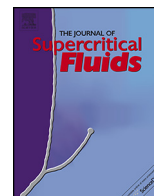




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Thermodynamic model for biomass processing in pressure intensified technologies

Mariana González Prieto, Francisco A. Sánchez, Selva Pereda*

Planta Piloto de Ingeniería Química (PLAPIQUI-UNS-CONICET), Camino La Carrindanga Km 7, 8000 Bahía Blanca, Argentina

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ABSTRACT

Pressure intensified technologies have a great potential in the context of biomass refining. A thermodynamic model able to predict phase behavior of typical mixtures found in biomass processing technologies, containing for instance 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. It has already been proved that the Group Contribution with Association Equation of State (GCA-EoS) is able to predict the complex phase behavior of mixtures containing natural products and biofuels. In the last few years, several contributions agree that 2,5-dimethylfuran has a great potential as a sugar-derived fuel additive. In this work, as a case study, we extend the GCA-EoS to represent the phase equilibria of furan derivatives with hydrocarbons and alcohols. In addition, we show that the GCA-EoS is able to predict, based on the performed parameterization, high pressure data of 2,5-hydroxymethylfurfural solubility in CO₂ and ethanol as co-solvent.

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1. Introduction

During the last decade, bio-based economy, also known as bioeconomy, attracts increasing attention driven by the high price of fossil fuels. Aligning policies and governmental incentives have also been pushing new studies on biomass processing. On the other hand, the current petroleum-based economy has taught us to process raw materials maximizing atomic efficiency while minimizing the use of energy. As a consequence, refineries have been developed for high energy integration in the processing and conversion of all petroleum fractions. Nowadays the same efficient approach reached in refineries is expected in the biomass processing plants, giving birth to the concept of biorefineries.

On the other hand, pressure-intensified technologies have shown in many studies a great capability to enhance the efficiency of reactions, extractions and fractionations, as well as to control of the final quality of materials and particulate products. Moreover, they have been widely applied in the processing of natural products and bio-based materials. Therefore, they have a great potential to contribute to the development of more efficient biomass processing

poles. In addition, pressure-intensified technologies have already achieved maturity and slowly are coming out from the academic milieu to industry.

Researchers working on the development of pressure-intensified technologies with different aims highlighted the need of predictive thermodynamic models at the Workshop of Supercritical Fluids and Energy (SFE'13) held at Campinas (Brazil). The requirements were clear; modeling biomass derived multi-component systems with compressed gases up to high pressures, which show complex multiphase behavior. Special emphasis was given to the need of models with capabilities to predict real mixtures. Equations of state (EoS) are an adequate tool for describing high pressure systems since they use the same model to describe liquid and vapor phases, avoiding inconsistencies in the near critical region (φ - φ approach). In that sense, classic cubic equations of state, like Soave-Redlich-Kwong [1] or Peng-Robinson [2], do a great job when dealing with non-polar compounds, even though of their mathematical simplicity. Thus, these models were and still are key tools in the understanding of conventional fossil fuel exploration and downstream processing. Nevertheless, biomass derived mixtures are characterized by containing polar compounds (like water and many other organo-oxygenated compounds), where association and solvation effects are present. It is known that cubic EoS are not able to describe the complex multiphase behavior that

* Corresponding author. Tel.: +54 29 14 86 1700; fax: +54 29 14 86 1600.
E-mail address: spereda@plapiqui.edu.ar (S. Pereda).

arises in mixtures containing these types of compounds with a single set of parameters [3].

A well-known concept applied in modeling associating solutions is the chemical theory [4,5], which postulates the existence of distinct chemical species in solution. However, new generation EoS are applying a different approach, based on statistical-mechanics, recognized as Wertheim's perturbation theory [6,7] for fluids with highly oriented attractive forces. Wertheim's theory has been used, e.g. in the Statistical Associating Fluid Theory (SAFT) [8,9] and the Perturbed Chain SAFT (PC-SAFT) [10,11], the Group Contribution Associating EoS (GCA) [12], and the Cubic plus Association EoS (CPA) [13–15]. All these models are semi-empirical, which means that the theoretical background is not sufficient to predict thermodynamic properties; however, after training them with experimental data (fitting parameters) they can predict phase behavior under conditions beyond that of the experimental study to a certain extent. Furthermore, models such as the GCA, and other group contribution SAFT derived EoS, like the GC-PPC-SAFT [16,17] and GC-SAFT-VR [18,19] can also predict behavior of additional similar compounds, not included in the parameterization using the group contribution approach.

Besides of semiempiricals, there are fully predictive models. For instance, numerical simulation techniques such as Monte Carlo and molecular dynamics have received increasing attention in the last years [20]. These types of models have a great potential and are normally used to compare qualitatively the effect of different components on a system behavior for a given application, for instance in a first approach for selecting completely unknown new solvents. However, nowadays the accuracy of the prediction is tightly bonded to the force field description, which is a current and very active research area. Ab initio or semi-empirical quantum mechanical calculations offer rigorous representation of structures and interactions. Nevertheless, the use of these models require high computing capacity, which is still not easily available to everyone [21], though this may change in the near future. Moreover, examples showing extension of fully predictive models to multicomponent mixtures is still limited.

As a case study, particularly in the field of biomass refining, 2,5-dimethylfuran (2,5-DMF) appears as a new promising fuel additive with better properties than ethanol. Román-Leshkov et al. [22] proposed a catalytic route for production of 2,5-DMF from biomass-derived carbohydrates broth. The removal of oxygen atoms from the sugar molecule can be accomplished in two steps: dehydration to produce 5-hydroxymethylfurfural (5-HMF) and hydrogenolysis of the latter to produce 2,5-DMF [22]. Gas-liquid reactions are one of the areas where the use of EoS is particularly attractive. In these reacting systems, EoS can handle subcritical and supercritical components in a wide range of conditions. Multiphase and supercritical conditions can be described with a proper EoS, going from the heterogeneous regions to the critical and homogeneous regions in a continuous way. Baiker et al. [23–25] have stressed the importance of having a proper knowledge of phase equilibria in gas-liquid catalyzed reactions. Advances in this area have been reviewed elsewhere [26–28].

In this manuscript we first introduce the advantages of modeling mixtures present in the biomass processing routes using the group contribution approach and the GCA-EoS. After presenting the equation, we discuss convenient algorithms to solve not only phase equilibrium but chemical equilibrium and finally we show the extension of GCA-EoS to a new family of organo-oxygenated compounds, furan and its derivatives. The developed tool can be applied in the future to evaluate the supercritical hydrogenolysis of 5-HMF to produce 2,5-DMF. In addition, we show that the GCA-EoS is able to predict, based on the performed parameterization, high pressure data of 2,5-hydroxymethylfurfural (HMF) solubility in CO₂ and ethanol as co-solvent.

2. Biomass conversion routes

Pressure intensified processes have been widely applied to the natural products industry, namely to food and functional food ingredients, cosmetic and pharmaceutical compounds. However, in the last decade, the need of diversifying the world resources for the fuel matrix has increased the use of biofuels, which are based on natural feedstock. These fuels are an alternative to petroleum fuels, though they are not expected to be totally replaced in the near future.

Biofuels have been classified by different authors [29,30] according to their source and processing pathway. The most commonly referred biofuels are bioethanol, produced from the fermentation liquors either of corn or sugarcane, and biodiesel usually obtained from the transesterification of oils and fats with alcohols such as methanol or ethanol. These fuels are produced in *first generation* biorefineries that use edible raw materials. They take advantage of high energy content raw materials and their conversion pathways are well-known, simple and relatively cheap. Nevertheless, raw material is limited by the availability of cultivable soils and they can directly lead to the increase of food price [30]. *Second generation biorefineries* use different biomass sources, for example, lignocellulosic materials, agricultural, industrial and urban residues, or non-edible crops. The conversion routes for these feedstocks are more expensive than that of the first generation and are still under development. In the last few years, scientists have defined also a *third generation biorefinery*, which employs microalgae and microbes as biological reactors. During their metabolism, these microorganisms can directly produce a great quantity of carbohydrates, oils, alcohols or added-value compounds [31].

There are several biomass conversion routes under development nowadays, some are recent developments but some are old refurbished technologies. Processing the great diversity of existing biomass species has some common basis given that, independently of the source, the processes should be able to convert the typical fractions of the biomass, i.e. carbohydrates, lipids, amino acids or proteins, cellulose or lignin. Therefore, from different raw materials the same family of compounds can be brought about of each fraction (refining concept). There is already a discussion going on about which will be the bio-based chemical building blocks of the future. The conversion routes are normally classified in three types: thermal, chemical and microbial/biochemical. In Tables 1–3 the more common compounds involved in each pathway are summarized. Thermal conversion route refers to biomass gasification, liquefaction, pyrolysis and direct combustion (Table 1). On the other hand, the most common chemical pathways are transesterification of lipids, hydrolysis and dehydration (Table 2). Last, the products of biochemical processes are summarized in Table 3, including anaerobic digestion, fermentation and enzymatic hydrolysis. Of course, these are only a fraction of a great deal of compounds that can be derived from biomass; nonetheless, these are the one among the more cited nowadays. It is important to highlight that pressure-intensified processes have a great potential in the development of new technologies not only in conversion routes but also in separation and purification steps of both, fuels and added-value compounds.

