Vapor–Liquid Equilibria of the Carbon Tetrafluoride–Chlorotrifluoromethane System at 199.80 K

Patricio C. Proust and Fred P. Stein*

Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

A vapor-recirculation apparatus was used to determine the vapor–liquid equilibrium conditions of the carbon tetrafluoride–chlorotrifluoromethane system at a temperature of 199.80 K over the full composition range, covering a pressure range of 1.544–15.272 bar. Liquid-phase activity coefficients were calculated from the experimental data by using a modified Redlich–Kwong equation of state to describe vapor-phase nonidealities. The activity coefficients were correlated with the Wilson equation, thus permitting the calculation of the equilibrium conditions at the temperature investigated.

Introduction

As part of a continuing program oriented toward the collection of thermodynamic properties of mixtures of light fluorocarbons, the vapor–liquid equilibria of the binary system carbon tetra-fluoride (Refrigerant 14) and chlorotrifluoromethane (Refrigerant 13) were determined at 199.8 K.

Experimental Section

The apparatus used was of the vapor-recirculation type; its description, construction, and mode of operation have been reported elsewhere.[1,2]

The temperature was measured to within ±0.01 K with a three-junction copper–constantan thermopile, the emf of which was determined by using a Leeds and Northrup type K-3 potentiometer. Calibration of the thermopile, which was referenced to melting ice, was effected against a platinum resistance thermometer, which, in turn, had been calibrated and certified by the U.S. National Bureau of Standards.

Equilibrium pressures were measured, to within ±7 mbar, with a Heise Bourdon-tube gage, previously calibrated against a Ruska Instrument Corp. deadweight gage.

Liquid and vapor samples were collected, both in the gas phase, in 75-cm³ sampling cylinders at gage pressures of about 2 bars and were analyzed chromatographically with a Beckman Instruments, Inc., GC-2A gas chromatograph with a di-*n*-butyl maleate column and a thermal conductivity cell. Peak areas were measured by means of an electronic integrator, consisting of a Hewlett-Packard Model 8875A differential amplifier, a Dymec Model 2210 voltage-to-frequency converter, and an Anadex Model CF-200R digital counter. Peak areas of the unknown samples were compared with peak areas of samples of known, similar composition; these reference samples had been prepared at a total, absolute pressure of about 2 bar, and their compositions calculated from measurements of partial pressures and appropriate corrections, utilizing the virial equation of state, to account for the very small gas-phase nonidealities. Both the unknown and the reference samples were always run in duplicate; the estimated error of the reported compositions is within ±0.3% of the lesser mole fraction. Pressure measurements required in the chromatographic technique and in the preparation of reference samples were performed by using a Ruska Instrument Corp. Model XR-38 quartz Bourdon-tube pressure counter, which had been calibrated by the manufacturer. Pressures could thus be read to within ±0.01 mmHg.

The supplier of the fluorocarbons, E.I. du Pont de Nemours and Co., indicated a purity of 99.7% for CF_4 and 99.9% for $CCIF_3$. These values were confirmed by chromatographic analysis, the major impurities being air for CF_4 and CF_4 for $CCIF_3$.

Results

Experimental liquid-phase and vapor-phase mole fractions and total pressures are reported in Table I and shown graphically in Figure 1.

Discussion of Results

At 199.80 K, the system CF_4–$CCIF_3$ showed a slight departure from liquid-phase ideal behavior, with both positive and negative deviations from Raoult's law, as observed in the liquidus line in Figure 1 and in the values of activity coefficients listed in Table I.

