Vapor−Liquid Equilibria and Densities for the System Butane + Hexacontane

Izak Nieuwoudt

Department of Chemical Engineering, University of Stellenbosch, Banhoekweg, 7600 Stellenbosch, South Africa

---

Liquid and vapor phase compositions and densities have been measured with a variable volume cell for the binary system butane + hexacontane (n-$C_{60}H_{122}$). Data sets at 433.15 K, 438.15 K, and 453.15 K are presented and include measurements in the mixture critical region.

Introduction

Knowledge of the phase behavior of binary mixtures of short and long chain normal paraffins is of importance in the understanding of the phenomena of retrograde condensation and the solubility of chain molecules in supercritical solvents. In these mixtures large deviations from ideality occur mainly as the result of the large differences in chain length (Glaser *et al*., 1985). These data are also important in developing equations of state to model the above mentioned processes. By far the most comprehensive study of binary systems of ethane and propane with long chain normal paraffins has been done by Peters and coworkers (Peters *et al*., 1987, 1988a,b, 1992, 1993; Glaser *et al*., 1985). Huang (1987) also measured vapor−liquid equilibria for binary systems containing ethane and long chain paraffins. The data of these authors include very few dew point measurements and no data points close to the critical points of the mixtures. For butane, no binary vapor−liquid equilibrium data with long chain paraffins beyond hexadecane have been reported.

In this paper bubble point and upper dew point compositions and densities for the binary system butane + hexacontane (n-$C_{60}H_{122}$) are reported.

Experimental Section

Materials. Butane with a certified purity of 99.5% was obtained from Messer Griesheim. The highest carbon number n-paraffin commercially available in a pure form is hexacontane. Reinhard and Dixon (1965) described a method for synthesizing higher molecular weight n-paraffins, but the prices and availability of the reagents needed in the synthesis make it impractical. Hexacontane was obtained from Fluka. According to Fluka the purity is better than 98%. Apart from degassing of the hexacontane, the chemicals were used without any further purification.

Apparatus. As discussed by McHugh and Krukonis (1986) and Fornari *et al*. (1990), the methods for studying high-pressure fluid phase equilibria can be lumped into two categories, namely dynamic and static methods. In the case of the dynamic methods, the feed and products are continuously fed to and withdrawn from the equilibrium cell, or one or both of the phases can be pumped around and sampled. Exorbitant chemical costs prevented the use of a dynamic method in this study. Because of the obvious difficulties in drawing and analyzing samples from a static cell for this binary system, the so-called synthetic method was used, i.e., the visual observation of dew- and bubble point pressures at various temperatures for mixtures of known composition. The variable volume static cell, shown in Figure 1, was built by SITEC-Sieber Engineering AG (Maur/Zürich Switzerland). The maximum allowable operating conditions are 473 K and 50 MPa. The cell volume can be varied from a maximum of 25 cm^3 down to 12.5 cm^3 by moving the piston. The cell was manufactured from sapphire and encased in a well-insulated metal mass that also contained the heating elements. The combined effect of the size of the piece of metal and the insulation ensured isothermal operation and a minimal temperature gradient between the heat source and the cell contents. The temperature in the cell was controlled to within ±0.1 K of the setpoint (TECON AG model 530 controller with type J thermocouple). The pressure in the cell was controlled with a counterbalance piston that varied the volume of the cell. Teflon and nylon seals were used to provide a seal between the piston and the sapphire cell wall. Nitrogen from a cylinder provided the force on the piston. A high-precision regulator (TESCOM Corp. model 44-1100) was used to control the nitrogen pressure. A bursting disk on the nitrogen line was used as overpressure protection. The pressure in the cell was directly measured with a pressure transducer specifically designed for high temperatures and pressures (Erich Brosa Messgeräte GmbH & Co KG). The pressure transducer was periodically calibrated against a high-precision dead weight gauge. To speed up the equilibration process, the cell content was stirred with a Teflon-coated magnetic stirrer bar. The optical transmission system consisted of two sapphire windows in the cell wall, a light source and fiber optic cables (FiberOptic model FOT 150), a closed circuit television camera (Sony model AVC-D5CE), and a monochrome display (TOA model CC-2091). High-pressure needle valves (SITEC-Sieber Engineering AG) were provided for filling and emptying the cell.

