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Ethylene + Olefin Binary Systems: Vapor–Liquid Equilibrium Experimental Data and Modeling

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New data on ethylene + 1-butene, 1-hexene, or 1-octene binary systems were obtained at different temperatures (around 293, 332, and 373 K) up to 9 MPa. Data on the ethylene + 1-butene system are compared to those from Bae et al. (*1*). Experimental data are represented using the Peng–Robinson equation of state and one adjusted binary interaction parameter.

Introduction

High-pressure vapor–liquid equilibrium data are required for plant design and for theoretical purposes such as checking the efficiency of the equations of state. Therefore, reliable data must be obtained. In order to check for systematic errors, our laboratory has designed and constructed several apparatus which are different in their basic principles (analytic and synthetic methods). In this work three apparatus have been used to obtain the new data, and consistent results were obtained.

Experimental Section

Apparatus. The three apparatus used to carry out the measurements in isothermal conditions at given temperatures were the following: Apparatus I is an apparatus based on a static method with sampling of both phases using valves as described by Figuiere et al. (*2*) and Laugier (*3*). Apparatus II, also based on a static method, uses special pneumatic capillary samplers (*4*). Apparatus III is based on a synthetic method; a variable-volume cell yields the bubble pressure; the overall composition of the loaded mixture is known through accurate weighings (*5*).

The reason for using three different measurement techniques, two of the analytic static type (apparatus I and II) differing only by the sampling method and one of the synthetic type, is to check for any possibility of systematic error and to benefit from the advantages of each method: faster measurements with the analytic method, higher accuracy in the synthetic method.

Due to small residence times, polymerization was negligible.

Chemicals. Ethylene was provided by CDF Chimie (Dunkerque plant). 1-Butene, purum (>99.3%), is from Hüls. 1-Hexene, purum (>99%), and 1-octene, purum (>99%), are from Ethyl-Corp. All these products have the polymer grade label. All compounds were used without any further purification except for a careful degassing of the liquids.

Results

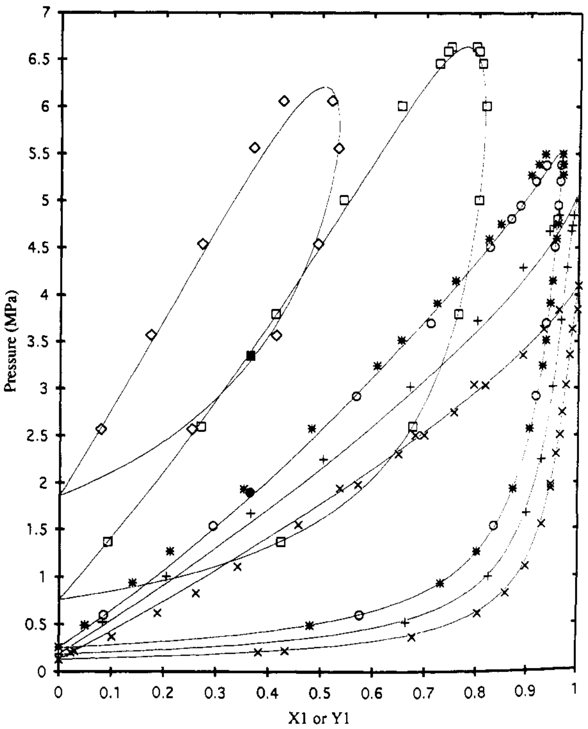

Figure 1. Pressure as a function of ethylene mole fraction in the ethylene (1) + 1-butene (2) system at different temperatures: Bae et al., 273 K (×), 283 K (+), 293 K (*); this work, 293 K (○, analytic method; ●, synthetic method), 333 K (□, analytic method; ■, synthetic method), 375 K (◇); (—) calculated results with the PR-EoS and $\delta_{ij} = 0$.

Experimental results for the three binary systems are reported in Tables 1–3 and displayed in Figures 1–6. Figures 1, 3, and 5 show phase envelopes and Figures 2, 4, and 6 partition coefficients (symbols are experimental data, while solid curves are calculated data). Estimates of experimental errors are given in the tables. σ_x and σ_y are calculated from uncertainties in GLC detector calibrations and dispersions observed on analyses of at least five samples.

