

## Modeling of Solid-Liquid Equilibria Using a Group Based NRTL Equation

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The NRTL equation has shown great capabilities in predicting phase equilibria data. However its major drawback is the non-availability of the required molecular interaction parameters. Consequently in the present study a new approach is proposed based on the introduction of the group contribution concept into the original NRTL equation to lead to the proposed Group Contribution NRTL model (GC-NRTL).

Similarly to UNIFAC the molecular activity coefficient is made of two parts: the first one is the combinatorial contribution which deals with differences in group sizes and shapes, and the second one is the residual contribution and is concerned with the different functional group interactions and is estimated by the proposed GC-NRTL model.

Group interaction parameters for the NRTL equation are calculated by minimizing an objective function defined in terms of the sum of the squared differences between the calculated values and the experimental ones reported in the literature.

As a first assessment, the GC-NRTL model was tested with a number of hydrocarbon binary solid - liquid systems mainly involving current functional groups like CH<sub>2</sub>, CH<sub>3</sub>, (CH<sub>2</sub>)<sub>cyclic</sub>, C, CH, ACH, ACCH<sub>3</sub>, ACCH<sub>2</sub>, AC and CH=CH.

The agreement between the predicted results and the experimental values was very encouraging and much better than the case when using the UNIFAC model. However the group interaction parameters matrix should be completed further including a greater number of functional groups.

### 1. Introduction

Thermodynamic models such as UNIQUAC and NRTL (*Non Random Two liquids*) have shown great capabilities in predicting the activity coefficient which is an important parameter required in any phase equilibria calculation. However their major drawback is the fact that they involve molecular interaction parameters which are not always available, hence excluding their use for a large number of chemical systems. The adopted approach to solve this problem in the case of UNIQUAC (Universal Quasichemical Activity Coefficient) (Abrams and Prausnitz, 1975) was to introduce the group contribution concept to give the well-known UNIFAC model (UNIQUAC Functional Activity Coefficient) (Fredenslund et al., 1975). Therefore in the present work the same group contribution approach is again applied and introduced into the initial NRTL equation leading to the GC-NRTL (Group Contribution NRTL) model, contrarily to the previous approach presented by the same authors where a completely different way for property additivity was proposed (Bouneb and Meniai, 2013).

For GC-NRTL, similarly to UNIFAC, the molecular activity coefficient is made of two parts: the first one concerns the contribution due to differences in molecule sizes and shapes and is estimated by using the athermal Staverman- Guggenheim equation Staverman (1950) and Guggenheim (1952) whereas the second one deals with the contribution due to molecular interactions.

In fact the fundamental idea of solution of a group model is to use existing phase equilibrium data for predicting phase equilibria for systems for which no experimental data are available.

The calculation of thermodynamic properties using molecular models requires information about all binary combinations in the mixture. Because of the large number of compounds which are relevant in the chemical industry, some binary parameters are often unknown. Group contribution methods such as ASOG (Derr and Deal, 1969), UNIFAC (Fredenslund et al, 1975) or modified UNIFAC (Larsen et al) offer a considerable simplification because the number of relevant groups can be restricted to a much more reduced size. The advantage of any group contribution method for the calculation of fluid phase equilibria key parameters is mainly due its ability to predict mixture properties for which no experimental data exist at all. The group contribution concept is based on the assumption that a chemical compound mixture can be treated, accurately enough as a mixture of functional groups making up these compounds.

*A priori* GC-NRTL group interaction parameters were estimated through the minimization of objective functions expressed in terms of the activity coefficients or/and the molar fractions of the considered system components. As usual the objective function is expressed as the sum of the squared deviations between the calculated and the experimental values, generally reported in the literature. The minimization method was based on the Nelder-Mead Simplex algorithm (Nelder and Mead, 1965).

The GC-NRTL model was tested considering a great number of binary solute-solvent liquid systems mainly involving current functional groups like CH, CH<sub>2</sub>, CH<sub>3</sub>, (CH<sub>2</sub>)<sub>cyclic</sub>, C, CH, ACH, ACCH<sub>3</sub>, ACCH<sub>2</sub>, AC and CH=CH. The agreement between the predicted results by means of the GC-NRTL and the experimental phase equilibrium data was encouraging and the interaction parameters table should be completed to include a greater number of functional groups.

