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Isothermal Vapor−Liquid Equilibria for the Systems 1-Chloro-1,1-difluoroethane + Hydrogen Fluoride, 1,1-Dichloro-1-fluoroethane + Hydrogen Fluoride, and Chlorodifluoromethane + Hydrogen Fluoride

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Isothermal vapor−liquid equilibria for the three binary systems (1-chloro-1,1-difluoroethane + hydrogen fluoride, 1,1-dichloro-1-fluoroethane + hydrogen fluoride, and chlorodifluoromethane + 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. All of the systems form minimum boiling heterogeneous azeotropes.

Introduction

1,1-Dichloro-1-fluoroethane (HCFC-142b), 1-chloro-1,1-difluoroethane (HCFC-142b), and 1,1,1-trifluoroethane (HFC-143a) are normally manufactured by fluorination of 1,1,1-trichloroethane (HCC-140a) or vinylidene chloride in the presence or absence of the catalyst. HCFC-142b, HCFC-141b, and HFC-143a are presently under consideration as new chlorofluorocarbon alternatives. For the effective separation of the reaction mixture into its components, the phase behaviors of these mixtures are required. The liquid−liquid equilibria for HCFC-142b + HCFC-141b + hydrogen fluoride and the vapor−liquid equilibria for the systems composed of HCFC-142b, HCFC-141b, and HCC-140a were reported by Kang and Lee (1995, 1996), but the vapor−liquid equilibria for HCFC-142b + hydrogen fluoride and HCFC-141b + hydrogen fluoride have not been reported in the literature. In this study, the isothermal vapor−liquid equilibria for the three binary systems HCFC-142b + hydrogen fluoride at 10.0 °C and 30.0 °C, HCFC-141b + hydrogen fluoride at 10.0 °C, and chlorofluoromethane (HCFC-22) + hydrogen fluoride at 25.0 °C were measured and correlated with the NRTL equation with the vapor-phase association model of Lenka and Anderko (1993).

Experimental Section

Chemicals. HCFC-142b (Allied-Signal, Inc.), HCFC-141b (Elf Atochem, Inc.), and HCFC-22 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 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 (1995). The equilibrium temperature was measured with a T-type thermocouple converter (Yokogawa Electric Corp., Model STED-210-TT*B) having an accuracy of ±0.1 deg. The equilibrium pressure was determined by a gauge pressure transmitter (Yokogawa Electric 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 both phases were estimated by using the association model combined with the Peng−Robinson cubic equation of state (1976) proposed by Lencka and Anderko (1993). The standard deviation of the liquid-phase composition was ±0.001.

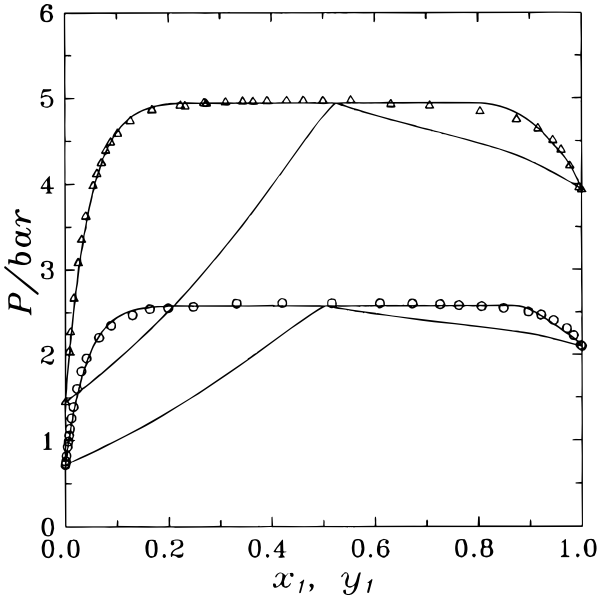

Figure 1. Equilibrium curve for HCFC-142b (1) + hydrogen fluoride (2) at 10.0 °C and 30.0 °C: (○) experimental at 10.0 °C; (△) experimental at 30.0 °C; (−) NRTL equation.