Data modeling was performed using several equations of state: the Redlich–Kwong–Soave equation of state (RKS-EoS) (*6*), the Peng–Robinson equation of state (PR-EoS) (*7*),

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Table 1. Vapor–Liquid Equilibrium Data, Temperature T, Pressure P, Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, and the Uncertainties σ, for the System Ethylene (1) + 1-Butene (2)

T/K	$\sigma(T)$/K	P_{exptl}/MPa	$\sigma(P)$/MPa	$x_{1,\mathrm{exptl}}$	$\sigma(x_1)/10^{-3}$	$y_{1,\mathrm{exptl}}$	$\sigma(y_1)/10^{-3}$	$P_{\mathrm{calcd}}{}^d$/MPa	$y_{1,\mathrm{calcd}}{}^d$
293.1	0.1	0.60^a	0.01	0.085	3	0.575	6	0.610	0.5772
293.1	0.1	1.54^a	0.01	0.293	7	0.833	4	1.537	0.8329
293.1	0.1	1.90^c	0.01	0.3638	0.2			1.875	0.8638
293.1	0.1	2.92^a	0.01	0.567	10	0.915	2	2.918	0.9153
293.1	0.1	3.70^a	0.01	0.710	9	0.935	2	3.737	0.9370
293.1	0.1	4.51^a	0.01	0.824	7	0.952	1	4.469	0.9513
293.1	0.1	4.81^a	0.01	0.865	4	0.955_7	1	4.761	0.9562
293.1	0.1	4.95^a	0.01	0.883	4	0.957_8	1	4.896	0.9584
293.1	0.1	5.21^a	0.01	0.913	3	0.961_7	0.8	5.132	0.9620
293.1	0.1	5.38^a	0.01	0.933	3	0.963_0	0.7	5.298	0.9642
332.9	0.1	1.37^a	0.01	0.092	2	0.424	6	1.382	0.4252
332.9	0.1	2.60^a	0.01	0.269	5	0.676	6	2.660	0.6798
332.9	0.1	3.35^c	0.01	0.3638	0.2			3.392	0.7382
332.9	0.1	3.80^a	0.01	0.412	5	0.764	6	3.778	0.7592
332.9	0.1	5.01^a	0.01	0.542	6	0.802	5	4.856	0.7969
332.9	0.1	6.01^a	0.01	0.652	6	0.814	3	5.787	0.8104
332.9	0.1	6.46^a	0.01	0.725	7	0.807	4	6.349	0.8048
332.9	0.1	6.59^a	0.01	0.740	6	0.800	4	6.448	0.7994
332.9	0.1	6.64^a	0.01	0.747	5	0.795	5	6.498	0.7908
374.8	0.1	2.57^b	0.02	0.078_2	2	0.252	4	2.585	0.2334
374.8	0.1	3.57^b	0.02	0.173	3	0.413	5	3.482	0.3885
374.8	0.1	4.54^b	0.02	0.271	5	0.493	5	4.418	0.4778
374.8	0.1	5.56^b	0.02	0.369	5	0.531	5	5.323	0.5233
374.8	0.1	6.06^b	0.02	0.425	5	0.518	6	5.786	0.5311

[a] Measured with apparatus I. [b] Measured with apparatus II. [c] Measured with apparatus III. [d] Calculated values with the PR equation of state and $\delta_{ij} = 0$.

Table 2. Vapor–Liquid Equilibrium Data, Temperature T, Pressure P, Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, and the Uncertainties σ, for the System Ethylene (1) + 1-Hexene (2)

