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Received September 8, 1986. The authors gratefully acknowledge the financial support of the United States Department of Energy through Subcontract No. 01-17001 with the International Coal Refining Co.

Mutual Binary Solubilities: Perfluorodecalin/Hydrocarbons

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Mutual solubility data for perfluorodecalin + *n*-hexane, + *n*-heptane, + *n*-octane, + *n*-nonane, + 1-hexene, and + 1-heptene are reported. The NRTL and UNIQUAC equations were used to correlate the data. UNIFAC group parameters for the interactions CH_2/CF_2(c) and $CH{=}CH_2/CF_2$(c) can also be obtained.

Introduction

Perfluorocarbon/hydrocarbon systems are particularly adequate to test the applicability of the activity coefficient models as multicomponent mixtures change swiftly from type to type of equilibrium pattern over a small temperature range.

As part of a program to study multicomponent mixtures containing perfluorodecalin (PFD) and hydrocarbons, this paper reports the results of measurements on liquid–liquid equilibrium for perfluorodecalin + *n*-hexane, + *n*-heptane, + *n*-octane, + *n*-nonane, + 1-hexene, and + 1-heptene. These experimental data are analyzed by the NRTL and UNIQUAC equations. UNIFAC group parameters for the interactions CH_2/CF_2(c) and $CH{=}CH_2/CF_2$(c) were obtained and published elsewhere (*1*). CF_2(c) refers to a cyclic molecule.

Experimental Section

The experimental work was carried out using a thermostated miniature cell similar to that described by Soares et al. (*2*). Temperature was controlled and was measured by means of a precision thermometer within an accuracy of 0.01 K. The mixtures were stirred with a magnetic stirrer for at least 30 min and allowed to settle for a period of 4 h. Once the equilibrium had been reached, samples of two conjugate phases were carefully withdrawn by using microsyringes and injected directly into the column of a gas–liquid chromatograph (Pye Unicam) combined with an electronic integrator (Varian CDS 111). Special care was taken with the measurements above the room temperature to avoid phase splitting due to cooling.

Calibration curves were obtained by using at least 10 mixtures of known concentration, of which four to six chromatograms were obtained. Four to six samples of both phases were

Table I. Mutual Solubility of PFD (1) and *n*-Hexane (2)

	solubility, wt %			solubility, wt %	
temp, K	x_1	x_{12}	temp, K	x_1	x_{12}
277.55	28.48	92.65	288.75	44.55	88.82
278.45	29.48	92.53	290.85	48.91	87.35
279.15	30.48	92.47	293.25	54.05	85.09
281.15	33.16	91.79	293.65	55.85	84.49
283.15	35.72	91.12	294.05	58.07	83.59
286.15	40.35	89.82	294.35	59.63	83.06
288.15	43.45	89.18	295.05	66.10	81.35

Table II. Mutual Solubility of PFD (1) and *n*-Heptane (2)

	solubility, wt %			solubility, wt %	
temp, K	x_{11}	x_{12}	temp, K	x_{11}	x_{12}
278.45	18.78	96.36	299.95	37.07	92.38
282.45	21.51	95.76	300.65	37.80	92.21
286.65	24.41	95.08	301.95	39.60	91.81
288.15	25.59	94.78	303.15	41.20	91.40
289.15	26.12	94.56	304.25	42.49	91.02
291.15	27.95	94.35	306.75	46.68	89.79
293.15	29.72	93.98	308.15	49.30	88.99
295.75	32.30	93.49	310.55	56.49	87.08
297.65	34.35	92.97	311.25	60.48	85.68
298.15	34.80	92.88	311.75	65.03	83.78

Table III. Mutual Solubility of PFD (1) and *n*-Octane (2)

	solubility, wt %			solubility, wt %	
temp, K	x_{11}	x_{12}	temp, K	x_{11}	x_{12}
278.55	13.58	97.02	316.35	39.61	90.66
287.75	17.57	96.32	324.05	50.81	84.57
298.15	23.48	94.98	325.65	54.08	82.67
298.55	24.01	94.87	326.45	55.84	82.00
307.85	30.09	93.44	327.25	58.22	81.35
313.15	36.22	91.53			

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Table IV. Mutual Solubility of PFD (1) and *n*-Nonane (2)

	solubility, wt %			solubility, wt %	
temp, K	x_{11}	x_{12}	temp, K	x_{11}	x_{12}
287.85	12.52	97.39	326.15	39.48	91.72
298.35	16.70	96.28	330.15	45.44	90.49
307.35	22.60	95.19	332.15	47.02	89.16
315.45	28.44	94.07	334.85	50.52	88.09
323.15	36.00	92.51	336.65	53.12	87.00
324.65	37.57	91.97	340.35	60.34	82.55
325.45	38.60	91.68			

