Molecular structures and thermodynamic Phase equilibrium models

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Abstract

A great number of chemical engineering applications involve processes such as distillation, absorption, liquid-liquid extraction, etc. For the design of the necessary equipment to carry out these operations, it is important to have equilibrium data which is not always available. Therefore predictive models can be very useful and are necessary.

Various models exist but the most accurate ones are those which take into account the nature and the size of the molecule. Consequently, this present work is an attempt to establish an eventual relationship between the thermodynamic models and the molecular structure, for chosen binary systems such as Hydrocarbons, Hydroxylic, Aromatic, etc.

Known systems have been considered to validate the approach and examine any relationship between the molecular structure and the calculated property.

Keywords: *Phase equilibria; UNIQUAC; UNIFAC; NRTL; Activity coefficient; Molecular.*

I. Introduction

The calculation of the equilibrium between the phases of systems of many components is based on the J W Gibbs concept of a same chemical potential for each component in each phase, at the prevailing temperature and pressure. The equilibrium conditions between two phases is then the isofugacity criteria which is written as follows [1]:

$$f_i^{(1)} = f_i^{(2)} \qquad (i = 1,2,\dots,n) \qquad (1)$$

with f_i denoting the fugacity of component i.

For a vapour-liquid equilibrium, the fugacities in each phase can be calculated from the following equations:

- For the fugacity in vapor phase:

$$\varphi_i(T,P,y_i) = \frac{f_i^V(T,P,y_i)}{P\cdot y_i}$$

Where y_i is the molar fraction of component i in vapor phase, P the pressure and ϕ_i the fugacity coefficient of component I defined as:

$$\ln\varphi_i = \frac{1}{RT}\cdot\int_0^P\left(\bar{v}_i - \frac{RT}{P}\right)\cdot dP$$

$\bar{v}_i$ is partial molar volume.

- For the fugacity in liquid phase:

$$f_i^L(T,P,x_i) = f_i^{L*}(T,x_i)\cdot\exp\int_0^P \frac{\bar{v}_i^L}{RT}\cdot dP \qquad (2)$$

f_i^L is the fugacity of component i in the liquid mixture at the pressure P;

f_i^{L*} is the fugacity of component i in the liquid mixture, brought back to null pressure;

$\bar{v}_i^L$ is molar volume partial in the liquid mixture of component i.

Hence:

$$f_i^L(T,P,x_i) = f_i^{L*}(T,x_i)\cdot\exp\frac{v_i^{0L}\cdot P}{RT} \qquad (3)$$

The activity coefficient is independent of the pressure and is defined as follows:

$$\gamma_i(T,x_i) = \frac{f_i^{L*}(T,x_i)}{x_i\cdot f_i^{0L*}(T)} \qquad (4)$$

f_i^{L*} is as defined above and the selected standard state for this fugacity of reference is the pure liquid i at the temperature T, under null pressure. The coefficients of activity are then defined according to the symmetrical convention, expressed by the following condition for each component i in the mixture: $\gamma_i \rightarrow 1$ when $x_i \rightarrow 1$.

The use of the symmetrical convention is justified here by the fact that in the considered mixtures, the components are often at a temperature lower than their critical temperature [1].

$$f_i^{0L*} = P_i^S(T)\cdot\varphi_i^S(T,P_i^S)\cdot\exp\left(-\frac{v_i^{0L}\cdot P_i^S}{RT}\right) \qquad (6)$$

P_i^S indicates the saturated vapour pressure of the pure substance I at the temperature T;

φ_i^S is the coefficient of fugacity of the vapour saturated with component i given by the following expression :

$$\ln\varphi_i^S = \frac{P_i^S\cdot B_{ii}}{RT} \qquad (7)$$

The coefficient B $_{ii}$ of a pure substance i is given by:

$$B_{ii} = \frac{RT_{Ci}}{P_{Ci}}\cdot f(T_{Ri},\omega_i) \text{ Avec } T_{Ri} = \frac{T}{T_{Ci}}$$

$$f(T_{Ri},\omega_i) = 0.1445 - \frac{0.33}{T_{Ri}} - \frac{0.1385}{T_{Ri}^2} - \frac{0.0121}{T_{Ri}^3} + \omega_i\cdot\left(0.073 + \frac{0.46}{T_{Ri}} - \frac{0.5}{T_{Ri}^2} - \frac{0.097}{T_{Ri}^3} - \frac{0.0073}{T_{Ri}^8}\right) \qquad (8)$$

