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Vapor−Liquid Equilibria for the Hexane + Tetracosane and Hexane + Hexatriacontane Systems at Elevated Temperatures and Pressures

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Vapor and liquid equilibrium compositions have been measured for the hexane + tetracosane and hexane + hexatriacontane systems at temperatures from 473.0 K to 622.9 K and pressures from 6.2 bar to 64.5 bar. A continuous-flow apparatus was used so that the low wax concentrations in the vapor phase could be accurately measured. Mixture critical pressures and compositions were also measured. The effects of chain length, branching, and substituent groups on the phase behavior of binary systems containing hexane + a long-chain alkane are summarized in the form of a pressure versus temperature projection.

Introduction

Vapor−liquid equilibrium (VLE) compositions are being measured by our group for binary mixtures of short- and long-chain alkanes at elevated temperatures and pressures. Such fundamental measurements are of interest for several reasons. For example, although modern equations of state based on statistical mechanics have been developed for chainlike molecules (e.g., SAFT; Chapman et al., 1990), these approaches are still largely unproven for their ability to accurately predict the effect of molecular shape on fluid properties. In addition, data such as ours also provide a difficult test for molecular-force models being proposed for use in molecular simulation (Nath et al., 1998). A more practical application of our work is the separation of Fischer−Tropsch waxes from reactor catalyst via supercritical extraction, as proposed by Biales et al. (1999). The proposed process uses near or supercritical solvents such as pentane and hexane for extraction and recovery of the waxes, which consist of paraffins, olefins, and alcohols up to C_{200} in size.

Comprehensive VLE measurements for systems containing mixtures of dense alkane solvents (i.e., C_3 or larger) with long-chain alkanes are surprisingly scarce. Nieuwoudt (1996) has examined the VLE behavior of hexacontane (n-$C_{60}H_{122}$) in butane at temperatures from 433 to 453 K, but only at pressures near the mixture critical point. Nederbragt and de Jong (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. Peters et al. (1992, 1993) have measured VLE data for binary mixtures of propane + tetratriacontane (n-$C_{34}H_{70}$) and propane + hexacontane. However, limited vapor-phase data are presented. Joyce and Thies (1997, 1998) and Joyce et al. (1999) have studied binary VLE for hexane + squalane (a branched C_{30} alkane), hexane + hexadecane, hexane + 1-hexadecanol, and hexane + 1-hexadecene from 473 to 623 K. In this paper, we report on the binary phase behavior of two long-chain alkanes, tetracosane (n-$C_{24}H_{50}$) and hexatriacontane (n-$C_{36}H_{74}$), in near and supercritical hexane.

Experimental Section

Apparatus and Procedure. As shown in Figure 1, a continuous-flow apparatus was used to measure the vapor−liquid equilibrium for the two systems of interest. The configuration of the apparatus was identical to that used for the hexane + 1-hexadecanol system (Joyce and Thies, 1998), so only a brief description is given below. For an experimental run, hexane and the wax compound are pumped at a combined flow rate between 150 and 250 mL·h^{-1}. Because both tetracosane (mp = 54 °C) and hexatriacontane (mp = 76 °C) are solids at room temperature, the wax feed reservoir, the feed lines, and the pump head are heated with electrical heating tape and maintained at approximately 100 °C. Next, the hexane and the wax component are brought to the desired operating temperature within the isothermal nitrogen bath 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 flashed to ambient pressure after passing through micrometering valves. The top-phase valve is used to control the pressure, while the

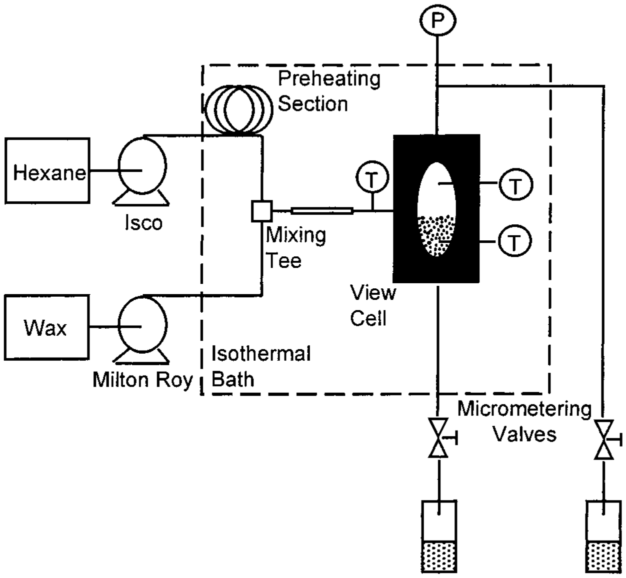

Figure 1. Schematic of the continuous-flow apparatus.

