

Figure 1. Plot of temperature against time. The melting point is calculated by using the graphical and mathematical analysis of Taylor and Rossini.

melting point. The lack of scatter of the data points in Figure 1 indicates that the precision of the temperature measurements is not a limiting factor in determining the melting point. Eight replicate measurements yields $-54.53\text{ }^{\circ}\text{C}$ as the mean melting

point of PC with 95% confidence limits of $\pm 0.02\text{ }^{\circ}\text{C}$. The melting point depression constant was estimated from the melting point of a $0.0985\text{ }m$ LiClO_4 solution (four measurements) and the melting point of a $0.0978\text{ }m$ tetrabutylammonium bromide (TBAB) solution (two measurements). LiClO_4 was selected because there is evidence that it behaves as a 1:1 strong electrolyte in PC without significant ion pair formation (10). The value of the molal melting point depression constant estimated from the LiClO_4 solution is $4.38 \pm 0.16\text{ }^{\circ}\text{C } m^{-1}$, and that estimated from the TBAB solution is $4.25 \pm 0.23\text{ }^{\circ}\text{C } m^{-1}$.

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Isothermal Vapor-Liquid Equilibria for the Ethylene-Carbon Dioxide System at High Pressure

Hyo Kwang Bae, Kunio Nagahama, and Mitsuho Hirata*

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Metropolitan University, 2-1-1, Fukusawa, Setagaya-Ku, Tokyo 158 Japan

Isothermal vapor-liquid equilibria (VLE) of the $\text{C}_2\text{H}_4 + \text{CO}_2$ system were measured at -10.01 , 0.01 , 10.01 , 20.03 , and $25.00\text{ }^{\circ}\text{C}$. The critical properties of the mixture and the azeotropic points at several temperatures were also obtained. The experimental data of this work could be successfully correlated by using the Peng-Robinson equation of state with a binary interaction parameter except for the $25\text{ }^{\circ}\text{C}$ isothermal data.

Introduction

VLE data for the $\text{C}_2\text{H}_4 + \text{CO}_2$ system are of interest because it forms an azeotropic mixture. Isothermal measurements of the VLE for this system were extensively carried out by Hakuta et al. (1), Nagahama et al. (2), and Mollerup (3) in the temperature range from -50 to $20\text{ }^{\circ}\text{C}$. Haselden et al. (4, 5) measured dew and bubble points at several compositions.

In the present work, the isothermal vapor-liquid equilibrium data at -10.01 , 0.01 , 10.01 , 20.03 , and $25.00\text{ }^{\circ}\text{C}$ were measured and compared carefully with those of other investigators (1, 3-5).

The data obtained were correlated by utilizing the Peng and Robinson equation of state (6), and it appeared to provide a good representation of the experimental data except for the $25\text{ }^{\circ}\text{C}$ isotherm.

Critical properties and azeotropic points were also determined.

Experimental Section

The measurement of vapor-liquid equilibria were carried out by using a newly constructed apparatus described recently in detail (7). The visual type of static apparatus was distinguished by the inclusion of a direct liquid-sampling device to reduce experimental error during sampling and of a magnetically driven agitator by which the vapor phase was dispersed into the liquid phase within the equilibrium cell to attain the equilibrium state.

The cell was placed in a bath containing ethanol as a bath fluid. The temperature of the bath was controlled within $\pm 0.03\text{ }^{\circ}\text{C}$ of the temperature of interest and measured by a calibrated platinum resistance thermometer connected to a digital potentiometer for measurement of its resistance. It was assumed that the bath temperature was identical with that of the equilibrium cell because the bath temperature was held for at least 1 day.

The pressure measurement was carried out by using an Aminco pressure balance. The accuracy of the measurement was believed to be within 0.035 atm . A Bourdon gauge was also employed for reading the pressure rapidly.

The equilibrium liquid of $\sim 8\text{ }\mu\text{L}$ was sampled through a specially designed device mounted directly into the cell wall, which had a construction similar to that of Fredenslund et al. (3, 8). On the other hand, a small portion of vapor was released into an evacuated chamber. At least three samples of liquid and vapor, respectively, were analyzed by gas chromatography. A 3-m column packed with activated charcoal (40/60

Table I. Isothermal Vapor-Liquid Equilibrium Data for the Ethylene (1)-Carbon Dioxide (2) System