In the case of a mixture, the critical parameters necessary for the calculation of the coefficient B$_{ii}$, are given by the following mixing rules:

$$T_{Cij} = \left(T_{Ci}\cdot T_{Cj}\right)^{0.5} \quad \omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

$$P_{Cij} = 4\cdot T_{Cij}\cdot\left(\frac{P_{Ci}\cdot v_{Ci}}{T_{Ci}} + \frac{P_{Cj}\cdot v_{Cj}}{T_{Cj}}\right)\Big/\left(v_{Ci}^{1/3} + v_{Cj}^{1/3}\right)^3 \qquad (9)$$

II. Activity coefficient models

Various models for the calculations of the activity coefficients are proposed in the literature. Each one depends on the manner, the expression for the excess free energy, G^E, is chosen. The coefficient of activity is then obtained, on a molar basis, as follows:

$$RT\ln\gamma_i = \frac{\partial g^E}{\partial x_i} \qquad (10)$$

- **van Laar model**

The excess free energy according to this model is given by the following expression:

$$\frac{G^E}{R\cdot T} = \frac{A_{12}\cdot A_{21}\cdot X_1\cdot X_2}{A_{12}\cdot X_1 + A_{21}\cdot X_2} \qquad (11)$$

Where A$_{12}$, A$_{21}$ the parameters of van Laar which are function of the temperature. The activity coefficients are as follows [2]:

$$\ln\gamma_1 = \frac{A_{12}}{\left[1 + \frac{A_{12}\cdot X_1}{A_{21}\cdot X_2}\right]^2} \qquad (12)$$

$$\ln\gamma_2 = \frac{A_{21}}{\left[1 + \frac{A_{21}\cdot X_2}{A_{12}\cdot X_1}\right]^2} \qquad (13)$$

- **Margules model**

The excess free energy is expressed as follows:

$$\frac{G^E}{R\cdot T} = B\cdot x_1\cdot x_2 \qquad (14)$$

After differentiation, the activity coefficients are given expressed as follows [2]:

$$\ln\gamma_1 = B\cdot x_2^2 \qquad \ln\gamma_2 = B\cdot x_1^2$$

The parameter B is calculated by means of infinite dilution activity coefficient as $\ln\gamma_{12}^\infty = \ln\gamma_{21}^\infty = B$

The excess free energy for the Margules equation with three suffixes (third order) is given as follows:

$$\frac{G^E}{R\cdot T} = x_1\cdot x_2\cdot\left[A_{21}\cdot x_1 + A_{12}\cdot x_2\right] \qquad (15)$$

Similarly, after differentiation, the activity coefficients for binary systems are:

$$\ln\gamma_1 = x_2^2\cdot\left[A_{12} + 2\cdot x_1\cdot\left(A_{21} - A_{12}\right)\right] \qquad (16)$$

$$\ln\gamma_2 = x_1^2\cdot\left[A_{21} + 2\cdot x_2\cdot\left(A_{12} - A_{21}\right)\right] \qquad (17)$$

Parameters A $_{12}$ and A $_{21}$ are calculated by means of infinite dilution activity coefficients as $\ln\gamma_1^\infty = A_{12}$ and $\ln\gamma_2^\infty = A_{21}$

- **Wilson model**

The excess free energy according to this model is expressed as follows:

$$\frac{G^E}{R\cdot T} = -\sum_{i=1}^{n} Ln\left[\sum_{j=1}^{n}\Lambda_{ij}\cdot x_j\right] \qquad (18)$$

With

$$\Lambda_{ij} = \frac{V_j}{V_j}\cdot\exp\left[-\frac{(\lambda_{ij} - \lambda_{ii})}{R\cdot T}\right] \quad i\neq j \qquad (19)$$

$$\ln\gamma_i = 1 - \ln\left[\sum_{j=1}^{N} x_j\cdot\Lambda_{ij}\right] - \sum_{K=1}^{N}\frac{x_K\cdot\Lambda_{Ki}}{\sum_{j=1}^{N} x_j\cdot\Lambda_{Kj}} \qquad (20)$$

Λ_{ij} is the Wilson interaction parameter.

