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Vapor−Liquid Equilibrium for Mixtures of Hexane and Squalane at Temperatures from 469.8 K to 623.3 K

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Vapor and liquid equilibrium compositions have been measured for the hexane + squalane (2,6,10,15,19,23-hexamethyltetracosane) system at (469.8, 524.3, 574.6, and 623.3) K and at pressures ranging from (5.5 to 54.8) bar. A continuous-flow apparatus was used both to minimize squalane degradation and to measure the lower squalane concentrations in the vapor phase. Mixture critical pressures and compositions were also obtained.

Introduction

Supercritical fluid extraction is being considered for the recovery and fractionation of the wax products from the slurry bubble column (SBC) reactor of the Fischer-Tropsch process. In the proposed process, the waxes are extracted with a hydrocarbon solvent that has a critical temperature near the operating temperature of the SBC reactor, i.e., (473 to 573) K. The majority of these products are alkanes, both branched and straight chain, and their product distribution is rather broad, with alkanes up to C_{40} being present in nonnegligible amounts. Preliminary calculations indicate that product fractionation and recovery are most effective at temperatures near the operating temperature of the SBC reactor, that is, (473−573) K. Therefore, alkanes whose critical temperatures are within this range are of primary interest for use as the supercritical solvent.

Phase behavior measurements at elevated temperatures for systems containing such an alkane with components representative of those found in Fischer-Tropsch waxes are surprisingly scarce. To our knowledge, results are available from only one research group. Nederbragt and DeJong (1951) have measured binary VLE for pentane and heptane with several *n*-alkanes from C_{16} to C_{24} at temperatures from (519 to 630) K. However, none of the solutes that were used were of high purity. In this paper, we report on the binary phase behavior of hexane with a branched C_{30} alkane, squalane.

Experimental Section

Apparatus and Procedure. A continuous-flow apparatus was used to measure vapor−liquid equilibrium for the system of interest. A flow apparatus was chosen for this work (1) to allow us to more accurately measure the low concentrations of squalane in the vapor phase at the lower temperatures and (2) to minimize residence times at the higher temperatures and thus reduce the extent to which squalane degradation would occur. Although a similar apparatus has been used by Stevenson et al. (1994) to measure phase equilibria for the squalane + water system at temperatures to 660 K, several modifications were made.

A simplified schematic of the flow apparatus is depicted in Figure 1. Unless otherwise noted, all tubing was 1.59 mm o.d. with an i.d. of 0.76 mm. For an experimental run, squalane and hexane were pumped using an electronic syringe pump (Isco, Model LC-5000) and a metering pump (LDC/Milton Roy, model 396), respectively. The combined volumetric flow rate was generally between 150 and 250 mL/h. A surge tank filled with helium was attached to the hexane feed line to dampen pressure fluctuations caused by the metering pump. Helium was used because of its very low solubility in liquids.

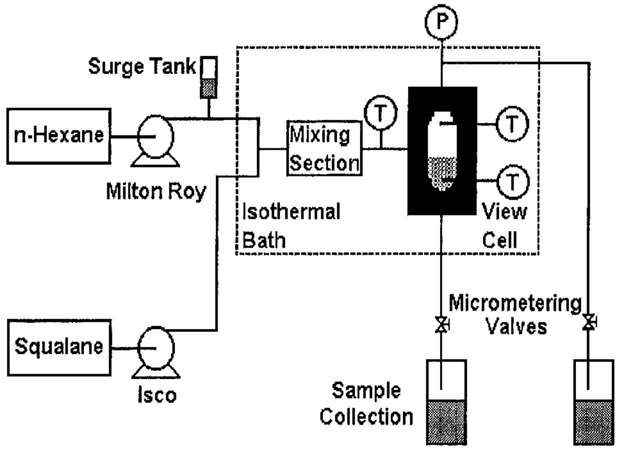

Figure 1. Schematic of the continuous-flow apparatus.

