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Guaiacol and its mixtures: New data and predictive models. Part 2: Gibbs energy of solvation

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ABSTRACT

Guaiacol is a model molecule for lignocellulosic biomass processing, and thus understanding its interactions with solvents is an important step when developing units for processing lignocellulosic biomass. In this work, activity coefficient measurements of different solvents (acetonitrile, ethanol, tetrahydrofuran) in guaiacol have been performed at different concentrations and temperatures. These measurements have been used to estimate the infinite dilution activity coefficients and the Gibbs energy of solvation of guaiacol in the different solvents, and of each solvent in guaiacol. These estimated values were compared to those obtained with different predictive models: UNIFAC DMD, Monte Carlo Molecular Simulation, COSMO-SAC and GC-PPC-SAFT. The predictions are in very good agreement with the Gibbs energies of solvation derived from experimental data. Some conclusions are also drawn regarding the inter- and intramolecular hydrogen bonding in guaiacol and about its affinity with different solvents on the basis of the inter- and intramolecular interactions taking place.

1. Introduction

Lignocellulosic biomass (LCB) can be a potential resource for the production of different chemical reagents and fuels. LCB usage will help to protect the environment and to reduce the dependence on fossil fuels, which is important for sustainable development of economics as well as for creation of new workplaces at the regional level and development of rural areas [1]. There is now a commitment from the chemical industry to develop new green chemistry-based processes [2–6], and LCB is called to play a major role as an alternative raw material. It has several advantages in comparison with fossil raw materials: renewable, widely available and better distributed throughout the world. As a matter of fact, lignocelluloses can be used to synthesize target molecules for many applications, which are consistent with the principles of green chemistry [6]. However, the development of effective processes to produce chemicals from LCB is limited by the availability of design tools that allow the prediction of physical-chemical properties of molecules when one only knows their structure.

It is expected that bioresources will be processed in plants called biorefineries. As in classic refineries, biorefineries consist of unit operations where separations are governed by chemical thermodynamics. The design of green and innovative processes for the valorisation of biomass requires the understanding of the thermodynamic behavior of species associated to LCB feedstocks. These mixtures are particularly complex due to the wide variety of oxygenated compounds they might contain. In particular, the decomposition of the LCB raw material leads to the formation of a large variety of multifunctional oxygen-bearing compounds. This leads to strong intra- and intermolecular interactions that make these mixtures highly non-ideal (from a thermodynamic point of view). The models used for hydrocarbons (models typically found in most process simulators) fail to reproduce these non-idealities. Therefore, the challenge for the design and optimization of biorefinery units is to have appropriate tools that can adequately reproduce the phase equilibrium and properties of these mixtures, in the same way as fossil mixtures are described in current industrial applications.

Another application that requires the development of thermodynamic models is the European regulatory context. The European legislation (REACH) pushes the chemical industry to provide adequate predictive estimations of the possible effects of molecules

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