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Vapor−Liquid Equilibrium Data for the Binary Decafluoropentane (HFC-43-10meec) + Heptane, Decafluoropentane + Butyl Ethyl Ether, Octafluorobutane (HFC-338pcc) + Butyl Ethyl Ether, and Heptafluoro Propyl Methyl Ether (HFE-347mcc) + HFC-338pcc Systems at 101.3 kPa

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Isobaric vapor−liquid equilibria were measured for the four binary systems of decafluoropentane (HFC-43-10meec) + heptane, decafluoropentane + butyl ethyl ether, octafluorobutane (HFC-338pcc) + butyl ethyl ether, and heptafluoro propyl methyl ether (HFE-347mcc) + HFC-338pcc systems at atmospheric pressure. The HFC-43-10meec + heptane system formed a minimum-boiling azeotrope. The experimental data were correlated by the Wilson and NRTL models. The Wilson and NRTL equations gave similar results.

Introduction

The development of new mixed cleaning solvents with no chlorine atoms has been pursued because hydrochlorofluorocarbons containing chlorine atoms have ozone depletion potential. To design and develop the manufacturing steps for new mixed cleaning solvents containing hydrofluoroethers, ASOG group pair parameters have been determined using vapor−liquid equilibrium (VLE) data measured in this project.[1]

This paper reports the experimental VLE data for the four binary systems decafluoropentane ($CF_3CHFCHFCF_2CF_3$,HFC-43-10meec) + heptane, decafluoropentane + butyl ethyl ether, octafluorobutane ($CHF_2CF_2CF_2CHF_2$, HFC-338pcc) + butyl ethyl ether, and heptafluoro propyl methyl ether ($CF_3CF_2CF_2OCH_3$, HFE-347mcc) + HFC-338pcc at 101.3 kPa. VLE data for the four binary systems are not available in the literature.

Experimental Section

Apparatus and Procedure. For this VLE measurement, we have used a modified Rogalski-Malanowski equilibrium still. This still described by Tochigi et al.[2,3] is a liquid−vapor ebullition type. The pressure in the still was measured using a Fortin-type mercury barometer. Because the barometric pressure changed slightly, the experimental temperatures were corrected to 101.3 kPa.[4] The equilibrium temperature was measured with a calibrated platinum resistance thermometer with an accuracy of ±0.01 K.

Analysis. Vapor and liquid samples were analyzed with a gas chromatograph (HP-GC6890 series) equipped with a flame ionization detector. Pora PLOT Q and HP-FFAP(GL Science Co.) were used as column packing, and helium was used as the carrier gas. The relationship between peak area and composition was determined from an analysis of samples of known composition. The accuracy of the equilibrium concentration was estimated to be ±0.004 in mole fraction.

Table 1. Purity, Densities ρ, and Normal Boiling Points T_b of the Components

		ρ(293.15 K)/(kg m^{-3})		T_b/K	
compound	purity/%	exptl	lit	exptl	lit[a]
HFC-43-1-meec	99.9	1586.3	-	327.04	-
HFC-338pcc	99.9	1562.9	-	317.39	-
HFE-347mcc	99.9	1409.2	1409.4[b]	307.31	307.33[b]
heptane	99.9	679.5[a]	679.46[c]	371.76	371.65[c]
butyl ethyl ether	99.8	745.3[a]	744.8[c]	365.35	365.35[c]

[a] This value was measured at 298.15 K. [b] The value is measured by RITE. [c] Riddick et al.[5]

Table 2. Antoine Constants[a] and Liquid Molar Volumes of Components

component	A	B	C	$\nu_i^L \times 10^6$ / m^3 mol^{-1}
HFC-43-10meec[b]	5.76802	912.407	−84.530	158.89
HFC-338ppc[b]	6.11874	1065.96	−58.223	129.28
HFE-347mcc[b]	5.60563	807.079	−83.116	141.94
heptane[c]	6.01980	1264.90	−56.606	146.50
butyl ethyl ether[c]	6.06345	1252.49	−56.685	136.24

[a] $\log(P/\text{kPa}) = A - B/[T/\text{K} + C]$. [b] The values were determined by RITE. [c] The values were published by Gmehling and Onken.

