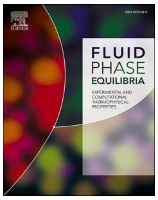
Fluid Phase Equilibria 582 (2024) 114104

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.journals.elsevier.com/fluid-phase-equilibria



Liquid-liquid equilibria and the interfacial properties of the ternary mixtures water + n-propanol + n-butyl acetate and water + n-butanol + n-butyl acetate

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ARTICLE INFO

Keywords:
Density gradient theory
NRTL model
Liquid-liquid equilibrium of ternary mixtures
Interfacial tension of ternary mixtures
Relative enrichment in the interface
Interfacial concentration profiles

ABSTRACT

In this work, a modified version of the Density Gradient Theory is used to predict the interfacial properties of two industrially relevant systems consisting of water + n-propanol + n-butyl acetate and water + n-butanol + n-butyl acetate and their demixing binary subsystems water + n-butanol and water + n-butyl acetate. Liquid-liquid equilibrium is calculated by applying the NRTL model. Through the combination of the NRTL model with the modified version of the Density Gradient Theory, the interfacial tension and the interfacial concentration profiles of the considered ternary mixtures are predicted based on the influence parameters of the binary demixed subsystems. It can be deduced that the predictions of the interfacial tension of both investigated ternary systems are trusted and experimental data sets from this work are in excellent agreement with the predictions. Phenomena like the selective enrichment of the solubilizing component in the interface are observed.

1. Introduction

The Working Party on Thermodynamics and Transport Properties of the European Federation of Chemical Engineering has recently published a paper [1] discussing the future of applied thermodynamics. In this paper [1], it is stated that: "The global challenges related to water, health, energy, and waste management open up new needs. These may be related not only to the types of mixtures (in particular bio-based molecules and electrolytes) but also to different properties that require innovative and accurate tools. In particular, properties under confinement and at interfaces or in the presence of external fields as well as transport and nonequilibrium phenomena require increased interest."

The change in feedstock, namely from fossil, like petroleum or crude oil, to renewable feedstocks requires modified separation technologies. One example is the production of platform chemicals, like alcohols, where liquid-liquid extraction is discussed for purification purposes. The liquid-liquid extraction relies on the liquid-liquid equilibrium (LLE) of the involved systems and mixtures. The interfacial tension between the coexisting phases, σ^{LLE}, is an important design parameter [2,3]. The current paper deals with the modeling of the LLE and the prediction of the interfacial tension, σ^{LLE}, for ternary mixtures, which play a significant role in the change in feedstock described above. Concerning these calculations, a thermodynamic model, which properly considers and describes the non-idealities in the liquid phases, is required. The abovementioned working party made the following statement related to the selection of a suitable thermodynamic model [1]: "Predictive modeling: An essential step in the industrial applications of thermodynamics is the selection and parameterization of an appropriate model in a process simulator. This choice is however far from straightforward. The answer will depend on the scope of the simulation task, the mixture at hand, the operating conditions, and most importantly, the availability of data for validation. Each of these issues should be further investigated, but it appears that industry prefers to have a "predictive" approach that works accurately for a large range of conditions."

Due to of the extremely small compressibility of liquid mixtures, an activity coefficient model should be selected. The Working Party [1] wrote: "Local composition models like NRTL and UNIQUAC are also useful as tools for multicomponent systems once binary parameters are available. All these models are still much used by industry, and there is a clear understanding that having a single predictive model for all applications is most likely an impossible task. Many companies have still traditional views on the model choice with the first category of the aforementioned models (cubic EoS, local-composition activity coefficients models) being far more used than the latter ones (association

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https://doi.org/10.1016/j.fluid.2024.114104
Received 5 February 2024; Received in revised form 27 March 2024; Accepted 15 April 2024

EoS and COSMO-RS), even if the latter ones are getting more popular. In this context, it is worth noting that these latter methods offer better prospects for multifunctional and complex materials, like bio-based and “smart” materials, and therefore may attract increased attention in the future."

Following these guidelines, the present paper deals with the calculation of the LLE and simultaneously the prediction of the interfacial tension for two ternary mixtures: a) water +n-butanol + n-butyl acetate and b) water + n-propanol + n-butyl acetate. Both mixtures show different miscibility behaviors. The selected mixture a) contains two binary subsystems having a miscibility gap, namely water + n-butanol and water + n-butyl acetate. In contrast, the selected mixture b) is composed of components, where only one binary subsystem (water + n-butyl acetate) shows a miscibility gap. Concerning the predictions to be made, an approach should be selected for an industrial application. Therefore, the thermodynamic model should be as simple as possible. The model parameters should be fitted only to binary experimental data. However, this is not possible for the selected mixtures, given that binary subsystems, which are homogeneous, are also considered. Therefore, the parameters describing these binary subsystems must be adjusted to ternary LLE data. The requirement for the application of only parameters fitted to binary subsystems can be fulfilled for the calculation of the interfacial properties by applying the modified or incompressible density gradient theory [4] in combination with a simple model for the excess Gibbs energy of mixing, g^E, which must be able to describe the real and non-ideal behavior of the involved systems. The modification of the density gradient theory of interfaces [5] consists of expanding the Gibbs energy of a nonuniform system, rather than its Helmholtz energy, in a Taylor series about the Gibbs energy of a solution of uniform concentration. The advantage of this approach is that a g^E-model, rather than an EoS, can now be applied for the calculation of the interfacial properties of systems and mixtures. Furthermore, the modification leads to several numerical simplifications [4]. The latter theoretical framework was already applied for binary [4,6–13], ternary [7,8,10,14–17], and quaternary mixtures [18,19] using different thermodynamic models for g^E. Recently, the dynamics of the interfacial properties due to chemical reaction [20–23], diffusion [19,24,25], or both [26,27] were studied by applying the modified density gradient theory. In this paper, we use the NRTL-model [28], given that some parameters, differing in the assumed temperature dependency, for the studied binary subsystems showing a miscibility gap are already available in the literature [29–31]. Those for the remaining binary systems were adjusted in this work to ternary LLE experimental data points.

Concerning the studied mixtures, some experimental data for the phase behavior and/or interfacial tension are available in the literature. Rao and Rao [32] and Costa et al. [33] measured the LLE, densities, viscosities, and interfacial tensions for the water + n-propanol + n-butyl acetate mixture. Ruiz Bevia et al. [29], Grob and Hasse [30], and Samarov et al. [34] investigated the LLE for the water +n-butanol + n-butyl acetate mixture. There are two binary subsystems in both considered ternary mixtures showing a miscibility gap, namely water +n-butanol and water + n-butyl acetate [29]. LLE experimental data of both binary systems water + n-butanol [35–38] and water + n-butyl acetate [30,37] are also available in the literature.

In addition, and concerning interfacial tensions, measurements for both binary demixed subsystems (water +n-butanol [8,9,39,40] and water + n-butyl acetate [39,41–44]) and for the ternary system water + n-propanol + n-butyl acetate [44] are found in the literature. However, and to the best of our knowledge, no experimental data regarding the interfacial tension for the ternary mixture water + n-butanol + n-butyl acetate are found in the literature. Therefore, experimental measurements were carried out by using the spinning-drop method for interfacial tension measurements and an oscillating U-tube for density measurements. These experiments were conducted not only for the ternary system of interest, namely water + n-butanol + n-butyl acetate, but also for all the other demixed binary and ternary mixtures to validate the experiments found in the literature [9,39–44]. Moreover, and by applying the theoretical framework described in the present paper, the interfacial concentration profiles and related enrichment effects in the interface can be calculated and predicted. The various impacts of the relative enrichment of one component in the inhomogeneous region are also discussed.

2. Experiments

Interfacial tensions and densities of the light (organic) and heavy (aqueous) bulk phases were measured for both studied demixed binary and ternary mixtures in this work. Interfacial tensions and phase densities at given temperatures were measured for the demixed binary mixtures water + n-butanol and water + n-butyl acetate. Concerning the ternary mixtures, these properties were acquired for the ternary mixture water +n-propanol + n-butyl acetate at 303.15 K over the whole concentration range where liquid-liquid phase separation is observed, starting from the binary subsystem water + n-butyl acetate up to the critical point of the system, and for the ternary mixture water + n-butanol + n-butyl acetate at 298.15 K starting from the binary subsystem water + n-butanol up to the binary subsystem water + n-butyl acetate. A spinning-drop tensiometer and an oscillating U-tube were used for experimentations.

2.1. Chemicals

All used chemicals are listed in Table 1. The chemicals were purchased from Sigma-Aldrich Chemie GmbH, Germany, and used without further purification. Furthermore, double distilled water was used for the experiments. Before mixing the pure substances and preparing the experimentally investigated mixtures, they were degassed for 10 min by using a Bandelin ultrasonic bath Sonorex RK150. In addition, it is important to give the prepared samples enough time so that the corresponding LLE is properly reached. Therefore, the mixtures were placed in a tempered water quench for 48 h. After phase separation has occurred, the bulk phases were removed with different syringes to measure phase densities and interfacial tensions.

2.2. Density measurements

To experimentally investigate interfacial tensions, the bulk phase densities of the mixtures at LLE have to be measured first. The density measurements in this work are carried out with an oscillating U-tube Anton Paar DMA 38. The measuring cell has a volume of 0.7 ml. The two open ends of the U-tube are firmly clamped. The vibration frequency of the oscillating U-tube is a direct function of the sample’s density. Before each experiment, the oscillating U-tube was calibrated with two substances, water, and air, with known densities at given temperatures. The apparatus has an accuracy of 1 mg/cm^3. During measurements, the temperature was maintained constant to within ±0.1 K.

2.3. Interfacial tension measurements

The interfacial tension between two liquid phases, σ^{LLE}, is measured in this work with a spinning-drop tensiometer SVT 20N from DataPhysics. The tempered and rotating fast exchange capillary tube FEC 622/400-HT has an outer diameter of 6.22 mm and an internal diameter

Table 1
Used chemicals for the conducted experiments.

Chemical	CAS	Purity /wt%
n-propanol	71–23–8	99.7 (water-free)
n-butanol	71–36–3	99.9
n-butyl acetate	123–86–4	99.5 (ReagentPlus)

of 4.0 mm. It fully contains the liquid phase with the higher density and approximately 1 μl of the fluid from the lower density phase which forms a droplet in the rotating capillary. This droplet is rotating at very high speed around its longitudinal axis, so that, in this case, the gravitational force can be neglected. Therefore, only two forces are acting on the rotating droplet: the centrifugal force and the interfacial force. While rotating, the droplet is stretched along the direction of its rotational axis. However, and due to the interfacial force, the droplet tends to take a spherical shape to shrink into the minimum surface area possible. At mechanical and gyrostatic equilibrium, the interfacial tension is given by the Vonnegut equation [45]:

$$\sigma^{LLE} = \frac{\Delta\rho \cdot r^3 \cdot \omega^2}{4} \tag{1}$$

where $\Delta\rho$ is the density difference between both liquid phases, r the radius of the droplet, and ω the angular velocity. The shape of the rotating droplet is obtained by the camera of the spinning-drop tensiometer, and the software determines the droplet radius from the number of pixels registered by the camera. Furthermore, the density difference $\Delta\rho$ is measured by the oscillating U-tube described in subsection 2.2. The angular velocity should be adjusted in such a way that the ratio of droplet length to droplet radius takes a value of at least four. In this case, a cylindrical shape can be assumed and Eq. (1) can thus be applied, given that the Vonnegut equation [45] is derived by assuming a cylindrical shape of the droplet. Therefore, the rotational speed of the capillary was varied between 1000 and 5000 rpm. The used tensiometer can measure interfacial tensions within ±0.05 mN/m, at temperatures within ±0.01 K. The obtained experimental data are collected in Tables 2–5.

