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Interfacial and bulk properties of vapor-liquid equilibria in the system toluene + hydrogen chloride + carbon dioxide by molecular simulation and density gradient theory + PC-SAFT

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ABSTRACT

Interfacial and bulk properties of vapor-liquid equilibria (VLE) in systems containing toluene, hydrogen chloride (HCl), and carbon dioxide (CO_2) are studied by molecular dynamics simulations and density gradient theory + PC-SAFT. The pure components, the three binary mixtures, and the ternary mixture are studied systematically. A new PC-SAFT model of HCl is developed and mixture models are adjusted to binary VLE data. The focus of the studies is on the temperatures 333 and 353 K for which both HCl and CO_2 are supercritical. The simulation results are compared to experimental data, where such data are available. VLE bulk properties are well described. For the interfacial tension, only pure component data are available, which are well predicted. For the mixtures, data on the interfacial tension are predicted. A strong adsorption of both HCl and CO_2 at the vapor-liquid interface is found from both methods.

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1. Introduction

Interfacial properties of the vapor-liquid equilibrium are important for many applications in process engineering, including separations like absorption but also multi-phase reactions. They are especially important for phenomena like nucleation and foaming. Experimental data on interfacial properties of mixtures are in most cases limited to the interfacial tension and even such data are rarely available. Hence, it is desirable to have models which enable predicting and analyzing interfacial properties. The most attractive methods are molecular simulation based on force fields and density gradient theory coupled with an equation of state [1–8].

Both methods are used in the present work for studying interfacial properties of toluene, carbon dioxide (CO_2) and hydrogen chloride (HCl), and their mixtures. These three molecules differ significantly in structure and polarity. HCl forms hydrogen bonds and is strongly dipolar, CO_2 is slightly larger and quadrupolar. Toluene is much larger and almost nonpolar. The system toluene + HCl + CO_2 can also be considered as a model system for similar mixtures, which are important in reaction engineering, where toluene stands for the solvent and HCl and CO_2 stand for reacting gases or gaseous products. The present study focuses on the temperature range 333–353 K where both HCl and CO_2 are supercritical and the binary vapor-liquid equilibria of toluene + HCl and toluene + CO_2 show wide-boiling behavior. There are many experimental studies on the VLE of toluene + CO_2 mixtures in the temperature range investigated in the present work [9–17]. The binary system CO_2 + HCl does not exhibit a VLE at temperatures in the range given above. A VLE is obtained in that system at 290 K, where it shows azeotropic behavior [18,19]. An overview of the experimental data of the binary mixtures used in the present work is shown in Table 1.

From a molecular point of view, at a vapor-liquid interface the density changes smoothly from its liquid bulk to its vapor bulk value. This transition from the vapor to the liquid phase along a coordinate normal to the interface can be described well by a hyperbolic tangent function for the density of a pure fluid [20–22]. For mixtures, however, complex phenomena are occasionally observed in that transition region [22–26]. This holds especially for wide-boiling mixtures [27–33]. While the density of such mixtures decreases monotonously from the bulk liquid to the bulk vapor, the

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Table 1
Literature overview of experimental data of the binary mixtures investigated in the present work.

Author	T/K		p/MPa	
	Min	Max	Min	Max
Toluene + CO_2 (VLE)				
Chen and Fang [9]	333	–	1.00	9.40
Yang et al. [10]	308	343	3.21	9.46
Tochigi et al. [11]	323	333	1.08	9.89
Park et al. [12]	333	393	3.98	15.4
Naidoo et al. [13]	283	391	0.41	12.1
Morris and Donohue [14]	353	413	0.26	13.2
Muhlbauer and Raal [15]	352	–	0.88	11.0
Kim et al. [16]	353	393	0.52	6.45
Walther et al. [17]	352	389	6.15	14.3
Toluene + CO_2 (Henry's law constant)				
Horvath et al. [104]	298	300		
Field [105]	283	313		
Fink and Hershey [81]	308	353		
Waeterling et al. [106]	476	–		
Sebastian et al. [107]	393	542		
Nig and Robinson [108]	311	477		
Zhang et al. [109]	275	328		
Piskovsky and Lakomy [110]	198	293		
Shenderei et al. [111]	228	248		
Toluene + HCl (Henry's law constant)				
Ahmed et al. [100]	195	293		
Bell [101]	293	–		
O'Brian and Bobalek [102]	293	–		
Brown and Brady [103]	195	–		
HCl + CO_2 (VLE)				
Ansdall [18]	273	320	2.82	9.34
Dorsman [19]	293	324	4.24	6.17