x	y	P , atm	x	y	P , atm
temp = 25.00 °C					
0.0	0.0	63.270	0.113	0.123	67.66
0.033	0.040	64.61	0.130	0.135	68.11
0.071	0.081	66.10	0.137	0.137	68.24
temp = 20.03 °C					
0.0	0.0	56.391	0.177	0.200	62.23
0.042	0.054	58.08	0.209	0.226	63.04
0.076	0.095	59.27	0.217	0.232	63.17
0.119	0.141	60.74	0.229	0.242	63.59
0.157	0.183	61.70	0.233	0.245	63.71
0.175	0.196	62.12	0.259	0.263	64.13
temp = 10.01 °C					
0.0	0.0	44.293	0.453	0.466	53.39
0.060	0.081	46.37	0.535	0.539	53.80
0.105	0.139	47.64	0.617	0.618	54.07
0.159	0.206	49.21	0.707	0.705	53.78
0.261	0.297	51.18	0.720	0.719	53.70
0.338	0.367	52.30			
temp = 0.01 °C					
0.0	0.0	34.303	0.667	0.666	42.85
0.039	0.056	35.53	0.684	0.681	42.83
0.089	0.125	36.87	0.725	0.721	42.58
0.155	0.202	38.35	0.754	0.751	42.59
0.226	0.273	39.68	0.817	0.809	42.19
0.316	0.355	40.92	0.884	0.878	41.66
0.433	0.458	42.07	0.952	0.950	40.88
0.526	0.539	42.62	1.0	1.0	40.387
0.594	0.598	42.81			
temp = -10.01 °C					
0.0	0.0	26.120	0.485	0.524	33.09
0.049	0.084	27.46	0.600	0.613	33.52
0.106	0.166	28.83	0.669	0.670	33.54
0.204	0.268	30.39	0.764	0.750	33.45
0.310	0.365	31.81	0.837	0.825	33.10
0.405	0.444	32.59	0.934	0.927	32.50
0.527	0.566	33.27	1.0	1.0	31.870

mesh) was used at 110 °C, hydrogen being employed as a carrier gas at a flow rate of 100 mL/min.

The mole fraction of the sample mixture is expressed as $(AR)F/[1 + (AR)F]$, where AR stands for the area ratio of C₂H₄ to CO₂ on the chromatogram and F stands for the calibration factor. The factor is defined as MR/AR , where MR indicates the mole ratio of C₂H₄ to CO₂. The values of F were determined by using several binary gas mixtures of known composition. The calibration mixtures were carefully prepared by measuring the isothermal partial pressure of each gas which was then admitted to an evacuated vessel of 1 L. The total pressure in the vessel never exceeded 2 atm. The mole fraction of the gas mixture was calculated from the virial equation by using second virial coefficients (B_{11} , B_{22} , and B_{12}) reported by Dymond and Smith (9) because of the nonideality of the mixture.

When one takes account of the error analysis of the preparation process as well as the reproducibility of the chromatographic analyses, the maximum experimental error of the mole fraction in either phase is ~ 0.003 .

All gases were of purities greater than 99.9% and were used without further purification. The gases were furnished by Takachiho Kagakugogyo Co. Ltd. Tokyo.

Results and Discussion

Isothermal VLE data are given in Table I and shown in Figures 1 and 2. The VLE data reported by other investigators are also plotted for comparison.

The saturated vapor pressures of pure C₂H₄ and CO₂ are in good agreement with those of previous investigators (1, 8, 10, 11).

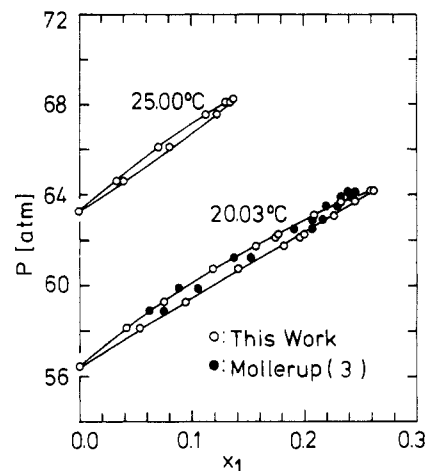
Figure 1. Pressure-composition diagram for the C₂H₄ (1) + CO₂ (2) system at 20.03 and 25.00 °C.

Table II. Azeotropic Data for the Ethylene (1)-Carbon Dioxide (2) System

temp, °C	x_1		press., atm	
	this work	lit.	this work	lit.
10.01	0.628	0.62 (8)	54.08	54.23 (8)
0.01	0.646	0.584 (2)	54.4	54.4 (2)
		0.586 (5)	42.83	43.4 (5)
		0.641 (2)		43.1 (2)
-10.01	0.675	0.667 (8)	33.55	33.56 (8)
		0.686 (2)		33.6 (2)

Table III. Critical Properties for the Ethylene (1)-Carbon Dioxide (2) System

t_c , °C	P_c , atm	x_{1c}
25.00	68.27	0.137
20.03	64.20	0.264
10.01	53.67	0.725

No earlier VLE data for the system at 25 °C can be found in the literature. The data for at 20 °C are coincident with the results of Mollerup (3) except the last several experimental points close to the critical point, as shown in Figure 1. In that respect, he reported that the reason for the unexpected increase in pressure was unknown (3). In the present study, the experimental data, however, do not show such unexpected behavior. Figure 2 illustrates the comparison of the present results with those of other investigators in lower temperature ranges. Both isotherms at -10.01 and 0.01 °C are in excellent agreement with those of Mollerup (3). However, there exists some discrepancy between our results and those obtained by interpolating the dew/bubble-point measurement reported by Haselden et al. (4, 5). The VLE data of Hakuta et al. (1) at 0 °C were not plotted in Figure 2 because large discrepancies from other data were observed in their pressure-composition relationship.

