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Vapor-Liquid Equilibria for 1,1,1-Trifluoro-2-(2,2,2-trifluoroethoxy)ethane +2-Methyl-2-propanol and Pentane+1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane System

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Abstract−Isobaric vapor-liquid equilibrium (VLE) for two binary systems of 1,1,1-Trifluoro-2-(2,2,2-trifluoroethoxy) ethane+2-methyl-2-propanol and pentane+1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane system have been measured at 101.3 kPa. The measurements were made in an equilibrium still, developed in a previous study, with circulation of both the vapor and liquid phases. The binary isobaric systems exhibit minimum boiling azeotropes. The thermodynamic consistencies of the experimental data were good by the Van Ness et al. and Herington methods. The experimental data for the binary systems investigated were correlated with activity coefficient equations. The nonrandom two-liquid (NRTL) equation yielded a good correlation of activity coefficients.

Key words: Hydrofluoroethers, Cleaning Solvents, VLE Data, Azeotrope, Activity Coefficient Equation

INTRODUCTION

Developments of advanced refrigerants, cleaning solvents and blowing agents to prevent the depletion of the ozone layer and global warming while at the same time saving energy are necessary for humankind immediately. Hydrofluoroethers (HFEs) and mixtures of HFEs with a solvent are useful substances that can be considered for this purpose. The goal of this project, the Research Institute of Innovative Technology for the Earth (RITE) in Japan, is to develop new refrigerants, cleaning solvents and blowing agents.

As a continuation of our studies [Hiaki and Kawai, 1999; Hiaki and Nanao, 2000; Hiaki et al., 2001, 2002] on the vapor-liquid equilibria (VLE) of HFEs+organic solvents systems, isobaric VLE for two binary systems 1,1,1-Trifluoro-2-(2,2,2-trifluoroethoxy)ethane (HFE-356mf-f) *i.e.* $CF_3CH_2OCH_2CF_3$, +2-methyl-2-propanol and pentane+1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane(HFE-347pc-f), *i.e.* $CHF_2CF_2OCH_2CF_3$, have been measured at 101.3 kPa. The measurements were made in an equilibrium still, which was developed in our previous work [Hiaki et al., 2001], with circulation of both the vapor and liquid phases. No isobaric or isothermal VLE data have been reported previously for these systems.

EXPERIMENTAL SECTION

1. Apparatus and Operation Procedure

A small capacity equilibrium still, with provisions for both vapor and liquid phases circulation, was developed in the previous study for the determination of VLE, shown in Fig. 1. The overall charge of the all-Pyrex-glass still was approximately 18 cm^3 of solution. An electric cartridge heater was inserted into the boiling flask (A), and a little glass dust was put on the wall of the heat-transfer surface

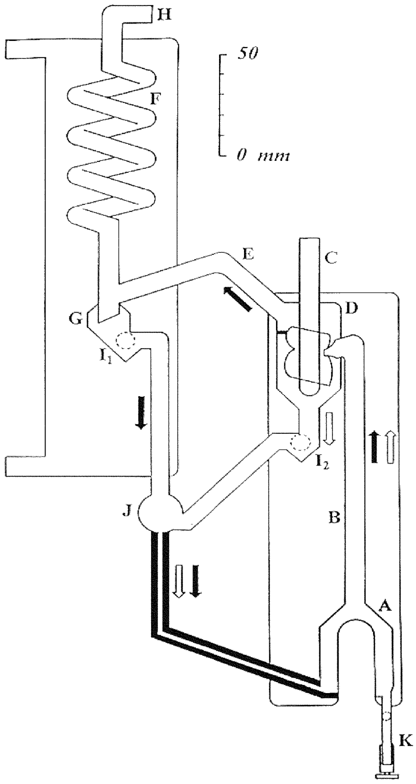

Fig. 1. Schematic diagram of the vapor-liquid equilibrium apparatus.

A: Boiling flask
B: Cottrell pump
C: Thermometer well
D: Equilibrium chamber
E: Heater for preventing partial condensation of vapor
F: Condenser
G: Drop counter
H: To atmosphere
I_1, I_2: Withdrawal of condensed vapor and liquid sample
J: Buffer for prevention of backward flow of mixing sample
K: Drain valve

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Table 1. Normal boiling point and Antoine constants of the components[a]

	Normal boiling point [K]			Antoine Constants			
	This work	Literature	Ref	A	B	C	Ref
HFE-356mf-f	337.00	336.91	1	6.324088	7.199185	1218.754	1
HFE-347pc-f	329.37	329.37	1	6.301521	7.176618	1176.625	1
2-methyl-2-propanol	355.62	355.497	2	6.35272	1105.198	171.894	3
pentane	309.21	309.215	2	5.99028	1071.187	232.766	3

