ϕ_1, ϕ_2 = coefficients of correction for nonideality of the vapor phase; components 1 and 2, respectively
π = total pressure, mm. of Hg

Subscripts

1, 2 = denote respectively the more volatile and the less volatile components of a binary system

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RECEIVED for review March 6, 1967. Accepted December 6, 1967. Work supported by the financial assistance of a grant from the National Research Council of Canada.

Heterogeneous Phase and Volumetric Equilibrium in the Ethane–*n*-Octane System

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Vapor-liquid equilibrium composition and liquid molar volumes for the binary system of ethane and *n*-octane are presented for six isotherms between 0° and 100° C. The Flory-Huggins model for liquid solutions is shown to fit the experimental data with considerably better accuracy than the Scatchard modification of regular solution theory.

EXPERIMENTAL examination of the volumetric and phase behavior of hydrocarbon systems continues to be of interest owing to their industrial importance and the lack of a sound theoretical model for obtaining equilibrium data on such systems. The literature through 1966 shows no existing experimental data on the vapor-liquid behavior of the ethane–*n*-octane system.

The behavior of the pure components has been extensively studied. Ethane has been investigated by several groups of experimenters (*1, 2, 13, 14*). Barkelew, Valentine, and Hurd (*1*) evaluated thermodynamic properties from the *PVT* data of Beattie, Hadlock, and Poffenberger (*2*). Rodrigues (*14*) obtained detailed information in the critical region. Michels, Van Straaten, and Dawson (*13*) present data for 0° to 100° C. and to 50 atm. The properties of *n*-octane have been established by several studies (*3, 8*). Eduljee, Newitt, and Weale (*3*) presented isotherms from 0° to 60° C. to 5000 atm. Data on the liquid density, vapor pressure, critical constants, and heat of fusion are reported by Rossini *et al.* (*15*).

EXPERIMENTAL

The equipment and experimental techniques were described by Kohn and Kurata (*11*) and were the same as those used in other recent studies of binary hydrocarbon systems (*9–11, 17, 18*). Temperatures were obtained with a platinum resistance thermometer, which was accurate to ± 0.01° C. and was frequently compared with a platinum resistance temperature standard calibrated by the National Bureau of Standards. Pressures were read on bourdon tube gages accurate to ±0.07 atm. Each gage was frequently checked against an accurate dead weight gage. The only change in procedure from the previous studies was that the equilibrium cell was immersed in an ice bath while being purged of air. The ice bath was needed to cool the cell to lower the vapor pressure of the octane and hence avoid its possible loss during purging. The equilibrium cells used in this study were made of borosilicate glass and were of the same type as those used in the earlier works.

Several experimental runs were taken at each isotherm to obtain a reasonably good assessment of experimental reproducibility. Compositions of ethane in the liquid and vapor phases were determined from stoichiometric analysis of the amount of pure ethane added to the cell from a thermostated reservoir. The gas was displaced from the reservoir by a manually operated mercury displacement pump. The pump has an accuracy of displacement of ±0.01 ml. The accuracy of the measured ethane composition was dependent on the temperature and pressure of the reservoir, the delivery line volume and temperature, and the volume and temperature of the neck of the equilibrium cell. The reservoir temperature was controlled to ±0.07° C. and the pressure to ±0.07 atm. The delivery line volume is approximately 0.7 ml., and its temperature was controlled manually to within ±2° C. Many hundreds of experimental runs with ethane in various binary and ternary systems have demonstrated that the equilibrium compositions in the cell are reliably reproduced within from 0.0005 to 0.003 mole fraction.

The ethane (Matheson Co.) was pure grade, stated by the supplier to have 99 mole % minimum purity, was purified before further use as described by Ma and Kohn (*12*), and was thought to have a purity of at least 99.7 mole %. Pure grade *n*-octane (Phillips Petroleum Co.) was stated by the supplier to be at least 99 mole % pure. The *n*-octane had a refractive index of 1.3971 at 20° C. in good agreement with the literature value (*15*) and was used as received without further purification.

