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Vapor–Liquid Equilibria in the Carbon Dioxide–1-Hexene and Carbon Dioxide–1-Hexyne Systems

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Vapor–liquid equilibrium data for CO_2–1-hexene mixtures at 309.3, 324.2, and 332.3 K and for CO_2–1-hexyne mixtures at 308.1, 323.0, and 332.6 K have been measured in a high-pressure recirculation apparatus. The pressure in the experiments ranged from 1.6 to 9.4 MPa. The experimental data were correlated by use of two simple equations of state: one containing three constants and the other containing four constants. The correlative capabilities of the two equations were found to be similar.

1. Introduction

The behavior of carbon dioxide–hydrocarbon mixtures has been of interest for many years because of their importance in natural gas and petroleum processing. More recently, these mixtures have received increased attention as solvent/cosolvent pairs in the supercritical extraction of coal as well as natural products. Phase equilibrium studies of carbon dioxide–alkane mixtures, with the *n*-alkane ranging from methane to decane, have been conducted by a large number of investigators (*1–3*). However, only a few investigators have studied carbon dioxide–alkene mixtures and there are no reported studies of carbon dioxide–alkyne mixtures. This work presents high-pressure vapor–liquid equilibrium data for the carbon dioxide–1-hexene and carbon dioxide–1-hexyne systems. There is some disagreement in the literature data presented by Wagner and Wichterle (*4*) and Orbey and Vera (*5*) for the CO_2–1-hexene system. The present work was carried out to verify the behavior of this system and to measure new data for the CO_2–1-hexyne system. Although the primary focus of the study was on experimental measurements, the ability of two simple equations of state to correlate the data was also examined and is discussed below.

2. Experimental Section

2.1. ***Apparatus.*** A schematic diagram of the apparatus used in this work is shown in Figure 1. The apparatus consisted of a stainless-steel view cell (similar to a Jerguson liquid level gauge of 40 cm^3 capacity) in which both the liquid and vapor phases were countercurrently recirculated in order to provide mixing of the phases and to ensure that equilibrium was established. An Emco magnetic pump (Model 101) was used for the recirculation of the vapor phase, while a Ruska magnetic pump (Model 2330-802) was used for the liquid phase. Each recirculation loop included ultra-low-volume high-pressure sampling valves manufactured by Valco Instruments Inc. The vapor sampling valve had a volume of 1.0 μL and the liquid valve 0.2 μL. The sampling valves were connected on-line to a Hewlett-Packard gas chromatograph (Model 5890A) equipped with a thermal conductivity detector. The carrier flow lines leading from the valves to the gas chromatograph were wrapped with heating tape to prevent condensation in the lines.

An additional feature of the apparatus was the use of an HIP pressure generator as a variable volume controller, similar to that used by Radosz (*6*). The variable volume allows the control and/or regulation of the system pressure and can be invaluable for correction of disturbances caused by sampling. It should be added that these disturbances were minimal in our apparatus because of the ultra-low-volume sampling valves used.

The entire assembly was placed in a constant-temperature air bath in which an Omega temperature controller (Model CN5001T1-A) connected to a heating element was used to control the air-bath temperature.

The pressure was measured by a digital Heise pressure gauge (Model 710A), and the temperature was determined by a thermistor inserted into the side of the view cell. The pressure gauge was calibrated against a Budenberg dead-weight tester and was estimated to be accurate to within ±0.014 MPa. The thermistor was calibrated by use of a Leeds and Northrup platinum resistance thermometer, and the temperature measurements were estimated to be accurate within ±0.1 K. The gas chromatograph was calibrated by preparing synthetic mixtures to determine response factors for the CO_2–1-hexene and CO_2–1-hexyne systems. The response factors were estimated to be accurate within 3%. The main source of error could be attributed to difficulties in the preparation of mixtures.

2.2. ***Experimental Procedure.*** The system was evacuated at the beginning of the experiment, and the liquid component was introduced into the equilibrium cell from the feed reservoir. Carbon dioxide was then charged into the apparatus. If pressures greater than cylinder supply pressure were desired, the carbon dioxide was liquified by passing through an ice bath and pumped into the apparatus by a Milton Roy simplex mini pump (Model 396-89). The recirculation pumps were then turned on and more CO_2 was introduced into the apparatus to achieve the desired pressures. Some trial and error in charging the apparatus to achieve acceptable liquid levels in the view cell was sometimes also necessary.