Table V. Mutual Solubility of PFD (1) and 1-Hexene (2)

	solubility, wt %			solubility, wt %	
temp, K	x_{11}	x_{12}	temp, K	x_{11}	x_{12}
278.45	26.39	93.08	293.15	44.94	87.40
280.15	28.32	92.61	293.85	46.28	87.06
282.15	30.66	92.15	295.75	49.65	85.05
284.15	32.91	91.45	298.00	56.33	81.49
286.75	35.99	90.77	298.15	56.60	81.19
288.15	37.60	90.19	298.50	58.20	80.43
298.00	38.58	89.90	298.75	59.36	79.73
291.55	42.28	88.31	298.95	60.16	79.28

Table VI. Mutual Solubility of PFD (1) and 1-Heptene (2)

	solubility, wt %			solubility, wt %	
temp, K	x_{11}	x_{12}	temp, K	x_{11}	x_{12}
279.25	14.67	95.97	306.25	35.00	91.62
282.85	16.92	95.48	311.75	40.90	89.18
288.15	19.67	95.02	315.25	44.92	87.42
292.45	22.74	94.40	318.15	49.02	84.99
298.15	28.02	93.50	320.65	53.07	81.89
303.15	31.89	92.30			

analyzed to minimize the experimental error. Weight fraction measurements were reproducible to within ±0.002. PFD (Aldrich-Europe, cis + trans, minimum purity 97%) and the hydrocarbons (Fluka, minimum purity 99%) were used as supplied.

Experimental results are presented in Tables I–VI.

Data Analysis

The NRTL (*3*), UNIQUAC (*4*), and UNIFAC (*5*) equations were used to correlate the experimental phase equilibrium data.

Combining the thermodynamic condition of equilibrium with the relevant stoichiometric relations yields a system of N nonlinear equations

$$F_i(A_1, A_2, \ldots, x_{1j}, \ldots, x_{Nj}, T) = \ln \frac{\gamma_{i1}}{\gamma_{i2}} - \ln \frac{x_{i2}}{x_{i1}} = 0 \qquad i = 1, N \tag{1}$$

A_1, A_2, ... are the adjustable parameters of the selected correlating equation, $x_{1j}, \ldots, x_{Nj}$ are the molar compositions of component 1 to N in phase j and T the temperature.

This system of equations was solved by using a Newton–Raphson method modified to avoid the trivial solution and to ensure rapid convergence enabling not only the determination of binary parameters from mutual solubility data of each temperature but also the calculation of the compositions of all components in the phases in equilibrium, once the parameters are known.

The NRTL and UNIQUAC parameters (A_K) were correlated with the temperature through

$$A_K = c + dT \tag{2}$$

Table VII. RMSD (10^3) Values for PFD/Hydrocarbon Mutual Solubility Data

system	α_{ij}	NRTL	UNIQUAC	UNIFAC[a]
PFD/*n*-hexane	0.4	13.4	7.4	7.8
PFD/*n*-heptane	0.3	7.9	9.6	12.2
PFD/*n*-octane	0.3	6.0	13.1	45.3[3]
PFD/*n*-nonane	0.3	10.0	7.8	8.4
PFD/1-hexene	0.4	5.7	6.2	34.0[2]
PFD/1-heptene	0.3	6.2	6.0	36.8[2]

[a] 2, 3 in the superscript are the number of tie lines (close to critical solution temperature) not included in the calculation.

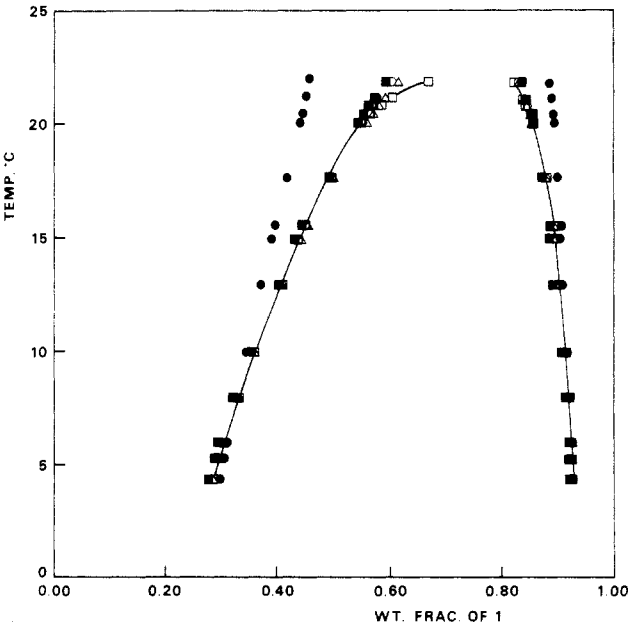

Figure 1. Mutual solubility of PFD/*n*-hexane: (□) experimental; (△) NRTL equation (α_{12} = 0.4); (○) UNIQUAC equation; (■) UNIFAC equation ($P = \phi(N_c)$); (●) UNIFAC equation (P, sim corr) (sim corr = simultaneous correlation).