Procedure. The hexacontane was degassed by recrystallizing it under vacuum. Hexacontane chips weighed to the nearest milligram were loaded into the cell, and the cell was evacuated (≈500 Pa) with a vacuum pump. At the lowest hexacontane concentration in Table 1 this yielded an accuracy of ±0.01 mass %. Residual air was displaced from the cell by filling the cell approximately halfway with liquified butane and then slowly venting off the butane through the topmost valve. This venting procedure was repeated five times. A sample bomb, with a volume of 25 cm^3, was used to transfer the butane solvent to the cell. To displace the air from the bomb, the bomb was filled with butane and vented. This venting procedure was repeated three times. To force the solvent from the bomb into the cell, the bomb was heated, using a hot water coil, to a temperature higher than that of the cell. The solvent condensed in the cell, leaving vapor in the bomb. It is important to note that this technique of transferring the solvent can only be used when the boiling range of the

S0021-9568(96)00017-9 CCC: $12.00

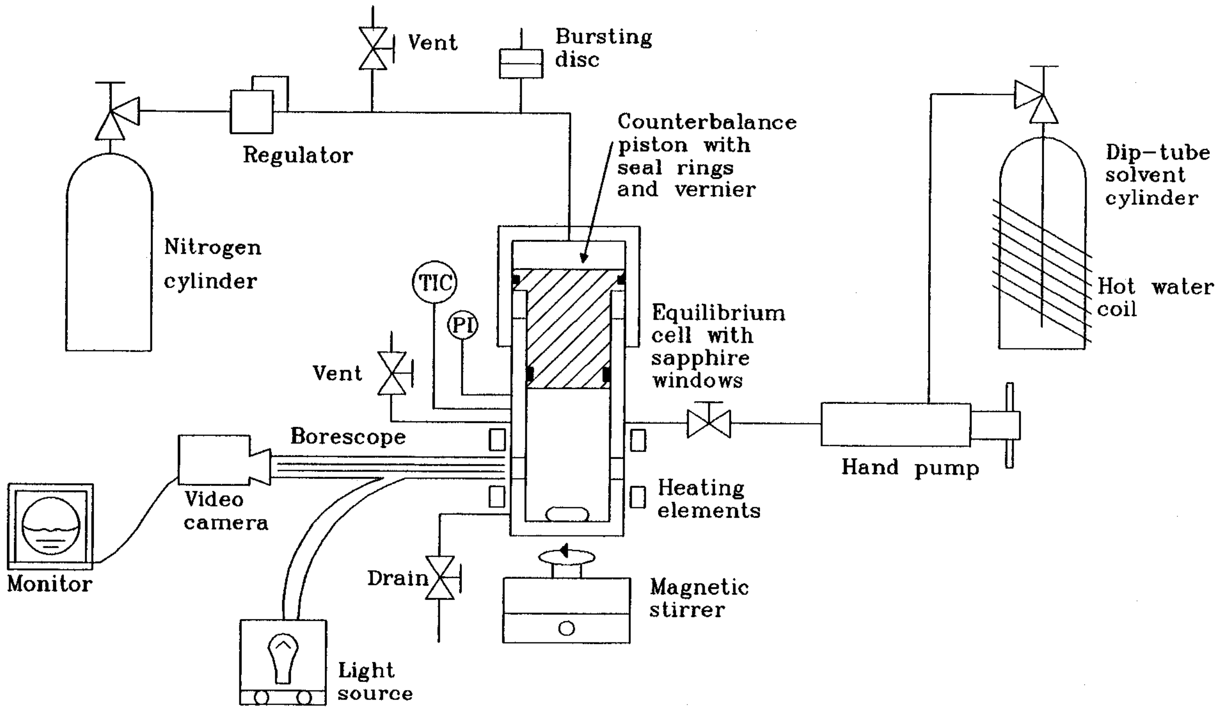

Figure 1. Schematic diagram of the variable volume cell and peripheral equipment.

