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Isothermal Vapor–Liquid Equilibria at Elevated Pressures for the Systems Containing Nitrogen, Carbon Dioxide, and Chlorodifluoromethane

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Isothermal vapor–liquid equilibrium (VLE) values were measured by means of a vapor-phase recirculation still for the ternary system nitrogen–carbon dioxide–chlorodifluoromethane ($CHClF_2$, R22) and its two constituent binary systems nitrogen–R22 and carbon dioxide–R22 at temperatures ranging from 263.2 to 288.2 K with pressures up to 5.128 MPa. With use of the recently proposed modified volume-translated Peng–Robinson equation of state, the binary interaction parameter k_{ij} values obtained from the experimental results for the two binaries and the literature values for the nitrogen–carbon dioxide system were used to predict the VLE values for the ternary system. The values obtained from a flash calculation yield an overall average absolute percentage deviation in composition of less than 0.005 mole fraction.

Introduction

Although halogenated hydrocarbons are mainly used as refrigerants, they are also useful at elevated pressures as a solvent in the separation of gas mixtures or as an absorbent in gas washing processes. In this work, we continued our investigation on the experimental determination and data correlation of vapor–liquid equilibrium (VLE) values for systems containing chlorodifluoromethane ($CHClF_2$, R22) and nitrogen/carbon dioxide.

Equilibrium values for the two binary systems nitrogen–R22 and carbon dioxide–R22 have been reported in the literature. Maslennikova et al. (*1*) reported VLE values for the binary system nitrogen–R22 at three isothermal conditions (295, 313, and 333 K) for a total of 21 data points. Leites and Argunova (*2*) presented graphically the solubility of nitrogen in R22 at pressures up to 1 atm. Nohka et al. (*3*) reported VLE values for the binary system nitrogen–R22 at 4 isothermal conditions (273, 293, 323, and 348 K) for a total of 37 data points, and for the binary system carbon dioxide–R22 at 8 isothermal conditions (273, 283, 293, 298, 303, 323, 333, and 348 K) for a total of 40 data points.

In this work, VLE values for these two binaries are reported at 5 isothermal conditions (263.2, 268.2, 273.2, 283.2, and 288.2 K) with a total of 50 data points for the nitrogen–R22 binary and a total of 81 data points for the carbon dioxide–R22 binary. In addition, VLE values are reported for the ternary system nitrogen–carbon dioxide–R22 at 2 isothermal conditions (273.2 and 283.2 K) for a total of 31 data points.

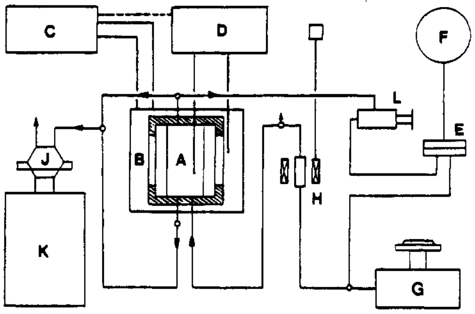

Figure 1. Schematic diagram of experimental VLE apparatus: (A) equilibrium cell; (B) jacket; (C) cooling source; (D) temperature controller; (E) pressure transducer; (F) gauge; (G) dead-weight balance; (H) magnetic pump; (J) six-way valve; (K) gas chromatograph; (L) volume compensator.

