LIQUID–LIQUID EQUILIBRIA OF SYSTEMS CONTAINING PERFLUOROMETHYLCYCLOHEXANE

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ABSTRACT

Bernardo-Gil, M.G. and Soares, L.J.S., 1990. Liquid–liquid equilibria of systems containing perfluoromethylcyclohexane. *Fluid Phase Equilibria*, 61: 121–130.

Liquid–liquid equilibria for the quaternary system perfluoromethylcyclohexane (PFMCH)–1-heptene–n-heptane–n-hexane at 288.15 K and for the ternary systems PFMCH–1-heptene–n-heptane, PFMCH–1-heptene–n-hexane and PFMCH–n-heptane–n-hexane at 279.15 K and 288.15 K are reported.

The experimental results are compared with predicted values calculated using the NRTL and the UNIQUAC models.

INTRODUCTION

Multicomponent mixtures consisting of perfluorocarbons and hydrocarbons change swiftly from type to type pattern over a small temperature range. Following our experimental determination of binary solubility data for some perfluoromethylcyclohexane–hydrocarbon systems (Bernardo-Gil and Soares, 1988), this paper reports the results of measurements on liquid–liquid equilibrium for ternary and quaternary systems containing perfluoromethylcyclohexane (PFMCH), 1-heptene, n-heptane and n-hexane.

Predictions of equilibrium data for these mixtures were made using NRTL and UNIQUAC perfluoromethylcyclohexane–hydrocarbon parameters obtained from binary data. Hydrocarbon–hydrocarbon parameters were calculated by correlating the ternary data. The results are compared with the experimental ones.

EXPERIMENTAL

Materials

PFMCH (Fluka, $\simeq 98\%$ (GC)), n-hexane, n-heptane (p. a., Merck) and 1-heptene (Fluka, $\simeq 95\%$) were used as supplied.

Procedure

The experimental work was carried out using a thermostatted miniature cell similar to that described by Soares et al. (1974). Temperature was measured within an accuracy of 0.01 K by means of a precision thermometer. The mixtures were stirred with a magnetic stirrer for at least 30 min and allowed to settle during a 4 h period. The tie-lines were obtained by analysing the compositions of the two conjugate phases in equilibrium by means of a gas chromatograph (Pye–Unicam) connected to an integrator (Varian CDS 111).

Calibration curves were obtained by using at least 10 mixtures of known composition, for which four to six chromatograms were obtained. Four to six samples of both phases were analysed to minimize the experimental error. The observation of the results shows also whether equilibrium has been reached.

TABLE 1

Experimental liquid–liquid equilibrium compositions for the ternary system PFMCH (1)–1-heptene (2)–n-heptane (3)

Temperature (K)	Weight fraction			
	X_{11}	X_{31}	X_{12}	X_{32}
279.15	0.9451	0.0159	0.2469	0.2200
	0.9410	0.0239	0.2510	0.2988
	0.9448	0.0242	0.2554	0.3320
	0.9447	0.0298	0.2556	0.3910
	0.9448	0.0362	0.2569	0.4609
	0.9432	0.0402	0.2658	0.5362
288.15	0.9188	0.0716	0.3555	0.5567
	0.9191	0.0686	0.3546	0.5294
	0.9193	0.0601	0.3427	0.4753
	0.9216	0.0425	0.3310	0.3586
	0.9230	0.0338	0.3233	0.2960
	0.9237	0.0266	0.3144	0.2422
	0.9260	0.0217	0.3094	0.2069
	0.9265	0.0135	0.3000	0.1250

TABLE 2

Experimental liquid–liquid equilibrium compositions for the ternary system PFMCH (1)–1-heptene (2)–n-hexane (3)

Temperature (K)	Weight fraction			
	X_{11}	X_{31}	X_{12}	X_{32}
279.15	0.9042	0.0750	0.4143	0.4254
	0.9179	0.0519	0.3598	0.3602
	0.9268	0.0392	0.3348	0.3162
	0.9345	0.0280	0.3212	0.2502
	0.9390	0.0207	0.2917	0.1973
	0.9412	0.0128	0.2691	0.1272
288.15	0.9158	0.0197	0.3399	0.1389
	0.9006	0.0330	0.3877	0.2113
	0.8969	0.0443	0.3902	0.2363
	0.8786	0.0660	0.4506	0.2732
	0.8593	0.0870	0.5024	0.2874
	0.8195	0.1252	0.6147	0.2579

Tables 1–3 summarize the experimental results obtained for the ternary systems. Quaternary tie-line data are presented in Table 4.

