Viscosity and Interfacial Tension of Ternary Mixtures Consisting of Linear Alkanes, Alcohols, and/or Dissolved Gases Using Surface Light Scattering and Equilibrium Molecular Dynamics Simulations

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Abstract
Ternary mixtures consisting of liquids and dissolved gases with either two solvents or solutes are characterized by determining their liquid dynamic viscosity $\eta_L$ and interfacial tension $\sigma$ using surface light scattering (SLS) and equilibrium molecular dynamics (EMD) simulations in the temperature range between (298 and 573) K and for mole fractions of the dissolved gas up to 0.20. The four ternary mixtures of interest are $n$-hexadecane + $n$-octacosane + carbon dioxide (CO$_2$), $n$-hexadecane + nitrogen (N$_2$) + CO$_2$, as well as 1-hexadecanol + $n$-octacosane with CO$_2$ or water (H$_2$O). With SLS, $\eta_L$ and $\sigma$ of the two ternary mixtures containing $n$-hexadecane are accessed with average relative expanded experimental uncertainties (coverage factor $k = 2$) of $u_r(\eta_L) = 0.021$ and $u_r(\sigma) = 0.019$. EMD simulations are performed for all four ternary mixtures and give access to $\eta_L$ and $\sigma$ with average relative expanded statistical uncertainties ($k = 2$) of $u_r(\eta_L) = 0.15$ and $u_r(\sigma) = 0.061$. The influence of the dissolved gases is investigated by comparing the thermophysical properties of the ternary mixtures to those of the pure solvent or the binary subsystems. The results for the ternary mixture consisting of $n$-hexadecane, $n$-octacosane, and CO$_2$, which include a variation of the composition of the binary subsystem, i.e. the solvent mixture, have shown the reduction of both properties, due to dissolving CO$_2$, to be independent of the solvent composition. For the ternary mixture consisting of $n$-hexadecane, N$_2$, and CO$_2$, the reduction in both properties can be estimated by adding up the reduction determined for the binary subsystems, i.e. $n$-hexadecane with dissolved N$_2$ or CO$_2$, which suggest that the presence of a further solute does not influence the impact of a dissolved gas.

Keywords Gases · Hydrocarbons · Interfacial tension · Molecular dynamics simulations · Surface light scattering · Ternary mixtures · Viscosity

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1 Introduction

Fluid systems consisting of liquids with dissolved gases with more than two different substances play an important role in many fields of chemical and biological engineering and energy technology. Applications where the working fluid consists of such a multicomponent system with dissolved gases include synthesis processes, for instance, the production of alcohols from carbon monoxide (CO) or carbon dioxide (CO₂) and hydrogen (H₂) in hydrogenation processes [1] or the production of methanol or dimethyl ether from synthesis gas using liquid-phase catalysis [2, 3]. In the latter example, mixtures will contain not only the desired products, but also intermediate reaction products, side products, as well as the reactants in the form of dissolved gases, and can be characterized as a multicomponent mixture with liquids and dissolved gases. For designing related equipment as well as modeling and optimization of involved processes, reliable knowledge on the thermophysical properties of such working fluids is required at process-relevant conditions. In this work, the liquid dynamic viscosity \( \eta_L \) and interfacial tension \( \sigma \) are of particular interest due to their requirement for the design and modeling of processes and related apparatuses in chemical and energy engineering. In addition, accurate knowledge on \( \eta_L \) and \( \sigma \) also helps to develop and validate prediction models which can be applied to novel systems. However, reliable data for \( \eta_L \) and \( \sigma \) of liquids with dissolved gases of representative fluid systems at process relevant conditions with respect to temperature \( T \), pressure \( p \), and composition, specifically for systems having more than two species, is still limited.