Table 1. Upper Dew Point and Bubble Point Pressures and Densities for the System Butane (1) + Hexacontane (2)

	T = 433.15 K		T = 438.15 K		T = 453.15 K	
$100\omega_2$	P/MPa	ρ/kg·m^{-3}	P/MPa	ρ/kg·m^{-3}	P/MPa	ρ/kg·m^{-3}
2.18	5.75	320	6.39	316	7.44	298
2.68	5.96	340	6.30	329	7.37	305
3.33	6.09	341	6.59	331	7.79	324
3.88	6.14	344	6.69	343	7.99	339
6.28	6.37	361	6.89	360	8.19	348
6.76	6.31	377	6.84	373	8.25	360
8.49	6.50	387	7.01	381	8.46	370
10.40	6.45	408	7.05	406	8.45	391
10.77	6.59	397	7.08	393	8.59	387
16.17	6.54	441	7.13	435	8.72	424
18.96	6.60	438	7.15	428	8.69	416
23.38	6.44	476	7.00	474	8.63	453
26.19	6.38	493	6.88	487	8.57	474
30.58	6.23	510	6.79	501	8.41	461
35.72	6.02	533	6.61	526	8.19	491
36.73	5.98	540	6.50	529	8.00	510
40.18	5.80	555	6.35	547	7.98	518
44.53	5.37	567	5.90	556	7.40	541

solvent is extremely small. The bomb was weighed to the nearest 10 mg before and after solvent transfer. The cell was heated to the extraction temperature and the pressure raised until a single phase was observed on the monitor. The magnetic stirrer was used to speed up the equilibration process. After the cell contents reached the operating temperature and the temperature difference between the heating element and the cell contents reached a minimum value, the pressure of the cell was slowly lowered to the point where a second phase was observed on the monitor. This was done by lowering the nitrogen pressure on the piston. The pressure was increased slowly, by increasing the nitrogen pressure on the piston, until the second phase disappeared. The process of increasing and decreasing the pressure was continued until a pressure change of less than 0.1 MPa yielded the appearance or disappearance of the second phase. Since the volume of the cell varies linearly with the piston position, a vernier was used to measure the piston travel and thus the cell volume.

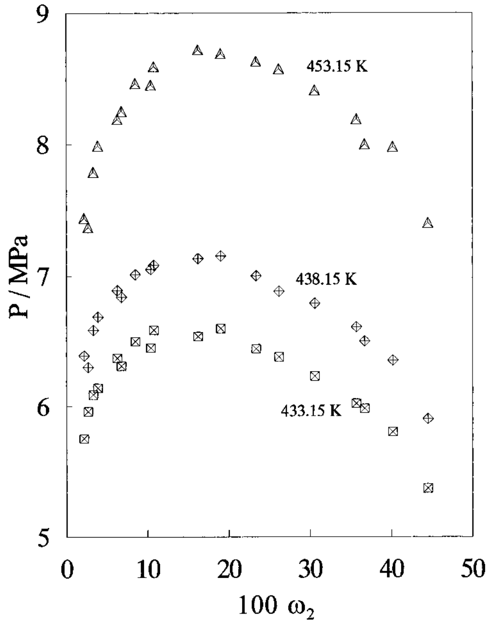

Figure 2. Vapor−liquid equilibria for the system butane (1) + hexacontane (2) at 433.15 K, 438.15 K, and 453.15 K.

With both the mass of the material inside the cell and the volume of the cell known, the density can be calculated at the phase boundary or at any pressure in the one-phase region. The accuracy of the density is estimated to be ±2%. Another advantage of the static method is that the phase boundaries and densities of a mixture could be measured at several temperatures without having to open the cell.

Results and Discussion

Upper dew point and bubble point pressures and densities at 433.15 K, 438.15 K, and 453.15 K are presented in Table 1. Although the pressure transducer shows excellent linearity and was calibrated regularly, the fact that phase transitions were observed with the human eye makes it

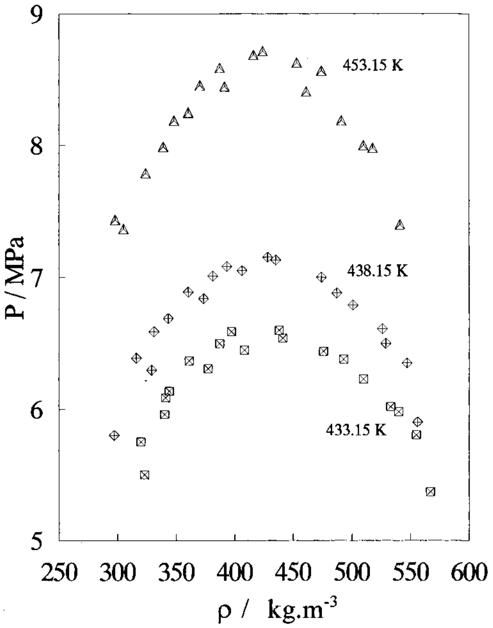

Figure 3. Pressure vs density of vapor and liquid phases in equilibrium for the system butane (1) + hexacontane (2) at 433.15 K, 438.15 K, and 453.15 K.