ANALYSIS OF RESULTS

Prediction of ternary and quaternary liquid–liquid equilibrium data was realized using the well-known NRTL and UNIQUAC models proposed by

TABLE 3

Experimental liquid–liquid equilibrium compositions for the ternary system PFMCH (1)–n-heptane (2)–n-hexane (3)

Temperature (K)	Weight fraction			
	X_{11}	X_{31}	X_{12}	X_{32}
279.15	0.8973	0.0812	0.4390	0.4208
	0.9094	0.0659	0.4091	0.3812
	0.9147	0.0550	0.3873	0.3521
	0.9239	0.0357	0.3482	0.2677
	0.9272	0.0268	0.3271	0.2199
	0.9324	0.0199	0.3136	0.1702
	0.9376	0.0098	0.2943	0.0968
288.15	0.9083	0.0124	0.3968	0.0750
	0.8908	0.0352	0.4501	0.1600
	0.8669	0.0627	0.4968	0.2205
	0.8455	0.0865	0.5572	0.2350
	0.8226	0.1054	0.5942	0.2350

TABLE 4

Experimental liquid–liquid equilibrium compositions for the quaternary system PFMCH (1)–1-heptene (2)–n-heptane (3)–n-hexane (4)

| Temperature (K)	Weight fraction					
	X_{11}	X_{31}	X_{41}	X_{12}	X_{32}	X_{42}
288.15	0.9148	0.0134	0.0063	0.3201	0.1137	0.0457
	0.9095	0.0258	0.0115	0.3485	0.1897	0.0755
	0.8782	0.0213	0.0530	0.4485	0.1119	0.2252
	0.8421	0.0183	0.0982	0.5228	0.0676	0.2849
	0.8355	0.0436	0.0933	0.5360	0.1324	0.2643
	0.8848	0.0559	0.0412	0.4396	0.2820	0.1838
	0.9002	0.0390	0.0334	0.4014	0.2477	0.1772
	0.9048	0.0394	0.0207	0.3880	0.2653	0.1175
	0.8865	0.0354	0.0479	0.4484	0.1834	0.2082
	0.8627	0.0317	0.0784	0.5245	0.1163	0.2519
	0.8309	0.0302	0.1126	0.5925	0.0799	0.2582
	0.8677	0.0409	0.0767	0.5320	0.1561	0.2540
	0.8787	0.0491	0.0537	0.4751	0.2213	0.2106
	0.8892	0.0521	0.0378	0.4270	0.2773	0.1842
	0.8981	0.0519	0.0288	0.4162	0.3043	0.1498
	0.9063	0.0537	0.0179	0.3869	0.3585	0.1042
	0.9081	0.0574	0.0113	0.3748	0.3904	0.0697
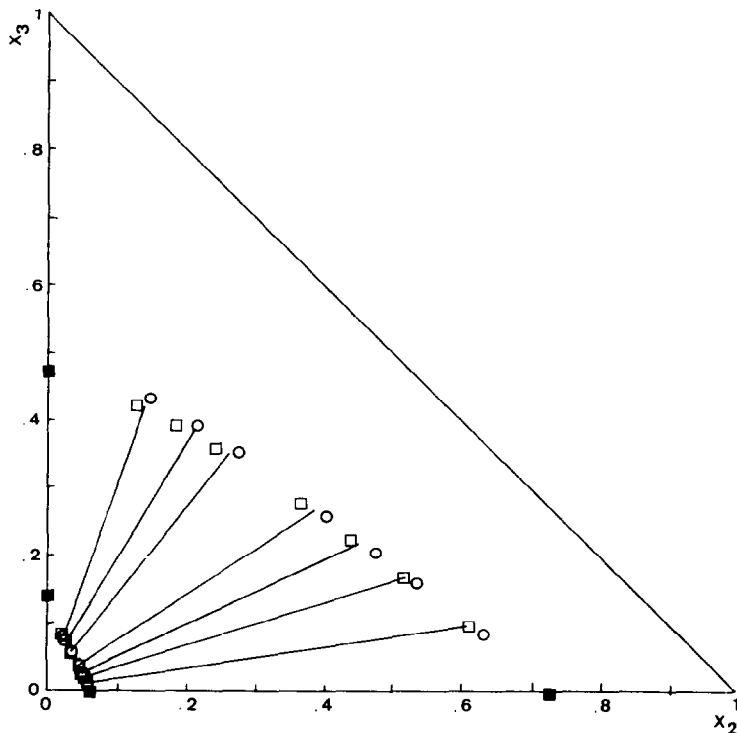
Fig. 1. Liquid–liquid equilibrium diagram for PFMCH–n-heptane–n-hexane at 279.15 K: (———) experimental tie-lines; (■) binary data; (□) NRTL equation ($\alpha_{12} = 0.3$, $\alpha_{13} = 0.4$, $\alpha_{23} = 0.3$); (○) UNIQUAC equation.

