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Thermodynamic modeling of phase equilibria in biorefineries

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ABSTRACT

A thermodynamic model for predicting phase behavior of mixtures of hydrocarbons, organo-oxygenated compounds and water is required for the development of a biorefinery process simulator. Moreover, the design of particular fuel/biofuel blends also requires the support of a thermodynamic model to predict the properties of the final products. These types of mixtures are highly non-ideal due to the presence of association and solvation effects. The GCA-EoS model has already proven to have excellent predictive capacity to represent the complex phase behavior of mixtures containing natural products and biofuels. In this work we extend GCA-EoS to represent the phase equilibria of mixtures of branched hydrocarbons with water and alcohols. It is a big challenge for the model to cover, with a single set of parameters, the wide range of operating conditions found in processing, transportation and storage of these fluid mixtures.

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1. Introduction

Second generation biorefineries include in their platform the processing of ligno-cellulosic biomass, in addition to oils and sugars, for the production of chemicals as well as materials and biofuels. The thermochemical route for ligno-cellulosic biomass conversion has three main alternatives: gasification, pyrolysis and hydrolysis [1]. In any of these processes, engineers have to deal with mixtures containing a wide variety of oxygenated organic compounds. The phase behavior of these mixtures is highly nonideal due to the presence of association and solvation effects. In some cases, important size asymmetry between components also contributes to non-ideality. Moreover, in the case of gasification, knowledge of gas solubilities in aqueous broths under a wide range of conditions is required. Even though the processing of ligno-cellulosic material produces numerous oxygenated species, all of them belong to certain families of organic compounds (alcohols, carboxylic acids, esters, etc.). Therefore, all these mixtures can be described by a reduced number of functional groups. For this reason the use of a group contribution approach is a logical choice for thermodynamic modeling. In this work we choose the Group Contribution with Association Equation of State (GCA-EoS) [2].

The group-contribution equation of state, originally proposed to predict gas solubilities in liquid solvents [3], has proved to have excellent predictive capacity to represent the phase behavior of mixtures containing natural products [4]. The model also shows very good performance in predicting hydrogen solubility in solutions of natural products with supercritical fluids [5]. The extension of the equation to multiple-associating and solvating solutions makes GCA-EoS a suitable model to predict the phase behavior of fluid mixtures typical of biomass processing [6]. On the other hand, the prediction of properties of fuel/biofuel blends calls for the extension of the model to represent mixtures containing also linear, branched, cyclic and aromatic hydrocarbons.

GCA-EoS has already been applied to predict the phase behavior of mixtures involving first generation biofuels (ethanol and biodiesel)[7–9]. In the present work we extend the GCA-EoS model to systems containing branched paraffins, water and alcohols. This information is of utmost importance for the prediction of the phase behavior of fuel/biofuel blends and contributes the required model parameters to describe the aqueous broth of different biomass processing units.

The final goal of this project is to build a thermodynamic package (THERMO/OS+LC) with predictive capacity for integrated second generation biorefineries, which include the processing not only of oils and sugars, but also of lignocellulosic material. This package will be based on the extension of GCA-EoS to the type of mixtures present in biomass processing. The model should be able to predict thermodynamic properties under a wide range of temperatures and pressures, as required by any of the thermochemical routes.

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2. Thermodynamic modeling

In the field of fossil fuels, the most frequently used equations of state are the classical cubic equations like Soave–Redlich–Kwong or Peng–Robinson. These models do not take into account association and solvation effects, which represent an important contribution to the non-ideality of fuel mixtures containing compounds such as alcohols. A well-developed approach applied in modeling association effects is Wertheim's perturbation theory [10,11] for fluids with highly oriented attractive forces. Wertheim's theory has been used in equations of state like the statistical associating fluid theory (SAFT) [12], the group contribution with association GCA-EoS equation [13] and the cubic plus association equation of state (CPA) [14].

2.1. GCA-EoS equation

There are three contributions to the residual Helmholtz energy in the GCA-EoS model: free volume, attractive and associating. The free volume and attractive contributions are based on Carnahan–Starling [15] and NRTL models respectively, and keep the same form as the original GC-EoS Skjøld–Jorgensen equation [3].

The attractive term is a group contribution version of the NRTL model, with density-dependent mixing rules. The attractive energy between like groups is calculated from pure group parameters; binary parameters are introduced to quantify interactions between unlike groups. Details of the model equations are given elsewhere [2–4].

The Carnahan–Starling repulsive term [15] follows the expression developed by Mansoori and Leland [16] for mixtures of hard spheres. It is a function of the critical hard sphere diameter d_c , characteristic of the pure-compound molecular size and has no binary or higher-order parameters. There are three different ways to calculate d_c of each component: (i) direct calculation with the values of critical temperature and pressure so that the model fulfills the critical point and its conditions (first and second derivatives of pressure with regard to volume equal to zero) [3], (ii) fit d_c to an experimental pure-component vapor pressure data point (T_{sat} , P_{sat}) [3], and (iii) computation with the correlation proposed by Bottini et al. [17] for high molecular weight compounds.

