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Vapor−Liquid Equilibria for the Hexane + Hexadecane and Hexane + 1-Hexadecanol Systems at Elevated Temperatures and Pressures

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Vapor and liquid equilibrium compositions have been measured for the hexane + hexadecane and the hexane + 1-hexadecanol systems at temperatures from 472.0 K to 623.0 K and pressures from 6.2 bar to 46.4 bar. A continuous-flow apparatus was used both to minimize possible thermal degradation and to accurately measure the lower hexadecanol concentrations in the vapor phase. Mixture critical pressures and compositions were also measured. Results indicate that the addition of the hydroxyl group to the C_{16} hydrocarbon backbone significantly affects the phase behavior with hexane.

Introduction

Fischer−Tropsch (F−T) synthesis produces a broad range of products (known as waxes) consisting primarily of paraffins, olefins, and alcohols with carbon numbers ranging from 1 up to about 200. Slurry bubble column (SBC) reactors are receiving increasing attention as the preferred way to carry out the F−T reaction. However, the separation of the reactor catalyst from the wax product is an issue that has yet to be satisfactorily resolved. Supercritical fluid (SCF) extraction was first proposed by Roberts et al. (1992) for the separation of the catalyst from the wax, followed by fractionation of the wax product itself. As has been demonstrated by White et al. (1996), a wax that contains as little as 0.05 mass % catalyst can be recovered with supercritical hexane (T_c = 507.5 K, P_c = 30.1 bar). Furthermore, preliminary calculations by Biales et al. (1997) indicate that product fractionation and recovery are most effective when SCF solvents with critical temperatures near the operating temperature of the SBC reactor (i.e., 473−573 K) are used.

A goal of this study is the development of a thermodynamic model applicable to the F−T wax/supercritical fluid system. However, phase equilibrium measurements at elevated temperatures for systems containing an appropriate supercritical solvent with model components representative of those found in F−T waxes are surprisingly scarce. Nederbragt and DeJong (1951) have measured elevated-temperature, binary VLE for pentane and heptane with several *n*-alkanes from C_{16} to C_{24}. However, none of the waxes were of high purity. The group at Delft (e.g., Gregorowicz et al. (1992) and Peters et al. (1988)) has measured liquid-phase compositions for light gases with a number of model F−T waxes, but no vapor-phase compositions or temperatures above 473 K are reported. Nieuwoudt (1996) has examined the VLE behavior of hexacontane (n-C_{60}) in butane at temperatures from (433 to 453) K. Joyce and Thies (1997) have studied binary VLE for hexane + squalane (a branched C_{30} alkane) from (470 to 623) K. In this paper we report on the binary phase behavior of two model F−T wax components, hexadecane and 1-hexadecanol, in near critical and supercritical hexane. Breman et al. (1994) have measured the solubility of hexane gas in hexadecane and 1-hexadecanol at temperatures from (420 to 525) K, but system pressures were always below 3 bar.

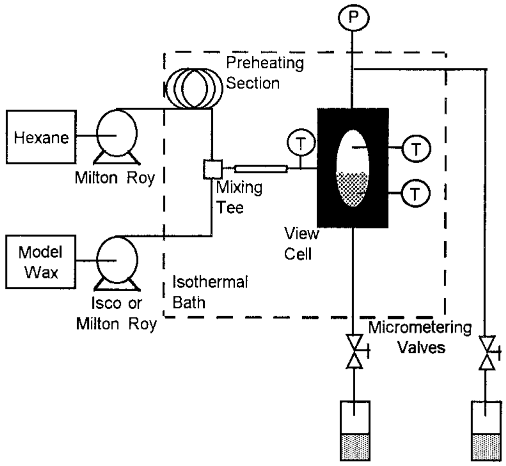

Figure 1. Schematic of the continuous-flow apparatus.

