Vapor−Liquid Equilibrium Data for the Four Binary Systems Containing Fluorocarbon, Hydrofluorocarbon, and Fluorinated Ethers at 101.3 kPa

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Isobaric vapor−liquid equilibria were measured for the four binary systems of perfluoro-2-methylpentane (FC-5114mmyc2) + perfluorooctane (FC-7118mc6), 1,1,1,2,2,3,3,4,4-nonafluorohexane (HFC-569mccf) + octane, 2,2,2-trifluorodiethyl ether (HFE-356mf-f) + butyl ethyl ether, and methylperfluoroisopropyl ether (HFE-347 mmy) + heptane at atmospheric pressure. The HFE-356mf-f + butyl ethyl ether system formed a minimum boiling azeotrope. The experimental data except for those for the FC-5114mmyc2 + FC-7118mc6 system were correlated by the Wilson and NRTL activity coefficient models. The Wilson and NRTL equations gave similar results. The VLE for the FC-5114mmyc2 + FC-7118mc6 system was predicted to be an ideal solution.

Introduction

The hydrochlorofluorocarbons (HCFCs) are widely used in the manufacture of cleaning solvents, but they contain chlorine atoms which result in an ozone depletion potential. Therefore, the development of the new purer cleaning solvents and mixed cleaning solvents with no chlorine atoms in place of HCFCs has been pursued. For the design and development of manufacturing processes using the new mixed cleaning solvents, it is necessary to have vapor−liquid equilibrium (VLE) data.

This paper reports the experimental VLE data for the four binary systems perfluoro-2-methylpentane ($(CF_3)_2CF$-$CF_2CF_2CF_3$, FC-5114mmyc2) + perfluorooctane ($CF_3(CF_2)_6$-CF_3, FC-7118mc6), 1,1,1,2,2,3,3,4,4-nonafluorohexane (CF_3-$(CF_2)_3CH_2CH_3$, HFC-569mccf) + octane, 2,2,2-trifluorodiethyl ether ($CF_3CH_2OCH_2CF_3$, HFE-356mf-f) + butyl ethyl ether, and methylperfluoroisopropyl ether ($CF_3CF(CF_3)OCH_3$, HFE-347mmy) + heptane at 101.3 kPa. These binary VLE data are not available in the literature.

Experimental Section

Apparatus and Procedures. For the VLE measurements, a modified Rogalski−Malanowski equilibrium still was used. This still has been described in detail by Hiaki et al.[1] and Kurihara et al.[2] It is a liquid−vapor ebullition-type. The pressure in the still was measured using a Fortin-type mercury barometer. Since the barometric pressure changed slightly, the experimental temperatures were corrected to 101.3 kPa.[3] The equilibrium temperature was measured with a calibrated platinum resistance thermometer with an accuracy of ±0.01 K.

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

component	purity/ %	ρ(298.15 K)/ (kg·m^{-3}) expt	lit.[a]	T_b/K expt	lit.[a]
FC-5114mmyc2	99.8	1710.2		330.80	
FC-7118mc6	99.9	1755.1		378.87	
HFC-569mccf	99.4	1415.8		340.74	
HFE-356mf-f	99.8	1402.8		336.74	
HFE-347mmy	99.9	1420.5[b]		302.49	
heptane	99.8	679.5	679.46	371.49	371.54
octane	99.9	698.5	698.62	398.70	398.82
butyl ethyl ether	99.9	745.3	744.8	364.25	365.39

[a] Riddick et al.[4] [b] This value was measured at 293.15 K.