In the case of permanent gases, the first procedure must be used. For ordinary solvents method (ii) is generally applied; the d_c values obtained by this way are usually within 5% of the d_c given by method (i), but this difference is significant since pure component vapor pressures are sensitive to d_c [3]. Even more sensitive to the d_c value are the predictions of liquid–liquid equilibria. In this case, better results are achieved when d_c is closer to the value calculated with the critical point conditions (method i)

The associating term *A*^{assoc} follows Wertheim's first order perturbation theory through a group-contribution expression [2]:

$$\frac{A^{assoc}}{RT} = \sum_{i=1}^{NGA} n_i^* \left\{ \sum_{k=1}^{M_i} \left[\ln X^{(k,i)} - \frac{X^{(k,i)}}{2} \right] + \frac{1}{2} M_i \right\}$$
(1)

In this equation NGA represents the number of associating functional groups, n_i^* the total number of moles of associating group *i*, $X^{(k,i)}$ the fraction of group *i* non-bonded through site *k* and M_i the number of associating sites in group *i*. The total number of moles of associating group *i* is calculated from the number $v_{assoc}^{(i,m)}$ of associating groups *i* present in molecule *m* and the total amount of moles of specie $m(n_m)$:

$$n_i^* = \sum_{m=1}^{NC} v_{assoc}^{(i,m)} n_m \quad NC = \text{number of components}$$
(2)

The fraction of groups *i* non-bonded through site *k* is determined by the expression:

$$X^{(k,i)} = \left[1 + \sum_{j=1}^{NGA} \sum_{l=1}^{M_j} \rho_j^* X^{(l,j)} \Delta^{(k,i,l,j)}\right]^{-1}$$
(3)

where the summation includes all *NGA* associating groups and M_j sites. $X^{(k,i)}$ depends on the molar density of the associating group ρ_i^* and on the association strength $\Delta_{(k,i,l_j)}$:

$$\rho_j^* = \frac{n_j^*}{V} \tag{4}$$

$$\Delta^{(k,i,l,j)} = \kappa^{(k,i,l,j)} \left[\exp\left(\frac{\varepsilon^{(k,i,l,j)}}{kT}\right) - 1 \right]$$
(5)

The association strength between site k of group i and site l of group j depends on the temperature T and on the association parameters κ and ε , which represent the volume and energy of association, respectively.

The thermodynamic properties required to calculate phase equilibria are obtained by differentiating the residual Helmholtz energy. The association contributions to the compressibility factor Z and to the fugacity coefficient ϕ_i of component i in the mixture are given by:

$$Z_{assoc} = -\frac{V}{n} \frac{\partial}{\partial V} \left(\left(\frac{A^R}{RT} \right)_{assoc} \right)_{T,n}$$
$$= -\frac{V}{n} \sum_{i=1}^{NGA} n_i^* \left[\sum_{k=1}^{M_i} \left(\frac{1}{X^{(k,i)}} - \frac{1}{2} \right) \left(\frac{\partial X^{(k,i)}}{\partial V} \right)_{T,n} \right]$$
(6)

$$\ln \hat{\phi}_{q}^{assoc} = \frac{\partial}{\partial n_{q}} \left(\left(\frac{A^{R}}{RT} \right)_{assoc} \right)_{T,V,n_{r \neq q}} \\ \ln \hat{\phi}_{q}^{assoc} \sum_{i=1}^{NGA} \left\{ \nu_{assoc}^{(i,q)} \left[\sum_{k=1}^{M_{i}} \left(\ln X^{(k,i)} - \frac{X^{(k,i)}}{2} \right) + \frac{M_{i}}{2} \right] \\ + n_{i}^{*} \left[\sum_{k=1}^{M_{i}} \left(\frac{1}{X^{(k,i)}} - \frac{1}{2} \right) \left(\frac{\partial X^{(k,i)}}{\partial n_{q}} \right)_{T,V,n_{r \neq q}} \right] \right\}$$
(7)

The final expressions of these contributions depend on the number of associating groups *NGA* and on the number of associating sites M_i assigned to each group *i*.

2.2. Calculation of association effects

Michelsen and Hendriks [18] demonstrate that the calculation of the association contributions to pressure and chemical potential from first order perturbation theory can be simplified by the minimization of a conveniently defined state function, which do not require the calculation of first derivatives of the fraction of non-associating molecules X_{A_i} . For species *i* in an associating mixture, these authors show that:

$$\frac{P^{assoc}}{RT} = -\frac{\partial (A^{assoc}/RT)}{\partial V} = -\frac{1}{2V} \left(1 - V\frac{\partial \ln g}{\partial V}\right) \sum_{i} n_{i} \sum_{A_{i}} (1 - X_{A_{i}})$$
(8)

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