TABLE 5

Recommended values for the NRTL and UNIQUAC parameters at 279.15 K and 288.15 K

System	T (K)	NRTL			UNIQUAC	
		α_{12}	b_{12} (K)	b_{21} (K)	c_{12} (K)	c_{21} (K)
PFMCH–n-hexane	279.15	0.4	392.1	545.1	131.0	3.579
	288.15	0.4	347.5	462.8	147.4	− 20.53
PFMCH–n-heptane	279.15	0.3	376.9	568.6	126.7	20.16
	288.15	0.3	339.5	538.7	122.0	15.56
PFMCH–1-heptene	279.15	0.3	387.9	602.1	141.1	18.02
	288.15	0.3	343.6	600.0	124.4	24.24

Renon and Prausnitz (1968) and by Abrams and Prausnitz (1975) respectively. Agreement between calculated and experimental data is expressed in terms of composition root-mean-square deviations (RMSD):
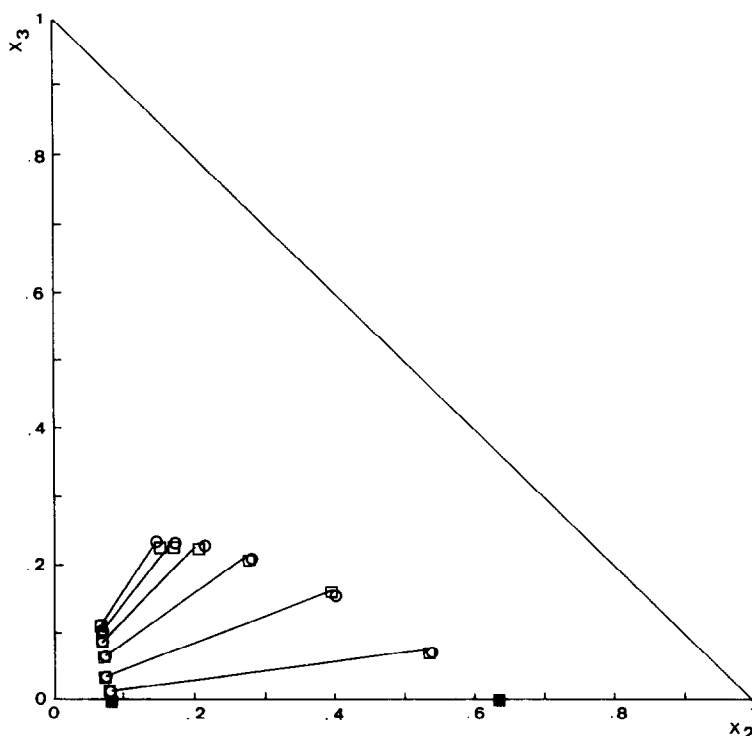
Fig. 2. Liquid–liquid equilibrium diagram for PFMCH–n-heptane–n-hexane at 288.15 K. Symbols as in Fig. 1.