T/K	$\sigma(T)$/K	P_{exptl}/MPa	$\sigma(P)$/MPa	$x_{1,\mathrm{exptl}}$	$\sigma(x_1)/10^{-3}$	$y_{1,\mathrm{exptl}}$	$\sigma(y_1)/10^{-3}$	$P_{\mathrm{calcd}}{}^c$/MPa	$y_{1,\mathrm{calcd}}{}^c$
293.2	0.1	0.77^a	0.01	0.118	3	0.9480	0.3	0.774	0.9696
293.2	0.1	1.81^a	0.01	0.289	5	0.9744	0.7	1.874	0.9843
293.2	0.1	3.00^a	0.01	0.482	7	0.9824	0.8	3.072	0.9874
293.2	0.1	4.11^a	0.01	0.681	7	0.9844	0.7	4.154	0.9874
293.2	0.1	4.98^a	0.01	0.839	6	0.9858	0.5	4.872	0.9866
293.2	0.1	5.41^a	0.01	0.913	4	0.9848	0.8	5.237	0.9859
293.2	0.1	5.61^a	0.01	0.944	3	0.9838	0.8	5.431	0.9853
293.2	0.1	5.66^a	0.01			0.9832	0.8		
332.9	0.1	0.93^a	0.01	0.081	2	0.856	8	0.864	0.8805
332.9	0.1	2.50^a	0.01	0.232	4	0.927	5	2.361	0.9439
332.9	0.1	2.52^a	0.01	0.238	4			2.421	0.9447
332.9	0.1	3.75^a	0.01	0.362	5	0.941	2	3.691	0.9540
332.9	0.1	5.19^a	0.01	0.503	6	0.943	2	5.143	0.9559
332.9	0.1	7.01^a	0.01	0.680	7	0.930	3	6.870	0.9446
332.9	0.1	7.53^a	0.01	0.729	6			7.298	0.9382
332.9	0.1	8.06^a	0.01	0.785	4	0.894	2	7.791	0.9258
373.6	0.1	1.49^b	0.02	0.105	6	0.773	5	1.608	0.7805
373.6	0.1	3.02^b	0.02	0.227	7	0.862	4	3.206	0.8624
373.6	0.1	5.06^b	0.02	0.374	9	0.898	4	5.196	0.8846
373.6	0.1	7.09^b	0.02	0.515	8	0.896	3	7.098	0.8800
373.6	0.1	8.78^b	0.02	0.632	7	0.877	3	8.537	0.8582

[a] Measured with apparatus I. [b] Measured with apparatus II. [c] Calculated values with the PR equation of state and $\delta_{ij} = 0.069$.

Table 3. Vapor–Liquid Equilibrium Data, Temperature T, Pressure P, Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, and the Uncertainties σ, for the System Ethylene (1) + 1-Octene (2)

T/K	$\sigma(T)$/K	$P_{\mathrm{exptl}}{}^a$/MPa	$\sigma(P)$/MPa	$x_{1,\mathrm{exptl}}$	$\sigma(x_1)/10^{-3}$	$y_{1,\mathrm{exptl}}$	$\sigma(y_1)/10^{-3}$	$P_{\mathrm{calcd}}{}^b$/MPa	$y_{1,\mathrm{calcd}}{}^b$
303.0	0.1	1.08	0.01	0.194	4	0.9916	0.5	1.085	0.9962
303.0	0.1	2.50	0.01	0.417	6	0.9954	0.8	2.511	0.9974
303.0	0.1	4.00	0.01	0.616	6	0.9962	0.6	3.982	0.9972
303.0	0.1	5.43	0.01	0.793	4	0.9946	0.4	5.444	0.9958
303.0	0.1	6.33	0.01	0.909	3	0.9909	1	6.406	0.9917
342.4	0.1	1.00	0.01	0.117	3	0.9740	0.6	1.003	0.9772
342.4	0.1	3.00	0.01	0.324	4	0.9884	0.5	2.976	0.9877
342.4	0.1	5.00	0.01	0.499	6	0.9890	0.7	4.932	0.9873
342.4	0.1	7.04	0.01	0.665	5	0.9838	0.8	7.077	0.9824
342.4	0.1	8.97	0.01	0.807	4	0.9651	0.9	9.060	0.9672

[a] Measured with apparatus II. [b] Calculated values with the PR equation of state and $\delta_{ij} = 0.011$.

the generalized form of the Patel–Teja equation of state (gPT-EoS) (*8*), and the generalized form of the Trebble–Bishnoï–Salim equation of state (gTBS-EoS) (*9*). A brief description of these equations is given in a previous paper (*10*).

