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Vapor−Liquid Equilibrium in Binary Systems Ethanol + C4 and C5 Hydrocarbons

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Isothermal vapor−liquid equilibrium data are measured for seven binary systems containing ethanol and different C4 and C5 hydrocarbons: *cis*-but-2-ene, *trans*-but-2-ene, 2-methyl-but-2-ene, pent-1-ene, 2-methyl-but-1-ene, cyclopentene, and cyclopentane. The experimental synthetic method does not require the sampling of the vapor and liquid phases. The results were correlated by Peng−Robinson equation of state with the Huron−Vidal mixing rules.

Introduction

Alcohols and ethers are being considered as octane enhancers without lead. Among the last ones methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME) are undoubtedly the most studied compounds. A typical plant for the production of ETBE can be ideally divided into two sections:

(1) a reaction section, in which all the chemical reactions necessary for the production of ETBE, as well as secondary reactions, take place;

(2) a separation section, in which the blending agent is separated from the other compounds and in which these compounds are also separated for their recycle.

The optimization of the separation section and the simulation of the whole process require the use of thermodynamic models that should predict with precision the vapor−liquid equilibria and in particular the presence of azeotropes for the compounds presents in the separation section. These include a C_4−C_5 hydrocarbon blend from the feed, ethanol and other alcohols from the feed, and secondary reactions and water from the secondary reactions as well as from a washing tower used for cleaning the hydrocarbon blend.

For this reason new experimental data for ethanol with various C4 and C5 hydrocarbons are presented.

Experimental Section

Apparatus and Procedure. The experimental equipment and the procedure have been described in details by Fransson et al. (1992). Measurements were made by the static method using well-degassed materials. From a knowledge of the volume of the cell, the masses of each component, the temperature, and the pressure and using an equation of state coupled with a flash algorithm the compositions of the liquid and vapor phases were calculated. The total volume of the cell was determined to be (60.44 ± 0.05) cm^3; the masses of the components were determined by successive weighing during the filling procedure with a precision balance (0.1 mg). The temperature stability of the thermostatic bath was 0.01 K. The temperature was measured with a platinum resistance thermometer (Thermo-Est, 100 Ω) calibrated using a reference thermometer (IPTS-68); the standard deviation in temperature was 0.005 K. The pressure was measured with a pressure transducer, and the expected standard deviation was 1.8 kPa.

Chemicals. The chemicals that are used are *cis*-but-2-ene, *trans*-but-2-ene with a purity higher than 99.5% from Praxair, 2-methyl-but-2-ene, pent-1-ene, 2-methyl-but-1-ene, cyclopentene, and cyclopentane with a purity higher than 99% from Fluka AG and ethanol with a purity higher than 99.9% from C. Erba. The ethanol was stored over molecular sieves 5 Å in order to reduce the water content.

To check the purity of the products and the reliability of our equipment, vapor pressure data were measured (Table 1) for the C4 and C5 hydrocarbons and compared with values reported in the literature (DIPPR, 1989). It is important to note that the accuracy of the correlation reported in the literature (DIPPR, 1989) is not better than 3%. For that reason since the relative deviations are always lower it is possible to be satisfied both for the performance of the equipment and for the purity of the chemicals used. Some duplicated or triplicated measurements were also performed in order to check the repeatability of the measurements. Also this check was very satisfactory.

Results and Discussion

The quantities experimentally determined are the temperature T, the pressure P, the total volume, and the masses of each compound m_1 and m_2, which give the overall mole fraction z_i. These data are reported for the different systems studied in the Tables 2−8. The liquid x_i and the

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Table 1. Vapor Pressures P of Pure Hydrocarbons at Temperature T: Literature (lit) Values Obtained by Interpolation from DIPPR (1989) and Percent Relative Deviation