Experimental Section

Apparatus and Procedure. A continuous-flow apparatus was used to measure vapor−liquid equilibrium for both of the systems examined; see Figure 1. The apparatus has previously been described in detail (Joyce and Thies, 1997), so only a brief description is given below. For an experimental run, hexane and the model wax compound are pumped to the system at a combined flow rate between 150 and 250 mL/h. The two components are preheated within the isothermal nitrogen bath in separate lines and are then combined in a specially designed mixing tee. After passing through an expansion and contraction to ensure adequate mixing, the two-phase stream enters the view cell (volume ∼ 12 mL), where the two phases are allowed to separate. The vapor and liquid phases flow out the top and bottom of the cell, respectively, and are reduced to ambient pressure after passing through micrometering (MM) valves. The top-phase MM valve is used to control the pressure, while the bottom-phase MM valve is used to control the liquid level within the view cell. Each phase then enters a sample collection vial, which is sealed to the tubing with an airtight rubber stopper. As the sample is collected, a slight positive pressure is created in the vial, so the sample losses are known to be negligible. The glass vials are kept cold in an ice bath to prevent the vaporization

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of hexane. Typically, triplicate samples weighing 2−6 g each are collected for each phase.

When 1-hexadecanol (mp = 55 °C) is used as the wax component, modifications to the apparatus and sample collection technique are required to prevent solids precipitation. The hexadecanol feed reservoir, feed lines, and Milton Roy pump head are heated with electrical heating tape (Glas-Col, Catalog No. DET025) and maintained at (75−100) °C. This heating tape is also used to maintain the temperature of the sampling lines exiting the bath at about 75 °C. The last 5 cm of sampling line is not wrapped with tape so that the line can be inserted into the sealed sample collection vial. To prevent this portion of the line from plugging due to hexadecanol solidification, the last 8 cm of each sampling line is made of copper, which remains hot by conduction. Because the sample lines are heated, some hexane (bp = 69 °C) flashes upon expansion to ambient conditions. To prevent the loss of hexane vapor, better sealing and colder collection vials are required. An improved seal is obtained by first threading the copper sample lines and screwing on tapped vial caps; the caps are then permanently sealed to the sample line with epoxy. Colder collection temperatures (∼−10 °C) are obtained by cooling the sample vials in a mixture of ice and salt.

Experimental Measurements. The temperatures of the feed to the cell and of the top and bottom phases were measured with three type K differential thermocouples referenced to an aluminum block located in the bath. The temperature of the block itself was measured with a secondary-standard PRT. A full description of the temperature measurement and calibration scheme, which is capable of measuring temperatures to an accuracy of ±0.1 K, is given elsewhere (Stevenson, 1994). The system pressure was measured using a Bourdon tube gauge (Heise, model CM, 0-1000 psig). The pressure gauge was calibrated against a Budenburg dead weight gauge (model 380H) to an accuracy of 0.04% of the indicated pressure.

All samples were analyzed with a Hewlett-Packard 5890A gas chromatograph (GC) equipped with a flame ionization detector and autosampler. Splitless injection was used to eliminate possible sample discrimination. Samples containing hexadecane were diluted with tetrahydrofuran, and those containing hexadecanol were diluted with toluene. Dodecane and hexadecane were used as internal standards for hexadecane and 1-hexadecanol, respectively. A 0.53 mm × 5 m capillary column with a 2.65 μm film thickness (Hewlett-Packard, HP-1) was used for the separation.

Materials. Hexane (99+%), hexadecane (99%), and 1-hexadecanol (99%) were purchased from Aldrich and used without further purification. The stated purities were verified by GC using a 0.53 mm × 60 m × 0.5 μm column (Restek, RTX-1) for the hexane and a 0.53 mm × 15m × 0.15 μm column (J&W Scientific, DB-1) for the two model waxes.

Results and Discussion

Measured compositions and corresponding pressures for the hexane + hexadecane system at 472.3, 524.4, 572.5, and 623.0 K are given in Table 1 and are depicted on a pressure−composition diagram in Figure 2. Mixture critical pressures and compositions are also reported at the three higher temperatures. For clarity, the vapor-phase compositions of the 472.3 K isotherm are also plotted in Figure 3a. For the liquid phase, the three samples collected at each temperature and pressure were generally reproducible to better than ±1% deviation in the minor component; for the vapor phase, to better than ±2%.

