

PERFLUORODECALINE/HYDROCARBON SYSTEMS PREDICTION AND CORRELATION OF LIQUID–LIQUID EQUILIBRIUM DATA

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ABSTRACT

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Experimental binary, ternary and quaternary liquid–liquid equilibrium data for systems containing perfluorodecaline (PFD) and some hydrocarbons were determined.

Binary NRTL, UNIQUAC and UNIFAC parameters were obtained, from the binary, the ternary and the quaternary experimental data: for the calculation of parameters from binary data a Newton–Raphson technique was used and the parameters so obtained—for each temperature (T)—were linearly correlated with T and $1/T$. Predicted binary, ternary and quaternary data were then compared with the experimental results; a Nelder–Mead method was used for the calculation of the binary parameters from ternary tie-line data.

UNIFAC group parameters for the interaction CH_2/CF_2 and $\text{CH}=\text{CH}_2/\text{CF}_2$ were obtained.

Attempts were made, and are discussed, to: correlate UNIFAC parameters with the number of carbon atoms and temperature; obtain a set of NRTL and UNIQUAC parameters yielding the overall best fit for the systems under consideration.

INTRODUCTION

Numerous equations have been proposed relating the activity coefficients to liquid mole fractions, namely equations based on the local composition model (Renon and Prausnitz, 1968; Abrams and Prausnitz, 1975; Fredenslund et al., 1975). The assessment of a correlating equation requires the availability of binary mutual solubility data, ternary and quaternary tie-line data and binary and ternary vapour–liquid equilibria data at the same temperature.

Perfluorocarbon/hydrocarbon systems are particularly adequate, as ternary and quaternary mixtures change swiftly from type to type of equilibrium pattern over a small temperature range. A comprehensive determina-

tion and analysis of binary, ternary and quaternary data was, therefore, undertaken.

The experimental results were obtained on an equilibrium still, similar to that described by Soares (1972) and Soares et al. (1974), using gas-liquid chromatographic analysis, and will be published elsewhere. The present paper concerns itself with the correlation of binary and multicomponent data, with particular emphasis on that building up to the quaternary system perfluorodecaline/*n*-heptane/1-hexene/*n*-hexane.

CALCULATION PROCEDURES

Methods using a system of non-linear equations

Combining the thermodynamic condition of equilibrium with the relevant stoichiometric relations yields (Soares, 1972; Soares et al., 1974) a system of N non-linear equations

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

A_1, A_2, \dots being the adjustable parameters of the selected correlating equation, x_{1j}, \dots, x_{Nj} the composition of components 1 to 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 (Soares, 1972) enabling not only the calculation of binary parameters from mutual solubility data, but also the prediction of binary and multicomponent data, once the correlating equation parameters were known.

The NRTL (Renon et al., 1971) and UNIQUAC (Abrams and Prausnitz, 1975) parameters (A_k) obtained from mutual solubility data were then correlated with the temperature, through

$$A_k = c + d \cdot T \quad (2)$$

$$A_k = c' + d'/T \quad (3)$$

Methods using an objective function and a Nelder-Mead minimization procedure

Binary NRTL, UNIQUAC and UNIFAC parameters were also obtained by correlation of ternary data, using a Nelder-Mead minimization procedure coupled with one of the following objective functions

$$F'_1 = \sum_{k=1}^M \sum_{i=1}^N \left[\ln \left(\frac{\gamma_{i1}}{\gamma_{i2}} \right)_k - \ln \left(\frac{x_{i2}}{x_{i1}} \right)_k \right]^2 \quad (4)$$

$$F'_2 = \sum_{k=1}^M \sum_{i=1}^N \sum_{j=1}^2 [x_{ijk}^{\text{cal}} - x_{ijk}^{\text{exp}}]^2 \quad (5)$$

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

The objective function F'_2 obviously yields a better agreement between experimental and calculated compositions, but requires a much longer computing time. As a result of that, F'_1 was used at the initial stages of the minimization procedure, changing later to F'_2 .