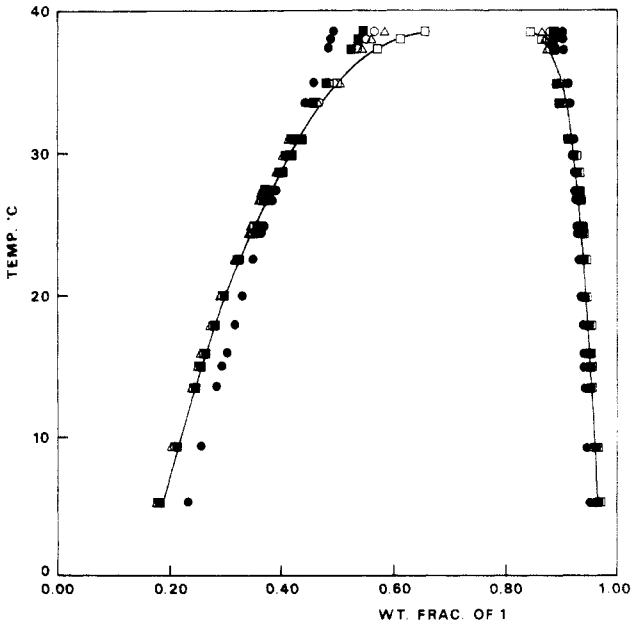

Figure 2. Mutual solubility of PFD/*n*-heptane: (□) experimental; (△) NRTL equation (α_{12} = 0.3); (○) UNIQUAC equation; (■) UNIFAC equation ($P = \phi(N_c)$); (●) UNIFAC equation (P, sim corr).

For fluorocarbon/hydrocarbon mixtures a value of $\alpha_{ij} = 0.4$ (NRTL equation) has been recommended by Renon et al. (*3*). However, no significant improvements on the predicted mutual solubility data have been found, when α_{ij} was changed.

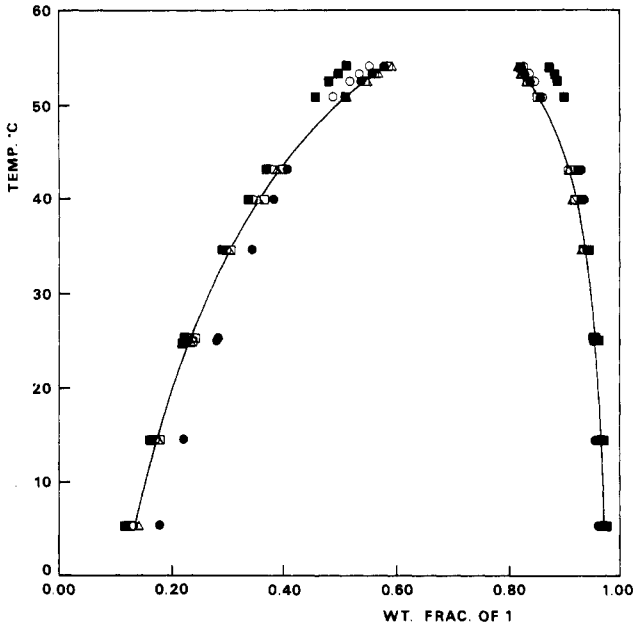

Figure 3. Mutual solubility of PFD/*n*-octane: (□) experimental; (△) NRTL equation (α_{12} = 0.3); (○) UNIQUAC equation; (■) UNIFAC equation ($P = \phi(N_c)$); (●) UNIFAC equation (P, sim corr).

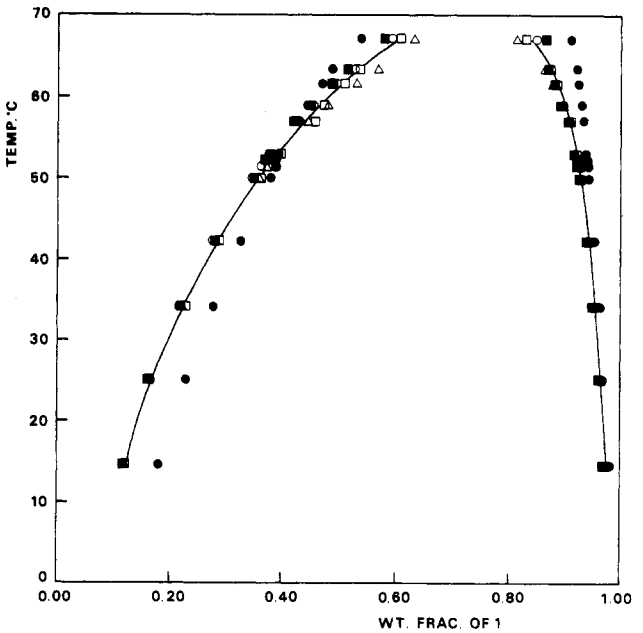

Figure 4. Mutual solubility of PFD/*n*-nonane: (□) experimental; (△) NRTL equation (α_{12} = 0.3); (○) UNIQUAC equation; (■) UNIFAC equation ($P = \phi(N_c)$); (●) UNIFAC equation (P, sim corr).

