MUTUAL BINARY SOLUBILITIES:
PERFLUOROMETHYLCYCLOHEXANE–HYDROCARBONS

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ABSTRACT

Bernardo Gil, M.G. and Soares, L.J.S., 1988. Mutual binary solubilities: perfluoromethyl-cyclohexane–hydrocarbons. *Fluid Phase Equilibria*, 41: 205–214.

Mutual binary solubility data for perfluoromethylcyclohexane + n-hexane, n-heptane, n-octane, n-nonane, 1-hexene and 1-heptene are reported.

NRTL and UNIQUAC parameters, for each experimental temperature, were obtained using a Newton–Raphson technique and the parameters so obtained were linearly correlated with T and T^{-1}.

UNIFAC group parameters for the interaction CH_2/CF_3 and $CH=CH_2/CF_3$ were obtained from mutual solubility data using the same technique.

UNIFAC parameters were correlated with the number of carbon atoms and temperature.

INTRODUCTION

As part of a program to study multicomponent mixtures containing perfluoromethylcyclohexane (PFMCH) and hydrocarbons, this paper reports the results of measurements on liquid–liquid equilibrium for PFMCH + n-hexane, + n-heptane, + n-octane, + n-nonane, + 1-hexene and + 1-heptene.

The correlation of the experimental data in terms of the NRTL, UNIQUAC and UNIFAC models is studied.

EXPERIMENTAL

Materials

PFMCH (Aldrich-Europe, minimum purity 99%), n-hexane, n-heptane, n-octane and n-nonane (Merck, minimum purity 99.5%) and 1-hexene and 1-heptene (Fluka, minimum purity 99%) were used as supplied.

TABLE 1

Experimental liquid–liquid equilibrium compositions for the binary system PFMCH + n-hexane

Temperature (K)	Phase compositions (wt. fraction)	
	X_{11}	X_{12}
276.25	0.4494	0.8840
276.45	0.4515	0.8790
277.25	0.4687	0.8751
278.45	0.5006	0.8671
279.15	0.5277	0.8571
279.55	0.5402	0.8500
280.55	0.5773	0.8344
281.55	0.6279	0.8086
281.75	0.6373	0.7981
281.85	0.6456	0.7976
281.95	0.6695	0.7680

Procedure

The experimental work was carried out using a thermostatted miniature cell similar to that described by Soares et al. (1974). Temperature was controlled within an accuracy of 0.01 K by means of a precision thermome-

TABLE 2

Experimental liquid–liquid equilibrium compositions for the binary system PFMCH + n-heptane

Temperature (K)	Phase compositions (wt. fraction)	
	X_{11}	X_{12}
278.15	0.2637	0.9454
279.15	0.2738	0.9416
281.15	0.2930	0.9375
283.25	0.3142	0.9318
285.75	0.3398	0.9244
288.15	0.3646	0.9145
290.45	0.3983	0.9018
293.15	0.4333	0.8868
295.65	0.4794	0.8707
298.15	0.5403	0.8422
299.15	0.5744	0.8248
299.35	0.5858	0.8200
299.65	0.6052	0.8107
300.35	0.6532	0.7718

TABLE 3

Experimental liquid–liquid equilibrium compositions for the binary system PFMCH + n-octane

Temperature (K)	Phase compositions (wt. fraction)	
	X_{11}	X_{12}
279.15	0.2034	0.9618
287.75	0.2479	0.9484
298.15	0.3189	0.9272
307.35	0.3991	0.8979
313.15	0.4606	0.8668
315.55	0.4954	0.8561
319.65	0.5555	0.8169
321.55	0.6399	0.7764

TABLE 4

Experimental liquid–liquid equilibrium compositions for the binary system PFMCH + n-nonane

Temperature (K)	Phase compositions (wt. fraction)	
	X_{11}	X_{12}
279.05	0.1347	0.9781
288.15	0.1808	0.9668
293.15	0.1924	0.9614
298.15	0.2209	0.9550
308.15	0.2710	0.9300
318.15	0.3383	0.8977
323.55	0.3893	0.8709
325.65	0.4247	0.8573
330.05	0.4902	0.8008

ter. The mixtures were stirred with a magnetic stirrer for at least 30 min and settled during a 4 h period. Mutual solubility data were obtained by analysing the compositions of the two conjugate phases using a gas chromatograph (Pye Unicam) combined with an electronic integrator (Varian CDS 111).

Special care was taken with measurements above room temperature to avoid phase splitting due to cooling.

Weight fraction measurements were accurate to within ±0.002.