product	T/K	P/bar	P_{lit}/bar	$100[P - P_{\mathrm{lit}}/P)]$
cis-but-2-ne	323.68	4.577	4.499	1.74
	323.75	4.549	4.507	0.93
	374.46	1.498	14.436	0.42
	374.56	14.503	14.465	0.26
trans-but-2-ene	323.76	4.897	4.902	−0.10
	323.79	4.875	4.906	−0.64
	374.56	15.378	15.691	−2.0
	374.59	15.372	15.701	−2.09
2-methyl-but-2-ene	323.66	6.177	6.235	−0.93
	323.79	6.144	6.256	−1.79
	323.75	6.194	6.249	−0.88
	323.83	6.194	6.262	−1.08
	374.45	18.563	18.879	−1.67
	374.52	18.569	18.904	−1.77
	374.53	18.693	18.907	−1.13
	374.59	18.642	18.929	−1.52
pent-1-ene	323.44	1.948	1.951	−0.15
	323.33	1.946	1.944	0.10
	373.54	7.002	6.954	0.69
	373.53	7.004	6.953	0.73
2-methyl-but-1-ene	323.42	1.886	1.886	0
	323.40	1.891	1.885	0.32
	323.43	1.890	1.887	0.16
	323.42	1.891	1.886	0.27
	373.56	6.879	6.875	0.058
	373.51	6.878	6.867	0.16
	373.54	6.875	6.872	0.27
cyclopentane	323.50	1.061	1.050	1.05
	323.44	1.067	1.048	1.81
	323.40	1.059	1.047	1.15
	323.41	1.061	1.047	1.34
	373.58	4.208	4.204	0.095
	373.61	4.200	4.207	−0.17
	373.59	4.201	4.205	−0.095
cyclopentene	323.37	1.244	1.233	0.89
	323.38	1.248	1.233	1.21
	323.42	1.249	1.235	1.13
	323.43	1.247	1.235	0.97
	373.49	4.850	4.830	0.41
	373.62	4.850	4.845	0.10
	373.53	4.853	4.835	0.37

Table 2. Experimental and Calculated Data for the *cis*-But-2-ene (1) + Ethanol (2) System: Masses m_i, Overall Mole Fractions z_1, Temperature T, Pressure P, Liquid Mole Fractions x_1, Vapor Mole Fractions y_1

m_1/g	m_2/g	z_1	T/K	P/bar	P_{calc}/bar	x_1	y_1
20.1165	0.2524	0.985	323.72	4.51	4.55	0.9849	0.9868
22.3172	0.82	0.957	323.75	4.54	4.53	0.9570	0.9715
22.6133	1.9964	0.903	323.81	4.52	4.48	0.9024	0.9579
17.8409	6.248	0.701	323.74	4.34	4.35	0.6986	0.9484
14.7277	11.6357	0.510	323.81	4.17	4.17	0.5063	0.9424
9.6121	17.4238	0.312	323.75	3.59	3.59	0.3078	0.9274
2.9279	24.6622	0.089	50.59	1.82	1.82	0.0865	0.8404
20.1165	0.2524	0.985	374.55	14.62	14.57	0.9850	0.9825
22.3172	0.82	0.957	374.53	14.62	14.61	0.9572	0.9567
22.6133	1.9964	0.903	374.55	14.58	14.53	0.9025	0.9230
17.8409	6.248	0.701	374.57	13.71	13.77	0.6970	0.8711
14.7277	11.6357	0.510	374.54	12.87	12.85	0.5035	0.8460
9.6121	17.4238	0.312	374.57	10.96	10.97	0.3039	0.8036
2.9279	24.6622	0.089	374.52	5.91	5.91	0.0847	0.6070

Table 3. Experimental and Calculated Data for the *trans*-But-2-ene (1) + Ethanol (2) System: Masses m_i, Overall Mole Fractions z_1, Temperature T, Pressure P, Liquid Mole Fractions x_1, Vapor Mole Fractions y_1

m_1/g	m_2/g	z_1	T/K	P/bar	P_{calc}/bar	x_{1c}	y_1
19.8336	0.3283	0.980	323.79	4.88	4.89	0.9802	0.9826
20.1261	1.1572	0.935	323.75	4.86	4.84	0.9342	0.9643
20.298	1.3649	0.924	323.79	4.85	4.83	0.9231	0.9621
17.0389	3.0689	0.820	323.70	4.78	4.75	0.8180	0.9543
19.3797	6.2833	0.717	323.78	4.68	4.70	0.715	0.9518
15.2772	11.6108	0.519	323.73	4.41	4.46	0.5161	0.9453
8.8683	9.5030	0.434	323.86	4.30	4.27	0.4251	0.9401
3.8539	25.5387	0.110	323.76	2.36	2.36	0.1077	0.8765
19.8336	0.3283	0.980	374.52	15.46	15.46	0.9804	0.9772
20.1261	1.1572	0.935	374.52	15.50	15.49	0.9344	0.9404
20.298	1.3649	0.924	374.51	15.47	15.47	0.9233	0.9340
17.0389	3.0689	0.820	374.50	15.15	15.09	0.8169	0.8955
19.3797	6.2833	0.717	374.60	14.66	14.69	0.7141	0.8764
15.2772	11.6108	0.519	374.57	13.63	13.67	0.5137	0.8506
8.8683	9.5030	0.434	374.62	12.96	12.93	0.4140	0.8351
3.8539	25.5387	0.110	374.53	7.213	7.21	0.1057	0.6752