Prediction of equilibrium compositions

Prediction of multicomponent equilibrium data was made using not only the parameters obtained from binary data alone but also those calculated from ternary data. Agreement between calculated and experimental data is expressed in terms of composition root mean square deviations (RMSD).

RESULTS

NRTL and UNIQUAC equations

From the temperature-dependence analysis for the NRTL parameters (τ_{ij} and τ_{ji}), obtained from perfluorodecaline/hydrocarbon mutual solubility data, it is possible to infer that:

Linear temperature-dependence yields a better correlation of binary parameters, whenever prediction of both mutual solubility and of multicomponent data is considered. For mutual solubility data alone (Table 1 and Fig. 1) better results can be obtained for PFD/*n*-hexane and PFD/*n*-nonane with $A_k = \phi(1/T)$.

Significant deviations are found when data close to the critical solution temperature (C.S.T.) are taken into consideration, due not only to the inability of the equation to describe the solution behaviour, but also the experimental uncertainty for that temperature-composition range: RMSD values for PFD/*n*-hexane are lowered, from 13.4×10^{-3} to 3.8×10^{-3} , if the experimental tie-line close to C.S.T. is not considered.

Predicted C.S.T. values are greater for PFD/*n*-hexane and PFD/*n*-heptane, lower for PFD/*n*-nonane and PFD/1-heptene, and not significantly different from the experimental C.S.T., for the other binaries.

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} was changed. That obviously does not apply to multicomponent equilibria.

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

TABLE 1
 RMSD (10^2) values for PFD/hydrocarbon mutual solubility data, using temperature-dependent NRTL, UNIQUAC and UNIFAC parameters

System	NRTL equation		UNIQUAC equation			UNIFAC equation					
	$\tau_{ij} = \phi(T)$		τ_{ij}	$\phi(1/T)$	Δu_{ij}	a	b	c			
	$\alpha_{ij} = 0.3$	$\alpha_{ij} = 0.4$	$\alpha_{ij} = 0.3$	$\alpha_{ij} = 0.4$	$\phi(T)$	$\phi(1/T)$	$\phi(1/T)$	a_{ij}			
PFD/n-hexane	9.6	13.4	5.1	4.8	7.4	6.1 ¹	7.4	5.8 ¹	7.5	37.3 ³	7.8
PFD/n-heptane	7.9	8.3	11.3	11.0	9.6	15.9	11.8	8.5	11.3	29.2	12.2
PFD/n-octane	6.0	6.8	11.1	12.4	13.1	13.7	18.5	16.7	12.1	21.4 ⁴	45.3 ³
PFD/n-nonane	10.0	8.8	4.4	3.9	7.8	3.2	8.5	3.7	3.5	42.0	8.4
PFD/1-hexene	5.7	5.0	7.7	7.5	6.2	8.5	7.3	9.0	7.0	25.0 ⁵	34.0 ²
PFD/1-heptene	6.2	6.7	7.3	7.9	6.0	8.2	8.0	9.0	8.1	22.4	36.8 ²