Results and Discussion

The experimental vapor−liquid equilibrium data for the three binary systems HCFC-142b + hydrogen fluoride at 10.0 °C and 30.0 °C, HCFC-141b + hydrogen fluoride at 10.0 °C, and HCFC-22 + hydrogen fluoride at 25.0 °C are shown in Tables 1−3 and in Figures 1−3. It was impossible to measure the vapor−liquid equilibria for the system HCFC-141b + hydrogen fluoride at 30.0 °C because of the reaction of their components. Figure 3 also shows a

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Table 1. Vapor−Liquid Equilibria for HCFC-142b (1) + Hydrogen Fluoride (2) at 10.0 °C and 30.0 °C

P/bar	x_1	y_1(calcd)	ϕ_1	ϕ_2
		t = 10 °C		
0.715	0.0000	0.0000	3.8850	0.4885
0.729	0.0003	0.0051	3.8246	0.4816
0.757	0.0009	0.0150	3.7115	0.4687
0.822	0.0022	0.0355	3.4964	0.4444
0.926	0.0042	0.0649	3.2281	0.4142
0.990	0.0056	0.0839	3.0741	0.3970
1.060	0.0071	0.1031	2.9325	0.3814
1.137	0.0089	0.1245	2.7881	0.3656
1.260	0.0120	0.1580	2.5876	0.3439
1.391	0.0156	0.1922	2.4090	0.3251
1.604	0.0227	0.2480	2.1624	0.3001
1.807	0.0310	0.2984	1.9759	0.2826
1.960	0.0408	0.3436	1.8317	0.2703
2.203	0.0652	0.4159	1.6356	0.2572
2.345	0.0885	0.4544	1.5450	0.2538
2.468	0.1301	0.4884	1.4719	0.2536
2.540	0.1637	0.4998	1.4485	0.2545
2.548	0.1991	0.5047	1.4388	0.2551
2.566	0.2478	0.5064	1.4348	0.2556
2.603	0.3316	0.5064	1.4348	0.2556
2.610	0.4202	0.5064	1.4348	0.2556
2.607	0.5164	0.5064	1.4348	0.2556
2.604	0.6097	0.5064	1.4348	0.2556
2.601	0.6725	0.5064	1.4348	0.2556
2.591	0.7261	0.5064	1.4348	0.2556
2.581	0.7624	0.5064	1.4348	0.2556
2.568	0.8061	0.5064	1.4348	0.2556
2.546	0.8489	0.5064	1.4348	0.2556
2.504	0.8967	0.5357	1.3766	0.2701
2.467	0.9211	0.6206	1.2333	0.3227
2.403	0.9452	0.7506	1.0714	0.4520
2.307	0.9707	0.8903	0.9605	0.7726
2.226	0.9836	0.9379	0.9453	0.9264
2.108	0.9977	0.9901	0.9434	1.0328
2.096	1.0000	1.0000	0.9438	1.0394
		t = 30 °C		
1.461	0.0000	0.0000	3.1893	0.5817
2.055	0.0073	0.1045	2.5308	0.4757
2.285	0.0106	0.1423	2.3508	0.4477
2.683	0.0171	0.2042	2.1006	0.4099
3.093	0.0253	0.2648	1.8968	0.3809
3.370	0.0321	0.3045	1.7806	0.3655
3.637	0.0402	0.3426	1.6793	0.3531
3.996	0.0546	0.3930	1.5581	0.3404
4.135	0.0618	0.4124	1.5153	0.3367
4.261	0.0705	0.4318	1.4739	0.3337
4.405	0.0794	0.4482	1.4403	0.3317
4.500	0.0884	0.4618	1.4130	0.3306
4.599	0.1019	0.4781	1.3816	0.3298
4.745	0.1267	0.4986	1.3435	0.3301
4.873	0.1685	0.5165	1.3115	0.3318
4.928	0.2234	0.5245	1.2974	0.3334
4.953	0.2691	0.5247	1.2972	0.3334
4.963	0.3111	0.5247	1.2972	0.3334
4.973	0.3641	0.5247	1.2972	0.3334
4.983	0.4299	0.5247	1.2972	0.3334
4.981	0.5000	0.5247	1.2972	0.3334
4.917	0.2327	0.5247	1.2972	0.3334
4.949	0.2736	0.5247	1.2972	0.3334
4.972	0.3441	0.5247	1.2972	0.3334
4.978	0.3918	0.5247	1.2972	0.3334
4.984	0.4619	0.5247	1.2972	0.3334
4.987	0.5541	0.5247	1.2972	0.3334
4.939	0.6317	0.5247	1.2972	0.3334
4.921	0.7069	0.5247	1.2972	0.3334
4.855	0.8043	0.5250	1.2966	0.3336
4.761	0.8745	0.5856	1.1983	0.3754
4.654	0.9162	0.6932	1.0620	0.4774
4.520	0.9449	0.8078	0.9600	0.6694
4.407	0.9607	0.8642	0.9272	0.8066
4.224	0.9771	0.9168	0.9122	0.9420
3.971	0.9952	0.9798	0.9111	1.0518
3.945	1.0000	1.0000	0.9124	1.0650