Experimental Section

Apparatus and Procedure. Isothermal vapor–liquid equilibrium values for the three systems were established in a vapor recirculation cell. A schematic diagram of the apparatus and the direction of fluid circulation is shown in Figure 1. A quartz glass tube (A) with an internal capacity of 13 cm^3, protected by a copper sleeve, was used as the equilibrium cell. It was immersed in an alcohol solution jacket (B). The temperature of the alcohol solution was maintained constant by recirculating it through a cooling source (C), the temperature of which was controlled by means of a precision bridge system (type QJ-18, Academia Sinica) and a controller (type DWT-702, Academia Sinica) (D) connected to a platinum resistance sensor installed on the wall of the copper sleeve. The equilibrium temperature was measured by a calibrated platinum resistance thermometer inserted in the cell. Furthermore, the cell and its fittings were placed in an air bath to minimize the possible variation of the system temperature with the ambient temperature. The accuracy of the temperature measurements is estimated to be within 0.1 K. Equilibrium pressures were measured through a pressure transducer (E) and a precision Bourdon pressure gauge (F), which was frequently calibrated throughout this work by means of a dead-weight balance (G). The uncertainty of the pressure measurements is estimated to be ±0.5%. To enhance the attainment of equilibrium, the vapor phase was recirculated by means of a magnetic pump (H). During the operation, samples were taken after the pressure and temperature of the cell reached constant values for a minimum of 1 h. The samples withdrawn from the cell were transferred through a six-way valve (J) to the gas chromatograph (K). Liquid samples were immediately vaporized in the sampling tubing before entering the valve. Whenever pressure reduction was observed due to repeated sampling, a volume compensator (L) was ap-

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Table I. Comparison of the Experimental and the Literature Vapor Pressure Values for CO_2 and R22

		P, MPa		
	T, K	this work	literature	$\|\Delta P/P\|^a$
CO_2	263.2	2.647	2.660 (5)	0.49
	268.2	3.045	3.050 (5)	0.16
	273.2	3.475	3.488 (5)	0.37
	283.2	4.459	4.505 (5)	1.02
	288.2	5.044	5.093 (5)	0.96
R22	263.2	0.355	0.355 (4)	0
	268.2	0.422	0.423 (4)	0.24
	273.2	0.499	0.499 (4)	0
	283.2	0.681	0.682 (4)	0.15
	288.2	0.788	0.790 (4)	0.25

[a] $\Delta P/P = [|P(\text{this work}) - P(\text{lit.})|/P(\text{lit.})] \times 100$.

Table II. Isothermal Vapor-Liquid Equilibria for the Nitrogen (1)-R22 (2) System

P, MPa	x_1	y_1	P, MPa	x_1	y_1
		263.2 K			
0.355	0.000	0.000	3.555	0.052	0.875
1.096	0.013	0.646	4.094	0.061	0.886
1.425	0.017	0.727	4.569	0.073	0.893
2.366	0.032	0.804	5.022	0.079	0.897
2.888	0.040	0.841			
		268.2 K			
0.422	0.000	0.000	2.990	0.044	0.835
0.832	0.008	0.478	3.598	0.054	0.852
1.554	0.020	0.686	4.076	0.065	0.863
2.030	0.028	0.737	4.572	0.073	0.872
2.597	0.037	0.811	5.128	0.083	0.878
		273.2 K			
0.499	0.000	0.000	2.588	0.033	0.798
0.816	0.006	0.372	3.083	0.045	0.797
1.137	0.011	0.542	4.126	0.063	0.840
1.597	0.019	0.662	5.013	0.077	0.857
2.010	0.027	0.724			
		283.2 K			
0.681	0.000	0.000	2.587	0.033	0.684
1.021	0.006	0.307	3.083	0.044	0.724
1.597	0.015	0.529	3.576	0.052	0.752
1.902	0.021	0.602	4.066	0.061	0.771
2.418	0.031	0.670	4.941	0.076	0.803
		288.2 K			
0.788	0.000	0.000	2.337	0.027	0.610
0.939	0.003	0.148	3.032	0.041	0.680
1.169	0.007	0.294	3.838	0.056	0.736
1.456	0.012	0.418	4.937	0.078	0.774
1.936	0.019	0.540			

