High-Pressure Vapor−Liquid Equilibria for Ethylene + 4-Methyl-1-pentene and 1-Butene + 1-Hexene

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Isothermal vapor−liquid equilibria (VLE) for the ethylene + 4-methyl-1-pentene and 1-butene + 1-hexene binary systems were measured by the static method at several temperatures for pressures in the range (0.3 to 8.5) MPa. Representations of VLE data by the Soave and Peng−Robinson cubic equations of state are compared in both modes: predictive and binary parameter adjustment. As the two binary systems behave almost ideally, there is no significant difference between their representation qualities through both equations of state.

Introduction

Special equipment for measuring vapor−liquid equilibria (VLE) up to 25 MPa and 500 K has been used here. The apparatus is based on a static−analytic method. Its very interesting feature is the ability of withdrawing small adjustable samples through patented capillary pneumatic samplers, coupled to an on-line gas chromatograph. The new data presented in this paper are a new contribution to a high-pressure database we have been building for a long time and extend the results on olefin systems (Laugier et al., 1994).

Experimental Section

Apparatus. The apparatus consists of a high-pressure cell immersed in a liquid bath. Pressure is measured in situ with a membrane pressure transducer. Representative samples of both liquid and vapor phases are withdrawn using capillary pneumatic samplers. They are improved versions of those described in a previous paper from Laugier and Richon (1986). Samples are analyzed using a gas chromatograph. Pressures are measured within 0.01 MPa, and temperatures are measured within 0.05 K. Uncertanties in composition are given in Tables 1 and 2.

Chemicals. Ethylene is from CdF Chimie (Dunkerque plant), its certified purity is 99.95% by GLC. 1-Butene, purum (>99.3%); is from Hülls and 1-hexene, purum (>99% by GLC), from Ethyl Corp. All three of these compounds have the polymer grade label. 4-Methyl-1-pentene was provided by Interchim (ref OM477848) with a certified purity of 99.95%. The liquids were carefully degassed prior to use.

Experimental Results

Experimental results obtained for the two binaries are given in Tables 1 and 2 along with uncertainties in each value. Uncertainties in temperatures (T/K) and pressure (P/MPa) are determined through calibrations against accurate measuring devices as described by Laugier and Richon (1986). Uncertainties $\sigma(x)$ and $\sigma(y)$ on liquid (x) and vapor (y) mole fractions are estimated from both calibration

Table 1. Vapor−Liquid Equilibrium Data for the System Ethylene (1) + 4-Methyl-1-pentene (2): Temperature T, Pressure P, Liquid Mole Fraction x_1, and Vapor Mole Fraction y_1

T/K	P/MPa	x_1	$10^3\sigma(x_1)$	y_1	$10^3\sigma(y_1)$	$P_{cal}{}^a$/MPa	$y_{1,cal}{}^a$
293.15	0.37$_5$	0.069	3			0.327	0.907
293.15	0.79	0.163	6	0.956	1	0.75	0.957
293.15	1.51	0.321	9	0.976	1	1.51	0.977
293.15	2.24	0.466	9	0.983	1	2.28	0.983
293.15	3.02	0.610	9	0.987	1	3.11	0.986
293.15	3.74	0.727	7	0.986	1	3.85	0.988
293.15	4.48	0.835	4	0.987	1	4.58	0.989
293.15	4.74	0.867	4	0.986	1	4.81	0.989
333.40	1.02	0.120	6	0.856	6	0.976	0.858
333.40	2.00	0.254	7	0.912	4	2.01	0.921
333.40	2.99	0.373	8	0.938	4	3.00	0.940
333.40	3.99	0.493	9	0.946	4	4.09	0.948
333.40	4.85	0.587	9	0.950	3	5.01	0.950
333.40	5.28	0.628	8	0.947	3	5.43	0.950
333.40	5.77	0.677	8	0.949	3	5.94	0.949
333.40	6.37	0.728	8	0.945	3	6.48	0.947
373.10	1.00	0.067	2	0.630	8	1.01	0.604
373.10	2.01	0.164	5	0.784	9	1.98	0.775
373.10	2.79	0.236	7	0.836	5	2.75	0.822
373.10	3.98	0.346	7	0.867	5	3.98	0.857
373.10	5.26	0.466	9	0.873	5	5.41	0.872
373.10	6.96	0.601	9	0.878	4	7.07	0.869
373.10	8.10	0.691	7	0.852	5	8.12	0.853
373.10	8.51	0.732	8	0.824	6	8.52	0.839

^{a} Calculated values with the RKS equation of state and mixing rule R0.