For a binary mixture the excess free energy is then given by [3]:

$$\frac{G^E}{R\cdot T}=-x_1\cdot\ln\left(x_1+x_2\cdot\Lambda_{12}\right)-x_2\cdot\ln\left(x_2+x_1\cdot\Lambda_{21}\right) \quad (21)$$

The coefficients of activity will be in this case:

$$\ln\gamma_1=-\ln\left(x_1+x_2\cdot\Lambda_{12}\right)+x_2\cdot\left(\frac{\Lambda_{12}}{x_1+x_2\cdot\Lambda_{12}}-\frac{\Lambda_{21}}{x_2+x_1\cdot\Lambda_{21}}\right) \quad (22)$$

$$\ln\gamma_2=-\ln\left(x_2+x_1\cdot\Lambda_{21}\right)+x_1\cdot\left(\frac{\Lambda_{12}}{x_1+x_2\cdot\Lambda_{12}}-\frac{\Lambda_{21}}{x_2+x_1\cdot\Lambda_{21}}\right) \quad (23)$$

Wilson parameters Λ_{ij} can be calculated, still, by means of infinite dilution activity coefficients:

$$\ln\gamma_1^\infty=-\ln\Lambda_{12}+1-\Lambda_{21} \quad \ln\gamma_2^\infty=-\ln\Lambda_{21}+1-\Lambda_{12}$$

NRTL model (Non Random Two Liquids)

The excess free energy for this model is given as follows [1]:

$$g^E=RT\cdot\sum x_i\cdot\frac{\sum_j x_i G_{ji}\tau_{ji}}{\sum_k x_k G_{ki}} \quad (24)$$

Where $G_{ji}=\exp\left(-\alpha_{ji}\cdot\frac{C_{ji}}{RT}\right)$ and $\tau_{ji}=\frac{C_{ji}}{RT}$

$$\ln\gamma_i=\frac{\sum_j^N\tau_{ji}\cdot G_{ji}\cdot x_i}{\sum_k^N G_{ki}\cdot x_k}+\sum_j^N\frac{x_j\cdot G_{ij}}{\sum_k^N G_{kj}\cdot x_k}\cdot\left(\tau_{ij}-\frac{\sum x_k\cdot\tau_{kj}\cdot G_{kj}}{\sum_k^N G_{kj}\cdot x_k}\right) \quad (25)$$

$$\ln\gamma_1^\infty=\tau_{21}+\tau_{12}\cdot\exp(-\alpha_{12}\cdot\tau_{12}) \quad (26)$$

$$\ln\gamma_2^\infty=\tau_{12}+\tau_{21}\cdot\exp(-\alpha_{21}\cdot\tau_{21}) \quad (27)$$

UNIQUAC (Universal Quasi-chemical Activity Coefficient) model

The excess free energy for this model is given by the following expression:

$$\frac{g^E}{RT}=\sum_i^N x_i\ln\frac{\Phi_i}{x_i}+\frac{z}{2}\cdot\sum_i^N q_i x_i\ln\frac{\Theta_i}{\Phi_i}-\sum_i^N q_i x_i\ln\left(\sum_j^N\Theta_i\tau_{ji}\right) \quad (28)$$

The coefficient of activity is made of two terms as [4]:

$$\ln\gamma_i=\ln\gamma_i^C+\ln\gamma_i^R \quad (29)$$

The first term is the combinatory and the second is the residual one and are given as follows:

$$\ln\gamma_i^C=\ln\frac{\Phi_i}{x_i}+\frac{z}{2}\cdot q_i\cdot\ln\frac{\Theta_i}{\Phi_i}+l_i-\frac{\Phi_i}{x_i}\cdot\sum_j x_j\cdot l_j \quad (30$$

$$\ln\gamma_i^R=q_i\cdot\left[1-\ln\left(\sum_j\Theta_j\cdot\tau_{ji}\right)-\sum_j\frac{\Theta_j\cdot\tau_{ji}}{\sum_k\Theta_k\cdot\tau_{kj}}\right] \quad (31)$$

