A SIMPLE CALCULATION PROCEDURE FOR ISOBARIC PHASE EQUILIBRIUM DATA ON CARBON DIOXIDE-PROPANE SYSTEMS

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Introduction

The phase behavior of carbon dioxide-alkane systems is of practical value in the processing of natural gas. Most natural gas contains sufficient carbon dioxide to warrant concern in processing plants, where solidified carbon dioxide can dangerously plug the low-temperature processing equipment. In addition, carbon dioxide has the undesirable effect of reducing the heating value of natural gas in direct proportion to its concentration. The importance of these systems is also reflected in the efforts at various laboratories in the last decade to measure isothermal vapor-liquid equilibrium data, as shown in **Table 1**. None of the investigators converted their information to isobaric form. However, isobaric data are difficult to obtain experimentally although they are the form required for most process calculations. Therefore, the engineering community should find the data presented for isobaric conditions especially convenient. In a previous publication[1] two plots of log P against $1/T$ were constructed for the system carbon dioxide-propane. From the smoothed P-X-Y data, one plot for constant liquid composition, and another for constant vapor composition were drawn to show the trend of the data available in the literature for the system. Hence, the purpose of this work is primarily to show that a very simple, long-neglected interpolation method can successfully be used for the calculation of the isobaric phase equilibrium data for these important mixtures of carbon dioxide + ethane or propane. These mixtures are highly nonideal, with the existence of azeotropes in the carbon dioxide-ethane system.

1. Representation of Vapor-Liquid Equilibria

In this work the empirical equation

$$\ln P = A - \frac{B}{T} \qquad (1)$$

where P is the pressure in MPa and T is the temperature in degrees Kelvin, was used to correlate the data. To develop this relation, P-X-Y curves were drawn through the experimental points. From the resulting plots at each temperature, pressures were determined at a series of constant vapor and liquid compositions differing by increments of 0.1 mole fraction. Thus, at each mole fraction two values for pressure were obtained: one for liquid and the other for vapor. The values were then plotted as log P versus $1/T$ at constant mole fraction. A total of 20 plots for each system were prepared, similarly to those reported earlier.[1] Data points which do not follow the general trend on P-X-Y curves were excluded and the remaining were correlated linearly using the least square criterion.

2. Results and Discussion

Table 2 lists the coefficients A and B thus determined. Equation (1) is then used to predict isobaric T-X-Y data over a pressure range of about 1-4 MPa for the carbon dioxide-ethane system, as shown in **Fig. 1**, and about 1.5-3 MPa for the carbon dioxide-propane system, **Fig. 2**. The overall average absolute deviations between the calculated and the smoothed experimental pressures for the carbon dioxide-ethane system are 0.86% and 1.15%, respectively, in the constant X and Y plots, with a maximum of 2%. For the system of carbon dioxide-propane the deviations are 0.66% and 0.75%, respectively, in the constant X and Y plots, with a maximum of 2.1%. The coefficients reported are useful for calculating VLE at isobaric conditions which are not available in the literature, as shown in Figs. 1 and 2 at different isobaric conditions.

The coefficients A and B of Eq. (1) as given in Table 2 were further correlated in terms of mole fraction. Using the following type of polynomial:

$$A = A_0 + A_1\xi + A_2\xi^2 + A_3\xi^3 + A_4\xi^4 + A_5\xi^5 \qquad (2)$$

$$B = B_0 + B_1\xi + B_2\xi^2 + B_3\xi^3 + B_4\xi^4 + B_5\xi^5 \qquad (3)$$

Table 1. Summary of recent isothermal vapor-liquid equilibrium measurements for carbon dioxide-ethane and carbon dioxide-propane systems

System	Authors	Temperature range (K)	Pressure range (MPa)	No. of experimental data points
CO₂-Ethane	Davalos et al.[2]	250	1.30 -2.13	15
	Fredenslund et al.[3]	223.15-293.15	0.552-6.30	65
	Gugnoni et al.[4]	241.45-283.15	1.01 -4.99	57
	Hamam et al.[5]	222.04-288.70	0.700-5.70	40
	Kurata et al.[9]	222.04-228.70	0.784-5.61	12
	Nagahama et al.[10]	252.95	1.43 -2.31	15
	Ohgaki et al.[12]	283.15-298.15	3.47 -6.63	74
	Robinson et al.[14]	288.70	3.56 -5.75	8
CO₂-Propane	Akers et al.[1]	233.15-273.15	0.101-3.50	15
	Hamam et al.[6]	244.26-266.48	0.504-2.61	21
	Nagahama et al.[10]	252.95-273.15	0.243-3.49	24
	Reamer et al.[13]	277.59-294.26	0.545-5.94	29

Table 2. Values of Constants A and B in Eq. (1). ln $P = A - B/T$ (P in MPa and T in K)

Mole fraction of CO₂	Carbon Dioxide–Ethane				Carbon Dioxide–Propane			
	Liquid		Vapor		Liquid		Vapor	
	A	B	A	B	A	B	A	B
0.0	7.4193	1788.9	7.4193	1788.9	7.5965	2281.7	7.5965	2281.7
0.1	7.6334	1726.6	7.6771	1835.0	6.3958	1751.9	7.9028	2337.7
0.2	7.2625	1671.5	7.7708	1829.0	6.2495	1616.4	8.0515	2350.6
0.3	7.5140	1713.8	7.8544	1827.3	6.4627	1610.0	8.2336	2365.9
0.4	7.6136	1741.5	7.7851	1787.0	6.7010	1628.2	8.4296	2372.9
0.5	7.8083	1767.2	7.7293	1756.3	7.0268	1683.1	8.6867	2388.2
0.6	7.9223	1791.1	7.9020	1786.9	7.4097	1759.3	8.9683	2399.4
0.7	8.0193	1814.8	8.0932	1836.3	7.7250	1823.7	9.1990	2391.4
0.8	8.1158	1843.2	8.3081	1898.4	8.0509	1893.6	9.2561	2318.6
0.9	8.1920	1873.4	8.4285	1943.1	8.3743	1964.2	8.5950	2048.9
1.0	8.5234	1987.0	8.5234	1987.0	8.5234	1987.0	8.5234	1987.0