One method, which enables the absolute determination of \( \eta_L \) and \( \sigma \) at macroscopic thermodynamic equilibrium is the optical technique surface light scattering (SLS). SLS probes the dynamics of thermal fluctuations at phase boundaries in a contactless manner via an analyzes of the temporal behavior of the light scattered at such boundaries. Using hydrodynamic theory to describe the dynamics of such surface fluctuations, this technique has been used to determine viscosity and surface or interfacial tension of various fluid classes, including reference fluids [4, 5], liquid mixtures [6–8] as well as liquids with dissolved gases [9–11], with typical relative expanded experimental uncertainties (coverage factor \( k = 2 \)) of \( u_r = 0.02 \) for both \( \eta_L \) and \( \sigma \). Complementary to experiments, a powerful tool used in thermophysical property research is molecular dynamics (MD) simulations. Based on an accurate description of the inter- and intramolecular interactions, MD simulations predict trajectories of molecules in a statistical ensemble by solving Newton’s equations of motion. From the resulting information, various thermophysical properties, including \( \eta_L \) and \( \sigma \), can be determined. Since MD simulations provide detailed information on the molecular and atomistic trajectories, an insight into the fluid structure is possible, which is helpful to develop an understanding of structure–property relationships. Another advantage of MD simulations is their ability to operate at thermodynamic states which are only hardly accessible by experiments. However, the accuracy of MD simulations relies on the underlying molecular force fields (FFs) describing the intra- and intermolecular interactions between atoms or molecules. To develop and validate
the FFs used in MD simulations for the prediction of thermophysical properties, reliable experimental data with low uncertainties are necessary.

The present work is part of an ongoing project at the institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP). With a special focus on \( \eta_L \) and \( \sigma \), the main aim of this project is to contribute to a reliable database of thermophysical properties of systems consisting of liquids with dissolved gases and to develop a fundamental understanding of structure–property relationships. For this purpose, long linear, branched, and cyclic hydrocarbons and related alcohols as well as their mixtures with and without dissolved gases are systematically investigated up to process-relevant conditions. The reliable data from SLS serve as the basis to validate and develop FFs used in equilibrium MD (EMD) simulations. The EMD simulation results are used to develop structure–property relationships, e.g., the influence of surface enrichment on the interfacial tension [9, 12, 13]. Within the overall project, which aims to get a fundamental understanding on how the molecular characteristics of the solvent and solute influence the thermophysical properties of the mixture, the first publication in the series reported thermophysical properties of 12 different long linear and branched alkanes and alcohols with a carbon number between 12 and 40 up to \( T = 573 \) K [14]. Within this context, based on the results from our own experiments, a modification to the optimized potentials for liquid simulations FF for long hydrocarbons (L-OPLS) [15, 16] could be proposed for a better representation of fluid behavior up to 573 K for all 12 pure liquids. This modification incorporates a \( T \)-dependency to the description of dispersive and repulsive interactions defined by the Lennard–Jones (LJ) potential and will be identified as L-OPLS-T FF [14]. Then, SLS and EMD simulations were extended to investigations of liquid–liquid and gas–liquid binary systems. \( \eta_L \) and \( \sigma \) of three binary liquid mixtures of \( n \)-hexadecane with \( n \)-octacosane, 1-hexadecanol, or 2,2,4,4,6,8,8-heptamethylnonane (HMN) over the complete composition range and up to \( T = 573 \) K were studied [13]. Furthermore, \( \eta_L \) and \( \sigma \) of binary gas–liquid systems were investigated up to \( T = 573 \) K and a solute mole fraction \( x_{\text{solute}} = 0.20 \). First, \( \eta_L \) and \( \sigma \) of binary gas–liquid mixtures based on six different solutes in the solvent \( n \)-hexadecane were investigated to probe the influence of solute characteristics on mixture properties [9]. The gases \( \text{H}_2 \), helium (He), methane (\( \text{CH}_4 \)), \( \text{H}_2\text{O} \), \( \text{CO} \), and \( \text{CO}_2 \) were selected due to their difference in size, weight, sphericity, and polarity. Investigations were then further extended to include an analysis of how solvent characteristics influence \( \eta_L \) and \( \sigma \) of binary mixtures consisting of liquids with dissolved gases. Systematic investigations were performed for binary systems based on the same six gases dissolved in solvents, featuring difference in molecular size, weight, branching, hydroxylation, and chain length [11]. These solvents are 1-hexadecanol, 2-butyl-1-octanol, HMN, 2,6,10,15,19,23-hexamethyloctacosane (squalane), \( n \)-octacosane, \( n \)-triacontane, and the liquid organic hydrogen carrier reference systems diphenylmethane (DPM) and its hydrogenated analogue dicyclohexylmethane (DCM).

