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Isobaric Vapor–Liquid Equilibria for the Systems $C_2Cl_2F_4$–$C_2Cl_3F_3$, $C_2Cl_2F_4$–$C_2Cl_4F_2$, and $C_2Cl_3F_3$–$C_2Cl_4F_2$

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Isobaric vapor–liquid equilibria for the three binary systems $C_2Cl_2F_4$–$C_2Cl_3F_3$, $C_2Cl_2F_4$–$C_2Cl_4F_2$, and C_2Cl_3F–$C_2Cl_4F_2$ were measured at 760 ± 1 mmHg pressure by using a modified Jones vapor recirculatory still. All the three binary systems show slight positive deviations from Raoult's law. The experimental data were well correlated with the Wilson equation.

Introduction

In the fluorination of perchloroethylene in the presence of an antimony catalyst, a reaction mixture comprising mainly 1,1,2-trichloro-1,2,2-trifluoroethane ($C_2Cl_3F_3$) and 1,2-dichloro-1,1,2,2-tetrafluoroethane ($C_2Cl_2F_4$) with a small amount of 1,1,2,2-tetrachloro-1,2-difluoroethane ($C_2Cl_4F_2$) is produced. The next step is to effectively separate the reaction mixture into their valuable components in an easy and economical manner. Hence, knowledge of vapor–liquid equilibrium data for their binary systems are essential in the design of separation equipment. However, no experimental data have been previously reported in the literature. In this study, the isobaric vapor–liquid equilibria for the three binary systems $C_2Cl_2F_4$–$C_2Cl_3F_3$, $C_2Cl_2F_4$–$C_2Cl_4F_2$, and $C_2Cl_3F_3$–$C_2Cl_4F_2$ were measured at 760 ± 1 mmHg and correlated with the Wilson equation.

Experimental Section

Chemicals. 1,2-Dichloro-1,1,2,2-tetrafluoroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, and 1,1,2,2-tetrachloro-1,2-difluoroethane supplied by PCR Research Chemicals, Inc., were of guaranteed reagent grade and used without further purification. A chromatographic analysis on them showed major peak areas of more than 99.9%.

Apparatus and Procedure. An all-glass modified Jones (*1*) vapor recirculation still was used to determine the VLE data. A still with a total capacity of about 50 mL was used. The condensate chamber was slightly heated to prevent the solidification of $C_2Cl_4F_2$ (mp 26 °C). When the equilibrium temperature was attained in the still, this temperature was maintained for 2 h to ensure equilibrium conditions. The temperature in the still was measured with an Omega digital thermometer having an accuracy of ±0.1 °C. The vapor and liquid compositions were determined by using a Yamagimoto 1800 gas chromatography provided with a thermal conductivity detector. The column packed with Chromosorb P was 25 ft long and $^1/_8$ in. in diameter. For all systems, the column was operated at 180 °C, the detector at 200 °C, and the injector at 200 °C. The flow rate of GC-grade helium carrier was maintained at 30 mL/min. The peak area ratio determined by using a Shimadzu Model 1 C-R1B data processor was converted to the weight composition of the mixture from the previous calibration analysis. The estimated accuracy of the equilibrium mixture composition measurements was better than ±0.5%.

Table I. Vapor–Liquid Equilibrium Data for $C_2Cl_2F_4$ (1)–$C_2Cl_3F_3$ (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
45.85	0.0279	0.1052	0.9572	0.9998
44.80	0.0416	0.1504	0.9688	0.9995
42.35	0.0662	0.2333	0.9868	0.9990
40.20	0.0971	0.3127	1.0048	0.9983
39.10	0.1106	0.3467	1.0111	0.9980
35.80	0.1462	0.4300	1.0240	0.9978
32.80	0.1877	0.5076	1.0328	0.9977
26.60	0.2962	0.6580	1.0352	1.0021
23.70	0.3614	0.7157	1.0290	1.0077
21.00	0.4425	0.7697	1.0216	1.0144
17.55	0.4972	0.8203	1.0131	1.0235
17.50	0.5133	0.8279	1.0116	1.0254
14.75	0.5872	0.8635	1.0059	1.0336
11.25	0.6944	0.9177	1.0029	1.0416
9.20	0.7705	0.9441	1.0013	1.0441
8.30	0.8207	0.9594	1.0013	1.0451
7.10	0.8818	0.9744	1.0010	1.0476