In any of the processes listed in Tables 1–3, engineers have to deal with mixtures containing a wide variety of organo-oxygenated compounds. The phase behavior of these mixtures is highly non-ideal due to the presence of association and solvation effects. In some cases, important size asymmetry between components also contributes to non-ideality. Moreover, cases like gasification or biological digestion require the knowledge of gas solubility in aqueous broths under a wide range of conditions. Even though the processing of biomass produces numerous oxygenated species, all of them belong to certain families of organic compounds (alcohols,

Table 1
Biomass thermal conversion routes.

| Chemical path | Compounds | Functional groups |
|--|---|---|
| Gasification and liquefaction [29,30,32,33] | Gases (hydrogen, carbon monoxide and dioxide, methane, nitrogen) | H ₂ , CO, CO ₂ , CH ₄ , N ₂ |
| | Hydrocarbons (pentanes, hexane, octane, hexene) (cyclopentane, cyclohexane, methylcyclohexane) (BTEX, alkylbenzenes, naphthenes) | CH _x , CH _x =CH _y cyCH _x , CH _x aCH, aCCH _x CH _x |
| Pyrolysis [29,32–35] | Organic acids (acetic, 2-hydroxybutanoic, pentanoic acids) | CH _x , COOH, OH |
| | Linear and cyclic aldehydes and ketones (acetone, glyoxal, 2-butenal, 2-butanone, cyclopentanone) | CH _x , CH _x =CH _y , cy-CH _x , CHO, CO |
| | Esters (2-propenyl acetate, methyl butanoate) | CH _x , CH _x =CH _y , CH _x COO |
| | Furanes (furfural) | aCH, a(CH _x OCH _y), CHO |
| | Alcohols and sugars (methanol, ethanol, levoglucosane) | CH _x , CH _x OH, cyCH _x , cyO |
| | Phenols (cresol, xylenol and other alkylated phenols) | aCH, aCCH _x , aCOH |
| | Phenolic ethers (guaiacol, methylguaiacol) | aCH, aCCH _x , aCOCH _x |
| | Hydrocarbons derivatives (2-methyl-1,4-Pentadiene, 2-hexene) | CH _x , CH _x =CH _y |

Table 2
Biomass chemical conversion routes.

| Chemical path | Compounds | Functional groups | |
|--|---|--|--|
| Supercritical water conversion (hydrolysis) [36–38] | Sugars (cellobiose, glucose, fructose) | cy-CH _x , cyO, CH _x OH | |
| | Alcohols and polyols (ethanol, xylosol, glycerol) | CH _x , CH _x OH | |
| | Glycoaldehydes and furans (glycoaldehyde, hydroxymethylfurfural, furfural) | aCH, a(CH _x OCH _y), CHO, CH _x OH, CH _x | |
| | Ketones and organic acids (butanone, formic acid, levulinic acid) | CH _x , COOH, CH _x CO | |
| | Aromatic (BTEX, polyphenols, acids) | aCH, aCOH, aCCOOH, CH _x | |
| | Amines (methylamine, ethanolamine, ethylamine) | CH _x , CH _x NH _y , CH _x OH | |
| | Aldehydes and ketones (formaldehyde, ethanol, acetone) | CH _x , CH _x CO, CH _x OH | |
| | Aminoacids (glycine, aspartic acid, serine, proline) | COOH, CH _x NH ₂ , CH _x , CH _x OH, aCH, cyCH _x , cyCH _x NH | |
| | Organic acids (formic, acetic, malic acid, glycolic acid, piruvic, malic, fumaric acids) | CH _x , CH _x CO, COOH, CH _x OH | |
| | Dehydration [22,39] | Cyclic ethers and sugars (fructose, THF, methyl-THF, tetrahydropyran) | cyCH _x , cyO, cyCH _x OH |
| | | Alcohols and polyols (methanol, ethanol, pentanediol, hexanetriol, xylosol, glycerol) | CH _x , CH _x OH |
| | | Furanes (furfural, hydroxymethylfurfural, dimethylfuran) | aCH, a(CH _x OCH _y), CHO, CH _x , CH _x OH |
| | | Gases (hydrogen, carbon monoxide and dioxide, methane, ethane) | H ₂ , CO, CO ₂ , CH ₄ , C ₂ H ₆ |
| Hydrocarbons (butane, pentane, hexane, octane) | | CH _x | |
| Organic acids (butanoic, pentanoic, hexanoic acid) | | CH _x , COOH | |
| Ketones (acetone, butanone, hexanone) | | CH _x , CH _x CO | |
| Acid hydrolysis [40] | | Monosaccharides (glucose, fructose) | cyCH _x , cyO, cyCH _x OH |
| | | Polyfunctional aromatics (methoxy-hydroxy-benzaldehydes, dihydroxy-benzoic acid, methoxy- α -hydroxy-benzenacetic acid) | aCH, aCOH, CH ₃ O, CHO, |
| | | Polyfunctional organic acids (acetic, oxo-pentanoic, hydroxy-propanoic, 2-butanedioic) | CH _x , COOH, CH _x OH, CH _x CO |
| | Furanic acids (furanocarboxylic, furanacetic, hydroxymethylfuranocarboxylic acids) | aCH, a(CH _x OCH _y), COOH, CH _x , CH _x OH | |
| | Transesterification [41–43] | Alcohols (methanol, ethanol, glycerol) | CH _x , CH _x OH |
| Mono, di and triglycerids and esters | | CH _x , COO, CH _x =CH _y , CH _x OH | |
| Fatty acids (linoleic, oleic, palmitic acids) | | CH _x , COOH, CH _x =CH _y | |

Table 3
Biological and biochemical conversion routes.

| Chemical path | Compounds | Functional groups |
|-----------------------------|---|---|
| Anaerobic digestion [44] | Gases (carbon dioxide, methane) Organic acids | CO ₂ , CH ₄ , CH _x , COOH |
| Fermentation [45–47] | Gases (carbon dioxide, hydrogen, methane, nitrogen) Polyfunctional alcohols (ethanol, butanol, glycerol, pentanol, hydroxyphenylethanol) Organic acids (propanoic, pentanoic, succinic, hydroxyphenylethanoic) Furans (furfural) Ketones (acetone) Oils | CO ₂ , H ₂ , CH ₄ , N ₂ CH _x , CH _x OH, aCH, aCOH CH _x , COOH, aCH, a CH _x OH aCH, a(CH _x OCH _y), COOH, CH _x , CH _x OH CH _x , CH _x CO CH _x , CH _x =CH _y , COOCH _x , |
| Enzymatic hydrolysis [48] | Sugars and alcohols (glucose, xylose, arabinose, glycerol) Aminoacids (glycine, aspartic acid, serine, proline) Furans (furfural, hydroxymethylfurfural) Organic acids (acetic, 4-oxopentanoic, fatty acids) | cyCH _x , cyO, cyCH _x OH, CH _x OH, CH _x COOH, CH _x NH ₂ , CH _x , CH _x OH, aCH, cyCH _x , cyCH _x NH aCH, a(CH _x OCH _y), CHO, CH _x OH, CH _x CH _x , COOH, CH _x CO, CH _x =CH _y |

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 reasonable choice for thermodynamic modeling. In this work we show the potential of the GCA-EoS [49].

The GCA-EoS is based in the Group Contribution Equation of State (GC-EoS) which was originally proposed by Skjold-Jørgensen to predict gas solubility in liquid solvents [50]. This model has proved an excellent predictive potential to represent the phase behavior of mixtures containing natural products [51–56]. The model also showed very good performance in predicting hydrogen solubility in solutions of natural products processed with supercritical fluids [57]. The extension of the equation to model multiple-associating and solvating compounds in solution, makes GCA-EoS a suitable model to predict the phase behavior of fluid mixtures typical of biomass processing [58]. On the other hand, the extension of the model to represent mixtures containing linear [59], branched [58], cyclic [60] and aromatic [61] hydrocarbons with the new compounds underway is needed not only to predict properties of fuel/biofuel blends, but also because there are currently under study several chemical pathways to produce hydrocarbons from biomass (for instance, green diesel).

In conclusion, our long term goal is to build up a thermodynamic package with predictive capacity for integrated second generation biorefineries, which include the processing not only of oils and sugars, but also of lignocellulosic material. The model should be able to predict thermodynamic properties under a wide range of temperatures and pressures, as required by any of the reviewed routes of synthesis. It is a big challenge for the model to predict, with a single set of parameters, the wide range of operating conditions found in processing, transportation and storage of these fluid mixtures. In the following section details of the GCA-EoS mathematical model are discussed.

3. Thermodynamic model: Group Contribution with Association Equation of State

The Group Contribution (GC) with Association Equation of State (GCA-EoS) is the first EoS of the SAFT family [8] that uses a GC approach of the Wertheim model [6,7]. As mentioned before, the GCA-EoS is an extension to associating systems of the original

GC-EoS [50], which is based on the Generalized van der Waals theory. There are three contributions to the residual Helmholtz energy in the GCA-EoS model: free volume, attraction and association.

$$A^R = A^{fv} + A^{att} + A^{assoc} \quad (1)$$

The free volume and attractive contributions are based on Carnahan-Starling [62] and Non Random Two Liquids (NRTL) [63] models respectively, and keep the same formulation as in the original GC-EoS proposed by Skjold-Jørgensen [50].