TABLE 6

RMSD ($\times 10^3$) between calculated and experimental values

System	T (K)	Type	NRTL		UNIQUAC	
			A [a]	B [b]	A [a]	B [b]
PFMCH–n-heptane–	279.15	II	9.5	9.5	8.9	15.5
n-hexane	288.15	I	4.2	9.9	8.4	10.2
PFMCH–1-heptene–	279.15	II	7.8	8.7	7.8	7.8
n-hexane	288.15	I	12.8	14.3	17.2	17.2
PFMCH–1-heptene–	279.15	II	9.7	10.8	9.6	11.3
n-heptane	288.15	II	4.7	5.2	4.2	4.4
PFMCH–1-heptene– n-heptane–n-hexane	288.15	II	10.5	12.1	13.2	18.0

[a] A: Direct correlation of ternary data, keeping α_{ij} constant.

[b] B: For the PFMCH–hydrocarbon parameters the linear correlation with temperature was used. The hydrocarbon–hydrocarbon parameters were determined from the ternary data.
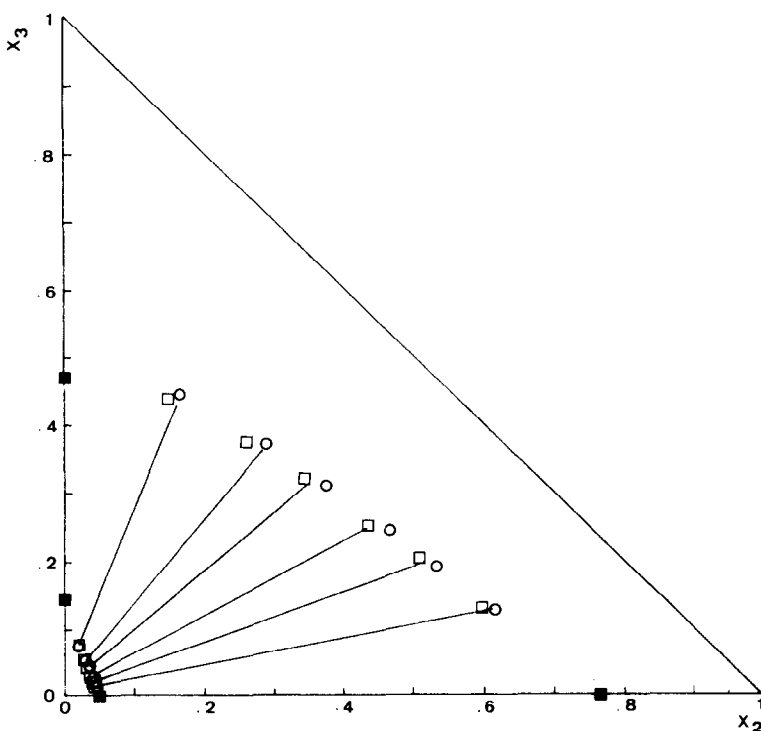
Fig. 3. Liquid–liquid equilibrium diagram for PFMCH–1-heptene–n-hexane at 279.15 K. Symbols as in Fig. 1.

$$\text{RMSD} = \left[\frac{\sum\limits_{k}^{M} \sum\limits_{i}^{N} \sum\limits_{j}^{2} \left(x_{ijk}^{cal} - x_{ijk}^{exp} \right)^2}{2N(M-1)} \right]^{1/2}$$

(1)