Table 1. Measured Equilibrium Pressures and Liquid (x) and Vapor (y) Compositions for the Hexane (A) + Hexadecane (B) System at (472.3, 524.4, 572.5, and 623.0) K

P/bar	x_B	y_B	P/bar	x_B	y_B
T = 472.3 K			T = 572.5 K		
6.18	0.548	0.0142	7.91	0.804	0.193
7.91	0.462	0.0107	14.80	0.629	0.117
9.63	0.363	0.00818	21.70	0.486	0.0887
11.36	0.277	0.00621	25.14	0.419	0.0828
13.08	0.195	0.00462	28.59	0.356	0.0801
14.80	0.123	0.00299	32.04	0.296	0.0804
16.53	0.0543	0.00145	35.49	0.240	0.0848
17.35	0.0230	0.000605	38.93	0.170	0.107
			39.45[a]	0.137	0.137
T = 524.4 K			T = 623.0 K		
7.91	0.676	0.0628	11.36	0.818	0.364
11.36	0.564	0.0463	16.53	0.719	0.274
14.80	0.450	0.0360	21.70	0.628	0.233
18.25	0.362	0.0304	25.14	0.566	0.210
21.70	0.276	0.0266	28.59	0.505	0.206
25.14	0.195	0.0234	32.04	0.443	0.201
28.59	0.132	0.0218	35.49	0.383	0.213
32.04	0.0717	0.0212	37.21	0.349	0.228
33.76[a]	0.0306	0.0306	38.24[a]	0.279	0.279

[a] Vapor−liquid critical point.

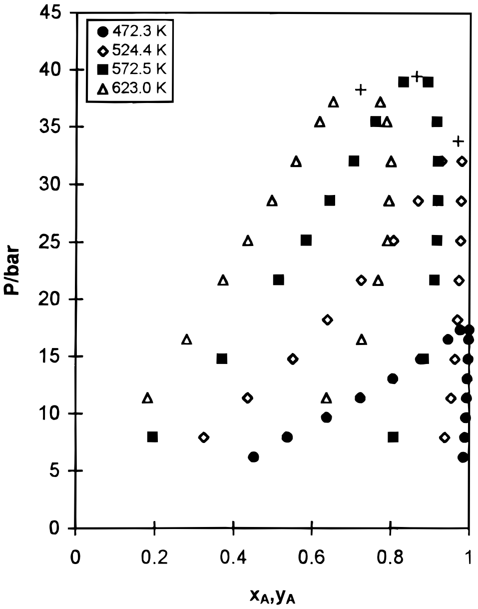

Figure 2. Pressure vs composition diagram for the hexane (A) + hexadecane (B) system at (472.3, 524.4, 572.5, and 623.0) K. The + denote mixture critical points.

Some variations in the temperature of the view cell are characteristic of a flow apparatus. Considering both the variations that occurred during experiments and the accuracy of the temperature measurement scheme, the temperatures reported for this binary are believed to be accurate to ±0.3 K. Similarly, the reported pressures are believed to be accurate to ±0.17 bar. Considering all sources of error, the reported liquid and vapor compositions are believed to be accurate to better than ±2 and ±3% deviation in the minor component, respectively.