Experimental results are presented in Tables 1–6.

TABLE 5

Experimental liquid–liquid equilibrium compositions for the system PFMCH + 1-hexene

Temperature (K)	Phase compositions(wt. fraction)	
	X_{11}	X_{12}
276.25	0.3761	0.9158
276.95	0.3841	0.9110
278.45	0.3995	0.8992
279.15	0.4095	0.8929
280.55	0.4284	0.8785
281.65	0.4481	0.8670
282.95	0.4810	0.8419
284.15	0.5119	0.8200
284.85	0.5403	0.8012
285.25	0.5596	0.7806
285.50	0.5691	0.7787
285.65	0.5808	0.7618
285.75	0.5902	0.7598
285.95	0.6668	0.7008
286.00	0.6851	0.6851

TABLE 6

Experimental liquid–liquid equilibrium compositions for the system PFMCH + 1-heptene

Temperature (K)	Phase compositions (wt. fraction)	
	X_{11}	X_{12}
279.15	0.2347	0.9464
283.15	0.2558	0.9404
288.15	0.2873	0.9283
293.15	0.3322	0.9141
298.15	0.3838	0.8882
300.65	0.4098	0.8720
303.15	0.4390	0.8558
305.55	0.4730	0.8318
306.15	0.4808	0.8245
307.75	0.5007	0.8009
308.15	0.5110	0.7960
309.35	0.5391	0.7762
310.65	0.5648	0.7423

CALCULATIONS

The thermodynamic equilibrium condition yields a system of N non-linear equations:

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

$$i = 1, N$$

A_1, A_2,... being the adjustable parameters of the selected correlating equation, x_{1j},..., x_{Nj} the composition of components $1-N$ in phase j, and T the temperature.

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

NRTL and UNIQUAC equations

The NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) parameters (a_{kl}) obtained from mutual solubility data were then correlated with the temperature, through:

$$a_{kl} = c_{kl} + d_{kl}T \tag{2}$$

$$a_{kl} = c'_{kl} + d'_{kl}/T \tag{3}$$

UNIFAC equation

One of the basic assumptions of a "contribution of groups" method is that the interaction parameters between groups are independent of the molecules where groups occur. This is obviously the main advantage of such methods, enabling predictions of multicomponent equilibria once the interaction parameters between groups (a_{ij}) are known.

For PFMCH/n-alkane mixtures the interaction parameters between groups, CH_3, CH_2, $CF_2(c)$, $CF(c)$ and CF_3 must be taken in account:

$$a_{CH_3/CH_2} = a_{CH_2/CH_3} = 0 \tag{4}$$

$$a_{CF_2(c)/CF(c)} = a_{CF(c)/CF_2(c)} = 0 \tag{5}$$

$$a_{CH_2/CF_2(c)} = a_{CH_3/CF_2(c)} = a_{CH_2/CF(c)} = a_{CH_3/CF(c)} \tag{6}$$

$$a_{CF_2(c)/CH_2} = a_{CF_2(c)/CH_3} = a_{CF(c)/CH_2} = a_{CF(c)/CH_3} \tag{7}$$

The interaction parameters $a_{CH_2/CF_2(c)}$ and $a_{CF_2(c)/CH_2}$ were obtained from mutual solubility data of perfluorodecaline/n-alkane systems (Bernardo Gil and Soares, 1986).

Considering in addition

$$a_{CH_2/CF_3} = a_{CH_3/CF_3} \tag{8}$$

$$a_{CH_3/CH_2} = a_{CF_3/CH_3} \tag{9}$$

the interaction parameters a_{CH_2/CF_3} and a_{CF_3/CH_2} can be obtained from mutual solubility data for any PFMCH/alkane system.

Having calculated the parameters from the experimental data for a given binary mixture we should be able to predict the mutual solubility data for any other PFMCH/n-alkane mixture. However, the analysis of PFMCH/ hydrocarbon binary equilibrium data revealed significant differences between the group interaction parameters obtained from experimental data for each PFMCH/hydrocarbon system. As a result the following alternative approaches were used.

(1) Simultaneous correlation of all mutual solubility data available for PFMCH/n-alkanes, allowing for the temperature dependence of the interaction parameters, through eqn. (2) or (3).

(2) Analysis of the parameter dependence on the number of carbon atoms of the alkane (N_c) and the temperature (T) using

$$a_{ij} = A_{ij} + B_{ij} N_c + C_{ij} N_c^2 \qquad (10)$$

where A_{ij}, B_{ij} and C_{ij} are temperature dependent.