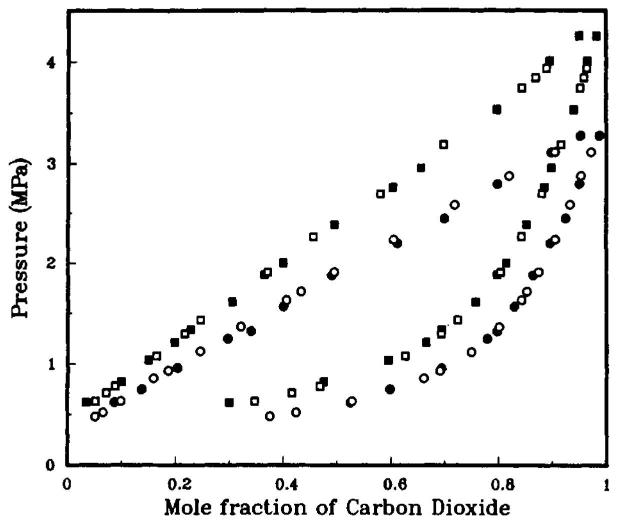

Figure 2. Comparison of the experimental and the literatre VLE values for the system CO_2 (1)-R12 (CCl_2F_2) (2). This work: ○, 273.2 K; □, 283.2 K. Work of Knapp et al. (6): ●, 273.2 K; ■, 283.2 K.

Table III. Isothermal Vapor-Liquid Equilibria for the Carbon Dioxide (1)-R22 (2) System

P, MPa	x_1	y_1	P, MPa	x_1	y_1
		263.2 K			
0.355	0.000	0.000	1.514	0.564	0.874
0.516	0.087	0.367	1.681	0.631	0.901
0.707	0.190	0.571	1.894	0.720	0.928
0.880	0.281	0.683	2.067	0.789	0.949
0.990	0.341	0.733	2.287	0.876	0.970
1.108	0.389	0.776	2.414	0.921	0.982
1.308	0.470	0.831	2.647	1.000	1.000
		268.2 K			
0.422	0.000	0.000	1.697	0.549	0.860
0.557	0.073	0.293	1.892	0.615	0.890
0.629	0.112	0.382	1.988	0.658	0.901
0.741	0.163	0.494	2.104	0.697	0.916
0.897	0.228	0.607	2.271	0.746	0.935
0.953	0.256	0.637	2.478	0.818	0.954
1.088	0.316	0.700	2.670	0.878	0.971
1.320	0.408	0.776	2.787	0.917	0.981
1.526	0.482	0.827	3.045	1.000	1.000
		273.2 K			
0.499	0.000	0.000	1.738	0.492	0.817
0.605	0.047	0.214	2.098	0.616	0.876
0.704	0.096	0.343	2.493	0.735	0.922
0.904	0.178	0.517	2.588	0.761	0.930
0.938	0.195	0.544	2.796	0.819	0.949
1.113	0.264	0.633	3.050	0.895	0.970
1.301	0.341	0.706	3.083	0.903	0.972
1.427	0.378	0.745	3.475	1.000	1.000
1.597	0.442	0.788			
		283.2 K			
0.681	0.000	0.000	2.057	0.444	0.761
0.808	0.051	0.188	2.423	0.532	0.826
0.936	0.100	0.323	2.587	0.583	0.841
1.017	0.123	0.383	2.871	0.647	0.874
1.142	0.170	0.466	3.083	0.708	0.899
1.254	0.208	0.523	3.576	0.816	0.936
1.354	0.234	0.565	3.636	0.831	0.945
		283.2 K			
1.597	0.314	0.649	4.066	0.907	0.971
1.744	0.357	0.694	4.459	1.000	1.000
		288.2 K			
0.788	0.000	0.000	2.319	0.437	0.754
0.894	0.034	0.139	2.709	0.538	0.815
1.035	0.083	0.278	2.884	0.572	0.836
1.218	0.142	0.406	3.477	0.702	0.893
1.408	0.199	0.504	4.062	0.826	0.937
1.438	0.206	0.516	4.654	0.933	0.975
1.751	0.296	0.627	5.044	1.000	1.000

plied to reduce the pressure disturbance during sampling. The total volume of liquid samples amounted to a very small fraction of a cubic centimeter. A column (3-m length, 3-mm i.d.) packed with GDX-104 was used for the analysis. The column temperatures were set to be 393 and 363 K, and thermal conductivity detector (TCD) temperatures were set to be 403 and 373 K for the binary and the ternary systems, respectively. The flow rate of the carrier gas (H_2, purity >99%) was 60 cm³/min. The uncertainty of composition measurements is estimated to be ±0.005 mole fraction.

