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Phase Equilibria Behavior of the Systems Carbon Dioxide + *n*-Dotriacontane and Carbon Dioxide + *n*-Docosane

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The phase behavior of the binary mixture carbon dioxide + *n*-dotriacontane was studied as a vapor–liquid system at 75, 100, and 125 °C and along the high-temperature branch of its solid–liquid–vapor locus to pressures of 1050 psia. The phase behavior of the binary mixture carbon dioxide + *n*-docosane was studied as a vapor–liquid system at 50, 75, and 100 °C and along the high-temperature branch of its solid–liquid–vapor locus to pressures of 1050 psia. The studies were carried out in a visual cell apparatus recently constructed by the investigators. The apparatus is described in detail herein. Properties of the systems reported are pressure, temperature, liquid-phase composition, and liquid-phase molar volume.

The purpose of this paper is to report phase equilibria data on the binary systems CO_2 + *n*-dotriacontane and CO_2 + *n*-docosane. The temperatures and pressures selected for study are characteristic of those encountered in CO_2-enhanced recovery projects. It is intended that the data herein will contribute to the current body of phase equilibria data on CO_2 with well-defined heavier hydrocarbons, in turn elucidating how species in the C7+ portion of a crude oil affect CO_2 + oil phase equilibria behavior.

There have been several earlier studies of CO_2–heavy hydrocarbon phase equilibria. Citation of previous studies herein will be restricted to those with *n*-paraffins as the heavy hydrocarbon, having a carbon number of at least 10. Reamer and Sage (*1*) extensively studied the CO_2 + *n*-decane system and obtained composition and volumetric data for vapor–liquid isotherms up to 460 °F. Kulkarni et al. (*2*) reported liquid–liquid–vapor (L–L–V) and solid–liquid–vapor (S–L–V) data for this same binary in the temperature range of −56 to −29 °C. Stewart and Nielsen (*3*) measured the solubility of CO_2 in *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane at 60 and 90 °C, observing L–L–V behavior in the *n*-tetradecane and *n*-hexadecane systems. Meldrum and Nielsen (*4*) studied L–L–V equilibria in the ternary systems CO_2 + propane + *n*-hexadecane and CO_2 + *n*-decane + *n*-hexadecane at about 70 °F. Schneider et al. (*5–7*) observed phase behavior in the binary systems of CO_2 with *n*-undecane, *n*-tridecane, and *n*-hexadecane at temperatures of −120 to 400 °C up to a maximum pressure of 3700 bar. This work emphasized L–L, L–L–V, and critical point locus phenomena.

Francis (*8*) observed partial miscibility in binary systems containing CO_2 and *n*-tetradecane, *n*-hexadecane, *n*-octadecane, and *n*-eicosane. Hayduk et al. (*9*) measured the solubility of CO_2 in *n*-dodecane and *n*-hexadecane from 10 to 50 °C at 1 atm absolute. King and Al-Najjar (*10*) measured the solubility at 1 atm absolute of CO_2 in *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane from 20 to 70 °C. Sebastian et al. (*11*) reported the solubility of CO_2 in *n*-decane and in *n*-hexadecane at pressures from 20 to 50 atm absolute at temperatures of 190 °C and above.

Huie et al. (*12*) studied L–V, L–L–V, and S–L–V phase equilibria of the binary system CO_2 + *n*-eicosane. The L–V data extended to 100 °C and 75 atm absolute. Hottovy et al. (*13*) detailed the L–L–V loci of CO_2 with *n*-dodecane, *n*-tridecane, *n*-tetradecane, and *n*-pentadecane, respectively. One salient feature of these two multiphase studies is that molar volume data on the liquid phases were reported, as well as the phase compositions.

In this paper, data are presented for S–L–V and L–V phase equilibria behavior for the binary systems CO_2 + *n*-dotriacontane and CO_2 + *n*-docosane. The effect of carbon number on CO_2 solubility in heavy *n*-paraffins is illustrated by comparing the behavior of the two systems. These binary systems do not exhibit L–L–V phase equilibria as the quadrupole point which would terminate the L–L–V locus at low temperature cannot form at a low enough temperature (below the upper critical end point L–L = V of the L–L–V locus). On the basis of the above cited studies, the L–L–V immiscibility locus shrinks in extent as one progresses upward in carbon number in the *n*-paraffins from 14 (*13*). It is only about 5 K in extent for the system CO_2 + *n*-eicosane (*12*). Preliminary results from an experimental study in progress by the authors indicate there is no immiscibility in binary systems of CO_2 + *n*-paraffins starting with *n*-docosane.