Table II. Vapor–Liquid Equilibrium Data for $C_2Cl_2F_4$ (1)–$C_2Cl_4F_2$ (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
88.00	0.0087	0.1318	1.4965	1.0000
80.00	0.0272	0.3267	1.4760	1.0003
69.20	0.0574	0.5211	1.1137	1.0013
61.20	0.0879	0.6311	1.4126	1.0030
33.80	0.2698	0.9052	1.2554	1.0292
25.00	0.3868	0.9437	1.1772	1.0621
14.40	0.5881	0.9749	1.0787	1.1544

Table III. Vapor–Liquid Equilibrium Data for $C_2Cl_3F_3$ (1)–$C_2Cl_4F_2$ (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
82.90	0.0917	0.3023	1.1231	1.0012
80.15	0.1313	0.3976	1.1120	1.0024
76.30	0.1915	0.5000	1.0963	1.0052
72.62	0.2497	0.5852	1.0824	1.0088
66.15	0.3852	0.7319	1.0546	1.0211
64.80	0.4094	0.7623	1.0503	1.0239
61.60	0.4940	0.8147	1.0367	1.0349
56.80	0.6318	0.8871	1.0193	1.0578
55.70	0.6573	0.8948	1.0167	1.0627
54.80	0.6939	0.9142	1.0133	1.0701
52.40	0.7595	0.9242	1.0082	1.0845
50.10	0.8413	0.9544	1.0035	1.1047

Results and Discussion

The vapor–liquid equilibrium data at 760 ± 1 mmHg for the three systems $C_2Cl_2F_4$–$C_2Cl_3F_3$, $C_2Cl_2F_4$–$C_2Cl_4F_2$, and $C_2Cl_3F_3$–$C_2Cl_4F_2$ are presented in Tables I–III, respectively. The liquid-phase activity coefficients for each component were

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Table IV. Constants for Vapor Pressure Correlation

compd	C_1	C_2	C_3	C_4	C_5
$C_2Cl_4F_2$[a]	549.23	-12237.8	0.379 87	-106.37	-0.000 201
$C_2Cl_3F_3$[b]	22.279	-4833.1	-0.031 09	0	0.000 027
$C_2Cl_2F_4$[b]	-95.566	-1811.9	-0.103 98	22.345	0.000 069

[a] From ref *3*. [b] From ref *4*.

Table V. Wilson Parameters and Mean Deviations of the Temperatures and Mole Fractions in the Vapor Phase

			mean deviation	
system	$\Delta\lambda_{12}$	$\Delta\lambda_{21}$	T	y_1
$C_2Cl_2F_4$ (1)–$C_2Cl_3F_3$ (2)	300.07	-201.02	0.47	0.0023
$C_2Cl_2F_4$ (1)–$C_2Cl_4F_2$ (2)	-194.48	751.30	0.71	0.0024
$C_2Cl_3F_3$ (1)–$C_2Cl_4F_2$ (2)	-390.42	947.14	0.50	0.0041

calculated from the $T-x-y$ data, taking into account the nonideality of the vapor phase, by employing the equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^{s}} + \frac{(B_{ii} - v_i)(P - P_i^{s})}{RT} + (1 - y_i)^2 \frac{P\delta}{RT} \quad (1)$$

where

$$\delta = 2B_{ij} - B_{ii} - B_{jj}$$

The pure component and cross second virial coefficients for the three binary mixtures were estimated from the method of Hayden and O'Connell (*2*). The vapor pressures of the pure components were calculated from an equation of the form

$$\ln P_i^{s} = C_1 + C_2/T + C_3 T + C_4 \ln T + C_5 T^2 \quad (2)$$

The constants C_1–C_5 for the pure components are listed in Table IV. The liquid molar volume v_i at a given temperature was calculated from the modified Rackett equation (*5*)

$$v_i = (RT_c/P_c) Z_{RA}^{1+(1-T_r)^{2/7}} \quad (3)$$

The values of the modified Rackett parameter, Z_{RA}, are 0.267 65 for $C_2Cl_4F_2$, 0.259 42 for $C_2Cl_3F_3$, and 0.281 26 for $C_2Cl_2F_4$. The activity coefficients tabulated in Tables I–III show that all of the three systems present a slight deviation from ideal solution behavior. An iterative nonlinear least-squares minimization procedure described in detail by Fredenslund et al. (*6*) was carried out to calculate the average absolute deviations between experimental and calculated y_1 values. The resulting AAD values are 0.007 14 for the $C_2Cl_2F_4$–$C_2Cl_3F_3$ system, 0.002 44 for the $C_2Cl_2F_4$–$C_2Cl_4F_2$ system, and 0.003 76 for the $C_2Cl_3F_3$–$C_2Cl_4F_2$ system. The experimental VLE data for the three binary systems are thus considered to be thermodynamically consistent. The activity coefficients were correlated with the Wilson equation (*7*)