vapor y_i mole fractions were obtained according to the procedure suggested by Fransson et al. (1992), applying an equation of state to the whole set of experimental data.

Thermodynamic Models. We have used the Peng−Robinson model (Peng and Robinson, 1976) associated with the volume correction proposed by Peneloux (Peneloux and Rauzy, 1982).

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{1}$$

$$a = a_c[1 + m(1 - T_r^{0.5})]^2 \quad T_r = T/T_c \tag{2}$$

The m parameter was fitted to force the equation of state to calculate the experimental vapor pressure of the pure components.

The volume correction c was considered independent of the temperature. It was calculated from the saturated molar volume at 293 K given in the DIPPR Data Compilation (DIPPR, 1989).

$$V_{\mathrm{corr},i} = V_i - C_i \tag{3}$$

$$c = \sum_i c_i z_i \tag{4}$$

The parameter b of the equation was calculated with the classical mixing rule:

$$b = \sum_i^N \sum_j^N x_i x_j b_{ij} \tag{5}$$

$$b_{ij} = \frac{b_i + b_j}{2} \tag{6}$$

For the evaluation of a parameter, the Huron−Vidal approach (Huron and Vidal, 1979) was followed

$$a = b\cdot\left[\sum_{i=1}^N x_i \cdot \frac{a_{ii}}{b_i} - \frac{g_\infty^E}{\Lambda}\right] \tag{7}$$

where Λ is a numerical constant depending on the cubic equation of state used: for the Peng−Robinson equation its value is given by the following expression:

$$\Lambda = \frac{1}{2\cdot\sqrt{2}} \ln\left[\frac{2 + \sqrt{2}}{2 - \sqrt{2}}\right] \tag{8}$$

g_∞^E, excess Gibbs energy at infinite pressure, is expressed with the N.R.T.L. model (Renon and Prausnitz, 1978) in which the concentrations are expressed in terms

Table 4. Experimental and Calculated Data for the 2-Methyl-but-2-ene (1) + Ethanol (2) System: Masses m_i, Overall Mole Fractions z_1, Temperature T, Pressure P, Liquid Mole Fractions x_1, Vapor Mole Fractions y_1

m_1/g	m_2/g	z_1	T/K	P/bar	P_{calc}/bar	x_1	y_1
18.0087	0.3326	0.978	323.80	6.14	6.16	0.9778	0.9842
15.2896	1.0552	0.922	323.80	6.13	6.07	0.9210	0.9695
18.8947	2.3757	0.867	323.78	5.97	6.00	0.8655	0.9655
16.4181	6.1735	0.686	323.79	5.79	5.82	0.6817	0.9603
13.5893	9.7131	0.535	323.78	5.52	5.49	0.5288	0.9545
7.2612	20.1951	0.228	323.81	4.06	4.07	0.2230	0.9296
3.2566	25.1649	0.096	323.78	2.68	2.68	0.0927	0.8886
18.0087	0.3326	0.978	374.59	18.65	18.69	0.9780	0.9775
15.2896	1.0552	0.922	374.50	18.47	18.50	0.9207	0.9415
18.8947	2.3757	0.867	374.53	18.11	18.21	0.8650	0.9218
16.4181	6.1735	0.686	374.61	17.05	17.04	0.6785	0.8878
13.5893	9.7131	0.535	374.56	15.86	15.77	0.5233	0.8663
7.2612	20.1951	0.228	374.53	11.28	11.32	0.2189	0.7919
3.2566	25.1649	0.096	374.64	7.49	7.48	0.0905	0.6785

