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Molecular Modeling Coupled To Reactive Separation Systems Design

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Process design in chemical engineering is based on kinetics models and thermophysical properties strongly dependent on experimental measurements which are generally expensive and very time consuming, or under specific conditions could be unfeasible. Computer simulations can be implemented to overcome some of these limitations. An important problem in chemical engineering is the accurate prediction of reaction and phase equilibrium for complex chemical systems in reaction-separation (or hybrid) process design, like reactive distillation, extraction or adsorption. There are two general approaches to solve this problem: 1) the standard one based on the equality of chemical potentials derived from cubic and empirical equations of state, as well as group contribution methods and 2) systems modeled by computer simulations, using specific intermolecular interactions between the constituent molecules. In this work we present results using molecular modeling coupled to a mass exchanger process design, where the reaction can take place into or between phases. The Reactive Monte Carlo method (Smith and Triska, 1994), (Johnson, et al, 1994). and the Statistical Associating Fluid Theory for Potentials of Variable Range (Gil-Villegas, et al, 1997) are applied to model phase equilibrium when chemical reactions are present in mixtures of industrial interest, such as a mixture of water, alcohols and organic acid mixtures.

1. Introduction

The reactive mass-exchange process is a process where the chemical reaction and separation of the reaction mixture occur simultaneously and combined (in one apparatus) with predominant removing of target reaction products. Process design in chemical engineering has been based on kinetics models and properties strongly dependents on experimental measurement whose determination generally is expensive, very time consuming, or under specific conditions are unfeasible. On the other hand, computer simulation can be implemented to overcome some of these problems, using molecular models. A particular case and important problem in chemical engineering is the accurate prediction of reaction and phase equilibrium for complex chemical systems for reaction-separation process (or hybrid process) design like reactive distillation,

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reactive extraction or adsorption. There are two general approaches to the solution of this problem , the conventional one based on chemical potential equality that utilizes cubic and empirical equations of state an contribution group methods. In these cases the input information are experimental data for the underlying pure components and binary mixture data of some type. The other approach involves modeling the intermolecular interactions between the constituent molecules of the system and the use of computer simulation techniques. In this work we present an efficient approach for coupling molecular modeling oriented to mass exchanger process design. Our methodology only requires the knowledge of intermolecular potentials between species, the stoichiometric conditions if chemical reactions take place. This approach is based on a Monte Carlo technique for reacting systems, (Smith and Triska, 1994), (Johnson, et al, 1994) and a statistical mechanical predictive equation of state like SAFT-VR (Gil-Villegas, et al, 1997), This approach enables to analyze at the same time salvation and association phenomena, which is of great practical importance as these effects determine, often dramatically, the phase behavior of many mixtures of industrial relevance. Some industrials mixtures examples like water, alcohols and organic acids mixtures are analyzed. In this paper we also present an algorithm for the calculation of simultaneous chemical and physical equilibrium, based on a Gibbs free-energy minimization with the constituent species elements conservation as a restriction. This robust and efficient scheme is oriented to be applied to reactive liquid-vapor and reactive liquid-liquid equilibrium. Common problems in others methodologies, like multiple or no physical solutions are avoided. We have implemented a non-stoichiometric formulation for chemical equilibrium in addition to the equality of chemical potentials for phases in equilibrium, and using the mass conservation law as a restriction. This algorithm is applied within the SAFT-VR approach to study the phase equilibrium of reacting fluids.

2.Equation of state

The statistical associating fluid theory (SAFT) (Chapman, et al, 1989, and Chapman, et al, 1990) provides an accurate description of the thermodynamic properties of non-ideal mixtures. This approach has been used to correlate and predict the phase behavior of a wide variety of complex systems (Muller and Gubbins, 2001). The general form of the SAFT Helmholtz free energy for associating chain molecules is given by:

$$\frac{A}{NkT} = \frac{A^{IDEAL}}{NkT} + \frac{A^{MONO}}{NkT} + \frac{A^{CHAIN}}{NkT} + \frac{A^{ASSOC}}{NkT} \tag{1}$$