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

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

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

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

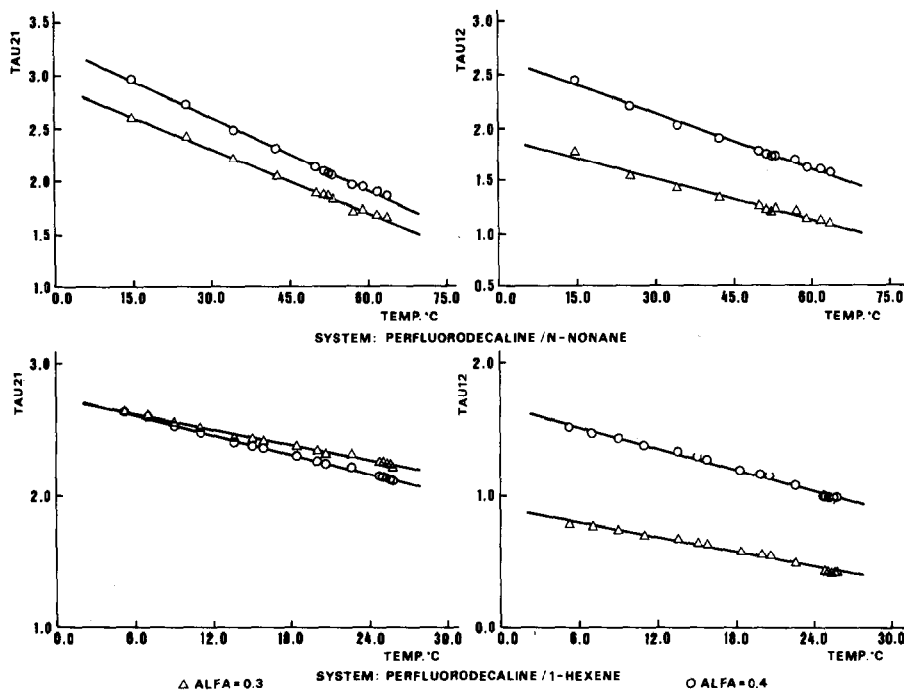


Fig. 1. NRTL equation: temperature dependence of the binary parameters.

For the analysis of ternary and quaternary data the following alternative approaches were adopted:

(1) prediction of equilibrium compositions using, for PFD/hydrocarbon binaries, the temperature-dependent parameters (obtained from correlation of mutual solubility data with the suggested values of α_{ij}), and assuming ideal behaviour for the hydrocarbon/hydrocarbon binaries. For temperatures above C.S.T. the binary parameters were obtained by extrapolation, assuming linear temperature-dependence of τ_{ij} ;

(2) direct correlation of ternary data, the number of adjusted parameters varying from 1 to 8, and keeping constant $\alpha_{ij} = 0.3$ for hydrocarbon/hydrocarbon systems; and

(3) using the temperature-dependent PFD/hydrocarbon parameters, obtained from mutual solubility data with the recommended α_{ij} , and adjusting the hydrocarbon/hydrocarbon parameters, using ternary tie-line data.

The overall comparative study of RMSD values for all the alternative methods and systems allows the recommendation of a set of NRTL temperature-dependent binary parameters that can be used for all the systems concerned (binary, ternary and quaternary). Tables 1 and 2 show RMSD values for some of the binary, ternary and quaternary PFD/hydrocarbon

TABLE 2
 RMSD ($\times 10^3$) values for some ternary and quaternary PFD/hydrocarbon systems

System	Temp.	Type	NRTL			UNIQUAC			UNIFAC		
			a	b	c	d	b	c	d	e	f
PFD/ <i>n</i> -heptane/ <i>n</i> -hexane	15	II	5.4	13.3	5.4	8.7	9.5	5.4	8.7	9.5	17.9
	25	I	5.5	6.3	5.5	5.7	20.4	13.9	14.7	15.0	51.0
	30	I	22.2	41.2	25.2	24.9	38.7	28.2	31.7	39.4	79.0
PFD/1-hexene/ <i>n</i> -hexane	15	II	3.6	14.0	14.0	14.0	15.6	7.1	8.0	17.1	25.5
	25	I	12.4	12.8	12.8	12.8	13.9	13.9	13.9	15.1	85.4
PFD/ <i>n</i> -heptane/ 1-hexene	15	II	8.4	18.5	11.3	17.4	9.9	8.4	9.6	10.2	18.4
	25	II	11.8	12.6	11.8	12.4	25.2	23.8	24.9	18.4	33.4
	30	I	14.9	42.5	17.0	16.4	27.8	15.2	16.6	23.2 ²	72.2 ¹
PFD/ <i>n</i> -heptane/ 1-hexene/ <i>n</i> -hexane	15	III	11.6	11.6	14.9	13.2	21.2	20.2	19.4	18.4	22.3
	25	II	11.9	11.4 ¹	11.7	11.9	13.1 ¹	43.3	13.5	13.4	47.0

^a Best agreement between predicted and experimental results, for the NRTL equation. Usually obtained by direct correlation of ternary data. Adjusted α_{ij} values may differ from the recommended values.