In the present work, \( \eta_L \) and \( \sigma \) of ternary gas–liquid mixtures are determined via SLS and EMD simulations with the L-OPLS-T FF [14–16] up to \( T = 573 \) K and solute mole fractions of up to 0.20. To investigate the influence of constituent species with different molecular characteristics on the thermophysical properties of a ternary system, one solvent with two different dissolved gases or two solvents with
one dissolved gas species are investigated. The ternary mixtures of interest for the former category are \(n\)-hexadecane with dissolved \(\text{N}_2\) and \(\text{CO}_2\) at different mole fractions of \(x_{\text{N}_2}\) and \(x_{\text{CO}_2}\). For the latter category, mixtures of the linear alkanes \(n\)-octacosane and \(n\)-hexadecane with dissolved \(\text{CO}_2\) are studied. To investigate the influence of hydroxylation and hydrogen bonding on the studied properties of ternary systems, mixtures of \(n\)-octacosane and \(1\)-hexadecanol with either dissolved \(\text{CO}_2\) up to \(x_{\text{CO}_2} = 0.20\) or dissolved \(\text{H}_2\text{O}\) up to \(x_{\text{H}_2\text{O}} = 0.09\) are investigated with EMD simulations.

In the following, first, the theory, experimental procedure, and data evaluation for the SLS experiments are presented. Afterwards, details necessary for the EMD simulations including the simulation parameters, applied FFs, and data evaluation methods used in this work are outlined. Finally, the results for \(\eta_L\) and \(\sigma\) of the ternary mixtures are presented and the influence of the dissolved gas are discussed by comparing the properties of the ternary mixtures to those of the binary subsystems or the pure solvents investigated in our previous studies.

## 2 Experimental Section

### 2.1 Materials and Sample Preparation

The names, sources, purities in mass fraction \(w\) or volume fraction \(\varphi\) as specified by suppliers, CAS numbers, and molar masses \(M\) of all substances used in this work are provided in Table 1. The solvents \(n\)-hexadecane (\(n\)-C\(_{16}\)H\(_{34}\)) and \(n\)-octacosane (\(n\)-C\(_{28}\)H\(_{58}\)) were filtered with a polytetrafluoroethylene filter with a pore size of 220 nm to remove particle-like impurities. Filtering was performed under ambient condition for \(n\)-hexadecane and approximately 20 K above its melting point for \(n\)-octacosane. The filtered alkanes were then degassed at around (313 and 353) K at \(p\) below 10 Pa for approximately 3 h and stored under an argon atmosphere for further usage. For each investigation, the cleaned sample cell is first filled with

| Substance                  | CAS number | Source      | \(M\) (g·mol\(^{-1}\)) | Weight fraction \(w\) or volume fraction \(\varphi\) purity | Purification method             |
|----------------------------|------------|-------------|---------------------|-------------------------------------------------|---------------------------------|
| \(n\)-hexadecane (\(n\)-C\(_{16}\)H\(_{34}\)) | 544-76-3   | Alfa Aesar  | 226.44              | \(w = 0.9910^a\)                               | Filtration and evacuation       |
| \(n\)-octacosane (\(n\)-C\(_{28}\)H\(_{58}\)) | 630-02-4   | Alfa Aesar  | 394.77              | \(w = 0.9934^a\)                               | Filtration and evacuation       |
| Nitrogen (\(\text{N}_2\))      | 7727-37-9  | Linde AG    | 28.013              | \(\varphi \geq 0.9980^a\)                      | None                            |
| Carbon dioxide (\(\text{CO}_2\)) | 124-38-9   | Linde AG    | 44.01               | \(\varphi \geq 0.9999^a\)                      | None                            |

\( \text{Purity as specified in the certificate of analysis of the supplier} \)
approximately 40 mL of the liquid sample. The cell is then flushed with He to create an inert atmosphere at 0.1 MPa before introducing the investigated gas or gases.

For the first ternary mixture of n-hexadecane + CO$_2$ + N$_2$, this 40 mL sample is entirely n-hexadecane and is filled into the sample cell under ambient conditions. The first investigated gas which is then introduced to the sample cell is CO$_2$ due to its high solubility. The cell temperature is adjusted to 298.15 K and CO$_2$ is introduced up to pressures to estimate (10 or 20)% dissolved CO$_2$ according to the solubility data of Breman et al. [17]. Once the system has equilibrated, the second gas N$_2$ is introduced with an added pressure to approximate (2.5 and 5.0)% dissolved N$_2$ at $T=298.15$ K according to the solubility data of Tremper and Prausnitz [18] and Lin et al. [19]. This totals four different ternary mixtures. The fill pressures of each gas are provided in the footnote of Table 2. It is assumed that the solubilities of the two gases in n-hexadecane are independent of each other. For each solute, the mole fraction in the liquid phase $x_i$ is estimated according to $x_i = p_i / H_{ij}$, where $p_i$ is the partial pressure of the solute in the vapor phase and $H_{ij}$ is the Henry’s law constant acquired from refs 17–19. Once filled, the cell is sealed, and the measurement series is performed under isochoric conditions.

