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Comparison of two modelling approaches for the interfacial tension of binary aqueous mixtures

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ABSTRACT

The present study focuses on the interfacial tension at liquid-liquid phase split of aqueous mixtures, namely water + 1-butanol, water + 1-hexanol and water + hexyl acetate. The interfacial tensions were calculated using the density gradient theory (DGT) coupled with the PC-SAFT equation of state and the incompressible version of DGT in combination with UNIQUAC or the NRTL-model. The application of the incompressible version of DGT in combination with the NRTL-model is a suitable tool for a very accurate correlation of the interfacial tension, including the correct modelling of the occurring maximum as function of temperature for water + 1-alcohol mixture. The prediction of the interfacial tension using DGT based on the influence parameters of the pure-components fails to a large extend. The problem could be solved, if the influence parameters of water were readjusted using binary data. The PC-SAFT allows also the prediction of the density difference between the coexisting phases which enter the spinning drop measurements. The predicted densities are not accurate enough in order to replaces the experiment.

1. Introduction

The investigation of interfacial properties in demixed fluids is of relevance from the theoretical as well as from the practical point of view. During the past decades there has been a great deal of progress in calculation of interfacial properties related to the liquid-liquid equilibrium (LLE) of binary [1–24] or ternary mixtures [21, 25–28]. Such calculations can be performed using density functional approaches [1, 5, 6, 9–13, 15, 17–23, 25–28], integral equation methods [2, 4] or molecular simulations (molecular dynamics [3, 5, 6, 14, 16, 24] or Monte-Carlo methods [8, 11]).

Applying the density functional approach, two principle procedures can be distinguished. In the simple approach, the so-called density gradient theory (DGT) [29–32], the functional of the Helmholtz free energy of the inhomogeneous system is expressed by a Taylor series around the homogenous (equilibrium) state. For numerical reasons, this method is widely used [1, 5, 6, 9–11, 13, 15, 18–23, 25–28]. The second method within the density functional approach is the direct minimization of the functional of the Helmholtz free energy, extensive discussed by Evans [33]. The second method, which requires more numerical effort, was utilized for calculation of interfacial properties of demixed systems by Llovell et al. [12] and Klink et al. [17]. Both methods necessitate an equation of state and the DGT requires additionally the so-called influence parameter (κ_i), which can be fitted to the surface tension of a pure substance at one temperature. For mixture without water, it could be shown that the surface tension σ^{VLE}, where VLE stands for vapor-liquid equilibrium, of binary (e.g. [34–38]), of ternary (e.g. [39, 40]) or of multi-component [41–43] mixture can be predicted with a high accuracy using a geometrical mixing rule for κ_{ij}. In the case of interfacial tension between demixed liquids (σ^{LLE}), a more complex picture arise [15, 27]. The fitted κ_i-value using the surface tension of the pure component can mostly not transferred to the LLE.

Molecular simulation for liquid–liquid systems is time consuming due to the large number of particle and the slow diffusional processes. This issue implies that simulations of liquid–liquid systems need to run for longer times than liquid–vapor simulations in order to accumulate appropriate statistical information for thermophysical properties calculations [16]. Using molecular dynamics for the calculation of interfacial tension of a binary mixture the correct trend related to the temperature dependence was obtained although scatter was observed caused by the closeness of the state points to the critical region [7]. In the case of surface properties related to a liquid-vapor equilibrium, Werth et al. [39] as well as Becker et al. [44] performed a detailed comparison of the modelling results obtained with molecular dynamic simulation and the DGT. They [39, 40] figured out that both methods are well suited for detailed studies of interfacial properties and that the independent methods yield similar results for the interfacial tensions and other properties (e.g. interfacial profiles) which cannot be studied experimentally.

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In summary, while DGT is a powerful tool for describing the interfacial properties of pure fluids and fluid mixtures, its main limitation for the prediction of σ^{LLE} is the limited transferability of the influence parameters.

For the special case of a LLE at atmospheric pressure, this inhomogeneous Helmholtz energy density can be replaced as an inhomogeneous Gibbs energy density [1]. The advantage of this simplification is to eliminate the pressure as a state variable which is justified by the incompressibility of liquids. This modified version (inc-DGT) was implicitly suggested by Cahn and Hilliard [31] in their seminal work when they used the regular solution theory for describing the homogenous contribution of Helmholtz energy density. Enders and Quitzsch [1] clearly formalized the use of inc-DGT version to describe the interfacial properties for LLE systems, where the homogeneous contribution of inc-DGT was described by the Koningsveld–Kleintjens activity coefficient model [45]. This version has been proved to work successfully, even better than the DGT, for the prediction of σ^{LLE} [1, 25, 26]. The reason for this finding is the better description of the LLE using an activity coefficient model in comparison with the modelling results obtained by sophisticated equations of state, like one out of the SAFT family. Of course, the Koningsveld–Kleintjens activity coefficient model can be replaced by other models, like the lattice cluster theory [9, 21, 22, 28] or the NRTL (Non-Random Two Liquids)-model [18, 23] depending on the considered mixture.

Beside the influence parameter, the other important ingredient of the DGT is the used EOS and in the inc-DGT framework the used activity coefficient model, especially for aqueous mixtures. The phase equilibria of these mixtures consist usually of a VLE and a LLE, where both equilibria reach each other at a vapor–liquid–liquid equilibrium (VLLE).