Table 2. Vapor−Liquid Equilibria for HCFC-141b (1) + Hydrogen Fluoride (2) at 10.0 °C

P/bar	x_1	y_1(calcd)	ϕ_1	ϕ_2
0.711	0.0000	0.0000	3.8623	0.4885
0.718	0.0003	0.0036	3.8180	0.4837
0.747	0.0014	0.0162	3.6707	0.4678
0.804	0.0038	0.0406	3.4143	0.4404
0.900	0.0082	0.0762	3.0946	0.4073
1.001	0.0137	0.1086	2.8482	0.3830
1.085	0.0217	0.1393	2.6440	0.3644
1.100	0.0318	0.1393	2.6440	0.3644
1.090	0.1469	0.1393	2.6440	0.3644
1.086	0.2083	0.1393	2.6440	0.3644
1.099	0.2999	0.1393	2.6440	0.3644
1.115	0.4628	0.1393	2.6440	0.3644
1.109	0.6396	0.1393	2.6440	0.3644
1.087	0.7873	0.1393	2.6440	0.3644
1.037	0.8954	0.1503	2.5308	0.3756
0.786	0.9573	0.4063	1.3455	0.5904
0.553	0.9883	0.7812	0.9913	0.9372
0.430	1.0000	1.0000	0.9837	1.0114

Table 3. Vapor−Liquid Equilibria for HCFC-22 (1) + Hydrogen Fluoride (2) at 25.0 °C

P/bar	x_1	y_1(calcd)	ϕ_1	ϕ_2
1.220	0.0000	0.0000	3.3744	0.5600
1.412	0.0012	0.0346	3.1067	0.5171
1.731	0.0036	0.0959	2.7198	0.4555
2.320	0.0086	0.1982	2.2441	0.3808
4.283	0.0295	0.4348	1.5682	0.2805
5.427	0.0457	0.5258	1.3900	0.2579
6.681	0.0687	0.6019	1.2598	0.2448
7.652	0.0939	0.6516	1.1814	0.2399
8.617	0.1301	0.6974	1.1126	0.2418
9.394	0.1756	0.7298	1.0670	0.2462
9.912	0.2259	0.7520	1.0372	0.2524
10.154	0.2703	0.7661	1.0193	0.2582
9.452	0.1793	0.7318	1.0642	0.2467
9.842	0.2205	0.7501	1.0398	0.2517
10.129	0.2753	0.7675	1.0176	0.2589
10.490	0.3703	0.7900	0.9908	0.2724
10.720	0.5000	0.8146	0.9639	0.2939
10.834	0.6642	0.8220	0.9562	0.3021
10.867	0.7922	0.8220	0.9562	0.3021
10.859	0.8684	0.8220	0.9562	0.3021
10.815	0.9298	0.8501	0.9320	0.3469
10.702	0.9724	0.9547	0.8605	0.7930
10.564	0.9925	0.9872	0.8543	1.0579
10.492	1.0000	1.0000	0.8550	1.1030

comparison with the results reported by Wilson et al. (1989). This graphical representation shows good agreement between our results and theirs. All of the binary systems form minimum boiling heterogeneous azeotropes at the experimental temperatures. The equation of vapor−liquid equilibrium for any component i is

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

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 (1976) proposed by Lencka and Anderko (1993) not using 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) has shown that the compressibility factor (Z) can be determined from the following equation:

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

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

component	T_c/K	P_c/bar	ω	Z_{RA}	C_1	C_2	$100C_3$	C_4
HCFC-142b	410.26	40.40	0.226	0.279	39.397	−3202.0	4.7794	−3.0449
HCFC-141b	477.31	42.50	0.222	0.269	124.63	−6560.4	2.1247	−17.147
HCFC-22	369.30	49.70	0.221	0.267	97.559	−4447.2	2.1188	−13.182
HF	461.00	64.80	0.372	0.120	110.01	−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	$100x_1$
HCFC-142b (1) + HF (2)	10.0	5.811	5.458	0.428	1.0	0.08	0.07
	30.0	5.670	5.596	0.428	0.8	0.12	0.04
HCFC-141b (1) + HF (2)	10.0	6.288	8.231	0.416	0.7	0.02	0.02
HCFC-22 (1) + HF (2)	25.0	6.545	4.591	0.449	0.3	0.08	0.04