Table 2. Vapor−Liquid Equilibrium Data for the System 1-Butene (1) + 1-Hexene (2): Temperature T, Pressure P, Liquid Mole Fraction x_1, and Vapor Mole Fraction y_1

T/K	P/MPa	x_1	$10^3\sigma(x_1)$	y_1	$10^3\sigma(y_1)$	$P_{cal}{}^a$/MPa	$y_{1,cal}{}^a$
373.6	0.405	0.093	2	0.322	6	0.410	0.331
373.6	0.575	0.214	4	0.550	6	0.570	0.561
373.6	0.820	0.391	6	0.736	5	0.817	0.742
373.6	1.125	0.591	6	0.846	5	1.117	0.859
373.6	1.295	0.695	6			1.283	0.902
373.6	1.430	0.769	5	0.919	4	1.407	0.929

^{a} Calculated values with the RKS equation of state and mixing rule R0.

of the GLC detector and dispersion of analyses (integrated peak areas) on at least five samples.

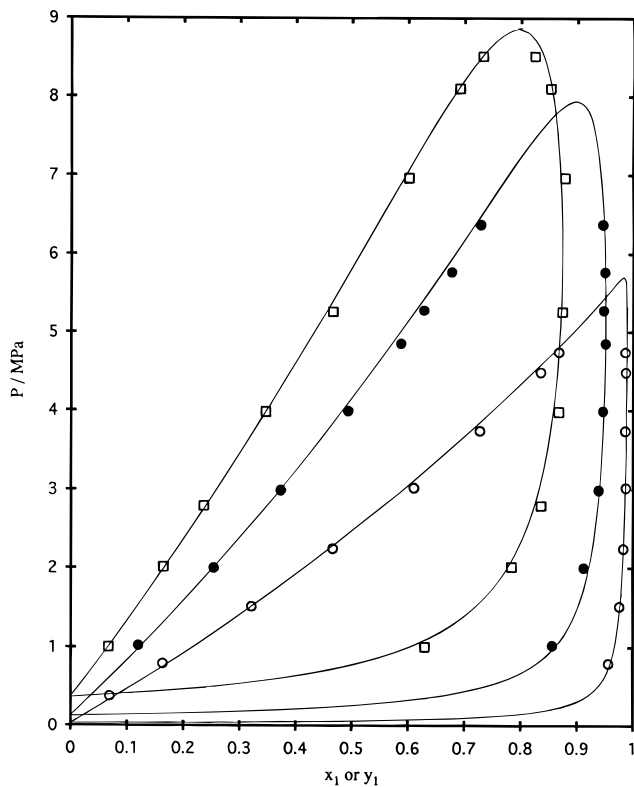* To whom correspondence should be addressed.

Figure 1. Pressure as a function of ethylene mole fraction in the ethylene (1) + 4-methyl-1-pentene (2) system at different temperatures: 293 K (○); 333 K (●); 373 K (□); solid lines were calculated with the RKS EoS and R0.
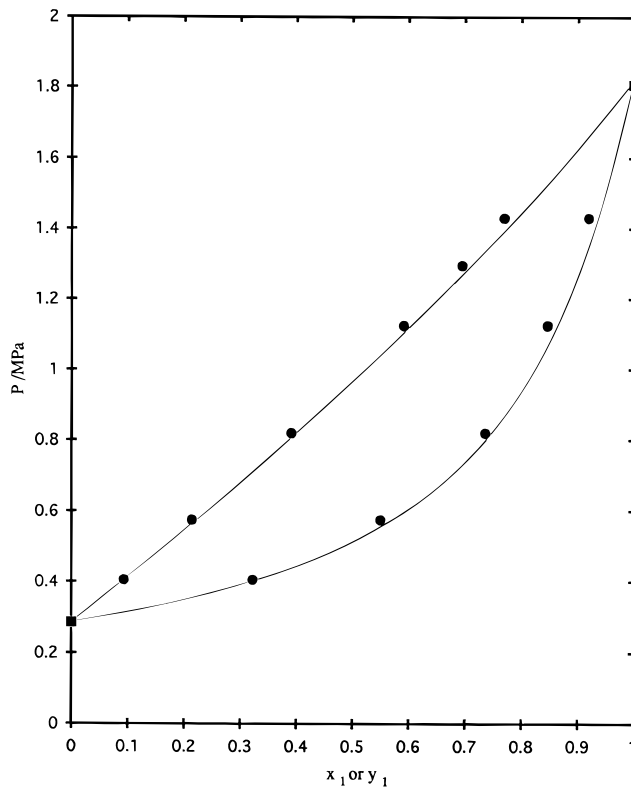

