. Three-dimensional bubble point pressure surface at 323.15 K: modified composition coordinates, X_2, X_3, versus pressure, P.

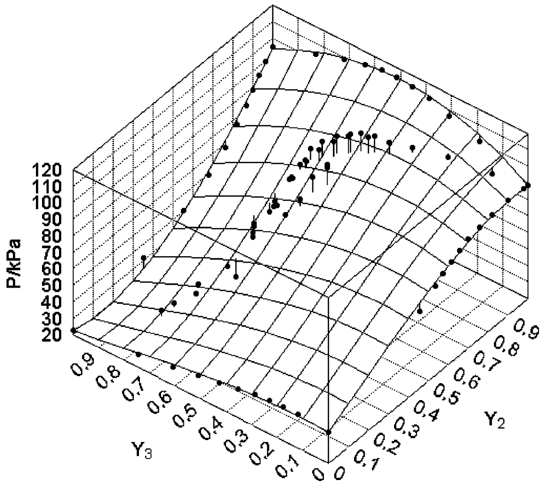

Figure 2. Three-dimensional dew point pressure surface at 323.15 K: modified composition coordinates, Y_2, Y_3, versus pressure, P.

By using the transformed composition coordinates, experimental bubble and dew point surfaces corresponding to chemical equilibrium at isothermal condition of 348.15 K are shown as a three-dimensional projection in Figures 1 and 2, respectively. All available (binary and quaternary) data were used as a basis for drawing the best fitted surface. The surface of both the dew and bubble pressures illustrates how the experimental points fit the data on reaction isotherm; bars attached to individual points show quantitative difference between smoothed and experimental value.

Recently, the same quaternary system was investigated by Calvar et al.[14] at 101.3 kPa isobaric conditions. In general, the isobaric data could be used for comparison, however, they are certainly not in chemical equilibrium since the authors did not catalyze the reaction. As it is shown in the present study, the reaction without catalyst is extremely slow and this is why any remarkable conversion could not be observed even after several hours. Therefore, the data[14] must be erroneous since the chemical equilibrium was not reached.

Conclusions

As can be observed from Table 2 and Figures 1 and 2, the new experimental data are well-correlated based on 12 NRTL parameters for four binary systems taken from the literature. The six remaining parameters for the two reacting binaries were optimized in this work. Mean absolute deviations between experimental data and the data correlated by using the NRTL equation are 0.0108 mole fraction in liquid phase and 0.0188 mole fraction in vapor phase; the mean absolute deviations of 0.06 kPa and 0.07 K were found for pressure and temperature, respectively. Deviations for some individual points are somewhat greater than expected, which is likely a combined effect of both the imperfection of the model and the relatively large analytical error in the boundary concentration regions. On the three-dimensional diagrams is shown how pressure of the system is dependent on composition and in which direction the distillation would proceed.

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Received for review March 28, 2006. Accepted September 27, 2006. The authors acknowledge partial support by the Grant Agency of Czech Republic (Grant 203/03/1588).

JE060143M