These parameters together with the parameters determined for the $CH_2=CH/CF_2(c)$ interactions (Bernardo Gil and Soares, 1986) and the mutual solubility data for PFMCH/1-hexene and PFMCH/1-heptene allow the calculation of the group interaction parameters for $CH_2=CH/CF_3$.

The parameters recommended by Jorgensen et al. (1979) and by Magnussen et al. (1981) for $CH_2=CH/CH_2$ interactions were used.

DISCUSSION OF RESULTS

From the temperature-dependence analysis for the NRTL parameters (τ_{ij} and τ_{ji}) obtained from PFMCH/hydrocarbon mutual solubility data (Table 7), it is possible to infer that linear temperature dependence yields a better correlation of binary parameters. However, better results can be obtained for PFMCH/n-nonane with $\tau_{ij} = \phi (1/T)$.

For fluorocarbon/hydrocarbon systems a value of $\alpha_{12} = 0.4$ has been recommended by Renon et al. (1968). No significant evidence of improvement on the predicted mutual solubility data has been found when α_{12} is changed. As for the perfluorodecaline/hydrocarbon systems (Bernardo Gil and Soares, 1986), $\alpha_{ij} = 0.4$ can be used for PFMCH/n-hexane and PFMCH/1-hexene, but $\alpha_{ij} = 0.3$ is recommended for the other PFMCH/ hydrocarbon binaries.

A similar analysis was conducted for the UNIQUAC equation with equivalent results (Table 7). It must be pointed out that in the temperature-dependence analysis of the UNIQUAC parameters, the relationships (2) and

TABLE 7

RMSD ($\times 10^3$) values for PFMCH/hydrocarbon mutual solubility data, using temperature-dependent NRTL, UNIQUAC and UNIFAC parameters

System	NRTL equation				UNIQUAC equation				UNIFAC equation		
	$\tau_{ij} = \phi(T)$		$\tau_{ij} = \phi(1/T)$		τ_{ij}		Δu_{ij}		a_{ij}		
	$\alpha_{ij}=0.3$	$\alpha_{ij}=0.4$	$\alpha_{ij}=0.3$	$\alpha_{ij}=0.4$	$\phi(T)$	$\phi(1/T)$	$\phi(T)$	$\phi(1/T)$	a	b	c
PFMCH/n-hexane	3.3	3.7	5.9	5.0	4.0	6.0	4.1	4.8	4.0	45.9[5]	18.2
PFMCH/n-heptane	10.9	11.9	13.9	6.8	12.3	57.4	14.9	58.2	5.8	39.7[3]	16.1
PFMCH/n-octane	8.3	7.4	8.8	9.2	6.9	10.8	8.4	12.2	10.3	36.4[2]	45.3[3]
PFMCH/n-nonane	8.3	6.4	5.2	6.1	5.7	9.8	4.8	7.0	5.0	78.6[1]	36.1[1]
PFMCH/1-hexene	5.4	7.4	7.9	7.8	10.7	10.0	6.7	6.1	12.8	36.4[5]	32.0[5]
PFMCH/1-heptene	6.3	6.1	6.2	7.9	6.0	9.6	5.7	7.3	10.7	33.7[1]	63.4[5]

a, $a_{ij} = \phi(T)$ directly adjustable for each binary system (varying, obviously, from system to system).

b, $a_{ij} = \phi(T)$ obtained from simultaneous correlation of all available mutual solubility data.

c, a_{ij} as a function of the number of carbon atoms of the hydrocarbons considered and a 2nd-degree dependence of temperature for all the mutual solubility data available.

Superscript numbers (1–5) denote the number of upper tie-lines (close to C.S.T.) not included in the calculation.

TABLE 8

Recommended parameters

System	NRTL equation			UNIQUAC equation	
	a_{12}	τ_{12}	τ_{21}	τ_{12}	τ_{21}
PFMCH/n-hexane	0.4	$7.574-0.221T$	$12.70-0.0385T$	$1.1300-2.882\times10^{-3}T$	$1.6990+9.623\times10^{-3}T$
PFMCH/n-heptane	0.3	$6.682-0.01191T$	$7.229-0.0186T$	$0.0228+2.193\times10^{-3}T$	$0.4014+1.895\times10^{-3}T$
PFMCH/n-octane	0.3	$5.861-0.0150T$	$5.649-0.0128T$	$0.0373+2.200\times10^{-3}T$	$0.7399+5.862\times10^{-3}T$
PFMCH/n-nonane	0.3	$8.232-0.0219T$	$4.969-0.0100T$	$-0.6742+4.691\times10^{-3}T$	$1.375\ -1.726\times10^{-3}T$
PFMCH/1-hexene	0.4	$16.14\ -0.0525T$	$7.369-0.0187T$	$-3.1340+1.339\times10^{-3}T$	$3.516\ -9.108\times10^{-3}T$
PFMCH/1-heptene	0.3	$7.503-0.0219T$	$4.474-0.0083T$	$-0.8195+5.097\times10^{-3}T$	$1.492\ -1.987\times10^{-3}T$
				$r(\text{PFMCH}) = 7.07$	$q(\text{PFMCH}) = 6.44$