3. Theory

By applying the NRTL model, g^E is given by the following expression [28]:

$$\frac{g^E}{RT} = \sum_{i=1}^{n} x_i \left(\frac{\sum_{j=1}^{n} \tau_{ij} G_{ij} x_j}{\sum_{k=1}^{n} G_{ik} x_k} \right) \tag{2}$$

where R is the universal gas constant, T the temperature and n the number of components in the mixture. Furthermore, τ_{ij} is defined as [28]:

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \tag{3}$$

and [28]:

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{4}$$

The parameter α_{ij} in Eq. (4) is a constant which is a characteristic of the non-randomness of the mixture ($\alpha_{ij} = \alpha_{ji}$). The parameters g_{ij} and g_{jj} in Eq. (3) describe the energies of interaction between a $i - j$ pair of different molecules and a $j - j$ pair of similar molecules in the mixture, respectively. The difference between the energies of interaction of different and similar molecules in Eq. (3) is considered in this work as a temperature-dependent parameter and is given by the following equation [31]:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}\mathrm{K}}{T} + c_{ij}\ln\left(\frac{T}{\mathrm{K}}\right) + d_{ij}\left(\frac{T}{\mathrm{K}}\right) \tag{5}$$

Table 2
Experimental data of the interfacial tension, σ^{LLE}, the density of the aqueous phase, ρ^I, and the density of the organic phase, ρ^{II}, for the binary system water +n-butanol at 298.15 K.

σLLE[mN/m]	ρ^I [g/cm^3]	ρ^{II} [g/cm^3]
1.69	0.985	0.844

Table 3
Experimental data of the interfacial tension, σ^{LLE}, the density of the aqueous phase, ρ^I, and the density of the organic phase, ρ^{II}, for the binary system water + n-butyl acetate at different temperatures.

σLLE[mN/m]	T [K]	ρ^I [g/cm^3]	ρ^{II} [g/cm^3]
12.9	298.15	0.996	0.877
12.58	303.15	0.995	0.872
12.06	313.15	0.991	0.862

Table 4
Experimental data of the interfacial tension, σ^{LLE}, the density of the aqueous phase, ρ^I, and the density of the organic phase, ρ^{II}, for different feed compositions, x_i^{feed}, of the ternary system water + n-propanol + n-butyl acetate at 303.15 K.

Xfeedwater	$x_{n-propanol}^{feed}$	σ^{LLE} [mN/m]	ρ^I [g/cm^3]	ρ^{II} [g/cm^3]
0.83	0.025	8.19	0.988	0.869
0.749	0.138	2.58	0.977	0.861
0.738	0.199	0.75	0.969	0.869

Table 5
Experimental data of the interfacial tension, σ^{LLE}, the density of the aqueous phase, ρ^I, and the density of the organic phase, ρ^{II}, for different feed compositions, x_i^{feed}, of the ternary system water + n-butanol + n-butyl acetate at 298.15 K.

xfeedwater	$x_{n-butyl\ acetate}^{feed}$	σ^{LLE} [mN/m]	ρ^I [g/cm^3]	ρ^{II} [g/cm^3]
0.9	0.03	3.15	0.989	0.853
0.88	0.071	5.31	0.991	0.863
0.86	0.12	9.65	0.993	0.872

where a_{ij}, b_{ij}, c_{ij} and d_{ij} are adjustable parameters that are fitted to equilibrium data. There are consequently nine adjustable parameters needed per binary system to describe a LLE using this form of the NRTL model. The adjustable NRTL parameters of the binary subsystems water + n-butyl acetate and water + n-butanol were taken from the literature [31], where they were fitted to binary LLE experimental data from Grob and Hasse [30] and from the Dortmund Data Bank. They are portrayed in Table 6. Those of the binary systems consisting of n-butyl acetate + n-butanol, water + n-propanol, and n-butyl acetate +n-propanol were estimated in this work by fitting them to ternary LLE experimental data from the literature [29,30,32–34]. Concerning the mathematical adjustment procedure, the least-squares method was applied and the following objective function (OF) that minimizes the difference of the composition values is used as an optimization tool:

$$\mathrm{OF} = \sum_{t=1}^{n_t} \sum_{i=1}^{n} \left[\left(x_{i,t}^{I,exp} - x_{i,t}^{I,cal} \right)^2 + \left(x_{i,t}^{II,exp} - x_{i,t}^{II,cal} \right)^2 \right] \tag{6}$$

where n_T is the number of tie-lines in the corresponding phase diagram

Table 6
Binary NRTL-parameters (Eqs. (4),(5)) for the binary subsystems water + n-butyl acetate and water + n-butanol taken from the literature [31].

Component i Component j	Water n-butyl acetate	Water n-butanol
a_{ij}	3554.89	35.867
a_{ji}	776.64	−0.1115
b_{ij}	−98,998.5	−3875.12
b_{ji}	−23,696.4	−5192.21
c_{ij}	−613.04	−1.838
c_{ji}	−130.77	7.599
d_{ij}	0.9254	−0.0297
d_{ji}	0.1666	−0.0825
$\alpha_{ij} = \alpha_{ji}$	0.25	0.45

and corresponding temperature, *I* refers to the aqueous phase and *II* to the organic one. The outer sum thus runs over all tie-lines and the inner sum over all components in the considered mixture. For the LLE calculations, the parameters of the binary subsystems showing a miscibility gap were taken from Table 6. The NRTL binary parameters estimated by this fitting procedure are presented in Table 7. The corresponding binary mixtures do not exhibit a miscibility gap. Therefore, the parameters c_{ij} and d_{ij} in Eq. (5) are not considered and will be set to zero.

$$\sigma^{LLE} = \int_{x_1^I}^{x_1^{II}} \sqrt{2\kappa' \Delta\Omega(x_1, x_2)}\, dx_1 \tag{7}$$

where x_1^I is the bulk mole fraction of component 1 in phase *I* and x_1^{II} the one in the coexisting bulk phase *II*. $\Delta\Omega$ is the grand thermodynamic potential, which can be calculated by using the applied thermodynamic model. The quantity κ' in Eq. (7) is related to the concentration gradients in the interface:

$$\kappa' = \kappa_{12}\left(\frac{dx_2}{dx_1}\right)^2 + \kappa_{13}\left(\frac{dx_3}{dx_1}\right)^2 \tag{8}$$

The parameters κ_{12} and κ_{13} in Eq. (8) are the influence parameters of the binary subsystems exhibiting a miscibility gap. Therefore, their values can be estimated by using the interfacial tension of the binary subsystems consisting of components 1 and 2, and components 1 and 3, respectively. For ternary mixtures, in which only one binary subsystem shows a miscibility gap, only one value of κ for the binary subsystem that demixes is needed for the calculation of the interfacial properties of the ternary system [7,8]. In that case, κ' is given by: $\kappa' = \kappa_{12}$. This applies to the ternary mixture water + n-propanol + n-butyl acetate. However, two values of κ are required for the second ternary mixture water + n-butanol + n-butyl acetate. It is also important to mention that κ' in Eq. (8) has units of Jmol/m^4, since the incompressible version of the DGT is applied. In the original framework of the DGT, the so-called influence parameter κ has units of Jm^5/mol^2 given that the density cannot be calculated with a g^E model. Furthermore, the interfacial concentration profiles can also be predicted by applying the DGT. The concentration profiles are given by the following expression:

$$z = z_0 + \int_{x_1^I}^{x_1(z)} \sqrt{\frac{\kappa'}{2\Delta\Omega(x_1, x_2)}}\, dx_1 \tag{9}$$

in which the reference coordinate, z_0, can be set to zero at $x_1(z_0) = \frac{x_1^I + x_1^{II}}{2}$ and the mole fraction $x_1(z)$ varies between both bulk concentrations. Thus, any value of the mole fraction inside the interface can be assigned to one spatial coordinate. By applying the incompressible version of the DGT, the calculated spatial coordinate *z* has units of mol/m^2. To obtain the interfacial coordinate in m, *z* has to be divided by the difference between the molar densities of the coexisting liquid phases. In addition, the molar fractions of all three components in the interface at LLE for a ternary mixture with two demixing binary subsystems are calculated by solving the following equation:

$$\sqrt{\kappa_{12}}\left(\frac{d\Delta\Omega}{dx_3}\right)_{x_2} = \sqrt{\kappa_{13}}\left(\frac{d\Delta\Omega}{dx_2}\right)_{x_3} \tag{10}$$

In the case of a ternary mixture with only one demixing binary subsystem, the interfacial molar fractions are obtained by solving the following equation:

$$\left(\frac{d\Delta\Omega}{dx_3}\right)_{x_2} = 0 \tag{11}$$

The grand thermodynamic potential is given for a ternary mixture by:

$$\Delta\Omega = g_0 - \sum_{i=1}^{3} x_i \mu_i^e \tag{12}$$

in which g_0 is the Gibbs energy of a homogeneous solution and the superscript *e* refers to the equilibrium value of the corresponding parameter. Thus, μ_i^e is the equilibrium chemical potential of component *i*.

Eqs. (7) and (9) are also applied for the predictions concerning binary mixtures that demix.

Table 7
Binary NRTL-parameters (Eqs. (4,5)) for the binary subsystems n-butyl acetate + n-butanol, water + n-propanol and n-butyl acetate + n-propanol estimated in this work by using Eq. 6 and ternary LLE data from the literature [29,30,32–34].

Component *i* Component *j*	n-butyl acetate n-butanol	Water n-propanol	n-butyl acetate n-propanol
a_{ij}	−2.7698	3.29014	5.91718
a_{ji}	3.1367	−1.49266	−3.67244
b_{ij}	894.7	−119.623	−1107.03
b_{ji}	−1618.76	431.795	886.271
$c_{ij} = c_{ji}$	0	0	0
$d_{ij} = d_{ji}$	0	0	0
$\alpha_{ij} = \alpha_{ji}$	0.4	0.425228	0.289351

For a ternary mixture, the interfacial tension, σ^{LLE}, is given by [7,8]:.

4. Results and discussion

4.1. Binary mixtures

4.1.1. water + n-butanol

In this paper, the NRTL parameters of the system water + n-butanol are adjusted to LLE data in [31] and presented from Table 6. Fig. 1 depicts the calculated LLE of the binary system water + n-butanol in a temperature-mole fraction diagram, compared to three experimental data sets from the literature [35,36,38]. As can be seen in Fig. 1, this system shows a phase behavior with an upper critical solution temperature, portrayed by the calculated critical point using the NRTL model. Furthermore, it can be deduced from Fig. 1 that the solubility of the alcohol in the water-rich phase is very low and hardly depends on temperature, whereas the solubility of water in the alcohol-rich phase increases significantly with temperature. The low solubility of the alcohol in the water-rich phase results from the highly nonpolar character of the carbon group of n-butanol. However, the hydroxyl group of n-butanol can form hydrogen bonds with the water molecules, thus contributing to the highly nonideal behavior of the binary water + n-butanol system. This observation was also deduced by Danzer and Enders [13] which calculated the LLE of the binary mixture water + n-butanol by applying the UNIQUAC activity coefficient model [46]. The application of the PC-SAFT EoS, where the self- and the cross-association are included, requires a quadratic temperature dependency for the binary interaction parameter to properly describe the LLE [13]. In addition, experimental data are reproduced over a significant range of temperatures in very good agreement with the calculations by the NRTL model. Nevertheless, the critical point, at approximately 400 K, is slightly underestimated by the g^E-model. This causes, however, no problem concerning thermal extraction processes since they are performed at temperatures way below the critical one.

Further deviations can also be observed at temperatures below 300 K due to the solid-liquid equilibrium (SLE) located at temperatures below 270 K. Grunert et al. [8] studied the system water + n-butanol using the Koningsveld-Kleintjens model [47] and came to the same conclusion.

