Vapor−Liquid Equilibrium Data for the Ethylene + Hexane System

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Vapor−liquid equilibrium data have been measured for the ethylene + hexane system at temperatures of (390 to 510) K and pressures up to 10 MPa. The bubble and dew point pressures of ethylene + hexane samples with fixed compositions were measured using the Cailletet apparatus. The critical points of ethylene + hexane mixtures were also measured experimentally. The experimental data were correlated with the modified Sanchez−Lacombe (MSL) equation of state. The experimental data are also compared with the predictions of the Peng−Robinson (PR) and Soave−Redlich−Kwong (SRK) equations of state using the binary interaction parameter obtained in the MSL correlation. The three equations of state produce comparable qualitative representations of the experimental phase boundaries.

Introduction

High-pressure vapor−liquid equilibrium data are required for process design and control. Vapor−liquid equilibrium data have previously been measured for the system of ethylene + hexane.[1−6] Most of the available experimental data are at low ethylene compositions, at temperatures below 390 K, and/or only the critical points. The purpose of this work is to obtain experimental bubble and dew point data for the ethylene + hexane system at temperatures of (390 to 510) K and pressures up to 10 MPa. The ranges of temperature and pressure have application in the solution polymerization process used to produce polyethylene industrially. The phase behavior of the ternary system polymer + solvent + ethylene and its binary subsystems should be known for the design of this process because hydrocarbons are used as solvents.

The experimental data are modeled with an equation of state for polymer solutions: the modified Sanchez−Lacombe (MSL) equation of state with one adjustable binary interaction parameter. The same value of the binary interaction parameter is also used to calculate a phase boundary using both the Peng−Robinson (PR) and Soave−Redlich−Kwong (SRK) equations of state.

Experimental Section

Materials and Sample Preparation. Ethylene (C_2H_4, certified GC purity >99.95%) was obtained from AGA Gas BV (product number AGA 3.5, The Netherlands). Hexane (C_6H_{14}, certified GC purity >99.5%) was obtained from Fluka Chemika (product number 52765, The Netherlands). Approximately (60 to 80) mg of liquid hexane was injected into the base of the Cailletet tube (capillary Pyrex glass tube) using an uncalibrated syringe. The mass of hexane was determined using a microbalance whose precision is estimated to be 0.05 mg. Immersing the base of the glass tube in liquid nitrogen to freeze the hexane and then applying a vacuum degases the sample. The degassing procedure is usually repeated between three and five times to ensure that the volatile components are completely removed. The hexane sample is frozen and the tube is evacuated before ethylene gas is dosed into a glass bulb.

Mercury is used to seal the ethylene in a glass bulb with a calibrated volume. The pressure and temperature are recorded at this point. The mass of ethylene was determined using the generalized virial expression[7] proposed by Pitzer and co-workers. Ethylene was nearly an ideal gas under filling conditions because the calculated compressibility factors were between 0.9998 and 0.9999. The mercury acts as a piston forcing the ethylene into the Cailletet tube and sealing the sample at the same time. The mixture of ethylene + hexane was prepared with an uncertainty in the mole fraction of less than ±0.0003.

Experimental Procedure. The experiments were carried out using the Cailletet apparatus that was described in detail by de Loos et al.[8] The Cailletet tube containing the sample of fixed composition was immersed in a bath of circulating silicon oil to maintain the temperature to within 0.03 K. Experiments were carried out at constant temperature starting in the two-phase region. The pressure was increased in small increments until one of the phases just disappears. Once the phase disappears, the pressure is decreased by the same increment to confirm that the phase reappears. If the incipient phase descends when formed, it is characteristic of dew point behavior; otherwise, if it ascends, it is characteristic of bubble point behavior. The critical temperature of the mixture was measured by determining the temperature interval in which the observed incipient phase changes from bubble point to dew point behavior.

