International Journal of Thermophysics, Vol. 15, No. 6, 1994

Vapor–Liquid Equilibria for the Ternary System $N_2 + CO_2 + n\text{-}C_4H_{10}$ at 250 and 270 K[1]

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The system studied was nitrogen + carbon dioxide + *n*-butane at 250 and 270 K and at pressures from 1.5 to 14 MPa. The Peng–Robinson equation was used to model the results, since it is the most widely accepted equation of state in the gas processing industry. In general, the predictions are most accurate at low and moderate pressures and poorest at high pressures, especially near the critical region.

KEY WORDS: binary system; butane; carbon dioxide; nitrogen; ternary system; vapor–liquid equilibria.

1. INTRODUCTION

This work is part of an ongoing experimental and modeling program aimed at increasing the accuracy of phase equilibria predictions for natural gas systems. Current thermodynamic models for vapor–liquid equilibria (VLE) are capable of a priori predictions only for very simple systems, and thus all models contain one or more adjustable parameters that must be obtained by fitting to binary experimental data. Since binary VLE data are used in developing the model, these data cannot be used to test the quality of the model; only multicomponent data can be used for that purpose. Ternary VLE data are by far the easiest multicomponent data to treat experimentally, and thus the combination of ternary measurements with the constituent binary systems provides the optimal data set for developing and evaluating models for predicting vapor–liquid equilibria.

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

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0195-928X/94/1100-1211$07.00/0

The system selected for study was the nitrogen + carbon dioxide + n-butane ternary and the three constituent binaries. Carbon dioxide was included in the system because the behavior of carbon dioxide with both the hydrocarbon and the nonhydrocarbon components of natural gas is becoming increasingly important to the gas processing industry. The future use of natural gas will require the processing of gases from wells with high concentrations of carbon dioxide, and the recovery of oil via carbon dioxide floods generates gases with high carbon dioxide concentrations. The large quadrupole moment of carbon dioxide makes it more difficult to model than the other components present in large quantities in natural gas and thus accurate experimental data for carbon dioxide systems are essential.

2. RESULTS

A complete literature survey and a thorough description of the equipment, calibrations, and operating procedures are available [1].

In order to obtain an internally consistent set of VLE data for a three-component system, it is necessary to measure the ternary system and the three constituent binaries at the same temperatures and on the same equipment. The binary systems were presented in a previous publication [2].

The nitrogen + carbon dioxide + n-butane ternary system was studied at 250 and 270 K and a total of nine different pressures ranging from 1.5 to 14.0 MPa. The highest pressures, 13.0 and 14.0 MPa at 270 K, are above the pressure of the nitrogen + carbon dioxide critical, and thus critical points exist in this ternary data. All of the normalized experimental data are in Table I.

Table I. The $N_2 + CO_2 + n\text{-}C_4H_{10}$ Ternary System

Pressure (MPa)	x_{N_2}	x_{CO_2}	$x_{C_4H_{10}}$	y_{N_2}	y_{CO_2}	$y_{C_4H_{10}}$
			250 K and 1.500 MPa			
1.502	0.0240	0.0000	0.9760	0.9666	0.0000	0.0334
1.499	0.0235	0.0000	0.9765	0.9654	0.0017	0.0329
1.501				0.8558	0.1109	0.0333
1.502	0.0200	0.0670	0.9129	0.7839	0.1833	0.0328
1.500	0.0177	0.1134	0.8689	0.6700	0.2978	0.0322
1.500	0.0157	0.1717	0.8126	0.5511	0.4179	0.0310
1.499	0.0111	0.2267	0.7222	0.4250	0.5451	0.0299
1.500	0.0105	0.3154	0.6741	0.3245	0.6467	0.0288
1.500	0.0081	0.4179	0.5740	0.2112	0.7620	0.0268
1.501	0.0064	0.4949	0.4987	0.1424	0.8320	0.0256
1.501	0.0054	0.5429	0.4517	0.1160	0.8594	0.0246
1.500	0.0000	0.7423	0.2577	0.0000	0.9798	0.0202

