Phase equilibria and excess properties for binary systems in reactive distillation processes. Part II. Ethyl acetate synthesis

Sarah Brandt[a], Sven Horstmann[a,*], Sven Steinigeweg[b], Jürgen Gmehling[c]

[a] LTP (Laboratory for Thermophysical Properties) GmbH, Associated Institute at the University of Oldenburg, Marie-Curie-Str. 10, D-26129 Oldenburg, Germany
[b] University of Applied Science Emden/Leer, EUTEC Institute, D-26723 Emden, Germany
[c] University of Oldenburg, Department of Industrial Chemistry, D-26111 Oldenburg, Germany

A B S T R A C T

In this investigation isothermal vapor–liquid equilibrium data (VLE) and excess enthalpy (H^E) data were measured for the binary systems required for the design of reactive distillation processes for the ethyl acetate production. The isothermal P–x data was measured with a static apparatus, the heat of mixing measurements were performed with a commercial isothermal flow calorimeter. To the experimental data from this work and mixture data from other authors temperature dependent UNIQUAC parameters were fitted.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

For the accurate design and optimization of separation processes like distillation columns the reliable knowledge of the phase equilibrium behavior is required. The ethyl acetate synthesis by esterification of acetic acid with methanol, and the back reaction, the hydrolysis of ethyl acetate, have received growing interest as a model for reactive distillation processes [1]. The synthesis and hydrolysis of methyl acetate, as first homologous of the row, was already published by Horstmann et al. [2].

While for most of the binary systems experimental data are available in literature (Dortmund Data Bank, DDB 2013) [3], there is a lack of experimental information for some systems. Therefore in this work, isothermal P–x data measured with the static method are presented for the binary systems ethanol + acetic acid and ethyl acetate + acetic acid. Excess enthalpy (H^E) data were measured for the binary systems ethyl acetate + ethanol, ethanol + acetic acid, ethanol + water, ethyl acetate + acetic acid,

and ethyl acetate + water, which are important for a correct description of the temperature dependence of activity coefficients following the Gibbs–Helmholtz equation:

$$\left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_{P,x} = \frac{\overline{H}_i^E}{R} \tag{1}$$
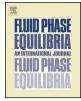
The experimental vapor–liquid equilibrium (VLE) and H^E data of this work as well as VLE, H^E, LLE, and azeotropic data from other authors are presented together with a UNIQUAC correlation which can be used in simulation software packages.

2. Experimental

2.1. Materials

Ethanol, ethyl acetate and acetic acid were purchased from commercial sources. The substances were dried over molecular sieves and afterwards distilled and degassed as described by Fischer and Gmehling [4]. Deionized water was prepared in our laboratory. The final purity and water content were determined by gas chromatography and Karl-Fischer titration and are given in Table 1.

Table 1
Properties of the pure components.

component	Supplier	purity (%GC)	water content (mass ppm)
Ethanol	Acros	>99.9	20
Ethyl acetate	Sigma-Aldrich	>99.8	30
Acetic acid	Acros	>99.9	40

Table 2
Experimental excess enthalpy data (H^E) for the system ethyl acetate (1) + ethanol (2) at 363.15 K and 1548 kPa.

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
0.0151	97.3	0.4226	1667
0.0305	198	0.4732	1717
0.0624	392	0.5265	1710
0.0956	578	0.5828	1690
0.1302	757	0.6424	1618
0.1664	926	0.7054	1486
0.2042	1083	0.7724	1276
0.2438	1228	0.8435	972
0.2853	1374	0.9192	555
0.3288	1489	0.9589	292
0.3745	1582		

2.2. Apparatus and procedure

The VLE measurements (isothermal P–x data) were carried out in a computer operated static device following the principle proposed by Gibbs and Van Ness [5]. The apparatus was described earlier [6,7]. The thermostated, purified, and degassed compounds are filled into the thermoregulated equilibrium cell by means of precise piston injectors. The injectors are driven by stepping motors. The pressure inside the equilibrium cell is measured with a calibrated pressure sensor (Model 245A, Paroscientific) or a dead weight pressure balance (Model 80005, Desgranges & Huot), respectively. For the temperature measurement a Pt100 resistance thermometer (Model 1506, Hart Scientific) is used. The feed compositions are determined from the known quantities of liquids injected into the equilibrium cell by piston injectors. The liquid phase compositions in equilibrium are obtained by solving mass and volume balance equations which are also taking the vapor–liquid equilibrium into account. The experimental uncertainties for both setups are $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa + 0.0001 × (P (Pa)), and $\sigma(x_i) = 0.0001$.