The Carnahan–Starling repulsive term follows the expression developed by Mansoori et al. [64]:

$$\frac{A^{fv}}{RT} = 3 \frac{\lambda_1 \lambda_2}{\lambda_3} (Y - 1) + \frac{\lambda_2^3}{\lambda_3^2} (Y^2 - Y - \ln Y) + n \ln Y \quad (2)$$

with

$$Y = \left(1 - \frac{\pi \lambda_3}{6V} \right)^{-1} \quad (3)$$

$$\lambda_k = \sum_j^{NC} n_j d_j^k \quad k = 1, 2, 3 \quad (4)$$

where n_i is the number of moles of component i , NC stands for the number of components, V represents the total volume, R stands for universal gas constant and T is temperature.

The following generalized expression is assumed for the hard sphere diameter temperature dependence:

$$d_i = 1.065655 d_{ci} \left[1 - 0.12 \exp \left(-\frac{2T_{ci}}{3T} \right) \right] \quad (5)$$

where d_c is the value of the hard sphere diameter at the critical temperature, T_c , for the i th component.

The critical hard sphere diameter (d_c) is 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) [50], (ii) fit d_c to an experimental pure-component vapor pressure data point (T_{sat} , P_{sat}) [50], and (iii) computation with the correlation proposed by Bottini et al. [52,65] for non-volatile compounds.

In the case of permanent gases and other single group compounds such as methane, hydrogen, water, or methanol, 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 [50]. 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), as it was shown elsewhere [58–60].

The attractive contribution to the residual Helmholtz energy, A^{att} , accounts for dispersive forces between functional groups. It is a van der Waals type of contribution, combined with a density-dependent local-composition expression, based on a group contribution version of the NRTL model. Integrating van der Waals EoS, $A^{\text{att}}(T,V)$ is equal to $-a \cdot n \cdot \rho$ being a the energy parameter, n the number of moles and ρ the mole density. For a pure component, a is computed as follows:

$$a = \frac{z}{2} q^2 g(T) \quad (6)$$

where g is the characteristic attractive energy per segment and q is the number of surface segments per mole as defined in the UNIFAC model [66]. The interactions are assumed to take place through each group surface and the coordination number, z , is set equal to 10 as usual. The extension of the GCA-EoS to mixtures is carried out using the two fluids NRTL model, but using local surface fractions like in UNIQUAC [67] rather than local mole fractions. Therefore, the A^{att} for the mixture becomes

$$\frac{A^{\text{att}}}{RT} = -\frac{(z/2)\tilde{q}^2 g_{\text{mix}}(T, V)}{RTV} \quad (7)$$

where \tilde{q} is the total number of surface segments and g_{mix} the mixture characteristic attractive energy per total segments, which are calculated as follows:

$$g_{\text{mix}} = \sum_{j=1}^{NG} \theta_j \sum_{k=1}^{NG} \frac{\theta_k g_{kj} \tau_{kj}}{\sum_{l=1}^{NG} \theta_l \tau_{lj}} \quad (8)$$

and

$$\tilde{q} = \sum_{i=1}^{NC} \sum_{j=1}^{NG} n_i v_{ij} q_j \quad (9)$$

where v_{ij} is the number of groups of type j in molecule i ; q_j stands for the number of surface segments assigned to group j ; θ_k represents the surface fraction of group k ;

$$\theta_j = \frac{q_j}{\tilde{q}} \sum_{i=1}^{NC} n_i v_{ij} \quad (10)$$

$$\tau_{ij} = \exp\left(\frac{\alpha_{ij} \Delta g_{ij} \tilde{q}}{RTV}\right) \quad (11)$$

$$\Delta g_{ij} = g_{ij} - g_{jj} \quad (12)$$

g_{ij} stands for the attractive energy between groups i and j ; and α_{ij} is the non-randomness parameter. The combination rule for the attractive energy between unlike groups is corrected by the corresponding binary interaction parameters between like groups:

$$g_{ij} = k_{ij} \sqrt{g_{ii} g_{jj}} \quad (k_{ij} = k_{ji}) \quad (13)$$

Furthermore, the energy and interaction parameters show the following temperature dependence:

$$g_{ii} = g_i^* \left[1 + g_i' \left(\frac{T}{T_i^*} - 1 \right) + g_i'' \ln \left(\frac{T}{T_i^*} \right) \right] \quad (14)$$

and

$$k_{ij} = k_{ij}^* \left[1 + k_{ij}' \ln \left(\frac{2T}{T_i^* + T_j^*} \right) \right] \quad (15)$$

where g_i^* is the attractive energy and k_{ij}^* the interaction parameter at the reference temperature T_i^* and $(T_i^* + T_j^*)/2$, respectively.

Last, the GCA-EoS associating contribution [49], A^{assoc} , is a group contribution version of the SAFT equation of Chapman et al. [8]:

$$\frac{A^{\text{assoc}}}{RT} = \sum_{i=1}^{NGA} n_i^* \left[\sum_{k=1}^{M_i} \left(\ln X_{ki} - \frac{X_{ki}}{2} \right) + \frac{M_i}{2} \right] \quad (16)$$

In this equation NGA represents the number of associating functional groups, n_i^* the total number of moles of associating group i , X_{ki} 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_{mi}^* of associating groups i present in molecule m and the total amount of moles of specie m (n_m):

$$n_i^* = \sum_{m=1}^{NC} v_{mi}^* n_m \quad (17)$$

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

$$X_{ki} = \left(1 + \sum_{j=1}^{NGA} \sum_{l=1}^{M_j} \frac{n_j^* X_{kl} \Delta_{ki,jl}}{V} \right)^{-1} \quad (18)$$

where the summation includes all NGA associating groups and M_j sites. As can be seen, X_{ki} depends on the association strength $\Delta_{ki,jl}$:

$$\Delta_{ki,jl} = k_{ki,lj} \left[\exp\left(\frac{\varepsilon_{ki,lj}}{RT}\right) - 1 \right] \quad (19)$$

Finally, 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 $\kappa_{ki,jl}$ and $\varepsilon_{ki,jl}$, which represent the volume and energy of association, respectively.

Thermodynamic properties for evaluating phase equilibria may be derived from the configurational Helmholtz free energy, following Maxwell relations. However, Michelsen and Hendricks [68] demonstrate that calculation of the associating contribution can be simplified by the minimization of a conveniently defined state function. Following their approach, Soria et al. [58] give expressions for the associating contribution to the compressibility factor, Z^{assoc} , and fugacity coefficient of component j in the mixture, φ_j^{assoc} :

$$Z^{\text{assoc}} = -\frac{1}{2} \sum_{i=1}^{NGA} \sum_{k=1}^{M_i} \frac{n_i^*}{n} (1 - X_{ki}) \quad (20)$$

$$\varphi_j^{\text{assoc}} = \sum_{i=1}^{NGA} v_{ji}^* \sum_{k=1}^{M_i} \ln X_{ki} \quad (21)$$

These equations are the result of assuming a constant value for the radial distribution function in the original SAFT equation. By assuming a value of one for the radial distribution function, it was possible to take into account the association contribution by a GC approach. In this way a single set of associating parameters of a given group can be applied to the corresponding homologue family of organic compounds, independently of the alkyl chain length. Therefore, the extension of the model to multicomponent mixtures is greatly simplified. Moreover, it reduces the number of equations to be solved in order to find each site non-associated fractions defined in Eq. (18), which is a time demanding procedure.

Table 4
 GCA-EoS parameters.

| Contribution | Parameter | | Attribute | |
|--------------------------|---------------|---------------------------------|-----------------------------------|-----------------------------------|
| Free-volume ^a | Pure compound | Hard sphere diameter | d_c | Fixed ^c |
| | | Critical temperature | T_c | Fixed |
| Attractive ^b | Pure group | Reference temperature | T_i^* | Fixed |
| | | Surface area | q_i | Fixed ^d |
| | | Energy ^d | $g_{ii}^*, g_{ii}^', g_{ii}^{''}$ | Adjustable ^e |
| | Binary | Energy interaction ^e | k_{ij}^*, k_{ij}' | Adjustable ^e |
| | | Non-randomness | α_{ij}, α_{ji} | Adjustable |
| Associating ^b | Pure group | Self association energy | ϵ_{ik-ik} | Fixed |
| | | Self association volume | κ_{ik-ik} | Fixed |
| | Binary | Cross association energy | ϵ_{ik-lj} | Comb.Rule/Adjustable ^f |
| | | Cross association volume | κ_{ik-lj} | Comb.Rule/Adjustable ^f |

^a Molecular term.
^b Group contribution term.
^c Calculated from critical point conditions for molecular compounds, density or vapor pressure data for compounds described by GC.
^d In certain cases, this parameter can be adjustable if it is not available.
^e See Eqs. (13) and (14) for details.
^f For groups that can only cross associate, these parameters are fitted to binary data.