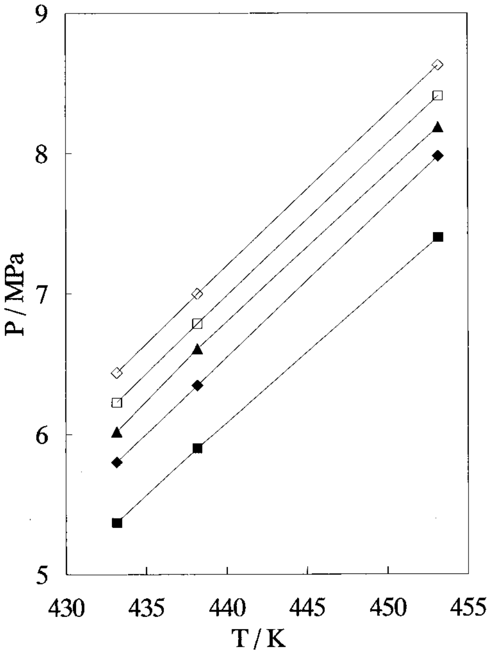

Figure 4. Isopleths of bubble point data for the system butane (1) + hexacontane (2): (◇) $\omega_2 = 0.2338$; (□) $\omega_2 = 0.3058$; (▲) $\omega_2 = 0.3572$; (♦) $\omega_2 = 0.4018$; (■) $\omega_2 = 0.4453$.

difficult to assign an uncertainty to the pressure values. It is estimated that the accuracy of the pressures of the phase boundaries reported in Table 1 is approximately ±0.05 MPa. The visual determination of phase boundaries has, however, gained general acceptance (Glaser *et al.*, 1985; McHugh and Krukonis, 1986; Peters *et al.*, 1992, 1993). The upper dew point and bubble point data in Table 1 are graphically presented in the form of an isothermal *P, x, y* plot in Figure 2, from which the compositions of co-existing phases can be read at a certain pressure.

The *P, T* plots in Figures 4 and 5 show that the isopleths form smooth curves that are virtually linear. This trend is also evident from the bubble point measurements by Peters and co-workers (Peters *et al.*, 1987, 1988a, 1992, 1993; Glaser *et al.*, 1985). This can be used to accurately interpolate between temperatures, but the fact that it is a nearly linear relationship means that limited extrapolations can be made with a fair degree of confidence. The fact that the isopleths are smooth almost linear curves can also be used to smooth the isothermal *P, x* and *P, y* values.

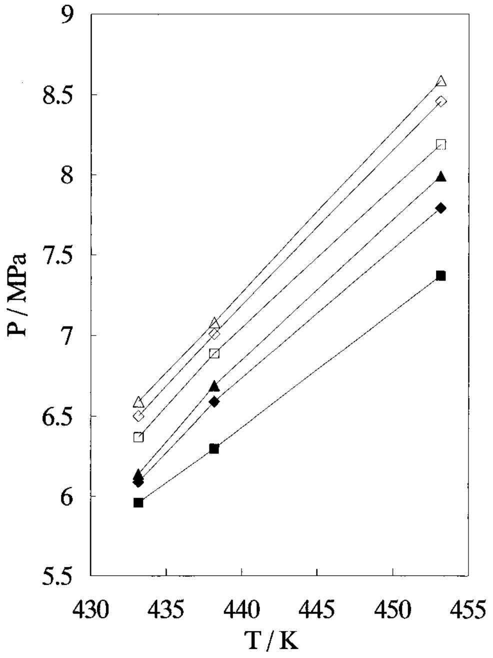

Figure 5. Isopleths of upper dew point data for the system butane (1) + hexacontane (2): (△) $\omega_2 = 0.1077$; (◇) $\omega_2 = 0.0849$; (□) $\omega_2 = 0.0628$; (▲) $\omega_2 = 0.0388$; (♦) $\omega_2 = 0.0333$; (■) $\omega_2 = 0.0268$.