For the determination of the excess enthalpy data a commercial isothermal flow calorimeter (Model 7501, Hart Scientific) described by Gmehling [8] was used. In this apparatus, two syringe pumps (Model LC-2600, ISCO) provide a flow of constant composition through a calorimeter cell (placed in a thermostat) equipped with a pulsed heater and a Peltier cooler. The Peltier cooler is working at

Table 3
Experimental excess enthalpy data (H^E) for the system ethyl acetate (1) + ethanol (2) at 413.15 K and 1307 kPa.

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
0.0151	108	0.4226	1773
0.0306	222	0.4732	1815
0.0624	439	0.5265	1812
0.0956	646	0.5829	1765
0.1302	841	0.6424	1663
0.1664	1028	0.7055	1502
0.2042	1198	0.7724	1261
0.2438	1360	0.8435	939
0.2853	1502	0.9192	524
0.3288	1623	0.9589	276
0.3745	1725		

Table 4
Experimental VLE data (P–x) for the system ethanol (1) + acetic acid (2) at 298.15 K.

x_1	P (kPa)	x_1	P (kPa)
0.0000	2.05	0.5095	4.26
0.0124	2.11	0.5694	4.62
0.0569	2.28	0.6449	5.14
0.1053	2.45	0.7231	5.72
0.1613	2.65	0.7978	6.29
0.2251	2.89	0.8606	6.78
0.2982	3.19	0.9124	7.18
0.3725	3.52	0.9520	7.48
0.4382	3.84	0.9853	7.71
0.4440	3.88	1.0000	7.82
0.4999	4.19		

Table 5
Experimental VLE data (P–x) for the system ethanol (1) + acetic acid (2) at 323.15 K.

x_1	P (kPa)	x_1	P (kPa)
0.0000	7.62	0.5026	15.92
0.0195	7.90	0.5724	17.54
0.0393	8.17	0.6485	19.48
0.0746	8.65	0.7270	21.62
0.1153	9.22	0.8018	23.75
0.1664	9.94	0.8644	25.56
0.2265	10.84	0.9158	27.01
0.2967	11.97	0.9547	28.09
0.3700	13.28	0.9868	28.96
0.4404	14.62	1.0000	29.32

Table 6
Experimental excess enthalpy data (H^E) for the system ethanol (1) + acetic acid (2) at 323.15 K and 1548 kPa.

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
0.0247	45.1	0.5464	148
0.0493	84.4	0.6467	111
0.0987	145	0.7473	80.3
0.1729	196	0.8229	60.8
0.2473	215	0.8987	38.9
0.3467	212	0.9493	21.1
0.4464	182	0.9746	11.7

Table 7
Experimental excess enthalpy data (H^E) for the system ethanol (1) + water (2) at 333.15 K and 1824 kPa.

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
0.0079	−39.9	0.2747	−190
0.0160	−79.5	0.3173	−147
0.0333	−155	0.3653	−101
0.0519	−217	0.4196	−52.3
0.0719	−266	0.4818	−7.3
0.0936	−297	0.5535	27.4
0.1172	−308	0.6372	41.8
0.1430	−306	0.7361	31.2
0.1712	−288	0.8548	0.6
0.2023	−259	0.9236	−15.5
0.2366	−231	0.9608	−12.1

constant power causing a constant heat loss from the calorimeter cell. To keep the temperature constant this heat flow is compensated by the pulsed heater. The heats of mixing effects are obtained from the change of frequency of the pulsed heater between the base line (pure components) and the investigated mixture. Endothermal heat effects cause an increase and exothermal heat effects cause a decrease in frequency. A back-pressure regulator serves to keep the pressure at a constant level at which evaporation and degassing effects can be prevented.