UNIFAC

$$a_{ij} = A_{ij} + B_{ij}N_c + C_{ij}N_c^2$$
$$a_{CH_3=CH/CH_2} = 2520.0 \text{ K}$$
$$a_{CH_2/CH_3=CH} = -200.0 \text{ K}$$

CH_2/CF_3
$A_{12} = 1.437\times10^4 - 2.093\times10^{-1}\,T^2$
$B_{12} = -2.555\times10^3 - 5.935\,T + 5.943\times10^{-2}\,T^2$
$C_{12} = 5.357\times10 - 7.909\times10^{-1}\,T - 4.256\times10^{-3}\,T^2$
$A_{21} = -2.025\times10^4 + 7.761\times10\,T$
$B_{21} = 4.826\times10^3 - 1.863\times10\,T$
$C_{21} = -2.721\times10^2 + 1.067\,T$

$CH_2=CH/CF_3$
$A_{12} = -9.913\times10^4 + 3.674\times10^2\,T$
$B_{12} = 1.217\times10^4 - 4.596\times10\,T$
$C_{12} = 0$
$A_{21} = 1.261\times10^4 - 6.493\times10\,T$
$B_{21} = -5.350\times10^2 + 5.240\,T$
$C_{21} = 0$

(3) were applied both to τ_{ij} and Δu_{ij}. The linear temperature dependence of τ_{ij} yields the best overall results, although better results can be obtained for PFMCH/n-nonane and PFMCH/1-hexene with $\Delta u_{ij} = \phi(T)$.

For the UNIFAC equation, the RMSD values between experimental and calculated compositions are, in general, much larger than for the other equations.

The correlation of the group interaction parameters with the number of carbon atoms of the hydrocarbons significantly improves the prediction. The simultaneous correlation of the available binary data does not seem suitable for the systems considered, although better results can be obtained for PFMCH/n-octane and PFMCH/1-heptene with this method.

For some tie-lines close to the critical solute temperature there are problems in convergence with UNIFAC parameters using either the temperature dependence obtained from simultaneous correlation of all available mutual solubility data or the correlation of the UNIFAC parameters with the number of carbon atoms of the hydrocarbons. This is due to the tendency of the equation to predict critical solution temperatures lower than the values obtained experimentally.

The RMSD values obtained when a_{ij} are directly adjusted for each binary system (varying from system to system) are given in Table 7 as references with which to compare the other results. Obviously, the parameters so calculated have no significance in terms of a "group contribution" method.

Owing to cumulative errors, resulting from the step-by-step method used for the calculation of group interaction parameters, the larger deviations found with UNIFAC for PFMCH/alkenes were expected: $CH_2=CH/CF_3$ interactions were the last to be accounted for using the values previously assumed for all the other groups.

Recommended parameters for NRTL, UNIQUAC and UNIFAC equations are presented in Table 8.

ACKNOWLEDGEMENTS

LIST OF SYMBOLS

a_{ij}(UNIFAC)   UNIFAC group parameters defined as (Fredenslund et al., 1975)

$$a_{ij} = \frac{U_{ij} - U_{jj}}{R}$$

g_{ij}, u_{ij}	measure of the interaction energy between molecules i and j.
U_{ij}	measure of the interaction energy between groups i and j.
$CF_2(c)$, $CF(c)$	denote cyclic molecules.
X_{ij}	weight fraction of component i in phase j.
τ_{ij}(NRTL)	NRTL adjustable parameters defined as (Renon and Prausnitz, 1968)

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}$$

τ_{ij}(UNIQUAC)   UNIQUAC adjustable parameters defined as (Abrams and Prausnitz, 1975)

$$\tau_{ij} = \exp\left(-\frac{u_{ij} - u_{jj}}{RT}\right) = \exp\left(-\frac{\Delta u_{ij}}{RT}\right)$$

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