

Liquid-Liquid Equilibrium and Interfacial Properties of the System Water + Hexylacetate + 1-Hexanol

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Dedicated to Prof. Dr. techn. Hans-Jörg Bart on the occasion of his 65th birthday

Experimental and theoretical investigations of the phase diagram and the interfacial tension are presented. The theoretical framework was able to predict the phase behavior and the interfacial tension with a high accuracy, where only binary experimental data enter the model parameter. The theory permits the calculation of the concentration profiles across the interface. The profiles show that 1-hexanol will be enriched, which was expected. In some circumstances a competition between hexylacetate and 1-hexanol was figured out leading to slight minima in the profile of 1-hexanol.

Keywords: Liquid-liquid equilibrium, Ternary mixtures, Interfacial tension, Density gradient theory, NRTL-model

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1 Introduction

Extraction is one of the most important unit operation in bio- and chemical engineering based on the liquid-liquid equilibrium (LLE) of at least ternary mixtures. The longtime challenges in the development of new processes or in the optimization of already existing processes and apparatus are the improvement of the mass transport across the interface between the coexisting liquid phases as well as the understanding of droplet breakage and coalescence [1–6]. The process efficiency and product quality in technical separation processes are substantially influenced by the specific interfacial area, which depends on droplet formation and the mutual effects of droplet breakage and coalescence [1–6]. Thus, the correct prediction of droplet phenomena, respectively, a detailed knowledge of the droplet size distribution in space and time is a vital requirement for precise process design. All these phenomena join one important feature, they depend strongly on the interfacial properties, like interfacial tension and concentration profiles across the interface, of the droplets and the surrounding continuous phase. Whereas, the interfacial tension can be measured, the mentioned concentration profiles can not. Usually, the measurements of interfacial tensions were performed in thermodynamic equilibrium. Regarding the speed-up of the process development it will be desirable to predict these interfacial properties using so less experimental data as possible, ideally only data of the binary subsystems. Such a theoretical framework, which permits the calculation of the interfacial tension related to the LLE was established twenty years ago [7]. The basic idea of this approach is the applica-

tion of the density gradient theory, originally developed by Van der Waals [8] and rediscovered by Cahn-Hilliard [9], to incompressible fluids, where the Helmholtz energy can be replaced by the Gibbs energy and consequently the thermodynamic properties can be modelled with a g^E model rather than an equation of state [10, 11]. The method was used for different binary [12–21], ternary [14, 21, 22–26] and quaternary mixtures [21, 27–29]. Recently, also the time-dependency of the interfacial tension caused by diffusion [14, 16, 24, 27] or caused by a chemical reactions [21, 29] were studied. Usually, the applied model was able to correlate or even predict the interfacial tension close to the experimental data. Regarding ternary mixture the phase diagram can exhibit different shapes depending on the miscibility gaps of the corresponding binary subsystems. For extraction the so-called closed system, where only one miscibility gap starting from the phase-forming binary subsystem occur, is desired. Ternary mixtures showing this phase behavior have a critical point, where the interfacial tension is zero. For these mixtures, the interfacial tension could be predicted based on data of the bulk-phase diagram and one value for the interfacial tension in the binary subsystem [14, 21, 22, 24–26]. For ternary mixtures, where two binary subsystems exhibiting a miscibility gap only one paper [23] dealing with the prediction of interfacial properties for the

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mixture water + 1-butanol + benzene is available in the literature. The purpose of this contribution is to study a second mixture, where two pairs show partial miscibility. We figure out similarities and differences of both systems. For this propose a similar mixture is chosen, where the middle-polar component 1-butanol is replaced by 1-hexanol having a lower polarity and to the same time the non-polar component benzene is replaced by hexylacetate having a slightly higher polarity. For the system under study only binary data belonging to the binary subsystems were measured [15, 19, 30–35]. LLE data for the binary subsystems water + 1-hexanol [30, 32, 34] as well as for the binary subsystem water + hexylacetate [32, 34] are available, this holds true also for interfacial tension data regarding the subsystems water + 1-hexanol [15, 19, 33, 35] and water + hexylacetate [19]. Considering the ternary system water + 1-hexanol + hexylacetate no experimental data, to the best of our knowledge, exists in open literature, regarding the LLE, as well as interfacial tension data at $T = 298.15$ K. Therefore, some experimental data with respect to the LLE and with respect to the interfacial tension were produced in order to verify or falsify the predictions.

2 Experiments

First, the LLE were measured with the analytical method using gas chromatography, whereas the interfacial tension was investigated experimentally applying spinning-drop tensiometry. This was done with the intent to validate the theoretical investigation of these properties, also performed in this work.

2.1 Chemicals and Sample Preparation

1-Hexanol (CAS: 111-27-3) with a purity of ≥ 98 % g g^{-1} , estimated with gas chromatography, was purchased by Carl Roth. Hexylacetate (CAS: 142-92-7) with a purity of 99 % g g^{-1} , also determined by gas chromatography, was purchased by Sigma Aldrich. Both chemicals were used without further purification. In case of water, bi-distilled water was used. Before the ternary mixtures were prepared, the pure components were degassed for 5 min using the ultrasonic bath Badelin Sonorex RK510. To ensure that the investigated ternary samples have reached thermodynamic phase equilibrium, they were put in a tempered water quench for 24 hours before they were investigated experimentally.

2.2 Density Measurements

The density of the coexisting liquid phases was measured in this work, using the oscillating U-tube density meter Anton Paar DMA 38 with a volume of the measuring cell of

0.7 mL. The reproducibility of the used operating apparatus was determined to $\Delta\rho = \pm 1$ mg cm^{-3} and $\Delta T = \pm 0.3$ K.

