Phase Equilibria of Ethylene and Certain Normal Paraffins

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The liquid–vapor and solid–liquid–vapor equilibria of the binary systems ethylene–*n*-eicosane and ethylene–*n*-dotriacontane are studied, with particular attention being paid to the critical end points of the *n*-paraffin-rich branches of the S–L–V loci. Pressure, temperature, liquid-phase composition, and molar volume are reported. These data are discussed in comparison with existing ethylene–hydrocarbon phase equilibria data, taken by us and other investigators, from both a systematic and correlational viewpoint.

Introduction

There is an interest in the solubility of polyethylene in gaseous ethylene relevant to the ethylene polymerization process and the subsequent separation of products from the process outstream. Because of the nature of polyethylene, vis-a-vis its molecular size distribution, correlation and prediction of ethylene–polyethylene phase equilibria behavior is at best a pseudo-two-component problem. More realistically, it is a complex multicomponent problem.

In an attempt to elucidate ethylene–polyethylene interactions, we have undertaken a study of well-defined, ethylene–*n*-paraffin binary systems, where the *n*-paraffin has an *even* carbon number. Attention is paid to those *n*-paraffins of carbon number of at least 16. The view being adopted here is that a correlation which purports to describe correctly the phase equilibria of ethylene-polyethylene systems should be able to describe the simpler equilibria behavior of well-defined binary systems, convincing the user that the physical basis of the correlation is fundamentally sound. Some additional remarks about correlations will be made at the end of this paper.

There is only a limited amount of relevant binary data in the literature (e.g., see ref *7*). For the binary systems of interest, there are three basic types of S–L–V phase equilibria behavior, as pictured in *P–T* space.

(A) The S–L–V locus extends from the solute triple point down to a Q point (S–S–L–V) near the triple point of the solvent ethylene. At pressures exceeding those of the S–L–V locus, there may be a L–L–V locus terminated by a K point (L–L = V) and a CST point (L = L–V). An example of this type of system is ethylene–*n*-hexadecane (*1*, *9*).

(B) The S–L–V locus extends from the solute triple point to a Q point (S–L–L–V), the lower terminus of a L–L–V locus, and then continues on to a Q point (S–S–L–V) near the triple point of the solvent ethylene. An example of this type of system is ethylene–*n*-octadecane (*1*).

(C) The S–L–V locus has two branches. The upper branch extends from the triple point of the solute to a critical end point (S–L = V), which generally occurs at a high pressure. The lower branch extends upward from the Q point (S–S–L–V) near the solvent triple point to a critical end point (S–L = V) near the solvent critical point. Systems containing *n*-eicosane (*1*) and heavier even-numbered *n*-paraffins are of this type.

Data are reported on the systems ethylene–*n*-octacosane and ethylene–*n*-hexatriacontane (*2*), specifically the two *P–T* loci described in paragraph C. However, the high-pressure critical end point was not located as the pressure exceeded the capability of the experimental method. A high-pressure critical end point has been reported for the binary system ethylene–naphthalene at 325.2 K and 176.4 bar (*10*).

In this present paper, the S–L–V upper branch loci for the systems ethylene–*n*-eicosane and ethylene–*n*-dotriacontane will be presented, including the critical end point. In addition to temperature and pressure, liquid-phase composition and molar volume are reported. Also, for each binary system, a vapor–liquid isotherm is reported, including its critical point termination, with similar detail.

Experimental Section

The equipment and experimental techniques which were employed at pressures below 70 atm have been described by Lee and Kohn (*6*). The apparatus used at higher pressures was similar in most respects to the low-pressure apparatus. A Jerguson sight glass gauge was used as an equilibrium cell in the high-pressure apparatus. Higher-range pressure gauges of the bourdon tube type were used in the high-pressure apparatus as well as a larger bath enclosure for the equilibrium cell. The high-pressure gauges were checked periodically against an Ashcroft dead-weight gauge and found to be accurate within 0.4 atm. Agitation of the contents of the high-pressure cell was achieved by periodic rotation of the yoke-mounted cell through an angle of ~160°. The temperature of the equilibrium cell was taken from a platinum resistance probe immersed along with the cell in a well-stirred water bath. The temperature of the bath was controlled within ±0.04 °C with a proportional controller. The platinum resistance probe was calibrated to within 0.03 K of IPTS 1968.

The volume of liquid phase inside the high-pressure cell was measured optically by use of a cathetometer. The calibration of liquid volume was precise to ±0.05 mL.