The thermodynamic consistency of the data was checked by using the integral test, whereby experimental values of log (γ_1/γ_2) are plotted vs. x_1 and the resulting positive and negative areas compared. The quantity [(positive area − negative area)/(positive area + negative area)] × 100 came to +4.3%, which is within the accepted limits for consistent data of this kind.[3]

Correlation of Experimental Data

The usual equation for vapor–liquid equilibrium was applied

$$\phi_i y_i P = \gamma_i x_i f_i^{ol} \tag{1}$$

The vapor-phase fugacity coefficient ϕ_i was calculated from the experimental temperature, pressure, and vapor composition through the use of a modified Redlich–Kwong equation of state.[4]

$$\ln \phi_i = \ln \frac{v}{v-b} + \frac{b_i}{v-b} - \frac{2\sum_{j=1}^{2} y_j a_{ij}}{RT^{1.5}b} \ln \frac{v+b}{v} + \frac{ab_i}{RT^{1.5}b^2}\left(\ln \frac{v+b}{v} - \frac{b}{v+b}\right) - \ln \frac{Pv}{RT} \tag{2}$$

where

$$a = y_1^2 a_{11} + 2y_1 y_2 a_{12} + y_2^2 a_{22} \tag{3a}$$

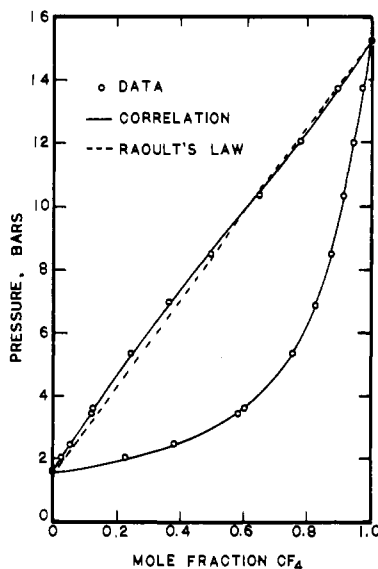$$b = y_1 b_1 + y_2 b_2 \tag{3b}$$

The constants of the equations were obtained from

$$a_{ii} = \frac{\Omega_{ai} R^2 T_{ci}^{2.5}}{P_{ci}} \qquad a_{12} = \frac{(\Omega_{a11} + \Omega_{a22}) R^2 T_{c12}^{2.5}}{2P_{c12}} \tag{3c}$$

$$b_i = \frac{\Omega_b R T_{ci}}{P_{ci}} \tag{3d}$$

Expressions for the binary constants T_{c12} and P_{c12} are available.[3] Only one binary, empirical interaction parameter is needed, namely, k_{12}. A value of 0.022 was used.[5] The resulting ϕ_1 and ϕ_2 are shown in Table I.

Table I. Experimental Vapor-Liquid Equilibria, Calculated Fugacity and Activity Coefficients, and Calculated Excess Gibbs Free Energy for the $CF_4/CClF_3$ System at 199.80 K

| pressure, bar | mole fraction of CF_4 | | ϕ_1 | ϕ_2 | γ_1 | γ_2 | G^E/RT |
	liquid	vapor					
1.544	0.0000	0.0000		0.956		1.000	0.0000
2.013	0.0277	0.2278	0.978	0.943	1.408	1.020	0.0290
2.448	0.0540	0.3805	0.971	0.932	1.454	1.009	0.0285
3.447	0.1192	0.5811	0.956	0.907	1.389	1.000	0.0393
3.599	0.1248	0.6017	0.954	0.904	1.430	0.994	0.0397
5.323	0.2422	0.7534	0.930	0.862	1.320	0.996	0.0646
6.895	0.3617	0.8283	0.909	0.826	1.222	1.015	0.0820
8.487	0.4942	0.8772	0.887	0.789	1.131	1.070	0.0953
10.349	0.6489	0.9165	0.862	0.747	1.058	1.201	0.1009
12.031	0.7783	0.9479	0.840	0.710	1.026	1.301	0.0782
13.755	0.8949	0.9737	0.817	0.672	1.012	1.489	0.0521
15.272	1.0000	1.0000	0.796		1.000		0.0000

Figure 1. Pressure-composition curves for $CF_4/CClF_3$ at 199.80 K.

The liquid-phase standard-state fugacity $f_i^{\circ l}$ was chosen as the pure liquid component at the system temperature and at zero pressure. Because the conditions covered in this investigation were well below the critical, no appreciable error was introduced when, for the pressure correction for activity coefficients, the molar volume of the pure liquid component was used. Also, the pure liquid was assumed incompressible.