| | Paraffin | | | | Biofuel | | | | Processing Broth | | | | Gas Solubilities | | | | | | |
|-------------------------|-----------------|----------|--------|----------|----------------|---------|---------|-----------|-------------------------|----------|-------|------------------|-------------------------|-----------|--------|----------------|----|-----------------|-----------------|
| | Linear | Branched | Cyclic | Aromatic | Methanol | Ethanol | Butanol | Biodiesel | Water | Glycerol | Amine | Carboxylic Acids | Sugars | Aldehydes | Furans | H ₂ | CO | CO ₂ | CH ₄ |
| Paraffin | | | | | | | | | | | | | | | | | | | |
| Linear | N | N | X | | X | X | X | X | X | X | X | | | X | T | X | X | X | X |
| Branched | | N | X | | X | X | X | | X | | | | | | | | | | |
| Cyclic | | | | X | X | X | X | | X | | | | | T | | X | X | X | X |
| Aromatic | | | | | X | X | X | | X | | | | | X | T | X | X | X | X |
| Biofuel | | | | | | | | | | | | | | | | | | | |
| Methanol | | | | | X | X | X | | X | X | X | | | | | X | | X | |
| Ethanol | | | | | | X | X | | X | X | X | | | T | | X | | X | |
| Butanol | | | | | | | X | | X | X | X | | | T | | X | | X | |
| Biodiesel | | | | | | | | X | X | X | | | | | | X | | X | |
| Processing Broth | | | | | | | | | | | | | | | | | | | |
| Water | | | | | | | | | X | X | | | | | | X | | X | |
| Glycerol | | | | | | | | | | | | | | | | | | | |
| Amines | | | | | | | | | | | | | | | | | | | X |
| Carboxylic Acids | | | | | | | | | | | | | | | | X | | X | |
| Sugars | | | | | | | | | | | | | | | | | | | |
| Aldehydes | | | | | | | | | | | | | | | | | | X | |
| Furans | | | | | | | | | | | | | | | | | | | |
| Gas Solubilities | | | | | | | | | | | | | | | | | | | |
| H ₂ | | | | | | | | | | | | | | | | X | X | X | |
| CO | | | | | | | | | | | | | | | | | X | X | |
| CO ₂ | | | | | | | | | | | | | | | | | | | X |
| CH ₄ | | | | | | | | | | | | | | | | | | | |

Fig. 1. Family of compounds already included in the table of GCA-EoS parameters. X=from previous work; P= to be published; T= this work; N= attractive energy mixing rule does not require binary interaction parameters.

On the other hand, a similar approach than that used for solving the non-association fraction, can be used to solve the chemical equilibrium. In fact the former was developed based on solving elemental conservation equations originally developed for reversible reactive system [69,70]. There are different methods for solving the chemical equilibria formulation that can be classified as stoichiometric and non-stoichiometric approaches. Quite frequently, papers that deal with simultaneous phase and chemical equilibrium place the emphasis on the computational algorithms required to perform the calculations, but disregard the importance of the thermodynamic model applied. It is common to find the use of inappropriate equations of state with conventional mixing rules for highly non-ideal systems, which somehow invalidates the numerical results of the complex algorithms proposed. Pereda et al. reviewed the used of equations of states in the calculation of phase equilibria in reactive mixtures [27,28].

3.1. Model parameterization

Table 4 summarizes the model parameters required for each contribution described in the preceding section. It also shows which parameters can be calculated (noted as fixed) and which are fitted to experimental data (adjustable) [59]. GCA-EoS was applied to several mixtures containing multiple associating and solvating compounds: paraffinic and aromatic hydrocarbons + linear alcohols + water [61], *n*-alkanes + alcohols + amines + water [71,72] (also used to predict the solubility of hydrocarbons in aqueous alkanolamine solutions), esters + methanol + glycerol + water [73,74], dimethyl sulfoxide + water + CO₂ [75]. For all these systems model predictions compare favorably with experimental data.

Fig. 1 shows the matrix of binary interaction parameters available for describing, the phase behavior of several families of compounds that are of interest for biorefineries and biofuels.

As it was introduced, biomass has been a historical source of food and natural products; however, it has also become a promising feedstock for industrial and commercial applications in the long term. In the last years, several oxygenated organic compounds have been studied as fuel additives in order to reduce the nonrenewable fuels consumption, to enhance fuel properties and decrease greenhouse gas emissions. Ethanol is today one of the most used fuel substitute and additive. However, it has some disadvantages because of its water affinity, high volatility and low energy density. This has encouraged the search for alternative oxygenates, such as methyl-tertbutylether or butanol. Recently, furan derivatives like 2-methylfuran, 2,5-dimethylfuran, 2-methyl-tetrahydrofuran have been proposed also as renewable fuel additives since they exhibit better blending properties than ethanol [76,77]. The knowledge of vapor–liquid equilibria of furan derivatives with hydrocarbons present in gasoline and alcohols provides useful information for process and products evaluation.

The equilibrium data available in the literature for systems containing furan and its derivatives is scarce, highlighting the importance of developing a predictive tool. However, the larger the number of experimental data incorporated in the parameterization process, the more robust is the model. Given the current applications for furan and derivatives, the ranges of pressure and temperature of the available equilibrium data are limited to near atmospheric pressure and temperatures from 298.15 K up to 390 K, approximately.

A new aromatic ether-group family has been defined in order to model the furan derived compounds. These groups are a(CHOCH), a(CHOC) and a(COC), needed to model not only furan but also its substituted derivatives. The three groups share the same pure group surface energy (g_{ii}) and the interaction parameters (k_{ij} , α_{ij}) with other groups evaluated in this work. The only difference between them is their number of surface segments (q_i), which is a

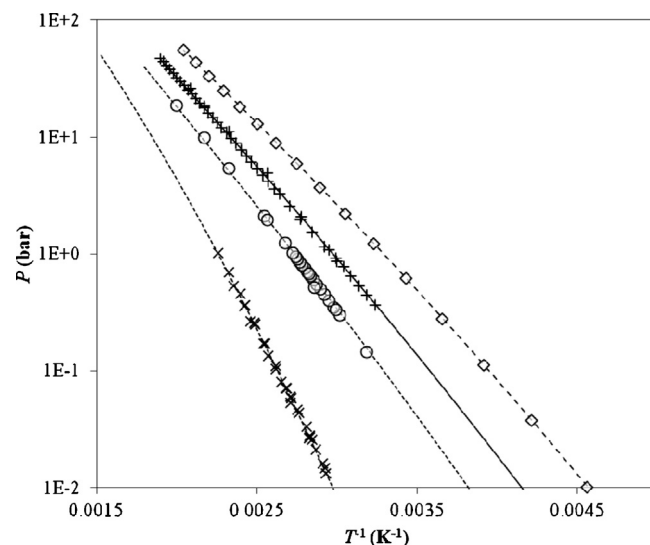


Fig. 2. Pure component vapor pressure. Symbols: experimental data (\diamond) furan [88], (+) 2-methylfuran [79–81], (\circ) 2,5-dimethylfuran [82,83] and (\times) furfuryl alcohol [84–86]. Dashed lines: GCA-EoS correlation, solid line: GCA-EoS prediction.

geometric parameter. For example, the furan molecule is build with one a(CHOCH) group plus two aCH groups as defined by Skjold-Jørgensen [50]; 3-methylfuran with one a(CHOCH) group, one aCH and one aCCH₃; while 2,5-dimethylfuran is formed by one a(COC), two aCH and two CH₃.

The energy pure group parameter and the binary parameters required to correctly represent furan vapor pressure and furane + alkanes or aromatic hydrocarbons phase equilibria were fitted together. This was required mostly due to the fact that the aCH group is present in both furanic and aromatic molecules. Therefore, the furan vapor pressure, the binary VLE of the system furan + *n*-hexane at 1 atm and the VLE of the 2-MF + benzene at 323.15 K were used for correlation. Moreover, since furanic groups are not included in the UNIFAC parameter lists, the number of surface segments of the group a(CHOCH)

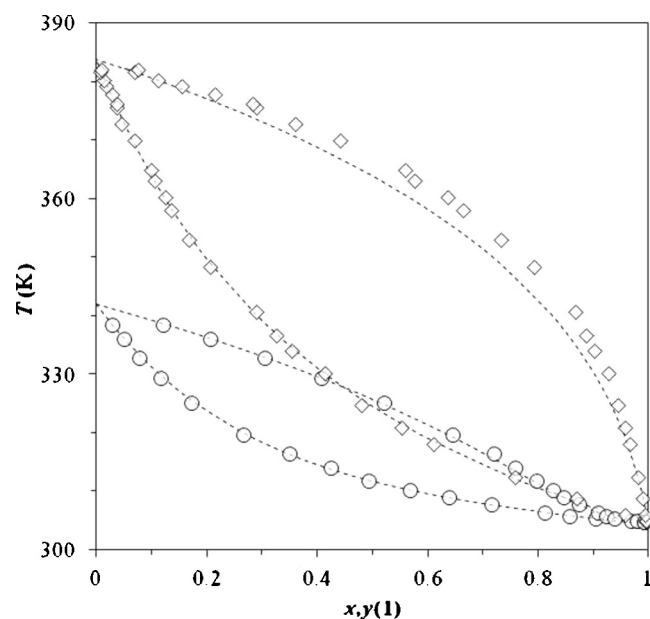


Fig. 3. Vapor liquid equilibria of the furan + hydrocarbon binary systems at atmospheric pressure. (\circ) Furan (1) + *n*-hexane (2) and (\diamond) furan (1) + toluene (2). Symbols: experimental data [83]. Dashed lines: GCA-EoS correlation.