Based on the calculated phase equilibrium (Fig. 1), the next step will be to investigate the interfacial tension of the binary water + n-butanol mixture. To do so, the influence parameter of the binary subsystem, κ_{ij}, must be determined. Predicting interfacial properties through the

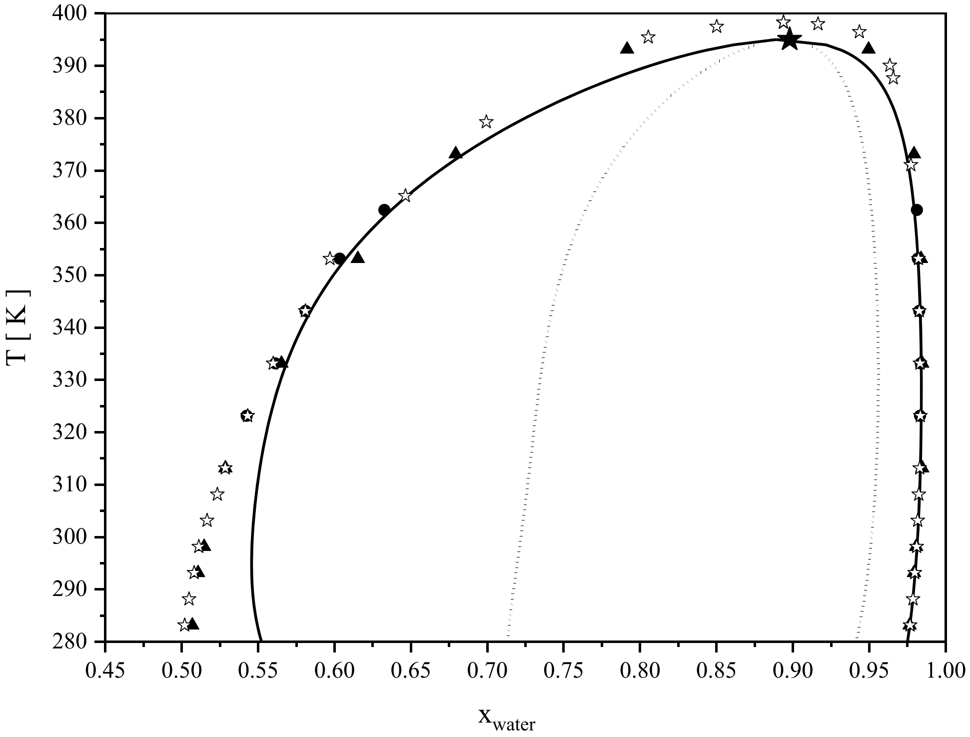

Fig. 1. Comparison between the calculated phase diagram using NRTL and the parameters in Table 6 (solid line: binodal line, dotted line: spinodal line, solid star: critical point) and experimental data taken from the literature (solid triangles [35], open stars [36], solid circles [38]) of the binary system water + n-butanol.

combination of the NRTL model with Eq. (7) requires the adjustment of the influence parameter to one interfacial tension experimental data of the binary system at a given temperature. Fig. 2 shows the calculated interfacial tension of the water + *n*-butanol mixture compared to experimental data from the literature [9,40], as well as from own measurements (Table 2). In their work, Cárdenas et al. [9] used an oscillating U-tube to measure bulk densities and a spinning-drop tensiometer to measure interfacial tensions of n-alkanol + water and ether + water demixed mixtures. The authors [9] also studied the binary system water + n-butanol and used the NRTL model in combination with Eq. (7)

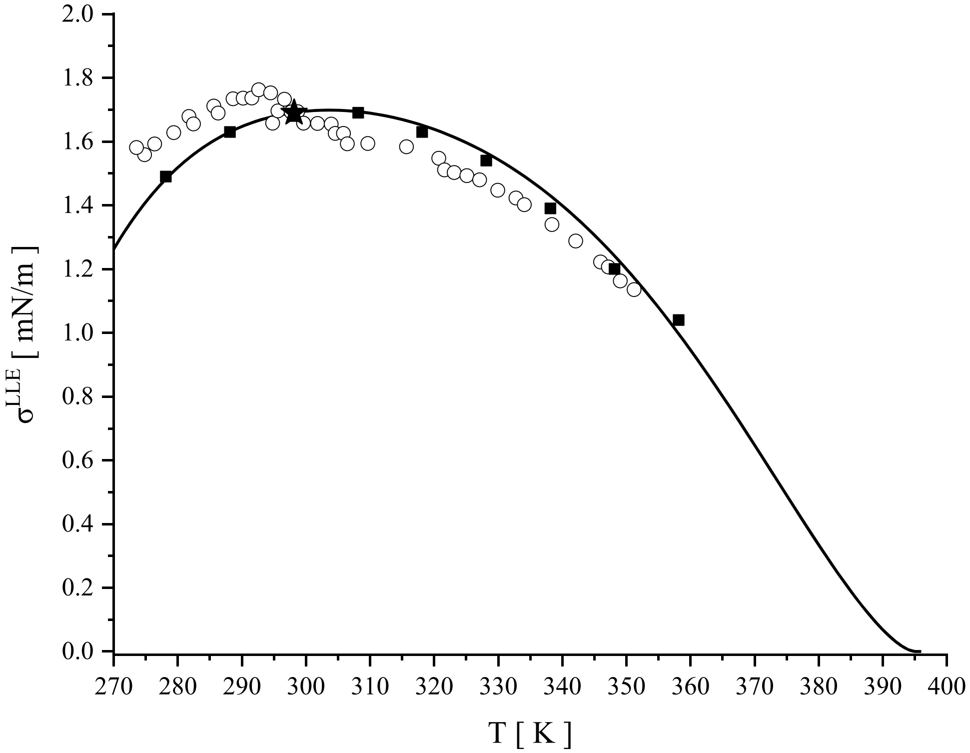

Fig. 2. Comparison between the calculated interfacial tension using Eq. (7) in combination with NRTL and the parameters in Table 6 and Table 8 (solid line), and experimental data (solid squares [9], open circles [40], solid star Table 2) for the binary system water + n-butanol.

to predict the interfacial properties of the investigated systems. They [9] found very good agreement between calculations of interfacial tensions and experimental data sets from their work [9]. Cárdenas et al. [9] used a slightly different temperature dependency for τ_{ij} in Eq. (5) and set $d_{ij} = 0$. On the other hand, they [9] used a quadratic function for the temperature dependency of κ_{ij}.

In addition, Villers and Platten [40] measured interfacial tensions between water and long-chain alcohols by using the Wilhelmy plate method. They [40] also investigated the water + n-butanol mixture. In the present paper, the influence parameter κ_{ij} of the binary system water + n-butanol is fitted to the experimental data of Cárdenas et al. [9]. The data set of Villers and Platten [40] was not taken into consideration because the Wilhelmy plate method is way less accurate than the spinning-drop method for measuring interfacial tensions. However, as depicted in Fig. 2, the experimental data points of Villers and Platten [40] are located in the tolerable range of uncertainty of those measured by Cárdenas et al. [9], so that they can also be trusted. In addition, the interfacial tension of the system water + n-butanol was measured in this work at 298.15 K. The experimental results are shown in Table 2. As can be seen in Fig. 2, the latter measurement at 298.15 K is in very good agreement with the experimental data from the literature [9,40]. The next step consists of fitting the influence parameter κ_{ij} to the data of Cárdenas et al. [9]: the experimental data points at both temperatures 278.15 K and 308.15 K were used for the adjustment. As a result, a linear temperature-dependency of the influence parameter is assumed, and the fitting result is given by the following equation:

$$\kappa_{ij} = a + bT \tag{13}$$

The numerical values of a_{ij} and b_{ij} are provided in Table 8. The linear temperature-dependency of κ_{ij} provides a much better agreement with the experimental data set (Fig. 2). Cárdenas et al. [9] also used a temperature-dependent influence parameter and κ_{ij} was given by a quadratic polynomial temperature function. In addition, as depicted in Fig. 2, applying the NRTL model in Eq. (7) reflects excellently the interfacial tension of the binary water + n-butanol mixture over a wide temperature range. In addition, the interfacial tension shows a maximum at a given temperature. Furthermore, its location is strongly related to the demixing behavior of the water + n-butanol mixture. In fact, and by closely examining Eq. (7), the interfacial tension is proportional to the integral over the grand thermodynamic potential $\Delta\Omega$. In addition, for binary mixtures with an upper critical solution temperature, the grand thermodynamic potential decreases with temperature and converges to zero at the critical point. It is related to the length of the tie-lines, thus the difference between the bulk phase concentrations at thermodynamic equilibrium. For ternary liquid-liquid equilibria, the grand thermodynamic potential also decreases with smaller tie-lines and converges to zero at the critical point of the ternary mixture. Therefore, the larger the tie-lines, the higher will be the value of $\Delta\Omega$. Subsequently, and according to Eq. (7), a large grand thermodynamic potential implies a high interfacial tension and vice versa. Therefore, the maximum of the interfacial tension in Fig. 2 is directly located at the same temperature where the LLE of the system water + n-butanol has the longest tie-line in Fig. 1, thus at approximately 300 K. The interfacial tension then converges to zero for temperatures near the critical temperature of the binary mixture. In fact, at the critical point, both liquid phases become one single phase, so that the interfacial tension tends to a value of zero. These observations were also deduced by Cárdenas et al. [9], Grunert et al. [8], and Danzer and Enders [13], where the maximum of the interfacial tension of the mixture of water + n-butanol as a function of the temperature was calculated. Cárdenas et al. [9] and Grunert et al. [8] studied the interfacial properties of the binary system water + *n*-butanol by applying the combination NRTL + DGT and Koningsveld-Kleintjens + DGT, respectively, and found very good agreement between calculations and experimental data. Danzer and Enders [13] used the combination UNIQUAC + DGT and found, however, qualitative modeling precision for temperatures below 300 K.

Table 8
Adjusted parameters in Eq. (13).

Component i	Component j	10^{-6} a_{ij} [Jmol/m^4]	10^{-9} b_{ij} [Jmol/(Km^4)]
water	n-butanol	1.282	−2.988
water	n-butyl acetate	0.852	−2.001

Another important interfacial property are the concentration profiles across the interface. These are not experimentally accessible because of the negligible thickness of the interface. Fig. 3 shows the interfacial concentration profiles of both components in the water + n-butanol mixture at three different temperatures. It can be seen from Fig. 3 that the interfacial concentrations of water and n-butanol varies continuously across the interface from the aqueous phase (left) to the organic phase (right). In addition, the interfacial thickness increases, and the local concentration gradient decreases as the temperature increases. At the critical point, the interfacial thickness converges to infinity and the local concentration gradient to zero because the bulk phase concentrations of each component become equal.

4.1.2. water + n-butyl acetate

The next binary subsystem to be studied is the water + n-butyl acetate mixture that is found in both investigated ternary systems in this work. Fig. 4 shows the calculated LLE of the binary system water + n-butyl acetate in a temperature-mole fraction diagram, compared to two experimental data sets from the literature [30,37]. Furthermore, the NRTL parameters used for the binary water + n-butyl acetate mixture in this work are also taken from Grob [31] and listed in Table 6. As can be seen in Fig. 4, a very good agreement between the calculated LLE of the water + n-butyl acetate mixture and experimental data [30,37] is observed. In addition, small deviations between calculations and the experimental measurements of Stephenson and Stuart [37] in the organic phase in the temperature range between 300 K and 320 K and between 340 K and 360 K are observed. The authors [37] measured the concentrations of water and n-butyl acetate by using a gas chromatograph with a thermal conductivity detector. The internal standard method was used for calibration [37]. On the other hand, Grob and Hasse [30] used a batch reactor with online gas chromatography and a thermal conductivity detector for LLE measurements. The authors [30] investigated a strongly nonideal esterification system and thus used the batch reactor under conditions where chemical reactions are negligible to properly measure the LLE of the binary system water + n-butyl acetate. However, both authors [30,37] do not provide any information concerning the time that was given for the mixtures to reach phase equilibrium. In addition, and as depicted in Fig. 4, the solubility of n-butyl acetate in the water-rich phase as well as the solubility of water in the ester-rich phase are even lower than those in the binary system water + n-butanol. This can be deduced by the nonpolar character of the ester, given that n-butyl acetate, in contrast to n-butanol, does not possess a hydroxyl group, which contributes to the poor solubility in water.

The next step consists of calculating the interfacial tension of the binary mixture water + n-butyl acetate. The calculations are found in Fig. 5 and are presented in comparison with experimental data sets from the literature [39,41–43] and with own measurements performed with the spinning-drop tensiometer (Table 3).