Materials. HFC-43-10meec, HFC-338pcc, HFE-347mcc, and butyl ethyl ether were provided by the Research Institute of Innovative Technology for the Earth (RITE). Heptane was a special grade pure reagent (Wako Pure Chemical Industry, Inc., Japan). These materials were used without further purification. In Table 1, the purity and

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Table 3. Isobaric Vapor−Liquid Equilibrium Data, Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, Temperature T, and Activity Coefficients γ_i for the Four Binary Systems at 101.3 kPa

x_1	y_1	T/K	γ_1	γ_2	x_1	y_1	T/K	γ_1	γ_2	x_1	y_1	T/K	γ_1	γ_2
							HFC-43-10meec (1) + Heptane (2)							
0.000	0.000	371.76		1.000	0.729	0.863	326.77	1.196	2.347	0.957	0.950	326.73	1.003	5.513
0.184	0.766	333.00	3.384	1.045	0.797	0.869	326.56	1.109	3.035	0.979	0.971	326.83	1.000	6.570
0.210	0.789	330.85	3.295	1.057	0.830	0.876	326.65	1.071	3.398	1.000	1.000	327.04	1.000	
0.622	0.850	327.07	1.366	1.821	0.900	0.898	326.60	1.014	4.774					
							HFC-43-10meec (1) + Butyl Ethyl Ether (2)							
0.000	0.000	365.35		1.000	0.450	0.749	334.20	1.299	1.277	0.817	0.890	328.82	1.023	2.061
0.116	0.503	346.71	2.255	1.005	0.471	0.761	333.64	1.283	1.294	0.841	0.904	328.42	1.024	2.104
0.194	0.608	341.58	1.924	1.038	0.497	0.772	333.13	1.256	1.321	0.875	0.921	328.05	1.016	2.230
0.250	0.657	339.20	1.737	1.065	0.526	0.782	332.69	1.221	1.363	0.907	0.938	327.75	1.009	2.373
0.277	0.675	338.21	1.667	1.083	0.598	0.807	331.59	1.151	1.480	0.936	0.956	327.49	1.005	2.510
0.317	0.700	337.11	1.565	1.103	0.698	0.842	330.27	1.076	1.701	0.966	0.975	327.26	1.002	2.669
0.342	0.708	336.46	1.496	1.142	0.787	0.875	329.25	1.028	1.983	1.000	1.000	327.04	1.000	
0.387	0.728	335.27	1.415	1.193										
							HFC-338pcc (1) + Butyl Ethyl Ether (2)							
0.000	0.000	365.35		1.000	0.459	0.818	330.15	1.152	1.120	0.747	0.924	322.26	1.047	1.368
0.153	0.526	346.31	1.340	1.034	0.484	0.832	329.24	1.146	1.123	0.775	0.932	321.65	1.040	1.411
0.196	0.594	342.94	1.306	1.050	0.542	0.856	327.41	1.119	1.165	0.804	0.940	321.06	1.033	1.465
0.234	0.644	340.67	1.271	1.047	0.573	0.867	326.62	1.101	1.190	0.832	0.948	320.51	1.026	1.515
0.264	0.676	338.91	1.249	1.056	0.601	0.877	325.84	1.091	1.215	0.862	0.957	319.94	1.021	1.562
0.295	0.706	337.26	1.229	1.063	0.634	0.889	324.83	1.085	1.245	0.891	0.965	319.41	1.015	1.645
0.338	0.743	335.01	1.213	1.075	0.661	0.897	324.20	1.074	1.279	0.917	0.973	318.92	1.012	1.701
0.372	0.767	333.51	1.194	1.087	0.690	0.908	323.49	1.067	1.286	0.946	0.982	318.38	1.010	1.783
0.395	0.783	332.57	1.183	1.089	0.718	0.916	322.89	1.056	1.322	1.000	1.000	317.39	1.000	
0.436	0.806	330.95	1.164	1.110										
							HFE-347mcc (1) + HFC-338pcc (2)							
0.000	0.000	317.39		1.000	0.373	0.463	312.57	1.027	1.025	0.655	0.723	309.95	1.002	1.062
0.059	0.087	316.43	1.066	1.005	0.394	0.480	312.39	1.014	1.034	0.727	0.782	309.30	1.000	1.083
0.116	0.164	315.67	1.050	1.008	0.441	0.529	311.88	1.016	1.035	0.754	0.805	309.07	1.001	1.085
0.172	0.235	314.90	1.042	1.013	0.460	0.547	311.70	1.014	1.038	0.782	0.828	308.85	1.001	1.090
0.222	0.298	314.25	1.047	1.013	0.509	0.593	311.24	1.010	1.044	0.811	0.851	308.63	1.000	1.098
0.240	0.320	314.03	1.048	1.013	0.524	0.606	311.12	1.007	1.047	0.839	0.874	308.42	1.000	1.099
0.260	0.343	313.82	1.044	1.013	0.552	0.631	310.84	1.005	1.053	0.941	0.955	307.67	1.002	1.103
0.299	0.384	313.37	1.033	1.020	0.584	0.660	310.55	1.004	1.056	0.968	0.976	307.49	1.002	1.092
0.337	0.425	312.95	1.029	1.023	0.613	0.686	310.30	1.003	1.059	1.000	1.000	307.31	1.000	
0.356	0.444	312.75	1.025	1.026										

