

"SOME DIFFICULTIES ON THE APPLICATION OF THE UNIFAC MODEL FOR  
THE PREDICTION OF LIQUID-LIQUID EQUILIBRIUM COMPOSITIONS"

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ABSTRACT

*UNIFAC group parameters for the interaction between  $CH_2$  and  $CF_2$  (c) and  $CH_2$  and  $CF_3$  were obtained using experimental liquid-liquid equilibrium data for hydrocarbon - perfluorodecaline (PFD) and hydrocarbon - perfluoromethylcyclohexane (PFMCH) systems.*

*Some difficulties were experienced on the use of the UNIFAC method with those particular systems, namely the group parameters dependence on the length of the hydrocarbon chain.*

*Attempts were made to correlate UNIFAC parameters with the number of carbon atoms and temperature and the results compared with those obtained with NRTL equations.*

INTRODUCTION

One of the basic assumptions of the "contribution of groups" method is that the interactions between molecules can be obtained adding the contribution of all the interactions between the molecules functional groups. Therefore the properties of a liquid mixture depend both on the interaction between groups and the size and shape of those groups.

The relatively small number of functional groups that need to be considered, when compared with the number of mixtures of industrial interest makes any contribution method attractive particularly in a preliminary study of a project: once the group interaction and size parameters are obtained we are able to predict activity coefficients and phase equilibrium data for a particular mixture without any experimental results.

UNIFAC is one of such methods, combining the solution of groups concept with the UNIQUAC model. The calculation of the molecular activity coefficients is separated into two parts: a combinatorial part, essentially due to differences in size

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and shape of the molecules in the mixture, and a residual part essentially due to energetic interactions.

Fredenslund et al (1975, 1977), Jorgensen et al (1979), Gmehling et al (1982), Macedo et al (1983) present values of interaction parameters suitable for vapor-liquid equilibrium data calculations, and Magnussen et al (1981) published a different set of values adequate to the calculation of liquid-liquid equilibrium data.

Perfluorocarbon/hydrocarbon systems are particularly adequate for the assessment of any correlating equation because ternary and quaternary mixtures change swiftly from type to type of equilibrium pattern over a small temperature range. The experimental liquid-liquid equilibrium data of Bernardo-Gil (1984 a, b, 1985), Packer (1979) and Soares (1972) and vapor-liquid equilibrium data of Packer (1970) and Soares (1972) were used in the present study.

## CALCULATION PROCEDURES

### . METHODS USING A SYSTEM OF NON-LINEAR EQUATIONS

Combining the thermodynamic condition of equilibrium (1) with the stoichiometric relation (2) yields a system of  $N$  non-linear equations:

$$\ln(\gamma_{i1} x_{i1}) - \ln(\gamma_{i2} x_{i2}) = 0 \quad i=1, N \quad (1)$$

$$\sum_{i=1}^N x_{ij} = 1 \quad j=1, 2 \quad (2)$$

$\gamma_{ij}$  and  $x_{ij}$  being the activity coefficient and com

### . METHODS USING AN OBJECTIVE FUNCTION

UNIFAC parameters were also obtained correlating all available mutual solubility data for PFD/n-alkanes, and PFMCH/n-alkanes, assuming temperature dependent parameters (equation 4) and using a Nelder-Mead minimization procedure coupled with one of the following objective functions:

$$F_1 = \sum_{k=1}^M \sum_{i=1}^N \left[ \ln \left( \frac{\gamma_{i1}}{\gamma_{i2}} \right) - \ln \left( \frac{x_{i2}}{x_{i1}} \right) \right]^2 \quad (5)$$

position of component  $i$  in phase  $j$ . Selecting an activity coefficient - composition relationship (3), such as

$$\ln \gamma_{ij} = F(x_{1j}, \dots, x_{Nj}, T, A_1, A_2, \dots, A_L) \quad (3)$$

$A_L$  being the adjustable parameters and  $T$  the temperature, it is possible to solve the system of  $N$  non-linear equations. A Newton-Raphson technique was used to determine both the parameters, from mutual solubility data, and the predicted equilibrium compositions for a binary or multicomponent mixture, once the correlating equation parameters  $A_L$  were known.

Having calculated the parameters from the experimental data for a given binary mixture, they were then correlated with the temperature through:

$$A_K = c + d.T \quad (4)$$

#### APPLICATION TO PERFLUOROCARBON/HYDROCARBON MIXTURES

For PFD/n-alkane mixtures the interaction parameters between the groups  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CF}_2(c)$  and  $\text{CF}(c)$  must be taken in account. Considering:

$$- a_{\text{CH}_3/\text{CH}_2} = a_{\text{CH}_2/\text{CH}_3} = 0 \quad (7)$$

$$- a_{\text{CF}_2(c)/\text{CF}(c)} = a_{\text{CF}(c)/\text{CF}_2(c)} = 0 \quad (8)$$

$$- a_{\text{CF}_2(c)/\text{CH}_2} = a_{\text{CF}(c)/\text{CH}_2} = a_{\text{CF}_2(c)/\text{CH}_3} = a_{\text{CF}(c)/\text{CH}_3} \quad (9)$$

$$- a_{\text{CH}_2/\text{CF}_2(c)} = a_{\text{CH}_2/\text{CF}(c)} = a_{\text{CH}_3/\text{CF}_2(c)} = a_{\text{CH}_3/\text{CF}(c)} \quad (10)$$

$$F_2 = \sum_{k=1}^M \sum_{i=1}^N \sum_{j=1}^2 [x_{ijk}^{\text{ca}} - x_{ijk}^{\text{exp}}]^2 \quad (6)$$