One of the most challenging tests for any molecular theory involves the representation of aqueous mixtures of hydrocarbons. The fluid phase behavior of aqueous solutions of hydrocarbons is highly nonideal due to the strong polarity and associating interactions among water molecules leading to marked hydrophobic interactions with the hydrocarbon. Recently [46], the demixing behavior of these mixtures could be modelled very close to experimental data using the PC-SAFT approach [47, 48], where it was found, that the binary interaction parameter, k_{ij}, depends strongly on temperature. This approach allows the description of the minimum of *n*-alkane solubility in water as a function of temperature [46].

Zheng et al. [49] modelled then VLE and VLLE equilibria for systems involving highly non-ideal components, namely, water, alcohols, alkanes, ketones, aldehydes, esters, and ethers using (PC-SAFT EOS) and two widely used activity coefficient models, that is, the universal quasichemical (UNIQUAC) and universal functional-group activity coefficients (UNIFAC). It was found that all the three models yield reliable correlations/predictions for VLE calculations [49]. However, UNIQUAC and UNIFAC were observed to be unreliable for LLE and VLLE calculations despite successful reproductions of experimental data in some cases [49]. The calculated results deviate significantly from experimental data in many cases; particularly, both models predict artificial liquid–liquid phase splitting for a number of miscible mixtures [49].

Alcohols are oxygen bearing hydrocarbons which consist of a hydrocarbon chain and a terminal OH group. They have a tendency to form hydrogen bonds with themselves and with water. Because of the strength of attraction of the OH group, the first three alcohols (methanol, ethanol, 1-propanol) are completely miscible in water. However, the hydrocarbon chain in alcohol is water repellent and hence in the homologous series alcohols with a higher carbon number then three shows a LLE in water. The thermodynamics of hydrogen bonding in 1-alcohol + water binary mixtures was studied using MD simulation and the polar PC-SAFT [50]. The analysis shows that hydrogen bonding in pure alcohols is best predicted using a two-site model within the SAFT framework [50]. On the other hand, molecular simulations show that increasing the concentration of water in the mixture increases the average number of hydrogen bonds formed by an alcohol molecule [50] and hence a transition in association scheme occurs at high water concentrations where hydrogen bonding is better captured within the SAFT framework using a three-site alcohol model [50]. The knowledge gained in understanding hydrogen bonding is applied to model VLE and LLE of mixtures using polar PC-SAFT [50]. The selection of appropriate association schemes is also investigated using spectroscopic data [51]. For pure water, a four-site scheme is shown to be the most appropriate scheme [51]. In the case of pure alcohols, a three-site scheme is best for methanol; two- or three-site schemes perform about equally for ethanol; for higher alcohols, a two-site scheme is preferred [51]. This can be interpreted using steric arguments [51]. Kontogeorgis et al. [52] proposed the incorporation of the spectroscopic data in the parameter fitting procedure, otherwise remarkable deviation between the experimental data and the modelling results for the LLE occur [53]. A new association scheme within the SAFT-framework is presented for more-accurate predictions of 1-alcohol + water phase equilibria than with the 2B or 3B association schemes [54]. The new association scheme consists of one bipolar association site and one negative electron donor site and is a combination of the 1A and 2B/3B association schemes [54]. For systems made of water and oxygenated compound, Nguyen et al. [55] proposed to consider cross-association in addition to a binary interaction parameter l_{ij} on the combining rules for the cross-segment diameter between water and the investigated oxygenated compound. Ahmed et al. [56] incorporated a nonadditive hard sphere term [57] in the equation of state leading to a good description of the involved phase equilibria. de Villiers et al. [58] provide an overview over the performance of different versions of the SAFT-EOS in modelling water - alcohol mixtures. However, no model is able to model the LLE with a high accuracy.

The DGT was combined with original SAFT EOS in order to describe both the phase behavior and interfacial properties with respect of association [6]. It was found that for water alcohol mixtures the simultaneous correlation of both phase equilibrium and interfacial properties with the SAFT EOS in combination with the DGT is possible, however, the used model does not allows the description of the maximum in interfacial tension as function of temperature in the system water and 1-butanol [6]. Llovell et al. [13] modelled the surface tension for two mixtures, namely water + ethanol and water + 1-propanol, applying the DGT. However, they [13] avoid the modelling of the interfacial tension. Grunert et al. [25] was able to model the maximum in σ^{LLE} as function of temperature using the inc-DGT in combination with Koningsveld-Kleintjens model. Similar results were obtained by Cárdenas et al. [18] utilized also the inc-DGT with the NRTL model. This approach allows also the calculation of the maximum of σ^{LLE} as function of temperature for alcohols with different chain length [18].

Esters are polar molecules and are capable of associating with water molecules although they do not self-associate. Low molecular mass esters are somewhat soluble in water, and this solubility decreases drastically with increasing carbon atoms; borderline solubility occurs in esters containing three to five carbon atoms. The phase equilibria of mixtures containing water and ester are already calculated using the SAFT-approach [56, 59]. del Pozo et al. [23] investigated the interfacial tension for methyl ester (from methyl formate to methyl heptanoate) in water as function of temperature, where the interfacial tension run through a maximum. The experimental data could be correlated using inc-DGT in combination with NRTL activity coefficient model [23]. To the best of our knowledge, the interfacial behavior of mixture of acetates + water was not studied yet.

The purpose of this work is a detailed comparison of the DFT and the inc-DGT for three technical important mixtures, specifically, this work is devoted to binary demixed aqueous-organic mixtures, where the organic compound is 1-alkanol (1-butanol to 1-hexanol), or hexyl acetate. We would like to carve out the advantages and the disadvantages of both methods, where we focus our attention to the transferability of the influence parameter, κ_i, obtained from the surface tension of the