The experimental procedure for vapor–liquid and vapor–liquid–solid equilibrium points was essentially identical for the low- and high-pressure apparatus. For a vapor–liquid two-phase equilibrium determination, the cell was thermostatically controlled at the desired temperature. A known amount of *n*-eicosane or *n*-dotriacontane was injected into the cell by means of a hypodermic syringe. The mass of the component was established to ±0.02 mg by weighing techniques. The cell was then purged free of air by repeated flushing with ethylene gas. A series of increasing equilibrium pressures was achieved in the cell by incremental additions of ethylene gas. The ethylene gas was displaced accurately from a stainless steel reservoir which was kept at constant temperature and pressure. A precision mercury pump which could be read to ±0.001 mL was used for the displacement. Agitation of the cell contents generally secured equilibrium at each pressure within 5 or 6 min. At the equilibrium point, readings of the cell pressure, the liquid volume in the cell, and the accumulated mass of ethylene in the cell were taken. These data permitted a straightforward stoichiometric computation of the composition of the liquid phase, assuming that the vapor phase in the cell is pure ethylene gas. An experimental run was concluded when either the cell was full of liquid phase or the pressure had exceeded 70 atm (for the low-pressure apparatus). Each run generally furnished ~7–8 data points.

The procedure for determination of the three-phase solid–liquid–vapor equilibrium points was experimentally very similar to that just described for vapor–liquid two-phase points. In the three-phase determination, the equilibrium cell was not kept at

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Table I. Smoothed Values of Pressure; Composition and Molar Volume at 50 °C for the Ethylene-*n*-Eicosane System in the Two-Phase Vapor-Liquid Region

press., atm	composition of liquid phase, mole fraction ethylene	molar volume of liquid phase, mL/mol
	0.000	367.0
10.0	0.168	315.7
20.0	0.325	267.5
30.0	0.441	232.0
40.0	0.537	202.0
50.0	0.611	178.0
60.0	0.681	156.0
70.0	0.740	138.1
80.0	0.787	123.5
90.0	0.822	112.7
100.0	0.845	105.5
110.0	0.859	101.2
120.0	0.870	98.8
130.0	0.881	94.8
140.0	0.903	91.9
150.0	0.930	86.9
154.1[a]		

[a] Vapor-liquid critical point.

a constant temperature throughout an experimental run. The equilibrium cell was charged with heavy component and flushed of air as previously described. Addition of ethylene gas with simultaneous agitation of the cell contents was accomplished as the cell bath was being cooled. When crystallization of material in the cell began, the cooling was stopped and the bath temperature was made to rise very slowly in temperature. The highest temperature of which a few small crystals remained in the cell with agitation was taken as the equilibrium crystal point. The readings of cell pressure, temperature, liquid volume, and accumulated ethylene added to the cell were taken and used in a stoichiometric computation of the liquid-phase coomposition. Then additional ethylene was added to the cell, and other crystal points were determined until the cell was filled with liquid.

Materials

The ethylene used was Linke CP gas stated to have a minimum purity of 99.5%. Dew-bubble isotherms determined on the cylinder gas showed it to have a difference between the bubble and dew-point pressures of 0.3 atm. The ethylene was used without purification. The *n*-eicosane was 99% pure grade from Humprey-Wilkinson, Inc. It had a freezing point within 0.2 °C of the literature value for *n*-eicosane. The *n*-dotriacontane was 97% pure from Humprey-Wilkinson, Inc. It had a freezing point within 0.4 °C of the literature value for *n*-dotriacontane. Both of these components were used without further purification.

Results

Table I is the smoothed 50 °C isotherm for the ethylene-*n*-eicosane vapor-liquid system, based on a total of 32 data points. Below 60 atm, the standard deviations in pressure and liquid-phase composition are 0.5 atm and 0.005, respectively; above 60 atm, they are 2.0 atm and 0.008, respectively. The standard deviation for molar volume for the entire isotherm is 1.0 ml/mol. Table II is the upper branch of the S-L-V locus for ethylene-*n*-eicosane, presented in smoothed form based on 25 data points. The standard deviation for pressure is 0.4 atm below 60 atm and 1.5 atm above 60 atm. The standard deviations of liquid-phase composition, molar volume, and temperature are 0.005, 0.8 ml/mol, and 0.1 K, respectively. The data in Table II agree with that reported by Colmenares (*1*) within experimental uncertainty up to 60 atm, beyond which pressure Colmenares did not take measurements. Noteworthy are the two critical end points in Tables I and II which make up two points on the critical point (L = V) locus of ethylene-*n*-eicosane. This (upper) part of the critical point locus starts at the S-L = V point of 99.9 atm and 290.60 K and moves upward (positive slope) rapidly in *P*-*T* space (see Table I) and will enventually terminate at the critical point of pure *n*-eicosane.

Table II. Smoothed Pressure-Temperature-Composition Diagram in the Solid-Liquid-Vapor Region of the Ethylene-*n*-Eicosane System

press., atm	temp, K	composition of liquid phase, mole fraction ethylene	molar volume of liquid phase, mL/mol
5.0	308.67	0.112	328.6
10.0	307.30	0.211	298.1
15.0	305.92	0.300	271.0
20.0	304.50	0.375	248.1
25.0	303.07	0.444	227.2
30.0	301.64	0.512	206.5
35.0	300.20	0.575	187.5
40.0	298.60	0.630	170.9
45.0	296.98	0.681	155.7
50.0	295.22	0.730	141.0
55.0	293.80	0.775	126.8
60.0	292.71	0.815	113.8
65.0	292.10	0.845	103.1
70.0	291.74	0.861	97.7
75.0	291.41	0.874	93.1
80.0	291.15	0.887	87.8
85.0	290.93	0.897	84.5
90.0	290.77	0.909	81.8
95.0	290.62	0.925	78.0
99.9[a]	290.60		

[a] Type-K singular point.