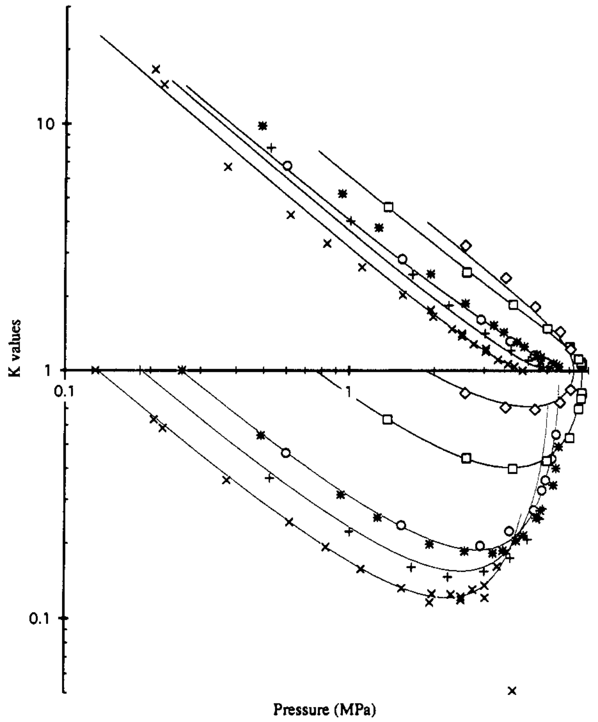

Figure 2. Partition coefficients as a function of pressure in the ethylene (1) + 1-butene (2) system at different temperatures: Bae et al., 273 K (×), 283 K (+), 293 K (*); this work, 293 K (○), 333 K (□), 375 K (◇); (—) calculated results with the PR-EoS and $\delta_{ij} = 0.0$.

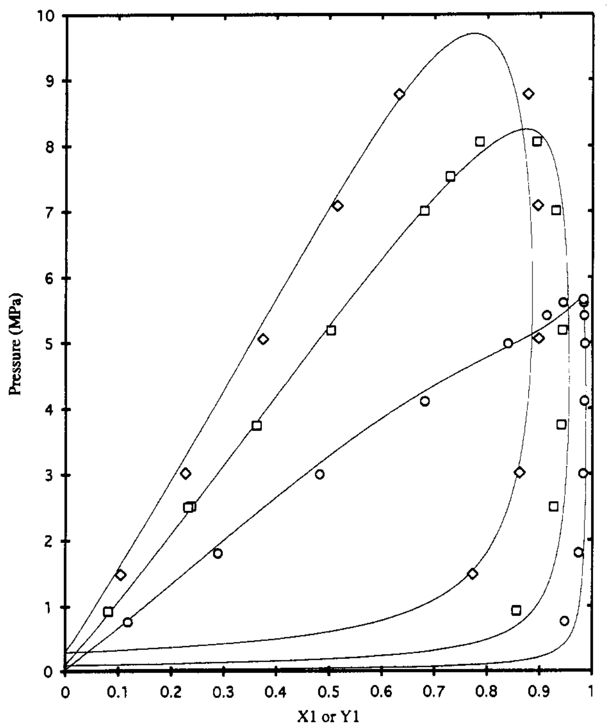

Figure 3. Pressure as a function of ethylene mole fraction in the ethylene (1) + 1-hexene (2) system at different temperatures: 293 K (○); 333 K (□); 374 K (◇); (—) calculated results with the PR-EoS and $\delta_{ij} = 0.069$.