2.3 Phase Composition

The measurement of the mole fractions in the coexisting organic phases was carried out with the gas chromatograph Agilent 6890 auto sampler, equipped with the column Hewlett Packard INNOWax[®]. The front injector injects one microliter of the assay. The split-injector works at a temperature of $T = 493$ K, a pressure of $P = 0.365$ bar and with a split ratio of 20:1, using helium as carrier gas. The total volume flow rate is $\dot{V} = 30.8$ mL min^{-1} . The mentioned separation column has a length of 38 m, with an inner diameter of $d_i = 0.35$ mm and a film thickness of 0.5 μm . The working pressure is again $P = 0.365$ bar, with a constant oven temperature of $T = 403$ K, and a through flow of $\dot{V} = 0.7$ mL min^{-1} . The run time was adjusted to 16 min. Additionally, the separation column was equipped with a flame ionization detector (FID) for the detection of 1-hexanol and hexylacetate and a thermal conductivity detector (TCD) for the detection of water. The FID works at a temperature of $T = 513$ K with a H_2 flow of 40 mL min^{-1} , an air flow of 450 mL min^{-1} , and a H_2 makeup flow of 20 mL min^{-1} . The TCD works also at a temperature of $T = 513$ K, a reference volume flow of 20 mL min^{-1} and a H_2 makeup flow of 6.3 mL min^{-1} .

The data analysis was performed with the help of the HP-GC-Chem Station [36]. A typical chromatogram of the FID is shown in Fig. 1, showing the separation of 1-hexanol and hexylacetate in the organic phase by the selected column. The composition of the studied phase can be estimated via a calibration, where the weight fraction is related to the peak area [21].

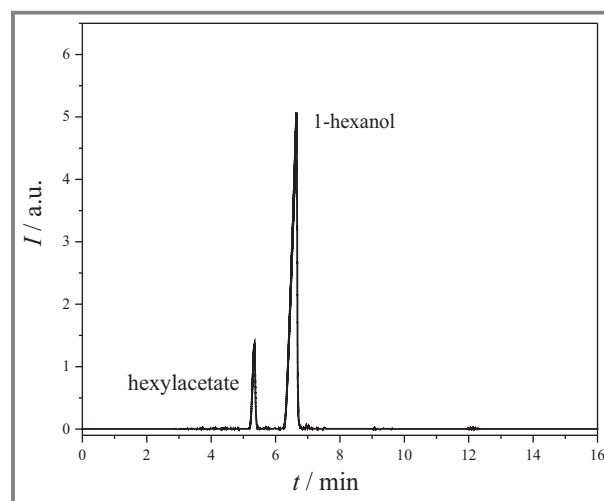


Figure 1. Separation of 1-hexanol and hexylacetate in the organic phase, where the feed composition is given by $x_{1\text{-hexanol}}^{\text{feed}} = 0.075$ and $x_{\text{hexylacetate}}^{\text{feed}} = 0.025$, obtained by gas chromatography equipped with the FID.

The detection of water with the TCD serves as control of the condition that the sum over all mole fractions in one phase has to be 1. This condition was always fulfilled, within the experimental accuracy. The mole fractions of 1-hexanol and hexylacetate in the water-rich phase are below the detection value. Modelling results using the activity coefficient model NRTL reveal mole fractions in the order of magnitudes 10^{-4} – 10^{-6} for the alcohol and in the order of magnitudes 10^{-6} – 10^{-8} for the ester. Therefore, the composition was not measured.

2.4 Interfacial Tension Measurements

The tension between two liquid bulk phases, the interfacial tension, σ^{LLE} , was measured with a spinning-drop tensiometer Data Physics SVT 20N. The measurement principle is based on the fact that gravitational acceleration has little effect on the shape of a droplet rotating at sufficient speed around its longitudinal axis. A tempered, rotating capillary (outer diameter: 6.22 mm, inner diameter: 4.0 mm) tube is filled with fluid from the higher density phase. Some microliters of the fluid (1 μL) from the lower density phase are injected in the middle of the rotating capillary tube and form a droplet. The interfacial tension is dependent on the diameter of the droplet, the rotating speed of the capillary tube and the difference of the density of both bulk phases:

$$\sigma^{\text{LLE}} = \frac{\Delta\rho r^3 \omega^2}{4} \quad (1)$$

whereas r is the radius, ω is the rotating speed of the capillary tube and $\Delta\rho$ is the density difference. The density difference $\Delta\rho$ were estimated from the experiments performed with a U-tube density meter. It is necessary that the length of the droplet is four times larger than the width so that Eq. (1) can approximate the interfacial tension as its best. During measurements the rotating speed was varied from five to nine thousand rpm to get a better average of the interfacial tension. The reproducibility of the apparatus used was evaluated to be $\sigma^{\text{LLE}} = \pm 0.05 \text{ mN m}^{-1}$ and $\Delta T = \pm 0.03 \text{ K}$.