Table 4. Results[a] of Thermodynamic Consistency Tests of VLE Data for Four Binary Systems at 101.3 kPa

test	HFC-43-10meec (1) + heptane (2)	HFC-43-10meec (1) + butyl ethyl ether (2)	HFC-338pcc(1) + butyl ethyl ether (2)	HFE-347mcc(1) + HFC-338pcc(2)
point[b]	+	+	+	+
Δy_1	0.009	0.008	0.005	0.005
area[c]	+	+	+	-
$D - J$/%	−15.78	−7.11	−3.07	-

[a] Results of the tests are characterized by the signs "+" (pass) and "−" (fail). [b] The criterion for passing the test is $\Delta y_1 \le 0.010$ absolute in mole fraction.[6,8] [c] The criterion for passing the test is $D - J \le 10\%$.[7,8]

Table 5. Parameters for the Four Binary Systems Using the Wilson and NRTL Equations

system	Wilson equation		NRTL equation		
	$\lambda_{12} - \lambda_{11}$[a]	$\lambda_{12} - \lambda_{11}$[a]	$g_{12} - g_{22}$	$g_{21} - g_{11}$	α_{12}
HFC-43-10meec (1) + heptane (2)	3058.2	3812.1	3522.2	2807.0	0.40
HFC-43-10meec (1) + butyl ethyl ether (2)	1972.6	1643.4	1220.1	2308.6	0.45
HFC-338pcc (1) + butyl ethyl ether (2)	256.1	1333.3	1737.2	−111.3	0.47
HFE-347mcc (1) + HFC-338pcc (2)	172.6	100.6	−195.8	468.2	0.35

[a] J mol^{-1}.

Table 6. Deviations between the Calculated and Experimental Vapor-Phase Mole Fractions Δy_1 and Temperature Change ΔT for the Four Binary Systems Using the Wilson and NRTL Equations[a]

system		Wilson equation		NRTL equation	
		Δy_1	ΔT/K	Δy_1	ΔT/K
HFC-43-10meec (1) + heptane (2)	ave	0.009	0.56	0.009	0.51
	max	0.028	2.30	0.023	2.32
HFC-43-10meec (1) + butyl ethyl ether (2)	ave	0.006	0.40	0.006	0.41
	max	0.012	0.76	0.013	0.80
HFC-338pcc (1) + butyl ethyl ether (2)	ave	0.007	0.36	0.008	0.35
	max	0.021	0.93	0.019	0.85
HFE-347mcc (1) + HFC-338pcc (2)	ave	0.005	0.03	0.005	0.03
	max	0.010	0.06	0.010	0.06

[a] $\Delta y_1 = \sum_k |y_{1,\text{exptl}} - y_{1,\text{calcd}}|_k/N$, $\Delta T = \sum_k |T_{\text{exptl}} - T_{\text{calcd}}|_k/N$, N = number of data points.

some measured properties of the samples are shown together with literature values.

