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# Enrichment of Components at Vapour - Liquid Interfaces: A Study by Molecular Simulation and Density Gradient Theory

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In separation processes not only thermodynamic bulk but also interfacial properties play a crucial role. In classical theory, a vapour-liquid interface is a two-dimensional object. In reality it is a region in which properties change over a few nanometres and the density changes continuously from its liquid bulk to its gas bulk value. Many mixtures show unexpected effects in that transition region. While the total density changes monotonously from the bulk vapour to the bulk liquid, this does not hold for the molarities of the components. The molarities of the light boiling component can have a distinct maximum at the interface. That maximum would be an insurmountable obstacle to mass transfer according to Fickian theory. Even if that argument is not adopted, it shows that there is good reason to believe that the maximum may affect mass transfer and, hence, fluid separation processes like absorption or distillation. Unfortunately, there are currently no experimental methods that can be used for direct studies of density profiles in such interfacial regions. But such data can be obtained with theoretical methods, namely with molecular dynamics simulations (MD) as well as with density gradient theory (DGT) or with density functional theory (DFT) combined with an equation of state (EOS).
Studies from our group on the vapour-liquid interface of several real mixtures and a model fluid using these methods yield consistent results and reveal an important enrichment in some cases. Strong enrichment is found at vapour-liquid interfaces in the systems in which one of the components is supercritical. These results indicate that mixtures, which are typical for absorption processes usually show an important enrichment, whereas this is not the case for mixtures that are typically separated by distillation. Possible consequences of this finding for the modelling of these separation processes are discussed.

## 1. Introduction

In separation technology, mass transport between phases is a key factor for apparatus design. This transport is accounted for by models like the two-film theory, assuming that the transport resistance in the interface is negligible. In separation technology, mass transport between phases is a key factor for apparatus design. This transport is accounted for by models like the two-film theory, assuming that the transport resistance in the interface is negligible. If, however, light boiling components like inert gases are present in the mixture, enrichment of these components at the interface can occur. It is known that surfactants, which also show enrichment at the interface, reduce mass transfer rates (Carey et al., 1980). We argue that the same holds for the enrichment of other chemicals, provided that this enrichment is high enough.

We introduce the enrichment in a density profile of a component $i$ in the interface $\rho_i(z)$ as

$$E_i = \frac{\max\left(\rho_i\left(z\right)\right)}{\max\left(\rho_i`, \rho_i``\right)} \tag{1}$$

Where $z$ is the spatial coordinate perpendicular to the interface, $\max\left(\rho_i\left(z\right)\right)$ is the maximum density of the light boiling component in the density profile and $\max\left(\rho_i`, \rho_i``\right)$ the higher of the two bulk densities. The

enrichment at the interface cannot be studied directly in experiments and therefore theoretical methods must be employed to study it.
In the present work, the enrichment at fluid interfaces is studied by molecular simulations and density gradient theory for two real mixtures and a model fluid mixture:

a) toluene + carbon dioxide
b) ethanol + carbon dioxide
c) binary mixture of Lennard-Jones truncated and shifted (LJTS) fluids.

Molecular simulations and density gradient theory have been applied before for studies of the enrichment, e.g. (Becker et al., 2016, Werth et al., 2016, Lee et al., 1984, Lee et al., 1985, Protsenko et al., 2016a, Protsenko et al., 2016b, Mejia et al., 2005, Baidakov et al., 2008, Miqueu et al., 2005, Miqueu et al., 2011, Eckelsbach and Vrabec, 2015).
For describing the real fluids in the molecular simulations, force fields from previous work of our group are used (Merker et al., 2010, Huang et al., 2011, Schnabel et al., 2005). In the density gradient theory approach the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state (Gross and Sadowski, 2001) is used to model the real fluids and the PeTS (Perturbed truncated and shifted) equation of state is used for describing the LJTS fluid (Heier et al., 2018). The LJTS fluid is one of the computationally cheapest fluid models that reasonably captures the physical behaviour of pure fluids, e.g. (Vrabec et al., 2006). The results from molecular simulations and density gradient theory are consistent for all studied mixtures. They show that enrichment is always observed for the light-boiling component but not for the heavy-boiling component. The enrichment depends on the type of mixture and the composition.