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

The objective function  $F_2$  yields better agreement between experimental and calculated compositions, but requires a much longer computing time. So  $F_1$  was used at the initial stages of the minimization procedure changing later to  $F_2$ .

the interaction parameters  $a_{\text{CH}_2/\text{CF}_2(c)}$  and  $a_{\text{CF}_2(c)/\text{CH}_2}$  can be obtained from mutual solubility data for any PFD/n-alkane system.

For PFMCH/n-alkane mixtures the interaction parameters between the groups  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CF}_2(c)$ ,  $\text{CF}(c)$  and  $\text{CF}_3$  must be accounted for. Considering the previous results and:

$$a_{\text{CF}_2(c)/\text{CF}_3} = a_{\text{CF}_2(c)/\text{CF}(c)} = a_{\text{CF}_3/\text{CF}_2(c)} = a_{\text{CF}_3/\text{CF}(c)} = 0 \quad (11)$$

$$a_{\text{CF}_3/\text{CH}_2} = a_{\text{CF}_3/\text{CH}_3} \quad (12)$$

$$a_{\text{CH}_2/\text{CF}_3} = a_{\text{CH}_3/\text{CF}_3} \quad (13)$$

the interaction parameters  $a_{\text{CH}_2/\text{CF}_3}$  and  $a_{\text{CF}_3/\text{CH}_2}$  can be obtained from mutual solubility data for any PFMCH/n-alkane mixture.

Having calculated the parameters it should be possible to predict the mutual solubility data for any other PFD/n-alkane. The analysis of PFD/hydrocarbon and PFMCH/hydrocarbon equilibrium data revealed however significant differences between the group interaction parameters obtained from experimental data determined for each system.

The following alternative approaches were then used to overcome this problem and the results were compared in terms of the root mean square deviations (RMSD) between predicted and experimental compositions

- simultaneous correlation of all available mutual solubility data for PFD/alkanes, allowing for the temperature dependence of the interaction parameters;
- analysis of the parameter dependence on the number of carbon atoms of the alkane ( $N_c$ ) and the temperature ( $T$ ):

$$a_{ij} = A_{ij} + B_{ij} \cdot N_c + C_{ij} \cdot N_c^2 \quad (14)$$

with  $A_{ij}$ ,  $B_{ij}$  and  $C_{ij}$  temperature dependent.

Using the calculated parameters, together with those recommended by Jorgensen et al (1979) for  $\text{CH}_2=\text{CH}/\text{CH}_2$  and PFD / PFMCH/n-alkane mutual solubility data, the group interaction parameters for  $\text{CH}_2=\text{CH}/\text{CF}_2(c)$  and  $\text{CH}_2=\text{CH}/\text{CF}_3$  were calculated.

Recommended parameters were published elsewhere ( Bernardo-Gil and Soares 1984, 1985 ).

## RESULTS

For comparative purposes the calculated RMSD values for binary mixtures are included in TABLE 1, together with those obtained using:

- 1) - the NRTL and UNIQUAC equations;
- 2) -  $\text{CH}_2/\text{CF}_2$  and  $\text{CF}_2/\text{CH}_2$  parameters recommended by Gmehling et al (1982).

According to Shapovalov and Yurkin (1983) the assumption of  $a_{\text{CH}_2/\text{CH}_3} = a_{\text{CH}_3/\text{CH}_2} = 0$  leads to the hypothesis, contradictory to the experiment, of athermal hydrocarbon mixtures. On that basis they recommended the use of non-zero interaction parameters between groups  $\text{CH}_3$  and  $\text{CH}_2$ , calculated from hydrocarbon-hydrocarbon phase equilibrium data. All the calculations were reworked on that basis (TABLE 1) but the initial problem was not overcome: experimental data for each perfluorocarbon/hydrocarbon binary leads to a different set of group interaction parameters.

TABLE 2 presents some results for multicomponent systems, using UNIFAC model and, for comparative purposes, RMSD values obtained with the NRTL and UNIQUAC equations are also included (Bernardo-Gil and Soares, 1984 a, b; 1985).

Experimental vapor-liquid equilibrium data were determined by Packer (1970), for n-heptane/PFD, 1-heptene/PFD, PFMCH/n-heptane and PFMCH/1-heptene at 700 mmHg and Soares (1972) for PFMCH/n-hexane and PFMCH/1-hexene at 700 mmHg and 55°C. RMSD values between experimental and calculated vapor composition (Y), temperature (T) and pressure (P), for UNIFAC model .../...