^b Temperature-dependent PFD/hydrocarbon parameters obtained from mutual solubility data. Hydrocarbon/hydrocarbon mixtures assumed ideal.

^c Direct correlation of ternary data. Recommended α_{ij} are used for NRTL equation.

^d Temperature-dependent PFD/hydrocarbon parameters obtained from mutual solubility data. Hydrocarbon/hydrocarbon parameters adjusted with ternary equilibrium data.

^e UNIFAC parameters dependent on the number of carbon atoms.

^f UNIFAC parameters obtained from simultaneous correlation of all available data.

¹⁻² denote the number of upper tie-lines (close to C.S.T.) not included in the calculation.

TABLE 3
Recommended parameters

System	α	NRTL		UNIQUAC	
		τ_{12}	τ_{21}	τ_{12}	τ_{21}
PFD/ <i>n</i> -hexane	0.4	7.449 - 0.0214 <i>T</i>	10.760 - 0.0295 <i>T</i>	0.8239 - 8.170 × 10 ⁻⁴ <i>T</i>	-0.4420 + 5.15 × 10 ⁻³ <i>T</i>
PFD/ <i>n</i> -heptane	0.3	5.292 - 0.0143 <i>T</i>	8.349 - 0.0208 <i>T</i>	0.4511 + 4.350 × 10 ⁻⁴ <i>T</i>	0.1505 + 3.050 × 10 ⁻³ <i>T</i>
PFD/ <i>n</i> -octane	0.3	6.317 - 0.0169 <i>T</i>	7.067 - 0.0159 <i>T</i>	0.0906 + 1.820 × 10 ⁻³ <i>T</i>	0.6864 + 1.000 × 10 ⁻³ <i>T</i>
PFD/ <i>n</i> -nonane	0.3	5.406 - 0.0129 <i>T</i>	8.395 - 0.0201 <i>T</i>	0.6964 - 1.348 × 10 ⁻⁴ <i>T</i>	0.0033 + 3.178 × 10 ⁻³ <i>T</i>
PFD/1-hexene	0.4	8.953 - 0.0267 <i>T</i>	9.363 - 0.0242 <i>T</i>	0.0770 + 1.737 × 10 ⁻³ <i>T</i>	0.4668 + 1.951 × 10 ⁻³ <i>T</i>
PFD/1-heptene	0.3	5.459 - 0.0151 <i>T</i>	7.641 - 0.0174 <i>T</i>	0.2640 - 1.143 × 10 ⁻³ <i>T</i>	0.4331 + 1.891 × 10 ⁻³ <i>T</i>
UNIFAC					
$a_{ij} = A_{ij} + B_{ij} \cdot N_c + C_{ij} \cdot N_c^2$					
$a_{\text{CH}_2-\text{CH}/\text{CH}_2} = 2520.0 \text{ K}$					
$a_{\text{CH}_2/\text{CH}_2-\text{CH}} = -200.0 \text{ K}$					
$\text{CH}_2 = \text{CH}/\text{CF}_2(\text{c})$					
$A_{12} = 3942.0 - 13.16 \text{ T}$					
$B_{12} = -96.11 + 3.151 \text{ T}$					
$C_{12} = 61.98 - 0.1999 \text{ T}$					
$A_{21} = -4190.0 + 13.75 \text{ T}$					
$B_{21} = 1113.00 - 3.469 \text{ T}$					
$C_{21} = 72.18 + 0.2218 \text{ T}$					
$A_{12} = 3.142 \times 10^4 - 2.195 \times 10^2 \text{ T} + 3.816 \times 10^{-1} \text{ T}^2$					
$B_{12} = -4.796 \times 10^3 + 3.397 \times 10 \text{ T} - 5.954 \times 10^{-2} \text{ T}^2$					
$C_{12} = 0$					
$A_{21} = -9.402 \times 10^4 + 6.557 \times 10^2 \text{ T} - 1.140 \text{ T}^2$					
$B_{21} = 1.422 \times 10^4 - 9.898 \times 10 \text{ T} + 1.721 \times 10^{-1} \text{ T}^2$					
$C_{21} = 0$					