[a] $\log(P/kPa) = A - B/[(T/K) + C]$

Ref. 1: Otake, Ref. 2: Riddick et al., Ref. 3: Boublik et al.

to stabilize the boiling. Both vapor and liquid mixture flow through a Cottrell pump (B) and flash on the wall of the thermometer well (C). The separated vapor, which is kept warm by a flexible heating tape (E), flow into the condenser (F). The condensed vapor phase is stirred naturally at the withdrawal of the vapor sample (I_1). The liquid, which flows through the withdrawal of the liquid sample (I_2), and condensed vapor phases returned again to the boiling flask. The steady state corresponding to equilibrium was attained within about 30 minutes.

2. Materials and Auxiliary Equipment

2-methyl-2-propanol and pentane were special grade reagents, supplied by the Wako Pure Chemical Co. Ltd. HFE-356mf-f and HFE-347pc-f were provided by the RITE. Gas-chromatographic analysis of all seven materials indicated that each had a purity of at least 99.9 mol%. Normal boiling point of compounds are listed in Table 1 along with literature values.

The equilibrium temperature was measured with a calibrated platinum resistance thermometer (Automatic System Laboratories model F250, England) with maximum error of 0.03 K. The pressure in the apparatus was measured by means of a silicon resonant precision barometer (Tokyo Suzuki Seisakusho Co., model T60, Japan) with an accuracy of ±0.015 kPa. Since the barometric pressure changed slightly, the experimental temperatures were corrected to 101.3 kPa [Hiaki et al., 1999].

The equilibrium composition of the samples were determined using a gas chromatograph (Hewlett Packard HP6890, USA) equipped with a flame ionization detector, auto sampler and HP computer. Gas chromatograph column were used HP-624 (60 m in length and 0.25 mm in diameter) for HFE-356mf-f+2-methyl-2-propanol system and HP-FFAP (25 m in length and 0.5 mm in diameter) for pentane+HFE-347pc-f system. The relationship between the peak area and composition was determined from analysis of samples of known composition. The maximum error of liquid and vapor composition measurements is estimated to be 0.003 mole fraction.

RESULTS AND DISCUSSION

The isobaric VLE were measured for the two binary systems, HFE-356mf-f+2-methyl-2-propanol and pentane+HFE-347pc-f at 101.3 kPa. The activity coefficients γ_i were calculated using the following equation:

$$Py_i = \gamma_i P_i^S x_i \tag{1}$$

In principle, it is better to calculate the activity coefficients including fugacity coefficients and Poynting factor correction. However, not all the required physical property data for HFEs needed to calculate these terms correctly are available. The activity coefficients were therefore calculated on the assumption of an ideal vapor phase. The vapor pressures of the pure components, P_i^S, were obtained using the Antoine equation constants, which are given in Table 1.

The VLE data for the HFE-356mf-f (1)+2-methyl-2-propanol (2) and pentane (1)+HFE-347pc-f (2) are reported in Table 2 along with the activity coefficients calculated using Eq. (1). The experimental VLE data are shown graphically in Figs. 2 and 3.

The two binary isobaric systems form minimum boiling azeo-

Table 2. Isobaric vapor-liquid equilibrium data, temperature, T, liquid phase, x_1, and vapor phase, y_1, mole fractions, and activity coefficient, γ_i, for the HFE-356mf-f (1)+2-methyl-2-propanol (2) and pentane (1)+HFE-347pc-f (2) at 101.3 kPa

Temperature (K)	x_1	y_1	γ_1	γ_2
HFE-356mf-f (1)+2-methyl-2-propanol (2) at 101.3 kPa				
355.62	0.000	0.000	-	1.000
350.05	0.060	0.242	2.613	1.003
348.00	0.086	0.320	2.551	1.008
346.00	0.117	0.388	2.425	1.022
343.44	0.168	0.468	2.216	1.054
341.99	0.209	0.517	2.076	1.071
341.24	0.234	0.542	1.994	1.084
340.30	0.271	0.562	1.844	1.134
339.76	0.297	0.578	1.760	1.162
339.10	0.328	0.603	1.699	1.179
338.10	0.379	0.633	1.600	1.233
337.81	0.406	0.642	1.532	1.273
337.66	0.421	0.647	1.497	1.297
337.25	0.449	0.662	1.456	1.329
336.80	0.489	0.684	1.402	1.369
336.15	0.604	0.721	1.225	1.606
335.82	0.676	0.747	1.147	1.809
335.69	0.705	0.759	1.125	1.897
335.59	0.725	0.769	1.112	1.961
335.49	0.771	0.792	1.079	2.139
335.42	0.805	0.810	1.060	2.295
335.61	0.876	0.859	1.026	2.668
335.75	0.921	0.899	1.016	2.974
336.34	0.963	0.948	1.003	3.204
337.00	1.000	1.000	1.000	-

