

Temperature Effect on the Interaction Parameters of GC-NRTL Model Using the Genetic Algorithm

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Liquid-liquid equilibrium data is imperatively needed for the design of separation processes, particularly solvent extraction. The experimental measuring approach is complex and costly for a great number of chemical systems, and hence the need for reliable predictive models.

A great number of thermodynamic models have been developed and are reported in the literature. Among these the NRTL (Non Random Two Liquids) model has shown a great capability for predicting reliable liquid-liquid equilibrium data. However its major drawback is that it requires molecular interaction parameters which are not always available.

Consequently, the aim of the present work is to present a new approach where the group contribution concept is incorporated into the NRTL equation, leading to the group contribution NRTL model (GC-NRTL).

This GC-NRTL equation was tested by calculating liquid-liquid equilibrium data, particularly distribution coefficients, for a wide variety of liquid binary systems, at different temperatures.

The required interaction parameters were calculated, minimizing an objective function using the genetic algorithm (GA) which generally leads to the global minimum. The effect of temperature on the interaction parameter values was also investigated, considering five different temperatures and ten different chemical systems.

The agreement between experimental data and the predicted phase equilibrium results was encouraging. Correlations of binary group interaction parameters in term of temperature were proposed and recommended for predicting LLE by means of the GC-NRTL model which had proven to be reliable.

1. Introduction

Generally any modelling of separation processes like liquid-liquid extraction, distillation, absorption, crystallisation, etc. is based on known thermodynamic models like the NRTL, UNIQUAC, UNIFAC, etc. However the use of these models depends upon interaction parameters which are not always available and the problem is worse for those which are based on molecular rather than group interaction parameters.

In a previous work an approach had been proposed and consisting of introducing the group contribution concept into the NRTL equation leading to GC-NRTL (Group Contribution NRTL) model (Bounab et al., 2010). This was mainly guided by the fact that a large number of compounds and mixtures can be handled with a reduced number of functional groups (Fredenslund et al., 1975).

Also for most thermodynamic models, it is a common practice to assume that the interaction parameters are temperature independent. However this may lead to important errors and hence in the present study the effect of temperature on the GC-NRTL interaction parameters was considered. The parameter fitting was solved by means of the genetic algorithm (GA).

2. Theoretical aspects

2.1 The NRTL equation

The NRTL (Non Random Two Liquids) model equation was described in detail for the first time by Renon and Prausnitz (1968) and was applied to a large variety of mixtures for the calculation of the vapour-liquid and

liquid-liquid equilibria Henley and Seader, 1981). The model is based on the molecular local composition concept for local mole fractions (x_{ji}) of species j in a liquid cell occupied by a central molecule i expressed as:

$$x_{ji} = \frac{x_j \exp(-\alpha_{ji} \tau_{ji})}{\sum_{k=1}^c x_k \exp(-\alpha_{ki} \tau_{ki})} \quad (1)$$

For the binary pair ij τ_{ji} and τ_{ij} are adjustable parameters and $\alpha_{ji}(=\alpha_{ij})$ is the non-randomness parameter $\alpha_{ji}(=\alpha_{ij})$ that can be fixed or adjusted. Excess free energy for the liquid system is expressed by an extension of Scott's cell theory, wherein only binary molecular interactions are considered leading to the following expression:

$$\frac{g^E}{RT} = \sum_{i=1}^c x_i \left[\sum_{j=1}^c x_{ji} \tau_{ji} \right] \quad (2)$$

The expression for the activity coefficients can then be obtained as:

$$\ln \gamma_i = \frac{\sum_{j=1}^c (\tau_{ji} G_{ji} x_j)}{\sum_{k=1}^c (G_{ki} x_k)} + \sum_{j=1}^c \left[\frac{(x_j G_{ij})}{\sum_{k=1}^c (G_{kj} x_k)} \left(\tau_{ij} - \frac{\sum_{k=1}^c (x_k \tau_{kj} G_{kj})}{\sum_{k=1}^c (G_{kj} x_k)} \right) \right] \quad (3)$$

Where

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (4)$$

The τ parameters are given by:

$$\tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT} = \frac{A_{ij}}{T} \quad (5)$$

$$\tau_{ji} = \frac{(g_{ji} - g_{ii})}{RT} = \frac{A_{ji}}{T} \quad (6)$$

with g_{ij} the interaction energy between molecules i and j . In the above equations, $g_{ji} \neq g_{ij}$, $\tau_{ij} \neq \tau_{ji}$, $g_{ii} = g_{jj} = 1$ and $\tau_{ii} = \tau_{jj} = 0$. A_{ij} and A_{ji} are the interaction parameters between each pair of molecule in the unit of Kelvin. The parameter α_{ji} characterizes the tendency of species j and species i to be distributed in a non-random manner.