The two components are preheated within the isothermal nitrogen bath in separate lines. The hexane is preheated in an 8-m length of tubing and the squalane in a shorter section that is only 1 m long to minimize degradation at high temperatures. The two components are then combined in a mixing tee whose configuration has been previously described (Stevenson, 1994). In order to promote further mixing, the squalane + hexane mixture subsequently flows through two lengths of 1.5-m tubing separated by a 1.75 mm i.d. × 3-m section. The combined streams then enter the view cell.

The two phases separate within the cell and are then drawn off from sample ports located at the top and bottom of the view cell. Lines run from the sample ports out of the oven and connect to micrometering valves (Autoclave Engineers, Model 60VRMM). The top-phase micrometering valve is used to control the pressure, while the bottom-phase micrometering valve is used to control the liquid level within the view cell.

The view cell was designed by Roebers (1991) to operate at temperatures up to 673 K and pressures up to 350 bar. For this system, two different view cell volumes have been used, 50 and 12 mL. The 12-mL cell was used for the higher temperature runs to decrease the squalane residence time in the oven. The cell windows are made of high-temperature aluminosilicate glass (Hoya Optics) and are sealed with graphite gaskets (Grafoil, UCAR). Both the

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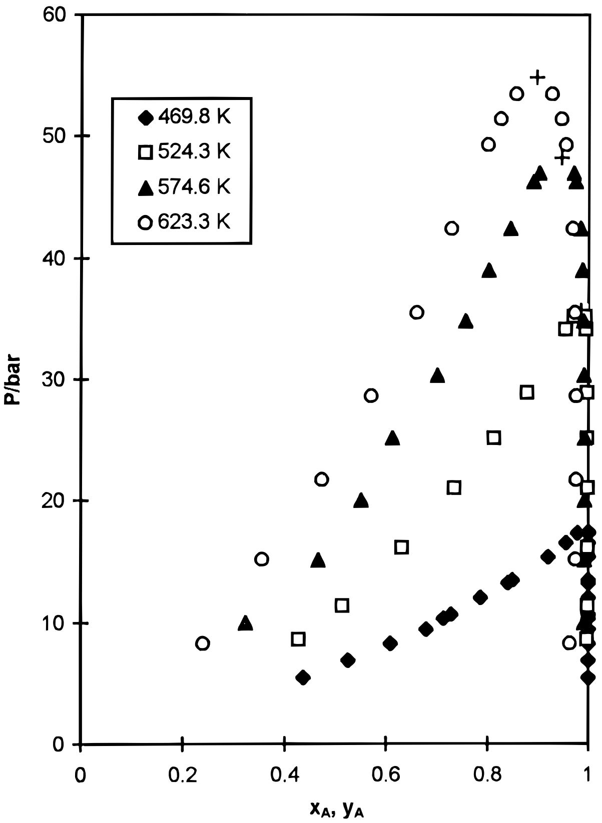

Figure 2. Pressure vs composition diagram for the hexane (A) + squalane (B) system at (469.8, 524.3, 574.6, and 623.3) K.

Table 1. Measured Equilibrium Pressures and Liquid (x) and Vapor (y) Compositions for the Hexane (A) + Squalane (B) System at (469.8, 524.3, 574.6, and 623.3) K

P/bar	x_B	y_B	P/bar	x_B	y_B
		T = 469.8 K			
5.52	0.564	0.000173	12.07	0.213	0.0000975
6.89	0.474	0.000152	13.24	0.159	0.0000960
8.27	0.392	0.000131	13.44	0.150	0.0000939
9.45	0.321	0.000121	15.38	0.0781	0.0000620
10.34	0.287	0.000113	16.55	0.0437	0.0000397
10.69	0.271	0.000111	17.31	0.0219	0.0000065
		T = 524.3 K			
8.62	0.572	0.00189	28.89	0.122	0.00232
11.38	0.486	0.00161	34.13	0.0457	0.00461
16.13	0.369	0.00155	35.16	0.0294	0.00627
21.03	0.266	0.00169	35.65[a]	0.0147	0.0147
25.17	0.187	0.00168			
		T = 574.6 K			
10.00	0.677	0.00915	38.95	0.198	0.0130
15.10	0.534	0.00779	42.40	0.155	0.0162
19.99	0.450	0.00727	46.26	0.110	0.0262
25.17	0.387	0.00746	46.95	0.0986	0.0303
30.34	0.300	0.00864	48.23[a]	0.0543	0.0543
34.82	0.243	0.0101			
		T = 623.3 K			
8.27	0.761	0.0362	42.40	0.272	0.319
15.17	0.643	0.0256	49.30	0.199	0.0455
21.72	0.527	0.0238	51.37	0.174	0.0547
28.61	0.429	0.0242	53.43	0.144	0.0733
35.51	0.340	0.0260	54.81[a]	0.104	0.104