Table 2. Continued

Temperature (K)	x_1	y_1	γ_1	γ_2
Pentane (1)+HFE-347pc-f (2) at 101.3 kPa				
329.37	0.000	0.000	-	1.000
316.90	0.096	0.418	3.386	1.031
310.19	0.220	0.591	2.601	1.104
306.81	0.349	0.665	2.067	1.251
305.24	0.426	0.694	1.871	1.384
304.97	0.463	0.697	1.745	1.483
304.65	0.537	0.714	1.557	1.650
304.52	0.553	0.713	1.518	1.725
304.35	0.599	0.722	1.428	1.871
304.24	0.673	0.729	1.288	2.249
304.20	0.750	0.744	1.180	2.792
304.16	0.753	0.742	1.175	2.848
304.26	0.816	0.762	1.110	3.507
304.64	0.884	0.793	1.052	4.739
304.83	0.901	0.808	1.044	5.150
305.33	0.926	0.834	1.030	5.806
306.52	0.960	0.888	1.015	6.952
309.21	1.000	1.000	1.000	-

Table 3. Experimental azeotropic temperature, T(AZ), and composition, X(AZ), for the HFE-356mf-f (1)+2-methyl-2-propanol (2) and pentane (1)+HFE-347pc-f (2) at 101.3 kPa

System	T(AZ) [K]	X(AZ)
HFE-356mf-f (1)+2-methyl-2-propanol (2)	335.40	0.817
pentane (1)+HFE-347pc-f (2)	304.17	0.742

tropes. The azeotropic data, which were determined on the basis of the experimental VLE data, are shown in Table 3.

The experimental data were tested for thermodynamic consistency by the Van Ness et al. [1973] and the Herington [1951] methods. The results of the consistency tests for all systems indicate that the VLE data are shown in Table 4. The results from two consistency tests indicate that the VLE data for system of HFE-356mf-f (1)+2-methyl-2-propanol (2) is thermodynamically consistent. The other of pentane (1)+HFE-347pc-f (2) is perfectly good by Method II and slightly good by Method I.

The activity coefficients for four binary systems were correlated with the nonrandom two-liquid (NRTL) [Renon and Prausnitz, 1968] equation. The parameters are obtained by using the Marquardt method [1963]. The sum of the squares of relative deviations in activity coefficients was minimized during optimization of the parameters.

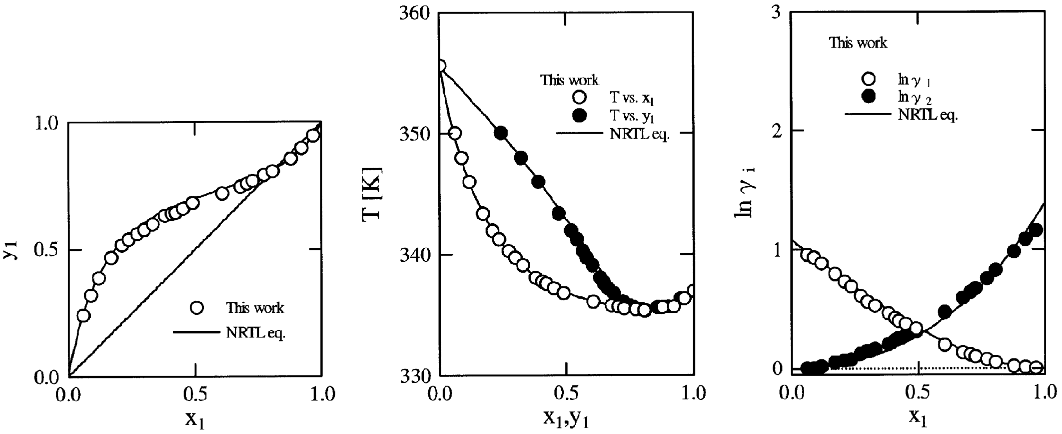

Fig. 2. Vapor-liquid composition, temperature-composition, and activity coefficient-liquid composition diagram HFE-356mf-f (1)+2-methyl-2-propanol (2) at 101.3 kPa.