Table 5
GCA-EoS pure group surface energy parameters of the attractive contribution for the aromatic ether groups defined in this work.

| Group <i>i</i> | q_i | T_i^* (K) | g_i^* (atm cm ⁶ mol ⁻²) | g_i' | g_i'' | Correlated data |
|----------------|-------|-------------|--|---------|---------|---------------------------------------|
| a(CHOCH) | 1.611 | | | | | Furan vapor pressure |
| a(CHOC) | 1.331 | 600 | 349,174 | -0.2688 | -0.3665 | VLE furan + <i>n</i> -hexane at 1 atm |
| a(COC) | 1.051 | | | | | VLE 2MF + benzene at 323.95 K |

Table 6
GCA-EoS binary energy interaction parameters of the attractive contribution for the aromatic ether groups defined in this work.

| Group <i>i</i> | Group <i>j</i> | k_{ij}^* | k_{ij}' | α_{ij} | α_{ji} | Correlated data |
|---------------------------------|---|------------|-----------|---------------|---------------|---|
| a(CHOCH)/ a(CHOC)/ a(COC) | CH ₃ /CH ₂ /cyCH ₂ | 0.940 | 0.0 | 0.0 | 5.0 | VLE F + <i>n</i> -hexane at 1 atm |
| | aCH | 0.985 | 0.0 | 0.0 | 0.0 | VLE 2-MF + benzene at 323.95 K VLE F + <i>n</i> -hexane at 1 atm |
| | aCCH ₃ | 1.050 | 0.0 | 0.0 | 0.0 | VLE F + Toluene 1 atm |
| | C ₂ H ₅ OH | 0.950 | 0.0 | 0.0 | 0.0 | VLE 2,5-DMF + ethanol at 0.927 atm |
| | CH ₂ OH | 1.100 | 0.0 | 0.0 | 0.0 | 2,5-DMF + 1-butanol at 393.15 K. |

F, furan; MF, methylfuran; DMF, dimethylfuran.

Table 7
Associating parameters for aromatic ether and alcohol groups solvation.

| Site <i>k</i> | Group <i>i</i> | Site <i>l</i> | Group <i>j</i> | $\varepsilon_{ki,lj} R^{-1}$ (K) | $\kappa_{ki,lj}$ (cm ³ mol ⁻¹) | Correlated data |
|---------------|----------------|---------------|----------------|----------------------------------|---|--|
| (-) | aO | (+) | OH | 1650 | 1.50 | Vapor pressure of furfuryl alcohol VLE 2,5-DMF + 1-butanol at 393.15 K VLE 2,5-DMF + ethanol at 0.94 bar |

DMF, dimethylfuran.

was included in the parameterization. The surface segments for the other new groups were calculated decreasing the corresponding area for a covalent single bond (-0.28) [78]. No temperature dependent parameters were needed and only in the case of aliphatic hydrocarbons one non-randomness parameter different from zero is required. This means that most of binary interactions were defined using a single parameter. In the case of the aCCH₃ group, the binary equilibrium data of the system furan+toluene at atmospheric pressure were used

for correlation. Fig. 2 depicts GCA-EoS correlation of furan vapor pressure while Fig. 3 shows the binary VLE correlated data with hexane and toluene.

Regarding those cases where association effects are present, furanic compounds are assumed to have two electronegative association sites: the aromatic ring and the oxygen atom. Due to the nature of these sites, no self-association is possible. However, cross-association with the positive site of the alcohol group could take place. In this case, the cross-association strength parameters

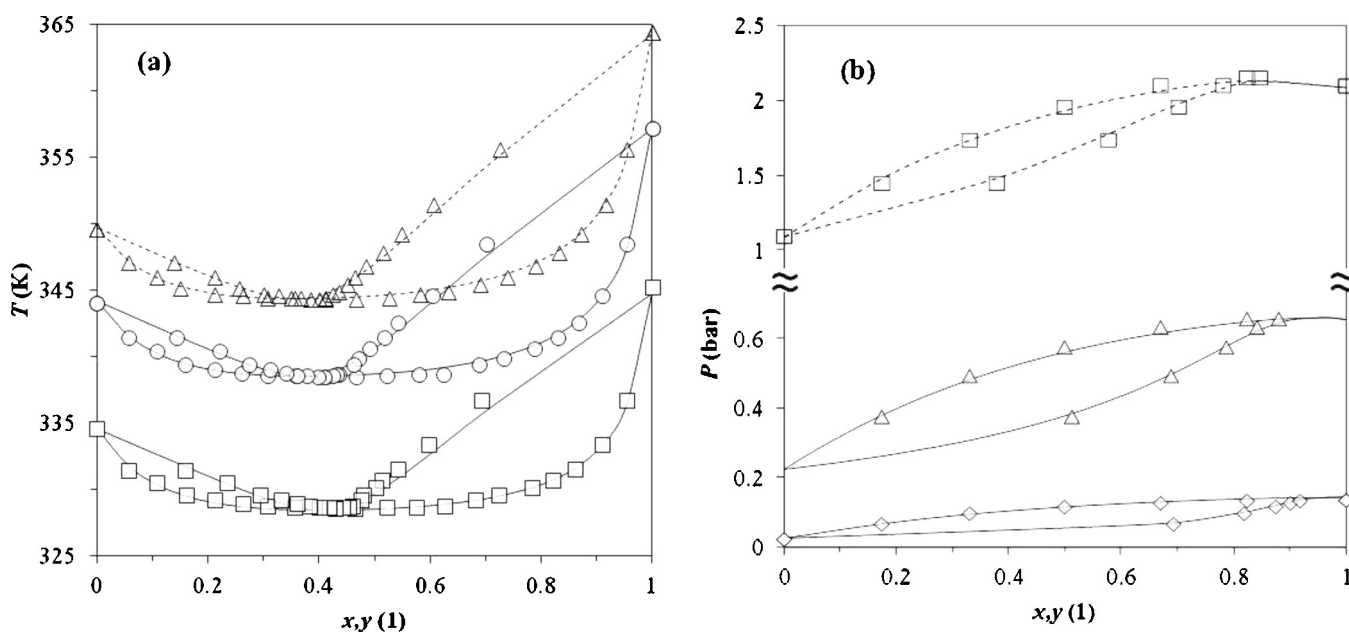


Fig. 4. Vapor liquid equilibria of the binary systems 2,5-DMF(1)+: (a) ethanol(2) at (□) 0.5 bar (○) 0.75 bar and (△) 0.94 bar. (b) 1-Butanol (2) at (◇) 313 K (△) 353 K and (□) 393 K. Symbols: experimental data from [82,87]. Dashed lines: GCA-EoS correlation. Solid lines: GCA-EoS prediction.

Table 8
Free-volume contribution to the GCA-EoS.

| Compound | T_c (K) | $(T_{sat}/K, P_{sat}/bar)^a$ | d_c (cm mol ^{-1/3}) |
|------------------|--------------------|------------------------------|---------------------------------|
| Furan | 490.2 [88] | (304.5, 1.01) [88] | 4.0465 |
| 2-MF | 528.0 [81] | (338.9, 1.08) [80] | 4.3919 |
| 3-MF | Idem 2-MF | (360.0, 1.94) [83] | 4.4932 |
| 2,5-DMF | 559.0 [89] | (366.8, 1.01) [82] | 4.7181 |
| 2,3-DMF | Idem 2,5-DMF | (367.7, 1.01) [90] | 4.7927 |
| Furfuryl alcohol | 632.0 [88] | (443.1, 1.01) [88] | 4.5296 |
| 5-HMF | 803.0 ^c | (539.1, 1.01) ^c | 4.707 ^b |

^a Saturation point used to calculate d_c .

^b Calculated with Espinosa et al. correlation [51] for non volatile compounds.

^c Not available in open literature, predicted using GCA-EoS.

were fitted together with the binary interaction parameter of the attractive contribution between the alcohol and the ether-aromatic groups. Vapor pressure of furfuryl alcohol and part of the binary VLE data available for systems 2,5-DMF + 1-butanol and 2,5-DMF + ethanol were used to fit the alcohol/aromatic ether group binary interaction. Fig. 2 shows the model correlation of furfuryl alcohol vapor pressure. Fig. 4 shows the correlated binary data (dashed lines) and GCA-EoS predictions of data left out of the parameterization (solid lines). The association interaction is needed to correctly describe the azeotropic behavior of 2,5-DMF + alcohol system.

Tables 5–7 report the pure group parameters, binary energy interaction parameters and cross association parameters used in this work, respectively. Last, Table 8 summarizes the critical temperatures and diameters, required for the repulsive contribution, of all the furanic compounds evaluated in this work.

It is important to mention that for 3-MF and 2,3-DMF, the critical temperature of their respective isomers, 2-MF and 2,5-DMF, were used for the free volume contribution calculation (see Table 8).

The performance of the model to correlate and predict pure compounds vapor pressure and VLE binary data is reported in Tables 9 and 10, respectively.