The classical quadratic mixing rule is used for the parameter a

$$a_m = \sum_i \sum_j a_{ij} x_i x_j \tag{1}$$

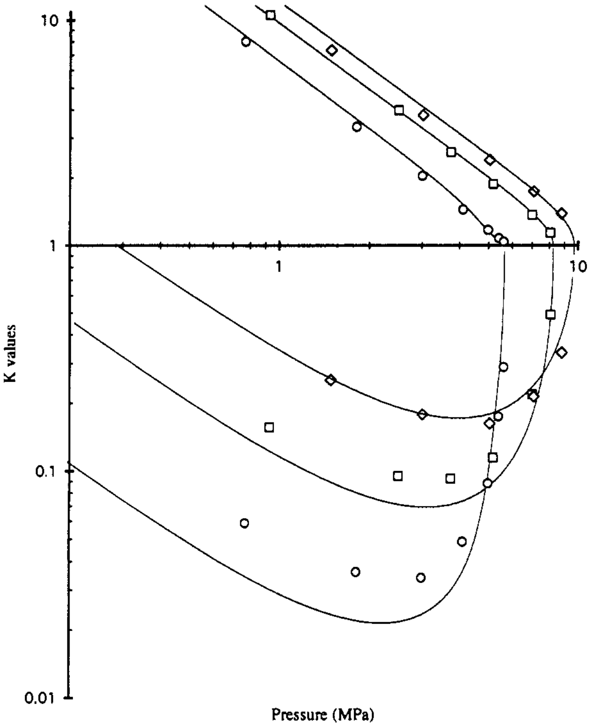

Figure 4. Partition coefficients as a function of pressure in the ethylene (1) + 1-hexene (2) system at different temperatures: 293 K (○); 333 K (□); 374 K (◇); (—) calculated results with the PR-EoS and $\delta_{ij} = 0.069$.

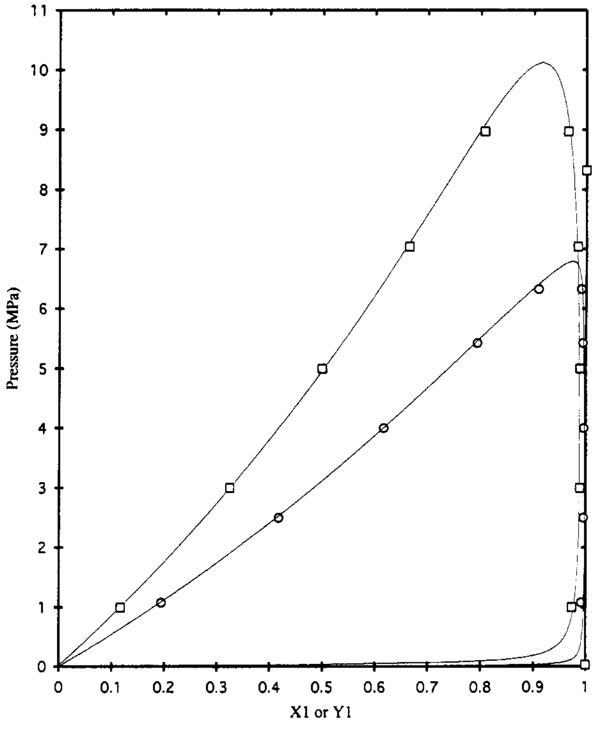

Figure 5. Pressure as a function of ethylene mole fraction in the ethylene (1) + 1-octene (2) system at different temperatures: 303 K (○); 342 K (□); (—) calculated results with the PR-EoS and $\delta_{ij} = 0.011$.

with the following combining rule:

$$a_{ij} = (1 - \delta_{ij})(a_i a_j)^{1/2} \tag{2}$$

Characteristic parameters of the pure compounds used in the PR and RKS equations of state are listed in Table 4. The corresponding values of the adjusted parameters δ_{ij} are given

Table 4. Critical Properties and Acentric Factors Used in the Cubic Equations of State

compound[a]	critical pressure/MPa	critical temp/K	acentric factor
ethylene	5.040	282.40	0.085
1-butene	4.023	419.60	0.187
1-hexene	3.206	504.20	0.285
1-octene	2.675	567.40	0.386

[a] Data taken from ref 11.

