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Vapor−Liquid Equilibria for the Systems Composed of 1-Chloro-1,1-difluoroethane, 1,1-Dichloro-1-fluoroethane, and 1,1,1-Trichloroethane at 50.1 °C

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Isothermal vapor−liquid equilibria for the three binary systems 1-chloro-1,1-difluoroethane + 1,1-dichloro-1-fluoroethane, 1-chloro-1,1-difluoroethane + 1,1,1-trichloroethane, and 1,1-dichloro-1-fluoroethane + 1,1,1-trichloroethane and the ternary system 1-chloro-1,1-difluoromethane + 1,1-dichloro-1-fluoroethane + 1,1,1-trichloroethane have been measured at 50.1 °C. The experimental data for the binary systems are correlated with the Peng−Robinson equation of state, and the relevant parameters are presented. The predicted results for the ternary system were found to be in good agreement with the experimental data.

Introduction

1,1-Dichloro-1-fluoroethane (HCFC-142b), 1-chloro-1,1-difluoroethane (HCFC-142b), and 1,1,1-trifluoroethane are normally manufactured by fluorination of 1,1,1-trichloroethane (HCC-140a) or vinylidene chloride in the presence or absence of the catalyst. HCFC-141b and 1,1,1-trifluoroethane are presently under consideration as a new foam blowing agent and new promising alternative refrigerants blended with difluoromethane, pentafluoroethane, and/or 1,1,1,2-tetrafluoroethane, respectively. HCFC-142b is the major raw material for the production of poly(vinylidene fluoride). For the effective separation of the reaction mixture into its valuable components, the vapor−liquid equilibrium (VLE) data for the various mixtures are required. No measurements have been reported in the literature. In this study, the isothermal vapor−liquid equilibria for the three binary systems and the ternary system composed of HCFC-142b, HCC-140a, and HCFC-141b were measured at 50.1 °C and correlated with the Peng−Robinson equation of state.

Experimental Section

Chemicals. HCFC-142b (Allied-Signal, Inc.), HCFC-141b (Elf Atochem, Inc.), and HCC-140a (Tosoh Corp.) were of guaranteed reagent grade and were used without any further purification. A chromatographic analysis on the reagents showed major peak areas of more than 99.8%.

Apparatus and Procedure. A static equilibrium apparatus was used to determine the isothermal VLE. The equilibrium cell, which was manufactured with 316 stainless steel pipe of 65 mm diameter, was placed in an isothermal water bath controlled with an accuracy of ±0.1 °C using a Haake circulator (model F3-K). The liquid phase was mixed with a magnetic stirrer. A cooling coil, 15 cm long and 1.6 mm in diameter, was installed in the vapor phase to reach the equilibrium compositions quickly by condensing the vapor phase. A electrical heater around the connecting tubing between the equilibrium cell and sampling loop for the vapor was used to prevent condensation of vapor. The volume of the equilibrium cell was 545 cm^3. When the equilibrium pressure was attained in the cell, this pressure was maintained for 1 h to ensure equilibrium conditions. 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 °C. The equilibrium pressure was determined by a gauge pressure transmitter (Yokogawa Electric Corp., model UNE43-SAS3*B) and a barometer having accuracies of ±0.5 kPa and ±0.05 kPa, respectively.

After the cell was evacuated to 1 Pa, a known mass of the component having a higher normal boiling point was introduced into the cell. The mass was determined with a digital balance having an accuracy of ±0.01 g. A known mass of the component having a lower normal boiling point was added. To change the compositions in the cell, the additional masses of the second component were added. The compositions of the vapor phase were measured using a GowMac gas chromatograph provided with a thermal conductivity detector. The total mass of the vapor-phase samples used for three gas chromatographic analyses to obtain one set of VLE data was about 0.3 g. The mass of each sample was calculated using an estimated vapor density at the pressure of the sampling cylinder. The volume of the sampling cylinder was 155 cm^3. A 6 m long, 3.2 mm diameter Porapak Q column was operated at 210 °C, with the detector at 220 °C and the injector at 220 °C. The peak areas were converted to the mass fractions using weight factors determined by the gas chromatographic analysis of mixtures of known composition. The standard deviation of the above analysis method between analyzed and known mole fractions was found to be ±0.003. The compositions of the liquid phase were calculated by mass balance from the known mass existing in the vapor phase. The densities of both phases were estimated using the Peng and Robinson (1978) equation of state (PR EOS) 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 loss caused by the vapor-phase sampling, the accuracy of the estimated densities of the both phases, and error in the analysis of the vapor phase. The effect of 10% errors in the estimated densities for the liquid and vapor phases gives errors of approximately 0.0001 and 0.0005 in the respective mole fraction. The standard deviation of the liquid-phase mole fractions was ±0.001.