Furthermore, applying the NRTL model in Eq. (7) requires the adjustment of the influence parameter κ_{ij} to interfacial tension experimental data of the considered binary subsystem. Therefore, both experimental data points measured in this work at 298.15 K and 303.15 K (Table 3) were considered in the fitting procedure, a linear temperature-dependency of the influence parameter is assumed (Eq. (13)), and the fitting result for the system water + n-butyl acetate is given in Table 8. Considering the calculated interfacial tension of the binary water + n-butyl acetate mixture in Fig. 5, it can be noted that the

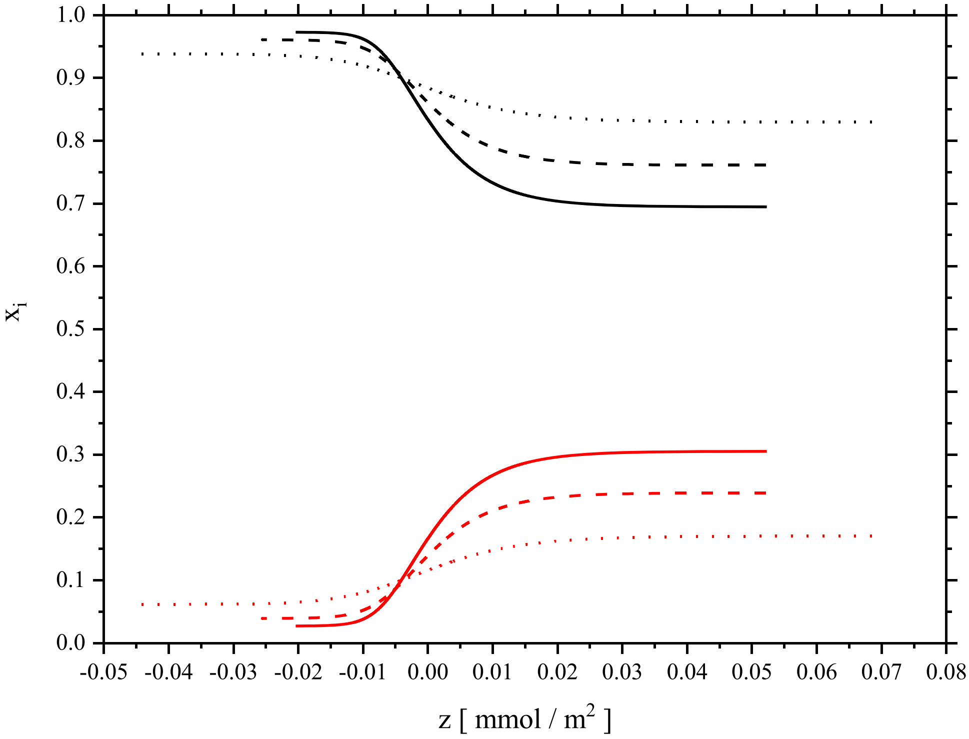

Fig. 3. Calculated interfacial concentration profiles of water (black lines) and n-butanol (red lines) in the binary water +n-butanol mixture using Eq. (9) in combination with NRTL and the parameters presented in Table 6 and Table 8 at different temperatures: 375 K (solid lines), 385 K (dashed lines) and 392 K (dotted lines).

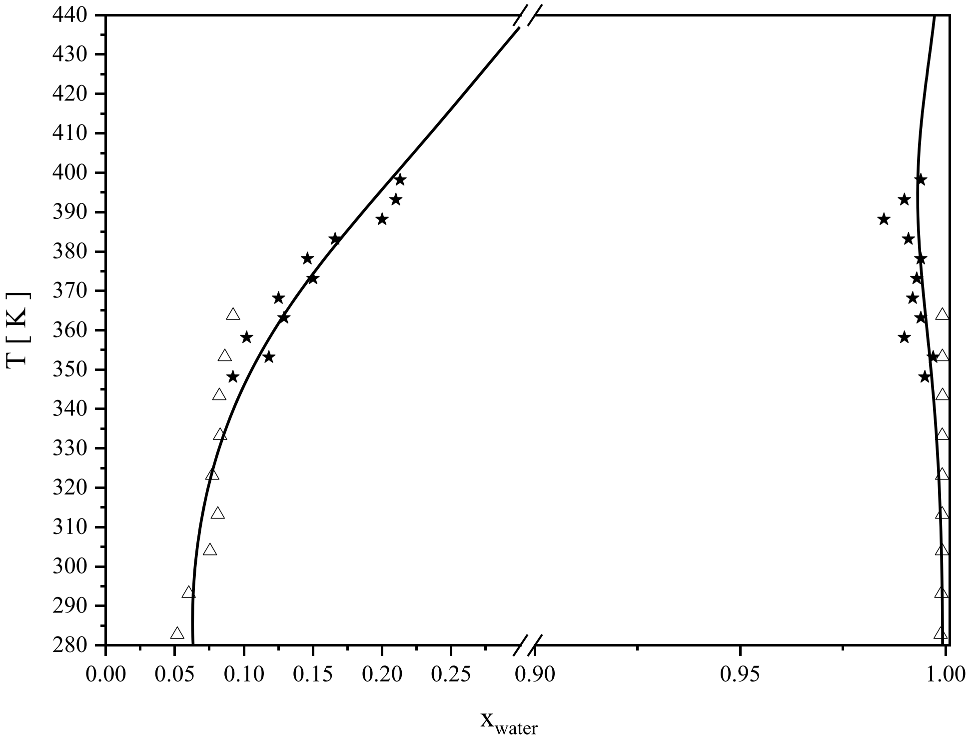

Fig. 4. Comparison between the calculated phase diagram using NRTL with the parameters presented in Table 6 (solid line) and experimental data (open triangles [37], solid stars [30]) for the binary system water + n-butyl acetate.

experimental data from this work is reproduced with high accuracy by the applied theoretical framework. The predicted interfacial tension decreases continuously with temperature. As portrayed in Fig. 4, the tie-lines of the investigated system become smaller with higher temperatures, thus, and as explained in subsubsection 4.1.1, the interfacial tension of the system should decrease with temperature. Moreover, many experimental data sets for the interfacial tension of the binary mixture water + n-butyl acetate can be found in the literature [39, 41–43], but since these measurements were conducted with methods way less accurate than the spinning-drop method, they are not trusted in

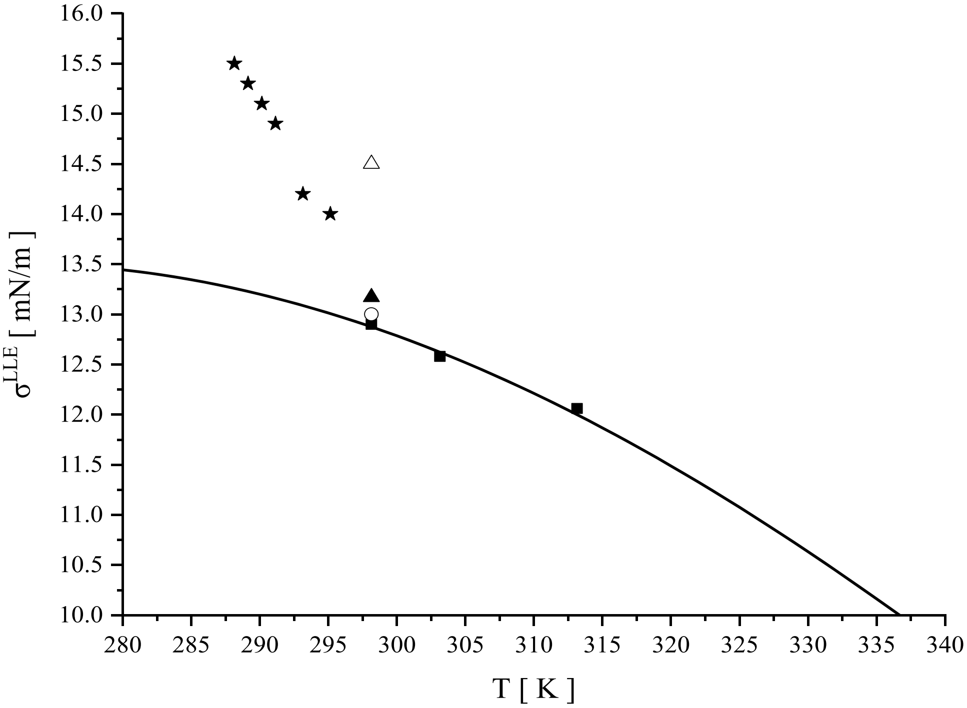

Fig. 5. Comparison between the calculated interfacial tension using Eq. (7) in combination with the NRTL model and parameters from Table 6 and Table 8 (solid line), and experimental data (open triangle [39], open circle [41], solid triangle [42], solid stars [43], solid squares Table 3) for the water + n-butyl acetate mixture.

this work (Fig. 5). For instance, Saien et al. [43] used the drop-volume method, which is an excellent method for measuring surface tensions. However, the spinning drop method is more accurate for the measurements of interfacial tensions. Furthermore, a remarkable difference in the measured density of the organic phase can be observed: the densities found in [43] are higher than the ones provided in Table 3.

In addition, interfacial concentration profiles are also calculated with the applied theoretical framework using Eq. (9). Fig. 6 shows the concentration profiles across the interface for both components in the water + n-butyl acetate mixture and at three different temperatures. A

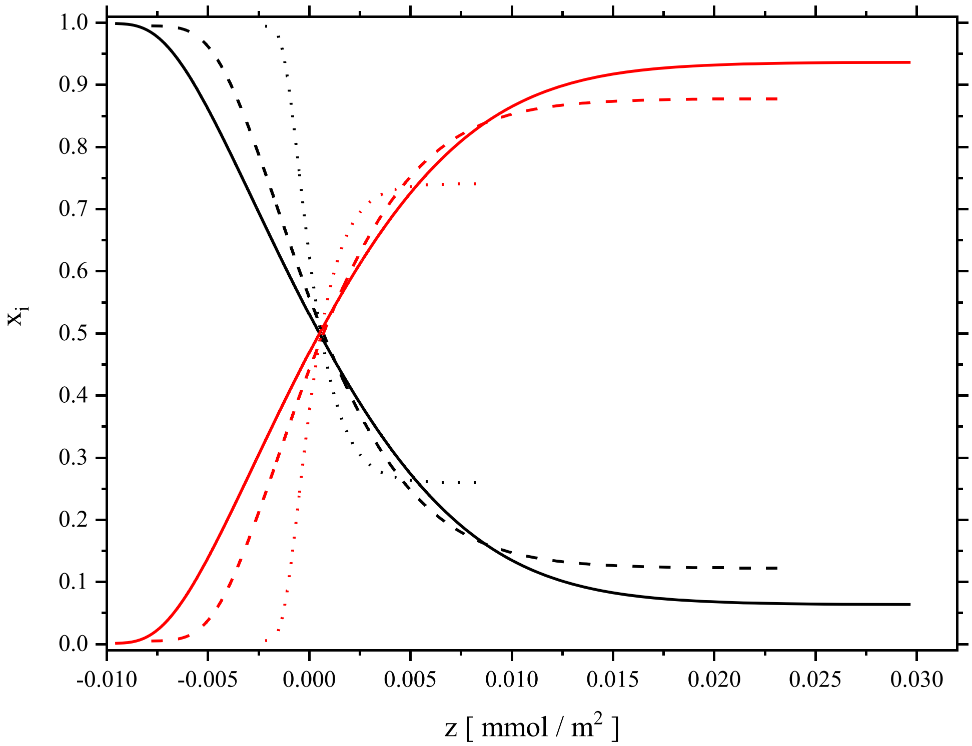

Fig. 6. Calculated interfacial concentration profiles of water (black lines) and n-butyl acetate (red lines) in the binary water + n-butyl acetate mixture using Eq. (9) in combination with the NRTL model and the parameters listed in Table 6 and Table 8 at different temperatures: 280 K (solid line), 360 K (dashed line) and 420 K (dotted line).

similar behavior regarding the binary subsystem water + n-butanol can also be observed here. The interfacial concentration profiles of water and n-butyl acetate vary continuously inside the interface from the aqueous phase (left) to the organic phase (right).