Table 5. Experimental and Calculated Data for the Pent-1-ene (1) + Ethanol (2) System: Masses m_i, Overall Mole Fractions z_1, Temperature T, Pressure P, Liquid Mole Fractions x_1, Vapor Mole Fractions y_1

m_1/g	m_2/g	z_1	T/K	P/bar	P_{calc}/bar	x_1	y_1
4.1141	22.2639	0.108	323.39	1.14	1.15	0.1068	0.7571
9.4065	17.0065	0.267	5323.49	1.67	1.65	0.2646	0.8436
14.9441	13.2154	0.426	323.43	1.85	1.87	0.4248	0.8722
20.0218	7.7981	0.628	323.39	1.98	1.98	0.6269	0.8873
22.2045	5.0401	0.743	323.42	1.99	2.00	0.7427	0.8914
23.5520	2.7377	0.850	323.39	2.02	2.01	0.8495	0.8985
25.3915	1.5748	0.914	323.41	2.03	2.02	0.9137	0.9133
26.8203	0.2532	0.986	323.39	2.01	1.98	0.9859	0.9735
4.1141	22.2639	0.108	373.52	4.66	4.66	0.1051	0.5340
9.4065	17.0065	0.267	373.61	6.33	6.31	0.2624	0.6787
14.9441	13.2154	0.426	373.60	7.03	7.06	0.4235	0.7337
20.0218	7.7981	0.628	373.54	7.46	7.47	0.6265	0.7743
22.2045	5.0401	0.743	373.56	7.59	7.60	0.7427	0.7986
23.5520	2.7377	0.850	373.56	7.63	7.64	0.8498	0.8355
25.3915	1.5748	0.914	373.59	7.56	7.55	0.9141	0.8768
26.8203	0.2532	0.986	373.57	7.27	7.15	0.9860	0.9701

Table 6. Experimental and Calculated Data for the 2-Methyl-but-1-ene (1) + Ethanol (2) System: Masses m_i, Overall Mole Fractions z_1, Temperature T, Pressure P, Liquid Mole Fractions x_1, Vapor Mole Fractions y_1

m_1/g	m_2/g	z_1	T/K	P/bar	P_{calc}/bar	x_1	y_1
6.7815	21.3460	0.173	323.41	1.334	1.338	0.1713	0.8000
11.9464	16.6728	0.32	323.44	1.693	1.676	0.3186	0.8520
18.5555	9.6451	0.558	323.41	1.879	1.897	0.5572	0.8827
22.0608	5.2175	0.735	323.41	1.933	1.942	0.7347	0.8915
24.5825	2.2020	0.880	323.42	1.965	1.960	0.8799	0.9033
25.9346	0.8604	0.952	323.42	1.967	1.955	0.9520	0.9334
27.2525	0.2977	0.978	323.47	1.967	1.935	0.9783	0.9610
6.7815	21.3460	0.173	373.59	5.284	5.292	0.1697	0.6045
11.9464	16.6728	0.32	373.55	6.451	6.422	0.3171	0.6987
18.5555	9.6451	0.558	373.58	7.193	7.223	0.5565	0.7638
22.0608	5.2175	0.735	373.55	7.440	7.455	0.7347	0.7997
24.5825	2.2020	0.880	373.58	7.478	7.479	0.8803	0.8527
25.9346	0.8604	0.952	373.58	7.289	7.274	0.9523	0.9157
27.2525	0.2977	0.978	373.52	7.125	7.089	0.9785	0.9552

of volumetric fractions at infinite pressure defined as

$$\phi_i = \frac{x_i \cdot b_i}{\sum_{i=1}^{N} x_i \cdot b_i} = \frac{x_i \cdot b_i}{b_m} \tag{9}$$

instead of mole fractions.