The final expression for the activity coefficient is

$$\gamma_i = \frac{\phi_i y_i P}{x_i P_i^s \phi_i^s \exp\left[\dfrac{(P - P_i^s)v_i^l}{RT}\right]} \quad (4)$$

The experimentally determined vapor pressure of each component, P_i^s, was used, and the ϕ_i^s terms were calculated from the same modified Redlich-Kwong equation of state but in this case applied to the pure, saturated vapor. The pure-component properties are given in Table II.

The resulting activity coefficients are shown in Table I, where the dimensionless excess Gibbs free energy G^E/RT for this system is also reported, as calculated from

$$G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (5)$$

Subsequently, the experimental activity coefficients given by eq 4 were correlated by using the Wilson equation.[8] As mentioned previously, this system shows both positive and negative deviations from Raoult's law. The Wilson equation is not suitable for such behavior; however, the negative deviations are quite minor, as shown by the values of γ_2 at $x_1 = 0.1248$

Table II. Properties of the Pure Components

	CF_4	$CClF_3$	ref
critical temp, K	227.50	302.00	6, 7
critical pressure, bar	37.45	38.70	6, 7
critical vol, cm^3/mol	140.7	180.8	6, 7
acentric factor	0.1777	0.1703	calcd from 6, 7
Ω_a	0.4408	0.4400	this work
Ω_b	0.0896	0.0894	this work
liquid vol at 199.8 K, cm^3/mol	69.9	70.1	6, 7

and $x_1 = 0.2422$ in Table I. Accordingly, it was decided to use the Wilson equation in view of its numerous advantages.[3]

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \quad (6a)$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \quad (6b)$$

The parameters Λ_{12} and Λ_{21} were determined in such a way that the root-mean-square percentage difference between calculated and experimental activity coefficients for both components was a minimum. Equal weight was given to each experimental point. As has been shown several times (see, for example, ref 9), there is no unique optimum pair of Wilson parameters, and this fact was verified in this work. The final values selected were

$$\Lambda_{12} = 1.011$$

$$\Lambda_{21} = 0.589$$

With these values, the resulting root-mean-square percentage difference for the calculated activity coefficients was 2.79%.

Once expressions for fugacity and activity coefficients are available, the equilibrium conditions can be calculated. For a given liquid composition, the total pressure and the vapor composition are fixed and can be determined. For 199.80 K, these calculations gave a root-mean-square difference in pressure of 0.064 bar, and a root-mean-square difference in vapor composition of component 1 of 0.0060 mole fraction.

The results of this correlating scheme are shown in Figure 1.

Acknowledgment

Glossary

a, b	constants of the Redlich-Kwong equation of state
f_i	fugacity, bar

G^E/RT	dimensionless excess Gibbs free energy
k_{12}	interaction constant
P	pressure, bar
R	gas constant
T	temperature, K
v	molar volume, cm^3/mol
x_i	liquid-phase mole fraction
y_i	vapor-phase mole fraction
γ_i	liquid-phase activity coefficient
$\Lambda_{12}, \Lambda_{21}$	parameters of the Wilson equation
ϕ_i	vapor-phase fugacity coefficient
Ω_a, Ω_b	dimensionless constants in the modified Redlich–Kwong equation of state