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Table 1. Measured Equilibrium Pressures and Liquid (x) and Vapor (y) Compositions for the Hexane (A) + Tetracosane (B) System at (473.0, 524.3, 573.4, and 622.9) K

P/bar	x_B	y_B	P/bar	x_B	y_B
	T = 473.0 K			T = 573.4 K	
6.18	0.532	0.000 460	7.91	0.691	0.0185
7.91	0.450	0.000 406	14.80	0.549	0.0127
9.63	0.359	0.000 348	18.25	0.475	0.0119
11.35	0.276	0.000 301	21.70	0.413	0.0116
13.08	0.204	0.000 255	25.14	0.365	0.0118
14.80	0.128	0.000 201	32.11	0.267	0.0134
16.53	0.0606	0.000 141	38.93	0.186	0.0177
17.42	0.0325	0.000 093	44.10	0.122	0.0274
			46.72[a]	0.0591	0.0591
	T = 524.3 K			T = 622.9 K	
7.91	0.629	0.003 89	7.91	0.768	0.0652
11.35	0.501	0.003 19	14.80	0.638	0.0429
14.80	0.408	0.002 87	21.70	0.516	0.0367
18.25	0.328	0.002 70	28.59	0.429	0.0359
21.70	0.254	0.002 72	35.49	0.350	0.0386
25.14	0.182	0.002 98	42.38	0.272	0.0457
28.59	0.124	0.003 52	45.83	0.233	0.0530
32.04	0.0657	0.004 46	48.59	0.201	0.0630
35.28[a]	0.0154	0.015 4	51.83[a]	0.111	0.111

[a] Vapor–liquid critical point.

bottom-phase valve is used to control the liquid level within the view cell. Heating tape is used to maintain the top- and bottom-phase sampling lines exiting the bath at about 85 °C. After being flashed, each sample enters a sealed collection vial that is cooled to approximately −10 °C to prevent the vaporization of hexane. Typically, triplicate samples of the top and bottom phases weighing from 2 to 6 g each are collected.

All samples were analyzed with a Hewlett-Packard 5890A gas chromatograph (GC) equipped with a flame ionization detector and an autosampler. For tetracosane, samples were diluted with hexane, and squalane was used as the internal standard. A 0.53 mm i.d. by 10 m long capillary column with a 1.2 μm film thickness (Alltech, RSL-150) was used for the separation; the column operating temperature was ramped from 200 to 250 °C. For hexatriacontane, samples were diluted with heptane, and squalane was again used as an internal standard. A 0.53 mm i.d. by 5 m long high-temperature capillary column with a 0.1 μm film thickness (Analytical Controls, Part No. 40.01.060) was used for this analysis; this column was ramped at 15 °C·min^{-1} from 150 to 250 °C.

Materials. Hexane (99+%) and tetracosane (99%) were supplied by Aldrich; hexatriacontane (99%) was supplied by Alfa Aesar. The stated purities were confirmed by gas chromatography. All chemicals were used without further purification.

Results and Discussion

Hexane + Tetracosane. Measured compositions and corresponding pressures for the hexane + tetracosane system at 473.0, 524.3, 573.4, and 622.9 K are given in Table 1 and are depicted on a pressure–composition diagram in Figure 2. For clarity, selected vapor-phase isotherms are also enlarged in Figure 3. Mixture critical pressures and compositions are also reported at the three temperatures above the critical temperature of hexane (T_c = 507.5 K, P_c = 30.1 bar; Reid et al., 1987). A discussion of the experimental method used to measure the mixture critical points is given elsewhere (Joyce and Thies, 1998). For the liquid phase, the three samples collected at a given temperature and pressure were typically reproducible to <±1% deviation in tetracosane composition. For the vapor phase, the samples were typically reproducible to ±2% deviation in the minor component tetracosane. The percent deviation was higher at 473.0 K and 17.42 bar (i.e., ±6%) because the concentration of tetracosane in the vapor phase changes significantly as the vapor pressure of hexane is approached. The temperature and pressure uncertainties for a given isotherm were always <±0.3 K and <±0.17 bar, respectively. Considering all sources of error, the reported liquid- and vapor-phase compositions are believed to be accurate to ±2 and ±3%, respectively.

