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Guaiacol and its mixtures: New data and predictive models part 1: Phase equilibrium

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ABSTRACT

In the present work, new experimental data of guaiacol mixture with methane were investigated. The results have been evaluated using several thermodynamic approaches. Predictive calculations using the GC-PPC-SAFT (Group Contribution-Polar Perturbed Chain- Statistical Associating Fluid Theory) equation of state and Molecular Simulation using the Anisotropic United Atoms (AUA4) force field were performed. Data from literature for the binary systems of guaiacol with CO_2, ethanol, octanol, acetone, butyl acetate and water were used to evaluate the thermodynamic models. The effect of the association scheme is discussed at length. Predictive phase equilibrium for systems containing small and toxic compounds, such as hydrogen, carbon monoxide, hydrogen sulfide and ammonia were also performed. In GC-PPC-SAFT, two configurations of associative sites for guaiacol were considered. The predicted values showed to be consistent with new experimental data. The effect of conformational structure of guaiacol on phase equilibria was detected.

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1. Introduction

The increase in the energy demand coupled with the gradual depletion of fossil fuels and the political and environmental requirements have motivated the search of new energy sources. Recently, the biomass conversion into hydrocarbon fuels has gained special attention due to its attractive characteristics in terms of availability and sustainability.

The use of bioresources in the production of energy and chemicals involves major environmental, economic and geostrategic implications. Indeed, creating new opportunities for bio-products in the field of energy, chemicals and materials should lead to a reduction of greenhouse gas emissions. The general objective behind this strategy is to ensure the protection of human beings and their environment while ensuring also the continuity of the economic activities with a reduced dependence on fossil energies. Unlike fossil fuels, bioresources are renewable, widely available and better distributed throughout the world, and their valorisation will certainly have a very positive impact at the regional level on the preservation of jobs and development of rural areas [1].

Chemical and petrochemical industries are now aiming at developing new green chemistry-based processes [2] [3], and lignocellulosic biomass (LCB) is called to play a major role as an alternative raw material. Indeed, the lignocellulosic material may be conditioned to obtain already “functionalised” molecules for specific applications, unlike hydrocarbons that require additional processing steps for the synthesis of specific chemicals.

The mixtures associated with the conversion of LCB include a large number of oxygenated molecules belonging to different families produced through the decomposition of the main constituents of LCB: cellulose, hemicellulose (polymers of sugars) and lignin (phenolic-derivatives polymers). The fast pyrolysis of LCB, for instance, produces solid, liquid (bio-oil) and gaseous fractions, in which the bio-oil is a source of several attractive compounds, including lighter components from different chemical families such as carboxylic acids, ethers or ketones and heavier compounds such as phenolic or furan derivatives. Recent studies have used guaiacol (or 2-methoxyphenol) as a model compound of bio-oil due to its

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molecular structure: it contains two oxygen-containing functional groups (phenolic –OH- and methoxy -OCH_3- groups) that facilitate its repolymerization [4-6].

The processing and refining of these products is needed to improve their quality and to promote their use as a fuel. Several treatments can be considered: cracking, hydrocracking, decarbonylation, decarboxylation, hydrodeoxygenation, catalytic hydrotreatment, hydrogenation, others. However, in order to carry out studies on the technological and economic potential of LCB conversion process, it is necessary to develop predictive thermodynamic models with strong theoretical basis able to deal with multifunctional molecules where complex polar and associating interactions take place.

There have been several previous studies aiming at modeling systems with phenol derivatives. Lee et al. [7] evaluated the phase equilibria of CO_2 + guaiacol and the data was correlated by different equations of state (EoS): the Soave–Redlich–Kwong, the Peng–Robinson, and the Patel–Teja EoS with the van der Waals mixing rules. They all require two binary interaction parameters for a good modeling and can therefore not be called predictive. Hwang et al. [8] evaluated the phase equilibria of guaiacol + 1,2-dimethoxybenzene and guaiacol + diphenylmethane with several versions of the UNIFAC model. They were unable to predict the phase behavior of these systems, indicating that the interaction parameters of AC–OCH_3 binaries had to be re-evaluated. On the other hand, good data correlation was obtained using the Wilson, the NRTL, and the UNIQUAC models (not predictive). Espinosa et al. [9] applied the Group Contribution Associating Equation of State (GCA-EoS) to predict the phase equilibria of different phenol derivative systems; however, this work did not involve the mixtures evaluated here.