Figure 3. Pressure as a function of butene mole fraction in the 1-butene (1) + 1-hexene (2) system at 373 K (●) and from DIPPR (373 K) (■); solid lines were calculated with the RKS EoS and R0.
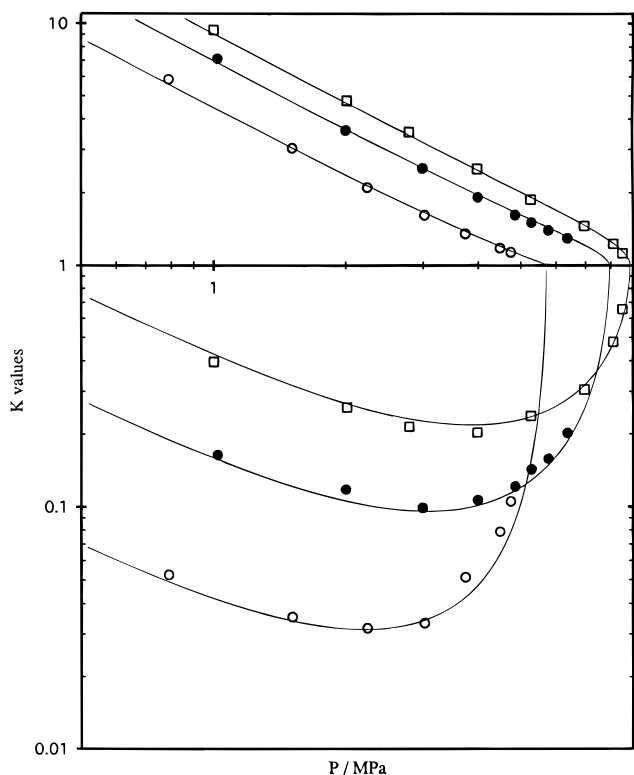

Figure 2. Partition coefficients as a function of pressure in the ethylene (1) + 4-methyl-1-pentene (2) system at different temperatures: 293 K (○); 333 K (●); 373 K (□); solid lines were calculated with the RKS EoS and R0.

Phase envelopes for ethylene + 4-methyl-1-pentene and 1-butene + 1-hexene systems are shown in Figures 1 and 3 while corresponding $K_i(y_i/x_i)$ values appear in Figures 2 and 4.
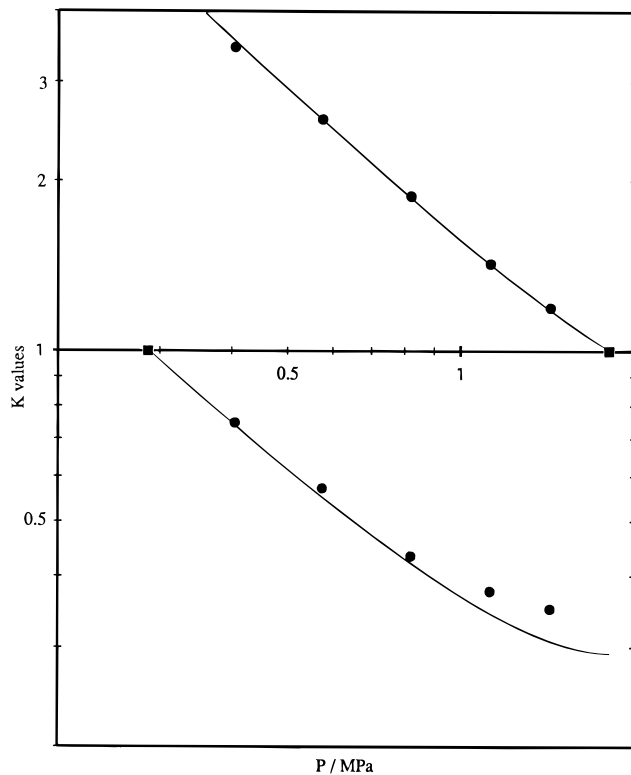

Figure 4. Partition coefficients as a function of pressure in the 1-butene (1) + 1-hexene (2) system at 373 K (●) and from DIPPR (373 K) (■); solid lines were calculated with the RKS EoS and R0.