3 Theory

3.1 Incompressible Density Gradient Theory (inc-DGT)

The density gradient theory [8, 9] was originally developed for the description of the interface between a vapor and a liquid phase for pure components. Therefore, it needs to be combined with an equation of state due to the fact that the density is the only property, which changes continuously across the interface. However, the assumption of incompressible fluids is valid due the fact, that the LLE does not depend on pressure and therefore just the concentration changes during the interface. In this case, the density

gradients in the inhomogeneous region will be replaced by concentration gradients and the inhomogeneous region within the interface can be described by the Gibbs energy, g . This incompressible consideration [7] comes with the advantage that the Gibbs energy, g , can be described with a thermodynamic model for the activity coefficients (g^{E} -model), which are superior in the description of systems, which inhabit a liquid-liquid phase split. For ternary mixtures the expressions for calculating the interfacial tension is given by [22, 23]:

$$\sigma^{\text{LLE}} = \int_{x_1^{\text{I}}}^{x_1^{\text{II}}} \sqrt{\bar{\kappa} \Delta g(x_1, x_2)} dx_1 \quad (2)$$

where x_1^{I} is the bulk mole fraction of component 1 in phase I, x_1^{II} is the bulk mole fraction of component 1 in phase II, $\bar{\kappa}$ is the influence parameter of the ternary mixture and Δg the difference between the Gibbs energy of the inhomogeneous and the homogeneous system. The influence parameter $\bar{\kappa}$ in case of a ternary mixture, with two binary subsystems showing liquid-liquid demixing (and that are the only systems considered here), is given by [22, 23]:

$$\bar{\kappa} = \kappa_{1,2} + \sqrt{\kappa_{1,2} \kappa_{1,3}} \left(\frac{\partial x_2}{\partial x_1} \right)_T + \kappa_{1,3} \left(\frac{\partial x_3}{\partial x_1} \right)_T^2 \quad (3)$$

whereas $\kappa_{1,2}$ is the influence parameter of the binary subsystem 1,2, which established a LLE and $\kappa_{1,3}$ refers to the binary subsystem 1,3, also showing liquid-liquid demixing. Furthermore, the inc-DGT allows calculating the mole fraction profiles inside the interface by [22, 23]:

$$z - z_0 = \frac{\int_{x_1^{\text{I}}}^{x_1(z)} \sqrt{\frac{\bar{\kappa}}{\Delta g}} dx_1}{\frac{x_1^{\text{I}} + x_1^{\text{II}}}{2}(z_0)} \quad (4)$$

In order to utilize Eqs. (2)–(4) in regard to calculate interfacial properties of demixed liquid-liquid systems, additionally, a suitable model for the Gibbs energy of mixing is required. The used one is presented in the following.

3.2 Non Random Two Liquid model (NRTL-model)

The application of the NRTL-model for the studied mixture was suggested by Schmitt and Hasse [34]. The selected standard state for this model is the ideal mixture. In contrast, the model utilized by Grunert and Enders [23] for the description of water + 1-butanol + benzene to refer to the ideal-athermic mixture, where the size difference of the molecules are taken into account.

The NRTL-model for a mixture, containing NC components, reads:

$$\frac{g^E}{RT} = \sum_{i=1}^{NC} x_i \left(\frac{\sum_{j=1}^{NC} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{NC} G_{li} x_l} \right) \quad (5)$$

with

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \quad (6)$$

and

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (7)$$

Thereby, τ_{ij} is assumed to be temperature-dependent in the following way:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad (8)$$

The parameters of the NRTL-model, a_{ij} , b_{ij} , and α_{ij} were taken from the literature [34] for all binary subsystems and are listed in Tab. 1. The parameters were adjusted to binary data alone [34], in case of water + 1-hexanol and water + hexylacetate to binary LLE data, in case of 1-hexanol + hexylacetate to binary VLE data.

Table 1. Values of the NRTL-parameters for the binary subsystems water + 1-hexanol, water + hexylacetate and 1-hexanol + hexylacetate taken from the literature [34].

component <i>i</i> component <i>j</i>	water 1-hexanol	water hexylacetate	1-hexanol hexylacetate
a_{ij}	-0.1522	-1.7481	2.1656
a_{ji}	-3.177	-1.3148	-1.1818
b_{ij}	1945.07	3545.58	-174.40
b_{ji}	1381.31	998.70	236.42
$\alpha_{ij} = \alpha_{ji}$	0.3323	0.2	0.3

Table 2. Measured mole fractions in the organic phase (x_i^1) and the feed compositions (x_i^{feed}) in the ternary mixture water + 1-hexanol + hexylacetate at $T = 298.15$ K using gas chromatography.

Sample	$x_{\text{hexylacetate}}^{\text{feed}}$	$x_{1\text{-hexanol}}^{\text{feed}}$	x_{water}^1	$x_{1\text{-hexanol}}^1$	$x_{\text{hexylacetate}}^1$
I	0.01	0.09	0.2727	0.6566	0.0706
II	0.018	0.082	0.2285	0.6363	0.1351
III	0.025	0.075	0.2177	0.5901	0.1921
IV	0.08	0.02	0.0846	0.1789	0.7364
V	0.085	0.015	0.0725	0.1362	0.7911
VI	0.09	0.01	0.0701	0.0898	0.8401

The implementation of Eq. (5), together with the parameters provided in Tab. 1, permits the phase equilibrium calculation by equating the chemical potentials of every component present in the mixture in the coexisting phases. Additionally, the spinodal line, separating the meta-stable region from the instable region can be calculated with the help of the stability theory.