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

component	A	B	C	$v_i^L \times 10^6$/ (m^3·mol^{-1})
FC-5114mmyc2[b]	5.732 67	960.556	−73.068	197.660
FC-7118mc6[b]	5.792 15	1141.890	−77.296	249.588
HFC-569mccf[b]	6.075 06	1169.9045	−53.248	175.228
HFE-356mf-f[b]	6.326 51	1218.754	−54.673	129.786
HFE-347mmy[b]	6.004 16	1004.638	−51.233	127.459
heptane[c]	6.019 80	1264.370	−56.510	146.499
octane[c]	6.056 90	1358.800	−63.295	163.422
butyl ethyl ether[c]	6.084 70	1256.361	−56.243	136.237

[a] $\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C]$. [b] The values were given by RITE.[5] [c] The values were published by Gmehling and Onken.[6]

10.1021/je000192d CCC: $20.00
Published on Web 06/09/2001

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
FC-5114mmyc2 (1) + FC-7118mc6 (2)									
0.000	0.000	378.87		1.000	0.398	0.736	351.86	0.967	1.034
0.112	0.320	369.43	0.934	1.015	0.528	0.835	345.85	0.985	1.021
0.165	0.444	365.62	0.969	0.994	0.612	0.875	342.42	0.987	1.068
0.229	0.549	361.36	0.965	1.001	0.710	0.926	338.85	1.006	0.969
0.265	0.600	359.14	0.968	1.002	0.858	0.972	334.28	1.010	0.895
0.307	0.649	356.74	0.965	1.010	1.000	1.000	330.80	1.000	
HFC-569mccf (1) + Octane (2)									
0.000	0.000	398.70		1.000	0.577	0.874	347.29	1.229	1.612
0.014	0.152	393.31	2.551	1.002	0.602	0.878	346.84	1.200	1.688
0.066	0.484	377.83	2.514	1.026	0.651	0.888	346.02	1.152	1.825
0.101	0.590	371.73	2.347	1.031	0.680	0.894	345.58	1.126	1.917
0.148	0.678	365.14	2.201	1.066	0.724	0.904	344.90	1.092	2.067
0.164	0.701	363.38	2.157	1.072	0.748	0.910	344.47	1.079	2.159
0.174	0.714	362.28	2.136	1.079	0.774	0.917	344.03	1.066	2.259
0.198	0.737	360.20	2.055	1.099	0.805	0.924	343.61	1.046	2.438
0.212	0.748	359.22	2.004	1.110	0.839	0.934	343.10	1.031	2.617
0.252	0.776	356.68	1.882	1.139	0.886	0.949	342.40	1.015	2.937
0.292	0.798	354.65	1.773	1.169	0.903	0.955	342.11	1.012	3.081
0.316	0.806	353.85	1.695	1.197	0.935	0.968	341.64	1.005	3.332
0.380	0.825	351.83	1.533	1.285	0.956	0.977	341.34	1.002	3.582
0.462	0.848	349.60	1.387	1.399	0.976	0.987	341.04	1.001	3.757
0.505	0.859	348.61	1.325	1.465	1.000	1.000	340.74	1.000	
0.548	0.866	347.85	1.260	1.570					
HFE-356mf-f (1) + Butyl Ethyl Ether (2)									
0.000	0.000	364.25		1.000	0.521	0.727	340.20	1.237	1.263
0.063	0.246	357.41	1.980	0.996	0.558	0.743	339.72	1.200	1.311
0.076	0.278	356.41	1.912	0.999	0.581	0.753	339.41	1.181	1.344
0.082	0.300	355.75	1.952	0.995	0.603	0.763	339.15	1.163	1.374
0.093	0.327	354.78	1.933	1.000	0.632	0.776	338.85	1.140	1.416
0.100	0.343	354.35	1.912	0.997	0.654	0.785	338.58	1.125	1.460
0.109	0.362	353.66	1.891	1.000	0.681	0.797	338.30	1.108	1.510
0.137	0.412	351.97	1.806	1.006	0.715	0.812	337.99	1.087	1.583
0.160	0.451	350.69	1.764	1.007	0.741	0.824	337.77	1.072	1.644
0.181	0.477	349.67	1.704	1.018	0.765	0.835	337.58	1.060	1.710
0.235	0.543	347.23	1.617	1.035	0.788	0.846	337.42	1.048	1.780
0.267	0.576	345.90	1.578	1.049	0.818	0.862	337.23	1.036	1.871
0.293	0.597	345.06	1.532	1.064	0.841	0.875	337.08	1.028	1.951
0.308	0.610	344.65	1.510	1.067	0.861	0.887	336.97	1.022	2.025
0.324	0.620	344.18	1.482	1.082	0.924	0.930	336.71	1.008	2.317
0.351	0.635	343.62	1.428	1.104	0.926	0.931	336.70	1.007	2.346
0.376	0.654	342.94	1.404	1.115	0.930	0.935	336.70	1.007	2.336
0.402	0.667	342.38	1.365	1.142	0.953	0.954	336.68	1.003	2.464
0.429	0.682	341.88	1.330	1.162	0.958	0.959	336.67	1.004	2.459
0.458	0.693	341.37	1.289	1.204	0.968	0.967	336.68	1.001	2.597
0.475	0.704	340.93	1.281	1.217	0.982	0.981	336.69	1.001	2.657
0.499	0.717	340.53	1.259	1.237	1.000	1.000	336.74	1.000	
HFE-347mmy (1) + Heptane (2)									
0.000	0.000	371.49		1.000	0.515	0.926	308.47	1.452	1.540
0.029	0.461	355.25	3.217	0.918	0.546	0.927	308.03	1.392	1.656
0.032	0.493	353.28	3.276	0.924	0.643	0.936	307.43	1.219	1.898
0.046	0.604	347.53	3.240	0.889	0.779	0.950	305.35	1.099	2.640
0.086	0.750	334.69	3.064	0.929	0.810	0.951	304.96	1.073	3.065
0.128	0.813	324.89	2.989	1.067	0.842	0.955	304.79	1.043	3.412
0.150	0.837	322.42	2.837	1.056	0.863	0.959	304.52	1.032	3.631
0.173	0.853	320.03	2.704	1.081	0.887	0.963	304.21	1.020	4.032
0.190	0.867	318.38	2.639	1.070	0.903	0.966	304.00	1.013	4.359
0.273	0.901	313.58	2.236	1.092	0.915	0.970	303.80	1.011	4.431
0.288	0.902	313.08	2.158	1.129	0.931	0.974	303.56	1.006	4.785
0.298	0.905	312.67	2.122	1.130	0.947	0.979	303.31	1.003	5.092
0.320	0.909	312.09	2.024	1.147	0.962	0.985	303.07	1.002	5.132
0.403	0.922	310.17	1.741	1.221	0.977	0.990	302.85	1.000	5.712
0.448	0.924	309.33	1.616	1.336	1.000	1.000	302.49	1.000	
0.488	0.926	308.78	1.515	1.438					