As evident from the previous tables, part of the available experimental data was left out of the parameterization database in order to test the model predictive capacity. Figs. 5 and 6 show GCA-EoS predictions of VLE binary systems of furanic compounds

Table 9
Vapor pressure correlation and prediction.

| Compound | ΔT_r | ARD(P)% | Reference |
|--------------------|--------------|---------|-----------|
| <i>Correlation</i> | | | |
| Furan | 0.44–0.96 | 0.79 | [88] |
| 2,5-DMF | 0.56–0.90 | 2.2 | [82,83] |
| Furfuryl alcohol | 0.53–0.70 | 4.1 | [84–86] |
| <i>Prediction</i> | | | |
| 2-MF | 0.58–0.99 | 2.0 | [79–81] |
| 3-MF | 0.68–0.91 | 1.4 | [83] |
| 2,3-DMF | 0.63–0.89 | 2.2 | [83] |

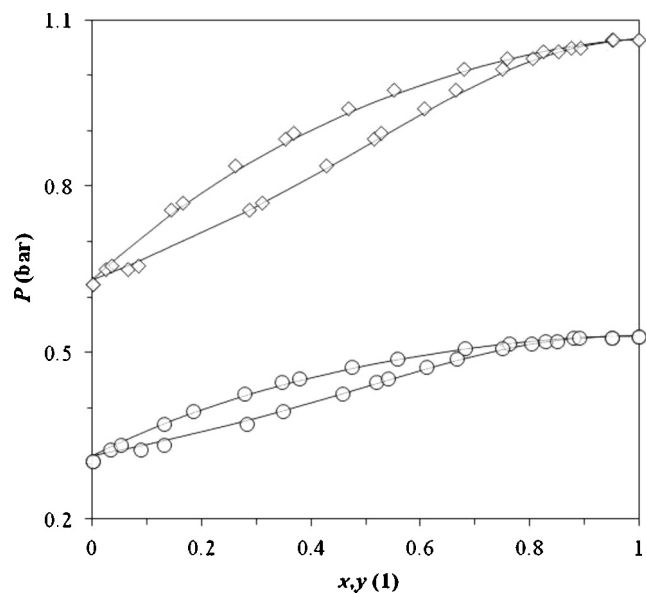


Fig. 5. Vapor liquid equilibria of the binary system 2-MF(1) + cyclohexane (2) at 318.85 K (○) and at 339.95 K (◇). Symbols: experimental data from [80]. Solid lines: GCA-EoS predictions.

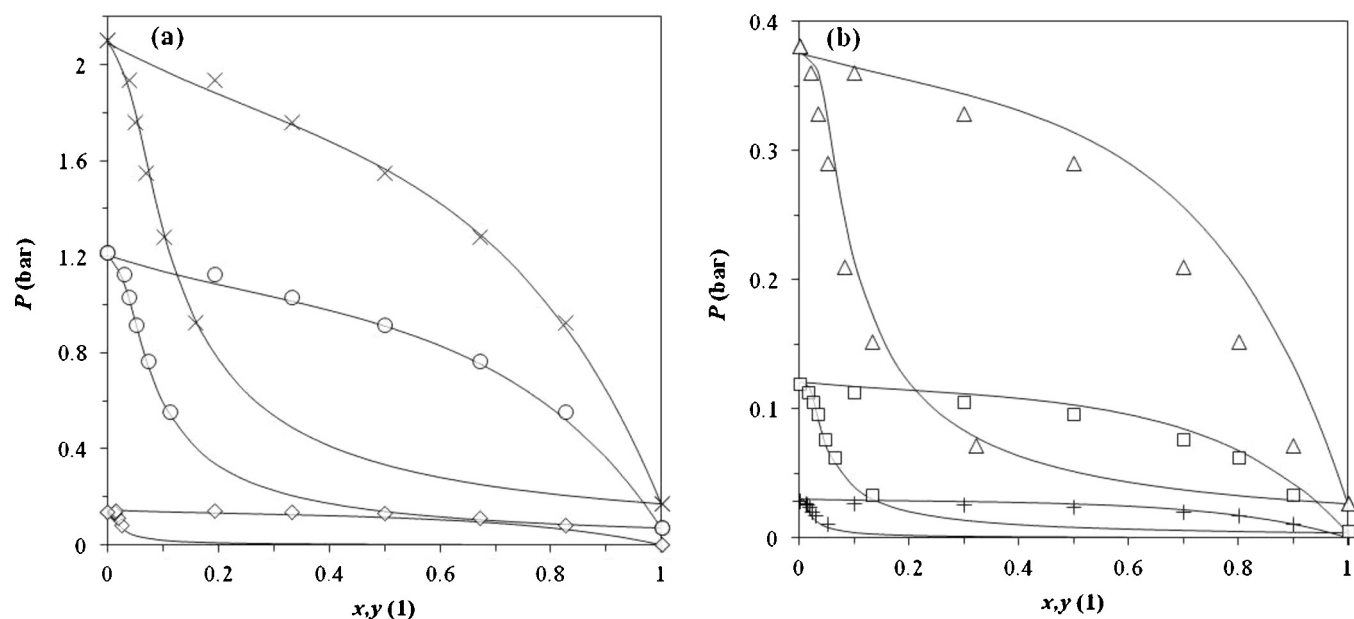


Fig. 6. Vapor liquid equilibria of the binary systems furfuryl alcohol (1)+: (a) 2,5-DMF(2) at (◇) 313 K, (○) 373 K and (×) 393 K and (b) toluene (2) at (+) 293 K, (□) 323 K and (△) 353 K. Symbols: experimental data [92]. Solid lines: GCA-EoS predictions.

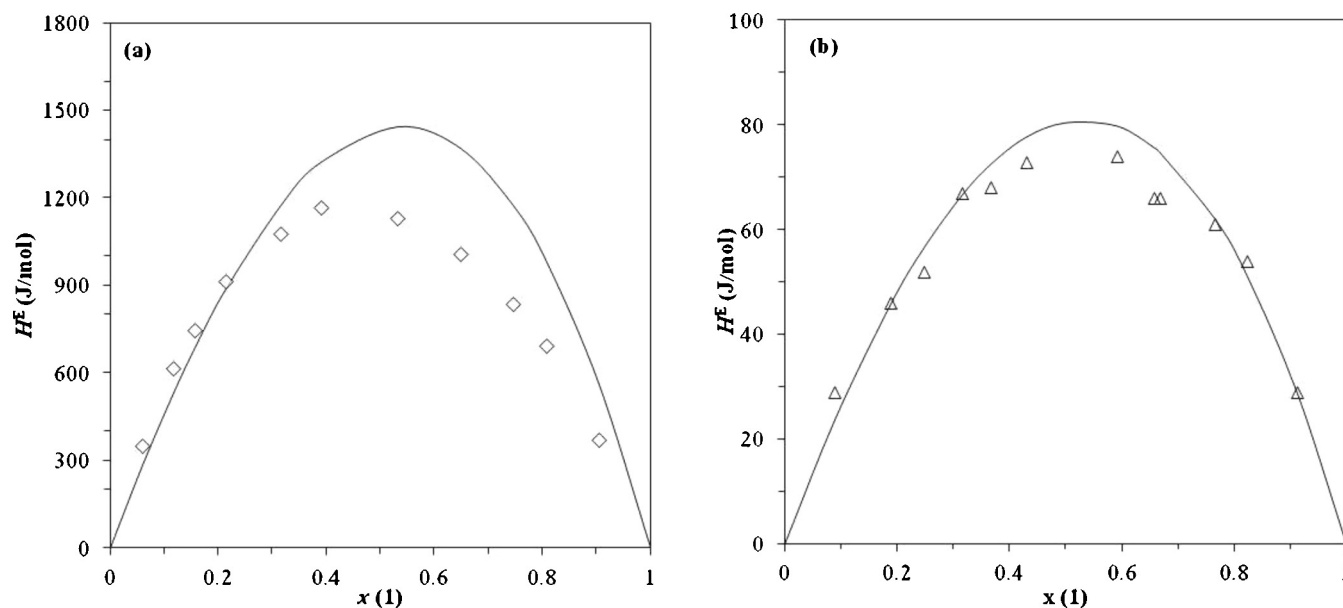


Fig. 7. Excess enthalpy of the binary systems: (a) furan (1) + *n*-hexane (2) at 303.15 K; (b) furan(1) + benzene(2) at 298.15 K. Symbols: experimental data [93,94]. Solid lines: GCA-EoS predictions.

in non-associating and associating systems, respectively. Moreover, the predictive capability of the model was also tested with excess enthalpy data of furan + *n*-hexane and furan + toluene systems (Fig. 7). Finally, Figs. 8 and 9 show the model prediction of ternary liquid–liquid equilibria data.