4 Results and Discussion

In order to access the interfacial properties with the inc-DGT in combination with an appropriate activity coefficient model, in a first step the LLE of the considered mixture must be known. In Fig. 2, the calculated LLE is depicted in comparison to experimental data of the ternary mixture, where the experimental data are collected in Tab. 2. Addi-

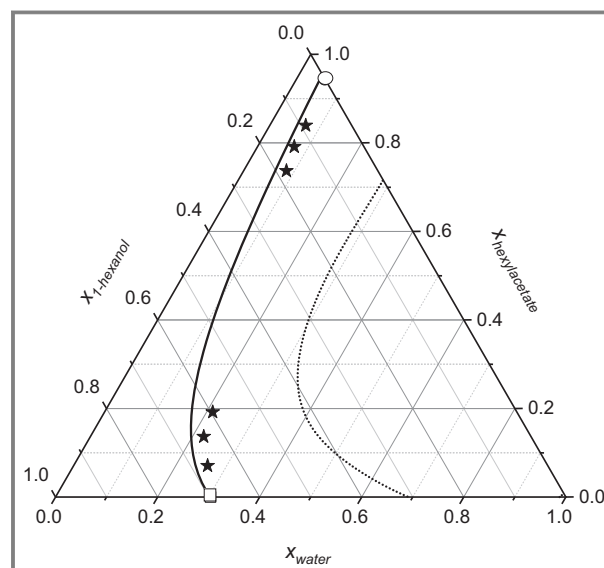


Figure 2. Comparison between experimental binodal points (stars, Tab. 2) and calculated LLE (solid line: binodal, dashed line: spinodal) using NRTL-model for the ternary system water + 1-hexanol + hexylacetate at $T = 298.15$ K, where the experimental data of the binary subsystems are included (squares [29], circles [30]).

tionally, the literature data [31, 32] of the corresponding binary subsystems are included in Fig. 2. The binary data from the literature [31, 32] and the measured ternary data in Fig. 2 fit nicely together.

In Fig. 2, only the binodal curve of the organic phase is visible due to the fact that it coexists with a nearly pure water phase, the solubility of 1-hexanol and hexylacetate in the water-rich phase is minimal. Detailed information regarding the solubility of 1-hexanol in water can be found in the literature [37]. According to our calculations, the solubility varies in the order of magnitudes 10^{-4} – 10^{-6} for the alcohol and in the

order of magnitudes 10^{-6} – 10^{-8} for the ester, depending on the considered tie line. As opposed to this, much higher mutual solubility occurs in the organic phase. As one can see in Fig. 2, the NRTL-model is very much capable of predicting the LLE, this holds true for the binary subsystems water + 1-hexanol and water + hexylacetate as well as the ternary mixture. This is remarkable judging from the fact that the parameters of the NRTL-model are adjusted to binary data alone [34]. In case of the binary subsystems water + 1-hexanol and water + hexylacetate they were adjusted to binary LLE data, for the binary subsystem 1-hexanol + hexylacetate to binary VLE data [34]. Having this in mind, the binodal curve is predicted very close compared to the experimental data points. The ternary mixture considered here, exhibits an open miscibility gap nearly over the whole ternary concentration range, showing no critical point at all. Only for very low values of the mole fraction of water the ternary mixture shows no liquid-liquid demixing phenomena. The mole fraction of water, where no liquid-liquid demixing occurs, ranges from $x_{\text{water}} = 0.045$ to $x_{\text{water}} = 0.3$, depending on the mole fraction of 1-hexanol. This can be explained by the molecular structure of the alcohol. It can act as a solubilizer between the polar water molecules and the non-polar ester molecules, containing a non-polar hydrocarbon chain and a polar hydroxy group itself. The higher the amount of 1-hexanol in the ternary mixture, the higher the amount of water can be, without the appearance of a liquid-liquid split up.

Grunert et al. [22] investigated the ternary system water + 1-butanol + benzene, which shows some similarities to the system investigated here. It also forms a closed miscibility gap, caused by the two miscibility gaps of two binary subsystems, namely water + 1-butanol and water + benzene. Compared to the ternary system water + 1-hexanol + hexylacetate the ternary miscibility gap of the system water + 1-butanol + benzene is much smaller. This is astonishing on a first sight, regarding that the ester (hexylacetate) is substituted by an aromatic compound (benzene), which is classified as a hydrocarbon. In other words, benzene is completely non-polar, whereas hexylacetate contains an ester group which is capable of participating in hydrogen bonding when present in mixtures with, for example, water. However, the smaller miscibility gap can be explained by the shorter hydrocarbon chain of 1-butanol compared to 1-hexanol. This also becomes obvious when comparing the binary subsystems water + 1-butanol and water + 1-hexanol at $T = 298.15$ K. The alcohol rich phase in the system water + 1-butanol nearly consists of fifty mole percentage of water [22], whereas in the system water + 1-hexanol, it only compromises approximately thirty mole percentage (Fig. 2). From this point of view, it's safe to say that the enlargement of the miscibility gap in the ternary mixture water + 1-hexanol + hexylacetate compared to the ternary mixture water + 1-butanol + benzene is mainly triggered by the extension of the hydrocarbon chain of the alcohol. From the theoretical point of view, both g^E -models (NRTL and Koningsveld

Kleintjens model [22]) belong to the class of semi-empirical models containing adjustable parameters. This situation can be explained by the different chosen standard state. Taking into account the size differences of the molecules for example relating the molecular masses of the molecules permits the saving of one adjustable parameter. Generally speaking, both models predicts the ternary LLE with high accuracy.