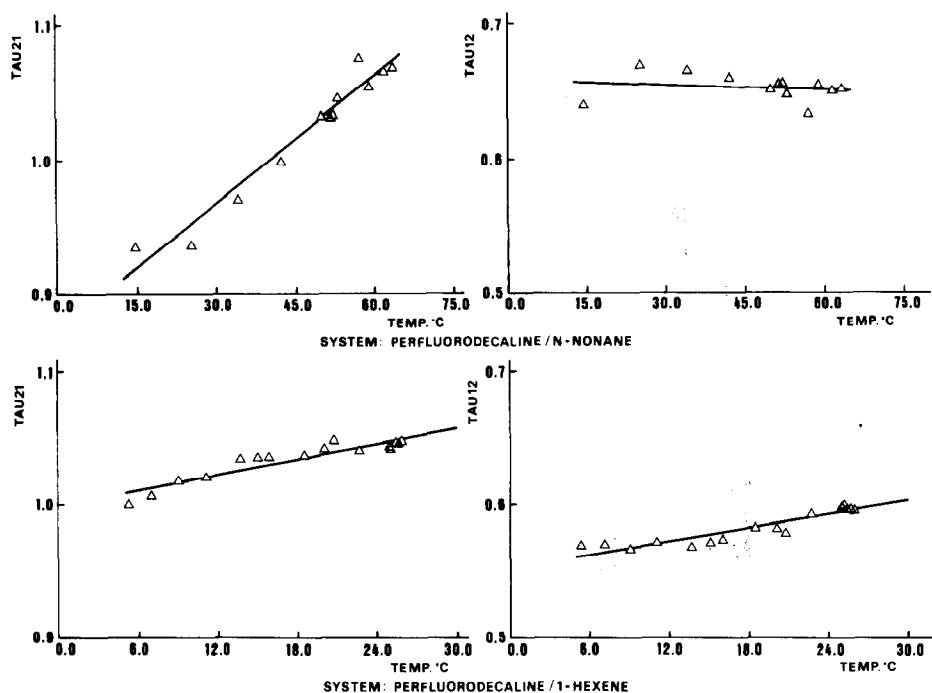


Fig. 2. UNIQUAC equation: temperature dependence of the binary parameters.

systems studied (building up to the quaternary system PFD/*n*-heptane/1-hexene/*n*-hexane). The lowest RMSD values (usually obtained by direct correlation of ternary data) were retained as a standard of reference to judge the relative adequacy of a given method for a particular system.

A similar analysis was conducted for the UNIQUAC equation with equivalent results (Tables 1, 2, 3 and Fig. 2). It must be pointed out that:

(1) in the temperature-dependence analysis of the UNIQUAC parameters, the relationships (1) and (2) were applied both to τ_{ij} and Δu_{ij} (Table 1). The linear temperature dependence of τ_{ij} yields the best overall results, when binary and multicomponent data are accounted for; and

(2) although a worst fit in terms of τ_{ij} is obtained for the UNIQUAC equation, if compared with the NRTL equation (Figs. 1 and 2), the deviations are smoothed out in terms of compositions (Table 1), due to the difference in the definition of τ_{ij} , for the two correlating equations.

