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Liquid−Liquid Equilibria for Hydrogen Fluoride + 1,1-Dichloro-1-fluoroethane + 1-Chloro-1,1-difluoroethane at −20 and 20 °C

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Liquid−liquid equilibria for the ternary system (hydrogen fluoride + 1,1-dichloro-1-fluoroethane + 1-chloro-1,1-difluoroethane) have been measured at −20 and 20 °C. The results are correlated with the NRTL model, and the relevant parameters are presented.

Introduction

1,1-Dichloro-1-fluoroethane (hereinafter referred to as HCFC-141b) is presently under consideration as a replacement for trichlorofluoromethane, which is widely used as a foam blowing agent. 1-Chloro-1,1-difluoroethane (hereinafter referred to as HCFC-142b) is the major raw material for the production of poly(vinylidene fluoride). These two materials are normally manufactured by the fluorination of 1,1,1-trichloroethane or vinylidene chloride with hydrogen fluoride. The product stream from which hydrogen chloride is primarily removed contains mainly HCFC-141b, HCFC-142b, and unreacted hydrogen fluoride (*1, 2*). A phase separator is normally used to retrieve hydrogen fluoride from the product stream. To design the phase separator, liquid−liquid equilibrium data are required. In this study, the liquid−liquid equilibria for the ternary system hydrogen fluoride + HCFC−141b + HCFC−142b was measured at −20 and 20 °C and correlated with the NRTL model.

Table 1. Liquid−Liquid Equilibrium Data for Hydrogen Fluoride (1) + HCFC-141b (2) + HCFC-142b (3) at −20 and 20 °C

	light phase			heavy phase		
t/°C	x_1	x_2	x_3	x_1	x_2	x_3
−20	0.9859	0.141	0.0000	0.0179	0.9821	0.0000
	0.9739	0.0125	0.0135	0.0237	0.7102	0.2661
	0.9631	0.0110	0.0259	0.0381	0.5149	0.4470
	0.9472	0.0089	0.0439	0.0436	0.3425	0.6139
	0.9353	0.0064	0.0583	0.0691	0.1915	0.7394
	0.9125	0.0000	0.0875	0.1424	0.0000	0.8576
20	0.9761	0.0239	0.0000	0.0928	0.9072	0.0000
	0.9574	0.0231	0.0195	0.1326	0.6249	0.2425
	0.9559	0.0168	0.0273	0.1731	0.4432	0.3837
	0.9434	0.0145	0.0421	0.2330	0.2870	0.4800
	0.9102	0.0075	0.0823	0.2434	0.0991	0.6575
	0.8528	0.0000	0.1472	0.3091	0.0000	0.6909

Table 2. NRTL Parameters and Standard Errors for Hydrogen Fluoride + HCFC-141b + HCFC−142b at −20 and 20 °C

		NRTL parameters			
t/°C	system component i + component j	Δg_{ij}/ (kJ·mol^{-1})	Δg_{ji}/ (kJ·mol^{-1})	α_{ij}	SD (%)
−20	HF + HCFC-141b	5.598	5.682	0.15	
	HF + HCFC-142b	4.261	3.278	0.30	0.3
	HCFC-141b + HCFC-142b	0.431	−0.553	0.50	
20	HF + HCFC-141b	7.089	1.816	0.15	
	HF + HCFC-142b	5.037	2.250	0.30	1.1
	HCFC-141b + HCFC-142b	−2.621	−0.134	0.50	

Experimental Section

Chemicals. HCFC-141b and HCFC-142b (PCR Research Chemicals, Inc.) and anhydrous hydrogen fluoride (ULSAN Chemical Co.) were of guaranteed reagent grade and were used without further purification. Chromatographic analysis on organic materials showed major peak areas of more than 99.5 mass %.

Apparatus and Procedure. The static apparatus was used to measure LLE. The equilibrium cell, which was manufactured with 316 stainless steel, was placed in an isothermal methanol bath, and the bath temperature was controlled within an accuracy of ±0.1 °C by using a Haake circulator (Model F3-K). The volume of the equilibrium cell was 150 cm^3. To reduce the dead volume in the sampling lines, narrow tubes of 0.8 mm i.d. and 3.2 mm o.d. for both phases were installed.

The equilibrium cell containing about 50 cm^3 of hydrogen fluoride and 70 cm^3 of HCFC mixture was shaken and then was held to equilibrate for a period of 20 h in an isothermal bath. The cell was pressurized to 7 bar with nitrogen gas. The boiling points of the pure components hydrogen fluoride, HCFC-141b, and HCFC-142b at 7 bar are 85, 102, and 51 °C, respectively. To measure the concentration of hydrogen fluoride in the heavy phase (the HCFC-rich phase), about 25 g of a liquid sample was placed in a 150 cm^3 pressure cylinder which was filled with 100 cm^3 of water. The mass of the sample was measured with a balance having an accuracy of ±0.1 g. The water-rich phase containing hydrogen fluoride was titrated with standard NaOH solution. To determine the ratio of HCFC-141b to HCFC-142b in the heavy phase of the ternary system, about 5 g of a liquid sample in the pressure cylinder was removed and then mixed with about 150 g of perchloroethylene. The organic sample which contains perchloroethylene was analyzed with a Varian Model 2440-10 gas chromatograph using a flame ionization detector. Finally, about 5 g of the light phase (hydrogen fluoride-rich phase) was mixed with about 150 g of perchloroethylene. The ratio of HCFC-141b to HCFC-142b and the total amount of the HCFC mixture in the light phase were quantified by a gas chromatographic analysis. There are two reasons for mixing the two liquid phases with perchloroethylene. The first reason is that the bubble point temperature of the organic phase at atmospheric pressure was higher than room temperature, so the analysis of the liquid sample by gas chromatograph could be possible. The other reason is that the amount of the HCFC mixture existing in the organic phase of the mixture containing perchloroethylene could be minimized because the solubil-