In a next step, the interfacial properties of the ternary mixture are investigated. Due to the fact that two binary subsystems showing liquid-liquid demixing, two binary influence parameters $\kappa_{i,j}$, namely $\kappa_{\text{water/hexanol}}$ and $\kappa_{\text{water/hexylacetate}}$, must be known in order to obtain the influence parameter of the ternary mixture $\bar{\kappa}$ according Eq. (3). Danzer et al. [19] adjusted the influence parameter $\kappa_{\text{water/hexanol}}$ and $\kappa_{\text{water/hexylacetate}}$ to one data point of the interfacial tension at $T = 298.15$ K to $\kappa_{\text{water/hexanol}} = 3.82 \cdot 10^{-7} \text{ J mol m}^{-4}$ and $\kappa_{\text{water/hexylacetate}} = 2.96 \cdot 10^{-7} \text{ J mol m}^{-4}$. With regard to the very accurate modelling results of interfacial properties in the binary systems water + 1-hexanol and water + hexylacetate from Danzer et al. [19], the influence parameters mentioned above were used in this work investigating the ternary mixture water + 1-hexanol + hexylacetate. However, it should be mentioned that the influence parameter of the ternary mixture, $\bar{\kappa}$, shows a dependency of the mole fraction gradients inside the interface (Eq. (3)), in other words it depends also on the applied activity coefficient model. Therefore, $\bar{\kappa}$ is not specified solely by the values of the influence parameters of the binary subsystems $\kappa_{\text{water/hexanol}}$ and $\kappa_{\text{water/hexylacetate}}$ (Eq. (3)).

In Fig. 3, the calculated interfacial tension as a function of the hexylacetate mole fraction in phase I (organic phase) is shown in comparison to experimental data points obtained from spinning-drop measurements performed also in this work. The experimental data (feed composition, interfacial tension and densities of the coexisting phases) are listed in Tab. 3. As it can be seen in Fig. 3 the combination NRTL + inc-DGT gives a very accurate description of the interfacial tension in the ternary mixture. As a matter of fact, this is no surprise regarding the binary subsystems water + 1-hexanol ($x_{\text{hexylacetate}}^I = 0$) and water + hexylacetate ($x_{\text{hexylacetate}}^I = 0.952$) due to the fact that the influence parameters $\kappa_{\text{water/hexanol}}$ and $\kappa_{\text{water/hexylacetate}}$ are adjusted to these interfacial tension data points of the binary subsystems. However, the trajectory of the interfacial tension in the ternary mixture ($0 < x_{\text{hexylacetate}}^I < 0.952$) is highly non-linear, but very well predicted using the combination of NRTL and inc-DGT. The deviations between modelling and experimental data slightly increases when approaching the binary subsystem water + hexylacetate (Fig. 3). This finding could have its origin in the description of the aqueous phase, considering the fact, that the organic phase is predicted very close to experimental data (Fig. 2). The solubility of 1-hexanol and hexylacetate in the water-rich phase is extremely low for all tie lines in the phase diagram [37] (Fig. 2), but especially low for tie lines near the binary subsystem water

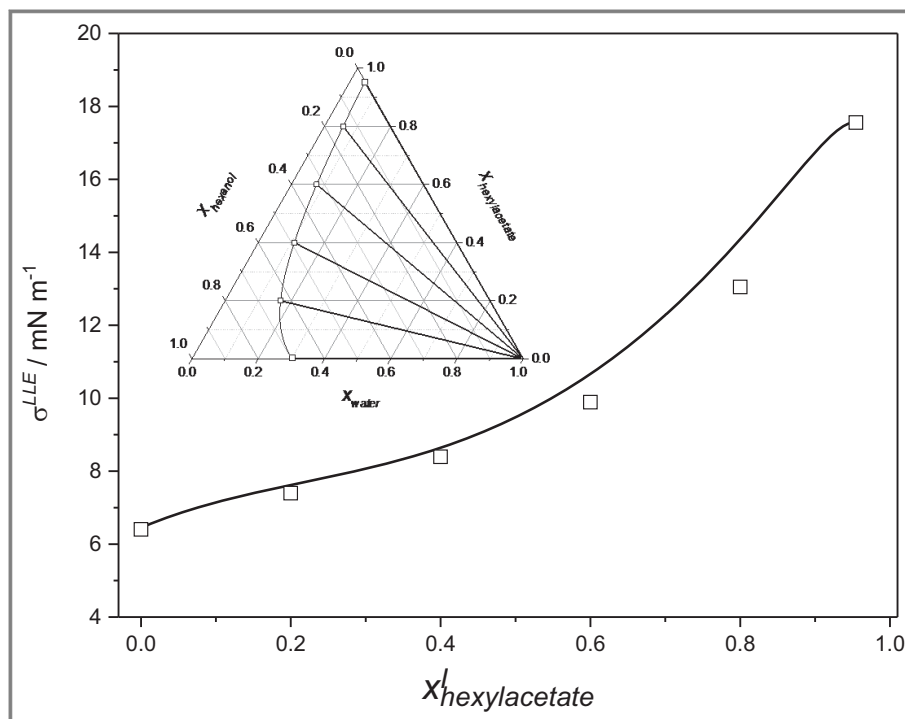


Figure 3. Comparison between experimental interfacial tension data (squares, Tab. 3) and calculated interfacial tension (solid line) using NRTL + inc-DGT in the ternary mixture water + 1-hexanol + hexylacetate at $T = 298.15$ K. In the left top corner the underlying LLE is illustrated, additionally the tie lines are depicted for which the interfacial tension was measured.

Table 3. Experimental data of the interfacial tension (σ^{LLE}), the densities of the light phase (ρ^{I}) and of the heavy phase (ρ^{II}) and the feed compositions (x_i^{feed}) in the ternary mixture water + 1-hexanol + hexylacetate at $T = 298.15$ K.