Table 7. Experimental and Calculated Data for the Cyclopentane (1) + Ethanol (2) System: Masses m_i, Overall Mole Fractions z_1, Temperature T, Pressure P, Liquid Mole Fractions x_1, Vapor Mole Fractions y_1

m_1/g	m_2/g	z_1	T/K	P/bar	P_{calc}/bar	x_1	y_1
7.2272	20.5213	0.188	323.44	0.959	0.962	0.1870	0.7214
12.0236	17.0298	0.317	323.38	1.099	1.088	0.3160	0.7681
17.0807	12.6155	0.471	323.45	1.166	1.172	0.4701	0.7978
23.2103	7.2102	0.679	323.36	1.204	1.206	0.6787	0.8173
23.9029	5.3019	0.748	323.44	1.205	1.211	0.7474	0.8189
27.6455	2.3039	0.887	323.46	1.207	1.210	0.8875	0.8249
29.2850	0.8626	0.957	323.42	1.183	1.173	0.9573	0.8680
7.2272	20.5213	0.188	373.55	4.417	4.422	0.1857	0.5314
12.0236	17.0298	0.317	373.56	4.934	4.896	0.3150	0.6021
17.0807	12.6155	0.471	373.63	5.193	5.204	0.4695	0.6541
23.2103	7.2102	0.679	373.53	5.303	5.333	0.6788	0.7034
23.9029	5.3019	0.748	373.55	5.313	5.335	0.7478	0.7178
27.6455	2.3039	0.887	373.56	5.198	5.200	0.8883	0.7670
29.2850	0.8626	0.957	373.63	4.867	4.841	0.9578	0.8502

Table 8. Experimental and Calculated Data for the Cyclopentene (1) + Ethanol (2) System: Masses m_i, Overall Mole Fractions z_1, Temperature T, Pressure P, Liquid Mole Fractions x_1, Vapor Mole Fractions y_1

m_1/g	m_2/g	z_1	T/K	P/bar	P_{calc}/bar	x_1	y_1
6.3734	21.6858	0.166	323.46	0.950	0.953	0.1649	0.7235
12.5024	16.3523	0.341	323.40	1.234	1.223	0.3399	0.8064
19.6672	11.2306	0.542	323.42	1.301	1.322	0.5416	0.8340
24.7867	7.1053	0.702	323.45	1.339	1.340	0.7020	0.8413
26.7273	4.9892	0.784	323.41	1.347	1.343	0.7836	0.8456
28.2575	2.8313	0.871	323.41	1.350	1.345	0.8710	0.8600
31.1045	1.2763	0.943	323.43	1.340	1.327	0.9429	0.9004
6.3734	21.6858	0.166	373.57	4.307	4.310	0.1637	0.5221
12.5024	16.3523	0.341	373.58	5.196	5.169	0.3387	0.6395
19.6672	11.2306	0.542	373.55	5.560	5.578	0.5412	0.7036
24.7867	7.1053	0.702	373.53	5.676	5.693	0.7021	0.7411
26.7273	4.9892	0.784	373.50	5.675	5.694	0.7838	0.7631
28.2575	2.8313	0.871	373.53	5.676	5.626	0.8715	0.8007
31.1045	1.2763	0.943	373.53	5.430	5.389	0.9432	0.8677

The final expression for a is

$$a = b \cdot \sum_{i=1}^{N} x_i \cdot \left[\frac{a_{ii}}{b_{ii}} - \frac{1}{\Lambda} \cdot \frac{\sum_{j=1}^{N} x_j \cdot G_{ji} \cdot C_{ji}}{\sum_{k=1}^{N} x_k \cdot G_{ki}} \right] \tag{10}$$

with

$$G_{ji} = b_j \exp\left(-\alpha_{ji} \frac{C_{ji}}{RT}\right) \tag{11}$$

where $\alpha_{ij} = \alpha_{ji}$, C_{ij} and C_{ji} with $C_{ii} = C_{jj} = 0$ and with are the parameters of the model.

For sake of comparison also the classical mixing rules with one binary parameter were also used:

$$a = \sum_{i}^{N} \sum_{j}^{N} x_i x_j a_{ij} \tag{12}$$

$$a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij}) \tag{13}$$

The values of the critical properties and the acentric factor are given in Table 9 (DIPPR, 1989).