Experimental Results

The four experimentally determined binary VLE data points are shown in Table 3 and Figures 1 to 8. The activity coefficients γ_i in Table 3 and Figures 5 to 8 were calculated by the following equation

$$Py_i = x_i \gamma_i P_i^{\text{S}} \qquad (1)$$

in which the vapor phase is assumed to be an ideal gas because it was not possible with the available information to calculate the vapor-phase fugacity coefficients of HFC-43-10meec, HFC-338pcc, and HFE-347mcc. In eq 1,

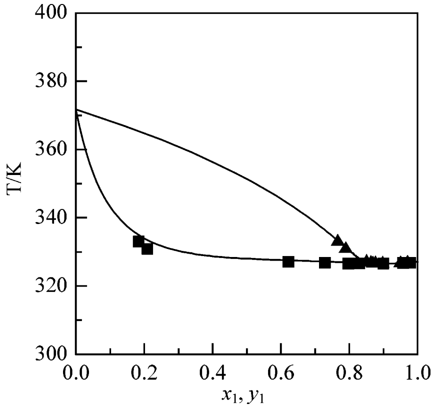

Figure 1. Temperature–composition diagram for the HFC-43-10meec (1) + heptane (2) system: ■, experimental liquid-phase mole fractions x_1; ▲, experimental vapor-phase mole fractions y_1; –, NRTL equation.

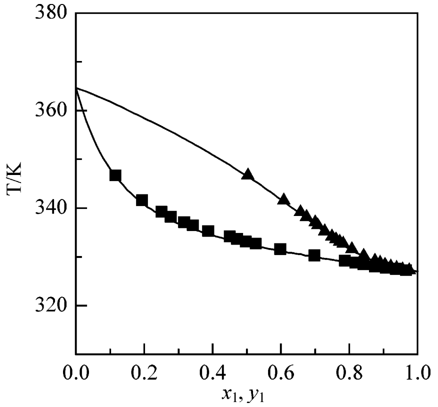

Figure 2. Temperature–composition diagram for the HFC-43-10meec (1) + butyl ethyl ether (2) system: ■, experimental liquid-phase mole fractions x_1; ▲, experimental vapor-phase mole fractions y_1; –, NRTL equation.

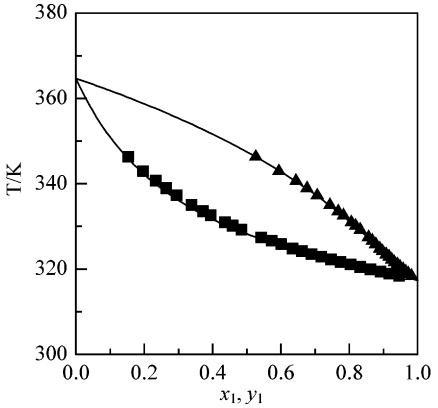

Figure 3. Temperature–composition diagram for the HFC-338pcc (1) + butyl ethyl ether (2) system: ■, experimental liquid-phase mole fractions x_1; ▲, experimental vapor-phase mole fractions y_1; –, NRTL equation.

the vapor pressures of the pure components P_i^S were calculated from the Antoine equation constants shown in Table 2.

The experimental VLE data were examined by thermodynamic consistency using the point test of Fredenslund et al.[6] and the area test of Herington[7] as described by Gmehling and Onken.[8] The consistency of the data for the HFE-347mcc + HFC-338pcc system was checked only by the point test because all of the γ_i values were close to 1, indicating that this system at atmospheric pressure is

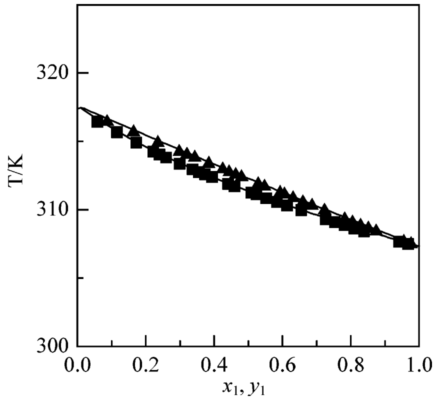

Figure 4. Temperature–composition diagram for the HFE-347mcc (1) + HFC-338pcc (2) system: ■, experimental liquid-phase mole fractions x_1; ▲, experimental vapor-phase mole fractions y_1; –, NRTL equation.