## 2. Theoretical aspects

GC-NRTL model like UNIFAC is mainly based on the assumption that the contribution to the activity coefficient of compound can be separated into two parts, namely, a combinatorial, entropic contribution due to differences in molecular size and shape and a residual, enthalpy contribution due primarily to differences in intermolecular forces.

In GC-NRTL, the Staverman- Guggenheim equation was used for the combinatorial part of the activity coefficient and the NRTL equation was used for the determination of group residual activity coefficients.

The activity coefficient of compound *i* can then be calculated using the following equation:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (1)$$

with C and R denoting combinatorial and residual, respectively.

The combinatorial part of the activity coefficient depends only on the number size groups, in the various molecules that make the mixture. The Staverman- Guggenheim equation was used for the combinatorial part as:

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (2a)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (2b)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (2c)$$

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (2d)$$

In these equations,  $x_i$  is the mole fraction of compound *i*,  $\theta_j$  is the area fraction, and  $\phi_i$  is the segment fraction, which is similar to the volume fraction. Pure component parameters  $r_i$  and  $q_i$  are measures of molecular van der Waals volumes and molecular surface areas. Parameters  $r_i$  and  $q_i$  are calculated as the sum of group volume and area parameters  $R_k$  and  $Q_k$ .

$$r_i = \sum_k v_k^{(i)} R_k \quad (3a)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (3b)$$

Where  $v_k^{(i)}$ , always an integer, is the number of groups of type *k* in molecule *i*. group parameters  $R_k$  and  $Q_k$  are obtained from the van der Waals group volume and surface area  $V_k$  and  $A_k$  given by Bondi [16]

$$R_k = \frac{V_k}{15,17} \quad (4a)$$

$$Q_k = \frac{A_k}{2.5 \cdot 10^9} \quad (4b)$$

The residual part of the activity coefficients are calculated from the basic NRTL equation and the molecular activity coefficients term is expressed as:

$$\ln \gamma_i = \sum v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (5)$$

With  $\gamma_i$  the molecular activity coefficient,  $v_k^{(i)}$  the number of group (k) in the molecule (i),  $\Gamma_k$  the activity coefficient of group (k) in the mixture,  $\Gamma_k^{(i)}$  the activity coefficient of group (k) in reference solution containing only molecules of type (i).

The term  $\ln \Gamma_k^{(i)}$  is necessary to attain the normalization that molecular activity coefficient  $\gamma_i$  becomes unity as  $x_i \rightarrow 1$ .

The activity coefficient of group (k) is calculated as follows:

$$\ln \Gamma_k = \frac{\sum_l \tau_{lk} G_{lk} X_l}{\sum_k G_{lk} X_l} + \sum_l \frac{G_{kl} X_l}{\sum_m G_{ml} X_m} \left( \tau_{kl} - \frac{\sum_m \tau_{ml} G_{ml} X_m}{\sum_m G_{ml} X_m} \right) \quad (6a)$$

With  $x_k$  is the mole fraction of group (k) in the mixture is calculated as follows:

$$X_k = \frac{\sum_i^{nc} v_k^{(i)} x_i}{\sum_m^{ng} \sum_j^{nc} v_m^{(j)} x_j} \quad (6b)$$

$x_i$  is the mole fraction of molecule (i).

$$G_{lk} = \exp(-a_{lk} \tau_{lk}) \quad (6c)$$

$\tau_{lk}$  is the interaction parameters between group (l) and (k) is expressed as follows:

$$\tau_{lk} = \left( \frac{g_{lk} - g_{kl}}{RT} \right) = \left( \frac{a_{lk}}{T} \right) \quad (6d)$$

with  $g_{lk}$  the interaction energies between the corresponding groups,  $a_{lk}$  the group interaction parameters between the corresponding groups. Note that  $a_{lk}$  has units in Kelvins  $a_{lk} \neq a_{kl}$ .