Materials. The reagent R22 (purity > 99.85%) was supplied by Du Pont Co., and its purity was verified by a gas chromatograph. The specified purities of carbon dioxide and nitrogen were 99.9% and 99.99 vol %, respectively.

Results and Discussion

In order to verify the capability of the apparatus for reliable VLE measurements, vapor pressures of pure carbon dioxide and R22, as well as the VLE values for the binary system carbon dioxide-dichlorodifluoromethane (CCl_2F_2, R12), were

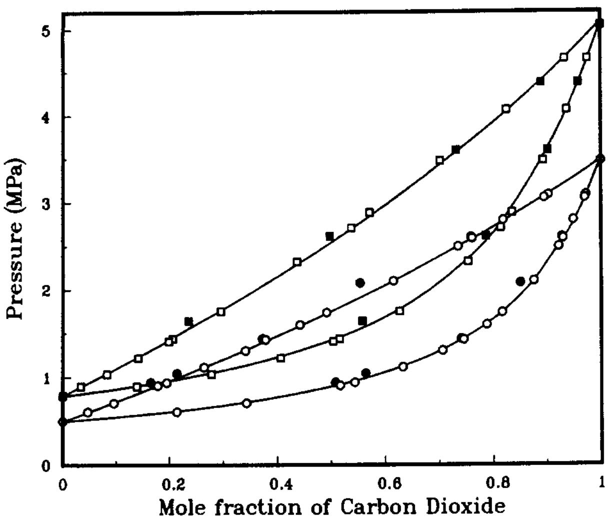

Figure 3. Comparison of the experimental and the literature VLE values for the system CO_2 (1)–R22 ($CHClF_2$) (2). This work: ○, 273.2 K; □, 288.2 K. Work of Nohka et al. (*3*): ●, 273.2 K; ■, 288.2 K. Lines indicate correlated results.

Table IV. Isothermal Vapor–Liquid Equilibria for the Nitrogen (1)–Carbon Dioxide (2)–R22 (3) System

P, MPa	x_1	x_2	y_1	y_2
		273.2 K		
1.597	0.018	0.030	0.606	0.049
1.597	0.009	0.252	0.284	0.437
1.597	0.007	0.308	0.200	0.538
2.588	0.029	0.150	0.615	0.170
2.588	0.023	0.301	0.462	0.356
2.588	0.019	0.396	0.361	0.478
2.588	0.015	0.474	0.286	0.571
2.588	0.006	0.690	0.074	0.838
3.083	0.028	0.368	0.470	0.382
3.083	0.025	0.409	0.432	0.429
3.083	0.023	0.482	0.366	0.509
3.083	0.019	0.541	0.313	0.574
3.083	0.015	0.628	0.234	0.673
		283.2 K		
1.597	0.012	0.075	0.397	0.159
1.597	0.010	0.149	0.277	0.307
1.597	0.003	0.250	0.102	0.523
2.587	0.028	0.128	0.535	0.176
2.587	0.020	0.252	0.383	0.359
2.587	0.015	0.346	0.274	0.492
3.083	0.032	0.200	0.516	0.245
3.083	0.024	0.329	0.377	0.414
3.083	0.018	0.425	0.280	0.586
3.576	0.044	0.170	0.590	0.188
3.576	0.036	0.276	0.491	0.310
3.576	0.031	0.374	0.399	0.421
3.576	0.024	0.498	0.279	0.572
3.576	0.018	0.576	0.215	0.657
4.066	0.043	0.310	0.510	0.312
4.066	0.034	0.423	0.406	0.440
4.066	0.029	0.528	0.314	0.554
4.066	0.015	0.727	0.149	0.770

determined over the temperature range useful to this work and compared with the values available in the literature (*4–6*). The experimentally determined vapor pressure values are reported in Table I, and the VLE values are depicted in Figure 2. These results indicate that the apparatus used in this work is suitable for the intended measurements.