3.2. High pressure phase equilibria prediction of polyfunctional biomass derived compounds

In this section we show the performance of the model to predict high pressure data and solubility of furan derivatives in CO_2 , based on parameters fitted to low pressure data. For instance, the

extension of the GCA-EoS table of parameters to furan derivatives allows us predicting solubility data of 5-hydroxymethylfurfural (5-HMF) in CO_2 and the effect of using ethanol as cosolvent (experimental data reported by Jing et al. [96]). The 5-HMF is a complex molecule that includes the aromatic, furanic, alcohol and aldehyde groups. Espinosa [97] reported interaction parameters for the aldehyde groups with the paraffinic, aromatic and CO_2 groups. On the other hand, parameters for the aromatic– CO_2 and alcohol– CO_2 interactions were reported by Bamberger et al. [98] and González Prieto et al. [99], respectively. Moreover, the associating interaction between hydroxyl and aldehyde groups was assumed to be the same as that of the ether–hydroxyl associating interaction reported

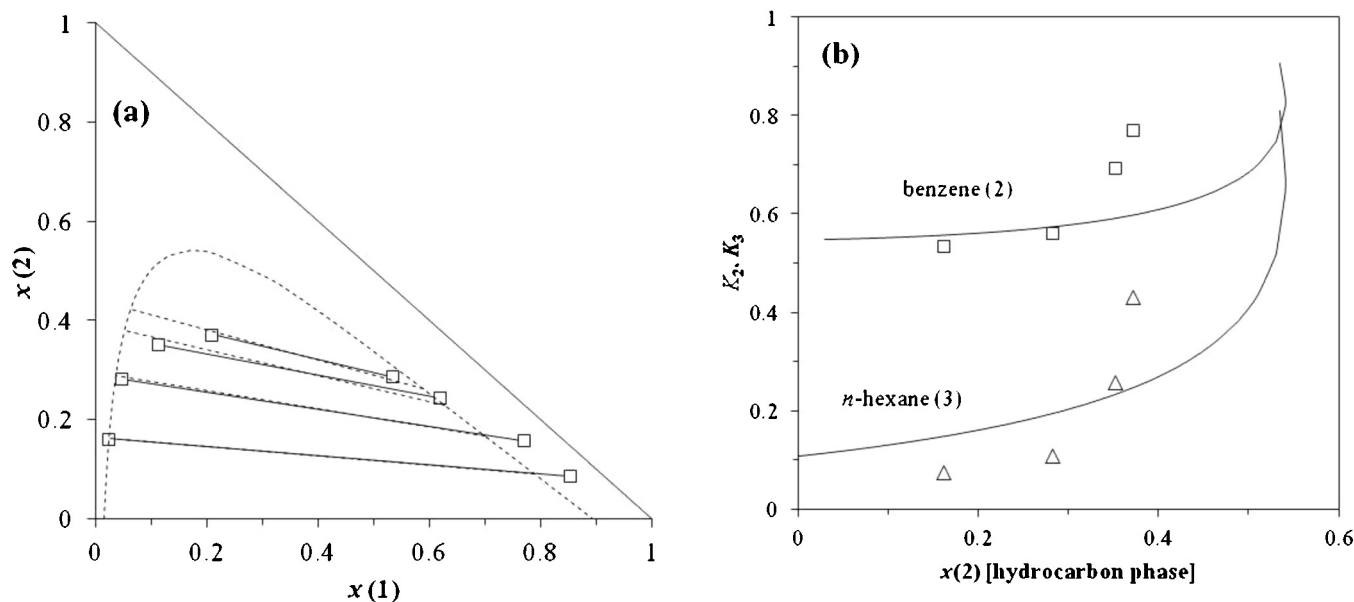


Fig. 8. Liquid–liquid equilibria of the ternary system furfuryl alcohol (1) + benzene (2) + *n*-hexane (3) at 298 K and 1.01 bar. (a) Symbols and solid lines: experimental data [95]. Dashed lines: GCA-EoS predictions. (b) GCA-EoS prediction (lines) of benzene (\square) and *n*-hexane (\triangle) partition coefficients.

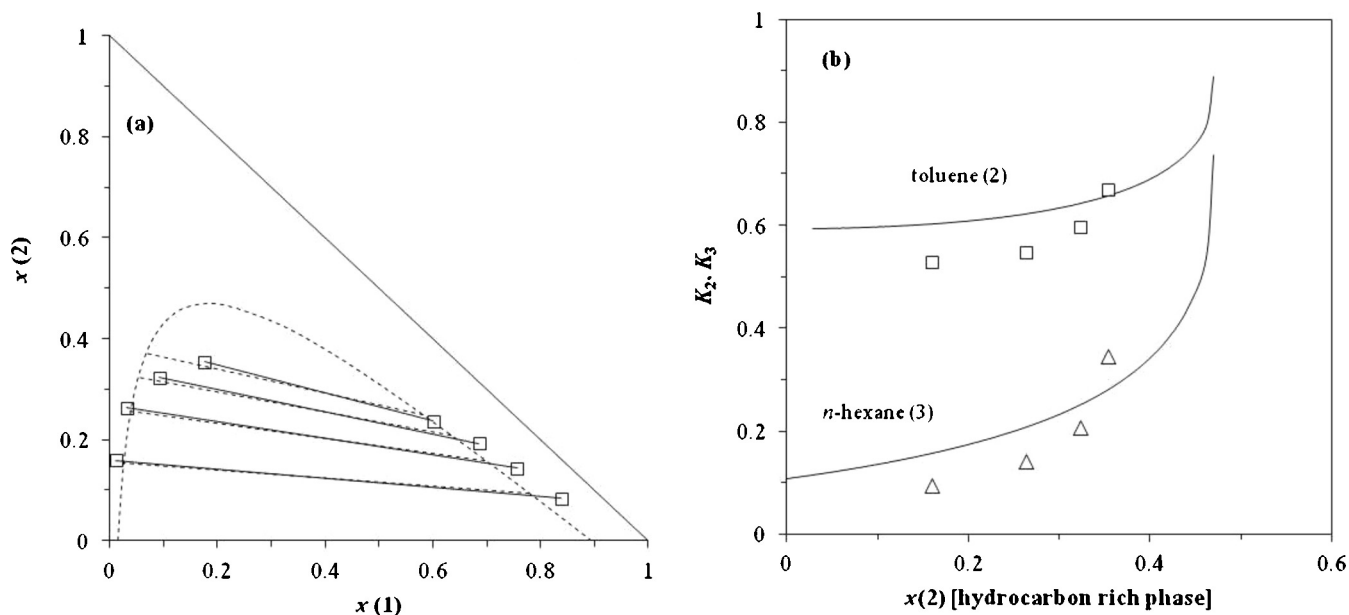


Fig. 9. Liquid–liquid equilibria of the ternary system furfuryl alcohol (1)+toluene (2)+*n*-hexane (3) at 298 K and 1.01 bar. (a) Symbols and solid lines: experimental data [95]. Dashed lines: GCA-EoS predictions. (b) GCA-EoS prediction of toluene (□) and *n*-hexane (Δ) partition coefficients.

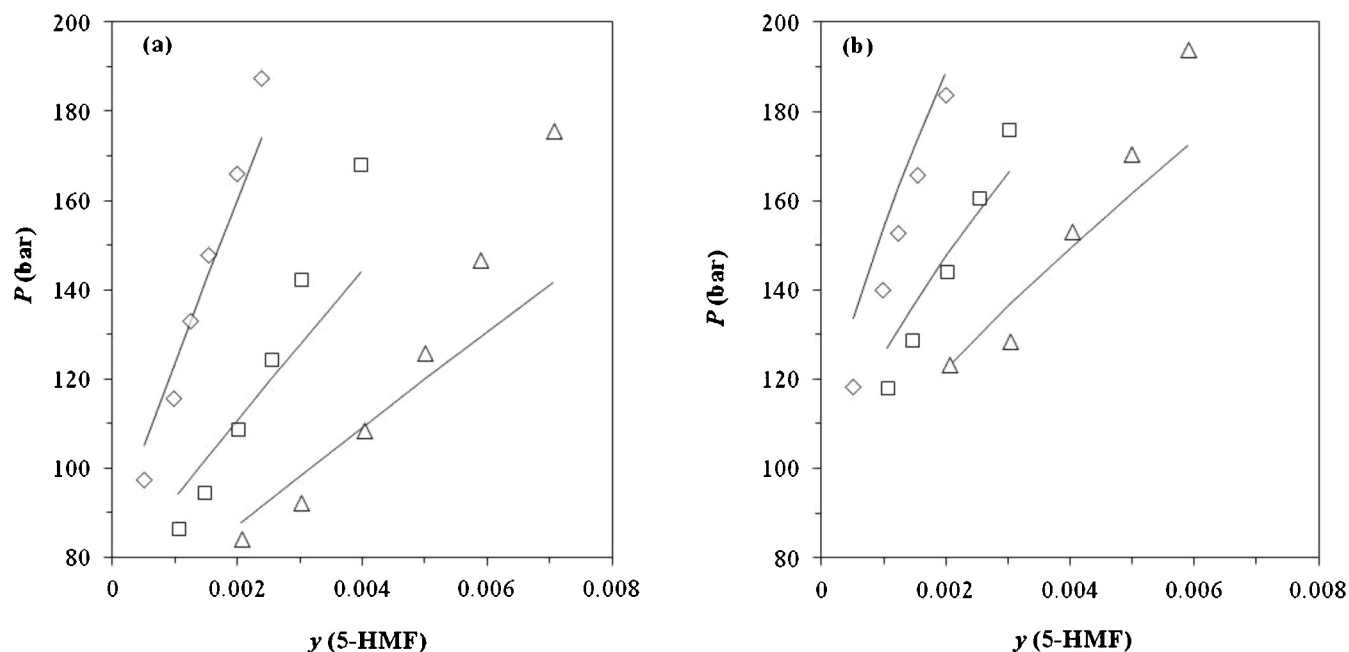


Fig. 10. 2,5-Hydroxymethyl furfural solubility in CO₂ at (a) 314 K and (b) 334 K, and its enhancement by co-solvent addition (ethanol) Symbols experimental data [96]: (◇) $y_{\text{ethanol}} = 0$; (□) $y_{\text{ethanol}} = 0.025$; (Δ) $y_{\text{ethanol}} = 0.05$ Solid lines: GCA-EoS predictions.

by Soria [100]. Last, the three missing attractive interaction parameters were assumed as $k_{ij} = 1$ and $\alpha_{ij} = \alpha_{ji} = 0$ (alcohol-aldehyde, furan-aldehyde and furan-CO₂).