4.2. Ternary mixtures

4.2.1. water + n-propanol + n-butyl acetate

The first ternary mixture to be investigated is the water + n-propanol + n-butyl acetate mixture. Fig. 7 shows the phase diagram of the ternary LLE of the studied system, calculated with the NRTL model at 323.15 K in comparison with experimental data from the literature [33]. Fig. 8 portrays the predicted LLE of the same mixture at 303.15 K compared with another experimental data set from the literature [32]. Costa et al. [33] measured phase equilibria of the system water + n-propanol + n-butyl acetate at 323.15 K by using a gas chromatograph with the internal standard method for the calibration of the detector response. The authors [33] also predicted the LLE of the ternary mixture by applying the UNIFAC group contribution method [48] and found excellent agreement with their measurements [33]. To properly model the LLE of the ternary system water + n-propanol + n-butyl acetate, the binary NRTL-parameters of the subsystems water + n-propanol and n-butyl acetate + n-propanol were fitted in this work to the experimental data set of both authors [32,33] at both temperatures 323.15 K and 303.15 K (Figs. 7 and 8). They are listed in Table 7. The predictions based on the NRTL modeling by using the fitted parameters in Tables 6 and 7 are also in very good agreement with the experimental data of both papers [32, 33]. The experimental values of both authors [32,33] are thus reproduced outstandingly through the NRTL model, as shown in Figs. 7 and 8. Furthermore, increasing the concentration of n-propanol in the mixture leads to an increase in the physical similarities between both coexisting phases at LLE. n-propanol thus acts as a solubilizer in the investigated system water +n-propanol + n-butyl acetate and ensures better miscibility of the system, resulting in closed miscibility gaps (Fig. 7 and 8).

After calculating the ternary phase equilibrium, the prediction of the interfacial properties at 303.15 K by applying the NRTL-model in combination with Eq. (7) follows. The binary subsystem water + n-butyl acetate is the only subsystem in the ternary water + n-propanol + n-butyl acetate mixture that demixes at 303.15 K. In addition, for ternary mixtures with just one binary demixing subsystem, Grunert et al. [7,8] assumed that the influence parameter $\kappa^{'}$ of the ternary system used in Eq. (8) is equal to the influence parameter κ_{ij} of the binary subsystem that demixes. Therefore, $\kappa^{'}$ in Eq. (8) is equal to the influence parameter κ_{ij} of the binary system water + n-butyl acetate. The latter is given by the parameters in Table 8 at a temperature of 303.15 K. Moreover, Costa et al. [33] and Johnson et al. [44] measured interfacial tensions of the ternary water + n-propanol + n-butyl acetate mixture at 323.15 K and 303.15 K, respectively. However, both authors [33,44] used the Du Noüy ring-detachment method for measuring the interfacial tensions, and, since this method is less accurate than the spinning-drop method, their experimental results are not trusted in this paper (Fig. 9 concerning the results of Johnson et al. [44]). Therefore, measurements are carried out by applying a spinning-drop tensiometer. The measured interfacial tensions, densities and applied feed concentrations are presented in Table 4. Fig. 9 shows the calculated interfacial tension as function of the concentration of n-propanol in the aqueous phase, and in comparison with own experimental measurements (Table 4) and with the literature [44]. As can be deduced from Fig. 9, and through the combination NRTL

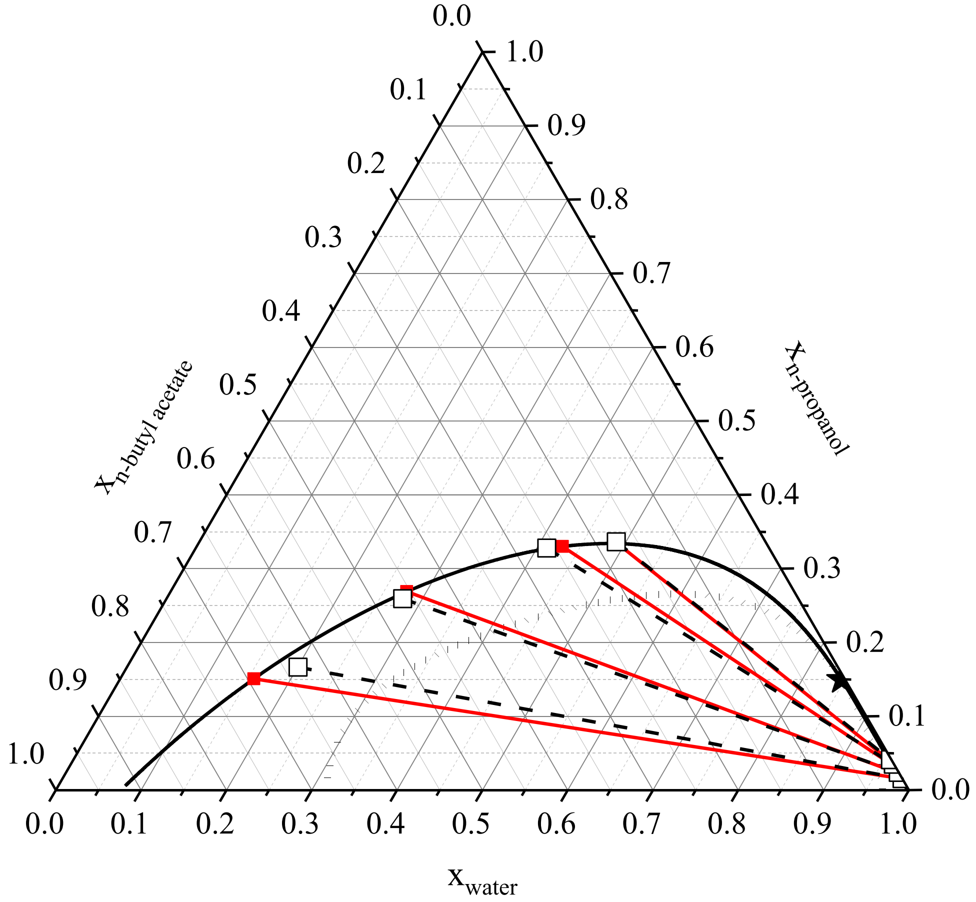

Fig. 7. Comparison between the calculated phase diagram using the NRTL model and parameters in Table 6 and Table 7 (solid black line: binodal line, dotted line: spinodal line, solid star: critical point) and experimental data (open squares [33]) for the ternary system water + n-propanol + n-butyl acetate at 323.15 K. The dashed lines represent experimental tie-lines, and the solid red lines and solid squares are the calculated tie-lines which correspond to the experimental ones.

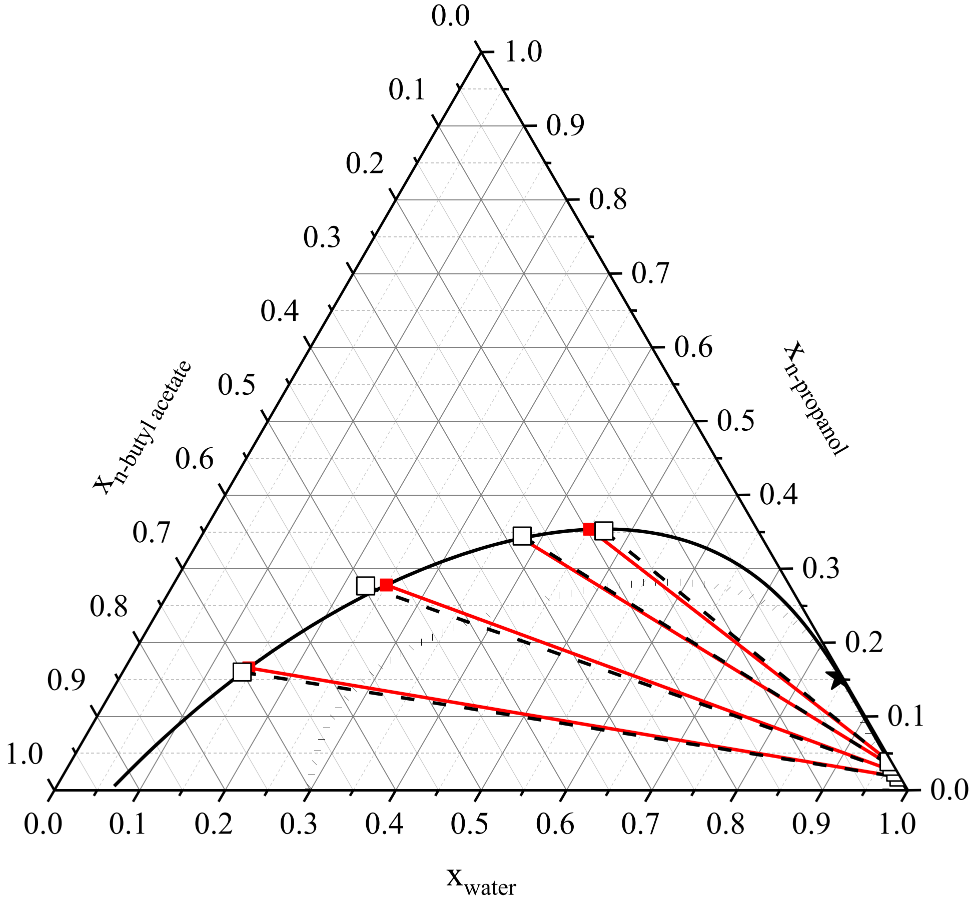

Fig. 8. Comparison between the calculated phase diagram using the NRTL model and parameters in Table 6 and Table 7 (solid black line: binodal line, dotted line: spinodal line, solid star: critical point) and experimental data (open squares [32]) for the ternary system water + n-propanol + n-butyl acetate at 303.15 K. The dashed lines represent experimental tie-lines, and the solid red lines and solid squares are the calculated tie-lines which correspond to the experimental ones.

+ DGT, an excellent agreement between calculations and own experimental results can be observed over the entire concentration range going from the binary subsystem water + n-butyl acetate up to the critical point of the mixture. In fact, this observation is remarkable given that the prediction of interfacial tensions, and much generally interfacial properties, of ternary mixtures at LLE can be achieved only based on the bulk phase properties of the ternary system and the influence parameter κ_{ij} of the binary demixing subsystem. Furthermore, and because n-propanol acts as a solubilizer in the studied ternary mixture, increasing its concentration in the ternary system water + n-propanol + n-butyl acetate decreases the interfacial tension of the mixture, as shown in Fig. 9. This behavior is directly related to the length of the tie-lines in the phase diagram of the ternary LLE. As explained in subsubsection 4.1.1, the value of the interfacial tension is related to the length of the tie-lines: by increasing the concentration of n-propanol, the tie-lines become smaller and the interfacial tension thus decreases and finally vanishes at the critical point of the ternary system at approximately $x_{n-propanol} = 0.15$, where the tie-lines become zero in length and both liquid phases merge to one single phase.