Subsequently, VLE values were measured for the binary systems nitrogen–R22 and carbon dioxide–R22 at temperatures ranging from 263.2 to 288.2 K. The experimentally determined pressure, P, and liquid and vapor compositions, x_1 and y_1, for the isothermal equilibrium of the two systems at temperatures T are listed in Tables II and III. The VLE values reported by Nohka et al. (*3*) for the system carbon dioxide–R22 at 273 and 288 K are compared with our results in Figure 3. Pressure differences of about 20–30 kPa are observed between the two sets of data.

In addition, VLE values for the ternary system N_2–CO_2–R22 were measured at 273.2 and 283.2 K. The experimental P–T–x–y values are reported in Table IV.

An attempt was made in this work to predict the ternary VLE values from the VLE values of the constituent binary systems by means of an equation of state. A modified volume-translated Peng–Ribinson equation of state (MTPR) (*7*) was adopted for this purpose. It is of the following form

$$P = \frac{RT}{v - b} - \frac{a(T)}{v^2 + (2 - 4c/b)bv + (2c^2/b^2 - 1)b^2} \quad (1)$$

where

$$a(T) = \alpha \Omega_{ac} R^2 T_c^2 / P_c, \quad \Omega_{ac} = 0.457\,24$$

$$b = \Omega_{bc} R T_c / P_c, \quad \Omega_{bc} = 0.3112/(2 + u)$$

$$c = (2 - u)b/4$$

$$\alpha = 1 + A_1(1 - T_r) + A_2(1 - T_r)^2 + A_3(1 - T_r)^3$$

$$u = u_0 + u_1(1 - T_r) + u_2(1 - T_r)^2 + u_3(1 - T_r)^{0.1}$$

In these expressions, T_c is the critical temperature, P_c is the critical pressure, and $T_r = T/T_c$ is the reduced temperature.

The parameters A_k (k = 1–3) and u_k (k = 0–3) for the three substances are listed in Table V. The mixing rules used and the related expression for calculating the fugacity coefficient $\hat{\phi}_i$ ($=\hat{f}_i/y_iP$) are as follows

$$a = \sum\sum x_i x_j (a_i a_j)^{1/2}(1 - k_{ij}) \quad (2)$$

$$b = \sum b_i x_i \quad (3)$$

$$c = \sum c_i x_i \quad (4)$$

$$\ln \hat{\phi}_i = -[\ln (Z - B)] + \frac{b_i}{v - b} + \frac{\sum x_k a_{ki}}{DRT} \ln \left(\frac{Q - D}{Q + D}\right) + \frac{a(b_i - 2c_i)}{(Q^2 - D^2)RT} - \frac{2^{1/2} a (b_i - c_i)}{2D^2 RT} \left[\ln \left(\frac{Q - D}{Q + D}\right) + \frac{2QD}{Q^2 - D^2}\right] \quad (5)$$

where

$$Q = v + b - 2c$$

$$D = 2^{1/2}(b - c)$$

$$Z = Pv/(RT)$$

$$B = bP/(RT)$$

The results obtained from a bubble point calculation for the binary systems nitrogen–R22 and carbon dioxide–R22 are presented in Table VI. The average absolute percentage deviations (AAPD) between the measured and the calculated pressures, the average absolute deviations (AAD) between the experimental and the calculated vapor mole fraction of component 1, and the values of the binary interaction parameters k_{ij} are also reported in the table. The k_{ij} values were calculated by minimizing the deviations between the predicted and the experimental bubble point pressures by using $\sum(1 - P(\text{calcd})/P(\text{exptl}))^2$ as the objective function.