where $\xi = x$ for liquid, and $\xi = y$ for vapor. The polynomial coefficients were determined, using the least square fit criterion, to be

for CO₂-ethane liquid

$A_0 = 7.4284 \ A_1 = 1.6844 \ A_2 = 5.9930 \ A_3 = 4.6854$

$A_4 = -19.960 \ A_5 = 12.057$

$B_0 = 1791.6 \ B_1 = -1103.7 \ B_2 = 3550.5$

$B_3 = -2371.1 \ B_4 = -2082.4 \ B_5 = 2200.9$

for CO₂-ethane vapor

$A_0 = 7.4103 \ A_1 = 4.1230 \ A_2 = -14.464 \ A_3 = 17524$

$A_4 = -1.8177 \ A_5 = -4.2642$

$B_0 = 1787.2 \ B_1 = 856.4 \ B_2 = -4010.1 \ B_3 = 4975.1$

$B_4 = -358.67 \ B_5 = -1266$

for CO₂-propane liquid

$A_0 = 7.5871 \ A_1 = -18.664 \ A_2 = 86.140$

$A_3 = -162.38 \ A_4 = 146.60 \ A_5 = -50.767$

$B_0 = 2277.9 \ B_1 = -7709.8 \ B_2 = 31327 \ B_3 = -57951$

$B_4 = 51902 \ B_5 = -17863$

for CO₂-propane vapor

$A_0 = 7.5732 \ A_1 = 7.1407 \ A_2 = -43.939 \ A_3 = 127.87$

$A_4 = -146.66 \ A_5 = 56.49$

$B_0 = 2274.0 \ B_1 = 1809.7 \ B_2 = -13136 \ B_3 = 38116$

$B_4 = -45012 \ B_5 = 17922$

Agreement between the temperatures calculated from Eq. (1) with A and B reported in Table 2 and those predicted from Eqs. (1), (2) and (3) is excellent. Also, note that at each isothermal condition reported by Fredenslund and Mollerüp,[3] the polynomials were used to calculate the isothermal VLE curves. The lines were passed and the azeotropic points were determined and compared with the experimental data points. It was found that the calculated azeotropic
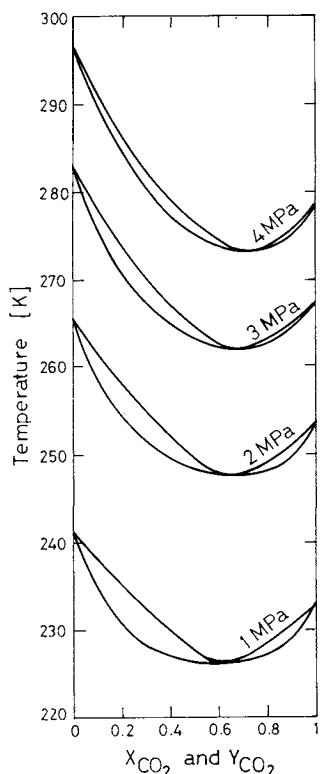
Fig. 1. Calculated T-X-Y values for carbon dioxide-ethane system.
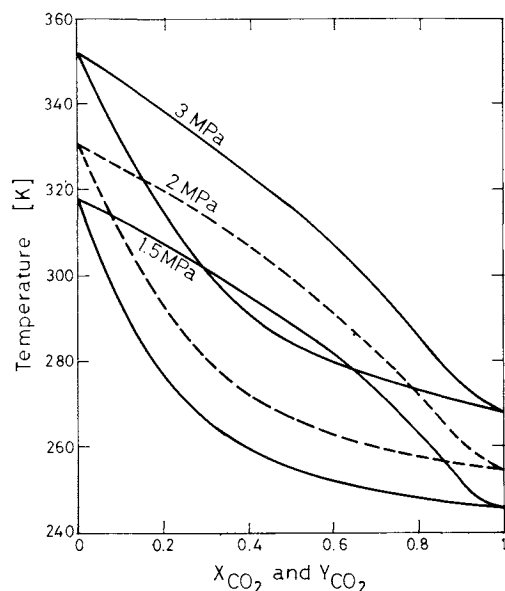

Fig. 2. Calculated T-X-Y values for carbon dioxide-propane system.

pressures agree well with the experimental data within an average absolute deviation of 1%. The compositions at the azeotropic points are calculated within 0.03 mol fraction. These levels are accept-

able with the degree of generalization of the data presented.

In conclusion, all the recently available vapor-liquid equilibria data on the carbon dioxidé-ethane and carbon dioxide-propane systems were compiled. The smoothed P-X-Y data were presented as log P versus $1/T$ plots at regular intervals. These data points were correlated by means of a simple linear relationship. The coefficients reported are useful for obtaining isobaric conditions in a relatively simple way. More complex and perhaps more satisfying models could have been used for obtaining isobaric data. One of these is the use of an equation of state with a binary interaction parameter, as shown for isothermal data.[5-9,11] However, the results could not have been much more precise than those presented here. The present approach is simple and more direct.

Nomenclature

A, B	= coefficients of Eq. (1)	[—]
P	= pressure	[MPa]
T	= temperature	[K]
X	= liquid-phase mole fraction	[—]
Y	= vapor-phase mole fraction	[—]

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