The experimental apparatus and procedures are described in the following sections in some detail as these are the initial studies performed in this laboratory.

Experimental Apparatus and Procedures

The data are taken by using a stoichiometric approach, with the experimental phase equilibria system being contained in a glass visual cell, illustrated in Figure 1. The glass cell is fabricated from Pyrex glass, having a $^1/_2$ in. o.d. thick-walled body, a $^1/_2$ in. o.d. solid base, and a $^1/_4$ in. o.d. capillary neck. The cell is attached to a gas feed line with a standard Swagelok $^1/_4$-in. stainless steel fitting with a Teflon ferrule to achieve the metal-to-glass seal. A cell holder is required to keep the cell from slipping longitudinally out of the Teflon ferrule. The internal volume of the glass cell is typically about 7–8 mL, and phase volumes within the cell can be accurately measured with a cathetometer, once the volume correspondence of height relative to a fiducial line on the cell exterior is known. This volumetric calibration is obtained by making incremental microburet additions of a liquid to the cell accompanied by cathetometer readings. This calibration procedure allows volumes to be read in the cell to ±0.005 mL. The contents of the cell can be stirred to achieve phase equilibria by using a steel ball manually actuated by an overriding horseshoe magnet. This glass cell arrangement is reliable to pressures of at least 1500 psia.

The visual cell is housed in a visual cell unit (see Figure 2) consisting of a stirred bath contained in an unsilvered 4-L Dewar vessel. The bath fluid is either water or a glycerol–water mixture at temperatures exceeding 75 °C. The temperature of the bath can be readily controlled to at least ±0.01 K by using two 400-W quartz immersion heaters linked through a variable transformer to a Sargent-Welch Thermonitor temperature controller with probe, which has a sensitivity of ±0.001 K. The input of the quartz heaters is offset with a water-circulating cooling coil. The temperature in the bath is determined by a 25.5-Ω metal-sheathed platinum-resistance thermometer linked to a Mueller bridge and a null detector, both supplied by Leeds and Northrup. The thermometer is calibrated against a Leeds and Northrup standard platinum resistance thermometer in the laboratory and should provide temperature measurement

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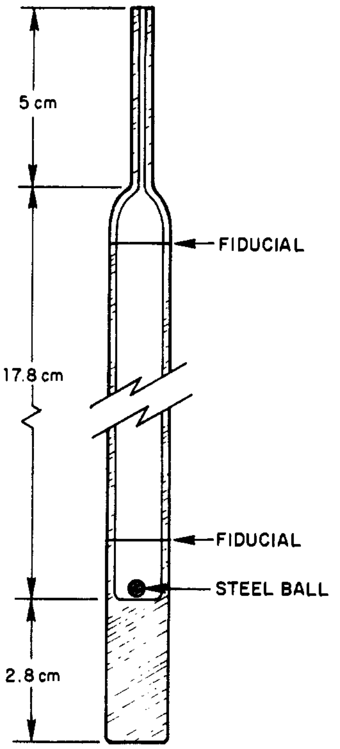

Figure 1. Diagram of the glass visual cell.

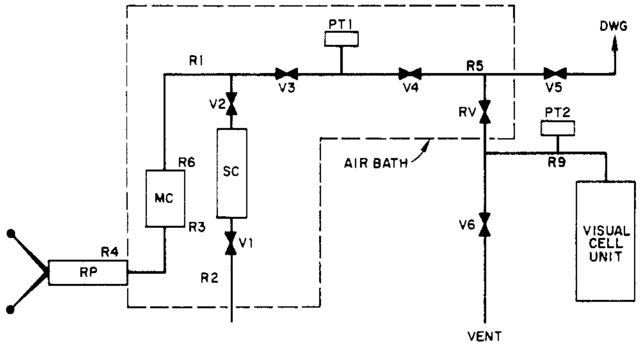

Figure 2. Schematic diagram of the experimental unit.

reliability to ±0.01 K, IPTS-68.

