Vapor−Liquid Equilibria for the Systems Difluoromethane + Hydrogen Fluoride, Dichlorodifluoromethane + Hydrogen Fluoride, and Chlorine + Hydrogen Fluoride

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Isothermal vapor−liquid equilibria for difluoromethane + hydrogen fluoride, dichlorodifluoromethane + hydrogen fluoride, and chlorine + hydrogen fluoride have been measured. The experimental data for the binary systems are correlated with the NRTL equation with the vapor-phase association model for the mixtures containing hydrogen fluoride, and the relevant parameters are presented. The binary system difluoromethane + hydrogen fluoride forms a homogeneous liquid phase, and the others form minimum boiling heterogeneous azeotropes at the experimental conditions.

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. A small amount of chlorodifluoromethane, dichlorodifluoromethane (hereinafter referred to as CFC-12), and chloromethane 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 affect the purity of the product and the economics of the HFC-32 production process. If a trace amount of the byproduct is not removed from the process, it may build up to very large levels in a recycle loop. 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 to produce HFC-32 is required. However, very limited experimental data for the related binary systems to produce HFC-32 have been reported in the literature (Kang and Lee, 1996; Lee et al., 1996). In this study, the isothermal vapor−liquid equilibria for the three binary systems HFC-32 + hydrogen fluoride at 6.0 °C and CFC-12 + hydrogen fluoride and chlorine + hydrogen fluoride at 30.0 °C were measured and correlated with the NRTL equation with the association model of Lencka and Anderko (1993) for the mixtures containing hydrogen fluoride.

Experimental Section

Chemicals. HFC-32 prepared in our pilot plant was used. Chlorine (Hanwha Chem., Co.) and CFC-12 and anhydrous hydrogen fluoride (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 liquid phase was mixed with a magnetic stirrer. 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 an accuracy 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 since the hydrogen fluoride is toxic and very reactive with the packing materials of the gas chromatography column. 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 association model combined with the Peng−Robinson cubic equation of state (1978) proposed by Lencka and Anderko (1993). The estimated accuracy of the liquid-phase mole fraction was 0.001.

Results and Discussion

The experimental vapor−liquid equilibrium data for the three binary systems HFC-32 + hydrogen fluoride at 6.0 °C, CFC-12 + hydrogen fluoride at 30.0 °C, and chlorine + hydrogen fluoride at 30.0 °C are shown in Tables 1−3 and in Figures 1−3. The binary system difluoromethane + hydrogen fluoride forms a homogeneous liquid phase, and the others form minimum boiling heterogeneous azeotropes at the experimental conditions. The equation of vapor−liquid equilibrium for any component i is

$$y_i\phi_i P = x_i\gamma_i\phi_i^{s} P_i^{s} \exp((P - P_i^{s})\nu_i^{L}/RT) \tag{1}$$

where y_i is the vapor-phase mole fraction, ϕ_i is the fugacity coefficient of the vapor phase, P is the pressure, x_i is the liquid-phase mole fraction, γ_i is the activity coefficient, ν_i^{L} is the saturated-liquid molar volume, T is the temperature, and the superscript s indicates the saturation state. The fugacity coefficient ϕ_i was calculated by the association model combined with the Peng−Robinson cubic equation of state (1978) proposed by Lencka and Anderko (1993)

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Table 1. Vapor−Liquid Equilibria and Fugacity Coefficients ϕ for HFC-32 (1) + Hydrogen Fluoride (2) at 6.0 °C

P/kPa	x_1	y_1 (calc)	ϕ_1	ϕ_2
68.6	0.0000	0.0000	4.0743	0.4679
80.7	0.0020	0.0683	3.5563	0.4119
102.6	0.0060	0.1801	2.9059	0.3423
140.2	0.0133	0.3234	2.2907	0.2782
210.0	0.0284	0.4983	1.7550	0.2263
317.7	0.0581	0.6558	1.3887	0.1991
425.5	0.0935	0.7350	1.2197	0.1964
520.9	0.1343	0.7840	1.1256	0.2033
600.5	0.1802	0.8177	1.0682	0.2140
658.6	0.2241	0.8391	1.0276	0.2322
711.4	0.2768	0.8545	0.9971	0.2523
973.7	1.0000	1.0000	0.8741	1.0751
968.3	0.9885	0.9791	0.8752	1.0537
964.1	0.9751	0.9752	0.8766	1.0117
954.2	0.9517	0.9675	0.8791	0.9223
937.3	0.9189	0.9599	0.8831	0.8014
924.4	0.8779	0.9522	0.8885	0.6823
904.2	0.8057	0.9412	0.8971	0.5526
881.3	0.7147	0.9304	0.9064	0.4667
860.8	0.6264	0.9209	0.9158	0.4114
836.6	0.5373	0.9117	0.9276	0.3653
807.5	0.4683	0.9032	0.9392	0.3334
774.0	0.3858	0.8923	0.9573	0.2991
737.8	0.3215	0.8799	0.9781	0.2706
702.8	0.2712	0.8666	0.9997	0.2502