Recirculation of the phases was continued until equilibrium had been established. Both phases were then sampled, with the liquid phase being sampled first. Multiple samples (typically 4–6) were taken. After sampling the liquid phase, the vapor sample valve was heated by use of heating tape. The valve temperature was maintained slightly above the bath temperature to prevent any condensation of heavier components in the vapor valve sample slot. The heating was kept minimal to prevent disturbance of equilibrium. Several samples of the vapor phase were then taken until vapor-phase analyses became reproducible. The first few were often found to give

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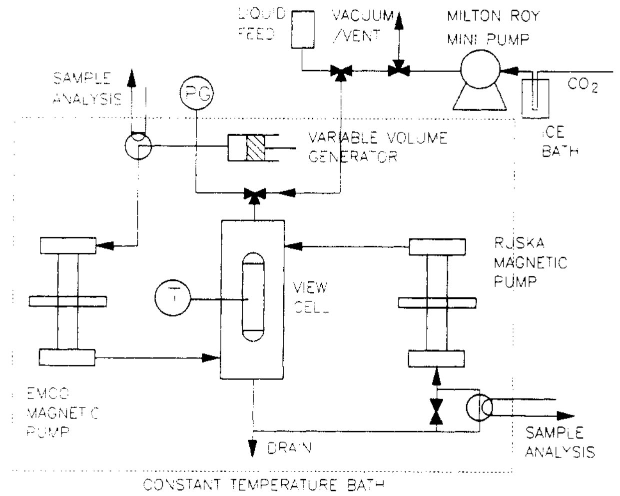

Figure 1. Schematic diagram of apparatus.

slightly higher compositions of the heavy component. This was believed to be a result of some condensation in the vapor valve slot. After a few initial samples or after flushing, this problem disappeared and analysis of vapor compositions gave reproducible results. Three or four samples of the vapor phase were typically taken after stability had been achieved. The liquid-phase composition was determined from the average of all samples whereas the vapor-phase composition was determined from the average of the samples taken after flushing.

After sampling of the two phases, the heating tape around the vapor sampling valve was turned off and the system pressure was reduced for further phase equilibrium measurements. Reduction of the system pressure was obtained by simply venting some of the vapor phase.

3. Source and Purity of the Materials

Coleman grade CO_2 of minimum purity 99.99% was obtained from Matheson Gas Products, and 1-hexene and 1-hexyne were obtained from the Aldrich Chemical Co. The 1-hexene had a stated purity of 99+%, and the 1-hexyne had a stated purity of 97% (97.4% lot analysis). All compounds were used without further purification.

4. Reproducibility of Measurements

The reproducibility of data taken depended on the pressure and temperature stability during sampling. Temperature stability during sampling was generally within 0.1 K. Most of the temperature change could be attributed to an increase caused by the heating of the vapor sampling valve. Pressure stability was directly related to the temperature stability and was generally within ±0.007 MPa. Since disturbances from sampling were generally negligible, no reductions in system volume were required to compensate for any pressure changes. The maximum recorded deviation between temperatures along an "isotherm" for a series of pressures was 0.47 K.

Reproducibility of the vapor-phase composition was generally within ±0.0007 mole fraction, whereas that of the liquid-phase composition was ±0.005 mole fraction with occassional differences of ±0.01 mole fraction in the CO_2–1-hexene system. This is reflected in the scatter in the liquid-phase data in the CO_2–1-hexene system. The reproducibility of the CO_2–1-hexyne liquid-phase compositions was generally better.

5. Results and Discussion

Vapor–liquid equilibrium data for CO_2–1-hexene at 309.3, 324.2, and 332.3 K are presented in Table I.