Pressure in the cell is measured by a Sensotec Super TJE transducer (PT2 in Figure 2) read on a Sensotec indicator (Model 450D). The transducer is frequently calibrated to ±1 psia with a Ruska dead-weight gauge (DWG) pressure calibration system (Model no. 2400-601) on site in the laboratory. It should be mentioned that the pressure measurement system is somewhat sensitive to the temperature of the transducer. Therefore, the transducer is maintained at a given temperature to ±0.1 K for all experimental runs and is calibrated at that operating temperature. Also the pressure indicator is devised to read to a pressure of 2000.0 psia with a sensitivity of ±0.1 psi. The sensitivity enables one to determine when equilibrium is attained in the cell while stirring at a given temperature. It is not meant to imply accuracy.

Referring to Figure 2, one can deliver gas to the visual cell with a 100-cm^3 Ruska manual pump (RP) which drives the gas with a mercury "piston" from a bomb (MC) to the visual cell. This gas delivery system is separated from the line to the visual cell by a regulating valve (RV). The amount of gas that passes the regulating valve can be determined by the advance of the manual pump. The gas addition system is housed in an air bath with a temperature controller which can hold the bomb MC and all connecting lines at a constant temperature to ±0.1 K. The temperature of the gas is determined by platinum-resistance temperature devices (R1, R2, R3, etc.) which are calibrated to ±0.1 K. The pressure of the gas to the left of the regulating valve RV is determined by a pressure transducer PT1 of the same kind as the earlier described system PT2. The sensitivity of PT1 (±0.1 psi) enables one to maintain a constant pressure to the left of RV throughout an experimental run. In case of a need to provide more gas to the bomb MC, additional gas is stored in a larger storage bomb SC.

The procedure for studying a vapor-liquid isotherm is as follows. An empty volume-calibrated visual cell is tared. Then the heavy hydrocarbon species is added as a liquid to the cell by a syringe with a long tip (to extend through the capillary neck of the cell), and the visual cell is reweighed. The cell is placed in the bath (Dewar) in the cell holder and attached to the unit. Without stirring the liquid hydrocarbon phase, the vapor space of the cell and the line to the right of the valve RV is flushed several times with the gas to be added. Upon completion of flushing, the Ruska manual pump is balanced at its pressure, to be maintained throughout the run

The liquid level in the visual cell is measured with the cathetometer, so that the volume of the vapor space can be known, since it contains the gas at atmospheric pressure. In addition the line from the valve RV to the top of the visual cell also contains the gas at the same pressure as the visual cell. This line is kept at a constant known temperature (R9) by means of a heating tape controlled with a variable transformer. The line is carefully calibrated with respect to volume prior to the run.

A gas addition is made slowly through valve RV, with the pump being advanced at constant pressure to avoid adiabatic thermal disturbances to the left of valve RV. The valve RV is then shut and the visual cell is stirred for several minutes, until the cell pressure stabilizes to ±0.1 psi. The liquid level in the cell is then remeasured. In the gas solubility studies reported herein, the computation of the liquid-phase composition is relatively straightforward. The gas that was present in the line and the cell vapor space after flushing *plus* the gas that was adddd by the manual pump RP are now in one of the three places: (1) in the line to the right of valve RV, (2) in the cell vapor space, or (3) dissolved in the liquid phase. One can calculate 1 and 2 with the aid of compressibility factor $Z = Z(P,T)$ information for the gas and obtain 3 by process of elimination. The composition of the liquid phase and its molar volume can thus be computed.

A few comments are in order. It is assumed in these present studies that the heavy hydrocarbons are nonvolatile, and therefore no hydrocarbon is present in the vapor space of the visual cell. The gas used is CO_2, and so the air bath and line temperatures are held at $T > 50$ °C (about 20 K supercritical) in order to reduce the sensitivity of Z to the variables P and T. The IUPAC equation of state (*14*) was used to determine single-phase $Z = Z(P,T)$ information for CO_2.