Data Treatment

Several equations of state have been tested for modeling experimental data: the Redlich−Kwong−Soave equation of state (RKS EoS) (Soave, 1972), the Peng−Robinson equation of state (PR EoS) (Peng and Robinson, 1976), the

Table 3. Critical Parameters and Acentric Factors, ω, Used in the Cubic Equations of State

compound	ref	P_c/MPa	T_c/K	ω
ethylene	Reid et al. (1977)	5.040	282.40	0.085
1-butene	Reid et al. (1977)	4.023	419.60	0.187
1-hexene	Reid et al. (1977)	3.206	504.20	0.285
4-methyl-1-pentene	DIPPR (1987)	3.220	496.00	0.239

Table 4. Binary Interaction Parameter, δ_{ij}, Values Associated with the Redlich–Kwong–Soave (RKS) and Peng–Robinson (PR) Equatiosn of State

mixture	number of experimental data	δ_{ij} RKS	δ_{ij} PR
1-butene + 1-hexene	5	−0.002	0.002
ethylene + 4-methyl-1-pentene	22	−0.001	0.002

generalized form of the Patel–Teja equation of state (Patel and Teja, 1982), and the generalized form of the Trebble–Bishnoï–Salim equation of state (Salim and Trebble, 1991).

The generalized form of cubic equations of state is

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + uv + wb}$$

For the PR EoS, we have $u = 2b$ and $w = -b$. For the SRK EoS, we have $u = b$ and $w = 0$. The mixing rules for all equations of state are

$$a_\mathrm{m} = \sum_i \sum_j a_{ij} x_i x_j$$

$$b_\mathrm{m} = \sum_i b_i x_i$$

$$u_\mathrm{m} \sum_i u_i x_i$$

$$w_\mathrm{m} = \sum_i w_i x_i$$

Two combining rules have been used for the a_{ij} term:

R0: no adjustable parameter

$$a_{ij} = (a_i a_j)^{1/2}$$

R1: one adjustable parameter, δ_{ij}

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

Only the results for the RKS EoS and PR EoS are reported because other equations do not lead to any significant representation improvements. Characteristic parameters of pure compounds used with the PR EoS and RKS EoS are listed in Table 3. The values of binary interaction parameters (Table 4) and the relative standard deviations between experimental and calculated values (Table 5) are reported.

Table 5. Representation of Vapor–Liquid Equilibria of Mixtures Using Cubic Equations of State[a]

mixture	combining rule	σ_P^R/% RKS	σ_P^R/% PR	σ_{y1}^R/% RKS	σ_{y1}^R/% PR
1-butene +	R0	1.1	2.0	1.8	1.4
1-hexene	R1	1.1	2.0	1.8	1.4
ethylene +	R0	2.4	2.5	1.1	1.2
4-methyl-1-pentene	R1	2.4	2.4	1.1	1.2

[a] $\sigma_u^R = 100[\sum_{j=1}^n ((u_{j,\exp} - u_{j,\mathrm{cal}})/u_{j,\exp})^2/(n - k)]^{1/2}$ with $u =$ either P or y and $k =$ number of model parameters.

Binary interaction parameters were adjusted using the following objective function:

$$Q = \sum_{j=1}^n \left[\left(\frac{P_{j,\exp} - P_{j,\mathrm{cal}}}{P_{j,\exp}} \right)^2 + \left(\frac{y_{1j,\exp} - y_{1j,\mathrm{cal}}}{y_{1j,\exp}} \right)^2 \right]$$

$n =$ the number of experimental data points, and exp stands for an experimental quantity while cal stands for a calculated one.

The two binaries ethylene + 4-methyl-1-pentene and 1-butene + 1-hexene behave as ideal mixtures. Adjusting one binary interaction parameter does not improve the representation as seen in Table 5.

Acknowledgment

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