The applied theoretical framework also allows to spatially examine the interface of a multicomponent system, for instance, to predict the concentration profiles of the various components in the inhomogeneous region between both bulk phases as a function of the interfacial spatial coordinate z, perpendicular to the planar interface. Fig. 10 depicts the concentration profiles of water, n-butyl acetate, and n-propanol in the ternary mixture water + n-propanol + n-butyl acetate over the spatial coordinate z at 303.15 K and for three different tie-lines: one tie-line is located near the binary subsystem water + n-butyl acetate at infinite dilution of n-propanol and another one near the critical point of the mixture. As can be deduced from Fig. 10, there is a pronounced maximum in the local concentration profile of n-propanol across the one-dimensional interface at infinite dilution of n-propanol in the ternary mixture, thus for the tie-line near the binary subsystem water + n-butyl acetate (solid, blue line in Fig. 10). The observed maximum in the concentration profile of n-propanol thus refers to the enrichment of that component in the interface. In fact, at very low feed concentrations of the alcohol and because of the poor solubility in the polar, water-rich phase and the nonpolar, ester-rich phase, an enrichment of n-propanol in the interface is mostly probable to occur. Moreover, and due to the increased concentration of n-propanol in the interface, in contrast to both bulk phases, high local concentration gradients are observed in the inhomogeneous region since the concentration of n-propanol must decrease continuously from the highest concentration value at the place of the enrichment to the lowest value in the aqueous phase. Considering the tie-line far away from the binary subsystem water + n-butyl acetate, the enrichment of n-propanol becomes much less pronounced (dashed blue line in Fig. 10), and for the tie-line located near the critical point of the ternary mixture, the enrichment of the alcohol vanishes in the interface (dotted blue line in Fig. 10). Therefore, it can be deduced that the peak in concentration becomes less sharp as the feed concentration of n-propanol increases. n-propanol possesses a polar molecular part due to the hydroxyl group and a nonpolar part due to the presence of the hydrocarbon chain. The ester-rich bulk phase has also a nonpolar character and the water-rich bulk phase, on the other hand, is strongly polar. Therefore, at very low feed concentrations of n-propanol, thus at infinite dilution of the alcohol, its presence in the interface is preferred, since the hydroxyl group can be directed at the water-rich phase and the hydrocarbon chain at the ester-rich phase. However, and by moving

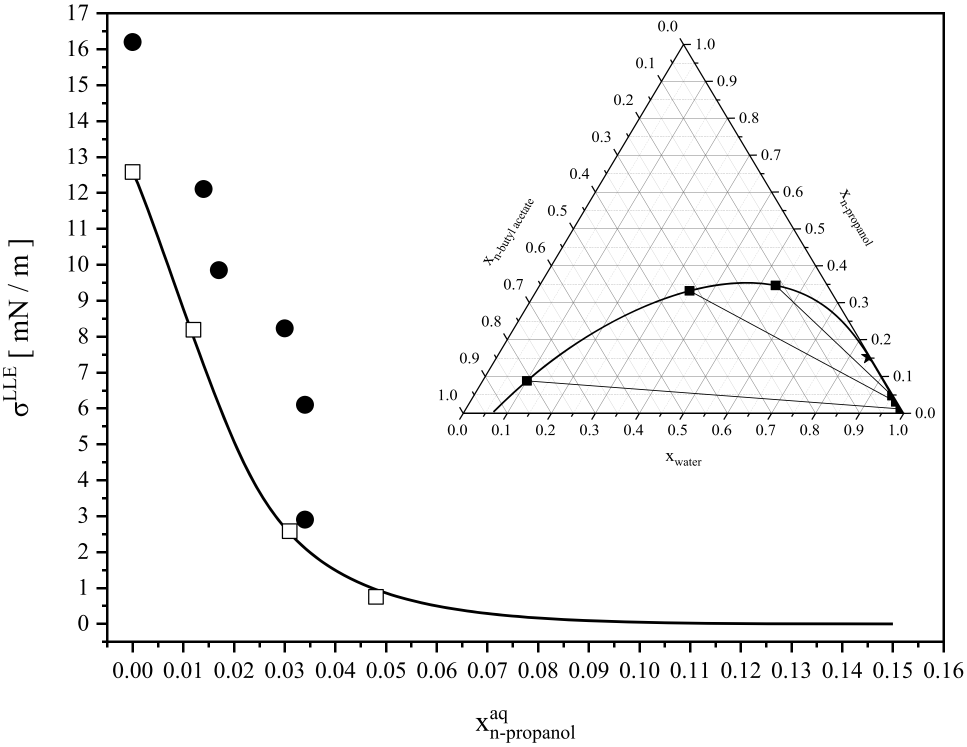

Fig. 9. Comparison between the predicted interfacial tension using Eq. (7) in combination with the NRTL model and the parameters listed in Table 6, Table 7, Table 8 (solid line), and experimental data (solid circles [44], open squares Table 4) for the ternary system water + n-propanol + n-butyl acetate at 303.15 K. In the upper right corner, the phase diagram of the ternary LLE is shown, and the tie-lines, for which the interfacial tensions were measured, are also plotted.

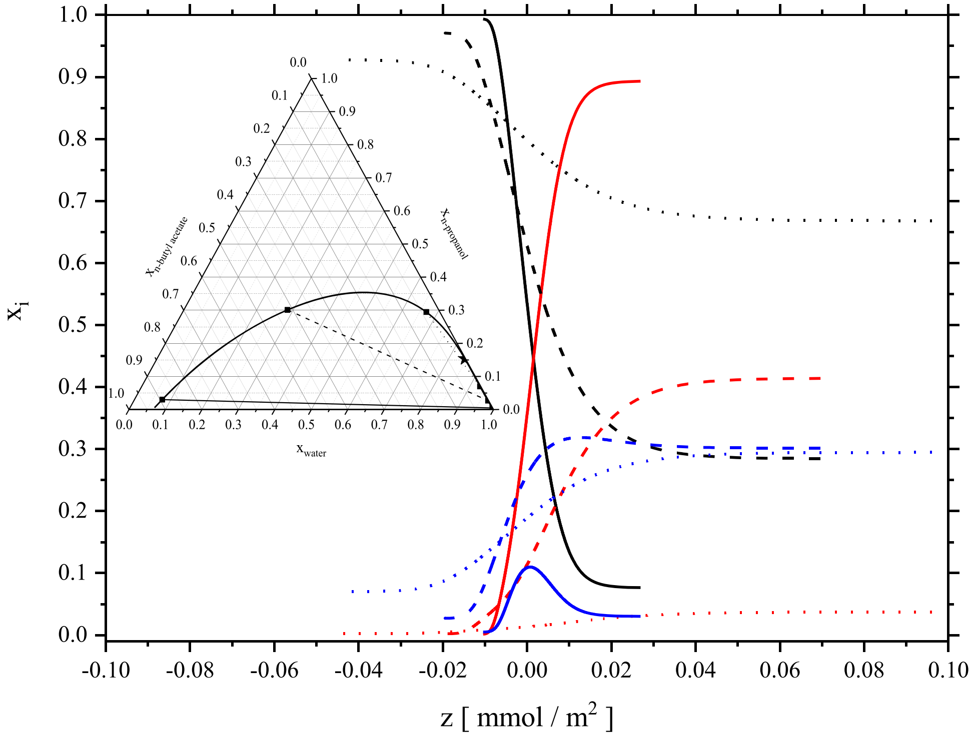

Fig. 10. Calculated interfacial concentration profiles of water (black lines), n-butyl acetate (red lines), and n-propanol (blue lines) using Eq. (9) in combination with the NRTL-model and the parameters listed in Table 6, Table 7, and Table 8 at 303.15 K for three different tie-lines. In the upper left corner, the phase diagram of the ternary LLE is shown, and the three tie-lines, for which the interfacial concentration profiles were calculated, are also plotted: solid lines concentration profiles correspond to the solid tie-line, dashed lines to the dashed tie-line, and dotted lines to the dotted tie-line.

away from the binary subsystem water + n-butyl acetate, thus by increasing the feed concentration of n-propanol, the interface no longer provides sufficient space for the n-propanol molecules to enrich, so that the bulk phase concentration of n-propanol increases, especially in the ester-rich phase. As the bulk phase concentration of n-propanol increases, the alcohol molecules will find a more favorable environment for them in the bulk phase, so that the interfacial enrichment disappears and the peak in the interfacial concentration profile vanishes (dotted blue line in Fig. 10). Danzer and Enders [16] studied the interfacial properties of both systems water + 1-hexanol + acetic acid and water + hexyl acetate + acetic acid and found the same behavior concerning the solubilizer acetic acid in both ternary mixtures. On the other hand, and as shown in Fig. 10, the water concentration in the interface decreases continuously as the concentration of n-butyl acetate increases also continuously from the aqueous phase to the organic phase for all three investigated tie-lines. Therefore, only the solubilizer n-propanol in the ternary mixture water + n-propanol + n-butyl acetate will enrich inside the inhomogeneous interface, which confirms the explanation provided above. Moreover, the concentration profiles in Fig. 10 become broader, thus the interfacial thickness increases by increasing the feed concentration of n-propanol, going from the solid tie-line up to the dotted tie-line in Fig. 10, and converges to infinity at the critical point, where the interfacial tension vanishes and both bulk phases become one single critical phase.

4.2.2. *water + n-butanol + n-butyl acetate*

In order to extend the used theoretical framework to more complex ternary mixtures, the system water + n-butanol + n-butyl acetate with two binary demixing subsystems water + n-butyl acetate and water + n-butanol was investigated. While n-butyl acetate and n-butanol are perfectly miscible, a tube-formed miscibility gap in the LLE of the system is thus observed. Fig. 11 portrays the phase diagram of the ternary LLE of the studied system, calculated with the NRTL model at 298.15 K, in comparison with experimental data from the literature [29]. In addition, Fig. 12 shows the predicted LLE of the same mixture at 308.15 K, compared with another experimental data set from the literature [34]. Finally, the LLE of the system at 353.15 K is depicted in Fig. 13 in comparison with a third data set from the literature [30]. Ruiz Bevia et al. [29] measured the LLE of the ternary mixture water + n-butanol + n-butyl acetate at 298.15 K employing gas chromatography, the detection was carried out by thermal conductivity and the internal standard method was applied. All components used by the authors [29] contained negligible amounts of impurities. The prepared samples were settled, however, for only two hours at a constant temperature before the bulk phases were experimentally analyzed [29]. Furthermore, Samarov et al. [34] studied the LLE of the same mixture at 308.15 K and analyzed the samples of the water and organic phases using gas chromatography, the detection was also carried out by thermal conductivity and the method of internal standard and relative calibration were used. Nevertheless, the authors [34] considered that LLE is reached after the full separation of both phases is observed and when both phases become quite transparent [34]. Therefore, based on the assumptions of Ruiz Bevia et al. [29] and Samarov et al. [34], there is a certain degree of uncertainty as if the LLE of the investigated mixture has been really reached by the two authors [29,34] or not.

On the other hand, Grob and Hasse [30] used a batch reactor with online gas chromatography and thermal conductivity detector for LLE measurements of the system water + n-butanol + n-butyl acetate at

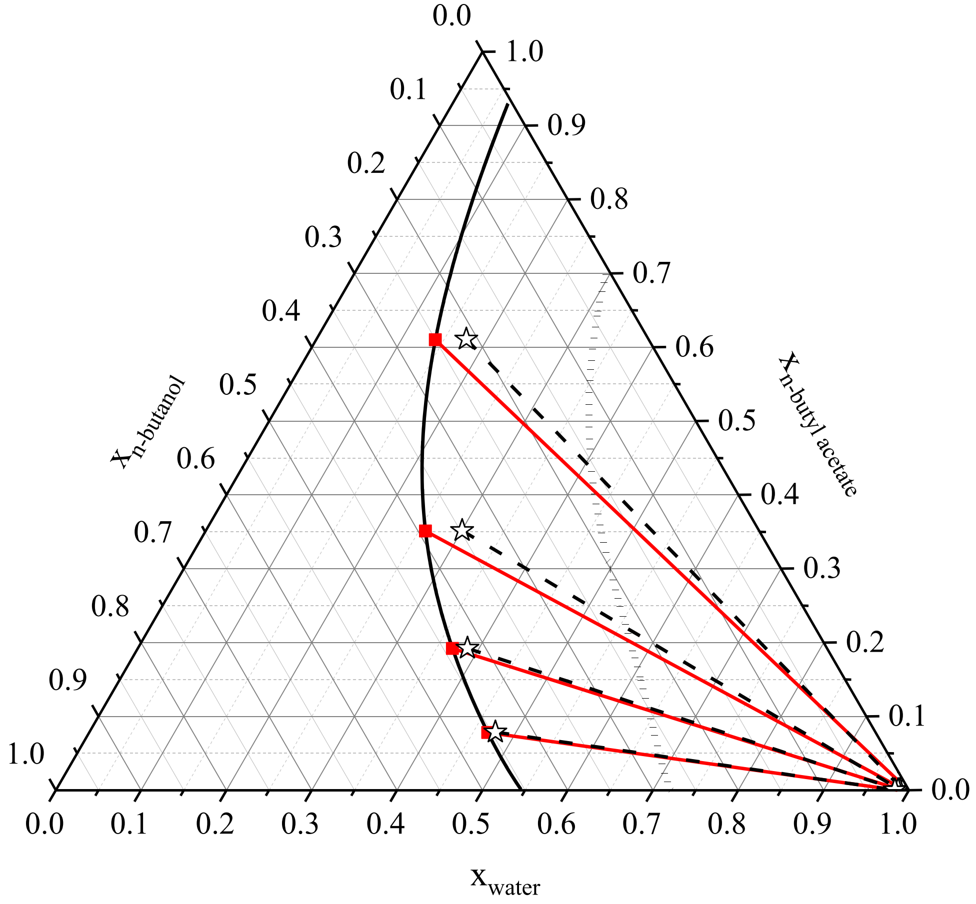

Fig. 11. Comparison between the calculated phase diagram using NRTL with the parameters listed in Table 6 and Table 7 (solid black line: binodal line, dotted line: spinodal line), and experimental data (open stars [29]) for the ternary system water + n-butanol + n-butyl acetate at 298.15 K. The dashed lines represent experimental tie-lines, and the solid red lines and solid squares are the calculated tie-lines which correspond to the experimental ones.