Predicted and experimental tie-line and binodal curve data are represented in Figs. 3 and 4, for PFD/*n*-heptane/*n*-hexane at 15 and 25°C.

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

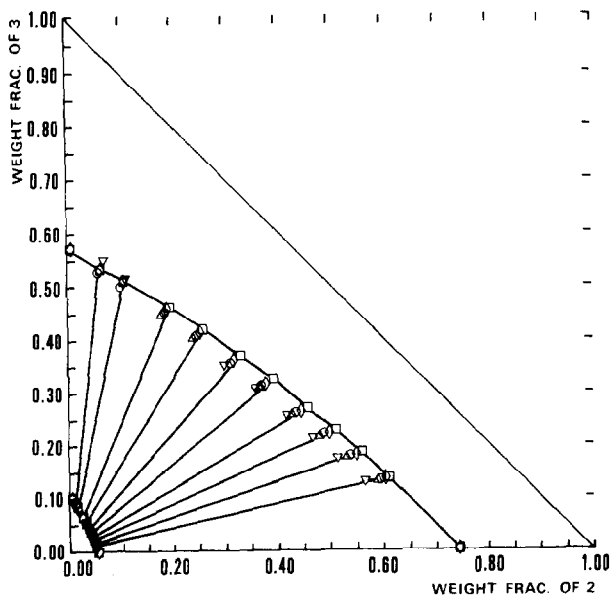


Fig. 3. PFD(1)/*n*-heptane(2)/*n*-hexane(3) Temp. = 15°C. □—□ Experimental; ◇ NRTL equation ($\alpha = 0.3, 0.4, 0.3$); ○ UNIQUAC equation; △ UNIFAC equation. ($P = F(NC)$); ▽ UNIFAC equation (P -sim. corr.).

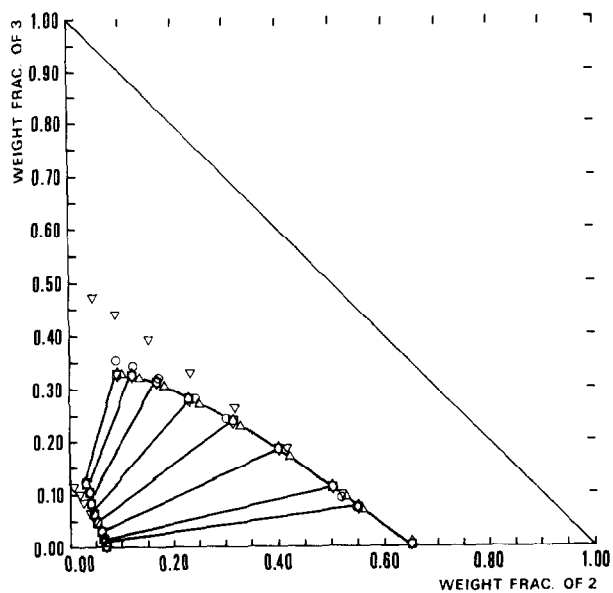


Fig. 4. PFD(1)/*n*-heptane(2)/*n*-hexane(3) Temp. = 25°C. □—□ Experimental; ◇ NRTL equation ($\alpha = 0.3, 0.4, 0.3$); ○ UNIQUAC equation; △ UNIFAC equation. ($P = F(NC)$); ▽ UNIFAC equation (P -sim. corr.).

where groups occur. That is obviously the main advantage of such methods, enabling predictions of multicomponent equilibria once the interaction parameters between groups (a_{ij}) are known.