With

$$l_i=\frac{z}{2}\cdot\left(r_i-q_i\right)-\left(r_i-1\right) \quad (32)$$

Where r_i and q_i are the van der Waals molecular volume and surface parameters, respectively,
z is the coordination number set equal to 10 . The surface and volume fraction are given as:

$$\Theta_i=\frac{q_i\cdot x_i}{\sum_j q_j\cdot x_j} \quad (33)$$

$$\Phi_i=\frac{r_i\cdot x_i}{\sum_j r_j\cdot x_j} \quad (34)$$

And the energy parameter is given by:

$$\tau_{ji}=\exp\left(-\frac{u_{ji}-u_{ii}}{R\cdot T}\right) \quad (35)$$

UNIFAC (UNIQUAC Functional Activity Coefficient) model

Similarly to the UNIQUAC, the UNIFAC is also made of two terms, combinatorial and residual expressed as follows [5]:

$$\ln\gamma_i=\ln\gamma_i^C+\ln\gamma_i^R \quad (36)$$

$$\ln\gamma_i^C=\ln\frac{\Phi_i}{x_i}+\frac{z}{2}\cdot q_i\cdot\ln\frac{\Theta_i}{\Phi_i}+l_i-\frac{\Phi_i}{x_i}\cdot\sum_j x_j\cdot l_j \quad (37)$$

With $l_i = \frac{z}{2}\cdot(r_i - q_i) - (r_i - 1)$; z=10 ;

$$\Theta_i = \frac{q_i \cdot x_i}{\sum_j q_j \cdot x_j} \ ; \qquad \Phi_i = \frac{r_i \cdot x_i}{\sum_j r_j \cdot x_j}$$

$$r_i = \sum_k \nu_k^{(i)} \cdot R_k \qquad q_i = \sum_k \nu_k^{(i)} \cdot Q_k$$

$$R_k = \frac{V_{wk}}{15.17} \qquad Q_k = \frac{A_{wk}}{2.5\times 10^9}$$

And

$$\ln\gamma_i^R = \sum_k \nu_k^i \cdot \left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \qquad (38)$$

With

$$\ln\Gamma_k = Q_k \cdot \left[1 - \ln\left(\sum_m \Theta_m \cdot \Psi_{mk}\right) - \sum_m \frac{\Theta_m \cdot \Psi_{km}}{\sum_n \Theta_n \cdot \Psi_{nm}}\right] \ ;$$

$$\Theta_m = \frac{Q_m \cdot X_m}{\sum_n q_n \cdot x_n} \ ; \qquad X_m = \frac{\sum_j \nu_m^{(j)} \cdot x_j}{\sum_j \sum_n \nu_n^{(j)} \cdot x_j}$$

$$\Psi_{mn} = \exp\left(-\frac{u_{mn} - u_{nn}}{R \cdot T}\right) = \exp\left(-\frac{a_{mn}}{T}\right)$$

In order to show the influence and importance of the nature and also the size of the molecules, present in the system, on the phase equilibrium calculations, different binary systems, frequently met, involving Hydroxylic, Aromatic, Acidic compounds, etc., are considered. A priori the choice of the systems has been made on the basis of the molecular weight, the number of carbon atoms, etc., to distinguish between light and heavy compounds. In the present work, it is assumed that the components having at least three carbon atoms, are regarded as light components while those having more than three carbon atoms are regarded as heavy.

The considered systems are mixtures where the first component is a light alcohol and the second one can be of similar or different nature such as a light or heavy alcohol, aromatic, an ester, an organic acid, etc.

III. Light alcohols- light alcohols binary systems

Six systems have been considered in this category. As an illustration, the results for the system Methanol-Ethanol are shown and compared with the experimental values [6] as follows:

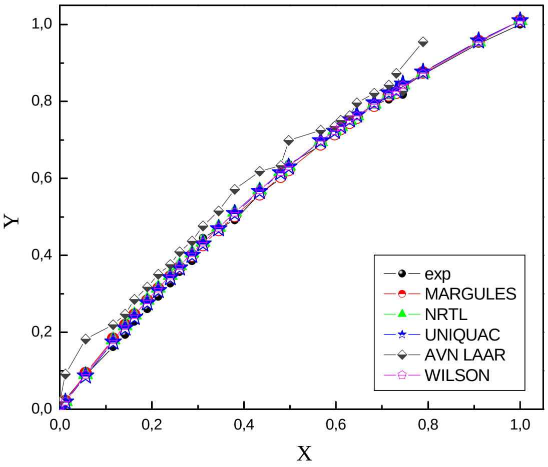

Figure 1 Methanol –Ethanol system

Table 1 shows the comparison of the deviations obtained for each model, for the same system Methanol – ethanol as follows:

Table 1 Comparison of the models for the system Methanol-Ethanol

System	Thermodynamic model	Deviation from experimental values
Methanol-ethanol	Margules	$1.003\ 10^{-2}$
	Van Laar	$1.244\ 10^{-2}$
	Wilson	$1.058\ 10^{-2}$
	NRTL	$1.060\ 10^{-2}$
	UNIQUAC	$9.807\ 10^{-3}$

On the six cases tested for this type of systems, the UNIQUAC model has given the most precise results.

IV. Light Alcohol – Organic acid binary systems

Four systems have been tested for this class and the results obtained by means of the UNIQUAC and the NRTL models, have shown the least and close deviations from the experimental data [6]

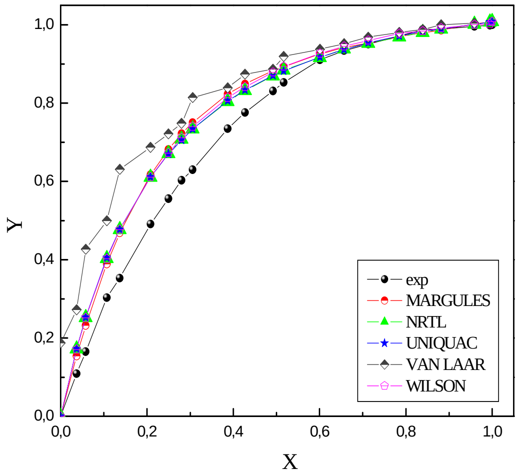

Figure 2 Methanol – Acetic acid system

Table 2 Models comparisons for Methanol-Acetic acid

System	Thermodynamic model	Deviation from the experimental values
Methanol – acid acetic	MARGULES	5.081 10 $^{-2}$
	VAN LAAR	6.086 10 $^{-2}$
	WILSON	5.099 10 $^{-2}$
	NRTL	3.79910 $^{-2}$
	UNIQUAC	3.801 10 $^{-2}$

V. Light Alcohols –Amines binary systems

Sixteen systems of this class have been tested and the results are shown for the mixture Methanol- Butylamine as follows [6]:

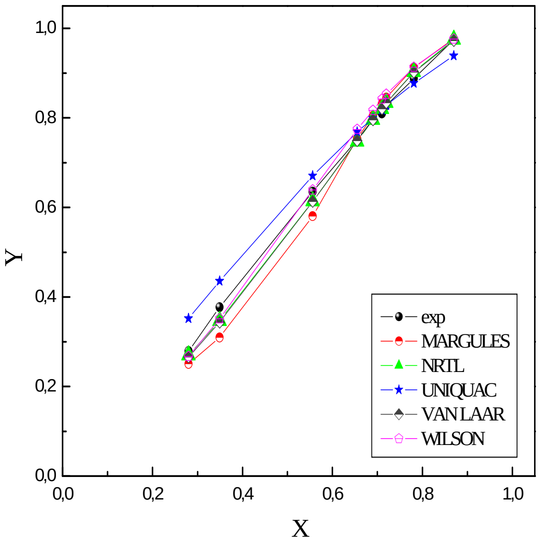

Figure 3 System Methanol Butylamine

Table 3 Models comparisons for Methanol-Butylamine

System	Thermodynamic model	Deviation from the experimental values
Methanol-butylamine	MARGULES	2.519 10 $^{-2}$
	VAN LAAR	1.152 10 $^{-2}$
	WILSON	1.863 10 $^{-2}$
	NRTL	1.063 10 $^{-2}$
	UNIQUAC	2.685 10 $^{-2}$

On the 16 treated systems, the NRTL model has proven once more to be the most precise in nine cases, followed by the UNIQUAC and Margules models in three cases, each, and only one case for the Wilson model. Thus on this basis, the NRTL model seems to be the most adequate for mixtures of light alcohols -amines.