Since 5-HMF is a non-volatile compound, the molecular free volume parameter, d_c , was calculated using the correlation of Espinosa et al. [52] using a van der Waals reduce volume for 5-HMF ($R_{5\text{-HMF}}$) of 4.2063. This parameter was

estimated by group contribution using the R_{furfural} value of furfural (3.1680), reported by Skjold-Jørgensen et al. [101] and that of the alcohol group reported by Fredenslund et al. [66].

Fig. 10 shows the prediction of 5-HMF solubility in CO₂ and its enhancement due to the addition of ethanol as cosolvent. The model is able to predict quantitatively well the system behavior.

Table 10
Correlation and prediction of VLE binary experimental data of furan derived compounds with hydrocarbons and alcohols.

| Comp. (1) | Comp. (2) | T/K | P/bar | AAD (ARD%) | | N | Source |
|---------------------|--------------------------|---------|-----------------|---------------------------------------|--------------------------|----|--------|
| | | | | T or P | y_1 | | |
| <i>Correlations</i> | | | | | | | |
| 2-MF | Benzene | 324 | 0.38–0.64 | 4×10^{-3} (0.7) ^P | 3×10^{-3} (1.1) | 12 | [80] |
| Furan | <i>n</i> -C ₆ | 304–338 | 1.01 | 0.21 (0.06) ^T | 7×10^{-3} (1.3) | 17 | [83] |
| Furan | Toluene | 305–382 | 1.01 | 0.52 (0.15) ^T | 0.035 (9.0) | 26 | [83] |
| 2,5-DMF | Ethanol | 344–364 | 0.94 | 0.19 (0.05) ^T | 8×10^{-3} (2.0) | 21 | [91] |
| 2,5-DMF | Butanol | 393 | 1.1–2.2 | 0.023 (1.2) ^P | 0.015 (2.3) | 5 | [87] |
| <i>Predictions</i> | | | | | | | |
| 2,5-DMF | <i>n</i> -C ₆ | 321–364 | 0.5, 0.75, 0.94 | 0.37 (0.11) ^T | 0.013 (3.9) | 64 | [82] |
| 2-MF | cy-C ₆ | 319–339 | 0.310–1.1 | 5×10^{-3} (0.8) ^P | 7×10^{-3} (2.7) | 32 | [80] |
| 2,5-DMF | Ethanol | 328–357 | 0.5, 0.75 | 0.17 (0.05) ^T | 9×10^{-3} (2.0) | 42 | [91] |
| 2,5-DMF | 1-Butanol | 313–383 | 0.030–1.7 | 0.013 (2.3) ^P | 0.014 (1.9) | 40 | [87] |
| 2,5-DMF | 1-Hexanol | 313–393 | 0.003–2.1 | 0.025 (5.7) ^P | 8×10^{-3} (0.9) | 45 | [87] |
| Furfuryl alcohol | Toluene | 283–363 | 0.010–0.5 | 0.016 (15) ^P | 0.020 (25) | 53 | [92] |
| Furfuryl alcohol | 2,5-DMF | 313–393 | 0.090–2.0 | 0.020 (6.0) ^P | 2×10^{-3} (6.1) | 42 | [86] |
| Furfuryl alcohol | Ethanol | 273–363 | 0.010–1.4 | 0.038 (25) ^P | 0.020 (41) | 54 | [92] |

MF, methylfuran; DMF, dimethylfuran. *P* and *T* indicate in each case if the reported deviation is in pressure or temperature, respectively.

4. Conclusions

Thermodynamic models able to predict multiphase equilibria of complex mixtures are required in order to design and optimize new technologies. Particularly, in biomass conversion and upgrading processes, the presence of organo-oxygenated compounds, gives rise to association and solvation effects, making classical models not suitable for this task. In that sense, SAFT derived equation of states are adequate tools since they specifically account for association effects. The biomass conversion routes involve the processing of mixtures with numerous organic compounds, making parameterization of molecular models a tough job. Therefore, the use of a group contribution approach is a logical choice for thermodynamic modeling of these multicomponent mixtures, since the great variety of species can be described by a reduced number of functional groups.

The Group Contribution with Association Equation of State (GCA-EoS) has already been successfully applied to predict the phase behavior of mixtures involving biofuels (ethanol and biodiesel) and many natural products. In this work, we extend the GCA-EoS to deal with mixtures containing furanic compounds. The model is able to correlate and predict well the phase behavior of all the relevant binary mixtures. On the other hand, it predicts fairly well liquid split in the ternary mixtures of furfuryl alcohol + *n*-hexane + benzene or toluene using the new set of parameters derived from binary VLE data. Finally, the predictive capability of the model was tested with high pressure data of 5-hydroxymethyl furfural solubility in supercritical carbon dioxide. It is also shown that GCA-EoS predicts quantitatively well the solubility enhancement due to the addition of ethanol as co-solvent. The developed model is a useful tool for future studies regarding alternative routes for the hydrogenolysis of 5-hydroxymethylfurfural to produce 2,5-dimethylfuran in supercritical CO₂, as well as to evaluate the behavior of the latter in fuel blends.

5. Perspectives and future directions

Pressure-intensified technologies have a great potential to enhance the efficiency of current biomass processing centers, giving alternatives to improve routes of synthesis, purification trains and the quality of the final products, while holding the principles of the green chemistry. In addition, these technologies that are nowadays slowly reaching commercial applications will probably play a role in the development of biorefineries. This relatively new concept of biorefineries calls for a substantial step in the

comprehensive utilization of all biomass fractions while approaching to the zero-waste philosophy, which encourages the redesign of resource life cycles so that all products are reused at maximum added value.

Phase equilibrium engineering principles can complement other disciplines in the rational design of experiments for studying biomass conversion routes. A thermodynamic model extended to describe typical mixtures of any conversion routes is a key tool. Partial enlightenment can be drawn from the behavior of binary mixtures; however, it is important that the models handle multicomponent systems. For the development of predictive tools, more equilibrium data is needed on phase behavior of the relevant substances involved in the different conversion routes, not only of the final products of interest but also of by-products. As in the development of technologies for natural products, in biomass conversion for many compounds there is no equilibrium data available at all; even though, already agreed as important players in the future bioeconomy.

In general, much more attention is given to phase behavior than to volumetric and second-derivative thermodynamic properties such as volume expansivity, isothermal compressibility, speed of sound, isobaric and isochoric heat capacities and Joule–Thomson coefficient. However, they are highly needed at the moment of designing experiments and equipments. In that sense, also models for predicting transport properties of multicomponent mixtures in the near critical region are underdeveloped. This fact delays, one way or another, the progress on theoretical backgrounds needed for scaling-up pressure intensified processes.

List of symbols

| | |
|-----------------------|---|
| <i>A</i> | Helmholtz free energy |
| AAD(<i>Z</i>) | average absolute deviation in variable <i>Z</i> : $(1/N) \sum_i Z_{\text{exp},i} - Z_{\text{calc},i} $ |
| ARD(<i>Z</i>)% | average relative deviation in variable <i>Z</i> : $(100/N) \sum_i (Z_{\text{exp},i} - Z_{\text{calc},i})/Z_{\text{exp},i} $ |
| <i>d_i</i> | effective hard sphere diameter of component <i>i</i> |
| <i>d_{ci}</i> | effective hard sphere diameter of component <i>i</i> evaluated at <i>T_c</i> |
| <i>g_i</i> | group energy per surface segment of group <i>i</i> |
| <i>k_{ij}</i> | interaction parameter between groups <i>i</i> and <i>j</i> |
| <i>M_i</i> | total number of associating sites in group <i>i</i> |
| <i>NC</i> | number of components in the mixture |
| <i>NG</i> | number of attractive groups in the mixture |

| | |
|----------|---|
| NGA | number of associating groups in the mixture |
| P | pressure |
| q_j | number of surface segments of group j |
| R | universal gas constant |
| R_k | Van der Waals reduce volume of component k |
| T | temperature |
| T_{ci} | critical temperature of component i |
| V | total volume of the mixture |
| X_{ki} | fraction of non-bonded associating sites of type k in group i |
| y_i | molar composition in vapor phase of component i |
| z | coordination number |

Greek symbols

| | |
|-----------------------|---|
| α_{ij} | non-randomness parameter between groups i and j |
| $\Delta Z\%$ | ARD% in variable Z |
| $\varepsilon_{ki,lj}$ | energy of association between site k of group i and site l of group j |
| $\kappa_{ki,lj}$ | volume of association between site k of group i and site l of group j |
| ν_{ij} | number of groups j in compound i |
| ν_{ij}^* | number of associating groups j in compound i |
| φ_i | fugacity coefficient of compound i |

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