The second investigated system, containing n-hexadecane + n-octacosane + CO$_2$, consists of six unique ternary mixtures. The 40 mL which is filled into the sample cell is a binary liquid mixture consisting of n-hexadecane and n-octacosane with mole fraction n-hexadecane of 0.25, 0.50, or 0.75. The binary liquid mixture is prepared with the same procedure as described in ref 13 and the uncertainty of the mixture compositions is estimated to be 0.01. The mixture is heated to approximately 373 K and then filled into the sample cell which is preheated to about $T=373$ K. The cell is flushed with Argon before and after filling. The investigated gas, CO$_2$, is then introduced at $T=373.15$ K and pressures to approximate (10 or 20)% dissolved CO$_2$ at this $T$. The solubility of CO$_2$ in the binary alkane mixture is approximated from a mole fraction-weighted Henry constant considering solubility data of the two binary mixtures of n-hexadecane + CO$_2$ and n-octacosane + CO$_2$ from Breman et al. [17] and Huang et al. [20]. These six mixtures are not investigated under isochoric conditions. At each temperature, $p$ may be adjusted to maintain the (10 or 20)% dissolved CO$_2$. Recorded experimental pressures for all mixtures at each temperature are provided in Table 2.

### 2.2 Surface Light Scattering: Liquid Viscosity and Interfacial Tension

The liquid dynamic viscosity $\eta_L$ and interfacial tension $\sigma$ are simultaneously determined in an absolute way at macroscopic thermodynamic equilibrium for all investigated mixtures via the contactless, optical technique surface light scattering (SLS). The reader is referred to the literature [21–24] as well as to our previous studies for a detailed description of the theory and application of this technique [6, 7, 9, 11, 13, 14, 25]. In the present work, the probed surface fluctuations exhibit an oscillatory behavior, identical in nature to that of our previous studies of binary mixtures containing n-hexadecane with n-octacosane [13] or with a dissolved gas [9].
Table 2  Liquid dynamic viscosity $\eta_L$ and interfacial tension $\sigma$ of the ternary mixtures of $n$-hexadecane and $n$-octacosane, with dissolved CO$_2$ or of $n$-hexadecane with dissolved N$_2$ and CO$_2$ obtained by SLS under saturation conditions as well as the estimated compositions of each component in the liquid phase $x_1$, $x_2$, and $x_3$, the liquid density $\rho_L$, vapor density $\rho_V$, and the vapor viscosity $\eta_V$ for each investigated temperature $T$ and pressure $p$.