Analysis. Vapor and liquid samples were analyzed with the gas chromatograph (HP-GC6890 series) equipped with a flame ionization detector. Pora PLOT Q (GL Science Co.) was used as column packing and helium as the carrier gas. The relationship between peak area and composition was determined from analysis of samples of known composition. The accuracy of the equilibrium concentration was estimated to be ±0.001 in mole fraction except for the HFE-347mmy + heptane system with an accuracy of ±0.003 mole fraction.

Materials. FC-5114mmyc2, FC-7118mc6, HFC-569mccf, HFE-356mf-f, and HFE-347mmy were provided by the Research Institute of Innovative Technology for the Earth (RITE). Heptane, octane, and butyl ethyl ether were special grade pure reagents (Wako Pure Chemical Industry, Inc., Japan, and Aldrich Chemical Co., Inc., Japan). These

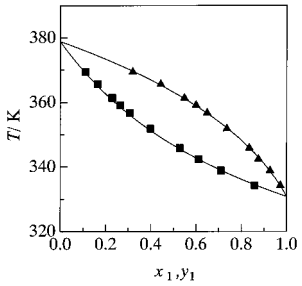

Figure 1. Temperature−composition diagram for the FC-5114mmyc2(1) + FC-7118mc6(2) system: (■) experimental liquid-phase mole fractions x_1; (▲) experimental vapor-phase mole fractions y_1; (—) ideal solution.

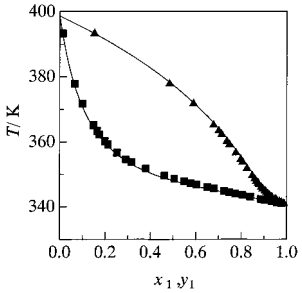

Figure 2. Temperature−composition diagram for the HFC-569mccf(1) + octane(2) system: (■) experimental liquid-phase mole fractions x_1; (▲) experimental vapor-phase mole fractions y_1; (—) Wilson equation.

