Isothermal Vapor−Liquid Equilibria for the Binary Systems of Chlorine with Difluoromethane, Chlorodifluoromethane, and Dichlorodifluoromethane at 10 °C

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Isothermal vapor−liquid equilibria for difluoromethane + chlorine, chlorodifluoromethane + chlorine, and dichlorodifluoromethane + chlorine have been measured. The experimental data are correlated with the Peng−Robinson equation of state, and the relevant parameters are presented. All of the binary systems form minimum boiling homogeneous azeotropes at the experimental conditions. The correlation of the vapor−liquid equilibria was found to be in good agreement with the experimental data.

Introduction

Difluoromethane (hereinafter referred to as HFC-32), which is presently under consideration as a new mixed refrigerant, is normally manufactured by the fluorination of dichloromethane with hydrogen fluoride. Chlorodifluoromethane (hereinafter referred as HCFC-22) is used as a low-temperature refrigerant, an intermediate in the production of Teflon, and also aerosol propellant formulations. Dichlorodifluoromethane (hereinafter referred to as CFC-12) is also used as a refrigerant and as a propellant in aerosols. HCFC-22 and CFC-12, which have been considered as chemicals depleting the ozone layer, are normally manufactured by the liquid-phase fluorination of trichloromethane and perchloromethane in the presence of the antimony catalyst. In the production of these materials, the other two components are produced by side reactions. A part of the chlorine that is added to the reactor to sustain the activity of the antimony catalyst flows out of the separation system. These byproducts and the chlorine may have an effect on the purity and the economics of the production processes of these organic products. To determine the structure of the separation system and to design the separation equipment, knowledge of the vapor−liquid equilibrium for the systems composed of the related components are required. A part of the experimental data for the related binary systems to produce these organic materials have been reported in our previous literature (Kang and Chung, 1996; Kang, 1998). In this study, the isothermal vapor−liquid equilibria for the three binary systems of chlorine with HFC-32, HCFC-22, and CFC-12 at 10.0 °C were measured and correlated with the Peng−Robinson equation of state (1976).

Experimental Section

Chemicals. HFC-32 prepared in our pilot plant was used. Chlorine (Hanwha Chem. Co.) and HCFC-22 and CFC-12 (ULSAN Chemical Co.) were of guaranteed reagent grade and were used without any further purification. A chromatographic analysis on organic materials and chlorine showed major peak areas of more than 99.8%.

Apparatus and Procedure. The static equilibrium apparatus and the procedures used for this work are described by Kang and Lee (1996). The equilibrium temperature was measured with a T-type thermocouple converter (Yokogawa Elec. Corp., model STED-210-TT*B) having an accuracy of ±0.1 °C. The equilibrium pressure was determined by a gauge pressure transmitter (Yokogawa Elec. Corp., model UNE43-SAS3*B) and a barometer having accuracies of ±0.5 kPa and ±0.05 kPa, respectively.

The mass of each component introduced into the cell was determined with a digital balance having an accuracy of ±0.01 g. The compositions of the vapor phase were not measured. The compositions of the liquid phase were calculated from the total composition by correction for the mass of each component existing in the vapor phase. The densities of the both phases were estimated by using the Peng−Robinson equation of state (1976) with the binary interaction parameters obtained by data reduction of the experimental data. Factors affecting the accuracy of the liquid-phase mole fractions would be the accuracy of the masses of each component introduced into the cell and the estimated densities of both phases. The effect of 10% errors in the estimated densities for the liquid and the vapor phase gives an error of approximately 0.0001 and 0.0005 in the respective mole fraction. The estimated accuracy of the liquid-phase composition was ±0.001.

Results and Discussion

The experimental vapor−liquid equilibrium data for the three binary systems HFC-32 + chlorine, HCFC-22 + chlorine, and CFC-12 + chlorine at 10.0 °C are shown in Tables 1−3 and in Figures 1−3. All of the binary systems form minimum boiling homogeneous azeotropes at the experimental conditions. The equation of vapor−liquid equilibrium for any component i with the equation of state is

$$x_i^{\mathrm{V}}\phi_i^{\mathrm{V}} = x_i^{\mathrm{L}}\phi_i^{\mathrm{L}} \tag{1}$$

where x_i is the mole fraction, ϕ_i is the fugacity coefficient, and the superscripts V and L indicate a vapor phase and a liquid phase, respectively. The fugacity coefficient ϕ_i in both phases was calculated by the Peng−Robinson equation of state (1976)

$$Z = \frac{v}{v-b} - \frac{a(T)v}{RT[v(v+b)+b(v-b)]} \tag{2}$$

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Table 1. Vapor−Liquid Equilibria for HFC-32 (1) + Chlorine (2) at 10.0 °C