Table III. Smoothed Values of Pressure Composition and Molar Volume at 75 °C for the Ethylene-*n*-Dotriacontane System in the Two-Phase Vapor-Liquid Region

press., atm	composition of liquid phase, mole fraction ethylene	molar volume of liquid phase, mL/mol
10	0.190	469
20	0.316	406
30	0.415	355
40	0.494	315
50	0.558	283
60	0.611	256
70	0.656	233
80	0.692	216
90	0.727	201
100	0.757	187
120	0.795	166
140	0.823	151
160	0.846	139
180	0.863	130
200	0.880	121
220	0.892	115
240	0.904	108
260	0.916	102
280	0.934	92
290.2[a]		

[a] Vapor-liquid critical point.

Table III is the smoothed 75 °C isotherm for the ethylene-*n*-dotriacontane vapor-liquid system, based on 72 data points. Below 60 atm, the standard deviations for pressure and volume are 0.8 atm and 1.0 ml/mol, respectively, whereas above 60 atm they are 4 atm and 2.0 ml/mol, respectively. The standard deviation for the liquid-phase composition for the entire isotherm is 0.007. Table IV is the smoothed S-L-V locus (upper branch) for ethylene-*n*-dotriacontane, based on 21 data points. The standard deviations are the same as for Table III, with the additional standard deviation of temperature being 0.1 K. The

Table IV. Smoothed Pressure-Temperature-Composition Diagram in the Solid-Liquid-Vapor Region of the Ethylene-*n*-Dotriacontane System

press., atm	temp, K	composition of liquid phase, mole fraction ethylene	molar volume of liquid phase, mL/mol
10	339.9	0.178	487.0
20	337.7	0.325	401.5
30	336.0	0.435	347.0
40	334.5	0.523	303.8
50	333.1	0.598	264.1
60	331.7	0.657	233.8
70	330.4	0.707	207.9
80	329.2	0.752	183.6
90	328.1	0.798	159.5
100	327.4	0.830	142.6
120	326.7	0.863	126.0
140	326.4	0.879	118.0
160	326.2	0.886	114.0
180	326.0	0.895	109.8
200	325.9	0.900	107.0
220	325.7	0.915	99.2
240	325.7	0.917	98.2
260	325.6	0.927	93.2
271[a]	325.5		

[a] Type-K sineular point.

large standard deviations of pressure at high pressures in all of the data are due to the steepness of the curves with respect to the pressure variable. As before, the two critical end points make up two points on the binary $L = V$ locus upper branch.

The S–L–V data in Tables II and IV can be correlated by using the Flory–Huggins theory (*4*, *5*) for the description of the nonideality of the liquid phase in concert with a solid–liquid fugacity equality formalism in the spirit of Prausnitz (*8*). However, to achieve a correlation of the accuracy desired for engineering design, one must modify the formalism in Prausnitz for pressure as the pressure effect is not negligible in these systems.

These systems presented herein also seem to be candidates for correlation using the perturbed hard-chain equation of state (*3*), which is designed parametrically for handling long molecules. We have not attempted to verify this conjecture.

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Glossary

CST	critical solution (temperature) point where two liquid phases become critical in the presence of the V phase
K	the critical end point, called the K point, where the L and V phases are critical in the presence of a third phase (either S or L)
L	liquid phase
P	pressure
Q	Q point, a four-phase invarient point, either S–L–L–V or S–S–L–V
S	solid phase
T	temperature
V	vapor phase

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Supplementary Material Available: Complete tables of raw data (Tables A1–A4) for both binary systems (6 pages). Ordering information is given on any current masthead page.

Study of the Critical and Azeotropic Behavior of Binary Mixtures. 1. Critical States of Perfluoromethylcyclohexane–Isomeric Hexane Systems

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The *PVT–x* diagrams of five binary systems composed of the isomers of hexane with perfluoromethylcyclohexane as the common component were determined in the critical region. All of these systems form positive azeotropes and exhibit a minimum temperature point in their critical locus curves. The measured critical points in these systems and their correlation and prediction using an extended corresponding states principle are reported in this paper.

Introduction

The *PVT–x* relations of mixtures at elevated pressures are of great practical as well as theoretical interest. Of particular interest are those systems whose solutions deviate from ideality to such an extent that azeotropes are formed. Because of the difficulty in separating such mixtures by using conventional distillation techniques, data on the characteristic properties of azeotropes or reliable methods for their prediction are of importance to chemists and chemical engineers in the design and operation of chemical processes. From a theoretical point of view, the study of azeotropy is of considerable interest because it yields fundamental information on the molecular behavior of fluids.

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