The GC-PPC-SAFT EoS has been used with some success on various mixtures of oxygenated compounds [11]. The objective of this study is to evaluate the GC-PPC-SAFT model and molecular simulations using the AUA4 force field, to predict the phase equilibria of systems with guaiacol. The behavior of its mixtures with associative, non-associative, polar and apolar compounds was evaluated. Phase equilibria of mixtures of guaiacol with methane, carbon dioxide, ethanol, octanol, water, acetone, butyl acetate, n-hexadecane and other light components such as H_2, CO, H_2S and NH_3 were evaluated in the present work. In order to evaluate the complexity of guaiacol, an analysis of its structure was also performed.

2. Experimental section

2.1. Materials

For carrying out the phase equilibrium experiments, the following reagents were used: methane from Air Liquide (purity ≥ 99.998%), and guaiacol from SAFC (purity ≥ 98%).

2.2. Apparatus and procedure

Experimental measurements were carried out using the static method. In an equilibrium cell, the solvent was first degassed by cryometry. The measurements were taken at a set temperature. Then known quantities of gas are introduced into the cell and the equilibrium pressure is measured. Mass and volume balances have been used in order to access to the partial pressure and the molar composition in the liquid phase. Before each set of measurement, the calibration of the temperature and the pressure sensors have been performed and the associated maximum uncertainties are: 0.05 K and 0.035 MPa. The relative uncertainties associated to the molar fraction in the liquid phase is estimated to 1%.

3. Models used

In this work, the predictions of phase envelope were done using the molecular-based Group Contribution Polar Perturbed-Chain Statistical Associating Fluid Theory (GC-PPC-SAFT) based equation of state as well as Monte Carlo Molecular Simulation with the AUA4 force field.

3.1. GC-PPC-SAFT

The GC-PC-SAFT EoS was originally proposed by Tamouza et al. [12] to model vapor–liquid equilibria of non-ideal mixtures. Later, Nguyen Huynh et al. [13] extended the application of this model to polar-chain containing mixtures (the so-called PPC-SAFT EoS) and applied it successfully to model the phase equilibrium behavior of different kind of chemical series, including alcohols, alkylbenzenes, esters, ethers, ketones, aldehydes [14–16] and small gas-containing systems [15,17,18].

The GC-PPC-SAFT EoS is a predictive model developed from the polar PC-SAFT equation proposed by Gross and Sadowski [19–21], coupled to a group contribution method (CG). It is expressed as a sum of Helmholtz energy contributions:

$$A^{res} = \left(mA^{hs} + A^{chain}\right) + A^{disp} + A^{assoc} + A^{multi-polar} \tag{1}$$

where the first four terms relate to the non-polar interactions and follow the theory developed by Gross and Sadowski, the last incorporate the contribution of polar interactions that was obtained by extending the Gubbins and Twu [22] theory to chain molecules using the so-called “segment approach” of Jog & Chapman [23], [24]. The details for the description of these terms can be found in the original papers.

3.1.1. Pure- components parameters

In GC-PPC-SAFT, the segment parameters (ε and σ) and the chain parameter m of the molecule are calculated from group contribution parameters ε_k, σ_k and R_k using the following relations inspired by the Lorentz-Berthelot combining rules [12,25],:

$$\varepsilon = \sqrt[\sum_{k=1}^{n_{groups}} n_k]{\prod_{k=1}^{n_{groups}} \varepsilon_k^{n_k}} \tag{2}$$

$$\sigma = \sum_{k=1}^{n_{groups}} n_k \sigma_k \Bigg/ \sum_{k=1}^{n_{groups}} n_k \tag{3}$$

$$m = \sum_{k=1}^{n_{groups}} n_k R_k \tag{4}$$

where n_k is the number of groups k in the molecule that is made of n_{groups} different groups.

In the case of polar compounds (water, aromatic compounds, alkanols, …) additional parameters shall be considered: for dipolar compounds (water, alkanols), the dipole moment μ and dipole fraction $x_p^{\mu}.m$, and for quadrupolar compounds (aromatic hydrocarbons), the quadrupole moment Q and its corresponding quadrupolar fraction $x_p^{Q}.m$. These parameters are only relevant to polar and quadrupolar groups.

Finally, association interactions are considered using a specific term that requires additional information and parameters: an association scheme and a self-association energy ε^{AB} and volume κ^{AB}. Self-association parameters are required for water and alkanols, and more generally, for all molecules containing both electron-

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