2.2 The GC- NRTL equation

The proposed version of NRTL model consisted in treating the solution as a mixture of functional groups rather than molecules (Bounab et al., 2010). For example, for a binary solution of ethanol and n-hexane, the involved contributing groups are 1 CH₃, 2 CH₂ and 1 OH from ethanol and 2 CH₃ plus 4 CH₂ from n-hexane. The group activity coefficients are calculated from the basic NRTL equation and the molecular activity coefficients are calculated by summing up the contribution of each group taking account of molar fractions of the different groups in each considered molecule type and of the compound mole fractions in the solution, respectively as follows:

$$\gamma_i = \sum_m X_i(x_m \gamma_m) \quad (7)$$

With γ_m the activity coefficient of Group m in molecule of Compound i, x_m and X_i the molar fractions of group m in a molecule of Compound i and that of Compound i in the solution.

The summation in Eqn. 7 is over all groups present in Molecule i.

The activity coefficient γ_m is calculated according to the NRTL equation as follows:

$$\ln \gamma_m = \frac{\sum_{m=1}^c (\tau_{jm} G_{jm} x_j)}{\sum_{k=1}^c (G_{km} x_k)} + \sum_{j=1}^c \left[\frac{(x_j G_{mj})}{\sum_{k=1}^c (G_{kj} x_k)} \left(\tau_{mj} - \frac{\sum_{k=1}^c (x_k \tau_{kj} G_{kj})}{\sum_{k=1}^c (G_{kj} x_k)} \right) \right] \quad (8)$$

$$G_{jm} = \exp(-\alpha_{jm} \tau_{jm}) \quad (9)$$

where τ_{mj} and τ_{jm} are interaction parameters between group m and j and are expressed as follows:

$$\tau_{mj} = \frac{(g_{mj} - g_{jj})}{RT} = \frac{A_{mj}}{T} \quad (10)$$

$$\tau_{jm} = \frac{(g_{jm} - g_{mm})}{RT} = \frac{A_{jm}}{T} \quad (11)$$

where any g_{mj} , g_{jm} , g_{jj} and g_{mm} denotes an interaction energy between the corresponding pair of groups and A_{mj} and A_{jm} are the group interaction parameters expressed in Kelvin between pair of groups m and j. Generally it is noted that $A_{mj} \neq A_{jm}$.

3. Parameter estimation procedure

The binary interaction parameters are obtained by minimizing the most common objective function which is the sum of the squared of the errors between the experimental and calculated mole fractions of all the components over the entire set of tie lines and can be expressed as follows:

$$\text{Min}(F) = \sum_{j=1}^n \sum_{l=1}^p \sum_{i=1}^{nc} (x_{\text{exp}}^l(j,i) - x_{\text{calc}}^l(j,i))^2 \quad (12)$$

where j, p and i denote system, phase and component, respectively.

The objective function is non-linear and non convex in terms of optimization variables and may have several local minima, maxima or saddle points within the considered variable ranges. Therefore, it is necessary to apply a robust technique that leads to the global optimum vector. Several techniques are reported in literature, like simulated annealing (SA), Hybrid simulated such as annealing Simplex simulated annealing (SSA), the modified Simplex simulated annealing (DSSA) (Hedar and Fukushima, 2002), and an evolutionary algorithm like the genetic algorithm (Mc Call, 2005) and later (El -Emary and Abd El- Kareem, 2008) and also work of (Sahoo et al., 2006) is adopted in the present work.

4. Results and discussion

The GC- NRTL was tested on seven different systems shown in Table 1 and where the corresponding liquid-liquid equilibria data at different temperatures were reported in the literature (Sørensen et al, 1979).

Table 1: Systems used to be tested by the GC-NRTL

N°	System	Temperature, K
1	Pentane – H ₂ O	
2	Heptane – H ₂ O	273-283-293-298-303
3	Ethanol-hexadecane	298
4	Hexadecane- Acetic Acid Nitril	298
5	Hexadecane- Methane Nitro	298
6	Propanone –hexadecane	298
7	trichloroethane-hexadecane	298

4.1 GC- NRTL binary group interaction parameters

The NRTL group binary interaction parameters were determined by means of the GA from experimental data for the seven above systems at 0, 10, 20, 25 and 30 °C, as shown in Table 2.