The calculation procedure starts with an initial guess of the binary interaction parameters for the model, and for each experimental point from the experimental measured

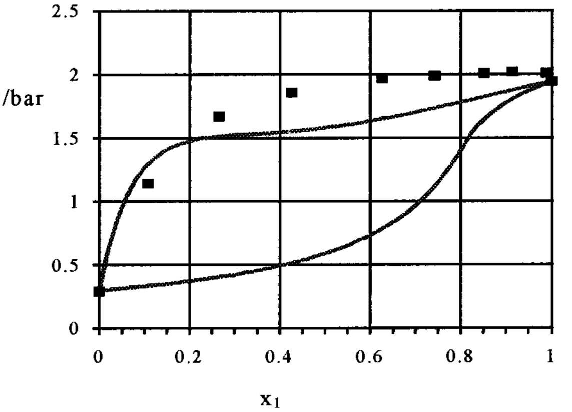

Figure 1. Correlation of the experimental data (■) for the system pent-1-ene (1) + ethanol (2) at 50.23 °C using the Peng−Robinson equation of state with classical mixing rules (—).

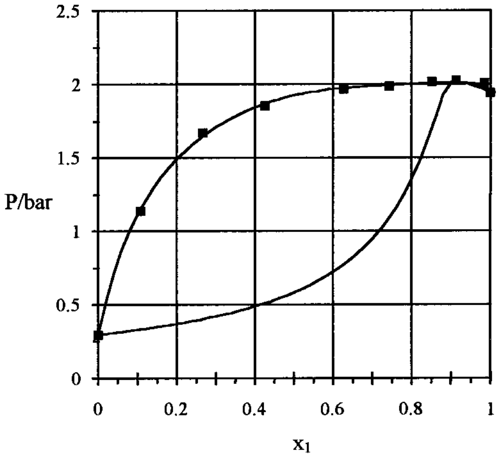

Figure 2. Correlation of the experimental data (■) for the system pentene-1 (1) + ethanol (2) at 50.23 °C using the Peng−Robinson equation of state with Huron Vidal mixing rules (—).

Table 9. Critical Temperature T_c, Critical Pressure P_c, and Acentric Factor ω for the Solutes Investigated

compound	T_c/K	P_c/bar	ω
cis-but-2-ene	435.6	42.0	0.202
trans-but-2-ene	428.6	39.9	0.205
2-methyl-but-2-ene	417.9	40.0	0.194
pent-1-ene	464.8	35.13	0.233
2-methyl-1-butene	465.0	37.8	0.232
cyclopentane	511.7	45.1	0.196
cyclopentene	507.0	47.9	0.194
ethanol	513.9	61.4	0.644

Table 10. Comparison between Different Mixing Rules and EOS for the Exploitation of Experimental Data for the System 2-Methyl-but-2-ene + Ethanol: Results Are the Sums of the Squares of the Deviations in Pressures

model	T/K	$\sum_i (P_i^{\text{calc}} - P_i)^2$/bar^2
PR classical	323.38	0.372
PRHV	323.38	0.239×10^{-2}
RKSHV	323.38	0.242×10^{-2}
PR classical	373.53	2.33
PRHV	373.53	0.143×10^{-1}
RKSHV	373.53	0.142×10^{-1}

Table 11. Binary Interaction Parameters for the Systems Considered

binary system	T/K	C_{ij}/ (cm^3 bar mol^{-1})	C_{ji}/ (cm^3 bar mol^{-1})	α
cis-but-2-ene (1) + ethanol (2)	323.75	7468.69	2244.68	0.45
	374.54	6903.11	1782.17	0.44
trans-but-2-ene (1) + ethanol (2)	323.77	7883.91	2988.61	0.48
	374.55	7046.75	2552.28	0.48
2-methyl-but-2-ene (1) + ethanol (2)	323.78	8053.19	3580.61	0.52
	374.56	7237.48	3324.91	0.56
pent-1-ene (1) + ethanol (2)	323.38	7734.16	2846.23	0.46
	373.53	7213.62	2582.93	0.46
2-methyl-but-1-ene (1) + ethanol (2)	323.42	7670.87	2660.50	0.46
	373.54	7149.28	2282.25	0.46
cyclopentane (1) + ethanol (2)	323.44	8378.91	3822.05	0.44
	373.60	7996.22	4080.66	0.47
cyclopentene (1) + ethanol (2)	323.40	7061.46	1585.34	0.37
	373.55	6891.83	2687.50	0.46