The procedure for determining an S-L-V data point is similar to that of the L-V data point. An L-V system is cooled until crystals of the hydrocarbon appear. (This usually requires some supercooling of the solute-solvent system.) The S-L-V system is then stirred and *slowly* heated until only a trace of crystals remains in equilibrium with the liquid and vapor phases. When the system is stabilized, the same measurements and calculations as before are performed, with the assumption that the amount of crystals is negligible; i.e., all the hydrocarbon is in the liquid phase.

Additional data points in either an L-V or an S-L-V run can be established by adding more gas to the system through valve RV, and proceeding as before.

Materials

The *n*-dotriacontaine and *n*-docosane were purchased from Alfa Products with a stated purity of 99%. Their melting points

Table I. Liquid-Phase Composition and Molar Volume as a Function of Pressure for Liquid-Vapor Isotherms of Carbon Dioxide + n-Dotriacontane

press., bar	$[CO_2]$, mole fraction	molar vol, mL/(g-mol)
	Temperature = 75 °C (348.15 K)	
9.52	0.1111	520.4
12.39	0.1501	499.1
20.92	0.2279	458.5
25.50	0.2793	430.3
34.05	0.3409	398.4
42.25	0.4037	364.6
48.35	0.4368	346.5
57.83	0.4941	315.8
63.44	0.5218	300.7
69.73	0.5503	286.2
72.08	0.5618	279.0
	Temperature = 100 °C (373.15 K)	
11.57	0.1223	523.7
27.08	0.2575	450.6
35.68	0.3114	423.3
42.86	0.3606	397.1
43.88	0.3687	391.2
49.68	0.4006	373.3
57.79	0.4457	349.9
58.13	0.4455	349.7
64.30	0.4724	333.7
70.34	0.5056	316.8
72.23	0.5087	315.0
	Temperature = 125 °C (398.15 K)	
9.46	0.0963	550.5
12.04	0.1168	536.2
14.76	0.1431	524.1
21.19	0.1990	493.1
26.86	0.2379	469.4
29.36	0.2553	460.6
34.51	0.2944	440.2
43.82	0.3438	411.1
44.31	0.3483	410.1
48.93	0.3760	393.1
53.89	0.3980	380.7
58.98	0.4186	369.6
64.42	0.4518	351.8
71.64	0.4821	333.8
72.29	0.4772	337.4

were determined to be 69.5 ± 0.1 and 43.5 ± 0.1 °C, respectively. They were used without further purification.

The CO_2 was obtained from Air Products and Chemicals, Inc., as "Coleman Grade" with a purity rating of 99.99%. It was transferred to the (initially evacuated) storage bomb as a liquid, with the bomb being jacketed with ice. In this two-phase condition, the vapor phase was vented and discarded to reduce the presence of any light gas impurities. A sample of this CO_2 was then liquefied in the visual cell at 25.00 °C. The difference in the bubble point and the dew point pressures at this temperature was about 1.3 psi, giving a Kuenen criterion of purity (this pressure difference divided by the critical pressure) of 0.0013. The vapor pressure at this temperature, and the critical temperature and pressure, agreed with the literature values (*15*) to within 1 psia (i.e., within experimental accuracy) and 0.06 K.

Results

Table I presents raw data for liquid-phase composition and molar volume of the binary L-V system CO_2 + *n*-dotriacontane at 75, 100, and 125 °C. Table II presents raw data for the S-L-V locus of the same binary system. The liquid-phase compositions and molar volume data are shown collectively in Figures 3 and 4.

Table III presents liquid-phase raw data for the binary system CO_2 + *n*-docosane for its L-V phase equilibria at 50, 75, and 100 °C. Table IV presents raw data for the system's S-L-V locus. Figures 5 and 6 graphically illustrate the data in Tables III and IV.