For PFD/*n*-alkane mixtures the interaction parameters between groups CH₃, CH₂, CF₂(c) and CF(c) must be taken into account. Considering

$$a_{\text{CH}_3/\text{CH}_2} = a_{\text{CH}_2/\text{CH}_3} = 0 \quad (6)$$

$$a_{\text{CH}_2/\text{CF}_2(\text{c})} = a_{\text{CH}_2/\text{CF}(\text{c})} = a_{\text{CH}_3/\text{CF}_2(\text{c})} = a_{\text{CH}_3/\text{CF}(\text{c})} \quad (7)$$

$$a_{\text{CF}_2(\text{c})/\text{CH}_2} = a_{\text{CF}(\text{c})/\text{CH}_2} = a_{\text{CF}_2(\text{c})/\text{CH}_3} = a_{\text{CF}(\text{c})/\text{CH}_3} \quad (8)$$

the interaction parameters $a_{\text{CH}_2/\text{CF}_2(\text{c})}$ and $a_{\text{CF}_2(\text{c})/\text{CH}_2}$ can be obtained from mutual solubility data for any PFD/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 PFD/*n*-alkane mixture. The analysis of PFD/hydrocarbon binary and multicomponent equilibrium data revealed, however, significant differences between the group interaction parameters obtained from experimental data determined for each PFD/hydrocarbon system. As a result the following alternative approaches were used, and their results compared, in terms of RMSD between predicted and experimental compositions:

(1) simultaneous correlation of all mutual solubility data available for PFD/*n*-alkanes, allowing for the temperature dependence of the interaction parameters; and

(2) analysis of the parameters dependence on the number of carbon atoms of the alkane (N_c) and the temperature (T), with

$$a_{ij} = A_{ij} + B_{ij} \cdot N_c + C_{ij} \cdot N_c^2 \quad (9)$$

with A_{ij} , B_{ij} and C_{ij} temperature-dependent. The overall analysis of all available data allows the recommendation of a set of interaction parameters (Table 3), dependent on the number of carbon atoms and the temperature.

The above-mentioned results, together with the parameters recommended by Jorgensen et al. (1979) or by Magnussen et al. (1981), for CH₂=CH/CH₂ and the mutual solubility data for PFD/1-hexene and PFD/1-heptene, allow the calculation of the group interaction parameters for CH₂=CH/CF₂(c). The best results are obtained when parameters recommended by Jorgensen et al. (1979) are used.

Recommended values are presented in Table 3. It must be pointed out that in the selection of a recommendable set of CH₂=CH/CF₂ parameters, both PFD/hydrocarbon and perfluoromethylcyclohexane/hydrocarbon data were considered. If PFD/hydrocarbon data alone were taken into account a different temperature-dependence law could be recommended.

For comparative purposes the calculated RMSD values for the systems previously referred to are included in Tables 1 and 2 and the experimental and calculated tie-line and binodal curve data are represented in Figs. 3 and 4, for PFD/*n*-heptane/*n*-hexane at 15 and 25°C.

CONCLUSIONS

Results can be summarized as follows:

(1) With a slight loss of accuracy (relative to the results obtained with the best parameters for each individual system) it is possible to obtain a set of NRTL, UNIQUAC and UNIFAC parameters applicable to all binary and multicomponent mixtures of perfluorodecaline and hydrocarbons.

(2) The overall results (considering all binary and multicomponent mixtures) are better for the NRTL equation, using the recommended values for α_{ij} , but the predicted multicomponent data are strongly dependent on the selected α_{ij} for the partially miscible binaries.

(3) Direct correlation of ternary data yields the best agreement between predicted and experimental data, but for the NRTL and UNIQUAC equations results do not significantly differ from those obtained with PFD/hydrocarbon parameters calculated from mutual solubility data and hydrocarbon parameters adjusted with ternary tie-line data.

(4) For the UNIFAC equation the RMSD values between experimental and calculated compositions are, in general, much larger than for the other equations and the simultaneous correlation of the binary data available does not seem recommendable for the systems considered. Correlation of group interaction parameters with the number of carbon atoms improves significantly the prediction of multicomponent data.

(5) 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 PFD/alkene mixtures were expected: CH₂=CH/CF(c) interactions were the last to be accounted for using the values previously assumed for all the other groups.

LIST OF SYMBOLS

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):

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

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 .

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