P/kPa	x_1	y_1 (calcd)	P/kPa	x_1	y_1 (calcd)
501.6	0.0000	0.0000	1164.4	0.4999	0.6545
744.0	0.0610	0.3282	1176.9	0.5497	0.6694
847.5	0.1006	0.4226	1187.7	0.5998	0.6859
941.2	0.1521	0.4956	1196.4	0.6493	0.7044
1002.7	0.2006	0.5388	1203.1	0.6986	0.7257
1048.0	0.2493	0.5689	1206.6	0.7495	0.7516
1083.0	0.2996	0.5919	1206.6	0.7967	0.7803
1110.8	0.3511	0.6106	1200.3	0.8494	0.8194
1132.6	0.4029	0.6266	1186.8	0.8975	0.8636
1149.9	0.4504	0.6403	1160.0	0.9494	0.9237
1164.4	0.5004	0.6546	1118.8	1.0000	1.0000
1177.7	0.5510	0.6698			
1190.2	0.6004	0.6861			

Table 2. Vapor−Liquid Equilibria for HCFC-22 (1) + Chlorine (2) at 10.0 °C

P/kPa	x_1	y_1 (calcd)	P/kPa	x_1	y_1 (calcd)
502.3	0.0000	0.0000	701.4	0.4509	0.5201
550.1	0.0501	0.1231	707.9	0.4994	0.5524
585.7	0.0998	0.2098	712.9	0.5491	0.5859
615.1	0.1521	0.2788	715.8	0.6003	0.6213
637.1	0.2003	0.3300	717.2	0.6477	0.6555
654.6	0.2481	0.3734	718.1	0.6996	0.6951
670.7	0.3012	0.4158	716.5	0.7492	0.7353
682.4	0.3499	0.4514	713.6	0.7995	0.7793
692.6	0.3999	0.4859	707.7	0.8490	0.8262
701.5	0.4504	0.5197	700.0	0.8979	0.8768
708.1	0.5002	0.5529	690.0	0.9478	0.9336
			676.8	1.0000	1.0000

Table 3. Vapor−Liquid Equilibria for CFC-12 (1) + Chlorine (2) at 10.0 °C

P/kPa	x_1	y_1 (calcd)	P/kPa	x_1	y_1 (calcd)
502.1	0.0000	0.0000	518.3	0.4495	0.4072
511.2	0.0484	0.0630	513.4	0.5004	0.4486
517.9	0.1000	0.1190	508.0	0.5487	0.4894
521.9	0.1520	0.1683	501.7	0.5988	0.5335
524.4	0.1995	0.2094	494.7	0.6487	0.5795
525.3	0.2503	0.2509	485.9	0.6995	0.6290
525.0	0.3013	0.2911	477.1	0.7517	0.6831
523.8	0.3497	0.3287	467.6	0.7995	0.7357
521.6	0.3997	0.3677	457.0	0.8504	0.7956
518.3	0.4502	0.4078	447.0	0.8952	0.8521
514.0	0.4993	0.4477	435.3	0.9501	0.9265
			422.6	1.0000	1.0000

where

$$a(T) = \frac{0.457\,24R^2T_c^2}{P_c}\alpha(T) \tag{3}$$

$$b = \frac{0.077\,80RT_c}{P_c} \tag{4}$$

with

$$\alpha(T) = (1 + m(1 - T_r^{0.5}))^2 \tag{5}$$

$$m = 0.374\,64 + 1.542\,26\omega - 0.269\,92\omega^2 \tag{6}$$

The mixture parameters used are defined by the classical quadratic mixing rule

$$a = \sum_i\sum_j x_ix_j(a_ia_j)^{1/2}(1 - \theta_{ij}) \tag{7}$$

$$b = \sum_i x_ib_i \tag{8}$$

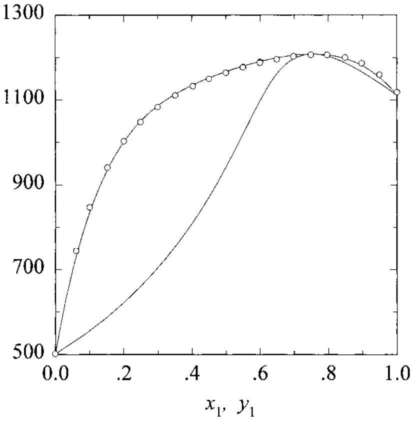

Figure 1. Equilibrium curve for HFC-32 (1) + chlorine (2) at 10.0 °C: (○) experimental; (—) Peng−Robinson equation of state.