Taking in account binary and multicomponent experimental results, $\alpha_{ij} = 0.4$ can be used for PFD/*n*-hexane and PFD/1-hexene, but $\alpha_{ij} = 0.3$ is recommended for the other PFD/hydrocarbon systems (*1*).

Table VII shows the root means square deviations (RMSD) between calculated and experimental compositions:

$$\mathrm{RMSD} = \left[\frac{\sum_{j=1}^{2} \sum_{K=1}^{N} (x_{1j}^{\mathrm{calcd}} - x_{1j}^{\mathrm{exptl}})_K^2}{2(N-1)} \right]^{1/2} \qquad (3)$$

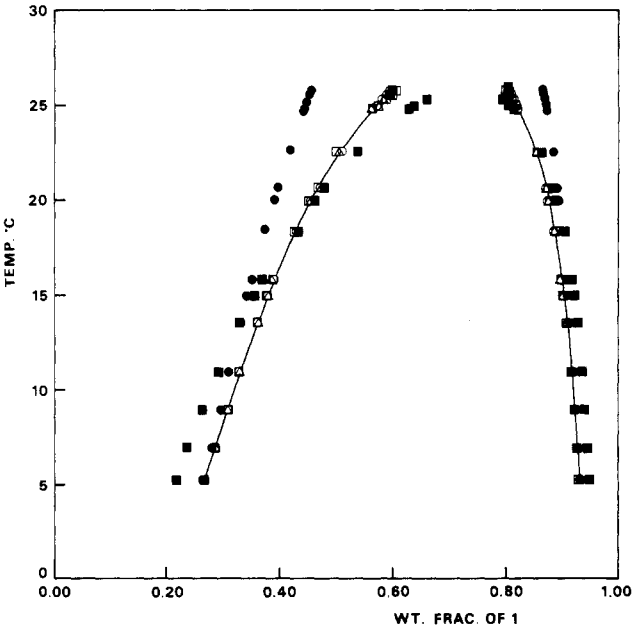

Figure 5. Mutual solubility of PFD/1-hexene: (□) experimental; (△) NRTL equation (α_{12} = 0.4); (○) UNIQUAC equation; (■) UNIFAC equation ($P = \phi(N_c)$); (●) UNIFAC equation (P, sim corr).

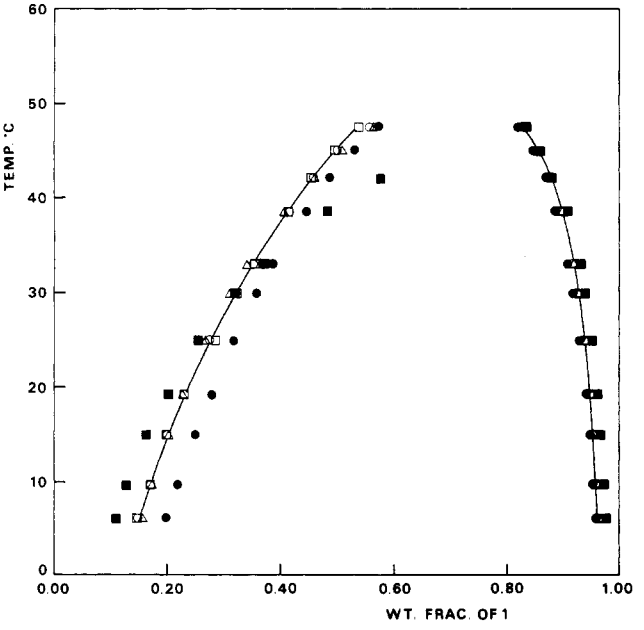

Figure 6. Mutual solubility of PFD/1-heptene: (□) experimental; (△) NRTL equation (α_{12} = 0.3); (○) UNIQUAC equation; (■) UNIFAC equation ($P = \phi(N_c)$); (●) UNIFAC, equation (P, sim corr).

The experimental and calculated solubility data are presented in Figures 1–6.

Registry No. Perfluorodecalin, 306-94-5; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; 1-hexene, 592-41-6; 1-heptene, 592-76-7.

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Received for review July 9, 1986. Accepted March 3, 1987.