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Vapour–liquid equilibria of aroma compounds in hydroalcoholic solutions: Measurements with a recirculation method and modelling with the NRTL and COSMO-SAC approaches

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Abstract

Aqueous solutions of aroma compounds are commonly encountered in the food and biofuel industries, and the knowledge of their thermodynamic properties is very important for process design. Here, we report the measurements of the vapour–liquid equilibria of water–ethanol solutions containing 13 aroma compounds (alcohols, aldehydes and esters), for temperatures between 351 and 366 K, and ethanol concentration ranging from 10 to 90% (v/v). The new data were obtained with a recirculation apparatus and are represented with the non-random two liquid (NRTL) activity coefficient model. It is observed that the partition coefficients of the aroma compounds can decrease of several orders of magnitude by increasing the proportion of ethanol. The COSMO-SAC (conductor-like screening model-segment activity coefficient) model provides reasonable predictions of the new data for alcohols and aldehydes, but underestimates the partition coefficients of the long ethyl esters. It is observed that the COSMO-SAC predictions depend a lot on the molecular conformations used to generate the sigma profiles, in agreement with previous studies. The COSMO-SAC predictions can be empirically improved by changing the real space cut-off distance employed in the *ab initio* calculations. The COSMO-SAC model is then reliable not only at infinite dilution but also over a whole composition range. The model is used to define a limit of validity for the infinite dilution approximation.

Keywords: Vapour–liquid equilibria; NRTL; COSMO-SAC; Henry's constant; Aroma compounds; Activity coefficients at finite dilution

1. Introduction

The knowledge of the vapour–liquid equilibria (VLE) in systems involving aroma molecules is of crucial importance for many applications in the food industry, such as the design of distillation processes in alcoholic beverage production. The flavour perception and the aromatic character of food products are governed by the partitioning of aromatic compounds between the vapour and liquid phases. This partitioning is related to the thermodynamic properties of the mixtures, and is characterized by the partition coefficients also called absolute volatilities. Aroma molecules such as furfural and ethyl decanoate are also encountered in the production of biofuels. Therefore, the knowledge of their thermodynamic properties is very important for the design of reactive and separation processes related to the biofuel industry.

Aroma compounds are often found at very low concentrations in alcoholic beverages: their mole fractions are usually lower than 10^{-4} [3]. For such low concentrations it can be assumed that the partition coefficient K_i of aroma i is proportional to the infinite dilution activity coefficient γ_i^∞ (or to Henry's constant H_i). Such an assumption should be considered with some care, as we will see later in this paper. Measuring the partition coefficients of aroma compounds at infinite dilution in hydroalcoholic solutions is a difficult task, mainly due to the small quantities of aromas that have to be measured and to the large proportion of

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ethanol in the vapour phase, which interferes in the chromatographic analysis. The development of efficient and reproducible experimental methods that truly achieve phase equilibrium is also a major concern [4]. Among the available techniques to measure activity coefficients at infinite dilution, one can find static methods such as the equilibrium partitioning in closed systems (EPICS) [5] and phase ratio variation (PRV) [6,7] methods, and dynamic methods such as recirculation (Gillespie-like still) [8,9] and inter gas-stripping (exponential dilutor) methods [10–12]. The reader is directed to the excellent reviews of Raal et al. [13–15] and Sandler [16] for a detailed discussion about the measurement techniques and engineering applications of the infinite dilution activity coefficients. In a previous work [17], we compared the performances of three different static headspace methods to determine the vapour–liquid partition coefficients of aroma compounds in hydroalcoholic solutions at the temperature $T = 298.15$ K. We found that the PRV method [6,7] was the most reliable method for measuring absolute volatilities. However, other experimental techniques are required to accurately measure the partition coefficients at higher temperatures. Following the recommendations of Raal and Mühlbauer [13], we decided to use here a dynamic method with a Gillespie-like recirculating still [8,9] to measure the vapour–liquid partition coefficients of the aroma compounds. The system is fully described in the experimental part of this paper. It has already been shown that this procedure is feasible for measuring the partition coefficients of compounds infinitely diluted in hydroalcoholic solutions [18].