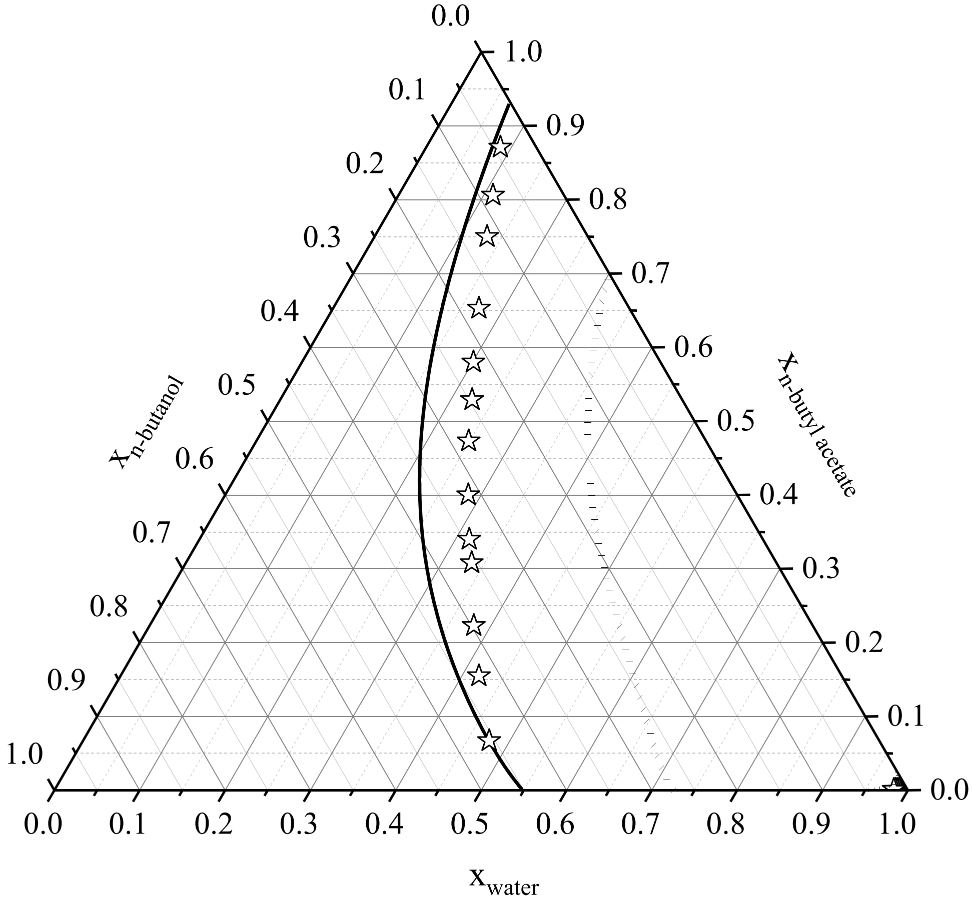

Fig. 12. Comparison between the calculated phase diagram using NRTL with the parameters listed in Table 6 and Table 7 (solid line: binodal line, dotted line: spinodal line), and experimental data (open stars [34]) for the ternary system water + n-butanol + n-butyl acetate at 308.15 K.

353.15 K. The same authors [30] also conducted measurements of the binary system water + n-butyl acetate with the same experimental apparatus, as explained in subsubsection 4.1.2 (solid stars in Fig. 4). However, Grob and Hasse [30] do not indicate how much time was given for the mixtures in the batch reactor to reach LLE. In addition, the NRTL binary parameters of the binary mixture water + n-butyl acetate were taken from Grob [31], who fitted the binary parameters of the system water + n-butyl acetate to own LLE experimental data (solid stars in Fig. 4) and to binary LLE experimental data sets from the Dortmund Data Bank, as described in Subsubsection 4.1.2. Again, Fig. 4 shows very good agreement between predictions and experimental data from not only Grob and Hasse [30] but also another author, namely Stephenson and Stuart [37]. Both experimental data sets [30,37] are also in very good compliance with each other. Therefore, and by relying on the above observations and deductions, the measured LLE of the ternary mixture water + n-butanol + n-butyl acetate from Grob and Hasse [30] at 353.15 K is more trusted than the measured LLE of the other authors Ruiz Bevia et al. [29] at 298.15 K and Samarov et al. [34] at 308.15 K. Therefore, to properly predict the LLE of the investigated ternary system water + n-butanol + n-butyl acetate, the binary NRTL parameters of the binary subsystem n-butyl acetate + n-butanol were adjusted in this paper to the ternary LLE experimental data set of Grob and Hasse [30, 31] at 353.15 K (Fig. 13). The NRTL binary parameters of the n-butyl acetate + n-butanol mixture are presented in Table 7. The experimental values of Grob and Hasse [30] are thus reproduced outstandingly through the NRTL model, as shown in Fig. 13. However, a satisfactory agreement between the calculated LLE at 298.15 K and experimental data of Ruiz Bevia et al. [29] and between the calculated LLE at 308.15 K and experimental data of Samarov et al. [34] can be deduced from Fig. 11 and 12, respectively. In both cases, the water concentration in the organic phase is not properly estimated by the theoretical model. This may be justified by the prepared samples not reaching phase equilibrium, as described above. Moreover, the right-hand side branch of the binodal curve, which depicts the concentrations of the aqueous phase, is not visible since the solubility of n-butyl acetate and n-butanol in the water-rich phase is extremely low. Considering the ester, it is in the range between 10^{-4} and 10^{-6} mole percent at 298.15 K and between 10^{-3} and 10^{-6} mole percent at 308.15 K; and for the alcohol, the solubility is in the range between 10^{-2} and 10^{-7} mole percent at both 298.15 K and 308.15 K. Given that one of the two coexisting phases consists almost entirely of pure water, water has thus in this ternary system a very high chemical potential which contributes to the strongly nonideal behavior of the system.

In addition, there is no experimental data concerning interfacial tensions of the ternary mixture water + n-butyl acetate + n-butanol in the literature. Therefore, own measurements are conducted in this paper by using a spinning-drop tensiometer. The investigated system is characterized by two demixing binary subsystems water + n-butyl acetate and water + n-butanol. Fig. 14 shows the interfacial tension calculated using the NRTL model in combination with Eq. (7). The interfacial tension is plotted as a function of the concentration of n-butyl acetate in the organic phase, in comparison with own measurements (Table 5). Since the ternary system water + n-butanol + n-butyl acetate includes two demixing binary subsystems (water + n-butyl acetate and water + n-butanol), the influence parameters κ_{ij} of both systems must be taken into consideration in calculating the interfacial properties of the ternary mixture. Both influence parameters are determined by Eq. (13) with the parameters listed in Table 8 at a temperature of 298.15 K. In addition, since the investigated ternary system shows a tube-formed miscibility gap, it has thus no critical point. Therefore, the interfacial tension of the

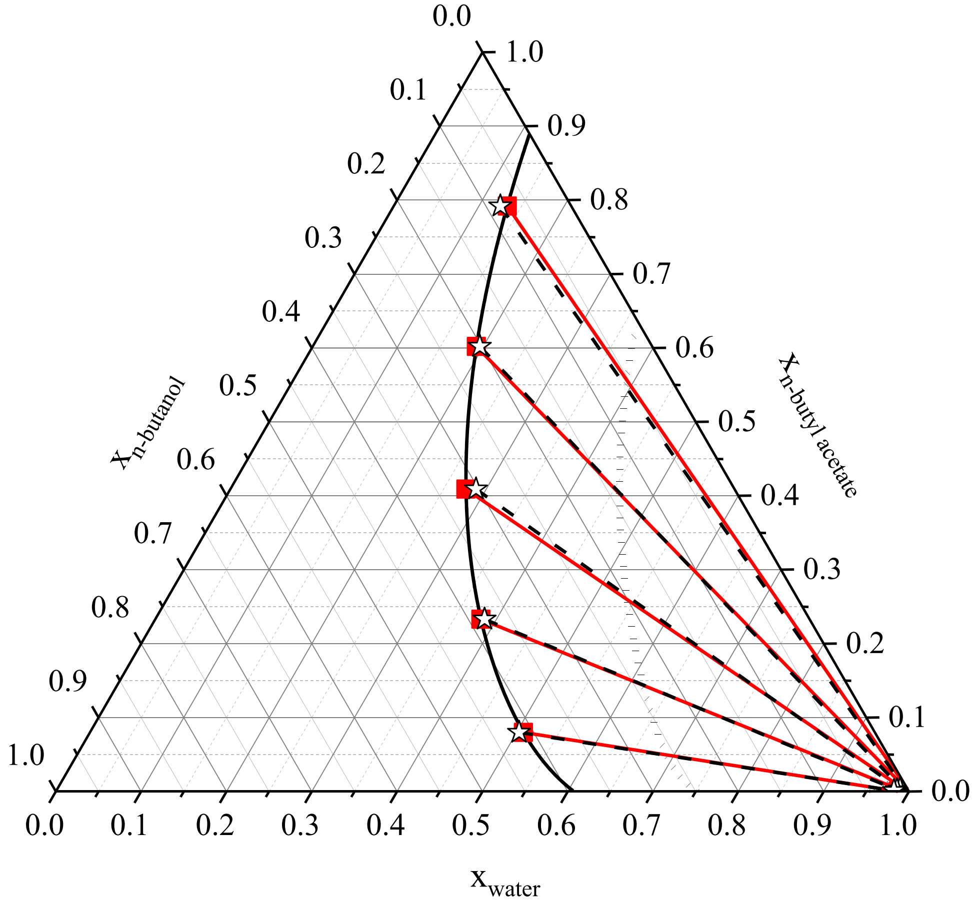

Fig. 13. Comparison between the calculated phase diagram using NRTL with the parameters listed in Table 6 and Table 7 (solid black line: binodal line, dotted line: spinodal line), and experimental data (open stars [30]) for the ternary system water + n-butanol + n-butyl acetate at 353.15 K. The dashed lines represent experimental tie-lines, and the solid red lines and solid squares are the calculated tie-lines which correspond to the experimental ones.

system, plotted over the entire concentration range, does not vanish, but changes continuously from the value corresponding to the demixing binary mixture water + n-butanol to the value corresponding to the demixing binary system water + n-butyl acetate, as shown in Fig. 14.

Fig. 14 also shows that the combination of the NRTL model with the modified DGT predicts the measured interfacial tension over the entire concentration range in an outstanding way and with excellent accuracy. This observation proves the strong predictive power of the applied theoretical framework concerning complex ternary mixtures and its ability to properly predict the highly nonlinear dependency of the interfacial tension on concentration.

Finally, the concentration profiles of the various components in the interface are calculated and predicted. Fig. 15 depicts the concentration profiles of water, n-butyl acetate, and n-butanol in the ternary mixture water + n-butanol + n-butyl acetate at 298.15 K and for three different tie-lines, one of which is located near the binary subsystem water + n-butyl acetate at infinite dilution of n-butanol.