Binary NRTL and UNIQUAC parameters were determined using two alternative approaches. Method A involved direct correlation of ternary data, the number of adjusted parameters varying from 1 to 6, keeping α_{ij} constant (0.3 for hydrocarbon–hydrocarbon systems (Renon and Prausnitz, 1968) and the recommended values for PFMCH–hydrocarbon binaries (Bernardo-Gil and Soares, 1988)). In method B, for the PFMCH–hydrocarbon binaries, the linear temperature dependence of parameters obtained from the correlation of binary solubility data was used; hydrocarbon–hydrocarbon parameters were calculated adjusting ternary tie-line data.
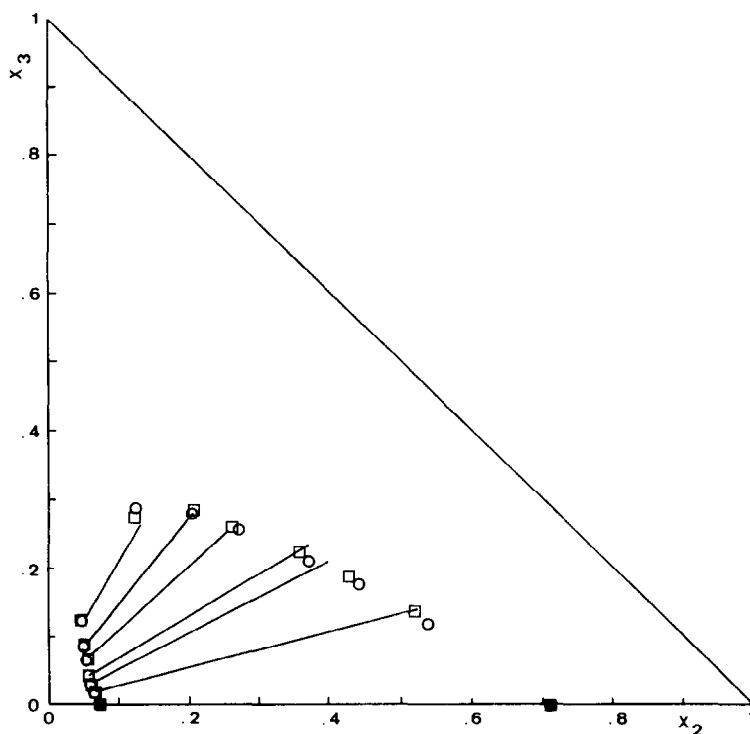

Fig. 4. Liquid–liquid equilibrium diagram for PFMCH–1-heptene–n-hexane at 288.15 K. Symbols as in Fig. 1.
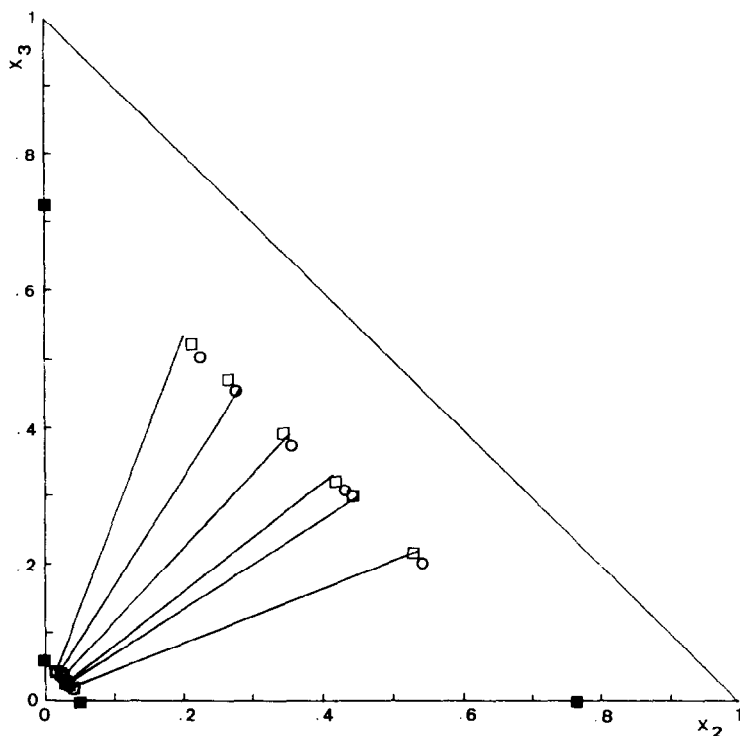
Fig. 5. Liquid–liquid equilibrium diagram for PFMCH–1-heptene–n-heptane at 279.15 K: (———) experimental tie-lines; (■) binary data; (□) NRTL equation ($\alpha_{12} = 0.3$, $\alpha_{13} = 0.3$, $\alpha_{23} = 0.3$); (○) UNIQUAC equation.