Table 2. Vapor−Liquid Equilibria and Fugacity Coefficients ϕ for CFC-12 (1) + Hydrogen Fluoride (2) at 30.0 °C

P/kPa	x_1	y_1 (calc)	ϕ_1	ϕ_2
146.9	0.0000	0.0000	3.2030	0.5817
147.7	0.0006	0.0312	2.9870	0.5428
182.2	0.0020	0.0949	2.6208	0.4769
234.1	0.0041	0.1721	2.2747	0.4149
298.2	0.0068	0.2482	2.0042	0.3665
371.5	0.0102	0.3196	1.7951	0.3294
449.1	0.0143	0.3817	1.6386	0.3013
531.4	0.0195	0.4383	1.5096	0.2793
612.7	0.0253	0.4824	1.4162	0.2636
683.1	0.0319	0.5177	1.3450	0.2519
745.1	0.0395	0.5459	1.2896	0.2431
810.6	0.0508	0.5731	1.2370	0.2353
868.4	0.0660	0.5945	1.1961	0.2311
883.6	0.0882	0.5945	1.1961	0.2311
886.4	0.1163	0.5945	1.1961	0.2311
750.1	1.0000	1.0000	0.8673	1.1034
781.6	0.9887	0.9661	0.8652	1.0147
811.8	0.9638	0.8786	0.8988	0.6099
849.4	0.9147	0.6293	1.1467	0.2503
868.5	0.8484	0.5945	1.1961	0.2311
880.6	0.7486	0.5945	1.1961	0.2311
888.0	0.6041	0.5945	1.1961	0.2311
884.2	0.4693	0.5945	1.1961	0.2311
903.1	0.3625	0.5945	1.1961	0.2311
901.4	0.2709	0.5945	1.1961	0.2311
893.7	0.2040	0.5945	1.1961	0.2311
887.3	0.1566	0.5945	1.1961	0.2311

without the use of a binary parameter. The complexity of the phase behavior for the mixtures containing hydrogen fluoride increases because of its unusually strong association. Anderko (1990, 1991) have shown that the compressibility factor (Z) can be determined from the following equation

$$Z = Z^{\mathrm{ph}} + Z^{\mathrm{ch}} - 1 \qquad (2)$$

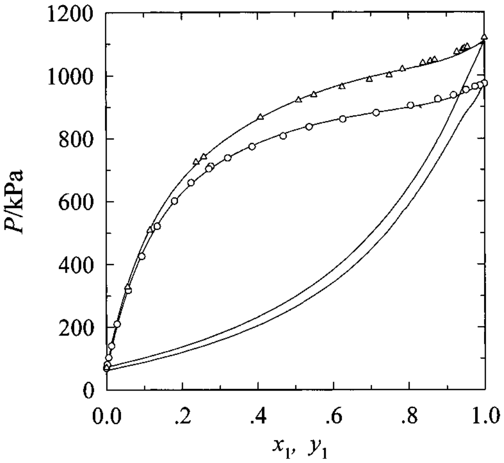

Figure 1. Equilibrium curve for HFC-32 (1) + hydrogen fluoride (2) at 6.0 °C: (△) experimental; (○) Lee et al. (1996) at 10.2 °C; (—) NRTL equation.

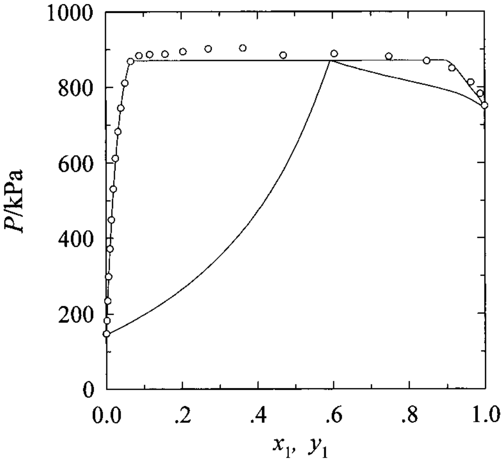

Figure 2. Equilibrium curve for CFC-12 (1) + hydrogen fluoride (2) at 30.0 °C: (○) experimental; (—) NRTL equation.

Table 3. Vapor−Liquid Equilibria and Fugacity Coefficients ϕ for Chlorine (1) + Hydrogen Fluoride (2) at 30.0 °C

P/kPa	x_1	y_1 (calc)	ϕ_1	ϕ_2
155.2	0.0000	0.0000	3.2214	0.5817
195.1	0.0015	0.0920	2.6611	0.4790
277.7	0.0049	0.2369	2.0764	0.3714
399.9	0.0101	0.3679	1.7167	0.3044
598.3	0.0196	0.4901	1.4581	0.2558
798.9	0.0317	0.5634	1.3227	0.2305
996.8	0.0498	0.6130	1.2347	0.2148
1044.2	0.0744	0.6279	1.2084	0.2110
1044.3	0.1098	0.6279	1.2084	0.2110
1049.5	0.1530	0.6279	1.2084	0.2110
1050.5	0.2017	0.6279	1.2084	0.2110
887.3	1.0000	1.0000	0.8988	1.0552
952.7	0.9837	0.9005	0.9240	0.6095
1021.9	0.9502	0.6279	1.2084	0.2118
1045.3	0.8873	0.6279	1.2084	0.2118
1058.7	0.7659	0.6279	1.2084	0.2118
1058.0	0.6328	0.6279	1.2084	0.2118
1054.9	0.4693	0.6279	1.2084	0.2118
1059.0	0.3508	0.6279	1.2084	0.2118
1058.3	0.2813	0.6279	1.2084	0.2118
1059.6	0.2256	0.6279	1.2084	0.2118