VI. Light alcohols -Esters binary systems

For this category, two possible cases have been considered, according to the nature of the mixture and whether azeotrope formation may occur or not. For the first case, *i.e.* with the presence of an azeotropy, for seven out of eight cases tested, the model of Wilson has given the best results. Whereas, with the absence of any azeotropy, the NRTL model has given the most precise results for the nine cases tested. The UNIQUAC has shown the largest deviation from the experimental values

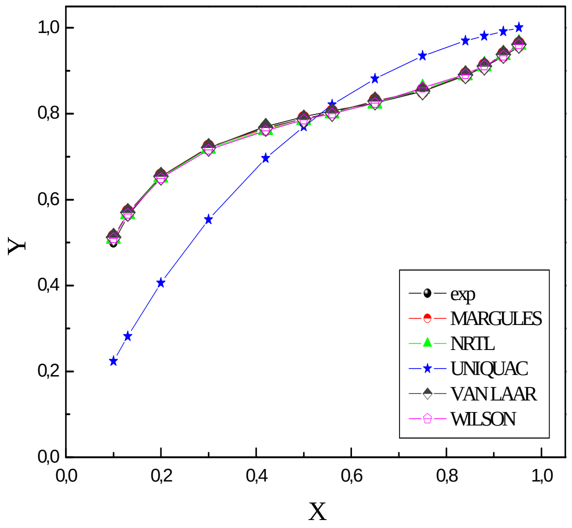

Figure 4 Methanol – Acrylate methyl system

Table 4 Models comparisons for Methanol – Acrylate methyl

System	Thermodynamic model	Deviation from the experimental values
Methanol – Acrylate methyl	MARGULES	5.192 10 $^{-3}$
	VAN LAAR	5.115 10 $^{-3}$
	WILSON	5.330 10 $^{-3}$
	NRTL	3.346 10 $^{-3}$
	UNIQUAC	1.137 $^{-1}$

VII. Light Alcohol – Aromatic binary systems

These systems are also treated according whether or not they may lead to the formation of azeotropy. For the fist case of a possible azeotropes formation, for the six treated systems, the Wilson model has given the best results. Consequently it is preferable to use this model for these types of systems. For the second case where a light alcohol and an aromatic do not form an azeotrope, the NRTL model has given the most precise results for the seven tested systems.

Table 5 Models comparisons for Methanol-Benzene system

System	Thermodynamic model	Deviation mpared to the rimental values
Methanol Benzene	MARGULES	1.303 10^{-2}
	VAN LAAR	1.181 10^{-2}
	WILSON	6.339 10^{-3}
	NRTL	6.989 10^{-3}
	UNIQUAC	1.882 10^{-1}

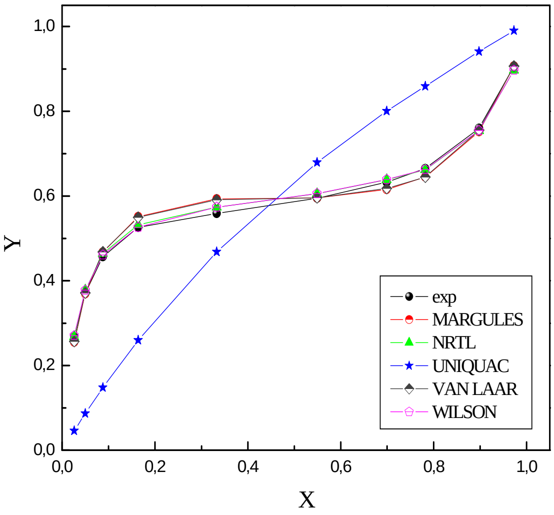

Figure 5 Methanol –Benzene System

VIII. Conclusion

From this study, one can see that it is not easy, a priori, to choose the best thermodynamic model for the activity coefficient calculations. Regarding to the importance of this parameter in process design, it is useful to have some guidance for making the most appropriate model choice.

Consequently, in the present study, an attempt has been made to relate the molecular structure (nature) of the compounds involved with the different thermodynamic models. Binary systems have been tested and the results show that the new models lead to more precise results than the old ones, due to the fact that they introduce parameters which take into account the size, interactions, the polarity, etc. of the components.

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