Table I. *(Continued)*

Pressure (MPa)	x_{N_2}	x_{CO_2}	$x_{C_4H_{10}}$	y_{N_2}	y_{CO_2}	$y_{C_4H_{10}}$
250 K and 6.000 MPa						
5.999	0.0908	0.0000	0.9092	0.9832	0.0000	0.0168
6.006	0.0925	0.1075	0.8000	0.8880	0.0948	0.0172
5.999	0.0895	0.1145	0.7960	0.8807	0.1025	0.0168
6.000	0.0932	0.2032	0.7036	0.8205	0.1628	0.0167
5.997	0.0933	0.3148	0.5919	0.7615	0.2226	0.0159
5.999	0.0972	0.4021	0.5007	0.7206	0.2637	0.0157
6.000	0.0983	0.5521	0.3496	0.6712	0.3145	0.0143
6.003	0.0967	0.7015	0.2018	0.6313	0.3567	0.0120
6.001	0.0912	0.8013	0.1075	0.6053	0.3858	0.0089
5.995	0.0918	0.8028	0.1054	0.6055	0.3858	0.0087
5.997	0.0874	0.8437	0.0689	0.5917	0.4011	0.0072
6.003	0.0755	0.9245	0.0000	0.5652	0.4348	0.0000
250 K and 12.000 MPa						
12.003	0.1739	0.0000	0.8261	0.9806	0.0000	0.0194
11.987	0.1854	0.1529	0.6617	0.8798	0.0986	0.0216
11.997	0.1918	0.2198	0.5884	0.8421	0.1354	0.0225
11.997	0.1875	0.2559	0.5566	0.8297	0.1481	0.0222
12.000	0.2011	0.2829	0.5161	0.8116	0.1655	0.0229
12.001	0.2111	0.3568	0.4321	0.7801	0.1968	0.0231
12.012	0.2245	0.4540	0.3215	0.7403	0.2368	0.0229
11.984	0.2380	0.5294	0.2326	0.7097	0.2677	0.0226
12.001	0.2483	0.6203	0.1314	0.6686	0.3118	0.0196
12.009	0.2492	0.6272	0.1236	0.6662	0.3150	0.0188
11.995	0.2452	0.6881	0.0667	0.6371	0.3489	0.0140
12.000				0.6368	0.3500	0.0132
12.005	0.2432	0.7015	0.0553	0.6317	0.3564	0.0119
11.997	0.2192	0.7808	0.0000	0.6050	0.3950	0.0000
250 K and 14.000 MPa						
14.004	0.2003	0.0000	0.7997	0.9780	0.0000	0.0220
13.982	0.2115	0.1321	0.6564	0.8896	0.0852	0.0252
14.006	0.2183	0.1912	0.5905	0.8565	0.1175	0.0260
13.987	0.2584	0.3962	0.3454	0.7601	0.2141	0.0258
14.009	0.2826	0.4805	0.2369	0.7072	0.2615	0.0313
13.998	0.3063	0.5516	0.1421	0.6599	0.3110	0.0291
14.007	0.3100	0.5607	0.1293	0.6496	0.3215	0.0289
14.000	0.3263	0.5996	0.0741	0.6049	0.3719	0.0242
13.993	0.2980	0.7020	0.0000	0.5470	0.4530	0.0000

(Continued)