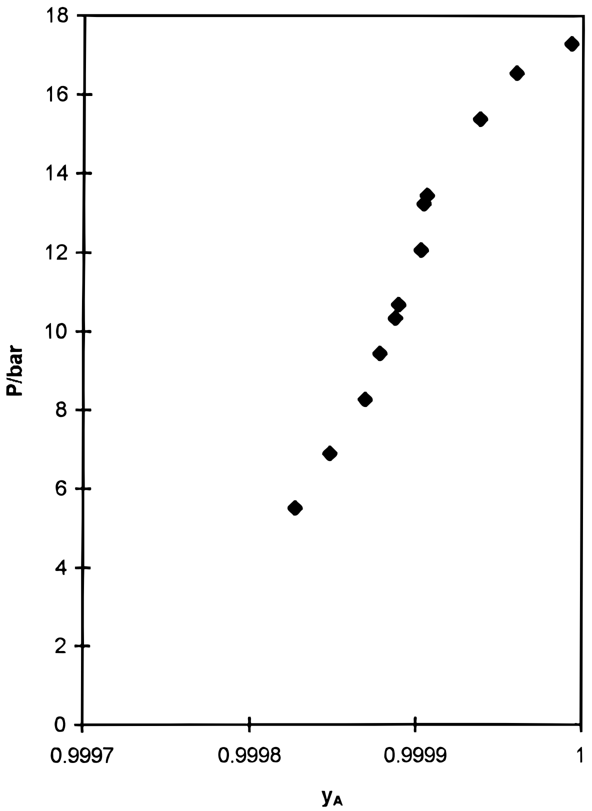

Figure 3. Vapor-phase compositions for hexane (A) + squalane (B) at 469.8 K.

mixing section and the view cell are located inside a nitrogen bath. The bath is of the forced-convection type and is discussed in detail elsewhere (Hutchenson et al., 1990). Several safety features are incorporated into the bath design: (1) A polycarbonate shield is mounted over the viewing window. In addition, the view cell is viewed indirectly with a mirror. (2) A high-temperature shut-off independent of the normal temperature control scheme is used. (3) When running the apparatus, the bath is continuously purged with nitrogen. The oxygen concentration inside the bath is regularly monitored by GC and is maintained below 2 mol % oxygen (well below the lower explosion limit).

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 (Tudor Technology) referenced to an aluminum block located in the bath. The temperature of the block itself was measured with a secondary-standard PRT (Burns Engineering). 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). Some variation of the temperature in the view cell and of the feed is characteristic of a flow apparatus. Based on the accuracy of the temperature measurements and accounting for the variations during an experimental run, the temperatures reported in this work are believed to be accurate to within ±0.3 K. 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. The cell pressure was controlled to within ±0.14 bar, resulting in an experimental uncertainty in the pressure measurements of ±0.17 bar.

For a given temperature and pressure, at least four samples each of the top and bottom phases were collected; sample sizes were typically 3−6 g. All samples were analyzed with a Hewlett-Packard 5890A GC equipped with a flame ionization detector and autosampler. Samples were diluted using tetrahydrofuran inhibited with 250 ppm BHT (Burdick and Jackson). Tetracosane (99%, Aldrich) was added as an internal standard. A 0.53 mm × 10 m capillary column with a 1.2-μm film thickness (Alltech, RSL-150) was used for the separation.