At infinite dilution of n-butanol, a pronounced maximum in its concentration can be observed (Fig. 16), similar to the enrichment of n-propanol in Fig. 10. In addition, the enrichment of n-butanol in the interface vanishes for both tie-lines located far away from the binary system water + n-butyl acetate (dashed and dotted blue lines in Fig. 15), which confirms the observed physical effect. However, and by comparing both investigated ternary systems, the interfacial enrichment of n-butanol (Fig. 16) is significantly less pronounced than that of n-propanol (Fig. 10), given that n-butanol begins already at lower feed concentrations to prefer the ester-rich organic phase, because of the stronger nonpolar character of n-butanol. This is due to its longer hydrocarbon chain compared to that of n-propanol. In addition, Fig. 15 shows that the concentrations of water (black lines in Fig. 15) and n-butyl acetate (red lines in Fig. 15) vary continuously for all three considered tie-lines, from the water-rich aqueous phase (lefthand side of Fig. 15) to the ester-rich organic phase (righthand side of Fig. 15), no enrichments of both components in the interface can thus be observed.

It can be generally concluded that in liquid-liquid systems at LLE, the more the phase-forming components in a mixture differ in polarity and the closer the distribution coefficient of the solubilizer is to the value of one, the greater the enrichment of the solubilizer in the interface will be. The solubilizer is the component in a system with both polar and nonpolar functional groups. Similarly, Danzer and Enders [16] came to the same conclusions concerning interfacial enrichment effects in liquid nonuniform systems.

5. Summary and conclusions

In conclusion, this work aimed at investigating theoretically the phase behavior and interfacial properties of mixtures relevant to extraction processes. It also aimed at investigating experimentally the interfacial tensions of these mixtures. Therefore, an oscillating U-tube and a spinning-drop tensiometer were used. The studied mixtures are composed of water + n-butanol, water + n-butyl acetate, water + n-propanol + n-butyl acetate, and water + n-butanol + n-butyl acetate. For modeling, the modified DGT in combination with the NRTL model was applied to these mixtures to perform the required calculations. In summary, it can be stated that the predictions based on the NRTL model in combination with the modified DGT are very promising for the investigated mixtures in this work, which are also relevant to liquid-liquid extraction processes. Excellent agreement between predictions

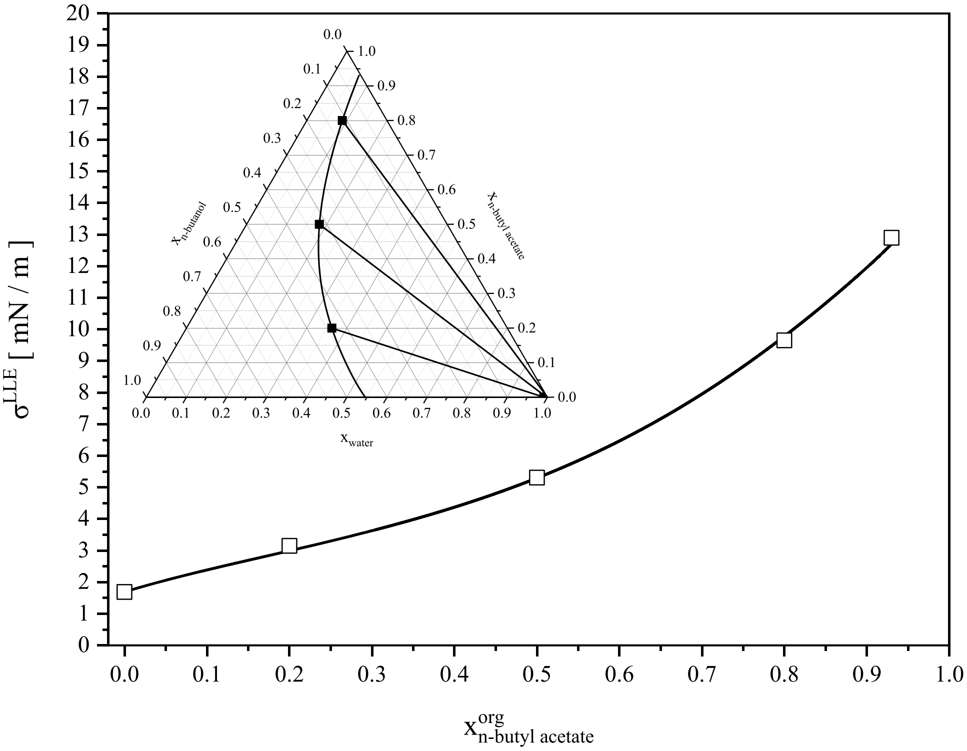

Fig. 14. Comparison between the predicted interfacial tension using Eq. (7) in combination with the NRTL-model and the parameters listed in Table 6, Table 7, and Table 8 (solid line), and experimental data (open squares Table 5) for the ternary system water + n-butanol + n-butyl acetate at 298.15 K. In the upper left corner, the phase diagram of the ternary LLE is shown, and the tie-lines, for which the interfacial tensions were measured, are also plotted.

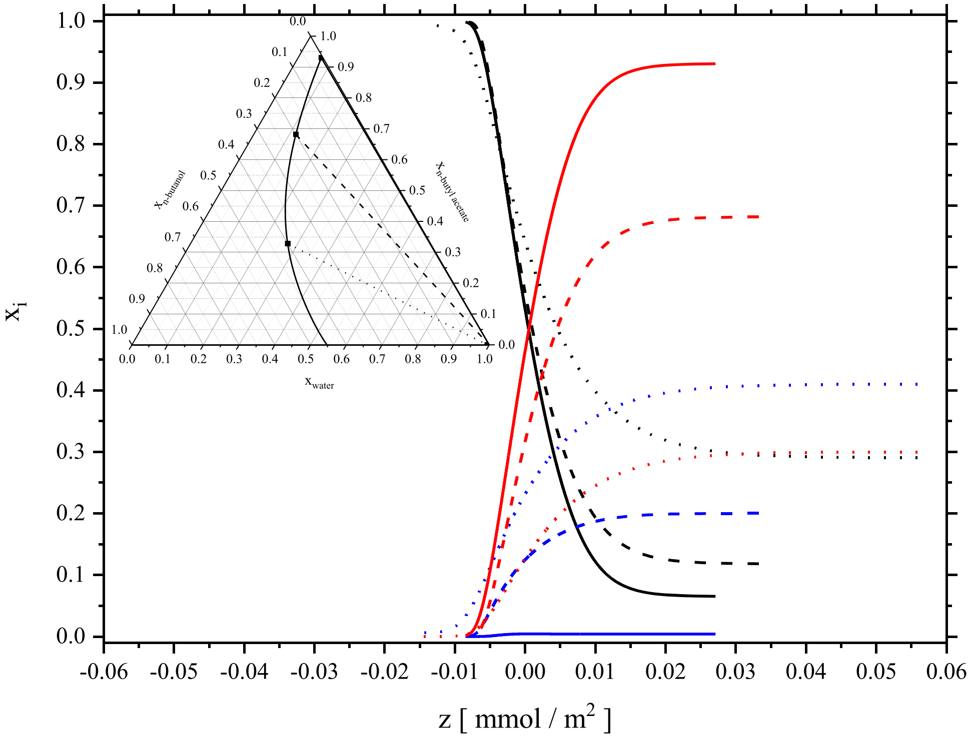

Fig. 15. Calculated interfacial concentration profiles of water (black lines), n-butyl acetate (red lines), and n-butanol (blue lines) using Eq. (9) in combination with the NRTL-model and the parameters listed in Table 6, Table 7, and Table 8 at 298.15 K for three different tie-lines. In the upper left corner, the phase diagram of the ternary LLE is shown, and the three tie-lines, for which the interfacial concentration profiles were calculated, are also plotted: solid lines concentration profiles correspond to the solid tie-line, dashed lines to the dashed tie-line, and dotted lines to the dotted tie-line.

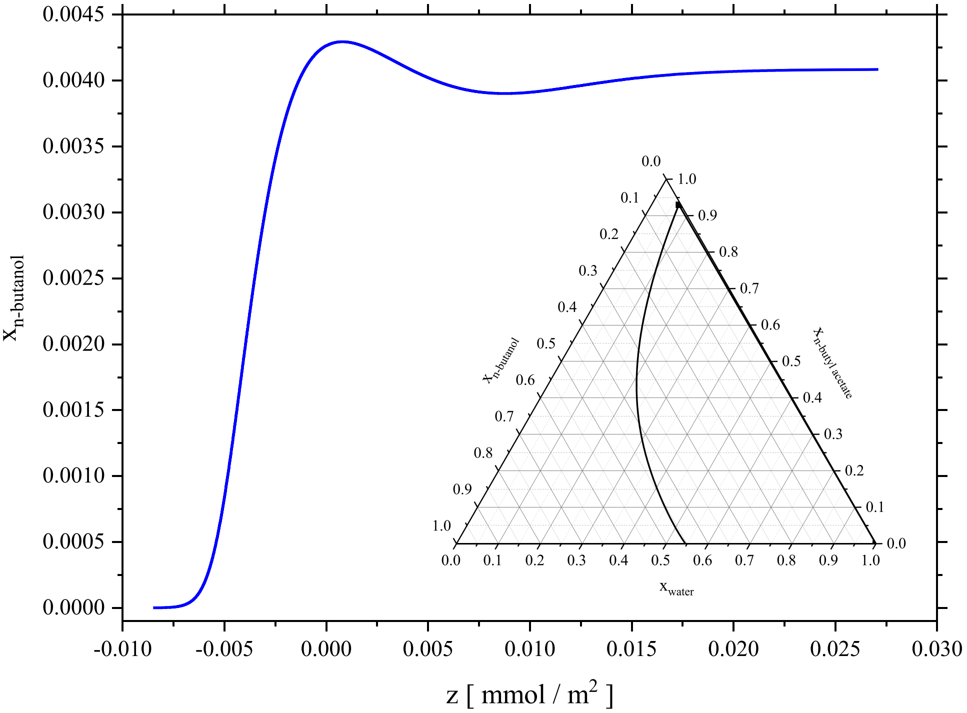

Fig. 16. Calculated interfacial concentration profile of n-butanol using Eq. (9) in combination with the NRTL-model and the parameters listed in Table 6, Table 7, and Table 8 at 298.15 K at infinite dilution of n-butanol. In the lower right corner, the phase diagram of the ternary LLE is shown, and the tie-line, for which the interfacial concentration profile was calculated, is also plotted.

and interfacial tension data sets from this work was found for the considered ternary mixtures. These systems can thus be theoretically and with high accuracy described. Starting from the theoretical framework of the original DGT, the modified DGT was developed by performing a simple mathematical transformation and by considering the Gibbs energy to be equal to the Helmholtz energy, if the pressure-dependency of the liquid densities is neglected. In this case, the prediction of the interfacial properties of mixtures at LLE using a g^E model can be achieved in a numerically more efficient way. In the case of a ternary system, and if the interfacial properties of the corresponding binary demixed subsystems and the phase equilibria data of the ternary mixture are known, all the interfacial properties of the ternary system at LLE can be predicted theoretically. For instance, the concentration profiles of the different components across the interface were predicted. Effects like the selective enrichment of the solubilizer in the interface for both investigated ternary systems were also observed in this work. In addition, the interfacial enrichment of the solubilizer decreases by increasing its concentration in the bulk phases at a given temperature.

Dedication

This paper is dedicated to the farewell of Ralf Dohrn in honor of his scientific achievements. I would like to thank him for his very fruitful cooperation in different fields and a long-time friendship. We wish Ralf a great time after his retirement.

CRediT authorship contribution statement

Joe Hajjar: Writing – original draft, Investigation, Data curation, Conceptualization. **Sabine Enders:** Writing – review & editing, Writing – original draft, Investigation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Sabine Enders reports financial support was provided by Karlsruhe Institute of Technology. Sabine Enders reports a relationship with Karlsruhe Institute of Technology that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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