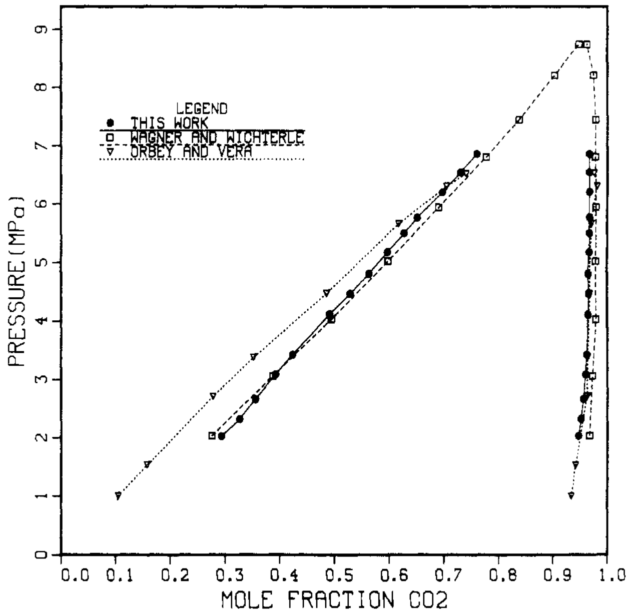

Figure 2. Data and comparisons for CO_2–1-hexene mixtures at 324.2 K.

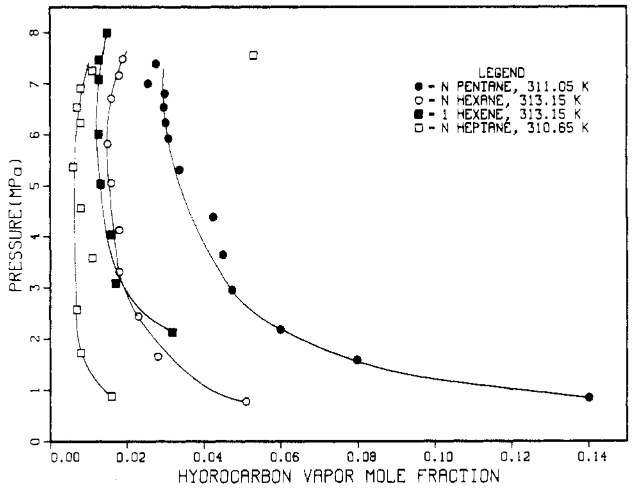

Figure 3. Comparisons of literature data for CO_2–hydrocarbon systems near 313.2 K.

The data at 324.2 K are compared with the measurements reported at 323.15 K by Orbey and Vera (*5*) and Wagner and Wichterle (*4*) in Figure 2. The data are in good agreement with the liquid-phase data of Wagner and Wichterle but show some disagreement with their vapor-phase data. On the other hand, good agreement was obtained with the vapor-phase data of Orbey and Vera, but there was considerable disagreement with their liquid-phase data. The data of Orbey and Vera at the highest two pressures appear to be displaced from the rest of their data. These two measurements give good agreement with our liquid-phase compositions and slight disagreement with our vapor-phase compositions.

Comparisons of Wagner and Wichterle's vapor-phase compositions for CO_2–1-hexene at 313.15 K with published data for CO_2–*n*-pentane (*2*), CO_2–*n*-hexane (*7*), and CO_2–*n*-heptane (*8*) at or near 313.15 K (Figure 3) show that their data lie between the *n*-hexane and *n*-heptane data. However, Dandge et al. (*9*) state that, for a given carbon number, "the solubility of the alkene (in the vapor phase of CO_2 is) ... noticeably higher than that of the *n*-alkane." Therefore, the CO_2–1-hexene data should lie between those of CO_2–*n*-pentane and CO_2–*n*-hexane systems. Wagner and Wichterle's vapor-phase compositions of CO_2–1-hexene are therefore perhaps low in the hydrocarbon composition. On the other hand, the values obtained in the present work are in agreement with the observations of Dandge et al.