Results and Discussion

The experimental vapor−liquid equilibrium data at 50.1 °C for the three binary systems and one ternary system, HCFC-142b + HCFC-141b, HCFC-142b + HCC-140a, HCFC-141b + HCC-140a, and HCFC-142b + HCFC-141b + HCC-140a, are given in Tables 1 and 2. The VLE data

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Table 1. Vapor–Liquid Equilibrium Data for Binary Systems at 50.1 °C

P/kPa	x_1	y_1	P/kPa	x_1	y_1
		HCFC-142b (1) + HCFC-141b (2)			
185.0	0.0000	0.0000	535.2	0.6969	0.8703
234.0	0.0924	0.2619	417.3	0.4625	0.7302
283.2	0.1879	0.4436	526.9	0.6822	0.8638
333.2	0.2866	0.5726	581.5	0.7924	0.9165
383.1	0.3880	0.6687	635.1	0.8993	0.9584
432.5	0.4895	0.7492	684.6	1.0000	1.0000
483.9	0.5932	0.8141			
		HCFC-142b (1) + HCC-140a (2)			
46.5	0.0000	0.0000	524.4	0.7354	0.9697
118.9	0.0878	0.6495	353.4	0.4354	0.9217
185.6	0.1769	0.7968	484.3	0.6662	0.9639
252.5	0.2664	0.8657	551.6	0.7854	0.9760
316.9	0.3707	0.9031	619.8	0.8971	0.9890
383.1	0.4807	0.9312	684.6	1.0000	1.0000
440.0	0.5829	0.9505			
		HCFC-141b (1) + HCC-140a (2)			
46.5	0.0000	0.0000	144.6	0.6991	0.9031
61.6	0.0970	0.3114	158.0	0.8003	0.9421
75.6	0.1946	0.5020	116.4	0.4893	0.8037
87.3	0.2802	0.6259	145.5	0.6943	0.9103
104.3	0.3960	0.7326	156.4	0.7975	0.9404
116.9	0.4972	0.8051	172.0	0.9000	0.9741
130.5	0.5985	0.8579	185.0	1.0000	1.0000

Table 2. Vapor–Liquid Equilibrium Data for HCFC-142b (1) + HCFC-141b (2) + HCC-140a (3) at 50.1 °C

P/kPa	x_1	x_2	y_1	y_2
93.4	0.1571	0.6240	0.2083	0.2131
211.9	0.1628	0.5737	0.3355	0.3075
231.6	0.1644	0.5101	0.5012	0.4161
255.0	0.1648	0.4592	0.6690	0.5063
302.4	0.3293	0.8067	0.1670	0.1070
318.7	0.3296	0.7380	0.3347	0.2036
335.8	0.3305	0.6771	0.5019	0.2956
404.5	0.4985	0.8682	0.1671	0.0848
418.2	0.5011	0.8137	0.3329	0.1622
195.0	0.1646	0.6717	0.1662	0.1637
265.3	0.2403	0.6570	0.3660	0.2681
500.0	0.6674	0.9084	0.1664	0.0712

Table 3. Physical Properties of Pure Components

component	formula	MW	T_b/K	T_c/K	P_c/kPa	ω
HCFC-142b	CH_3CClF_2	100.50	263.40	410.26	404.0	0.226
HCFC-141b	CH_3CCl_2F	116.95	305.37	477.31	425.0	0.222
HCC-140a	CH_3CCl_3	133.40	347.23	545.00	424.0	0.214

Table 4. Binary Parameters of the PR EOS and Standard Deviations for the Binary Systems at 50.1 °C

system component 1 + component 2	θ_{12}	standard deviations			
		P/kPa	T/°C	x_1/%	y_1/%
HCFC-142b + HCFC-141b	0.0076	0.1	0.05	0.02	0.60
HCFC-142b + HCC-140a	0.0259	0.2	0.06	0.05	0.92
HCFC-141b + HCC-140a	0.0074	0.3	0.05	0.02	0.99

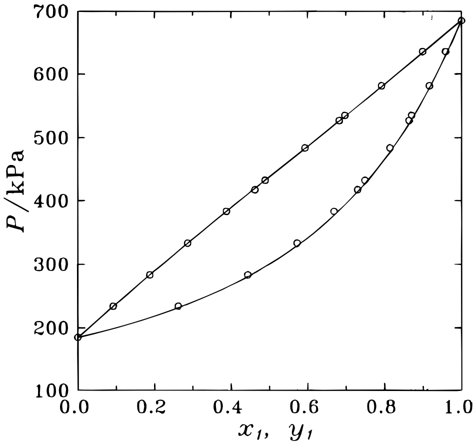

Figure 1. Equilibrium curve for HCFC-142b (1) + HCFC-141b (2) at 50.1 °C: (○) experimental; (—) PR EOS.