In all of these data, it is assumed that the gas phase is pure CO_2 and the solid phases are pure hydrocarbon. The tem-

Table II. Temperature, Pressure, Liquid-Phase Composition, and Molar Volume for the Solid-Liquid-Vapor Locus of Carbon Dioxide + n-Dotriacontane

temp, K	press., bar	$[CO_2]$ mole fraction	molar vol, mL/(g-mol)
341.12	9.25	0.1259	509.5
340.79	13.41	0.1677	486.8
340.04	20.09	0.2425	447.1
339.09	28.66	0.3229	404.0
338.73	32.69	0.3564	386.6
337.74	41.29	0.4164	353.7
337.29	48.78	0.4676	326.3
336.74	56.05	0.5100	304.3
336.36	61.74	0.5431	285.9
335.96	69.68	0.5814	265.5

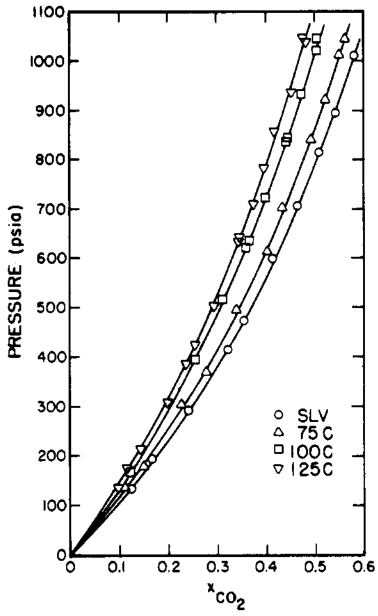

Figure 3. Pressure vs. liquid-phase mole fraction of CO_2 for the binary system CO_2 + *n*-dotriacontane (14.50 psia = 1 bar).

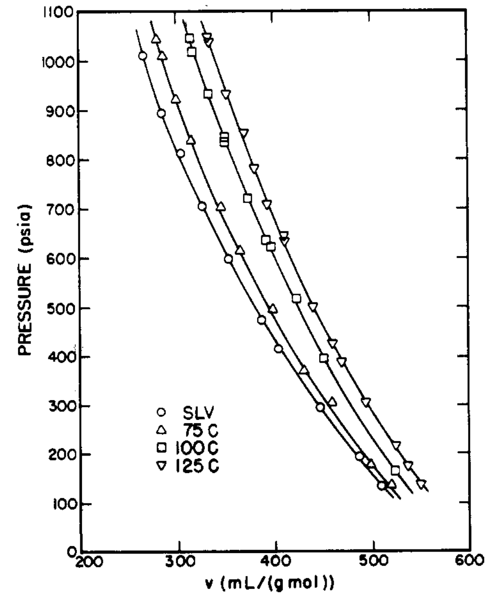

Figure 4. Pressure vs. liquid-phase molar volume for the binary system CO_2 + *n*-dotriacontane (14.50 psia = 1 bar).

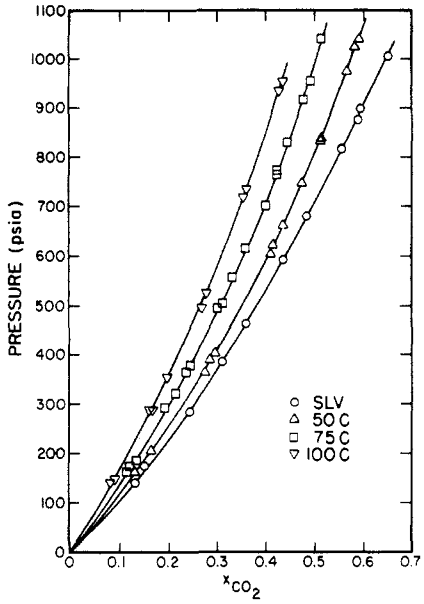

Figure 5. Pressure vs. liquid-phase mole fraction of CO_2 for the binary system CO_2 + *n*-docosane (14.50 psia = 1 bar).

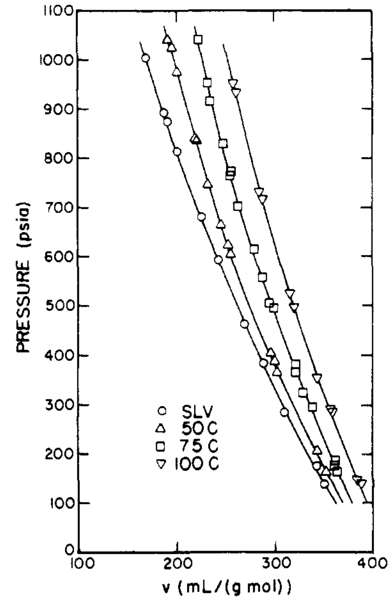

Figure 6. Pressure vs. liquid-phase molar volume for the binary system CO_2 + *n*-docosane (14.50 psia = 1 bar).