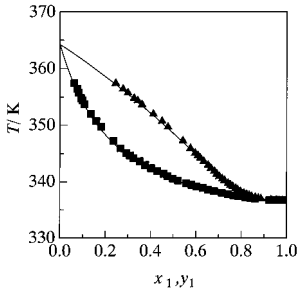

Figure 3. Temperature−composition diagram for the HFE-356mf-f(1) + butyl ethyl ether(2) system: (■) experimental liquid-phase mole fractions x_1; (▲) experimental vapor-phase mole fractions y_1; (—) Wilson equation.

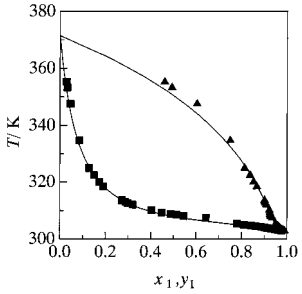

Figure 4. Temperature−composition diagram for the HFE-347mmy(1) + heptane(2) system: (■) experimental liquid-phase mole fractions x_1; (▲) experimental vapor-phase mole fractions y_1; (—) Wilson equation.

materials were used without further purification. In Table 1, the purity and some measured properties of the samples are shown together with the literature values.

Experimental Results

The experimental results of the four binary VLE data are shown in Table 3 and in Figures 1−8. The activity

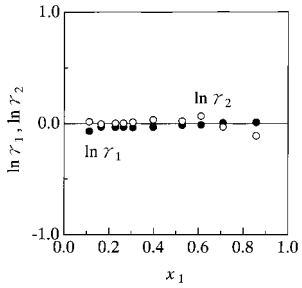

Figure 5. Activity coefficient−liquid composition for the FC-5114mmyc2(1) + FC-7118mc6(2) system: (●, ○) experimental.

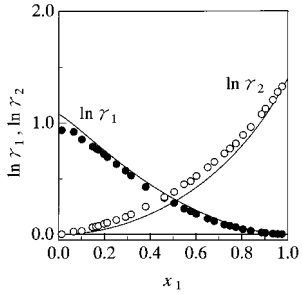

Figure 6. Activity coefficient−liquid composition for the HFC-569mccf(1) + octane(2) system: (●, ○) experimental; (—) Wilson equation.

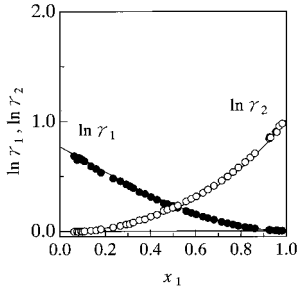

Figure 7. Activity coefficient−liquid composition for the HFE-356mf-f(1) + butyl ethyl ether(2) system: (●, ○) experimental; (—) Wilson equation.

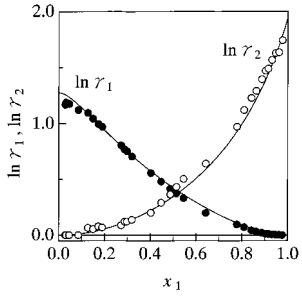

Figure 8. Activity coefficient−liquid composition for the HFE-347mmy(1) + heptane(2) system: (●, ○) experimental; (—) Wilson equation.

coefficients γ_i in Table 3 were calculated by the following equation which assumes ideal gas behavior:

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

because the vapor-phase fugacity coefficients of the FC-5114mmyc2, FC-7118mc6, HFC-569mccf, HFE-356mf-f, and HFE-347mmy could not be calculated. In eq 1, the vapor pressures of the pure components P_i^S were calculated from the Antoine equation constants shown in Table 2.

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

test	FC-5114mmyc2(1) + FC-7118mc6(2)	HFC-569mccf(1) + octane(2)	HFE−356mf-f(1) + butyl ethyl ether(2)	HFE−347mmy(1) + heptane(2)
point[b]	+	−	+	+
Δy_1	0.005_1	0.011_9	0.005_5	0.009_3
area[c]	n.a.[d]	+	+	+
$D-J$/%		−6.2	−6.2	−26.1

[a] Results of the tests are characterized by the signs "+" (pass) and "−" (not pass). [b] The criterion for passing the test is $\Delta y_1 \leq 0.010$.[6] [c] The criterion for passing the test is $D-J \leq 10\%$.[6] [d] n.a. = Not available.