Table I. Experimental Data for the CO_2-1-Hexene System

press., MPa	temp, K	liquid mole fraction CO_2	vapor mole fraction CO_2
6.467	309.06	0.8825	0.9813
6.185	309.34	0.8495	0.9807
5.874	309.43	0.8136	0.9798
5.509	309.42	0.7738	0.9786
5.081	309.14	0.7180	0.9801
4.826	309.33	0.6933	0.9798
4.482	309.20	0.6567	0.9793
4.130	309.10	0.6194	0.9787
3.799	309.22	0.5760	0.9773
3.399	309.17	0.5394	0.9764
3.096	309.32	0.5021	0.9749
2.744	309.43	0.4425	0.9734
2.420	309.40	0.3939	0.9715
2.124	309.36	0.3573	0.9689
1.655	309.27	0.2981	0.9628
	av 309.28		
6.860	324.30	0.7608	0.9669
6.543	324.33	0.7306	0.9670
6.205	324.32	0.6976	0.9673
5.771	324.23	0.6517	0.9677
5.502	324.21	0.6271	0.9674
5.178	324.25	0.5964	0.9672
4.806	324.17	0.5627	0.9649
4.468	324.18	0.5287	0.9659
4.116	323.99	0.4911	0.9647
3.434	324.32	0.4242	0.9621
3.096	324.21	0.3930	0.9598
2.668	324.22	0.3561	0.9560
2.324	324.23	0.3273	0.9519
2.034	324.22	0.2940	0.9472
	av 324.23		
9.349	332.31	0.8778	0.9335
8.970	332.33	0.8466	0.9451
8.612	332.30	0.8232	0.9507
8.246	332.41	0.7976	0.9526
7.157	332.15	0.7151	0.9557
6.702	332.22	0.6610	0.9554
5.764	332.29	0.5838	0.9569
5.481	332.39	0.5621	0.9561
5.137	332.36	0.5231	0.9555
4.737	332.39	0.4937	0.9531
4.268	332.39	0.4422	0.9506
3.758	332.33	0.3977	0.9490
3.413	332.34	0.3629	0.9435
3.054	332.34	0.3299	0.9390
2.744	332.35	0.3062	0.9364
2.227	332.33	0.2602	0.9265
	av 332.33		

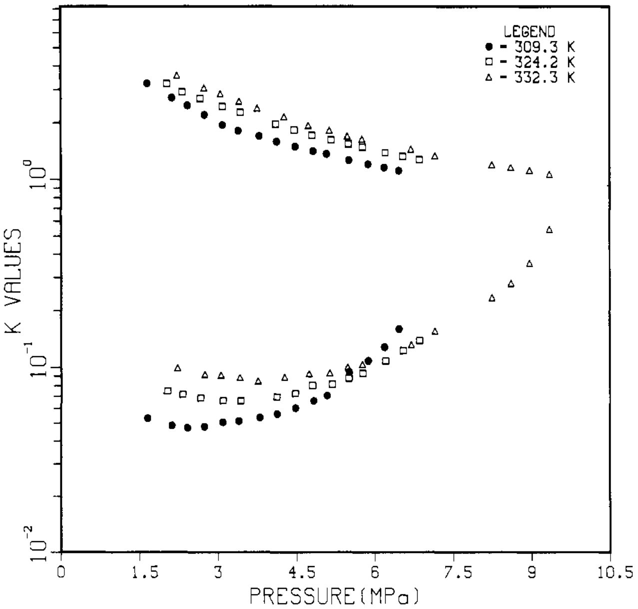

Figure 4. Experimental K values in the CO_2–1-hexene system.

Table II. Experimental Data for the CO_2-1-Hexyne System

press., MPa	temp, K	liquid mole fraction CO_2	vapor mole fraction CO_2
6.412	307.96	0.9260	0.9883
6.192	308.02	0.9051	0.9879
5.888	307.87	0.8807	0.9875
5.647	307.87	0.8540	0.9871
5.378	307.93	0.8204	0.9869
5.116	308.34	0.7730	0.9836
4.833	308.22	0.7366	0.9851
4.516	308.23	0.6962	0.9835
4.130	308.17	0.6466	0.9835
3.834	308.11	0.6130	0.9828
3.627	307.98	0.5928	0.9821
3.434	307.95	0.5644	0.9812
3.096	307.99	0.5271	0.9801
2.744	308.11	0.4798	0.9797
2.393	308.21	0.4387	0.9762
2.062	308.04	0.4058	0.9753
	av 308.06		
8.453	323.18	0.9181	0.9706
8.122	323.18	0.9044	0.9733
7.860	323.19	0.8905	0.9746
7.005	322.78	0.8273	0.9755
6.709	322.83	0.7959	0.9767
6.281	322.89	0.7593	0.9766
5.840	322.90	0.7132	0.9767
5.516	322.91	0.6792	0.9765
5.123	322.93	0.6431	0.9760
4.813	322.90	0.6117	0.9757
4.468	322.97	0.5818	0.9750
4.116	322.92	0.5455	0.9738
3.723	322.98	0.5068	0.9727
3.447	323.10	0.4812	0.9713
3.116	323.11	0.4514	0.9694
2.772	323.04	0.4168	0.9671
2.330	322.97	0.3762	0.9630
	av 322.99		
8.281	332.60	0.8373	0.9639
7.915	332.53	0.8101	0.9659
7.605	332.53	0.7852	0.9669
7.240	332.50	0.7561	0.9679
6.881	332.59	0.7296	0.9684
6.536	332.60	0.6973	0.9681
6.192	332.64	0.6665	0.9687
5.840	332.68	0.6381	0.9686
5.474	332.73	0.6067	0.9683
5.171	332.78	0.5783	0.9679
4.840	332.76	0.5459	0.9672
4.737	332.61	0.5391	0.9672
4.385	332.67	0.5089	0.9664
4.096	332.80	0.4804	0.9650
3.737	332.76	0.4483	0.9634
3.406	332.66	0.4225	0.9617
3.054	332.60	0.3908	0.9593
2.572	332.60	0.3490	0.9541
	av 332.65		