## 2. Methods

### 2.1 Molecular Simulation

Molecular dynamics simulations (MD) of equilibrated systems in which a vapour and a liquid phase are in direct contact are carried out in the *NVT* ensemble with $N$ = 16,000 particles. The *ls*1mardyn code (Niethammer et al., 2014) is used for the simulations, where the equations of motion are solved with the leapfrog integrator with a time step of 1 fs. After an equilibration of at least 500,000 time steps production runs for at least 2,500,000 time steps. Periodic boundary conditions are used. The simulation box contains a liquid slab in the middle surrounded by two vapour phases on either sides. The temperature is kept constant by velocity-scaling. The numbers of particles of the two components are chosen in such a way that mole fraction of the light boiling component in the liquid phase varies between about $x_2$ = 0.05 and $x_2$ = 0.85 to investigate the composition dependence of the enrichment. The cut-off radius is 17.5 Å for the real fluids in a) and b), while it is 2.5 $\sigma$ for the LJTS fluids in c).
The molecular models employed in this study consist of Lennard-Jones sites (describing the dispersion and repulsion between the particles) and eventually point multipoles (describing the polarity of the molecule and hydrogen bonding between molecules). Unlike electrostatic interactions, e.g. between charges and quadrupoles, are treated in a physically straightforward way, using the laws of electrostatics. The molecular model of ethanol, carbon dioxide, and toluene are taken from (Schnabel et al., 2005, Merker et al., 2010), and (Huang et al., 2011).
The size parameters of the two components in the LJTS model mixture are the same, i.e. $\sigma_{11} = \sigma_{22}$, the ratio of the energy parameters is $\varepsilon_{22} / \varepsilon_{11}$ = 0.5, so that component 2 is the light boiling component. The cut-off radius of the LJTS fluids is $r_c$ = 2.5 $\sigma$. For the representation of the results for the LJTS fluids dimensionless properties are used that are based on the size parameter $\sigma$ and the energy parameter $\varepsilon$ of the model (Allen and Tildesley, 1987).
For modelling interactions between unlike Lennard-Jones sites, the modified Lorentz-Berthelot combining rules are used:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{2}$$

$$\varepsilon_{ij} = \xi_{ij} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \tag{3}$$

The state-independent binary interaction parameter $\xi_{ij}$ is adjusted to a single experimental vapour pressure for the systems a) and b) resulting in $\xi_{\text{EtOH-CO}_2}$ = 1.08 (Werth et al., 2016) and $\xi_{\text{tolouene-CO}_2}$ = 0.95 (Becker et al., 2016). The binary interaction parameter for the LJTS mixture is set to $\xi_{\text{LJTS}}^{\text{MD}}$ = 1.0.

### 2.2 Density Gradient Theory

Density gradient theory (DGT) describes the continuous change of density in inhomogeneous systems, for example at vapour liquid interfaces, see e.g. (van der Waals, 1873, Cahn and Hilliard, 1958, Cornelisse et al., 1996). Applying density gradient theory requires an equation of state (EOS) for the Helmholtz free energy *A*. The so-called influence parameter $\kappa_{ij}$ describes the influence of the density gradients on the thermodynamic properties, cf. Eq. (4). The basic idea of DGT is the development of the free energy of an inhomogeneous system around the homogeneous equilibrium state in the spatial derivative of the density. Usually the series is truncated after the square gradient term (Miqueu et al., 2005), which results in

$$A\left[\rho(z)\right] = S\int_{-\infty}^{\infty}\left[a_0\left(\rho_i(z)\right) + \frac{1}{2}\sum_j\sum_i \kappa_{ij}\left(\frac{\mathrm{d}\rho_i}{\mathrm{d}z}\right)\left(\frac{\mathrm{d}\rho_j}{\mathrm{d}z}\right)\right]\mathrm{d}z \tag{4}$$

for an inhomogeneous system with a planar interface. Eq. (4) expresses the free energy as a functional of the density profiles $\rho_i(z)$. Here $S$ is the surface area, $a_0$ is the local free energy per volume, and $\rho_i$ is the molar density of component $i$. The interfacial profiles are determined using the method of (Miqueu et al., 2005). The pure component influence parameter $\kappa_{ii}$ is usually fit to experimental surface tension, e.g. (Niño-Amézquita et al, 2010a, Niño-Amézquita et al, 2010b), while a geometric mixing rule is applied for the binary influence parameters:

$$\kappa_{ij} = \sqrt{\kappa_{ii}\kappa_{jj}} \tag{6}$$

The PC-SAFT equation of state (Gross and Sadowski, 2001) is used in the present work for the calculation of the Helmholtz free energy of the real substances and the PeTS EOS for the truncated and shifted Lennard-Jones fluid (Heier et al., 2018). The pure component parameters for PC-SAFT are taken from (Gross and Sadowski, 2001) for toluene and carbon dioxide and from (Gross and Sadowski, 2002) for ethanol. The parameters for the unlike interaction energy $\xi_{ij}^{\text{EOS}}$ in the PC-SAFT EOS are taken from (Werth et al., 2016) for the toluene – carbon dioxide mixture and from (Becker et al., 2016) for the ethanol – carbon dioxide mixture. The unlike energy interaction parameters in the PeTS EOS for the LJTS mixtures have the same value as the one used in the mixing rule of the molecular model, cf. Eq. (3), i.e. $\xi_{ij}^{\text{EOS}} = \xi_{ij}^{\text{MD}}$. The influence parameters $\kappa_{ii}$ for carbon dioxide, ethanol, toluene, and the LJTS fluid are taken from (Enders et al., 2005, Becker et al., 2016, Werth et al., 2016), and (Heier et al. 2018), respectively.