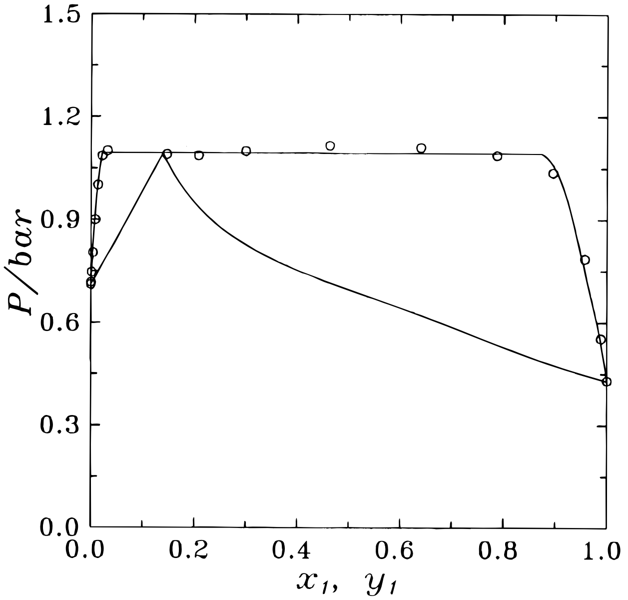

Figure 2. Equilibrium curve for HCFC-141b (1) + hydrogen fluoride (2) at 10.0 °C: (○) experimental; (—) NRTL equation.

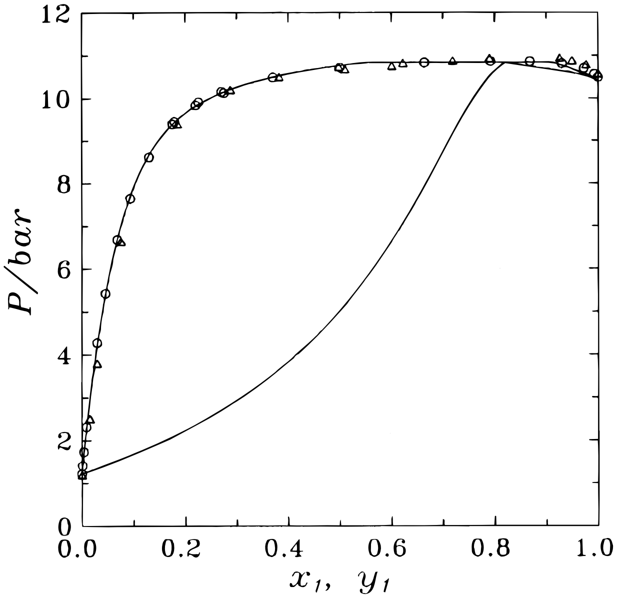

Figure 3. Equilibrium curve for HCFC-22 (1) + hydrogen fluoride (2) at 25.0 °C: (○) experimental; (△) data of Wilson et al. (1989); (—) NRTL equation.

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 equation of the form

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

The liquid molar volume v^L at a given temperature was calculated from the modified Rackett equation (Spencer and Danner, 1972). The physical properties from Sato et al. (1994) for the organic materials and Reid et al. (1988) for hydrogen fluoride, and the recalculated constants C_1–C_4 of the pure components in the above equations from Reid et al. (1988) are presented in Table 4. The activity coefficients in the liquid phase are correlated with the NRTL equation (Renon and Prausnitz, 1968):

$$\log(\gamma_i) = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \left[\frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k x_k G_{kj}} \right) \right] \quad (4)$$

where

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \quad (5)$$

$$\tau_{ji} = \Delta g_{ji}/RT \quad (6)$$

The binary interaction parameters of the NRTL equation, Δg_{ji}, 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):

$$F = \sum_j \left\{ \frac{(P^j_{\text{exptl}} - P^j_{\text{calcd}})^2}{\sigma_P^{\,2}} + \frac{(T^j_{\text{exptl}} - T^j_{\text{calcd}})^2}{\sigma_T^{\,2}} + \frac{(x^j_{1,\text{exptl}} - x^j_{1,\text{calcd}})^2}{\sigma_{x_1}^{\,2}} \right\} \quad (7)$$

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, we chose $\sigma_P = 1.0$ kPa, $\sigma_T = 0.1$ °C, and $\sigma_{x_1} = 0.001$. 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 (HCFC-142b + hydrogen fluoride, HCFC-141b + hydrogen fluoride, HCFC-22 + hydrogen fluoride) are presented in Tables 1−3. The comparison of the experimental and calculated equilibrium data is 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. As shown in the literature (Kang and Lee, 1995), the liquid-phase splits for the two binary systems (HCFC-142b + hydrogen fluoride and HCFC-141b + hydrogen fluoride) at the experimental temperatures were predicted, but the prediction of liquid−liquid equilibria using the NRTL binary parameters obtained by data reduction of the experimental vapor−liquid equilibrium data is poor.

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