### 3. Interaction parameters estimation

In this work, the required group interaction parameters were determined considering, *a priori*, only hydrocarbons. Experimental solid-liquid equilibrium data reported in the literature for different systems at different temperatures were used for this step.

The binary group interaction parameters required for the GC-NRTL model were retrieved in the present work using, as mentioned above, the Nelder-Mead method for the minimization of the following objective function (*Fobj*) defined as the sum of the squared deviations between the experimental and calculated mole fractions:

$$F_{obj} = \sum_{i=1}^N (x_{i(exp)} - x_{i(cal)})^2 \quad (7)$$

with N denoting the number of data points.

The obtained binary group and molecular interaction parameters for the GC-NRTL models are presented in the following table.

Table 1: Binary group interaction parameters for GC-NRTL model

	CH3	CH2	CH	C	ACH	AC	ACCH3	ACCH2	(CH2) <sub>cycl</sub>	CH=CH
CH3	0.00	217.95	757.72	-153.57	-10.17	-62.40	-0.33	-1180.85	153.78	1017.48
CH2	119.29	0.00	107.86	4159.72	-1873.86	51.28	8908.20	-890.08	164.42	633.13
CH	-226.74	-102.80	0.00	-2551.55	660.72	98.88	1581.83	1611.91	-142.95	-837.60
C	1072.13	-189.55	-111.53	0.00	-61.91	-702.54	432.14	-779.35	1113.39	-789.66
ACH	128.87	265.08	1435.34	1087.03	0.00	-824.88	-4377.34	4334.31	-293.55	1833.66
AC	441.46	-92.84	-93.94	1458.46	-348.89	0.00	301.81	-230.20	320.64	-1430.07
ACCH3	1812.02	1241.34	499.62	-519.67	3943.68	-567.70	0.00	336.00	15.81	1729.90
ACCH2	-917.34	-67.01	231.77	2578.85	771.80	294.60	332.84	0.00	-1676.07	-397.32
(CH2) <sub>cycl</sub>	-165.32	-321.69	-102.91	-515.64	-242.38	-675.75	-27.07	132.94	0.00	-1579.73
CH=CH	-345.37	-363.33	-660.67	-168.81	-1416.33	446.44	-2105.64	5483.26	-135.43	0.00

Table 2 shows the solubility data results obtained by means of GC-NRTL and UNIFAC equations as well as the experimental data reported by Acree Jr (2013) for the considered systems presented in this work.