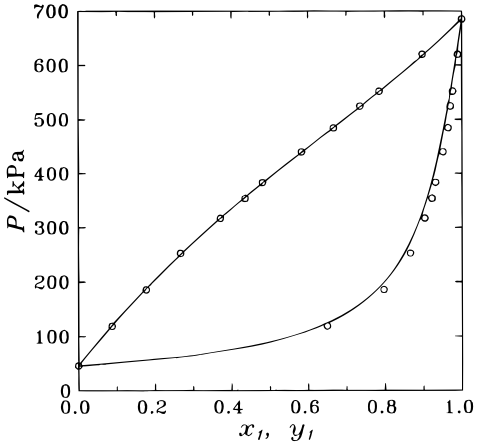

Figure 2. Equilibrium curve for HCFC-142b (1) + HCC-140a (2) at 50.1 °C: (○) experimental; (—) PR EOS.

for the three binary systems were correlated by the PR EOS:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{1}$$

where

$$a(T) = (0.45724R^2T_c^{\,2}/P_c)\alpha(T) \tag{2}$$

$$b = 0.07780RT_c/P_c \tag{3}$$

with

$$\alpha(T) = (1 + \kappa(1 - T_r^{\,0.5}))^2 \tag{4}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

The mixture parameters used are defined by the van der Waals one-fluid mixing rule:

$$a_m = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - \theta_{ij}) \tag{6}$$

$$b_m = \sum_i x_i b_i \tag{7}$$

In the above equations, T_c is the critical temperature, P_c the critical pressure, ω the acentric factor, and θ_{ij} the binary interaction parameter. The physical properties of pure components used in this work are given in Table 3. The binary interaction parameters of the PR EOS 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 (Z):

$$Z = \sum_j \left\{ \frac{(P^j_{\text{exptl}} - P^j_{\text{calcd}})^2}{\sigma_P^{\,2}} + \frac{(T^j_{\text{exptl}} - T^j_{\text{calcd}})^2}{\sigma_T^{\,2}} + \frac{(x^j_{1,\text{exptl}} - x^j_{1,\text{calcd}})^2}{\sigma_{x_1}^{\,2}} + \frac{(y^j_{1,\text{exptl}} - y^j_{1,\text{calcd}})^2}{\sigma_{y_1}^{\,2}} \right\} \tag{8}$$

where σ is the estimated standard deviation of each of the

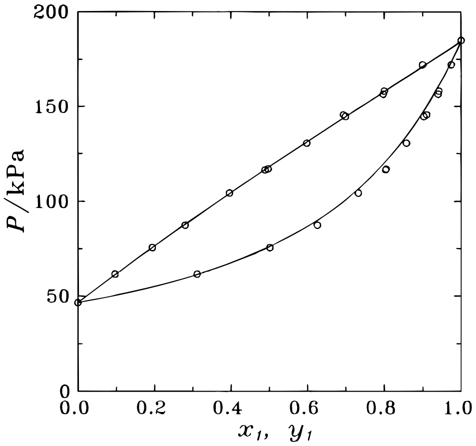

Figure 3. Equilibrium curve for HCFC-141b (1) + HCC-140a (2) at 50.1 °C: (○) experimental; (—) PR EOS.

measured variables, i.e., pressure, temperature, and liquid-phase and vapor-phase mole fractions. In data reduction, we chose $\sigma_P = 0.5$ kPa, $\sigma_T = 0.1$ °C, $\sigma_{x_1} = 0.001$, and $\sigma_{y_1} = 0.003$.

The binary interaction parameters obtained by data reduction and the standard deviations of the measured variables of the binary systems are presented in Table 4. The standard deviations of the measured pressure and vapor-phase mole fractions of the ternary system HCFC-142b (1) + HCFC-141b (2) + HCC-140a (3) calculated by the PR EOS were as follows: $\sigma_P = 1.5$ kPa, $\sigma_{y_1} = 0.0033$, $\sigma_{y_2} = 0.0042$, and $\sigma_{y_3} = 0.0039$. The experimental and calculated equilibrium data for the three binary systems HCFC-142b + HCFC-141b, HCFC-142b + HCC-140a, and HCFC-141b + HCC-140a at 50.1 °C are shown in Figures 1−3. As shown in these figures and by the low standard deviations of the measured variables, the calculated and experimental values for all systems including the ternary system are in good agreement.

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