Mixture critical pressures were obtained by the observation of critical opalescence within the equilibrium cell. To obtain critical point compositions, critical opalescence phenomena were maintained in the view cell while samples were collected as previously described. We have found that the flow apparatus can be used to measure both mixture critical pressures and critical point compositions to an accuracy comparable to our measurements for conventional vapor and liquid compositions. Results are believed to be

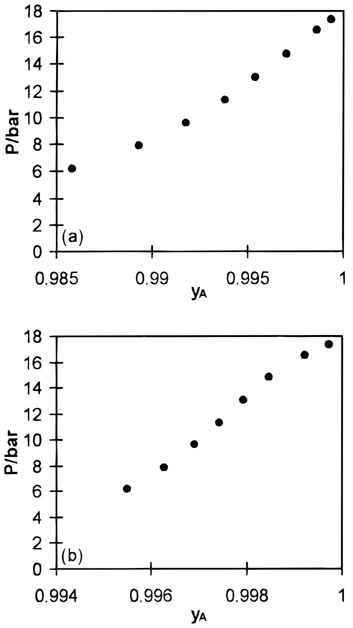

Figure 3. Vapor-phase compositions for (a) hexane (A) + hexadecane (B) at 472.3 K; (b) hexane (A) + 1-hexadecanol (C) at 472.1 K.

Table 2. Measured Equilibrium Pressures and Liquid (*x*) and Vapor (*y*) Compositions for the Hexane (A) + 1-Hexadecanol (C) System at (472.1, 524.4, 572.4, and 623.0) K

P/bar	x_C	y_C	P/bar	x_C	y_C
	$T = 472.1$ K			$T = 572.4$ K	
6.18	0.628	0.00452	7.91	0.826	0.0865
7.91	0.526	0.00373	11.36	0.756	0.0663
9.63	0.428	0.00310	14.80	0.678	0.0551
11.36	0.327	0.00258	18.25	0.598	0.0492
13.08	0.226	0.00207	23.15	0.504	0.0445
14.80	0.134	0.00155	28.59	0.393	0.0432
16.53	0.0589	0.000788	35.49	0.288	0.0470
17.35	0.0231	0.000279	38.93	0.215	0.0558
			42.38	0.144	0.0749
			43.21[a]	0.109	0.109
	$T = 524.4$ K			$T = 623.0$ K	
7.91	0.666	0.0250	11.36	0.835	0.184
11.36	0.588	0.0188	18.25	0.713	0.134
14.80	0.481	0.0160	21.70	0.659	0.127
18.25	0.393	0.0139	28.59	0.541	0.114
21.70	0.308	0.0129	32.04	0.491	0.113
25.14	0.220	0.0128	35.49	0.442	0.114
28.59	0.140	0.0123	38.93	0.374	0.116
32.04	0.0688	0.0134	42.38	0.325	0.126
34.35[a]	0.0302	0.0302	46.41[a]	0.199	0.199

[a] Vapor−liquid critical point.

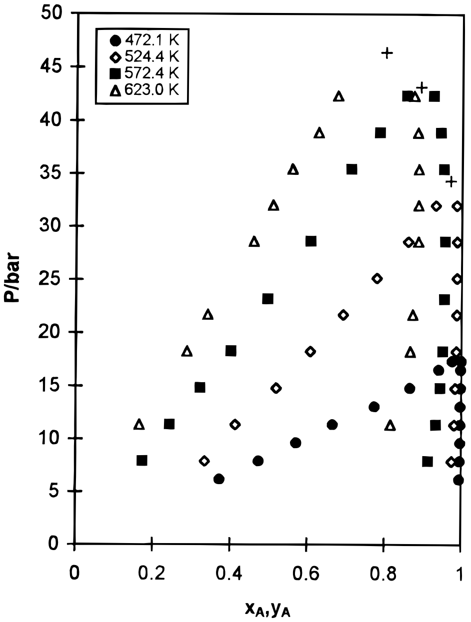

Figure 4. Pressure vs composition diagram for the hexane (A) + 1-hexadecanol (C) system at (472.1, 524.4, 572.4, and 623.0) K. The + denote mixture critical points.

Table 3. Measured Equilibrium Compositions and Nominal Flow Rates for the Hexane (A) + 1-Hexadecanol (C) System at 472.1 K and 11.36 Bar

total flow rate (mL/h)	x_C	y_C
100	0.324	0.00257
200	0.328	0.00254
300	0.328	0.00262

reliable because (1) the intense reddish color associated with opalescence is observed only over a narrow pressure range not exceeding ±0.10 bar, and (2) changes in the overall system composition of less than ±2% in the minor component cause the complete disappearance and reappearance of critical opalescence in the view cell. Taking into consideration all sources of uncertainty, including the range of temperatures, pressures, and compositions over which critical opalescence was observed, we believe the reported critical point compositions are accurate to ±4% in the minor component.