The temperature was measured using a platinum resistance thermometer (uncertainty ±0.01 K). The pressure was measured using a dead weight pressure gauge (uncertainty ±0.002 MPa at pressures below 5 MPa and ±0.01 MPa at pressures equal to and above 5 MPa). The total uncertainty in the temperature is estimated to be ±0.03 K as derived from the accuracy of the thermometer, its position in the thermostat fluid relative to the sample, and variances due to the circulation of the thermostat fluid. The total uncertainty in the pressure is ±0.003 MPa at pres-

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Table 1. Experimental Bubble (BP) and Dew (DP) Point Data for Ethylene (1) + Hexane (2)[a]

$x_1 = 0.0994$			$x_1 = 0.2002$			$x_1 = 0.3006$		
T/K	*P*/MPa	type	*T*/K	*P*/MPa	type	*T*/K	*P*/MPa	type
391.36	1.509	BP	390.99	2.746	BP	390.75	4.092	BP
396.27	1.584	BP	396.08	2.856	BP	395.93	4.237	BP
401.05	1.659	BP	401.12	2.961	BP	400.60	4.372	BP
406.13	1.744	BP	405.95	3.076	BP	405.66	4.517	BP
411.04	1.824	BP	410.91	3.201	BP	410.61	4.652	BP
415.98	1.919	BP	415.83	3.306	BP	415.58	4.787	BP
420.89	2.009	BP	420.74	3.416	BP	420.36	4.927	BP
425.84	2.104	BP	425.70	3.536	BP	425.44	5.057	BP
430.77	2.209	BP	430.74	3.656	BP	430.39	5.192	BP
435.67	2.309	BP	435.69	3.781	BP	435.36	5.312	BP
440.65	2.414	BP	440.72	3.901	BP	440.49	5.437	BP
445.66	2.529	BP	445.91	4.031	BP	445.31	5.542	BP
450.62	2.649	BP	450.74	4.151	BP	450.28	5.652	BP
455.59	2.769	BP	455.69	4.271	BP	455.26	5.737	BP
460.48	2.894	BP	460.59	4.386	BP	460.28	5.807	BP
465.43	3.024	BP	465.62	4.501	BP	465.16	5.847	BP
470.48	3.159	BP	470.54	4.611	BP	470.12	5.827	BP
475.48	3.289	BP	475.41	4.701	BP	474.98	5.707	BP
480.36	3.429	BP	480.37	4.766	BP	479.99	5.417	DP
485.34	3.564	BP	485.33	4.781	BP	484.83	4.887	DP
490.29	3.694	BP	491.31	4.516	DP			
495.25	3.804	BP						

$x_1 = 0.4002$			$x_1 = 0.4998$			$x_1 = 0.6006$		
T/K	*P*/MPa	type	*T*/K	*P*/MPa	type	*T*/K	*P*/MPa	type
391.04	5.434	BP	391.18	6.854	BP	391.03	8.299	BP
396.08	5.589	BP	396.13	7.039	BP	395.96	8.449	BP
401.00	5.754	BP	401.10	7.204	BP	400.85	8.559	BP
405.85	5.914	BP	405.95	7.359	BP	405.88	8.644	BP
410.85	6.064	BP	411.05	7.504	BP	410.95	8.674	BP
415.84	6.214	BP	415.98	7.629	BP	415.81	8.649	BP
420.76	6.349	BP	420.83	7.724	BP	420.68	8.564	BP
425.73	6.479	BP	425.97	7.794	BP	425.31	8.484	BP
430.62	6.594	BP	431.01	7.829	BP	430.71	8.229	DP
435.60	6.699	BP	435.78	7.791	BP	435.58	7.994	DP
440.59	6.784	BP	440.78	7.714	BP	440.56	7.699	DP
445.54	6.829	BP	446.00	7.534	BP	445.51	7.264	DP
450.41	6.849	BP	450.76	7.319	DP			
455.35	6.809	BP	455.65	6.989	DP			
460.24	6.694	BP	460.56	6.564	DP			
465.22	6.454	BP						
470.26	6.139	DP						
475.06	5.629	DP						

$x_1 = 0.7007$		
T/K	*P*/MPa	type
390.90	9.090	BP
395.79	9.080	BP
400.68	9.050	BP
405.74	8.950	DP
410.67	8.840	DP
415.61	8.670	DP
420.61	8.420	DP
425.46	8.050	DP

[a] Data are ethylene mole fraction x_1, temperature T, and pressure P.

sures below 5 MPa and ±0.02 MPa at pressures above 5 MPa. The total uncertainty in pressure is most strongly controlled by the accuracy of the dead weight pressure gauge. At a given composition, the accuracy of the measured critical temperature is ±0.1 K, and that of the critical pressure is ±0.03 MPa.