RESULTS

The pressure-composition diagrams of the system in vapor-liquid equilibrium are presented in Figures 1 and

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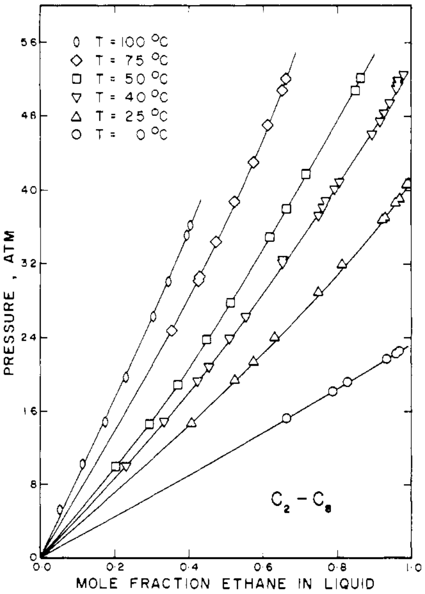

Figure 1. Pressure *vs.* liquid mole fraction ethane for the ethane–*n*-octane system

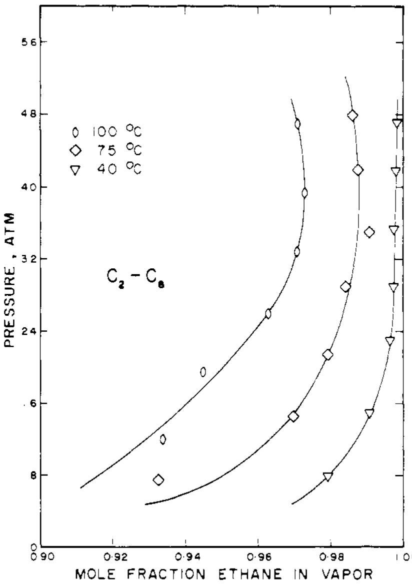

Figure 2. Pressure *vs.* vapor mole fraction ethane for the ethane–*n*-octane system

2. Figure 1 indicates pressure *vs.* mole fraction ethane in the liquid phase, while Figure 2 represents the experimental data in the vapor phase. Six isotherms were determined in the range 0° to 100° C. at pressures to 56 atm. Each isotherm was obtained by at least two runs in a 10-cc. equilibrium cell. The average deviations of the experimental bubble points were ±0.08 atm. and ±0.0024 mole fraction ethane. The average deviations for the vapor phase were ±0.32 atm. and ±0.0007 mole fraction ethane. Reliable dew point isotherms were obtained only at 40°, 75°, and 100° C. at pressures to 48 atm. A molar volume-composition diagram for the saturated liquid phase is presented in Figure 3. The average deviations for the liquid molar volume and the liquid mole fraction ethane were ±0.24 ml. per gram mole and ±0.0024 mole fraction, respectively.

Table I presents the smoothed properties of the coexisting vapor and liquid phases between 0° and 100° C. Vapor compositions were not measured below 40° C. because of the difficulty of accurately measuring octane compositions of less than a few tenths of a mole per cent. Because the vapor is essentially pure ethane at elevated pressures, its molar volume is almost identical to that of pure ethane at the same temperature and pressure. The values of the vapor molar volumes calculated from the data of the dew point runs showed this to be true, but did not display the desired precision, and thus were not reported here. The liquid molar volumes however were reproducible to ±0.2%.