## 3. Results and Discussion

A snapshot of a molecular simulation is shown in Figure 1. The simulation box contains the binary mixture toluene and carbon dioxide at 353 K and 3.1 MPa.

Figure 2, 3, and 4 show results for the binary mixtures toluene + carbon dioxide (Werth et al., 2016), ethanol + carbon dioxide (Becker et al., 2016), and the binary LJTS mixture. In these figures, panel (a) shows the phase behaviour, an exemplary density profile is shown in panel (b), and the enrichment of the light boiling component is depicted as a function of the liquid phase mole fraction of that component in panel (c).

Figures 2 and 3 show that molecular simulation results are in excellent agreement with the experimental data for the vapour-liquid equilibrium (panels a). The same holds for the PC-SAFT EOS except for the data near the critical point. Figure 4a, shows that the vapour-liquid equilibrium of the LJTS mixture is described very well by the PeTS EOS, although no adjustment of the binary interaction parameter was carried out. (As described above, that parameter was simply adopted from the molecular model).

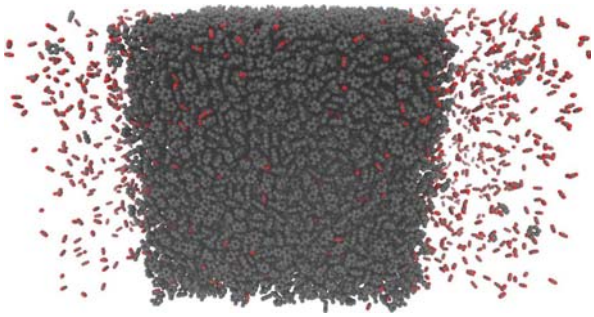

*Figure 1: Snapshot from a molecular simulation of the vapour-liquid equilibrium in the mixture toluene (grey) and carbon dioxide (red and grey) at $T$ = 353* K *and $p$ = 3.1* MPa*.*

The density profiles in Figures 2 - 4 (b) reveal that in all studied mixtures a significant enrichment of the light boiling component occurs at the interface. The density profiles predicted by MD and DGT are in good agreement. This is remarkable, as the methods are completely independent. The fact that the peak in the density of the light-boiling component in the interfacial region is slightly broader for MD than for DGT is due to the fluctuations that are present in MD but not in DGT.

The composition dependence of the enrichment of the light boiling component is shown in Figure 2 - 4 (c). In all systems, the highest enrichment is observed for low concentrations of the light boiling component. It is about 2.5 for all systems. The results from MD and DGT agree well, although DGT slightly overestimates the enrichment predicted by MD, which is probably again due to the absence of fluctuations in DGT.

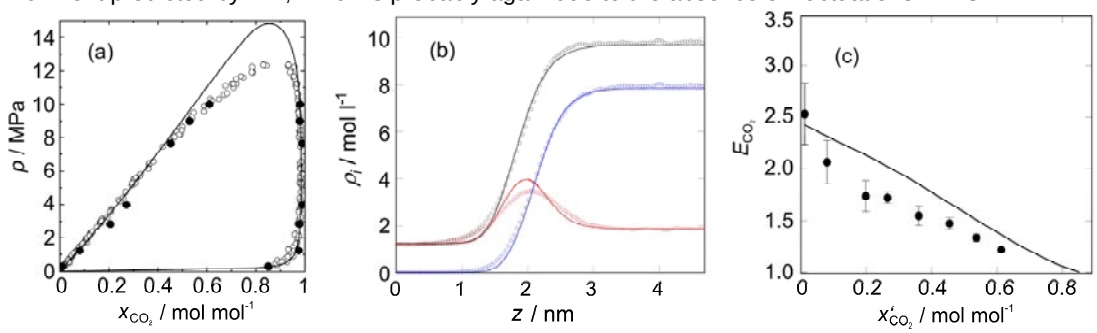


*Figure 2: Results for the system toluene + carbon dioxide at 353 K: (a) Phase behaviour; empty symbols are experimental data (Park et al., 1990, Naidoo et al., 2008, Morris and Donohue 1985, Muhlbauer and Raal 1991, Kim et al., 1986, Walther et al., 1992), full symbols are molecular simulation results, and the solid line is obtained from PC-SAFT. (b) Density profiles for $x'_{CO_2}$ = 0.2 mol/mol: solid lines are obtained from DGT, symbols are MD results. The black colour corresponds to the total density, blue to the toluene density, and red to carbon dioxide density. (c) Enrichment of carbon dioxide at the interface; solid line corresponds to DGT and symbols to MD results.*