densities of some of the individual components do not. Enrichment effects may occur, such that a maximum of the density of the light-boiling component is observed in the interfacial region, where it can reach values several times larger than its largest bulk value. Such interfacial enrichments in VLE of mixtures have been discussed in the literature [27–34], but no systematic evaluation of the phenomenon of interfacial enrichment has been conducted so far for complex systems like the ternary one studied in the present work. From the available VLE data, it can be deduced that high enrichments occur in mixtures of water and CO_2, where the component density of CO_2 is reported to be up to 7 times higher at the interface than in the bulk phases [33,35–37]. In mixtures of water and alcohols [7], as well as dimethylformamide + alkanes [26], component densities were found which were up to 10 times higher than the highest corresponding component density in the bulk phase. Only small enrichments were found for mixtures of alkanes [24,34], mixtures of poly(dimethylsiloxane) + acid gases [38], mixtures of carbon dioxide + sulfur dioxide, mixtures of carbon dioxide + hydrogen sulfide [39], mixtures of acetone + nitrogen and of acetone + oxygen [22].

In the present work, molecular dynamics (MD) simulations with the *ls*1 *mardyn* program [40] and calculations applying the density gradient theory coupled with the PC-SAFT equation of state are conducted to investigate the interfacial tension and the interfacial enrichment in multi-component systems. The force field models for the MD simulations are taken from previous work of our group [3,41]. The PC-SAFT parameters for toluene and CO_2 are taken from Gross and Sadowski [4]. A new model for HCl is developed in the present work. The molecular model parameters of the pure components were adjusted to describe the saturated liquid density, vapor pressure and enthalpy of vaporization, which is well done [3,41]. The molecular models for CO_2 and HCl were also evaluated with respect to transport properties. They show a very good agreement with experimental data for the self diffusion coefficient, shear viscosity and thermal conductivity [41,42].

The interfacial tension is usually not taken into account in the parameterization of molecular models. Molecular models from previous work of our group were adjusted to reproduce the vapor pressure and the saturated liquid density [43,44]. These models overestimate the interfacial tension by 20% on average [45–48]. Similar findings were obtained for other molecular models which were parameterized with respect to bulk properties only [22,27,49–56]. Attempts to reconciliate the quality of the results for bulk and interfacial properties by including the latter into the fit of the parameters of the molecular models have so far not been successful [47,57,58]. Despite these shortcomings, the molecular models from the literature were used straightforwardly in the present work. No parameters were changed. Hence, all results from the MD simulations in the present work are predictions of interfacial properties from bulk properties.

While molecular simulation resolves thermodynamic properties on the scale of atoms and molecules, density gradient theory (DGT) takes a continuum perspective. It was first introduced by van der Waals [59] and then rediscovered by Cahn and Hilliard [60] for application to pure compounds. Later it was generalized for the description of mixtures by Poser and Sanchez [24]. In combination with a physically based equation of state, DGT can describe with good accuracy the interfacial tension of both pure compounds [6] and mixtures [7].

In the present work, bulk and interfacial properties from both MD simulation and DGT + PC-SAFT of pure components as well as of binary and ternary mixtures are reported. The binary and ternary mixtures of toluene with HCl and CO_2 are investigated at the temperatures 333 and 353 K, while the mixtures of HCl and CO_2 are investigated at 290 K. Bulk properties, i.e. saturated densities, vapor pressures, compositions and Henry's law constants, are reported for a wide range of compositions. Interfacial properties, i.e. the interfacial tension, interfacial enrichment and interfacial adsorption are investigated systematically. Comparisons with experimental data are given if such data is available.

2. Modeling and simulation

2.1. Fundamentals

Thermodynamically, the interfacial tension γ is defined as the change in free energy upon a variation of the interfacial area

$$\gamma = \left(\frac{\partial A}{\partial S}\right)_{N,V,T}, \qquad (1)$$

where A is the Helmholtz free energy and S is the interfacial area. For determination of the interfacial tension in molecular simulation several methods can be used, either mechanical routes [61–63], the test-area method [64,65] or finite-size scaling based on grand-canonical sampling [66–70]. The mechanical route, which is used in the present work, can be realized straightforwardly based on the intermolecular virial [61–63], which is also used for the pressure calculation in MD simulation [61]. For planar interfaces, the thermodynamic and the mechanical route are equivalent. There are significant deviations for curved interfaces if the second order virial contributions are neglected in the application of the mechanical route [70–73].

Interfacial adsorption may lead to an enrichment of components of the studied mixture at interfaces between phases. To quantify this enrichment, the interfacial enrichment E_i of component i is introduced. It is defined in the present work as the ratio of the maximum of the local component density $\rho_i(y)$ in the interfacial region and of the highest density of the same component in the

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