## CONCLUSIONS

The conclusions can be summarized as follows:

1. The RMSD values, between experimental and calculated compositions, are, in general, much larger for the UNIFAC model than for the NRTL and UNIQUAC equations;
2. There is no set of interaction parameters that can, with accuracy, represent all the binary systems considered;
3. The simultaneous correlation of the available binary mutual solubility is not recommended, although the parameters so calculated allow, in some particular cases, a better agreement between predicted and experimental vapor-liquid equilibrium data;
4. The correlation of group interaction parameters with the number of carbon atoms of the hydrocarbon improves significantly the prediction of binary and multicomponent data;
5. The parameters obtained from liquid-liquid equilibrium data do not represent vapor-liquid equilibrium data accurately;
6. The larger deviations found with UNIFAC for PFD/alkene and PFMCH/alkene mixtures were expected:  
 $\text{CH}_2=\text{CH}/\text{CF}_3$  and  $\text{CH}_2=\text{CH}/\text{CF}_2(c)$  interactions were the last to be accounted for, using the values previously assumed for all the other groups.

TABLE 1: RMSD ( $\cdot 10^3$ ) values for perfluorocarbon/hydrocarbon binary mixtures using NRTL, UNIQUAC and UNIFAC parameters.

SYSTEM	NRTL EQUATION	UNIQUAC EQUATION	UNIFAC EQUATION				
			SIMULT. CORREL.	$a_{ij}=f(N_c)$	Gmehling et al.	PAR. FROM EACH BIN. ST.	
						$a_{CH_3/CH_2} = 0$	Shapov and Yu
PFD/n-hexane	13.4	7.4	37.3 <sup>III</sup>	7.8	38.7 <sup>V</sup>	7.5	16.
PFD/n-heptane	7.9	9.6	29.2	12.2	58.8 <sup>II</sup>	11.3	18.
PFD/n-octane	6.0	13.1	21.4 <sup>IV</sup>	45.3	42.4 <sup>IV</sup>	12.1 <sup>I</sup>	12.
PFD/n-nonane	10.0	7.8	42.0	8.4	83.2 <sup>IV</sup>	3.5	4.
PFD/1-hexene	6.7	6.0	25.4 <sup>V</sup>	34.0 <sup>III</sup>			
PFD/1-heptene	5.6	7.7	22.6	36.8 <sup>II</sup>			
PFMCH/n-hexane	3.7	4.0	45.9 <sup>V</sup>	18.2	60.0 <sup>IV</sup>	4.0	4.1
PFMCH/n-heptane	10.9	12.3	39.7 <sup>III</sup>	16.1	40.6 <sup>IV</sup>	5.8	7.6
PFMCH/n-octane	8.3	6.9	36.4 <sup>II</sup>	45.3	49.6 <sup>IV</sup>	10.3	13.9
PFMCH/n-nonane	8.3	5.7	78.6 <sup>I</sup>	36.1	56.2 <sup>III</sup>	5.0	5.4
PFMCH/1-hexene	7.4	6.0	36.4 <sup>V</sup>	32.0 <sup>VI</sup>			
PFMCH/1-heptene	6.3	10.0	33.7 <sup>I</sup>	83.4 <sup>V,III</sup>			

I - VIII . 1 - 8 tie lines (close to C.S.T.) are not included in the calculation.

TABLE 2: RMSD ( $\cdot 10^3$ ) values for some ternary and quaternary PFD/hydrocarbons and PFMCH/hydrocarbons systems.

SYSTEM	TEMP.	TYPE	NRTL EQUATION	UNIQUAC EQUATION	UNIFAC EQUATION	
					SIMULT. CORREL.	$a_{ij}=f(N_c)$
PFD/1-heptene/n-hexane	15	II	5.8	9.2	18.7	16.1
	25	I	7.0	8.6	43.3	15.5
PFD/1-heptene/n-heptane	15	II	1.4	1.5	19.2	1.8
	25	II	3.9	3.9	13.0	4.0
PFD/1-heptene/n-heptane/ /n-hexane	15	III	10.4	17.1	35.2	25.4
	25	II	11.6	13.0	27.3	15.2
PFMCH/1-heptene/n-hexane	15	I	14.3	17.2	66.8	31.3
	25	I	15.4	32.1	47.4	50.0
PFMCH/1-heptene/n-heptane	15	II	5.2	4.4	26.2	30.4
	25	II	9.8	13.9	44.4	41.4
PFMCH/1-heptene/n-heptane/ /n-hexane	15	II	12.1	18.0	*	20.0

II - number of tie-lines not included in the calculation.  
\* - convergence was only found for  $M \leq 3$  tie-lines.

are compared with those obtained with the NRTL and UNIQUAC parameters determined from vapor-liquid equilibrium data (VLE) and from liquid-liquid equilibrium data (LLE) (TABLE 3).

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