Table I. *(Continued)*

Pressure (MPa)	X_{N_2}	X_{CO_2}	$X_{C_4H_{10}}$	Y_{N_2}	Y_{CO_2}	$Y_{C_4H_{10}}$
270 K and 1.500 MPa						
1.503	0.0239	0.0000	0.9761	0.9254	0.0000	0.0746
1.500	0.0217	0.0558	0.9225	0.7126	0.2133	0.0741
1.498	0.0163	0.0892	0.8945	0.5928	0.3338	0.0734
1.501	0.0134	0.1236	0.8630	0.4793	0.4480	0.0727
1.500	0.0113	0.1492	0.8395	0.3976	0.5311	0.0713
1.500	0.0082	0.1865	0.8053	0.2944	0.6357	0.0699
1.501	0.0067	0.2189	0.7744	0.2104	0.7205	0.0691
1.501	0.0042	0.2650	0.7308	0.1096	0.8243	0.0661
1.497	0.0000	0.3109	0.6891	0.0000	0.9353	0.0647
270 K and 6.000 MPa						
5.994	0.0922	0.0000	0.9078	0.9659	0.0000	0.0341
5.998	0.0891	0.1152	0.7957	0.8313	0.1343	0.0344
5.998	0.0841	0.2420	0.6739	0.7100	0.2570	0.0330
6.006	0.0835	0.3150	0.6015	0.6538	0.3137	0.0325
6.001	0.0804	0.4578	0.4618	0.5621	0.4076	0.0303
6.004	0.0791	0.5669	0.3540	0.5073	0.4644	0.0283
6.000	0.0729	0.7345	0.1926	0.4290	0.5485	0.0225
6.002	0.0661	0.8547	0.0792	0.3718	0.6144	0.0138
5.998	0.0533	0.9467	0.0000	0.3262	0.6738	0.0000
270 K and 12.000 MPa						
11.991	0.1805	0.0000	0.8195	0.9656	0.0000	0.0344
12.000	0.1843	0.1506	0.6651	0.8406	0.1216	0.0378
11.993	0.1868	0.2137	0.5995	0.7947	0.1664	0.0389
11.998	0.1916	0.2800	0.5284	0.7510	0.2095	0.0395
12.009	0.1991	0.3394	0.4615	0.7143	0.2456	0.0401
12.008	0.2037	0.4018	0.3945	0.6739	0.2848	0.0403
11.997	0.2077	0.4393	0.3530	0.6527	0.3069	0.0404
12.011	0.2185	0.5213	0.2602	0.6002	0.3587	0.0411
11.995	0.2184	0.5854	0.1962	0.5398	0.4217	0.0385
11.995	0.2349	0.6235	0.1416	0.5231	0.4396	0.0373
11.990	0.2448	0.6707	0.0845	0.4726	0.4958	0.0316
12.009	0.2455	0.6778	0.0767	0.4644	0.5045	0.0311
11.998	0.2435	0.7565	0.0000	0.3644	0.6356	0.0000

Table I. *(Continued)*

Pressure (MPa)	X_{N_2}	X_{CO_2}	$X_{C_4H_{10}}$	Y_{N_2}	Y_{CO_2}	$Y_{C_4H_{10}}$
270 K and 13.000 MPa						
12.998	0.1946	0.0000	0.8054	0.9648	0.0000	0.0352
12.995	0.2009	0.1398	0.6593	0.8501	0.1105	0.0394
13.008	0.2033	0.1943	0.6024	0.8105	0.1491	0.0404
13.006	0.2090	0.2566	0.5344	0.7671	0.1913	0.0416
12.998	0.2224	0.3739	0.4037	0.6915	0.2645	0.0440
13.003	0.2289	0.4111	0.3600	0.6677	0.2875	0.0448
13.003	0.2445	0.4985	0.2570	0.6084	0.3453	0.0463
13.002	0.2626	0.5710	0.1664	0.5450	0.4086	0.0464
13.003	0.2709	0.5890	0.1401	0.5207	0.4334	0.0459
13.009	0.2866	0.6104	0.1030	0.4793	0.4756	0.0451
12.994	0.3002	0.6224	0.0774	0.4301	0.5261	0.0438
270 K and 14.000 MPa						
13.992	0.2084	0.0000	0.7916	0.9632	0.0000	0.0368
14.009	0.2250	0.2331	0.5419	0.7820	0.1740	0.0440
13.989	0.2401	0.3443	0.4156	0.7088	0.2448	0.0464
13.992	0.2465	0.3799	0.3736	0.6894	0.2662	0.0444

3. MODELING OF VAPOR–LIQUID EQUILIBRIA DATA

In recent years, numerous equations of state and mixing rules have been proposed for VLE calculations, but from an industrial perspective only a few are of any importance. The most generally accepted relations are simple cubic equations that are modifications of the van der Waals equation, generally used with the original van der Waals mixing rules with the introduction of a single binary interaction parameter, k_{ij}. In gas processing the equation proposed by Peng and Robinson [3] is widely used and this is the relation selected in this study. Their equation is