$x_{\text{water}}^{\text{feed}}$	$x_{\text{hexylacetate}}^{\text{feed}}$	σ^{LLE} [mN m ⁻¹]	ρ^{II} [g cm ⁻³]	ρ^{I} [g cm ⁻³]
0.9	0.024	7.39	0.996	0.839
0.9	0.045	8.39	0.995	0.848
0.9	0.065	9.89	1.018	0.877
0.9	0.085	13.04	1.007	0.872

+ hexylacetate. Danzer et al. [19] pointed out, that the prediction, or even the description, of this binodal curve is a huge challenge even for an activity-coefficient model, but can have a huge impact on the calculated the interfacial properties via inc-DGT.

Next up, the combination NRTL + inc-DGT is utilized to calculate the mole fractions profiles across the interfacial layer with spatial resolution in order to get insights of the enrichment phenomena in the ternary mixture investigated here. Danzer et al. [26] declared that enrichment phenomena in liquid-liquid systems are likely to happen, if the amount of substance of one component is rather small. Therefore, the mole fractions profiles with spatial resolution were calculated for tie lines near the binary subsystems water + 1-hexanol and water + hexylacetate. To begin with, Fig. 4

shows the mole fraction profiles of water, 1-hexanol and hexylacetate at $T = 298.15$ K for the tie line $x_{\text{hexylacetate}}^{\text{I}} = 0.001$ calculated with the combination NRTL + inc-DGT.

In Fig. 4 can be seen how the mole fractions of water, 1-hexanol and hexylacetate changes their values from bulk phase I ($z\Delta\rho = 0.15 \text{ mol m}^{-2}$) to bulk phase II ($z\Delta\rho = -0.025 \text{ mol m}^{-2}$) throughout the inhomogeneous region of the interface. Thereby, the trajectories exhibit the usual tangent hyperbolic curvature, $x_i = \tanh(z\Delta\rho)$, which can be explained theoretically and was already pointed out by Gibbs in the 19th century. The tangent hyperbolic curvature is clearly recognizable for the components water and 1-hexanol, but also holds true for hexylacetate, which becomes visible if amplified. As a consequence, no enrichment phenomena are encountered for this specific tie line, otherwise the mole fraction profile would develop a maximum or a minimum, depending on one component is enriched or degraded in the interfacial layer. As a matter of fact, no enrichment phenomena at all could be observed in the close proximity of the binary subsystem water + 1-hexanol. The absence of any enrichment phenomena near this binary subsystem can be explained considering the molecular structure of hexyl-

acetate. It's non-polar nature combined with it is high molecular weight does not admit an enrichment inside the interface, even at very small overall concentrations as depicted in Fig. 4. The water-rich phase is highly polar, whereas the water-poor phase is rather non-polar, containing mainly the long chain alcohol 1-hexanol. Hexylacetate itself is basically non-polar, so the enrichment inside the interface is not preferential. Instead, hexylacetate finds a suitable environment if distributed mainly in the water-poor phase. The calculated distribution coefficient, $K_{\text{hexylacetate}} = x_{\text{hexylacetate}}^{\text{I}}/x_{\text{hexylacetate}}^{\text{II}}$, which is $K_{\text{hexylacetate}} = 31645$ for the tie line $x_{\text{hexylacetate}}^{\text{I}} = 0.001$, confirms this statement. This very high value results from the limited solubility of the ester in the water-rich phase, which is according to our model $x_{\text{hexylacetate}}^{\text{II}} = 3.16 \cdot 10^{-8}$ for the considered tie line.

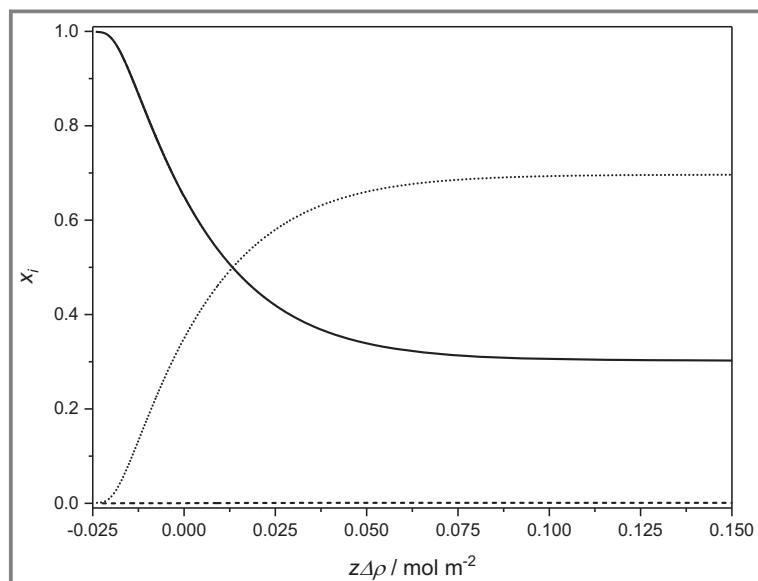


Figure 4. Calculated mole fraction profiles in the ternary mixture water, 1-hexanol and hexylacetate at $T = 298.15$ K for the tie line $x_{\text{hexylacetate}}^I = 0.001$ (bold line: water, dotted line: 1-hexanol, dashed line: hexylacetate) with the combination of NRTL + inc-DGT.