Table II presents the fugacity of ethane as a function of pressure along each isotherm. As mentioned previously and as is evident from Figure 2, the vapor phase is essentially pure ethane at the temperature of this study. Thus the compressibility factors of pure ethane were used in the calculation of the ethane fugacities. At the higher temperatures the Lewis and Randall fugacity rule was employed in order to correct for the small amounts of *n*-octane present in the vapor phase. The fugacities along each isotherm were fitted to both the Scatchard (*16*) modification of regular solution theory and the Flory-Huggins (*4*, *5*, *7*) solution model. The expressions for the component fugacity for these two models are as follows: For the Scatchard modification of regular solutions,

$$f_1 = f_1^\circ x_1 \exp\left\{\frac{\Delta u_{12}}{RT}\left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{1/2}\phi_2^2\right\} \qquad (1)$$

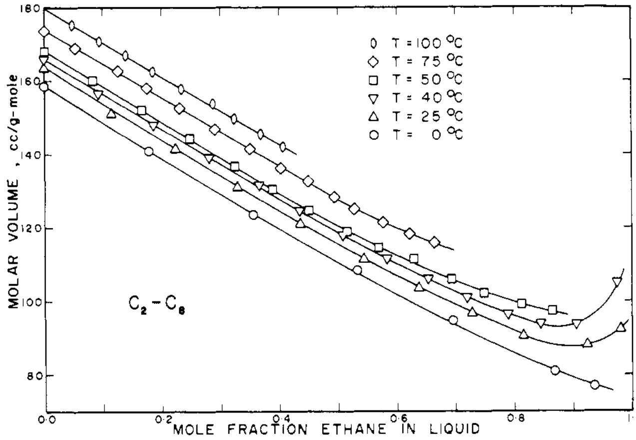

Figure 3. Liquid molar volume *vs.* liquid mole fraction ethane for the ethane–*n*-octane system

while for the Flory-Huggins model,

$$f_1 = f_1^\circ \phi_1 \exp\left\{\phi_2\left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right) + \frac{\Delta u_{12}}{RT}\left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{1/2}\phi_2^2\right\} \qquad (2)$$

where

$$\phi_1 = \frac{x_1\bar{V}_1}{x_1\bar{V}_1 + x_2\bar{V}_2} \text{ and } \phi_2 = \frac{x_2\bar{V}_2}{x_1\bar{V}_1 + x_2\bar{V}_2}$$

The standard state fugacity (f_1°) is the fugacity of the hypothetically pure incompressible liquid ethane at the temperature and pressure of the system. The standard state fugacity of the liquid ethane was computed with the thermodynamic equation:

$$f_1^\circ\big|_{(P,T)} = P_1^\circ \frac{f}{P}\Big|_{(P_1^\circ,T)} \exp\left[\frac{\bar{V}_1}{RT}(P - P_1^\circ)\right] \qquad (3)$$

Above the critical temperature of ethane, its vapor pressures were extrapolated using the equation proposed by Hougen, Watson, and Ragatz (*6*).

Table I. Properties of Coexisting Vapor and Liquid Phases of Ethane and *n*-Octane