Table 2: Comparison of experimental and calculated solubilities

SOLUTE	SOLVENT	T (K)	X <sub>exp</sub>	X <sub>GC-NRTL</sub>	X <sub>UNIFAC</sub>
Biphenyl	Cyclooctane	298.15	0.2194	0,2206	0.22530
	2,2,4 Trimethylpentane		0.1094	0,1095	0.21330
	Nonane		0.1551	0,1519	0.17170
	Decane		0.1636	0,1656	0.17430
	Hexadecane		0.2151	0,2278	0.19810
Biphenyl	Octadecane	298.57	0.266	0,2540	0.21500
Acenaphtane	Hexane	298.15	0.05192	0,0485	0.07896
	Cyclohexane		0.07043	0,0859	0.08235
	Octane		0.06826	0,0697	0.08227
	Nonane		0.0721	0,0762	0.08418
	Heptane		0.06075	0,0606	0.08034
	Hexadecane		0.1065	0,1043	0.10430
	Cyclooctane		0.09739	0,0835	0.08655
Phenantrene	Hexane	298.15	0.03189	0,0277	0.07018
	Heptane		0.03888	0,0373	0.07072
	Octane		0.04443	0,0449	0.07177
	Nonane		0.04785	0,0508	0.07297
	Decane		0.05531	0,0569	0.07531
	Undecane		0.0598	0,0614	0.07730
	Dodecane		0.06348	0,0653	0.07944
	Hexadecane		0.07972	0,0784	0.08918
	Cyclohexane		0.03648	0,0441	0.07138
	Methylcyclohexane		0.04572	0,0460	0.14290
	Cyclooctane		0.06002	0,0473	0.07507
	2,2,4 Trimethylpentane		0.02486	0,0247	0.11880
Phenantrene	methylbenzene	298.15	0.1901	0,1928	0.27420
		308.15	0.2486	0,2434	0.33930
		318.15	0.3200	0,3157	0.4145
		328.15	0.4000	0,4086	0.5000
Anthracene	Nonane	298.15	0.002085	0,0015	0.00253
			0.002345	0,0017	0.0026
			0.002585	0,0018	0.00268
			0.0028	0,0020	0.00276
			0.008458	0,0093	0.02369
			0.007056	0,0093	0.02380
Anthracene	2,2,4 Trimethylpentane	298.20	0.001187	0,0009	0.00448
		308.20	0.001515	0,0013	0.00669
		318.20	0.001768	0,0019	0.00975
Naphtalene	Heptane	290.25	0.05948	0,0583	0.09454
		294.30	0.07054	0,0686	0.1082
		297.85	0.07982	0,0785	0.1214
		301.37	0.08893	0,0895	0.1357
		303.04	0.09771	0,0964	0.1439
		309.63	0.12340	0,1245	0.1780
		312.60	0.14120	0,1413	0.1971
Naphtalene	Methylbenzene	291.35	0.23950	0,2442	0.2347
		301.45	0.31030	0,3148	0.3062
		308.53	0.37390	0,3727	0.3653
		318.55	0.47170	0,4685	0.4630
		327.55	0.58590	0,5695	0.5660
		299.42	0.29180	0,2946	0.2929

Table 2: Comparison of experimental and calculated solubilities (cont.d)

SOLUTE	SOLVENT	T (K)	$X_{exp}$	$X_{GC-NRTL}$	$X_{UNIFAC}$
Naphtalene	Dimethylbenzene (Mix)	309.84	0.37150	0,3800	0.3789
		319.25	0.47910	0,4719	0.4712
		330.46	0.60860	0,6027	0.6026
		337.97	0.71960	0,7045	0.7046
Trans- Stilbene	Hexane	298.15	0.00960	0,0092	0.09516
	Cyclohexane		0.01374	0,0141	0.09624
	Heptane		0.01085	0,0110	0.09551
	Octane		0.01241	0,0129	0.09717
	Ethyl Benzene		0.05331	0,0533	0.2653
	Benzene		0.06232	0,0624	0.3340

The results are assessed by calculating the average absolute relative deviation (AAD) defined as follows:

$$AAD = \frac{1}{n} \sum_{i=1}^n |x_{i(exp)} - x_{i(cal)}| \quad (8)$$

Where  $n$  is the number of experimental points;  $x_{i(cal)}$  is the solubility calculated using GC-NRTL and UNIFAC equation;  $x_{i(exp)}$  is the experimental solubility reported in literature Acree Jr (2013).