Where A^{IDEAL} is the ideal free energy, A^{MONO} is the excess free energy due to the monomer segments, A^{CHAIN} is the contribution due to formation of the chains of monomers, and A^{ASSOC} is the term that describes the contribution to the free energy due to intermolecular association. For more details see references (Gil-Villegas, et al,1997, Chapman, et al, 1989, and Chapman, et al, 1990) .The expression for the chemical potential is:

$$\frac{\mu_i}{m_i RT} = \frac{a_0^{mono}}{RT} + \left(Z_0^{mono} - 1\right)\left[\frac{2\sum_j X_j m_j \sigma_{ij}^3}{\sigma^3 \sum_j X_j m_j} - 1\right] + \frac{u_0^{mono}}{RT}\left[\frac{2\sum_j X_j m_j \varepsilon_{ij} \sigma_{ij}^3}{\varepsilon \sigma^3 \sum_j X_j m_j} - \frac{2\sum_j X_j m_j \sigma_{ij}^3}{\sigma^3 \sum_j X_j m_j}\right] \tag{2}$$

And the fugacity coefficient is given by:

$$\ln(\phi_i) = \frac{\mu_i}{RT} - \ln(Z) \tag{3}$$

Where:

$$Z = \eta \frac{\partial\left(A/NKT\right)}{\partial \eta} \tag{4}$$

3. Thermodynamic system

In the system under study only energy exchange is allowed, and there is not mass exchange. The system can be formed by one or many phases. Mass diffusion can occur only within the phases and chemical reactions are present. The system is defined by a set of equations named "abundance equations" and represents the mass conservation principle. Chemical elements are conserved, and this is described by a series of stoichiometric equations given by:

$$\sum_{i=1}^{N} a_{ki} n_i = b_k \qquad For \quad k = 1,2,.....,M$$

a_{ki} is the number of reaction invariants elements k, in molecule i. and b_k represents total element of k.

3.2 Simultaneous equilibrium formulation

If a thermodynamic system is in equilibrium in one or more phases, its free energy has a global minimum.

$$\min \; G(\eta) = \sum_{ii=1}^{N} n_i \mu_i (T, P, \eta) \tag{6}$$

Under non-stoichiometric conditions, this problem could be reduced to a free energy minimization at constant pressure and constant temperature, and subject to M conservation equations like restrictions. Using Lagrange multipliers to include the restrictions, we have that:

$$\ell(\eta,\lambda)=\sum_{i=1}^{N}n_i\mu_i+\sum_{k=1}^{M}\lambda_k\left(b_k-\sum_{k=1}^{N}a_{ki}n_i\right) \tag{7}$$

Equation (7) represents the lagrangian where λ is a vector of M unknowns Lagrange multipliers, therefore the necessary conditions give set of (N+ M) equations for (N+M) unknowns $\left(n_1,n_2,\ldots,n_N,\lambda_1,\lambda_2,\ldots\lambda_M\right)$.

3.3 Reactive liquid-vapor equilibrium

For systems where phase separation (i.e., liquid. vapor) as well as chemical reactions are present (Michelsen,1989), the previous procedure can be re-expressed as:

$$\theta_V\sum_{i=1}^{N}a_{ki}y_i+\theta_L\sum_{i=1}^{N}a_{ki}x_i-b_{kf}=0 \quad \text{And} \quad \begin{array}{l}\sum_{i=1}^{N}y_i-1=0\\ \sum_{i=1}^{N}x_i-1=0\end{array} \tag{8}$$

Where

$$y_i=\exp\left(\frac{\sum_{k=1}^{M}a_{ik}\lambda_k}{RT}-\frac{\mu_i^0(T)}{RT}-\ln\left(\phi_i^V\right)-\ln(P)\right)$$

$$x_i=\exp\left(\frac{\sum_{k=1}^{M}a_{ik}\lambda_k}{RT}-\frac{\mu_i^0(T)}{RT}-\ln\left(\gamma_i^L\right)-\ln\left(P_i^{sat}\right)\right) \tag{9}$$

Here, the dew or bubble point system is reached when the system reached a limit condition (Perdomo and Cardona, 2007) then θ^L or $\theta^V = 0$.