Table 5. Representation of Vapor–Liquid Equilibrium Data of the Mixtures Using the Cubic Equations of State

			PR-EoS			RKS-EoS		
mixture	no. of binary data	adjusted value	δ_{ij}	$\sigma^R{}_P$/ %	$\sigma^R{}_y$/ %	δ_{ij}	$\sigma^R{}_P$/ %	$\sigma^R{}_y$/ %
ethylene + 1-butene	24	no	0	2.2	2.2	0	2.3	2.3
(this work)		yes	0.000	2.2	2.2	0.000	2.3	2.3
ethylene + 1-butene	41	no	0	6.0	2.8	0	6.1	2.5
(Bae et al.)		yes	0.000	6.0	2.8	−0.004	5.9	2.7
ethylene + 1-hexene	19	no	0	19.	1.7	0	18.	1.8
		yes	0.069	3.9	1.6	0.070	3.9	1.6
ethylene + 1-octene	10	no	0	3.8	0.3	0	2.8	0.4
		yes	0.011	0.8	0.2	0.008	0.9	0.3

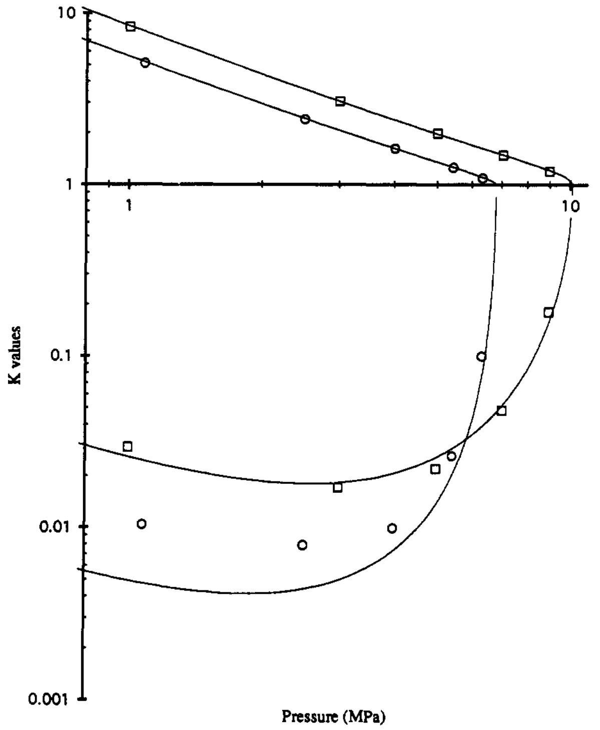

Figure 6. Partition coefficients as a function of pressure in the ethylene (1) + 1-octene (2) system at different temperatures: 303 K (○); 342 K (□); (—) calculated results with the PR-EoS and δ_{ij} = 0.011.

in Table 5. These binary interaction parameters were adjusted on data from this work using the objective function

$$Q = \sum_{j=1}^{n} \left(\frac{P_{j,\text{exptl}} - P_{j,\text{calcd}}}{P_{j,\text{exptl}}} \right)^2 + \left(\frac{y_{1j,\text{exptl}} - y_{1j,\text{calcd}}}{y_{1j,\text{exptl}}} \right)^2 \quad (3)$$

The optimum values are listed for each mixture for the PR and RKS equations of state. Representations are equivalent with the gTBS equation of state while the gPT equation of state is only slightly worse.

Data from Bae et al. (*1*) are compared to those of the present work in Figures 1 and 2. In Figure 2, we may notice that their data are in relatively good agreement with ours except at high pressures. Data from Bae et al. at the lowest temperature are very dispersed with an erroneous point. Solid curves obtained using PR-EoS and δ_{ij} adjusted on our data (see Table 5) represent both sets of data well. δ_{ij} adjusted on Bae et al.'s data is very small (close to zero). The average relative deviation on Bae et al.'s pressure data is about 2.5 higher than on our data.

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We thank other co-workers, A. Chareton and A. Valtz, who took part in the measurements.

Glossary

a	energetic parameter of the equations of state
K	partition coefficient
n	number of experimental points
P	pressure (MPa)
Q	objective function
T	temperature (K)
x	liquid mole fraction
y	vapor mole fraction

Subscripts

calcd	calculated property
exptl	experimental property
i, j	components i and j
P	pressure property

Greek Letters

δ_{ij}	binary interaction parameter
σ	uncertainty
σ^R	standard deviation

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