where the chemical (Z^{ch}) contribution is defined as the ratio of the number of moles of the true species in an associated mixture to the number of moles of the apparent species in the absence of association. The physical (Z^{ph}) contribution can be expressed by a common equation of state for the true monomeric species. The association model to obtain the Z^{ch} term for the mixtures containing hydrogen fluoride is well described by Lencka and Anderko (1993). The vapor pressures of the pure components were calculated from an

Table 4. Physical Properties and Constants for the Vapor Pressure Correlation of the Pure Components

component	T_c/K	P_c/kPa	ω	Z_{RA}	C_1	C_2	$100C_3$	C_4
HFC-32	351.3	5777	0.277	0.244	82.834	−4124.5	2.0285	−11.868
CFC-12	385.0	4129	0.179	0.280	75.732	−4127.3	1.6346	−10.581
chlorine	417.2	7710	0.069	0.281	64.451	−3855.6	1.2386	−8.522
HF	461.0	6480	0.372	0.120	103.102	−5179.4	2.8705	−15.705

Table 5. NRTL Parameters and Standard Deviations of the Measured Variables for the Binary Systems

					standard deviations		
system	t/°C	Δg_{12}/kJ·mol^{-1}	Δg_{21}/kJ·mol^{-1}	α_{12}	P/kPa	t/°C	$100x_1$
HFC-32(1) + HF(2)	6.0	4.300	2.910	0.525	0.4	0.09	0.05
CFC-12(1) + HF(2)	30.0	6.676	7.120	0.425	1.5	0.32	0.11
chlorine(1) + HF(2)	30.0	8.125	7.199	0.410	1.2	0.31	0.09

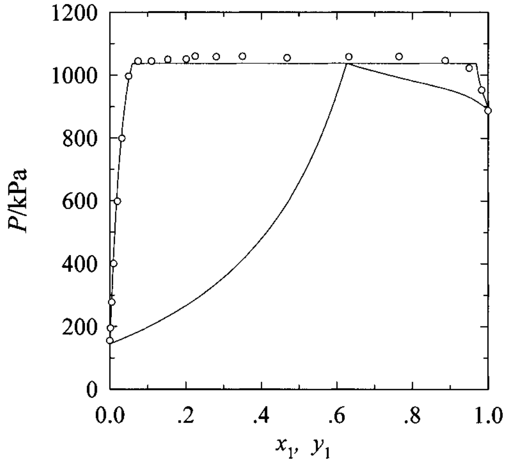

Figure 3. Equilibrium curve for chlorine (1) + hydrogen fluoride (2) at 30.0 °C: (○) experimental; (—) NRTL equation.

equation of the form

$$\ln(P_i^s/\mathrm{kPa}) = C_1 + C_2/(T/\mathrm{K}) + C_3(T/\mathrm{K}) + C_4 \ln(T/\mathrm{K}) \quad (3)$$

The liquid molar volume v^L at a given temperature was calculated from the modified Rackett equation (Spencer and Danner, 1972):

$$v^L = (RT_c/P_c)Z_{RA}^{1+(1-T_r)2/7} \quad (4)$$

The physical properties from Sato et al. (1994) for the organic materials, Reid et al. (1988) for hydrogen fluoride, Braker and Mossman (1980) for chlorine, and the recalculated constants C_1−C_4 of the pure components in the above equations are presented in Table 4. The activity coefficients in the liquid phase are correlated with the NRTL equation (Renon and Prausnitz, 1968)

$$\ln(\gamma_i) = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \left[\frac{x_j G_{ij}}{\sum_k x_k G_{ki}}\left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k x_k G_{kj}}\right)\right] \quad (5)$$

where

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \quad (6)$$

$$\tau_{ji} = \Delta g_{ji}/RT \quad (7)$$

The binary interaction parameters of the NRTL equation, Δg_{ji}, were evaluated by a nonlinear regression method based on 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)

$$F = \sum_j \left(\frac{(P^j_{\mathrm{exptl}} - P^j_{\mathrm{calcd}})^2}{\sigma_P^2} + \frac{(T^j_{\mathrm{exptl}} - T^j_{\mathrm{calcd}})^2}{\sigma_T^2} + \frac{(x^j_{1,\mathrm{exptl}} - x^j_{1,\mathrm{calcd}})^2}{\sigma_{x_1}^2} \right) \quad (8)$$

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 and the fugacity coefficients of each component calculated by the vapor-phase association model at the given experimental temperatures and liquid-phase mole fractions for the three binary systems (HFC-32 + hydrogen fluoride, CFC-12 + hydrogen fluoride, chlorine + hydrogen fluoride) 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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