One can expect that another picture arises near the binary subsystem water + hexylacetate. For tie lines there, a highly polar water-rich phase coexists with a basically non-polar ester-rich phase. The alcohol, containing a polar hydroxy group and a non-polar hydrocarbon chain, would benefit from staying inside the interface, due to the fact that the different functional groups can align to the water-rich phase or the ester-rich phase, respectively. In Fig. 5, the mole fraction profiles of water, 1-hexanol and hexylacetate at $T = 298.15$ K are depicted for for the tie line $x_{\text{hexylacetate}}^I = 0.9$, calculated with the combination NRTL + inc-DGT. As expected, the mole fraction profile of 1-hexanol exhibits now a maximum, which corresponds to an enrichment of that component inside the interfacial layer. This finding is consistent with the modelling results of Grunert et al. [23] in the ternary mixture water + 1-butanol + benzene. Here [23], also the alcohol 1-butanol shows an enrichment inside the interface, being the component with both polar and non-polar functional groups. Comparing the magnitude of the enrichment phenomena of 1-hexanol in

the ternary mixture water + 1-hexanol + hexylacetate to 1-butanol in the ternary mixture water + 1-butanol + benzene [23], one can find that 1-hexanol exhibits a much larger maximum in the mole fraction profile inside the interface. This confirms some general statements concerning enrichment phenomena made by Danzer et al. [26], who pointed out, that the magnitude of enrichment is to be expected higher, the larger the miscibility gap is. If the overall concentration of the alcohol is increased, the magnitude of enrichment in the interface is decreasing, due to the fact, that the bulk phase becomes more and more favorable, with an increasing amount of that specific component. This could be observed in the ternary mixture water + 1-butanol + benzene [23], as well as in the ternary mixture water + 1-hexanol + acetic acid and water + hexylacetate + acetic acid [26].

The overall concentration of the alcohol for the tie line illustrated in Fig. 5 is rather small, which benefits the occurrence of enrichment effects in general. If the overall concentration of the alcohol would be higher, an increasing amount would distribute to the bulk phases, where the organic phase will absorb more 1-hexanol than the aqueous phase. Therefore, the alcohol would find a more and more desirable environment in the organic phases itself, which precludes any enrichment effect inside the inhomogeneous

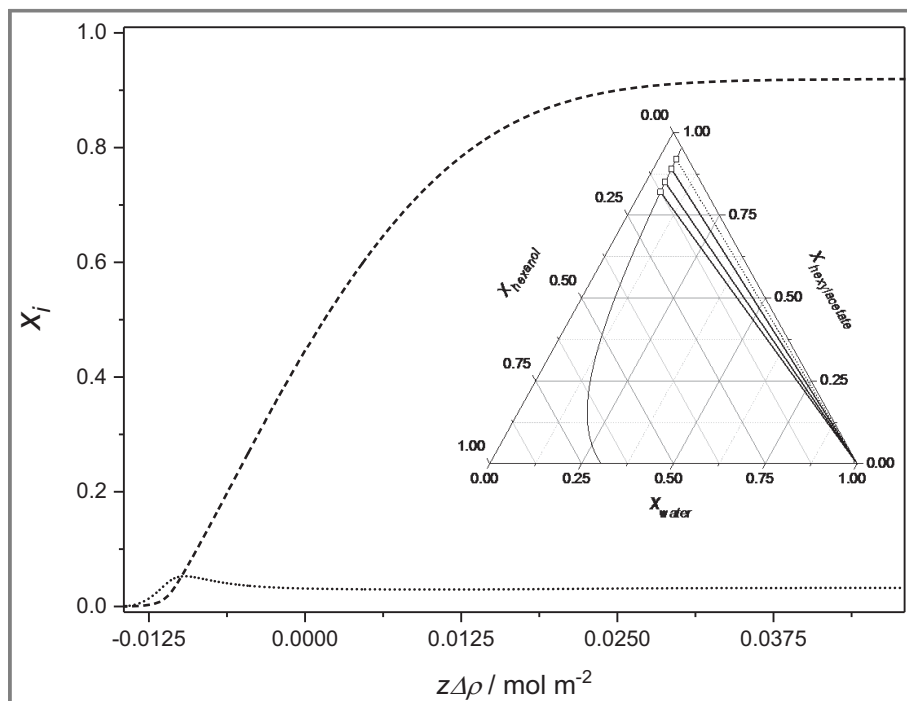


Figure 5. Calculated mole fraction profiles in the ternary mixture water (bold line), 1-hexanol (dotted line) and hexylacetate (dashed line) at $T = 298.15$ K for the tie line $x_{\text{hexylacetate}}^I = 0.92$ (dotted line in the insert) with the combination of NRTL + inc-DGT.

region of the interface. If these statements are correct, the enrichment effect of 1-hexanol near the binary subsystem water + hexylacetate should increase, if the mole fractions of hexylacetate in phase I, $x_{\text{hexylacetate}}^I$ increases too. This statement is supported by Fig. 6, in which it becomes clearly visible that the height of the maximum in the mole fraction profile of 1-hexanol compared to the bulk phase value in the organic phase is increasing if the mole fraction of hexylacetate in phase I is increasing. Another interesting fact is observed considering the interfacial tension for the tie lines shown in Fig. 6. If the mole fraction of hexylacetate in the organic phase ($x_{\text{hexylacetate}}^I$) is increasing, the binary subsystem water + hexylacetate is approached, therefore the mole fraction of 1-hexanol is decreasing. Nevertheless, the interfacial tension is increasing (Fig. 3). This can be explained simply by the fact that the highest interfacial tension in the system water + 1-hexanol + hexylacetate emerges in the binary subsystem water + hexylacetate. Therefore, it is possible that the interfacial tension increases with decreasing mole fraction of the alcohol.