Measured compositions and corresponding pressures for the hexane + 1-hexadecanol binary system at 472.1, 524.4, 572.4, and 623.0 K are given in Table 2 and are depicted on a pressure−composition diagram in Figure 4. For clarity, the vapor-phase compositions of the 472.1 K isotherm are plotted in Figure 3b. For the liquid phase, the three samples collected at a given temperature and pressure were generally reproducible to better than ±2% deviation in the minor-component composition. Only for the two liquid-phase compositions containing more than 80 mol % hexadecanol were larger errors obtained, that is, within ±5%. For the vapor phase, the samples were typically reproducible to ±3% in the minor component. Temperature and pressure uncertainties for a given isotherm were always less than ±0.25 K and ±0.17 bar, respectively. Considering all sources of error, the reported liquid- and vapor-phase compositions are generally believed to be accurate to ±3 and ±4%, respectively. Mixture critical points were measured as described for the hexane + hexadecane system.

To verify that equilibrium conditions exist in the view cell, samples were collected at different flow rates. As can be seen by the example for hexane + hexadecanol in Table 3, no effect of flow rate on the measured compositions was observed within the experimental uncertainties reported.

Because many of the phase compositions for the two binaries studied were measured at virtually the same temperatures and pressures (see Tables 1 and 2), a direct comparison of the effect of the added hydroxyl group on the system phase behavior can be made. The data indicate that even with an alkane as long as hexadecane, the impact on the phase behavior of adding an OH group is still significant. For example, hexadecanol has about one-third the solubility of hexadecane in the vapor phase at 472 K and about one-half the solubility at 572 K.

The measured mixture critical points were used to generate the critical locus for each binary; see Figure 5. Pure component critical points for hexane ($T_c = 507.5$ K, $P_c = 30.1$ bar) and hexadecane ($T_c = 722$ K, $P_c = 14.1$ bar) were taken from the literature (Reid et al., 1987). For

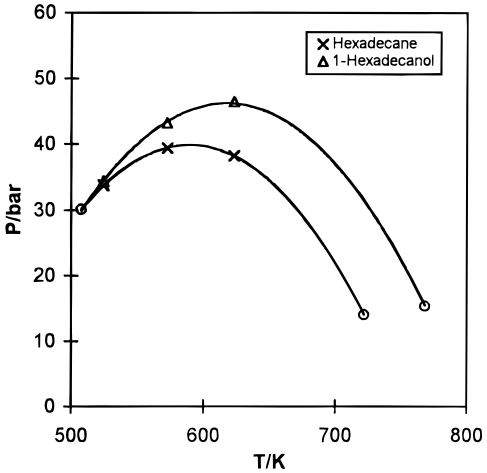

Figure 5. Critical loci for the hexane (A) + hexadecane (B) and hexane (A) + 1-hexadecanol (C) systems.

1-hexadecanol, the pure component critical properties (T_c = 768.4 K, P_c = 15.4 bar) had to be estimated from the correlation of Teja et al. (1990) for 1-alkanols, which was developed from critical point measurements for alkanols up to C_{12}. For clarity, a smooth curve connects the critical points. As expected, each system exhibits type I phase behavior (Rowlinson and Swinton, 1982), with the critical curves running through a maximum in pressure. However, the two-phase region for the hexane + 1-hexadecanol system extends to significantly higher pressures and temperatures.

In summary, the effect of an added hydroxyl group on the phase behavior of Fischer−Tropsch waxes in dense supercritical fluids is significant for hydrocarbon chains that are at least 16 carbons long. Future work will be necessary to determine just how long the hydrocarbon chain must be before the effect of an OH group becomes negligible.

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