Table 2: Group interaction parameters

Groups		A _{ij}						A _{ji}				
i	J	273 K	283 K	293 K	298 K	303 K	273 K	283 K	293 K	298 K	303 K	
-CH ₃	-CH ₂	4313.59	1681.32	2681.34	3451.65	2774.48	2251.21	4059.72	2319.65	833.37	3848.58	
-CH ₃	H ₂ O	1249.83	2085.02	2186.12	2218.99	2896.06	4995.17	2877.85	3378.03	1026.29	4752.53	
-CH ₂	H ₂ O	3365.68	1758.53	1903.24	3299.73	3830.45	4145.11	2887.7	2193.64	4923.20	2552.68	
-CH ₂	-CH	3649.93	3685.93	5330.55	2056.58	4327.78	2210.4	3002.84	1670.14	1178.61	3884.33	
-CH	-COH	1020.92	1719.12	2103.14	3684.87	2559.93	4696.64	1696.87	3194.09	-1188.2	1888.98	
-CH	H ₂ O	1356.39	2088.42	5924.79	4081.98	4958.25	1537.36	1210.95	1494.08	4539.74	1000.36	
-COH	H ₂ O	3897.83	1030.27	1030.27	-1512.22	4924.97	4875.43	4889.5	5801.68	2537.72	2605.62	
-CNH ₂	-CH	/	/	/	3551.18	/	/	/	/	-297.70	/	
-CNH ₂	H ₂ O	/	/	/	1798.18	/	/	/	/	4259.45	/	
-CH ₃	C≡N	/	/	/	-332.51	/	/	/	/	1798.18	/	
-CH ₂	C≡N	/	/	/	3227.03	/	/	/	/	3225.98	/	
-CH ₃	NO ₂	/	/	/	-152.71	/	/	/	/	1377.92	/	
-CH ₂	NO ₂	/	/	/	4495.93	/	/	/	/	2218.37	/	
-CH ₃	-C=O	/	/	/	2004.21	/	/	/	/	3034.07	/	
-CH ₂	-C=O	/	/	/	555.31	/	/	/	/	410.37	/	
-CHCl ₂	CH ₂ Cl	/	/	/	4071.91	/	/	/	/	-905.35	/	
-CHCl ₂	H ₂ O	/	/	/	433.03	/	/	/	/	433.03	/	
-CH ₂ Cl	H ₂ O	/	/	/	1943.26	/	/	/	/	1687.51	/	

4.2 Component equilibrium distributions

Equilibrium compositions were calculated using genetic algorithm that utilizes predicted activity coefficient applying the GC-NRTL model and are listed in Table 3 where calculated tie lines are compared with experimental ones. The absolute mean deviation (AMD) was calculated for each temperature.

Table 3: Liquid-liquid phase equilibria at different temperatures

Systems	Experimental		Calculated	
	phase I	phase II	phase I	phase II
	X _{exp}	X _{exp}	X _{calc}	X _{calc}
Temperature 273 K (AMD%)=0.058				
Pentane (1)	1.42E-05	0.99989	4.14E-004	0.99967
H ₂ O (2)	0.99954	1.04E-04	0.99999	1.99E-004
Heptane (1)	6.11E-07	0.99985	1.71E-008	0.99985
H ₂ O (2)	0.99999	1.5E-04	0.99999	1.41E-004
Temperature 283 K (AMD%)=0.28				
Pentane (1)	0.99998	1.84e-04	0.99996	2.74e-04
H ₂ O (2)	1.07E-5	0.99981	3.80E-005	0.99972
Heptane (1)	5.58E-07	0.997	2.98E-005	0.99978
H ₂ O (2)	0.99999	3E-03	0.99997	4.62E-004

Table 3: Liquid-liquid phase equilibria at different temperatures (Continued)

Temperature 293 K (AMD(%)=0.036)				
Pentane (1)	1.01E-05	0.99967	2.01E-09	0.99943
H ₂ O (2)	0.99989	3.29E-4	0.99999	5.66E-004
Heptane (1)	5.2E-07	0.99946	1.87E-009	0.99953
H ₂ O (2)	0.99999	5.34E-04	0.99999	4.62E-004
Temperature 298 K(AMD(%)=1.43)				
Pentane (1)	0.0000	0.9995	0.0000	0.9999
H ₂ O (2)	0.9999	0.0004	0.9999	0.0000
Heptane (1)	0.0000	0.9992	0.000	0.9999
H ₂ O (2)	0.9999	0.0007	0.9999	0.00
Hexadecane (1)	0.0466	0.9997	0.0466	0.9994
Methane Nitro (2)	0.9534	0.0003	0.9533	0.00001
Hexadecane (1)	0.0775	0.9995	0.0780	0.9999
Acetic Acid Nitril (2)	0.9225	0.0005	0.9219	0.00009
Ethanol (1)	0.3150	0.9570	0.3095	0.9879
Hexadecane (2)	0.6850	0.0430	0.6512	0.0358
Propanone (1)	0.6510	0.9065	0.6487	0.9131
Hexadecane (2)	0.3490	0.0935	0.3512	0.0868
Trichloro Ethane (1)	6.78e-04	0.9937	6.7742e-04	0.9937
Hexadecane (2)	0.9992	0.00626	0.9993	0.00626
Temperature 303 K (AMD(%)=0.18)				
Heptane (1)	4.73E-07	0.99904	1.04E-006	0.99995
H ₂ O (2)	0.99999	9.56E-04	0.99999	4.46E-005