In order to evaluate k_{ij} for the binary system nitrogen–CO_2, which is required in the ternary calculation by means of the

Table V. Values of Parameters A_k (k = 1–3) and u_k (k = 0–3) for the Three Substances Used in the MTPR Equation of State, Equation 1

substance	A_1	A_2	A_3	u_0	u_1	u_2	u_3
nitrogen	0.447 48	0.022 413	0.366 68	13.71	7.9377	−5.2914	−15.985
carbon dioxide	0.724 41	−0.055 058	1.153 4	19.65	16.193	−17.903	−23.872
R22	0.729 14	0.032 658	0.718 94	19.43	10.951	−7.1390	−22.735

Table VI. Comparison of the Experimental and the Correlated Values of P and y_1 for the Binary Systems (I) Nitrogen (1)–R22 (2) and (II) Carbon Dioxide (2)–R22 (2) by Means of the MTPR Equation of State

	no. of data points		AAPD(P)[a]		AAD(y_1)[b]		interaction param	
T, K	I	II	I	II	I	II	k_{13}	k_{23}
263.2	9	14	2.38	0.68	0.012	0.005	0.053 65	−0.006 72
268.2	10	18	1.45	1.22	0.015	0.004	0.035 56	−0.009 14
273.2	9	17	1.36	0.51	0.016	0.004	0.047 21	−0.011 03
283.2	10	18	1.14	1.03	0.014	0.003	0.045 13	−0.010 38
288.2	9	14	1.48	0.78	0.015	0.005	0.043 60	−0.006 36

[a] $\mathrm{AAPD}(P) = \{\sum[|P(\mathrm{exptl}) - P(\mathrm{corr})|/P(\mathrm{exptl})]/n\} \times 100$. [b] $\mathrm{AAD}(y_1) = \sum|y(\mathrm{exptl}) - y(\mathrm{corr})|/n$.

Table VII. Comparison of the Experimental and the Predicted Values of x_2, y_1, and y_2 for the Ternary System Nitrogen (1)–Carbon Dioxide (2)–R22 (3)

T, K	no. of data points	AAD(x_2)	AAD(y_1)	AAD(y_2)
273.2	13	0.001	0.003	0.002
283.2	18	0.001	0.005	0.004

equation of state, the VLE values reported by Yorizane et al. (*8*) were selected for the evaluation. The correlated values of k_{ij} for this system are −0.033 91 and −0.0202 at 273.2 and 283.2 K, respectively.

In the prediction of ternary VLE values, T, P, and x_3 values were assigned to determine the mole fractions x_2, y_1, and y_2 by a flash calculation procedure. A comparison of the calculated results with the experimental values, as shown in Table VII, indicates that the MTPR equation is successful in predicting the ternary VLE values from the data of its constituent binaries.

Glossary

a	parameter of equation of state, eq 1, cm^6·MPa·mol^{-2}
b, c	parameters of equation of state, eq 1, cm^3·mol^{-1}
A_1, A_2, A_3	coefficients for the temperature function of α, eq 1
AAD	average absolute deviation
AAPD	average absolute percentage deviation
$\hat{f}_i$	fugacity of components i in mixture, MPa
k_{ij}	binary interaction parameter for components i and j
n	number of data points
P	pressure, MPa
R	gas constant, 8.314 J·K^{-1}·mol^{-1}
T	temperature, K
u_1, u_2, u_3	coefficients for the temperature function of u, eq 1
v	molar volume, cm^3·mol^{-1}
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase

Greek Letters

α	$a(T)P_c/\Omega_{ac}R^2T_c^2$
$\hat{\phi}_i$	fugacity coefficient of component i in mixture
Ω_{ac}	0.457 24
Ω_{bc}	bP_c/RT_c

Subscripts

c	critical value
i	component identification
r	reduced value

Registry No. CO_2, 124-38-9; N_2, 7727-37-9; $CHClF_2$, 75-45-6.

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