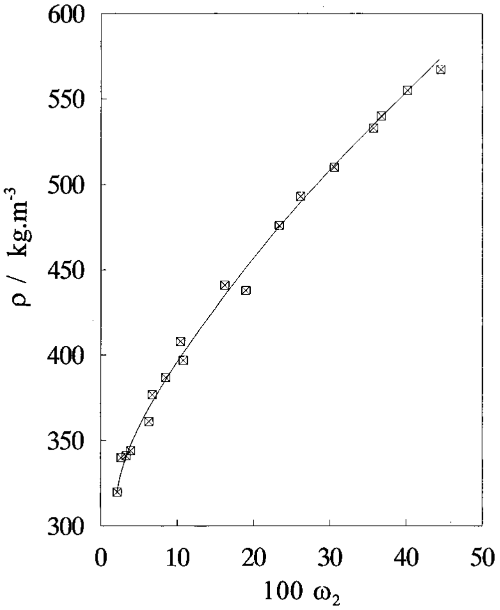

Figure 6. Density vs mass % hexacontane for the system butane (1) + hexacontane (2) at 433.15 K. Symbols represent experimental data, and the solid line is a polynomial fit.

The density data from Table 1 are graphically presented in the form of an isothermal *P*, *ρ* plot in Figure 3, from which the densities of the co-existing phases can be read at a certain pressure. A plot of density versus composition yields a smooth curve that can be used to smooth the experimental density data, as is shown in Figure 6.

Conclusions

Bubble point, upper dew point, and density data sets at three temperatures have been presented for the system butane + hexacontane. The data include several measurements in the mixture critical region.

List of Symbols

P	pressure
T	temperature
ρ	density
ω	mass fraction

Literature Cited

Fornari, R. E.; Alessi, P.; Kikic, I. High pressure fluid phase equilibria: Experimental methods and systems investigated (1978−1987). *Fluid Phase Equilib.* **1990**, *57*, 1−33.

Glaser, M.; Peters, C. J.; Van Der Kooi, H. J.; Lichtenthaler, R. N. Phase Equilibria of (Methane + n-Hexadecane) and (p, V_m, T) of n-Hexadecane. *J. Chem. Thermodyn.* **1985**, *17*, 803−815.

Huang, S. H.-W. Ph.D. Dissertation, Purdue University, U.M.I., Ann Arbor, MI, 1987.

McHugh, M.; Krukonis, V. *Supercritical Fluid Extraction − Principles and Practice*; Butterworth Publishers: Stoneham, MA, 1986.

Peters, C. J.; Van Der Kooi, H. J.; De Swaan Arons, J. Measurements and calculations of Phase Equilibria for (Ethane + Tetracosane) and (p, V_m^+, T) of Liquid Tetracosane. *J. Chem. Thermodyn.* **1987**, *19*, 395−405.

Peters, C. J.; Spiegelaar, J.; De Swaan Arons, J. Phase Equilibria in Binary Mixtures of Ethane + Docosane and Molar Volumes of Liquid Docosane. *Fluid Phase Equilib.* **1988a**, *41*, 245−256.

Peters, C. J.; De Swaan Arons, J.; Levelt Sengers, J. M. H.; Gallagher, J. S. Global Phase Behaviour of Mixtures of Short and Long n-Alkanes. *AIChE J.* **1988b**, *34*, 5, 834−839.

Peters, C. J.; De Roo, J. L.; De Swaan Arons, J. Measurements and Calculations of Phase Equilibria in Binary Mixtures of Propane and Tetratriacontane. *Fluid Phase Equilib.* **1992**, *72*, 251−266.

Peters, C. J.; De Roo, J. L.; De Swaan Arons, J. Phase equilibria in binary mixtures of propane and hexacontane. *Fluid Phase Equilib.* **1993**, *85*, 301−312.

Reinhard, R. R.; Dixon, J. A. Tetranonacontane. *J. Am. Chem. Soc.* **1965**, *30*, 1450−1453.

Received for review January 22, 1996. Accepted June 18, 1996.[⊗]

JE960017Q

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.