The design of a distillation process involving aroma compounds requires not only some experimental data but also a fast and accurate thermodynamic model for the determination of the vapour–liquid equilibria. The thermodynamic models that are applicable to aroma systems can be classified into two main categories: the equations of state for polar and associating compounds [19–22], and the excess Gibbs energy (or activity coefficient) models [23–28]. One should mention the hydration Gibbs energy models [29,30] that were developed for the specific case of organic compounds at infinite dilution in water. Molecular simulation can also be very useful to predict the PVT properties of aroma compounds [31] or Henry's constants via the Widom test particle insertion method [32]. Macroscopic approaches and molecular simulation can be complementary, for example, to understand highly non-ideal phase behaviours such as the evolution of the solubility of hydrocarbons in water with respect to temperature and alkyl chain length [33]. Equilibrium data for systems involving aroma compounds are scare; thus, predictive models that do not require any adjustment of parameters on experimental data are of crucial importance. Predictive models can be developed from a group contribution (GC) method, which consists in empirically linking the parameters of the thermodynamic model to the numbers of the various chemical groups constituting the molecules. GC methods have been developed both for equations of state [34–37] and activity coefficient models [38–41]. Faùndez et al. [28] recently employed the PSRK [35] equation of state and the UNIFAC activity coefficient model [38] to predict the phase equilibria of aromas + ethanol + water mixtures. The main advantages of GC methods are their simplicity and efficiency. However, GC approaches are limited to the types of molecules that were involved in the adjustment of the GC parameters, and they may be inaccurate for conditions ranges that were not considered in the fitting procedure.

A second way to develop predictive macroscopic models is to somehow involve quantum-chemical calculations [42,43]. One possible approach is to use an equation of state based on an intermolecular potential fitted to *ab initio* data. Such an approach is very similar to the methodology employed in classical simulation to develop new forcefields, and can provide very accurate predictions for spherical molecules [44]. However, this approach is still limited to simple cases as the development of general theories that would take all kinds of interactions (electrostatic, intramolecular, site–site and polarizability) into account is very difficult. Another strategy to involve first principle calculations consists in relating the parameters of a macroscopic thermodynamic model to *ab initio* calculations performed on the studied molecules. These parameters are the same for all molecules and they are determined by adjusting a large set of vapour–liquid and liquid–liquid (LLE) equilibria data. The only remaining inputs that characterize a given mixture are the *ab initio* data. The COSMO-RS activity coefficient model and its later versions [25–27] were developed based on the above idea. A review on continuum solvation models that use quantum-mechanical calculations has been recently proposed by Tomasi et al. [45]. A detailed description of the COSMO-RS model and a review of all the possible applications can be found in a book by Klamt [46]. In the COSMO approach molecular interactions are represented by interactions between surface segments. These surface segments are determined by the way surface charges are distributed over the cavity surface surrounding each molecule in the mixture. Each compound is characterized by *ab initio* calculations performed on one molecule solvated in a conductor. These calculations provide the molecular volume, the molecular surface area, and the so-called "sigma profile" that corresponds to the distribution of surface charges on the cavity surface. Lin and Sandler [27,47] proposed the COSMO-SAC (conductor-like screening model-segment activity coefficient) model, and an extensive database of *ab initio* calculations corresponding to this model was developed (the VT-2005 database [48]). A comparison between COSMO-like approaches and the UNIFAC group contribution model was recently made by Grensemann and Gmehling [49]. Mu et al. [50] performed an extensive analysis of the performances of the COSMO-RS and COSMO-SAC approaches, using different *ab initio* calculation packages for the generation of the sigma profiles.

Since we are interested only in phase equilibria at low pressures, we decided to use two activity coefficient approaches: the non-random two liquid (NRTL) model [23], which is very simple, fast, and implemented in most process simulation softwares, and the predictive COSMO-SAC model [27,47]. This paper is organised as follows: we first describe the experimental apparatus and present the new VLE measurements. We then use the NRTL model to represent the new experimental data, and investigate the prediction capabilities of the COSMO-SAC model on our experimental data and on other