Press., Atm.	Liquid Mole fraction ethane	Liquid Molar volume ml./gram mole	Vapor, Mole Fraction Ethane
	0.0° C.		
4.0	0.178	140.9	
8.0	0.350	123.6	
12.0	0.525	108.3	
16.0	0.697	94.6	
20.0	0.869	81.0	
22.0	0.952	76.7	
	25.0° C.		
4.0	0.112	151.2	
8.0	0.223	141.2	
12.0	0.334	130.8	
16.0	0.447	120.9	
20.0	0.547	111.4	
24.0	0.643	103.6	
28.0	0.735	96.6	
32.0	0.828	90.5	
36.0	0.922	87.7	
40.0	0.984	92.3	
	40.0° C.		
4.0	0.093	156.3	0.9704
8.0	0.186	147.8	0.9798
12.0	0.277	138.7	0.9868
16.0	0.363	131.6	0.9916
20.0	0.439	124.6	0.9947
24.0	0.514	117.7	0.9967
28.0	0.583	111.4	0.9977
32.0	0.652	105.7	0.9979
36.0	0.721	100.7	0.9979
40.0	0.792	96.6	0.9981
44.0	0.859	93.8	0.9984
48.0	0.921	93.6	0.9989
52.0	0.973	105.2	0.9994
	50.0° C.		
4.0	0.084	159.7	0.9464
8.0	0.162	151.7	0.9657
	50.0° C.		
12.0	0.248	143.8	0.9761
16.0	0.322	136.6	0.9827
20.0	0.392	130.2	0.9870
24.0	0.458	124.4	0.9900
28.0	0.517	119.1	0.9918
32.0	0.577	114.7	0.9929
36.0	0.636	111.4	0.9933
40.0	0.693	106.2	0.9934
44.0	0.749	102.2	0.9931
48.0	0.807	99.0	0.9924
52.0	0.863	97.6	
	75.0° C.		
4.0	0.057	168.8	0.9361
8.0	0.126	163.4	0.9518
12.0	0.173	158.0	0.9636
16.0	0.231	152.6	0.9721
20.0	0.288	147.1	0.9787
24.0	0.346	141.5	0.9823
28.0	0.399	136.6	0.9855
32.0	0.449	132.4	0.9875
36.0	0.493	128.1	0.9882
40.0	0.537	125.2	0.9881
44.0	0.578	121.6	0.9876
48.0	0.622	117.9	0.9863
52.0	0.663	115.7	
	100° C.		
4.0	0.047	175.6	0.8987
8.0	0.093	171.2	0.9146
12.0	0.139	166.9	0.9278
16.0	0.186	162.5	0.9400
20.0	0.232	158.1	0.9507
24.0	0.278	153.8	0.9596
28.0	0.324	149.3	0.9660
32.0	0.367	145.6	0.9702
36.0	0.405	142.0	0.9726

$$\log P_r^\circ = -\frac{A(1-T_r)}{T_r} - 10^{-8.68(T_r - b)^2} \tag{4}$$

where $A = 16.25 - 73.85\ Z_c + 90\ Z_c^2$ and $b = 1.80 - 6.20\ Z_c$.

The partial molar volumes of the components as used in Equations 1, 2, and 3 are presented in Table III. They were determined through use of the liquid molar volume data given in Table I and sketched in Figure 3. Apparently, Figure 3 shows that the molar volume *vs.* mole fraction lines are linear in the low ethane composition range and only deviate widely from linearity at compositions near the critical states. Therefore, the intercepts of the tangent lines to the molar volume lines in the dilute range were used as the partial molar volumes. These volumes are not true partial molar volumes, since the pressures along the molar volume lines are not constant; however, they are generally within a few per cent of the true partial molar volumes especially in the composition range below 0.5 mole fraction ethane.

The fugacity coefficients necessary in Equation 3 were computed from the reliable ethane data of Michels, Van Straaten, and Dawson (*13*). Thus, through the use of Equations 1 through 4 and the smoothed experimental data of Table II, values of the interchange energy Δu_{12} were computed at evenly spaced values of pressure for both solution models. These calculated energy parameters were relatively constant except at the highest pressures. The values of the energy parameters at the highest pressures and those which had excess deviations were deleted, and the remaining values were used in a least squares computer program in an attempt to determine the temperature effect on the energy parameters. The results indicated that the interchange energy parameter for both models were for all practical purposes statistically constant over the temperature range of Table II. The interchange energy parameter for the Flory-Huggins model was best represented by the value 582.5 cal. per gram mole with a standard deviation of 37.8 cal. per gram mole. The interchange energy parameter for the Scatchard model was best represented by the value of 222.6 cal. per gram mole with a standard deviation of 49.1 cal. per gram mole.