Binary parameters from ternary data were calculated using the Nelder–Mead method for the minimization of the following objective functions:

$$F1 = \sum_{k}^{M} \sum_{i}^{N} \left[\ln(\gamma_{i1}/\gamma_{i2}) - \ln(x_{i2}/x_{i1}) \right]_{k}^{2} \tag{2}$$

$$F2 = \sum_{k}^{M} \sum_{i}^{N} \sum_{j}^{2} \left(x_{ijk}^{cal} - x_{ijk}^{exp} \right)^{2} \tag{3}$$

with $3M > L$, M being the available number of tie-lines, N the number of components and L the number of parameters.

The NRTL and UNIQUAC parameters recommended for the PFMCH–hydrocarbon binaries are presented in Table 5.

Table 6 shows the values of RMSDs between experimental and calculated compositions. Figures 1–6 represent the experimental and calculated tie-lines.

CONCLUSIONS

The experimental results were correlated in terms of NRTL and UN-IQUAC equations, which represent the binodal curves and the tie-lines correctly either for type I or type II systems.

With a slight loss of accuracy (relative to the results obtained from direct correlation of data for individual ternary systems) it is possible to obtain a set of NRTL and UNIQUAC parameters applicable to all multicomponent mixtures of PFMCH and hydrocarbons.

The overall results are better for the NRTL equation with use of recommended values of α_{ij}, although the predicted multicomponent data are strongly dependent on the selected α_{ij} for the partially miscible binaries.
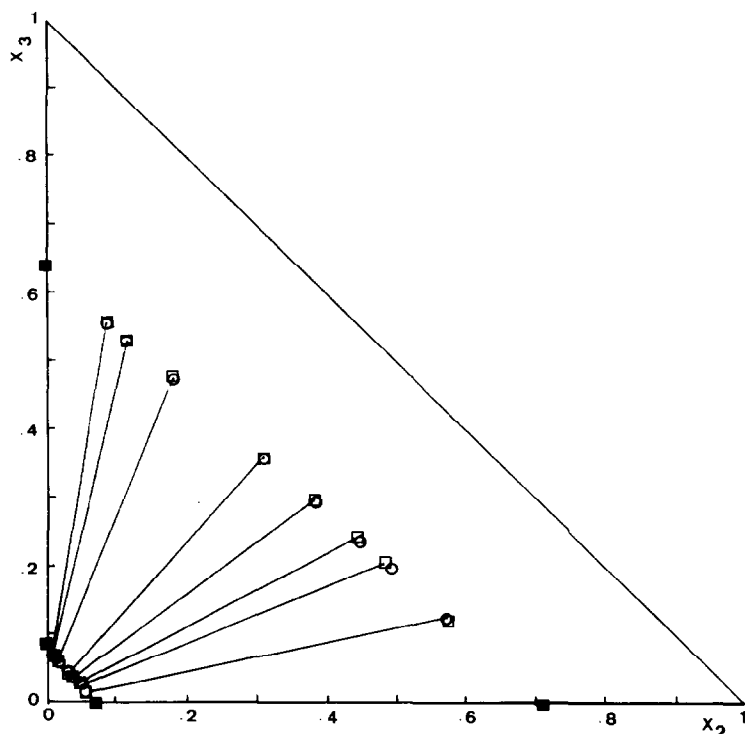

Fig. 6. Liquid–liquid equilibrium diagram for PFMCH–1-heptene–n-heptane at 288.15 K. Symbols as in Fig. 5.

LIST OF SYMBOLS

A, B   methods of correlation of ternary data (Table 6).

b_{ij} NRTL parameters, K, where $b_{ij} = (g_{ij} - g_{jj})/R$

c_{ij} UNIQUAC parameters, K, where $c_{ij} = (u_{ij} - u_{jj})/R$

g_{ij}, u_{ij} measures of the interaction energy between molecules i and j

x_{ij} molar fraction of component i in phase j

X_{ij} weight fraction of component i in phase j

U_{ij} measure of the interaction energy between groups i and j

α_{ij} non-randomness NRTL parameter

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