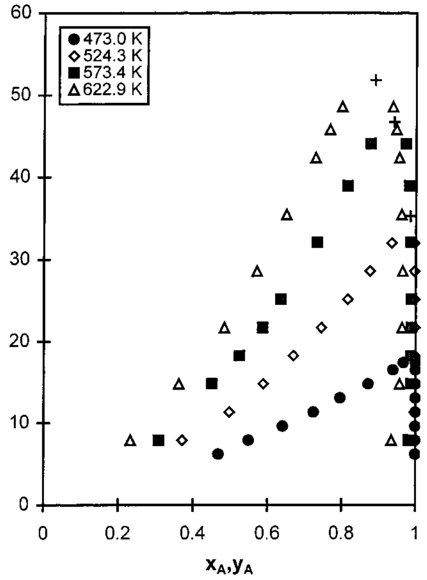

Figure 2. Pressure versus composition diagram for the hexane (A) + tetracosane (B) system at (473.0, 524.3, 573.4, and 622.9) K. The plus signs denote mixture critical points.

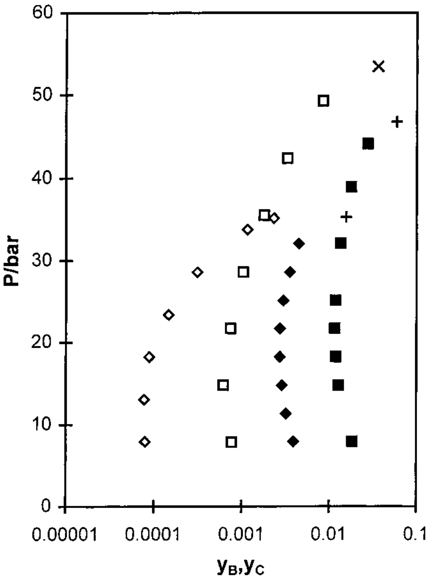

Figure 3. Vapor-phase compositions for hexane (A) + tetracosane (B) and hexane (A) + hexatriacontane (C) at selected temperatures: hexane + tetracosane at 524.3 (◆) and 573.4 (■) K; hexane + hexatriacontane at 521.7 (◇) and 573.1 (□) K. The plus and times signs denote mixture critical points for hexane + tetracosane and hexane + hexatriacontane, respectively.

Hexane + Hexatriacontane. Vapor–liquid equilibrium compositions and the corresponding pressures for the hexane + hexatriacontane system at 521.7, 573.1, and 621.8 K are presented in Table 2 and Figure 4. For clarity, selected vapor-phase isotherms are also enlarged in Figure

Table 2. Measured Equilibrium Pressures and Liquid (x) and Vapor (y) Compositions for the Hexane (A) + Hexatriacontane (C) System at (521.7, 573.1, and 621.8) K

P/bar	x_C	y_C	P/bar	x_C	y_C
	T = 521.7 K			T = 621.8 K	
7.91	0.591	0.000 079 5	7.91	0.765	0.004 66
13.08	0.411	0.000 077 7	14.80	0.626	0.003 47
18.25	0.292	0.000 088 3	25.14	0.449	0.003 64
23.42	0.199	0.000 146	35.49	0.330	0.004 93
28.59	0.117	0.000 310	45.83	0.240	0.008 12
33.76	0.0376	0.001 15	56.17	0.160	0.015 7
35.14	0.0191	0.002 31	62.38	0.116	0.030 6
35.42[a]	[b]	[b]	64.51[a]	0.0702	0.070 2
	T = 573.1 K				
7.84	0.711	0.000 773			
14.80	0.535	0.000 619			
21.70	0.412	0.000 745			
28.59	0.301	0.001 03			
35.49	0.221	0.001 79			
42.38	0.165	0.003 31			
49.28	0.102	0.008 41			
53.48[a]	0.0358	0.035 8			

[a] Vapor−liquid critical point. [b] Unable to maintain critical opalescence.