$$P = RT/(v - b) - a(T)/v(v + b) + b(v - b) \tag{1}$$

The constants are obtained from the relations

$$a(T) = a(T_c)\,\alpha(T_R, \omega) \tag{2}$$

$$b = b(T_c) \tag{3}$$

where

$$a(T_c) = 0.45724(R^2 T_c^2 / P_c) \tag{4}$$

$$b(T_c) = 0.07780(RT_c / P_c) \tag{5}$$

and

$$\alpha^{1/2} = 1 + \kappa(1 - T_R^{1/2}) \tag{6}$$

$$\kappa = 0.37464 + 1.542261 - 0.26992\omega^2 \tag{7}$$

The mixing rules are

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{8}$$

$$b = \sum_i x_i b_i \tag{9}$$

$$a_{ij} = (1 - k_{ij}) a_i^{1/2} a_j^{1/2} \tag{10}$$

where k_{ij} is the binary interaction coefficient. The original article should be consulted for details of the equation and its application to phase-equilibria calculations. In this work, the maximum-likelihood method of Niesen and Yesavage [4] was used to obtain the k_{ij} values.

The interaction parameters are given with the model variances in Table II. The interaction parameters that included both the 250 and the 270 K data were used for the binary and ternary predictions.

The predicted curves for the nitrogen + carbon dioxide + n-butane ternary system are shown in Figs. 1–4. The predictions are accurate at low pressures but poor at the high pressures near the critical region. At 270 K and 14.0 MPa, the Peng–Robinson equation predicts a continuous region of vapor–liquid equilibria when, in fact, a critical point exists.

Table II. Interaction Parameters for the Peng–Robinson Equation

System	Temperature (K)	No. of points	Interaction parameter	s^2
$N_2 + CO_2$	250	11	−0.043	96.11
	270	4	−0.006	8.89
	250–270	23[a]	−0.038	57.03
$N_2 + n\text{-}C_4H_{10}$	250	10	0.101	1.35
	270	12	0.096	2.40
	250–270	22	0.099	2.13
$CO_2 + n\text{-}C_4H_{10}$	250	19	0.129	40.67
	270	15	0.123	25.74
	250–270	34	0.126	36.72

[a] To weight the 270 K isotherm that had only 4 points approximately the same as the 250 K isotherm that had 11 points, the 270 K isotherm was weighted three times as heavily as the 250 K isotherm.

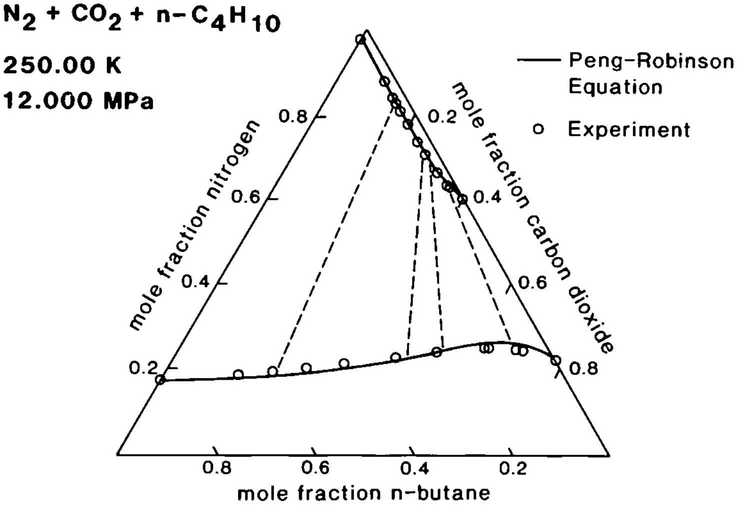

Fig. 1. Nitrogen + carbon dioxide + *n*-butane at 250.00 K and 12.000 MPa.

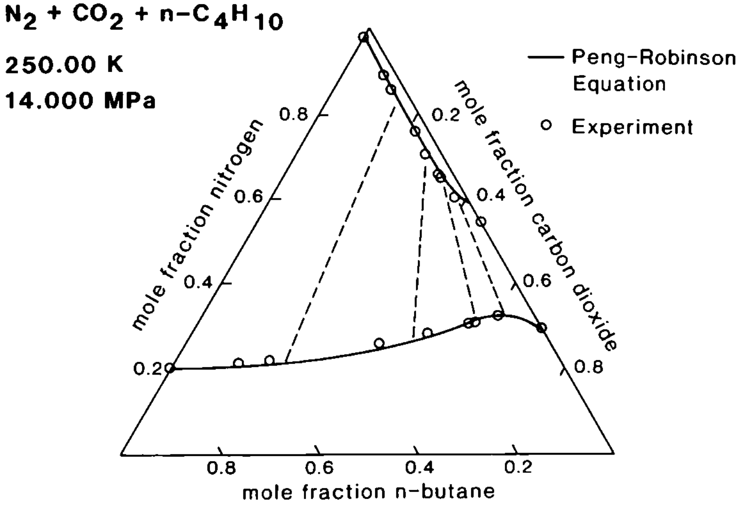

Fig. 2. Nitrogen + carbon dioxide + *n*-butane at 250.00 K and 14.000 MPa.