Table III. Liquid-Phase Composition and Molar Volume as a Function of Pressure for Liquid-Vapor Isotherms of Carbon Dioxide + *n*-Docosane

press., bar	$[CO_2]$, mole fraction	molar vol, mL/(g-mol)
Temperature = 50 °C (323.15 K)		
11.09	0.1338	352.8
14.14	0.1627	343.7
25.17	0.2778	302.2
26.83	0.2860	300.1
27.81	0.2957	296.5
41.62	0.4104	255.7
43.01	0.4175	253.0
45.66	0.4381	246.0
51.57	0.4763	232.1
57.65	0.5143	220.1
57.87	0.5157	218.3
67.29	0.5697	199.1
70.77	0.5827	195.0
71.78	0.5925	190.9
Temperature = 75 °C (348.15 K)		
11.08	0.1183	365.5
11.90	0.1231	362.9
12.67	0.1281	363.8
20.09	0.1918	339.4
22.09	0.2180	329.3
25.21	0.2379	321.8
26.14	0.2453	321.2
34.20	0.3028	300.0
34.72	0.3138	294.5
38.44	0.3348	287.2
42.40	0.3598	279.6
48.36	0.4011	263.0
52.92	0.4245	254.7
53.21	0.4225	257.0
57.21	0.4447	248.6
63.30	0.4796	234.9
65.69	0.4914	232.3
65.77	0.4919	230.5
71.75	0.5157	222.6
Temperature = 100 °C (373.15 K)		
9.62	0.0833	388.6
10.21	0.0928	384.2
19.77	0.1622	360.2
19.81	0.1678	357.8
24.33	0.2004	344.2
34.27	0.2705	319.4
36.20	0.2785	315.9
49.61	0.3546	287.6
50.44	0.3610	284.8
64.48	0.4284	260.4
65.64	0.4365	256.6

Table IV. Temperature, Pressure, Liquid-Phase Composition, and Molar Volume for the Solid-Liquid-Vapor Locus of Carbon Dioxide + *n*-Docosane

temp, K	press., bar	$[CO_2]$, mole fraction	molar vol, mL/(g-mol)
315.34	9.60	0.1335	350.4
315.21	11.93	0.1520	345.2
314.48	19.57	0.2454	311.1
313.45	26.61	0.3113	288.4
312.95	31.95	0.3621	268.9
311.84	40.85	0.4388	243.0
310.93	46.91	0.4869	225.6
309.92	56.42	0.5586	200.5
309.40	60.45	0.5907	189.3
309.40	61.65	0.5973	186.9
308.46	69.46	0.6518	167.8

peratures should be good to ±0.01 K for the L-V equilibria and ±0.03 K for the S-L-V equilibria. All pressures are estimated to be good to ±1 psi, even though they are tabulated to an additional significant figure. The mole fractions should be good to ±0.002 while the molar volumes should be good to at least ±1 mL/g-mol. These last two esimates are based on the average absolute deviations (AAD) of the raw data from the smoothed curves shown in Figures 3-6. The AAD for the liquid-phase molar volume for both systems is about 0.8 mL/g-mol, while the AAD for the mole fraction of CO_2 in the liquid phases for both systems is about 0.0016.

As a test of the integrity of the apparatus, an attempt was made to match the L-V isotherm of Huie et al. (*12*) for the binary system CO_2 + *n*-eicosane at 50 °C. The pressures observed at a given composition were typically 3-5% higher than those of Huie et al. However, our data agreed closely with the recent data of Robinson (*16*) on the same isotherm. It is suspected that the purity of the *n*-eicosane used by us and Robinson, stated as 99% and supplied by Alfa Products, is different from that used by Huie. In making any comparison of pressures between investigators, one should note that because of the steepness of the pressure-composition curves (see Figures 3 and 5) a small deviation in composition translates into an apparently large deviation in pressure.