Results

The experimental bubble and dew point measurements are given in Table 1, and the critical point measurements are given in Table 2. Only the upper portion of the ethylene + hexane phase boundary was measured. Isopleths are lines of constant composition and are presented in the *P*, *T* graphs shown in Figures 1 and 2. The critical points of the ethylene + hexane mixtures are located at higher temperatures than the maximum pressure of a mixture with given composition. The critical temperature T_c and critical pressure P_c as a function of the ethylene mole fraction x_1 are presented in Figures 3 and 4, respectively.

Table 2. Experimental Critical Point Data for Ethylene (1) + Hexane (2)[a]

$x_{1,c}$	T_c/K	P_c/MPa
0.2002	491.28	4.519
0.3006	479.65	5.437
0.4002	467.21	6.336
0.4998	449.90	7.346
0.6006	428.18	8.321
0.7007	402.32	9.021

[a] Data are critical ethylene mole fraction $x_{1,c}$, critical temperature T_c, and critical pressure P_c.

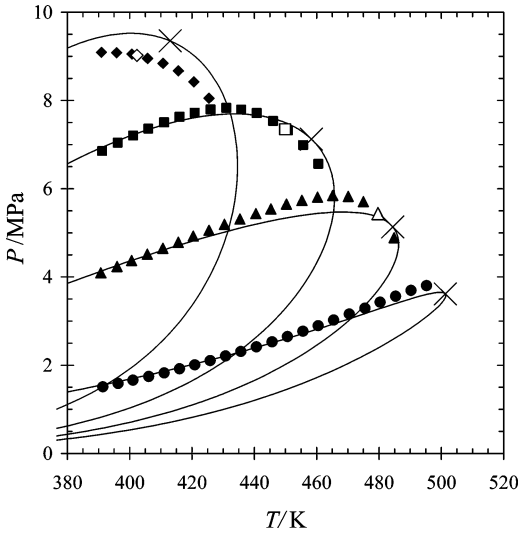

Figure 1. Vapor−liquid equilibrium data for the ethylene (1) + hexane (2) system. Filled symbols are bubble and dew points, empty symbols are critical points, curves are phase boundaries, and crosses (×) are critical points calculated using the MSL-EoS and $k_{ij} = 2.905 \times 10^{-2}$. Ethylene mole fraction: ●, $x_1 = 0.0994$; ▲, $x_1 = 0.3006$; ■, $x_1 = 0.4998$; ◆, $x_1 = 0.7007$.

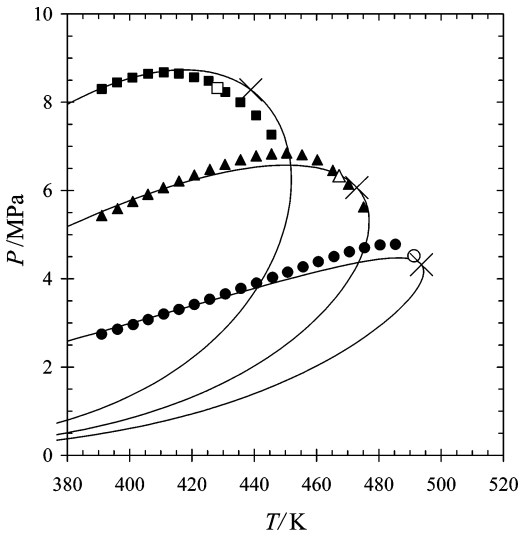

Figure 2. Vapor−liquid equilibrium data for the ethylene (1) + hexane (2) system. Filled symbols are bubble and dew points, empty symbols are critical points, curves are phase boundaries, and crosses (×) are critical points calculated using the MSL-EoS and $k_{ij} = 2.905 \times 10^{-2}$. Ethylene mole fraction: ●, $x_1 = 0.2002$; ▲, $x_1 = 0.4002$; ■, $x_1 = 0.6006$.