4. Computer simulation

In order to validate the theoretical approach and determine the conditions under which the approximations developed in this work are valid , the Reaction Ensamble Monte Carlo simulation have been performed to modeling the chemical reaction extent and the liquid-vapor phase coexistence. Such phases are monitored simultaneously in two disctinct regions , *a* and *b*, with volumes V^a and V^b $\left(V=V^a+V^b\right)$ and N^a and N^b, respectively $\left(N=N^a+N^b\right)$. The two regions are not in physical contact but in thermodynamic equilibrium to satisfy the conditions of phase equilibrium: the equality of the pressure p, temperature T, and chemical potential. The required conditions of vapor-liquid and chemical reaction equilibrium are ensured by performing a combination of four steps: particle displacements, volume changes, interphase particle transfers, and reaction moves. The transition probability for the transfer of a particle from box *a* into box *b* is:

$$\mathrm{P}^{a\to b} = \min\left\{1, \exp\left[-\beta\left(\Delta U^{a} - \Delta U^{b}\right) + \ln\frac{N^{a}V^{a}}{\left(N^{b}V^{a} + V^{a}\right)}\right]\right\} \tag{10}$$

For more details see references (McCabe, et al, 1999, Lísal, et al, 1999 and Lísal et al,2000), β is the Boltzmann factor, and ΔU is the energy change of the regions *a* and b.

5. Results

Vapor and liquid phase fugacity coefficient of component $\left(\phi_i^V, \phi_i^L\right)$ were calculated implemented the SAFT-VR equation of state. Figure (1) shows the MTBE (Methyl-Therbutyl-Eter) reaction production in vapor-liquid equilibrium for several reactants compositions, and Figure (2) shows the residue curve maps when the chemical reactions for MTBE (in inert presence) and Ethyl acetate production are presents and were pictured in elemental molar fractions.

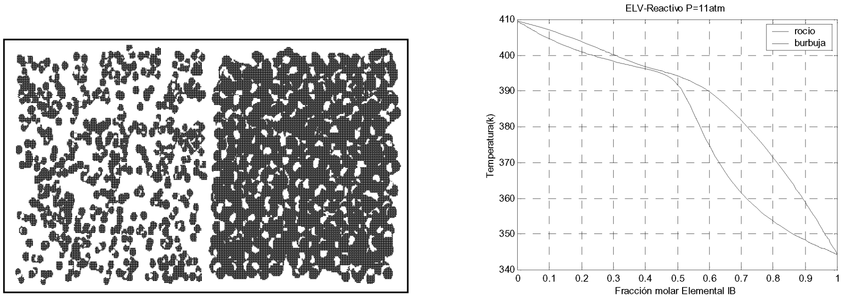

Figure 1. Simultaneous chemical reaction and vapour-liquid equilibrium for MTBE – isobutene – methanol system (inert absence and p=11 atm.).

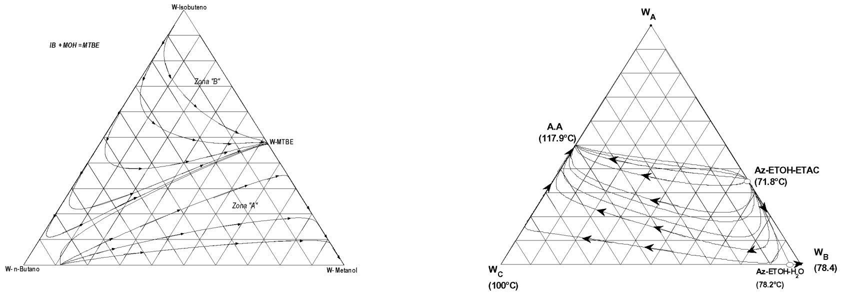

Figure (2) Residue curve maps when are present chemical reactions for a) MTBE production (p=11atm) and b) ethylacetate production. c) Chemical reaction simulation for (1a) case

Chemical reaction simulation was made using a Monte Carlo procedure , a cycle is defined by N particle displacements and fixed number of particle interchanges. The results presented here were obtained using 1728 particles and 40.000 cycles for equilibration, with another 40.000 for averaging. Additional details of the procedure followed are described in (MacCabe, et al, 1999, Martinez, et al,2007).

6. Conclusions

Has been implemented too a minimization free energy algorithm oriented to resolve the reactive liquid vapor problem for a several component mixture. The implemented algorithm satisfied the material conservation and chemical potential equality. The most important in the algorithm implementation is the singular and unphysical solutions avoid and it can converge to limit reacting compositions. In addition we have presented REMC simulation for the phase equilibrium when chemical reaction were presented and compared with the phase diagrams obtained with SAFT-VR. SAFT is a molecular based equation of satate enabling each term to be directly tested by computer simulation, which enables improvement of the theory. For the systems studied good agreement with the literature is seen.

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