J. Chem. Eng. Data **1984**, *29*, 417-419

Registry No. CO_2, 124-38-9; *n*-dotriacontane, 544-85-4; *n*-docosane, 629-97-0.

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Vapor–Liquid Equilibria in Mixtures of Cyclohexane and Methyl Methacrylate

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Isothermal vapor–liquid equilibrium values were measured for mixtures of cyclohexane and methyl methacrylate at 318.12, 333.13, and 348.14 K by using a modified Dvorak and Boublik recirculating still. The experimental results were correlated with the Wilson equation by fitting the total pressure and vapor composition values. A binary azeotrope was found to exist at all three temperatures.

Introduction

An ester interchange reaction between methyl methacrylate (MMA) and higher alcohols can be carried out in the presence of a catalyst to produce higher esters. This transesterification of alcohols is usually conducted in an inert solvent, such as hexane, benzene, or cyclohexane, which can form a low-boiling azeotrope with the liberated alcohols.

The data available in the literature on the vapor–liquid equilibrium (VLE) values for mixtures of cyclohexane and MMA are limited to those reported by Frolova et al. (*1*) at 760 mmHg (101.325 kPa). It appears that these values are of uncertain quality. The purpose of this work is to establish isothermal VLE values for the mixture at three temperatures by means of a recirculating still.

Experimental Section

***Chemicals*.** Phillips 66 Research-grade cyclohexane, supplied by the Phillips Petroleum Co., and Aldrich Analyzed-grade MMA, containing 65 ppm hydroquinone monomethyl ether, supplied by the Aldrich Chemical Co., were used without further purification. The purity of both liquids was estimated to be 99 mol % minimum. Physical constants of these materials are given in Table I. The vapor pressure data available in the literature for pure MMA are generally not in good agreement, and for this reason those that were obtained in this work were preferred.

***Apparatus*.** Vapor–liquid equilibria were established by means of a modified Dvorak and Boublik recirculating still, whose operation has been previously described (*2*, *3*). The temperature of the equilibrium mixture was measured by using a Hewlett-Packard (Model 2801 A) quartz thermometer, which was checked at the triple point of water. The accuracy of the temperature measurement is estimated to be ±0.01 K. For pressure measurements, a Texas Instruments pressure gauge (type 144-01) together with a Bourdon Capsule (0–174 kPa) was used. This instrument was calibrated by measuring the vapor pressure of distilled and demineralized water in a Swietoslawski type ebulliometer, and checked by a mercury manometer in conjunction with a cathometer. The system pressure was controlled by a two-liquid manostat. The accuracy of the pressure measurements is estimated to be ±0.05 torr.

Analyses of the condensed vapor and liquid samples were made with an Anton-Paar K.G. (Model DMA 02A) digital densimeter with its temperature maintained at 288.15 ± 0.01 K. The accuracy of the determined composition is estimated to be ±0.002 mole fraction.

Results and Discussion

The experimentally determined equilibrium pressure, P, and liquid and vapor compositions, x and y, together with the calculated activity coefficients, γ_i, are listed in Table II.

The values of ln γ_1 were obtained from

$$\ln \gamma_1 = \ln [y_1P/(x_1p_1^\circ)] + (B_{11} - v_1^\circ)(P - p_1^\circ)/RT + (1 - y_1)^2\delta_{12}P/RT \quad (1)$$

and similarly for ln γ_2. In these equations

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (2)$$

and x_1 and y_1 are the equilibrium mole fractions of cyclohexane in the liquid and vapor phases at pressure P. The quantities p_i°, B_{ii}, and v_i° are the vapor pressure, second virial coefficient, and liquid molar volume of component i and B_{12} is the cross second virial coefficient. The experimentally obtained p_i° values as listed in Table I were used in the calculation. The values of v_i° for cyclohexane and MMA were taken from Timmermans (*4*) and Matheson et al. (*5*).

Since values of B_{ii} and B_{12} are not available at the three temperatures investigated, they were estimated by using the

0021-9568/84/1729-0417$01.50/0