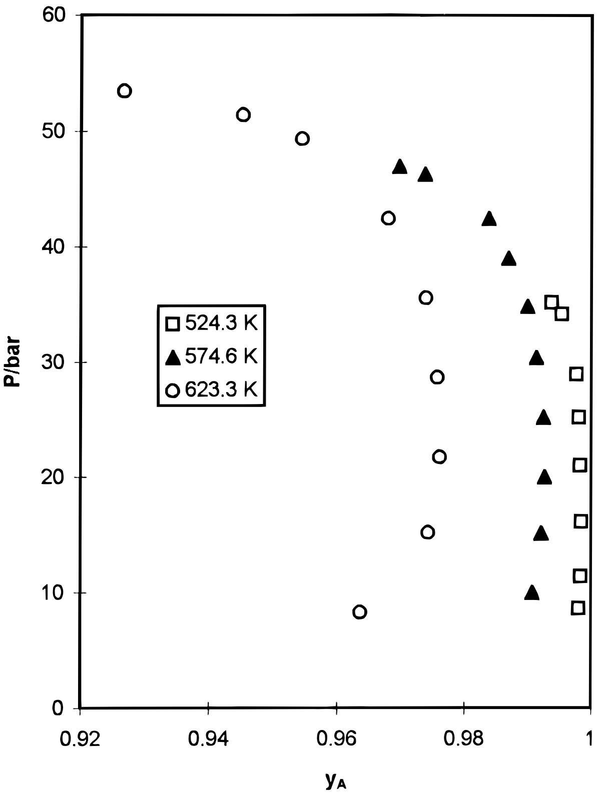

Figure 4. Vapor-phase compositions at (524.3, 574.6, and 623.3) K.

Materials. Both squalane (99%) and *n*-hexane (99+%) were supplied by Aldrich; the stated purities were confirmed by GC using the setup described above. Both chemicals were used without further purification.

Results and Discussion

Measured compositions and corresponding pressures for the hexane + squalane system at (469.8, 524.3, 574.6, and 623.3) K are given in Table 1 and are depicted on a pressure–composition diagram in Figure 2. For clarity, the vapor-phase compositions are also plotted in Figures 3 and 4. Using the classification system of Scott and van Konynenburg (Rowlinson and Swinton, 1982), we see that the system exhibits type I phase behavior, with the critical locus running through a maximum in pressure. For the liquid phase, the four samples collected at each temperature and pressure were generally reproducible to ±1–2% deviation in the squalane concentration. Liquid-phase compositions were somewhat less reproducible for the samples containing less than 5 mol % squalane, as deviations in squalane concentration of up to ±3% were measured. Deviations between the four vapor-phase samples for a given temperature and pressure were generally ±0.5–3%; in only a few cases were higher deviations (i.e., ±5–7%) observed. Such deviations were even typical for the higher pressures at 469.8 K, where only trace amounts of squalane were present. These results clearly demonstrate the versatility of a flow apparatus, as compositions encompassing a range of 4 orders of magnitude were accurately measured. On the basis of an error analysis, we believe that the reported liquid- and vapor-phase compositions are generally accurate to better than ±3% and ±4%, respectively.

Table 2. Measured Equilibrium Compositions and Nominal Flow Rates for the Hexane (A) + Squalane (B) System at 576.4 K and 34.82 bar

total flow rate (mL/h)	x_B	y_B
100	0.243	0.0101
200	0.244	0.0100
300	0.242	0.0101

Mixture critical pressures were obtained by observation of critical opalescence within the equilibrium cell. To obtain critical-point compositions, critical opalescence phenomena were maintained in the view cell while samples from the top and bottom sample ports were collected as previously described. Precise adjustment of the component flow rates was required for these measurements in order to obtain the critical composition in the cell. Samples were then analyzed in the manner previously described. 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 compositions are accurate to ±3%.

Verification that equilibrium conditions exist for this system was checked by collecting samples at several different flow rates; for these tests, the view cell with the smaller volume of 12 mL was used. As shown in Table 2, no effect of flow rate on composition was observed.

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