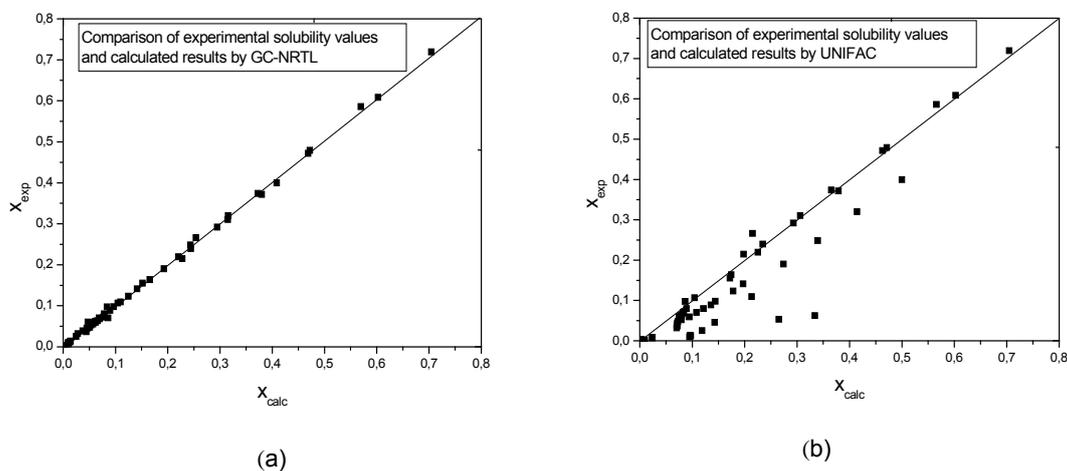


Figure 1: Assessment of the models a) GC-NRTL; b) UNIFAC

The obtained AAD values were 0.001432787 and 0.06656557 for GC-NRTL and UNIFAC models, respectively. This comparison is also shown by Figures 1a and b where clearly the predicted results using the proposed model i.e. GC-NRTL are in a very good agreement with the experimental values, contrarily to UNIFAC where important deviations are shown.

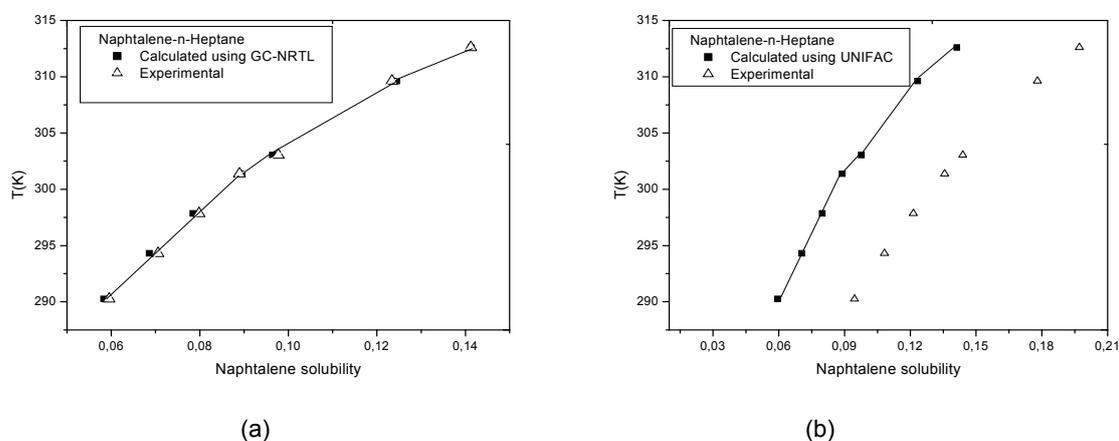


Figure 2: Solid-liquid equilibrium for Naphtalene- n-Heptane system by a) GC-NRTL and b) UNIFAC models

For a better representation of solid-liquid phase equilibrium, the corresponding diagrams are shown for a chosen system, namely Naphthalene in n-Heptane, for which experimental data are reported in the literature (Cui et al, 2009). Figures 2a & b show the comparisons of the obtained results by means of GC-NRTL and UNIFAC with the experimental values. Once more the GC-NRTL results were in a very good agreement with the experimental values, contrarily to UNIFAC.

#### 4. Conclusion

The GC-NRTL model was tested for different binary solid - liquid systems mainly involving current hydrocarbon functional groups like  $\text{CH}_2$ ,  $\text{CH}_3$ ,  $(\text{CH}_2)_{\text{cycl}}$ , C, ACH,  $\text{ACCH}_3$ ,  $\text{ACCH}_2$ , AC and  $\text{CH}=\text{CH}$ . The agreement between the predicted results by means of the GC-NRTL and the experimental phase equilibrium data is encouraging and the interaction parameters table should be completed to include a greater number of different functional groups.

Generally the models using molecular interaction parameters lead to more accurate results compared to models using group interaction parameters like the GC-NRTL or UNIFAC. This is perhaps due to the fact that any group contribution approach is assumed approximately to be additive.

However the non-availability of the required interaction parameters is also a serious limitation, justifying the introduction of the group contribution concept into the initial equation using molecular interaction parameters.

Also great efforts should be made in improving the minimization techniques very often local minima are reached rather than the global minimum, inducing errors.

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