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right] \quad (4)$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right]$$

where

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left[-\frac{\Delta\lambda_{12}}{RT} \right] \quad \text{and} \quad \Lambda_{21} = \frac{v_1}{v_2} \exp\left[-\frac{\Delta\lambda_{21}}{RT} \right]$$

The binary parameters of the Wilson equation were evaluated by a nonlinear regression method based on the maximum-likelihood principle (*8*) and are summarized in Table V. The mean deviations of the temperatures and mole fractions in the vapor phase calculated by the Wilson equation with these parameters are also included in Table V. Figures 1–3 show the equilibrium curves representing the mole fractions in the vapor phase calculated from Raoult's law and Wilson equation. The three binary systems exhibiting slight positive deviations from Raoult's law were well correlated with the two-parameter Wilson equation.

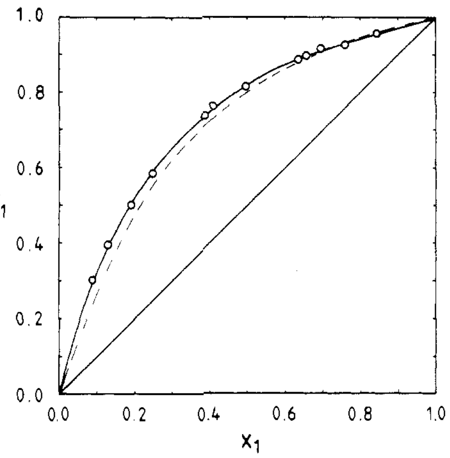

Figure 1. Equilibrium curve for the system $C_2Cl_2F_4$ (1)–$C_2Cl_3F_3$ (2) at 760 mmHg: (O) experimental; (—) Wilson equation; (- - -), Raoult's law.

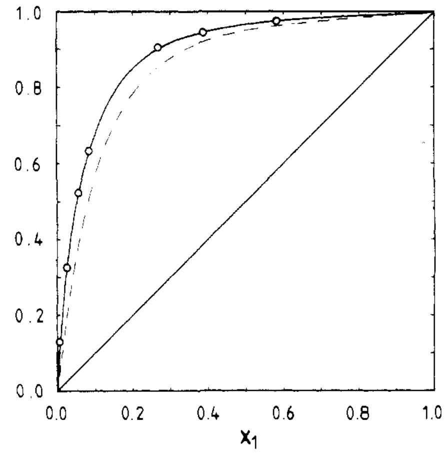

Figure 2. Equilibrium curve for the system $C_2Cl_2F_4$ (1)–$C_2Cl_4F_2$ (2) at 760 mmHg: (O) experimental; (—) Wilson equation; (- - -), Raoult's law.

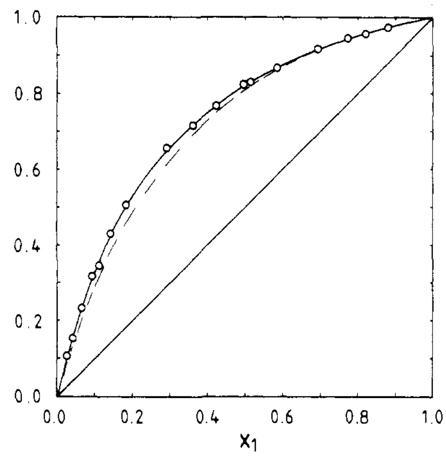

Figure 3. Equilibrium curve for the system $C_2Cl_3F_3$ (1)–$C_2Cl_4F_2$ (2) at 760 mmHg: (O) experimental; (—) Wilson equation; (- - -), Raoult's law.