The increase in the solubility of the alkene in the vapor phase (compared with the solubility of the n-alkane) could be because 1-hexene is more volatile than hexane. Therefore, it is not surprising that the CO_2–1-hexene vapor phase contains more hydrocarbon than the vapor phase of the CO_2–n-hexane system.

Vapor–liquid equilibrium data for CO_2–1-hexyne at 308.1, 323.0, and 332.6 K are presented in Table II. Analyses of the liquid phase showed the presence of a small amount of a third component during our measurements. The third component (impurity from the hexyne) was consistently in the range of 1% of the hexyne composition. It was assumed to be part of the hexyne in the calculation of the liquid-phase compositions. Equilibrium ratios (K values) for the CO_2–1-hexene and CO_2–1-hexyne systems are shown in Figures 4 and 5, respectively.

The effect of volatility on the hydrocarbon composition in the vapor phase may also be noted from the data on the CO_2–1-

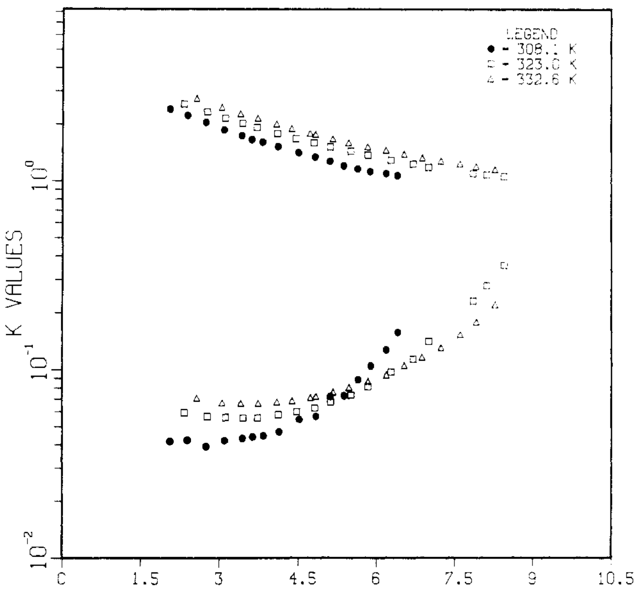

Figure 5. Experimental K values in the CO_2–1-hexyne system.

hexene and CO_2–1-hexyne systems. The effect of the double and triple bonds can be seen in the normal boiling points, which show a steady increase in going from 1-hexene → n-hexane → 1-hexyne. Therefore, the concentration of hexyne in the vapor phase is smaller than the corresponding concentration of hexene at the same temperature and pressure. Figure 6 shows a comparison of the phase equilibria between the two systems for the highest isotherm.

The main source of error in the measurement of the phase compositions is that associated with the response factors. This means that the largest errors in compositions occur when both components are present in roughly equal amounts. Inaccuracies in the response factors, however, have less effect on the error when one component predominates (as in the case of our vapor compositions). We estimate that the vapor-phase compositions are accurate to ±0.007 and the liquid-phase compositions are accurate to ±0.02.