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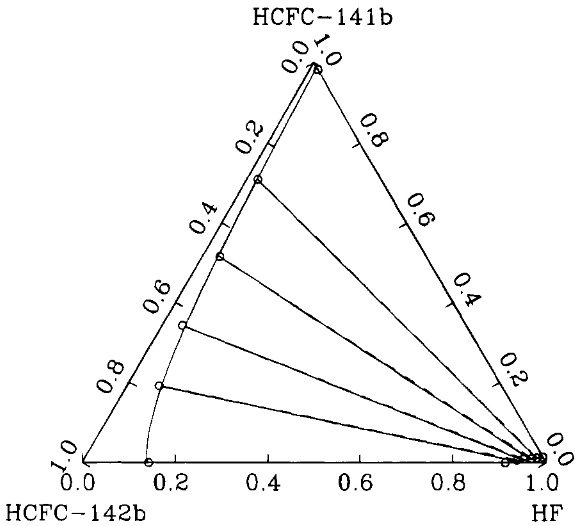

Figure 1. Liquid–liquid equilibria and NRTL correlation for hydrogen fluoride + HCFC-141b + HCFC-142b at −20 °C: (O- - -) experimental; (—) NRTL equation.

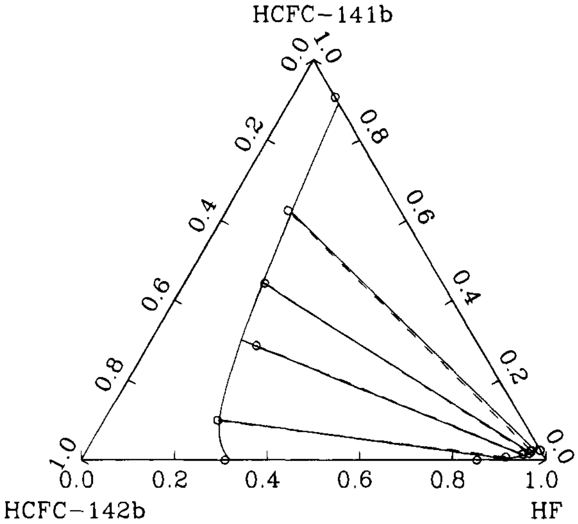

Figure 2. Liquid–liquid equilibria and NRTL correlation for hydrogen fluoride + HCFC-141b + HCFC-142b at 20 °C: (O- - -) experimental; (—) NRTL equation.

ity of perchloroethylene to hydrogen fluoride is very small. For the analysis of the light phase, the percentage of the HCFC mixture dissolved in the organic phase which contains perchloroethylene was more than 98 mass %. A 6 m long and 3.2 mm diameter DC-200 column was operated at 100 °C, with the detector at 200 °C and the injector at 200 °C. The peak area percents were converted to the mass percents using the weight factors determined by the analysis of mixtures of known composition. The standard deviation of the above analysis method between analyzed and known compositions was found to be about 0.2 mass fraction.

Results and Discussion

The experimental liquid−liquid equilibrium (LLE) results at −20 and 20 °C for the system hydrogen fluoride + HCFC-141b + HCFC-142b are shown in Table 1. The effect of temperature on the mutual solubility of hydrogen fluoride and HCFC was significant. The LLE data were correlated with the NRTL equation (*3*). To obtain the interaction parameters, $(g_{ij} - g_{jj})$ and $(g_{ji} - g_{ii})$, and nonrandomness parameter α_{ij}, the least-squares method proposed by Varhegyl and Eon (*4*) was used. The objective function (Z) in the data reduction is defined by

$$Z = \sum_{j=1}^{N} \sum_{i=1}^{3} \sum_{k=1}^{2} (x^{j}_{ik,\mathrm{exptl}} - x^{j}_{ik,\mathrm{calcd}})^2 \qquad (1)$$

where $x^j_{ik,\mathrm{exptl}}$ is the experimental mole fraction of component i in phase k and $x^j_{ik,\mathrm{calcd}}$ the calculated mole fraction using the NRTL model; j and N denote a tie line and the number of experimental tie lines, respectively. The interaction parameters, which were calculated from the solubility data for the binary systems hydrogen fluoride + HCFC-141b and hydrogen fluoride + HCFC-142b and by assuming an ideal solution for the system HCFC-141b + HCFC-142b, were used as the starting values for minimizing the objective function, Z. The binary interaction and nonrandomness parameters obtained by data reduction and standard errors at two different temperatures are presented in Table 2. The experimental and calculated equilibrium data for the ternary system at −20 and 20 °C are presented in Figures 1 and 2, respectively. As shown in these figures and by the low standard deviations in Table 2, the calculated and experimental data agree very well. However, some of the NRTL parameters obtained at two different temperatures showed considerably different values. Therefore, the NRTL parameters are recommended to apply in the narrow range of the experimental temperature for the prediction of LLE.

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