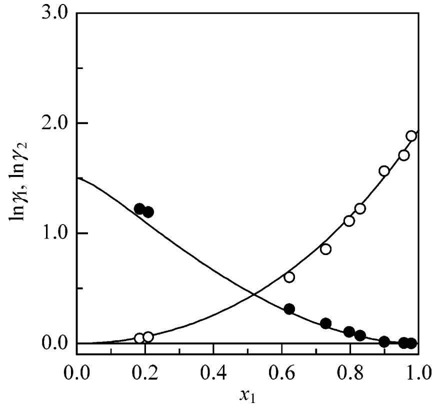

Figure 5. Activity coefficient–liquid composition for the HFC-43-10meec (1) + heptane (2) system: ● and ○, experimental; –, NRTL equation.

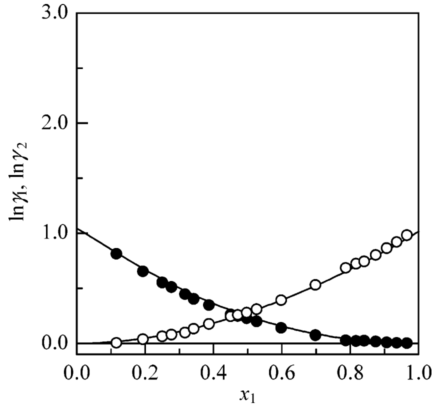

Figure 6. Activity coefficient–liquid composition for the HFC-43-10meec (1) + butyl ethyl ether (2) system: ● and ○, experimental; –, NRTL equation.

nearly an ideal solution. The results of these consistency tests are shown in Table 4. The reported data were found to be thermodynamically consistent according to the point and area tests.

The HFC-43-10meec + heptane system forms a minimum-boiling azeotrope. The binary azeotropic point was determined by a graphical method[9] on the basis of experimental VLE data and is $x_{1(AZ)} = 0.910$ and $T_{(AZ)} = 326.53$ K.

Correlation

The activity coefficients of the four binary systems were correlated by the Wilson[10] and NRTL[11] equations. The

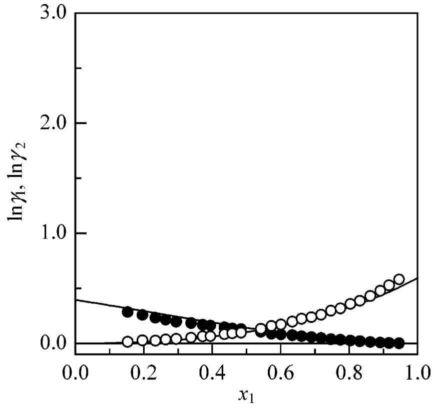

Figure 7. Activity coefficient−liquid composition for the HFC-338pcc (1) + butyl ehyl ether (2) system: ● and ○, experimental; −, NRTL equation.

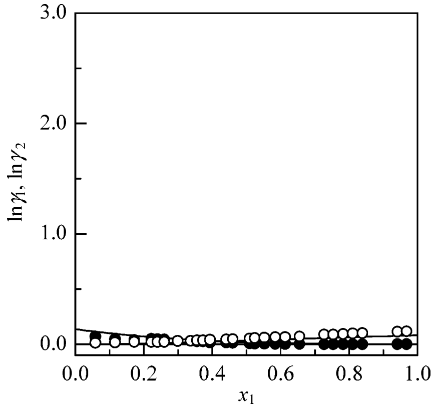

Figure 8. Activity coefficient−liquid composition for the HFE-347mcc (1) + HFC-338pcc (2) system: ● and ○, experimental; −, NRTL equation.

following objective function was minimized during optimization of the parameters in both equations.

$$F_{\mathrm{obj}} = \sum_{k=1}^{N}\left[\left(\frac{\gamma_{1,\mathrm{calcd}} - \gamma_{1,\mathrm{exptl}}}{\gamma_{1,\mathrm{exptl}}}\right)_k^2 + \left(\frac{\gamma_{2,\mathrm{calcd}} - \gamma_{2,\mathrm{exptl}}}{\gamma_{2,\mathrm{exptl}}}\right)_k^2\right]$$

$$N = \text{no. of data points} \quad (2)$$

Table 5 shows the estimated parameters of four binary systems. Table 6 also gives the deviations between experimental and calculated vapor-phase compositions and bubble-point temperatures. The liquid molar volumes ν_i^{L} in the Wilson equation are the constant values shown in Table 2. The Wilson and NRTL equations yielded similar results. The correlated results from the NRTL equation are illustrated in Figures 1 to 8.

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