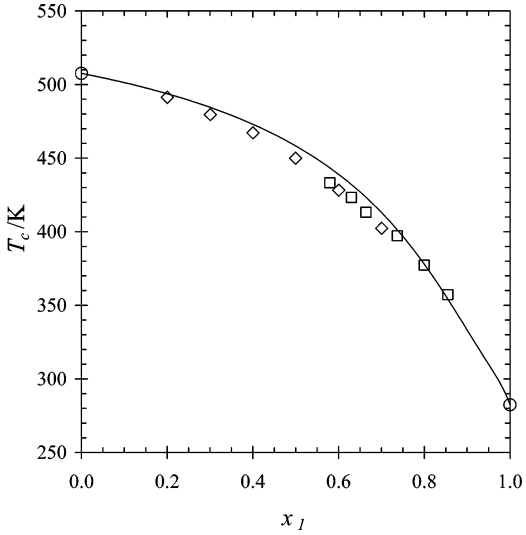

Figure 3. Critical temperature T_c versus ethylene mole fraction x_1 for the ethylene (1) + hexane (2) system. Empty symbols are experimental data, and curves are calculated using the MSL-EoS and $k_{ij} = 2.905 \times 10^{-2}$. Sources of data: ○, Poling et al.;[14] □, Rätzsch and Söll;[4] ◇, this work.

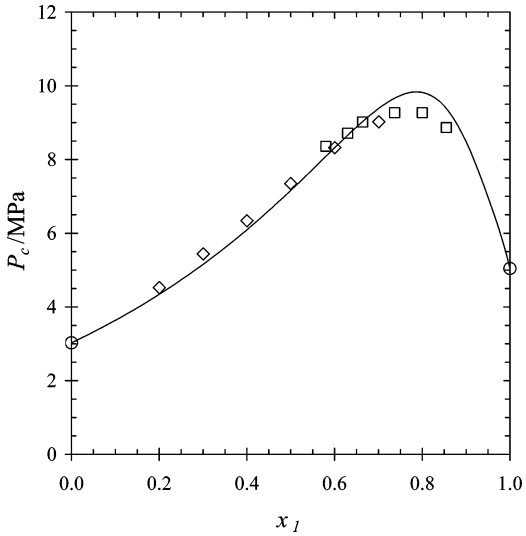

Figure 4. Critical pressure P_c versus ethylene mole fraction x_1 for the ethylene (1) + hexane (2) system. Empty symbols are experimental data, and curves are calculated using the MSL-EoS and $k_{ij} = 2.905 \times 10^{-2}$. Sources of data: ○, Poling et al.;[14] □, Rätzsch and Söll;[4] ◇, this work.

The critical point data measured by Rätzsch and Söll[4] are compared to those of the present work in Figures 3 and 4. The two sets of experimental data are in relatively good agreement over the entire range.

The modified Sanchez−Lacombe equation of state (MSL-EoS)[9] was used to perform the calculations using a parametrization that obtains the pure component parameters from the critical temperature, pressure, and acentric factor.[10] The MSL equation and correlation procedure are presented elsewhere in more detail.[11] The Peng−Robinson (PR)[12] and Soave−Redich−Kwong (SRK)[13] equations of state are also used to model the experimental data.

A classic quadratic mixing rule is used for the energetic parameter a in all three equations of state

$$a = \sum_i \sum_j x_i x_j a_{ij}(1 - k_{ij}) \qquad (1)$$

Table 3. Solvent Properties[14] [a]

solvent	M/g·mol^{-1}	ω ($T_r = 0.7$)	T_c/K	P_c/MPa
ethylene	28.054	0.087	282.34	5.041
hexane	86.177	0.300	507.60	3.025

[a] Molar mass M, acentric factor ω, critical temperature T_c, and critical pressure P_c.

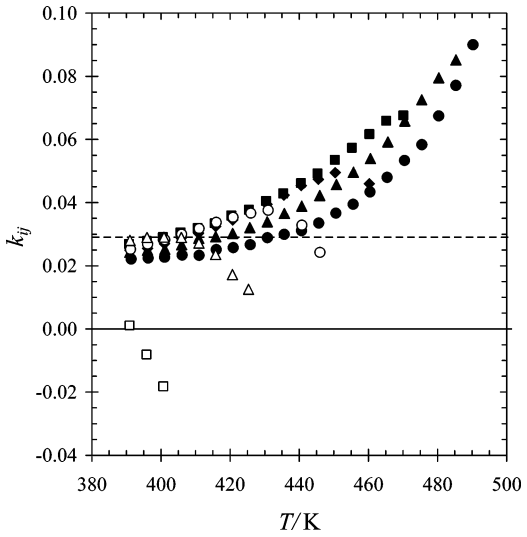

Figure 5. Ethylene (1) + hexane (2) binary interaction parameters k_{ij} required for the MSL-EoS to match each experimental data point. The dashed line is $k_{ij} = 2.905 \times 10^{-2}$. Ethylene mole fraction: ●, $x_1 = 0.0994$; ▲, $x_1 = 0.2002$; ■, $x_1 = 0.3006$; ◆, $x_1 = 0.4002$; ○, $x_1 = 0.4998$; △, $x_1 = 0.6006$; □, $x_1 = 0.7007$.

where x_i and x_j are the molar compositions, a_{ij} is the cross parameter, and k_{ij} is the binary interaction parameter. The properties of ethylene and hexane taken from ref 14 are listed in Table 3.