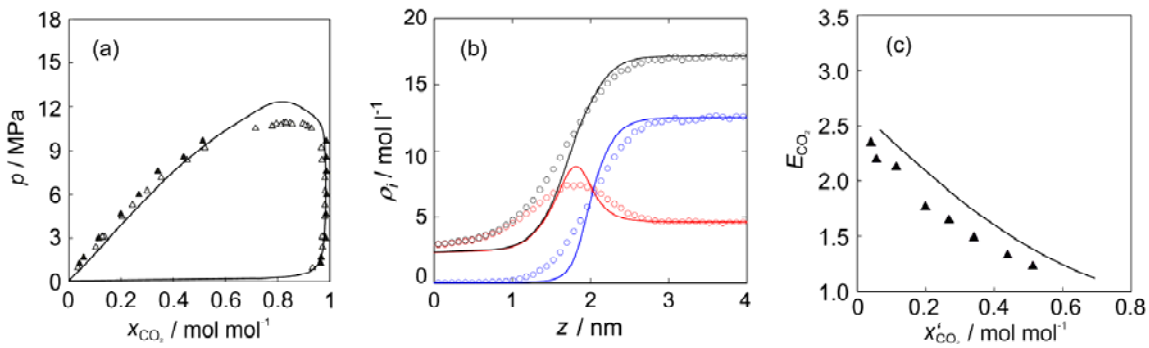


*Figure 3: Results for the system ethanol + carbon dioxide at 333 K: (a) Phase behaviour; empty symbols are experimental data (Secuianu et al., 2008), full symbols are molecular simulation results, and the solid line is obtained from PC-SAFT. (b) Density profiles for $x'_{CO_2}$ = 0.3 mol/mol: solid lines are obtained from DGT, symbols are MD results. The black colour corresponds to the total density, blue to the ethanol density, and red to carbon dioxide density. (c) Enrichment of carbon dioxide at the interface; solid line corresponds to DGT and symbols to MD results.*

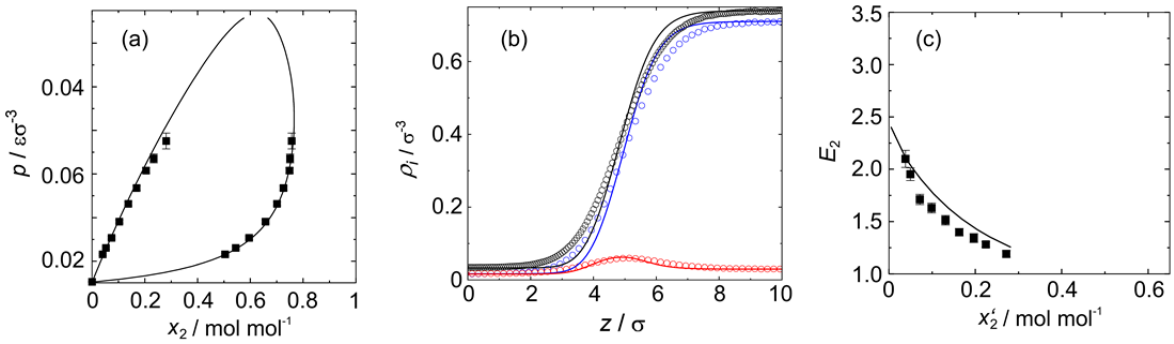


*Figure 4: Results for the binary LJTS mixture at $T$ = 0.7 $T_{c,1}$: (a) Phase behaviour; full symbols are molecular simulation results, and the solid line is obtained from the PeTS EOS. (b) Density profiles for $x'_2$ = 0.04 mol/mol: solid lines are obtained from DGT, symbols are MD results. The black colour corresponds to the total density, blue to the component 1 density, and red to the component 2 density. (c) Enrichment of component 2 at the interface; solid line corresponds to DGT and symbols to MD results.*

## 4. Conclusions

The present study reveals a significant enrichment in mixtures containing carbon dioxide as light boiling component as well as a corresponding LJTS mixture. Molecular simulation and density gradient theory, lead to consistent results for phase equilibria and interfacial behaviour. The enrichment predicted by MD and DGT agrees well for all three investigated mixtures. The results show that enrichment of low boiling components is important at low concentrations of that component in the liquid phase, i.e. for conditions that are typically encountered in absorption. It is a hypothesis for future work, that this influences mass transfer in absorption and should be accounted for explicitly.


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