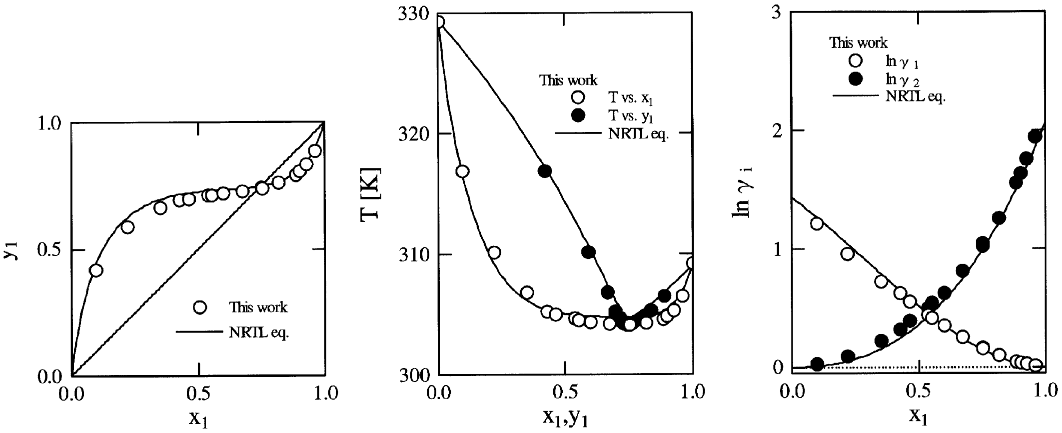

Fig. 3. Vapor-liquid composition, temperature-composition, and activity coefficient-liquid composition diagram pentane (1)+HFE-347pc-f (2) at 101.3 kPa.

Table 4. The results of the consistency tests for the VLE of HFE-356mf-f (1)+2-methyl-2-propanol (2) and pentane (1)+HFE-347pc-f (2) at 101.3 kPa

System	Thermodynamic consistency test	Criterion of consistency (character: +)	This work
HFE-356mf-f (1)+2-methyl-2-propanol (2)	Method I	$\Delta y_1<0.01$	0.007 (+)
	Method II	Δ-J<10%	−2.11 (+)
pentane (1)+HFE-347pc-f (2)	Method I	$\Delta y_1<0.01$	0.01 (±)
	Method II	D-J<10%	1.91 (+)

Method I: Van Ness et al. [1973], Method II: Herington [1951]

$A=100\left|\int_2^1 \ln(\gamma_1/\gamma_2)dx_1+\int_1^2 \varepsilon dx_1\right|$ $D=100|A'-B'|/(A'+B')$

$J=150|\Delta T_{max}|/T_{min}$ A'=area above the x axis

B'=area below the x axis of $\ln(\gamma_1/\gamma_2)$ vs. x_1 Δy_1=deviation between observed y_1 and calculated y_1

Table 5. Parameters and absolute deviations between calculated and experimental temperatures, ΔT, and vapor phase mole fractions, Δy_1, of NRTL equation for the experimental binary systems, HFE-356mf-f (1)+2-methyl-2-propanol (2) and pentane (1)+HFE-347pc-f (2) at 101.3 kPa

System	Parameters /kJ mol^{-1}	Deviation			
		Average		Maximum	
		ΔT/K	Δy_1	ΔT/K	Δy_1
HFE-356mf-f (1) +2-methyl -2-propanol (2)	$g_{12}=0.998$ $g_{21}=3.007$ $\alpha_{.}=0.308$ [-]	0.06	0.012	0.16	0.026
pentane (1) +HFE-347pc-f (2)	$g_{12}=1.483$ $g_{21}=4.191$ $\alpha_{.}=0.313$ [-]	0.44	0.013	1.04	0.031

average deviations: $\Delta T=\sum^{N}|T_{obs}-T_{calc}|/N$; $\Delta y_1=\sum^{N}|y_{1,obs}-y_{a,calc}|/N$
N=Number of data points.

The NRTL equation yielded a good correlation of activity coefficients for all systems. The parameter values and average and maximum absolute deviations of both vapor phase mole fractions and temperatures using the NRTL are shown in Table 5. The calculated results are shown by solid lines in Figs. 2 and 3.

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NOMENCLATURE

P : total pressure [kPa]
P_i^s : component vapor pressure [kPa]
R : molar gas constant, R=8.3144 J mol^{-1} K^{-1}
T : equilibrium temperature [K]
x : mole fraction in liquid phase
y : mole fraction in vapor phase
γ : activity coefficient

Subscript

i, j, 1, 2 : components

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