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Interfacial tension between benzene and water in the presence of caprolactam

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ABSTRACT

We studied the physical properties and the concentration profile of benzene + water + caprolactam mixtures near the fluid–fluid interface using self-consistent field (SCF) theory. This yields the interfacial tension which plays an important role in describing the stability of transient liquid droplets of one phase in the other. The studies were performed at a fixed temperature of 313 K. Flory–Huggins binary interaction parameters and the compound lattice segment numbers are input parameters for the applied SCF theory. These parameters were derived from activity coefficient relations, which are used to describe experimental liquid–liquid and vapor–liquid phase equilibrium measurements. Using first principles, the benzene–water interface was studied and the resulting interfacial tension was found to be in agreement with experimental values. This study illustrates that caprolactam accumulates at the benzene–water interface, acting as a weak surfactant. The interfacial tension is also demonstrated to be affected by the caprolactam concentration and the SCF results are in fair agreement with the experimental observations.

1. Introduction

Caprolactam (CPL) is the monomer unit of polyamide 6, one of the most commonly used polymers in engineering plastics and synthetic fibers. The worldwide production of CPL is about 3800 kton/year [1–3]. There are several routes to produce caprolactam, depending on the feedstock material (phenol, benzene, toluene, propylene) [3]. One of the central purification steps is the extraction of caprolactam from an aqueous solution containing impurities and dissolved salts. Benzene (B) is often used as extracting solvent since it offers a better partitioning for caprolactam, a higher selectivity with respect to impurities, and an easier downstream processing than other solvents like, for instance, toluene or chlorinated hydrocarbons [2]. The efficiency of benzene extraction is not only determined by the bulk equilibrium properties, but also by the local properties near the organic–aqueous interface, as we show in this study. Bulk equilibrium properties of the caprolactam–water–benzene (CPL/W/B) system, like liquid–liquid and vapor–liquid equilibria, have been studied experimentally and modeled using activity models like electrolyte NRTL [4,5]. The interfacial tension has also been studied in detail [6]. It is important to be able to predict and to understand the interfacial tension since it determines the stability of transient liquid droplets of one liquid phase in the other liquid phase which can reduce the efficiency of the extraction process.

In this paper, self-consistent field (SCF) computations are applied to study the local partitioning and interfacial properties of CPL/W/B dispersions theoretically. A simple lattice model is used in which the interactions between the different species are described using the Flory–Huggins binary interaction parameters and compound lattice segment numbers. Those inputs were determined from activity coefficient relations for B/W/CPL mixtures at $T = 313$ K (40 °C).

The interfacial properties (interfacial tension, local concentration profiles near the interface) as well as the bulk partition coefficient were evaluated. The numerical exact mean-field SCF lattice theory was developed by Scheutjens and Fleer [7,8]. Their method is based on Flory–Huggins theory [9,10], but additionally accounts for inhomogeneities, i.e. gradients in density profiles. This method is exact on the mean-field level. In order to be able to perform SCF computations we need the aforementioned Flory–Huggins parameters, which capture the association between the molecules. This work provides insight into the functionality of low molecular species at interfaces. Compounds such as caprolactam are usually not considered as surfactants because they are not amphiphilic. Here we demonstrate, however, that caprolactam does act as a surfactant simply because its interactions with the two molecules that dominate the two bulk phases (benzene and water) is such that the system prefers this compound to accumulate at the interface. This has significant consequences for phenomena such as emulsification and is relevant for understanding liquid–liquid interfaces in general.

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2. Determination of interaction parameters

Here we specify how to place all molecules on a lattice and compute the Flory–Huggins parameters between the three components. For the CPL/B/W mixture of interest we assume a benzene molecule occupies one lattice site. Hence we identify the size of one lattice site with the size of a benzene molecule. This fixes the size of one lattice site; it is derived from the density of benzene. The density of benzene is 858 kg/m^3. The molar mass of benzene is 78.11 g/mol, so the volume per molecule is 1.51×10^{-28} m^3. This means one lattice site has a length b of 0.53 nm [11].

In order to determine the Flory–Huggins parameters and the effective association numbers of the molecules involved, we used activity coefficients. These were calculated from the NRTL equation [12] using binary interaction parameters. The general expression for the chemical potential of molecules 2 in a binary mixture of molecules 1 and 2 is:

$$\mu_2 = \mu_2^0 + RT[\ln x_2 f_2], \tag{1}$$

where f_2 is the activity coefficient of component 2 and x_2 is the mole fraction of component 2 in a binary mixture of components 1 and 2. The Flory–Huggins expression for the chemical potential of component 2 is [10]:

$$\mu_2 = \mu_2^0 + RT[\ln \varphi_2 + (1-m)(1-\varphi_2) + m\chi(1-\varphi_2)^2], \tag{2}$$

where m is number of lattice sites occupied by a molecule 1 in comparison to molecule 2. The volume fraction φ_2 is related to the mole fraction through:

$$x_2 = \frac{m_2\varphi_2}{m_1\varphi_1 + m_2\varphi_2}. \tag{3}$$

Matching expressions (1) and (3) for a given set of experimental data (f_2, x_2), yields m and χ. We limit ourselves to $T = 313$ K. In Fig. 1 we plot experimental activity coefficients of water and benzene in water–benzene mixtures as a function of the mole fraction of water. The results for CPL/W and CPL/B mixtures are plotted in Figs. 2 and 3, respectively. We have performed a simultaneous fit to the data points in Figs. 1–3, using Eqs. (1) and (2) with the m's and χ_{B-W}, χ_{CPL-W} and χ_{CPL-B} as free parameters. Since the lattice theory imposes integer values for m we take the values from the second row in Table 1. It follows that the interaction between benzene and water is very repulsive, caprolactam-water interactions are quite favorable and benzene–caprolactam interactions are marginal.

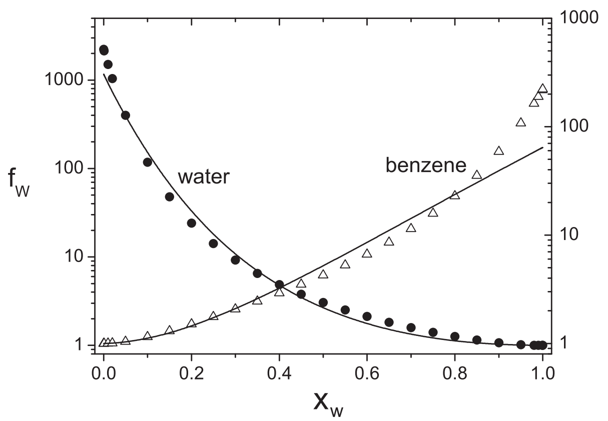

Fig. 1. Activity coefficients (data points) for water-benzene mixtures as a function of the mole fraction of water. Solid curves are the results of simultaneously fitting all activity coefficients of Figs. 1–3 using expression (3).

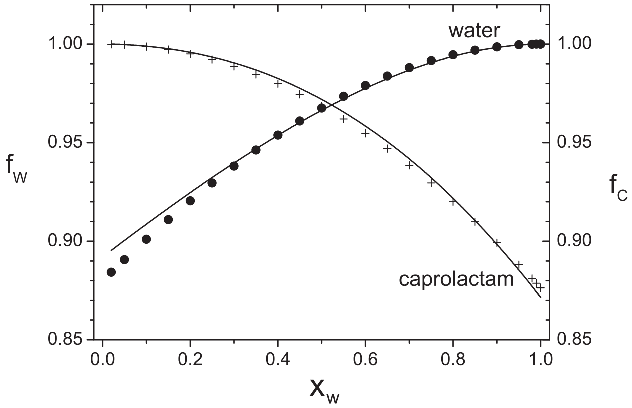

Fig. 2. Activity coefficients for water-caprolactam mixtures as a function of the mole fraction of water as data points. Solid curves are the results of simultaneously fitting all activity coefficients of Figs. 1–3 using expression (3).

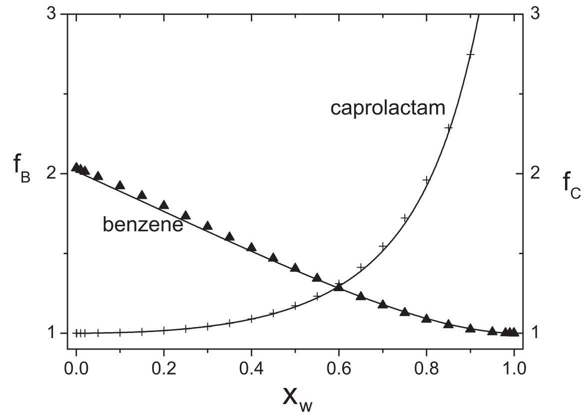

Fig. 3. Activity coefficients (data) for benzene–caprolactam mixtures as a function the mole fraction of benzene. Solid curves are the results of simultaneously fitting all activity coefficients of Figs. 1–3 using (3).

Table 1
Fitted Flory–Huggins parameters from Figs. 1–3 and values used in the SCF computations.

	$\chi_{B/W}$	$\chi_{CPL/W}$	$\chi_{CPL/B}$	m_W	m_B	m_C
Values from activity coefficients	7.23	−0.10	0.91	1.71	1	2.08
Values used for SCF	7	−0.1	0.9	2	1	2

The number of lattice sites effectively occupied by water and caprolactam are 2 for both. For water, every lattice site is already filled with many water molecules since the molecular size of water is much smaller than that of benzene. Apparently, however, water occupies two associated lattice sites. This corresponds with the experimental observation that the maximum water concentration in benzene is smaller than the maximum benzene concentration in water. A possible interpretation is that hydrogen bonding leads to effective clusters of water molecules which make permeation into a benzene-rich phase rather unfavorable.

A surprising feature is that caprolactam acts as a dimer as well. Relative to benzene this can be understood: the amide group of CPL can form a hydrogen bond with another CPL molecule. We have performed numerical SCF computations with the parameters of Table 1. They are presented in the next section.