The CO_2–1-hexene and CO_2–1-hexyne experimental data were correlated by using the Patel–Teja (*10*) and Trebble–Bishnoi (*11*) equations of state. These equations, which contain three and four constants, respectively, require the critical properties and acentric factors of the pure components. Critical properties and the accentric factor for CO_2 and 1-hexene were taken from Reid, Prausnitz, and Poling (*12*). Critical properties of 1-hexyne were estimated by using the Ambrose methods (*13*, *14*) since no published values are available. Similarly, the acentric factor for 1-hexyne was estimated by extrapolating a vapor pressure correlation given by Smith and Srivastava (*15*).

The two equations of state can be represented as follows:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v^2 + (b + c)v - bc - d^2} \tag{1}$$

For the Patel–Teja equation $d = 0$ and the constants a, b, and c are given by

$$a = \frac{\Omega_a R^2 T_c^{\,2} \alpha(T_r)}{P_c} \tag{2}$$

$$b = \frac{\Omega_b R T_c}{P_c} \tag{3}$$

$$c = \frac{\Omega_c R T_c}{P_c} \tag{4}$$

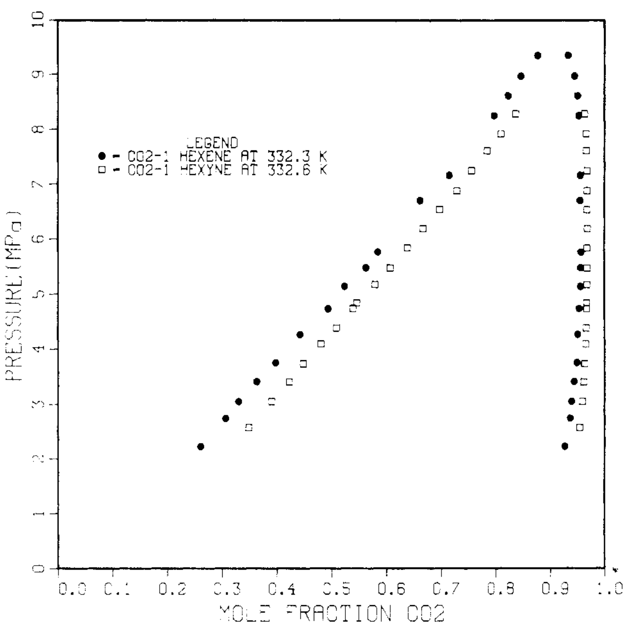

Figure 6. Effect of structure on vapor–liquid equilibria in CO_2–1-hexene and CO_2–1-hexyne systems at 332 K.

where $\alpha(T_r)$ is a function of reduced temperature and is given by

$$\alpha^{1/2} = 1 + F(1 - T_r^{\,1/2}) \tag{5}$$

P_c and T_c are the critical pressure and critical temperature, respectively, and the values of Ω_a, Ω_b, and Ω_c are constants for a given substance. In extending the equation of state to mixtures, the following mixing rules for a, b, and c were used:

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij} \tag{6}$$

$$b = \sum_{i=1}^{n} x_i b_i \tag{7}$$

$$c = \sum_{i=1}^{n} x_i c_i \tag{8}$$

where

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{9}$$

k_{ij} is a binary interaction coefficient, which is optimized to give the best fit to the experimental data.