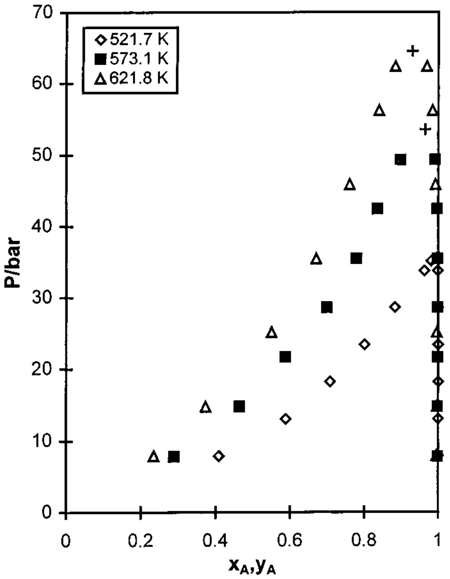

Figure 4. Pressure versus composition diagram for the hexane (A) + hexatriacontane (C) system at (521.7, 573.1, and 621.8) K. The plus signs denote mixture critical points.

3. Mixture critical points were measured at the two higher temperatures, but no critical point composition was obtained at 521.7 K, where the solubility of hexatriacontane is very low. For the liquid phase, the three samples collected at a given temperature and pressure were typically reproducible to <±2% deviation in the minor component composition. For the vapor phase, the samples at 573.1 and 621.8 K were typically reproducible to ±2% in the minor component (i.e., hexatriacontane). At 521.7 K, the reproducibility was not as good (i.e., ±3%) because of the lower solute concentrations in the vapor phase. Temperature and pressure measurements for a given isotherm are believed to be accurate to ±0.4 K and ±0.17 bar, respectively. Considering all sources of error, the reported liquid- and vapor-phase compositions are believed to be accurate to ±3 and ±4%, respectively.

Verification that equilibrium conditions are obtained when our flow apparatus is used for alkane mixtures at elevated temperatures and pressures was previously obtained (Joyce and Thies, 1997), so no such measurements were conducted during this study.

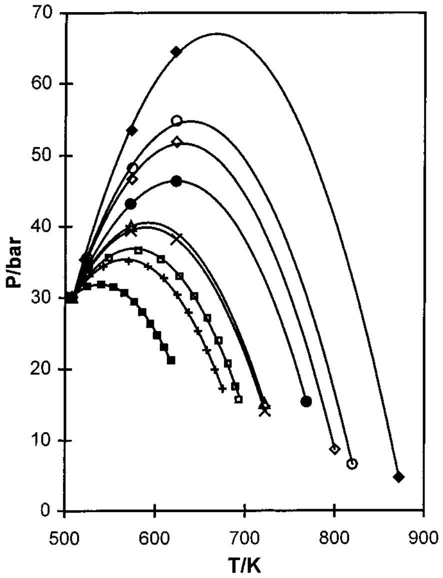

Figure 5. Critical locus curves for binary mixtures of hexane with long-chain alkanes: (■) decane, (+) tridecane, and (□) tetradecane (Pak and Kay, 1972); (×) hexadecane and (●) 1-hexadecanol (Joyce and Thies, 1998); (△) 1-hexadecene (Joyce et al., 1999); (○) squalane (Joyce and Thies, 1997); (◇) tetracosane and (◆) hexatriacontane (this work).

Over the past several years, our group has measured VLE for several binary systems containing hexane + a long-chain alkane. These measurements are succinctly summarized in the form of a pressure versus temperature projection; see Figure 5. For comparison, the early work of Pak and Kay (1972) is also given. The critical curves shown for each binary are simply smoothed fits to the measured mixture critical points. Pure component critical points for tetracosane (T_c = 800 K, P_c = 8.7 bar; Ambrose and Tsonopoulos, 1995) and hexatriacontane (T_c = 872 K, P_c = 4.72 bar; Nikitin et al., 1997) were taken from the literature. Note that no liquid−liquid equilibrium (LLE) was ever observed. This is consistent with the work of Peters and co-workers (1989), who examined the onset of LLE caused by system asymmetry in mixtures containing short- and long-chain alkanes. By extrapolation, they estimated that the long-chain alkane would need to be longer than n-$C_{60}H_{122}$ to observe LLE with hexane. Figure 5 also illustrates how similar the critical curves for hexane + C_{24} and hexane + squalane are to each other. This is consistent with the molecular simulation results of Zhuravlev and Siepmann (1997), who determined that the critical point of squalane agreed more closely with that of C_{24} (i.e., the "backbone" of squalane) than with that of triacontane (n-$C_{30}H_{62}$). Finally, as has been previously discussed (Joyce et al., 1999), the P−T projection shows that the effect on phase behavior of "adding" an hydroxyl group to hexadecane is significant, but the effect of "adding" a double bond is negligible.

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