The fugacities of ethane in solution were calculated using the constant values of the interchange energy in the two solution models. The standard deviation of ethane fugacities for all 64 data points of Table II is ±0.62 atm. by the Flory-Huggins model and ±0.76 atm. by the Scatchard model. The standard deviations were raised considerably by retaining the highest pressure values. If only the data at 36 atm. and below were considered, the standard devia-

Table II. Ethane Fugacity as a Function of Temperature and Pressures in Saturated Ethane–*n*-Octane Solution

Press., Atm.	Liquid Mole Fraction	Ethane Fugacity, Atm.
	0° C.	
4.0	0.178	3.83
8.0	0.350	7.33
12.0	0.525	10.52
16.0	0.697	13.40
20.0	0.869	15.98
22.0	0.952	17.14
σ_s = 0.40 atm.		
σ_f = 0.27 atm.		
	25.0° C.	
4.0	0.122	3.87
8.0	0.223	7.51
12.0	0.334	10.91
16.0	0.447	14.07
20.0	0.547	16.99
24.0	0.643	19.68
28.0	0.735	22.13
32.0	0.828	24.34
36.0	0.922	26.29
40.0	0.984	27.94
σ_s = 0.45 atm.		
σ_f = 0.29 atm.		
	40.0° C.	
4.0	0.093	3.79
8.0	0.186	7.44
12.0	0.277	10.94
16.0	0.363	14.25
20.0	0.439	17.37
24.0	0.514	20.29
28.0	0.583	22.99
32.0	0.652	25.49
36.0	0.721	27.78
40.0	0.792	29.87
44.0	0.859	31.76
48.0	0.921	33.43
52.0	0.973	34.79
σ_s = 0.71 atm.		
σ_f = 0.62 atm.		
	50.0° C.	
4.0	0.084	3.70
8.0	0.162	7.37
12.0	0.248	10.91
16.0	0.322	14.28
20.0	0.392	17.48
24.0	0.458	20.50
28.0	0.517	23.34
32.0	0.577	25.99
36.0	0.636	28.45
40.0	0.693	30.72
44.0	0.749	32.80
48.0	0.807	34.69
52.0	0.863	36.37
σ_s = 0.95 atm.		
σ_f = 0.84 atm.		
	75.0° C.	
4.0	0.057	3.68
8.0	0.126	7.34
12.0	0.173	10.94
16.0	0.231	14.44
20.0	0.288	17.82
24.0	0.346	21.04
28.0	0.399	24.14
32.0	0.449	27.10
36.0	0.493	29.71
40.0	0.537	32.53
44.0	0.578	35.02
48.0	0.622	37.36
52.0	0.663	39.60
σ_s = 1.17 atm.		
σ_f = 0.97 atm.		
	100.0° C.	
4.0	0.047	3.55
8.0	0.093	7.12
12.0	0.139	10.67
16.0	0.186	14.18
20.0	0.232	17.64
24.0	0.278	21.05
28.0	0.324	24.30
32.0	0.367	27.52
36.0	0.405	30.53
σ_s = 0.25 atm.		
σ_f = 0.12 atm.		

Table III. Partial Molar Volumes

Temp., ° C.	Ml./gram mole Ethane	 *n*-Octane
0.0	60.4	158.8
25.0	64.9	163.7
40.0	67.9	166.4
50.0	69.9	168.5
75.0	81.0	174.0
100.0	86.8	180.0

tion was reduced to ±0.36 atm. for the Flory-Huggins model and to ±0.51 atm. for the Scatchard model. Thus, the Flory-Huggins model is apparently better than the Scatchard model in fitting the fugacity data of ethane in the ethane–*n*-octane system. The data fit is not as good in the pressure region near the vapor-liquid critical state. In this region, the partial molar volume changes in the components cause deviations from the experimental fugacities, since both the solution models used are in reality isobaric, isothermal integrations of the Gibbs-Duhem equation, and in the critical region, the nonisobaric deviations become significant.