Table 5. Parameters and Deviations between the Calculated and Experimental Vapor-Phase Mole Fractions, Δy_1, and Temperature, ΔT, for the Three Binary Systems Using the Wilson and NRTL Equations[a]

parameter	HFC-569mccf(1) + octane(2)		HFE-356mf-f(1) + butyl ethyl ether(2)		HFE-347mmy(1) + heptane(2)	
			Wilson Equation			
$\lambda_{12}-\lambda_{11}$[b]	1536.54		928.72		2226.92	
$\lambda_{21}-\lambda_{22}$[b]	2854.10		2017.04		3212.83	
			NRTL Equation			
$g_{12}-g_{22}$[b]	2550.23		2464.08		3534.12	
$g_{21}-g_{11}$[b]	1491.91		357.80		1325.20	
α_{12}	0.3		0.3		0.3	
	$\Delta y_1 \times 100$	ΔT/K	$\Delta y_1 \times 100$	ΔT/K	$\Delta y_1 \times 10_0$	ΔT/K
			Wilson Equation			
average	1.3	0.47	0.3	0.17	0.3	0.64
maximum	2.3	1.18	1.0	0.50	0.9	2.97
			NRTL Equation			
average	1.3	0.52	0.4	0.17	0.4	0.70
maximum	2.4	1.22	1.1	0.47	1.6	2.54

[a] $\Delta y_1 = \sum_k |y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}|_k/N, \Delta T = \sum_k |T_{\mathrm{exp}} - T_{\mathrm{calc}}|_k/N$; N = number of data points. [b] J mol^{-1}.

The thermodynamic consistency of the experimental VLE data was checked using the point test of Van Ness et al.[7] and Frendenslund et al.[8] and the area test of Herington[9] and of Redlich and Kister[10] as described by Gmehling and Onken.[6] The consistency of the data for the FC-5114mmyc2 + FC-7118mc6 system was only checked by the point test, because all the values γ_i were close to 1, indicating that this system at atmospheric pressure is nearly an ideal solution. The results of the consistency test are shown in Table 4. The reported data except for those for the HFC-569mccf + octane system were found to be thermodynamically consistent according to the point test. But the difference between the calculated value ($\Delta y_1 = 0.012$) and the criterion ($\Delta y_1 = 0.010$) of the point test was small for this system. On the other hand, the area test also indicated that the data sets for the all-three-measures systems are reliable.

The HFE-356mf-f + butyl ethyl ether system forms a minimum boiling azeotrope. The binary azeotropic point was determined by a graphical method[11] on the basis of experimental VLE data and is $x_{1(\mathrm{AZ})} = 0.961$ and $T_{(\mathrm{AZ})} = 336.68$ K.

Correlation

The activity coefficients of the three binary systems (except the FC-5114mmyc2 + FC-7118mc6 system) were correlated by the Wilson[12] and NRTL equations.[13] The following objective function was minimized during optimization of the parameters in each of the two equations.

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

Table 5 lists the estimated parameters of three binary systems and the deviations between experimental and calculated vapor-phase compositions and bubble point temperatures. The liquid molar volumes v_i^{L} in the Wilson equation are the constant values shown in Table 2. The parameter α_{12} in the NRTL equation was set to 0.3 for all the binary systems in this work. The Wilson and NRTL equations yielded similar results. The correlated results from the Wilson equation are illustrated in Figure 2.

For the FC-5114mmyc2 + FC-7118mc6 system, the VLE was predicted to be an ideal solution. The predicted results give an absolute average deviation of 0.9 mol % in vapor-phase composition and 0.43 K in temperature. The predicted results are illustrated in Figure 1.

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Received for review June 28, 2000. Accepted April 17, 2001. The authors acknowledge the financial support of the New Energy and Industrial Technology Development Organization (NEDO).

JE000192D