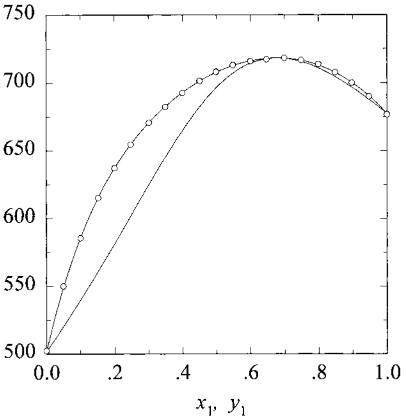

Figure 2. Equilibrium curve for HCFC-22 (1) + chlorine (2) at 10.0 °C: (○) experimental; (—) Peng−Robinson equation of state.

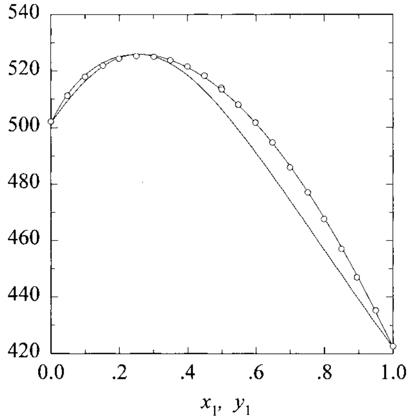

Figure 3. Equilibrium curve for CFC-12 (1) + chlorine (2) at 10.0 °C: (○) experimental; (—) Peng−Robinson equation of state.

In the above equations, T_c is the critical temperature, P_c is the critical pressure, v is the molar volume, R is the ideal gas constant, T_r is the reduced temperature, ω is the acentric factor, and θ_{ij} is the binary interaction parameter. The physical properties from Sato et al. (1994) for the organic materials and Braker and Mossman (1980) for chlorine are presented in Table 4. The binary interaction parameters of the Peng−Robinson equation of state, θ_{ij}, were evaluated by a nonlinear regression method based on the maximum-likelihood principle (Anderson et al., 1978), as implemented in the computer programs published by Prausnitz et al. (1980), with the following objective function (F)

Table 4. Physical Properties of the Pure Components

component	formula	M_W	T_b/K	T_c/K	P_c/kPa	ω
HFC-32	CH_2F_2	52.02	221.5	351.3	5777	0.277
HCFC-22	$CHClF_2$	86.47	232.4	369.3	4970	0.221
CFC-12	$CC1_2F_2$	120.91	243.4	385.0	4129	0.179
chlorine	Cl_2	70.91	238.7	417.2	7710	0.069

Table 5. Binary Parameters of the Peng−Robinson Equation of State and Standard Deviations of the Measured Variables for the Binary Systems

			standard deviations		
system	t/°C	θ_{12}	P/kPa	t/°C	$100x_1$
HFC-32 (1) + chlorine (2)	10.0	0.1460	1.0	0.07	0.03
HCFC-22 (1) + chlorine (2)	10.0	0.0556	0.2	0.01	0.00
CFC-12 (1) + chlorine (2)	10.0	0.0075	0.2	0.02	0.00

$$F = \sum_j \left(\frac{(P^j_{\mathrm{exptl}} - P^j_{\mathrm{calcd}})^2}{\sigma_P^2} + \frac{(T^j_{\mathrm{exptl}} - T^j_{\mathrm{calcd}})^2}{\sigma_T^2} + \frac{(x^j_{1,\mathrm{exptl}} - x^j_{1,\mathrm{calcd}})^2}{\sigma_{x_1}^2} \right) \quad (9)$$

where σ is the estimated standard deviation of each of the measured variables, i.e., pressure, temperature, and liquid-phase mole fraction. In data reduction, $\sigma_P = 1.0$ kPa, $\sigma_T = 0.1$ K, and $\sigma_{x_1} = 0.001$ are selected. The binary interaction parameters obtained by data reduction and the standard deviations of the measured variables of the binary systems are presented in Table 5. The predicted vapor-phase mole fractions at the given experimental temperatures and liquid-phase mole fractions for the three binary systems (HFC-32 + chlorine, HCFC-12 + chlorine, CFC-12 + chlorine) are presented in Tables 1−3. The comparison of the experimental and calculated equilibrium data are also shown in Figures 1−3. As shown in these figures and the low standard deviations in Table 5, the calculated results are in good agreement with the experimental values.

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