Glossary

P	total pressure, bar
P_c	critical pressure, bar
P_i^s	vapor pressure of pure component i, bar
R	gas constant, cal K^{-1} mol^{-1}
T	temperature, K
T_c	critical temperature, K
T_r	reduced temperature
v_i	liquid molar volume of pure component i
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
Z_{RA}	modified Rackett parameter

Greek Letters

γ_i	activity coefficient of component i
Λ	Wilson binary parameter
λ	Wilson energy parameter, cal mol^{-1}

Registry No. $C_2Cl_2F_4$, 76-14-2; $C_2Cl_4F_2$, 76-12-0; $C_2Cl_3F_3$, 76-13-1.

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Vapor–Liquid Equilibria of Tetrahydrofuran Systems

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Accurate vapor–liquid equilibrium data have been measured for tetrahydrofuran separately with hexane, with cyclohexane, and with ethyl acetate at both 313.15 and 333.15 K, for ethyl acetate with cyclohexane at 313.15 K, and for a ternary mixture of ethyl acetate, cyclohexane, and tetrahydrofuran at 313.15 K. The binary data reported satisfy thermodynamic consistency tests. The results of our measurements are correlated with five thermodynamic models using the maximum likelihood parameter estimation method. The ternary data are predicted accurately by both the multicomponent Wilson and NRTL models using parameters obtained from the binary vapor–liquid equilibrium data. Also, tetrahydrofuran is found to be an effective azeotropic distillation agent for changing the relative volatility of ethyl acetate to cyclohexane and breaking the azeotrope.

Introduction

Accurate vapor–liquid equilibrium (VLE) data are important to the design of separation processes and in the testing and further development of thermodynamic models. There are few VLE studies for cyclic ethers (e.g., furfural, tetrahydrofuran) with hydrocarbons or with oxyhydrocarbons, even though cyclic ethers have been found to be useful in breaking azeotropes (*1*). For example, furfural has been used as an extractive distillation agent in separating saturated and unsaturated hydrocarbons. Therefore, studies of these systems are both important to the chemical industry and helpful in improving the predictive ability of the UNIFAC (*2*, *3*) and TOM (*4*, *5*) group-contribution activity-coefficient models.

In this study we report the results of our measurements for binary mixtures of tetrahydrofuran separately with hexane, with cyclohexane, and with ethyl acetate at both 313.15 and 333.15 K, for ethyl acetate with cyclohexane at 313.15 K, and for a ternary mixture of ethyl acetate, cyclohexane, and tetrahydrofuran at 313.15 K. From the data we obtain the excess molar Gibbs free energy, G^E, for each isotherm. For mixtures for which G^E is available at two temperatures we also calculate molar heats of mixing which we compare with direct measurements of this quantity. Our experimental data are of high quality, as evidenced by this comparison and by using thermodynamic consistency tests.

Experiments

The experimental equipment and operating procedure have been described previously (*6*). The VLE measurements were done with a Stage-Muller dynamic still, temperature measurements were made with a platinum resistance thermometer (Rosemount Model 162N) accurate to 0.02 K with a resolution of 0.001 K, and pressures were measured with an accuracy of 0.02 kPa with a Wallace-Tiernan Model FA-187 precision mercury manometer. The vapor and liquid samples were analyzed by a Hewlett-Packard Model 5730 gas chromatograph with a Model 3390 integrator, after calibration with gravimetrically prepared samples. The compositions determined are accurate to better than 0.005 in mole fraction.

Since the purity of chemicals is essential to obtaining accurate VLE measurements, a check of the purity is very important. We checked the purity of each component first by gas chromatography, and then by comparing its vapor pressure measured in the Stage-Muller still with data in the literature. If the area fraction was greater than 0.995, and the vapor pressures were within 0.1 kPa of the reported vapor pressure data, we used the chemical for VLE measurements without purification. In this study all chemicals used were gold label quality from Aldrich Chemical Co. Tetrahydrofuran, cyclohexane, and ethyl acetate, as received, satisfied these purity tests. Our measured vapor pressure data, shown in Table I, agree with those reported in literature (*7*), as seen in Table II. However, tetrahydrofuran is hygroscopic at room temperature; tetrahydrofuran contamination by moisture is evident as anomalous vapor pressures. When this occurred, molecular sieves were used to remove the water. Hexane, which did not satisfy the purity tests, was purified by using a 13-stage Oldershaw distillation column at low pressure under a nitrogen blanket. The vapor

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