Subscripts

c	critical
i	component i
j	component j
1	CF_4
2	$CClF_3$

Superscripts

l	liquid
o	standard state
s	saturation

Literature Cited

(1) Stein, F. P., Sterner, C. J., Geist, J. M., *Chem. Eng. Prog.*, **58** (11), 70 (1962).
(2) Stein, F. P., Proust, P. C., *J. Chem. Eng. Data*, **16**, 389 (1971).
(3) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1969, pp 212, 157, 229.
(4) Chueh, P. L., Prausnitz, J. M., *Ind. Eng. Chem. Fundam.*, **6**, 492 (1967).
(5) Gupta, V. K., M.S. Thesis, Lehigh University, Bethlehem, Pa., 1970.
(6) Freon Products Division, E. I. du Pont de Nemours and Co., "Preliminary Thermodynamic Properties of Freon-14 Fluorocarbon", Technical Bulletin T-14 (1961).
(7) Freon Products Division, E. I. du Pont de Nemours and Co., "Freon-13 Refrigerant Thermodynamic Properties", Technical Bulletin T-13A (1967).
(8) Wilson, G. M., *J. Am. Chem. Soc.*, **86**, 127 (1964).
(9) Reid, R. C., Prausnitz, J. M., Sherwood, T. K., "The Properties of Gases and Liquids", 3rd ed., McGraw-Hill, New York, 1977, p 315.

Vapor–Liquid Equilibria in Hydrogen + 9,10-Dihydrophenanthrene Mixtures

Herbert M. Sebastian, James J. Simnick, Ho-Mu Lin, and Kwang-Chu Chao*

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907

Saturated fluid-phase compositions at vapor–liquid equilibrium were experimentally determined for hydrogen + 9,10-dihydrophenanthrene mixtures at temperatures of 188.3, 269.0, 349.7, and 429.9 °C over the pressure range of 20–250 atm.

Introduction

Vapor–liquid equilibrium data for mixtures of hydrogen and hydrocarbons are needed for engineering design of hydrotreating and hydrogenation processes. Data are especially needed at elevated temperatures and pressures. In this study we report experimentally observed saturated equilibrium phase compositions and K values for the system hydrogen + 9,10-di-hydrophenanthrene at conditions of industrial interest. The equilibrium phase behavior of this mixture system has not been previously reported in the literature.

Experimental Section

The experimental apparatus and procedure used in this study have been described (*1–3*).

Hydrogen gas was supplied by Airco with a minimum purity of 99.95% and was directly used without further purification. 9,10-Dihydrophenanthrene was purchased from Aldrich Chemical Co. with a reported purity of 97%. Before being used in this study it was zone refined to recover the colorless sections. The remaining colored portion from the zone refiner was fractionally distilled under a nitrogen blanket at a reduced pressure. The distillate was combined with the colorless sections from the zone refiner for use as feed to the equilibrium apparatus. The purity of this combined feed was found to be 99+% from gas chromatographic analysis.

Dihydrophenanthrene samples were taken from the cell effluents in all experimental runs and were analyzed by gas chromatography to test for possible thermal decomposition. No appreciable chemical change was detected at the three lower temperatures of the reported experiments. However, phenanthrene was found to be present to the extent of about 4–5% of the dihydrophenanthrene in the samples of the 430 °C runs. The reported mole fractions of dihydrophenanthrene at 430 °C include those of phenanthrene. We report the data at 430 °C in spite of the known chemical changes in the belief that equilibrium conditions are not substantially altered in view of the closely similar properties of phenanthrene and dihydrophenanthrene. It is, nevertheless, clear that the data at 430 °C are less accurate than the data at the lower temperatures.

Results

Compositions of equilibrium saturated vapor and liquid phases of hydrogen + 9,10-dihydrophenanthrene mixtures were determined at four temperatures, 188.3, 269.0, 349.7, and 429.9 °C, at seven pressures from 20 to 250 atm. The results are summarized in Table I. The phase compositions reported in the table represent the mean of duplicate samples. Individual samples are shown in Figures 1 and 2 as separate points when they can be distinguished. Saturated liquid compositions at all the four observed temperatures are shown in Figure 1, but the saturated gas compositions are shown in Figure 2 for only the two higher temperatures. The saturated gas phases are essentially all hydrogen at the lower temperature isotherms and could not be meaningfully presented in Figure 2.

Also tabulated in Table I are the equilibrium ratios of hydrogen and dihydrophenanthrene. These values were obtained from the averaged x's and y's. Figure 3 shows the K values of hydrogen as a function of pressure while Figure 4 shows the