Table II gives the azeotropic composition and the pressure which are determined by plotting the equilibrium ratio (K value) against either liquid composition or pressure. It is seen that there is good agreement between our azeotropic point and those reported by previous investigators (1, 3, 12). The azeotropic data were plotted on a P - T diagram as shown in Figure 3.

The critical properties were estimated by extrapolating the VLE data close to the critical point with the aid of direct visual observation in a windowed cell. The extrapolating method is identical with that of Muirbrook and Prausnitz (13). The properties are given in Table III and compared with those of Rowlinson et al. (14) in Figure 3. The maximum differences

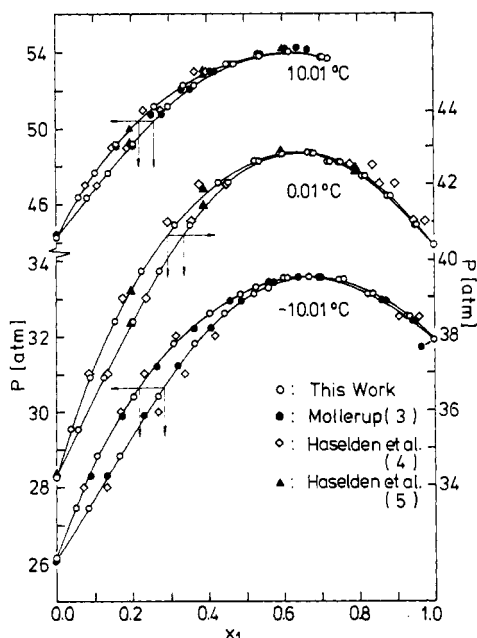


Figure 2. Pressure-composition diagram for the C_2H_4 (1) + CO_2 (2) system at -10.01 , 0.01 , and 10.01 °C.

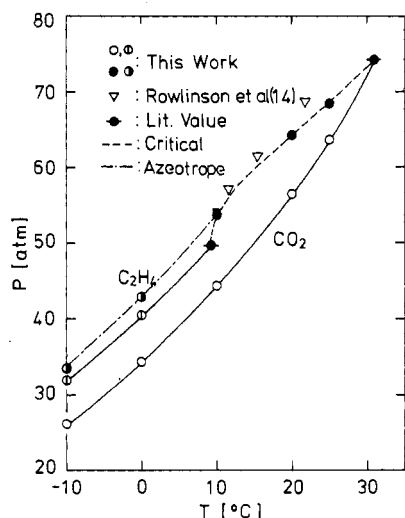


Figure 3. Critical and azeotropic locus for the C_2H_4 (1) + CO_2 (2) system.

between both investigators is ~ 2 atm in the critical pressure locus.

Data Correlation

The Peng-Robinson equation of state (6) was used to correlate the VLE data of this work. The mixing rules and the equations to compute VLE were identical with those reported by Peng and Robinson (6). The interaction parameter, $\theta_{12} = \theta_{21}$, was determined by nonlinear regression using all of the experimental points on the pressure-liquid composition curve of each isotherm. Critical properties of pure components and their acentric factors given in Table IV were employed for VLE calculations. The values of θ_{12} for each isotherm are summarized in Table V and appear to be independent of temperature. Also, Table V gives the correlated results except those at 25 °C by using the Peng-Robinson equation. Such calculations as shown above were made by employing the Soave-Redlich-Kwong equation (17) and the modified Redlich-Kwong equation (18). Each two-constant equation of state employed here provided nearly identical results for all isotherms except for the 25 °C isotherm. So Table V indicates only the correlated results by the Peng-Robinson equation. In the case of 25 °C, none of the three equations was able to predict the VLE

Table IV. Critical Properties and Acentric Factors for Pure Components^a

component	T_c , K	P_c , atm	ω
C_2H_4	282.36	49.66	0.0868
CO_2	304.19	72.85	0.231

^a Critical properties from ref 15. Acentric factor from ref 16.

Table V. Interaction Parameter and Mean Deviation between Experimental and Calculated Vapor Composition or Pressure for the Ethylene (1)-Carbon Dioxide (2) System

temp, °C	θ_{12}	Δy	ΔP , atm
-10.01	0.055	0.0041	0.117
0.01	0.056	0.0014	0.070
10.01	0.057	0.0047	0.059
20.03	0.056	0.0057	0.136
25.00			

region even though the values of the interaction parameter were varied over an appreciable range. This may be due to the insufficient capability of equations in VLE prediction for this binary very close to the critical region.

Except for the 25 °C isotherm, the Peng-Robinson equation of state provided a fairly good representation of the VLE data for the ethylene-carbon dioxide system, as shown in Table V. The Soave-Redlich-Kwong and the modified Redlich-Kwong equations also gave good results as the Peng-Robinson equation except for the 25 °C isotherm.

Glossary

K	equilibrium ratio ($=y/x$)
P	pressure, atm
T	temperature, K
t	temperature, °C
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Greek Letters

θ	interaction parameter
ω	acentric factor

Subscripts

c	critical value
1	ethylene
2	carbon dioxide

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