4.3 Temperature effect on the interaction parameters

From Table 2 it is clear that the temperature has a great effect on the interaction parameter values and therefore it is necessary to have correlations for their calculations at different temperatures. In fact polynomial functions giving A_{ij} and A_{ji} were obtained from the calculated results with correlation factors very close to unity for most cases, as shown in the following table:

Table 4: Polynomial approximation constants of the interaction parameters A_{ij} and A_{ji}

Group		$A_{ij} = C1 + C2T + C3T^2 + C4T^3 + C5T^4$					$A_{ji} = B1 + B2T + B3T^2 + B4T^3 + B5T^4$				
i	j	C1	C2	C3	C4	C5	B1	B2	B3	B4	B5
-CH ₃	-CH ₂	4313.59	-387.07	2.52	1.33	-0.035	2251.40	-320.72	114.31	-7.92	0.1510
-CH ₃	H ₂ O	1249.83	61.26	8.26	-0.81	0.0173	4995.17	-2345.40	378.30	-19.73	0.3240
-CH ₂	H ₂ O	3365.68	173.58	-68.55	4.21	-0.0701	4145.11	1598.28	-317.8	17.44	-0.2890
-CH ₂	-CH	3649.93	-2375.10	424.67	-22.27	0.359	2210.4	-137.91	54.97	-4.179	0.0854
-CH	-COH	1020.92	985.86	-166.20	8.93	-0.148	4696.64	-3671.30	591.23	-30.24	0.4838
-CH	H ₂ O	3365.68	674.22	-160.30	9.22	-0.154	1537.36	1880.27	-354.7	19.66	-0.3310
-COH	H ₂ O	3897.83	945.48	228.23	-15.18	0.288	4875.43	-4397.40	797.14	-42.70	0.6980

In order to test the reliability of these polynomial functions, they were tested on systems for which the NRTL interaction parameters were not available. The results are compared with experimental values reported in the literature (Sørensen et al, 1979) with a quite good agreement as shown in Table 5.

Table 5: Liquid-liquid phase equilibria at 298 K using calculated group interaction parameters

Methanol(1)-Cyclohexane(2) (AMD(%)= 0.41)				Methanol(1)-Hexadecane(2) (AMD(%)=2.16)				Phenol(1)-water(2) (AMD(%)=2.27)			
Experimental		Calculated		Experimental		Calculated		Experimental		calculated	
X_1^I	X_1^{II}	X_1^I	X_1^{II}	X_1^I	X_1^{II}	X_1^I	X_1^{II}	X_1^I	X_1^{II}	X_1^I	X_1^{II}
0.1244	0.8285	0.1224	0.8271	0.0475	0.9971	0.0287	0.9999	0.0164	0.32	0.034	0.3251
Toluene(1)-water(2) (AMD(%)=0.27)				Aniline(1)-water(2) (AMD(%)=1.04)							
Experimental		Calculated		Experimental		Calculated					
X_1^I	X_1^{II}	X_1^I	X_1^{II}	X_1^I	X_1^{II}	X_1^I	X_1^{II}				
0.0001	0.9973	0.00	0.9999	0.0067	0.782	0.001	0.7867				

5. Concluding remarks

The GC-NRTL model obtained by introducing the group contribution concept into the NRTL equation has proven to be reliable in predicting liquid-liquid phase equilibria for systems where the molecular interaction parameters required by the original NRTL model are not available. This has helped getting around the non availability interaction parameters problem. Therefore GC-NRTL can be regarded as a good predictive model, particularly with the use of the Genetic algorithm for the chosen objective function minimization. In this study polynomial functions giving the interaction parameters in terms of temperature have also been developed and proven their usefulness in solving problems due to the variation of the temperature which is a key parameter on processes involving phase equilibria.

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