The binary interaction parameters required for the MSL-EoS to match each experimental data point are shown in Figure 5. The binary interaction parameters required are not significantly dependent on the composition of the mixture. There is a definite curvature with respect to temperature in the binary interaction parameters. The binary interaction parameters as a function of temperature at different compositions have similar curvatures except near the critical point of each composition.

The sensitivity of the phase boundary to changes in the binary interaction parameters is more important. The objective function f_{xPT} used to obtain the MSL binary interaction parameter in this work is

$$f_{xPT} = \frac{1}{N_{xPT}}\left[\sum_{k=1}^{N_{xPT}} |T_{(k)} - T^{o}_{(k)}|\right] + \frac{(N^{o}_{xPT} - N_{xPT})}{N_{xPT}} \times 100 \qquad (2)$$

N^{o}_{xPT} is the total number of experimental data points, whereas N_{xPT} is the total number of converged points in the calculations. The subscript (k) refers to an experimental data point where the calculated temperature $T_{(k)}$ is compared to the experimental temperature $T^{o}_{(k)}$. It is more typical to report the absolute average deviation (AAD) in bubble and dew point temperatures for the converged points.

$$\text{AAD } T = \frac{1}{N_{xPT}}\left[\sum_{k=1}^{N_{xPT}} |T_{(k)} - T^{o}_{(k)}|\right] \qquad (3)$$

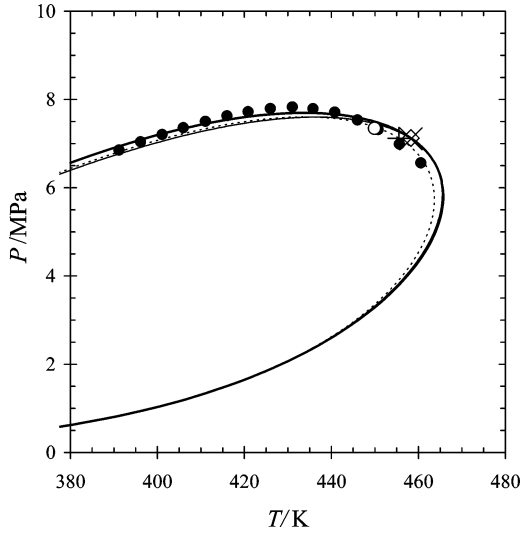

Figure 6. Phase boundary isopleth for a 0.4998 ethylene (1) + hexane (2) mixture. Experimental data: ●, bubble or dew point; ○, critical point. Curves are phase boundaries, and symbols are critical points calculated using different equations of state with $k_{ij} = 2.905 \times 10^{-2}$. − and ◇, MSL; - - - and +, PR; − and ×, SRK.

The MSL binary interaction parameter was $k_{ij} = 2.905 \times 10^{-2}$ based on 79 of 116 points converged. The absolute average deviation in temperature was AAD $T = 4.88$ K (1.15 %). Using a temperature-independent binary interaction parameter does not cause a significant decrease in accuracy over the entire range of temperature.

The MSL-EoS provides a qualitative representation of the experimental data presented in Figures 1 through 4 with a single binary interaction parameter. In Figures 1 and 2, the model deviates most from the experimental data at a given composition near the critical point. The MSL equation provides a fairly good representation of the critical temperature of an ethylene + hexane system as shown in Figure 3. Figure 4 demonstrates that the critical pressure of an ethylene + hexane system is only qualitatively represented by the MSL equation of state because the equation overpredicts the maximum critical pressure by approximately 0.6 MPa.

Phase boundary calculations performed with the PR and SRK equations of state that use the MSL binary interaction parameter are shown in Figure 6. There is a marginal difference in the accuracy of the calculations using the three equations of state. The critical point calculated using the PR equation is closer to the experimental critical point. The critical points are nearly the same using the same binary interaction parameter for the MSL and SRK equations. The three equations of state produce comparable-qualitative representations of the experimental phase boundaries.

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