Table 12. Mean Quadratic Relative Deviations in Pressure and Sums of the Squares of the Deviations in Pressures for the Different Binary Systems

system	T/K	100 σ_P%	$\sum_i (P_i^{\text{calc}} - P_i^{\text{exp}})^2 \times 10^2$
cis-but-2-ene + ethanol	323.75	0.47	0.31
	374.54	0.25	0.85
trans-but-2-ene + ethanol	323.77	0.56	0.52
	374.55	0.21	0.73
2-methyl-but-2-ene + ethanol	323.78	1.44	4.78
	374.56	0.36	2.33
pent-1-ene + ethanol	323.38	0.90	0.24
	373.53	0.58	1.43
2-methyl-but-1-ene + ethanol	323.42	0.87	0.19
	373.54	0.32	0.36
cyclopentane + ethanol	323.44	0.59	0.03
	373.60	0.45	0.36
cyclopentene + ethanol	323.40	0.82	0.08
	373.55	0.52	0.59

Table 13. Pressures and Azeotropic Compositions Calculated

system	T/K	experimental azeotrope	calculated azeotrope	x_{az}	P_{az}/bar
cis-but-2-ene + ethanol	323.75	no	no		
	374.54	no	yes	0.954	14.61
trans-but-2-ene + ethanol	323.77	no	yes	0.990	4.89
	374.55	yes	yes	0.954	15.51
2-methyl-but-2-ene + ethanol	323.78	no	no		
	374.56	no	yes	0.978	18.68
pent-1-ene + ethanol	323.38	no	yes	0.914	2.02
	373.53	yes	yes	0.824	7.64
2-methyl-but-1-ene + ethanol	323.42	no	yes	0.912	1.96
	373.54	yes	yes	0.812	7.50
cyclopentane + ethanol	323.44	yes	yes	0.820	1.21
	373.60	yes	yes	0.710	5.34
cyclopentene + ethanol	323.40	yes	yes	0.856	1.34
	373.55	yes	yes	0.754	5.70

total volume, temperature, and masses of the two components the equilibrium pressure is calculated; in this step the vapor−liquid equilibrium is calculated using the equation-of-state model and the equilibrium conditions, and as a consequence the volumes of the vapor and liquid phases and their compositions are calculated. A mean quadratic relative deviation is calculated

$$\sigma_P = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{P_{\text{calc}} - P}{P}\right)_i^2}{n}} \tag{14}$$

where n is the number of experimental points. The optimum values of the parameters of the model are obtained minimizing σ_P.

The compositions of the phases calculated following this procedure depend on the model used and cannot be accepted if the correlation of the pressure is bad.

In Figures 1 and 2 the results obtained for the system pent-1-ene + ethanol using the Peng−Robinson equation of state but with the classical mixing rules (PR classical) and with the Huron−Vidal (PRHV) approach are reported. It is evident that the classical mixing rules are unable to reproduce the experimental pressures within the experimental accuracy. To check the influence of the equation-of-state model, the same calculations were repeated also with the Redlich−Kwong−Soave equation of state (Soave, 1972) and with the Huron−Vidal mixing rules (RKSHV). The deviations in terms of pressure are very close to those obtained with the Peng−Robinson EOS. In Table 10 the results obtained with the three different approaches for the system pent-1-ene + ethanol are reported. The influence of the mixing rules is evident, whereas the type of equation of state has no effect on the quality of the data reduction.

On the basis of these results, all the data were correlated using the Peng−Robinson equation of state with the Huron−Vidal mixing rules. The compositions of the liquid and vapor phases obtained are reported in Tables 2−8. In Table 11 the numerical values of the binary parameters for the different binary systems are given, and in Table 12 the deviations in pressures for the different systems are reported both in terms of sum of squares of the deviations and as σ_P (see eq 14). Deviations are reasonable: the only system showing larger deviations is the system containing 2-methyl-but-2-ene.

From the experimental pressures measured and from the numerical values of the parameters of the model, it is possible to calculate the composition and the corresponding pressures of the binary azeotropes for the systems considered: the results of these calculations are presented in Table 13 and compared with the experimental data. It is always possible to calculate the existence of experimentally founded azeotropes; vice versa in some cases the model predicts the existence of azeotropes when there is not clear experimental evidence. However, it is necessary to remember that in these cases the azeotropic composition occurs at low mole fraction where both experimental methods and models give larger deviations.

Conclusions

New experimental data were measured for different binary systems of ethanol and hydrocarbons with four and five carbon atoms. The experimental results and the parameters of the model used to correlate the data will assist in the optimization of ETBE production plants.

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