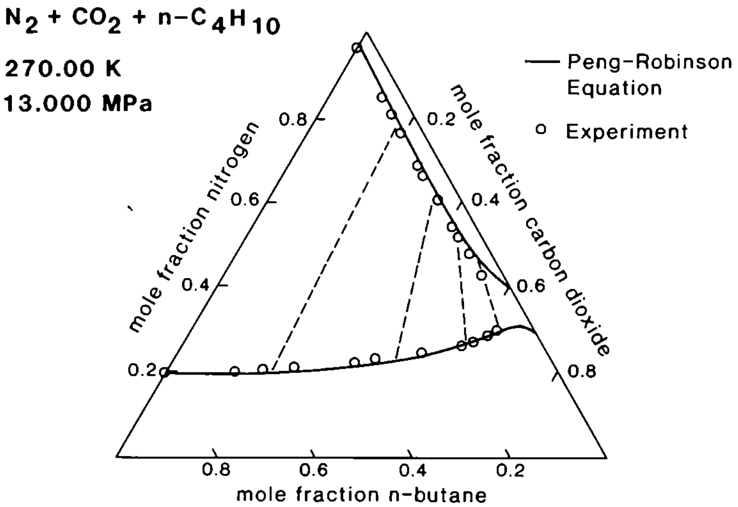

Fig. 3. Nitrogen + carbon dioxide + *n*-butane at 270.00 K and 13.000 MPa.

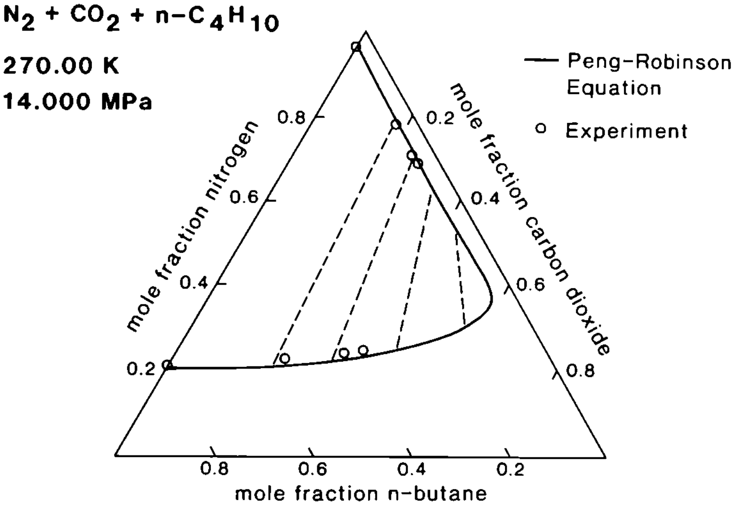

Fig. 4. Nitrogen + carbon dioxide + *n*-butane at 270.00 K and 14.000 MPa.

4. CONCLUSIONS

The Peng–Robinson equation can model all the binary data, in regions removed from the critical, with reasonable accuracy using only a single adjustable parameter, k_{ij}. The equation, however, is not satisfactory in the critical region. It is possible to obtain better agreement near the critical by adjusting the k_{ij}, but only at the sacrifice of accuracy in the lower-pressure regions.

The ternary system is also well represented by the Peng–Robinson equation, again in areas removed from the critical region. In this system, satisfactory representation of the ternary data is possible with binary interaction parameters only.

NOMENCLATURE

$a(T)$	Attraction parameter
b	Volume parameter
k	Binary interaction parameter
P	Pressure
R	Universal gas constant
T	Absolute temperature
x	Mole fraction
v	Molar volume
ω	Acentric factor

Subscripts

i, j	Identifies component
c	Critical property
R	Reduced property

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