For the Trebble–Bishnoi equation the constants a, b, c, and d are given by

$$a = \frac{A_c R^2 T_c^{\,2} \alpha(T_r)}{P_c} \tag{10}$$

$$b = \frac{B_c R T_c \beta(T_r)}{P_c} \tag{11}$$

$$c = \frac{C_c R T_c}{P_c} \tag{12}$$

$$d = \frac{D_c R T_c}{P_c} \tag{13}$$

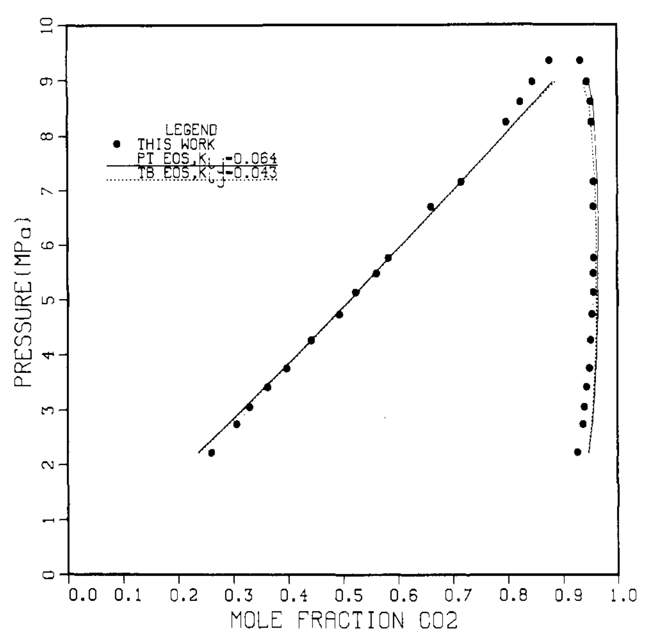

Figure 7. Experimental and calculated vapor–liquid equilibria in the CO_2–1-hexene system at 332.33 K.

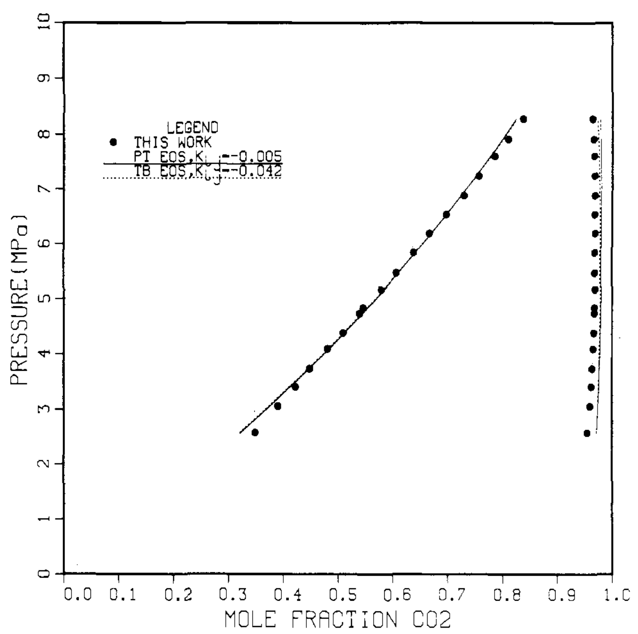

Figure 8. Experimental and calculated vapor–liquid equilibria in the CO_2–1-hexyne system at 332.65 K.

where $\alpha(T_r)$ and $\beta(T_r)$ are functions of reduced temperature given by

$$\alpha = \exp[q_1(1.0 - T_r)] \qquad (14)$$

$$\beta = 1.0 + q_2(1.0 - T_r + \ln T_r) \qquad \text{for } T \leq T_c$$

$$\beta = 1.0 \qquad \text{for } T > T_c \qquad (15)$$

and A_c, B_c, C_c, and D_c are constants for a given fluid.

The following mixing rules were used in extending the Trebble–Bishnoi equation of state to mixtures:

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij} \qquad (16)$$

$$b = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j b_{ij} \qquad (17)$$

$$c = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j c_{ij} \qquad (18)$$

$$d = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j d_{ij} \qquad (19)$$

where

$$a_{ij} = (a_{ii}a_{jj})^{1/2}(1.0 - k_{ij}) \qquad (20)$$

$$b_{ij} = \frac{1}{2}(b_{ii} + b_{jj}) \qquad (21)$$

$$c_{ij} = \frac{1}{2}(c_{ii} + c_{jj}) \qquad (22)$$

$$d_{ij} = \frac{1}{2}(d_{ii} + d_{jj}) \qquad (23)$$

The binary interaction coefficients, k_{ij}, were obtained by optimizing the following objective function:

obj function =

$$\sum_{k=1}^{\text{NPts}}\sum_{i=1}^{\text{NComp}}\left(\left|\frac{x_i^{\text{calcd}} - x_i^{\text{exptl}}}{x_i^{\text{exptl}}}\right| \times 100 + \left|\frac{y_i^{\text{calcd}} - y_i^{\text{exptl}}}{y_i^{\text{exptl}}}\right| \times 100\right) \qquad (24)$$

The experimental pressures and the average experimental "isotherm" temperatures were used in the calculations. The results of the modeling with the optimized binary interaction coefficients are shown along with the experimental data for the highest measured isotherms for each of the systems in Figures 7 and 8. Both equations of state give comparable results.

Registry No. CO_2, 124-38-9; 1-hexene, 592-41-6; 1-hexyne, 693-02-7.

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