NOMENCLATURE

f_i = fugacity of component i in atm., i = 1,2
f_i° = standard state fugacity of component i in atm., i = 1,2
P_c = vapor-liquid critical pressure, atm.
P_i° = vapor pressure of component i, atm.
P_r° = reduced vapor pressure = P/P_c
R = universal gas law constant = 1.987 cal./g. mole/° K.
T = temperature in ° K.
T_c = vapor-liquid critical temperature, ° K.
T_r = reduced temperature, T/T_c
t = temperature in ° C.
Δu_{12} = interchange energy for components 1 and 2 in cal./g. mole
V_i = partial molar volume of component i in a liquid solution in ml. per gram mole
x_i = mole fraction of component i in the liquid, i = 1,2
ϕ_i = liquid volume fraction of component i, i = 1,2
σ = statistically determined standard deviation

Subscripts

s = Scatchard
f = Flory-Huggins

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Received for review April 10, 1967. Accepted July 27, 1967. This work was made possible by a National Science Foundation Graduate Fellowship for D.S.M. and an Atomic Energy Commission Research Assistantship for A.B.J.R. The Radiation Laboratory of the University of Notre Dame is operated under contract with the U.S. Atomic Energy Commission. This is A.E.C. Document No. COO-38-532.

Liquid-Vapor Equilibria of the Hydrogen–Carbon Dioxide System

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The liquid-vapor equilibria of the hydrogen–carbon dioxide system were studied in a vapor recirculation apparatus. Six isotherms were studied, from 219.9° to 289.9° K., up to 200 atm. pressure. The accuracy is believed to be within about ±5% of the reported values. A comparison with other published data is made.

THE liquid-vapor equilibria of the hydrogen–carbon dioxide system were studied because of the lack of data in the literature. Prior to the initiation of the present work, the only available data were those of Abdullayev (*1*), Mills and Miller (*7*), and Greco, Casale, and Negri (*3*). The data of all three investigations were only presented graphically, and therefore were not in a particularly usable form. During the progress of this investigation, Kaminishi and Toriumi (*6*) published data sparsely covering the entire liquid-vapor region up to 200 atm.

The liquid-vapor equilibria of the hydrogen–carbon dioxide system were studied at six temperatures: 219.9°, 229.9°, 244.9°, 259.9°, 274.9°, and 289.9° K. These isotherms were studied up to 200 atm. pressure. In all, 96 data points were collected and are thought to be accurate within about ±5%. The data are presented in both graphical and tabular form. The data are also compared with those from the literature.

EXPERIMENTAL

The apparatus used was that of Herring and Barrick (*5*), originally designed for use below 200° K. Since the temperature range required was from 220° to 290° K., a few changes were necessary, but the system remained basically the same.

A diagram of the flow system and of the equilibrium cell are presented (*2*, *5*) with a fairly complete discussion of the apparatus and procedure. The primary changes in the apparatus (for use at the higher temperatures of this investigation) are illustrated in Figure 1. In the previous investigation of Herring and Barrick, the refrigeration was supplied by storing liquid nitrogen beneath the equilibrium cell, and boiling the liquid at a rate sufficient to keep the cell at the desired temperature. Actually, an excess amount of refrigeration was supplied, which was countered by an automatically controlled heater wrapped around the cell. This method was usable for temperatures below 200° K. At temperatures above 200° K., the refrigeration gas was so much colder than the cell temperature that large thermal

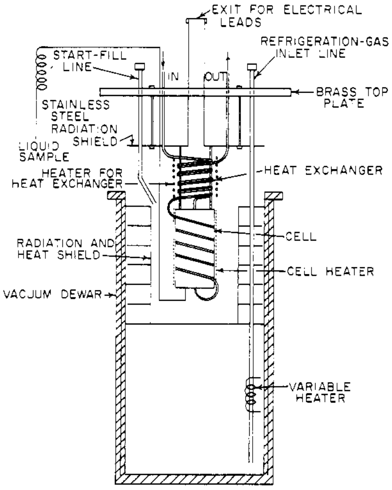

Figure 1. Apparatus modified for high temperature operation

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