Furthermore, the mole fraction profiles of 1-hexanol, illustrated in Fig. 6, show a minor minimum, additionally to the already discussed distinct maximum. Considering the fact, that hexylacetate has also a very low polarity and is also able to enrich at the interface. Therefore, hexylacetate can displace 1-hexanol. The minimum, depicted in Fig. 6, was not found in the mixture studied by Grunert and Enders [23]. Probably, the reason for this contrast lies in small difference in polarity of hexylacetate and benzene. However, this explanation needs a verification and requires the investigation of several other mixtures. To the best of our knowledge, the

occurrence of a maxima and simultaneously a minimum for one component was never before observed.

5 Summary

The experimental data base regarding the studied mixture water + hexylacetate + 1-hexanol were enlarged in terms of liquid-liquid equilibria and interfacial tension. The ternary LLE data fits to the already available binary data [31, 32]. Both properties could be predicted with a high accuracy, where the prediction of the miscibility gap was carried out with the NRTL-model with parameters taken from the literature [34]. For the prediction of the interfacial tension, the NRTL was inserted in the incompressible density gradient theory, where the necessary influence parameter were also taken from the literature [19]. The studied mixture shows very similar properties like the mixture water + 1-butanol + benzene, already investigated in the literature [23]. The common features are the shape of the miscibility gap running from one binary subsystem to the other binary subsystem. The extent of the miscibility gap depends strongly from the chain-length of the alcohol. The experimental as well as the predicted interfacial tensions depend on the concentration of the coexisting organic phase in a non-linear fashion. However, the interfacial profiles are different. In the mixture water + 1-butanol + benzene, always an enrichment of 1-butanol was predicted. In contrast, the concentration profile of 1-hexanol shows also a maxima, but also a slight minima. A possible explanation is the different polarity of benzene and hexylacetate. Hexylacetate carries a polar

group and can also be enriched in the interface. It is assumed that hexylacetate displaces 1-hexanol inside the interface resulting in the observed minimum in the mole fraction profile of the alcohol.

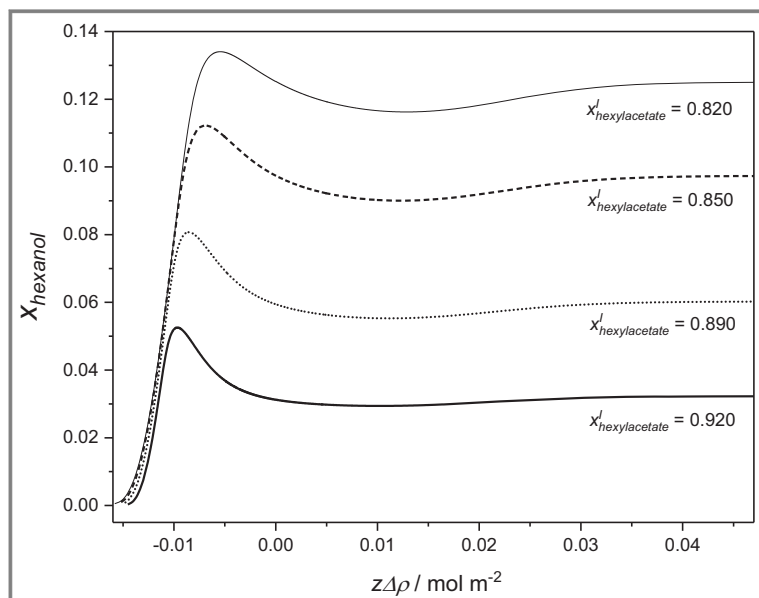


Figure 6. Calculated mole fraction profiles of 1-hexanol in the ternary mixture water, 1-hexanol and hexylacetate at $T = 298.15 \text{ K}$ for four different tie lines (solid line: $x_{\text{hexylacetate}}^I = 0.92$, dotted line: $x_{\text{hexylacetate}}^I = 0.89$, dashed line: $x_{\text{hexylacetate}}^I = 0.85$, thin line: $x_{\text{hexylacetate}}^I = 0.8205$) with the combination NRTL + inc-DGT. The tie lines are plotted in the insert of Fig. 5.

Symbols used

a	[-]	model parameter NRTL
b	[K]	model parameter NRTL
d	[m]	diameter
f	[J mol ⁻¹]	helmholtz energy
g	[J mol ⁻¹]	gibbs energy
G	[-]	model parameter NRTL
K	[-]	distribution coefficient
P	[Nm ⁻²]	pressure
T	[K]	temperature
\dot{V}	[m ³ s ⁻¹]	volume flow rate
x_i	[-]	mole fraction
$z\Delta\rho$	[mol m ⁻²]	interfacial coordinate

Greek symbols

α	[-]	model parameter NRTL
κ	[J mol ⁻⁴]	influence parameter
ρ	[kg m ⁻³]	density
σ	[Nm ⁻¹]	interfacial tension
τ	[-]	model parameter NRTL
ω	[s ⁻¹]	rotating speed

Abbreviations

DGT	density gradient theory
inc-DGT	incompressible density gradient theory
KK	Koningsfeld-Kleintjens
LLE	liquid-liquid equilibrium
NRTL	non random two liquid
VLE	vapor-liquid equilibrium

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Liquid-Liquid Equilibrium and Interfacial Properties of the System Water + Hexylacetate + 1-Hexanol

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Research Article: The phase behavior and interfacial properties in the ternary mixture water + 1-hexanol + hexylacetate are investigated both experimentally and theoretically. Whereas the experimental data could be predicted with high accuracy, also an enrichment of 1-hexanol in the interfacial layer could be observed.