| $T$ (K) | $p$ (MPa) | 100·($x_1$) | 100·($x_2$) | 100·($x_3$) | $\rho_L$ (kg·m$^{-3}$) | 100·$u_r$ ($\rho_L$) | $\rho_V$ (kg·m$^{-3}$) | 100·$u_r$ ($\rho_V$) | $\eta_V$ (μPa·s) | 100·$u_r$ ($\eta_V$) | $\sigma$ (mN·m$^{-1}$) | 100·$u_r$ ($\sigma$) |
|--------|-----------|-----------|-----------|-----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 373.22 | 1.44      | 22.14     | 66.71     | 11.14     | 745.7         | 0.30           | 21.05          | 18.68          | 2.042          | 1.5            | 20.78          | 1.6            |
| 398.22 | 1.59      | 22.23     | 66.96     | 10.81     | 729.8         | 0.30           | 21.97          | 19.81          | 1.429          | 1.7            | 18.86          | 1.6            |
| 423.23 | 1.78      | 22.27     | 67.08     | 10.65     | 713.7         | 0.30           | 22.74          | 20.92          | 1.107          | 2.3            | 17.86          | 1.4            |
| 473.22 | 2.08      | 22.28     | 67.13     | 10.58     | 680.8         | 0.30           | 23.76          | 23.05          | 0.7061         | 1.4            | 14.89          | 1.5            |
| 522.57 | 2.34      | 22.30     | 67.18     | 10.51     | 647.3         | 0.80           | 24.05          | 25.03          | 0.486          | 2.6            | 12.48          | 1.3            |
| 572.45 | 2.52      | 22.32     | 67.25     | 10.43     | 612.5         | 1.5            | 23.77          | 26.83          | 0.3365         | 2.7            | 9.62           | 1.8            |
| 0.223 $n$-hexadecane (1) + 0.670 $n$-octacosane (2) + 0.107 CO$_2$ (3) |
| 372.82 | 1.58      | 44.47     | 44.54     | 10.99     | 738.6         | 0.30           | 23.10          | 18.67          | 1.593          | 2.1            | 19.82          | 2.1            |
| 397.86 | 1.64      | 44.87     | 44.93     | 10.19     | 722.4         | 0.30           | 23.04          | 19.80          | 1.1673         | 0.59           | 18.32          | 1.6            |
| 422.80 | 1.82      | 45.06     | 45.13     | 9.81      | 706.0         | 0.30           | 23.25          | 20.90          | 0.895          | 1.7            | 16.9           | 2.3            |
| 472.71 | 2.11      | 45.11     | 45.17     | 9.72      | 672.3         | 0.30           | 23.89          | 23.02          | 0.589          | 1.9            | 14.2           | 1.6            |
| 523.15 | 2.33      | 45.04     | 45.10     | 9.86      | 637.0         | 0.80           | 24.13          | 25.00          | 0.4147         | 2.1            | 11.3           | 1.8            |
| 573.15 | 2.50      | 45.04     | 45.10     | 9.86      | 600.8         | 1.5            | 23.52          | 26.71          | 0.2940         | 2.0            | 8.7            | 1.7            |
| 0.449 $n$-hexadecane (1) + 0.450 $n$-octacosane (2) + 0.101 CO$_2$ (3) |
| 372.92 | 1.59      | 67.93     | 22.87     | 9.20      | 729.2         | 0.30           | 23.56          | 18.67          | 1.172          | 2.0            | 18.92          | 2.1            |
| 397.84 | 1.74      | 68.25     | 22.97     | 8.78      | 712.7         | 0.30           | 23.83          | 19.80          | 0.910          | 1.8            | 17.85          | 1.6            |
| 422.77 | 1.87      | 68.38     | 23.02     | 8.60      | 695.7         | 0.30           | 24.17          | 20.90          | 0.712          | 2.0            | 16.43          | 1.3            |
| 472.66 | 2.16      | 68.30     | 22.99     | 8.71      | 660.8         | 0.30           | 24.70          | 23.00          | 0.4622         | 2.2            | 12.95          | 1.8            |
| 522.59 | 2.39      | 68.15     | 22.94     | 8.91      | 624.3         | 0.80           | 24.63          | 24.94          | 0.3186         | 1.8            | 10.10          | 1.9            |
| 572.55 | 2.52      | 68.11     | 22.93     | 8.96      | 586.3         | 1.5            | 23.70          | 26.57          | 0.2303         | 2.4            | 7.43           | 1.8            |
| 0.682 $n$-hexadecane (1) + 0.230 $n$-octacosane (2) + 0.088 CO$_2$ (3) |
| 373.24 | 2.74      | 19.90     | 59.96     | 20.13     | 743.2         | 0.30           | 41.64          | 18.70          | 1.801          | 0.93           | 18.75          | 1.5            |
| 398.29 | 3.10      | 20.00     | 60.25     | 19.75     | 727.9         | 0.30           | 43.61          | 19.84          | 1.323          | 2.5            | 17.50          | 2.1            |
| 0.200 $n$-hexadecane (1) + 0.603 $n$-octacosane (2) + 0.197 CO$_2$ (3) |
| $T$ (K) | $p$ (MPa) | 100·($x_1$) | 100·($x_2$) | 100·($x_3$) | $\rho_L$ (kg·m$^{-3}$) | 100·$u_r$ ($\rho_L$) | $\rho_V$ (kg·m$^{-3}$) | $\eta_V$ (μPa·s) | $\eta_L$ (mPa·s) | 100·$u_r$ ($\eta_L$) | $\sigma$ (mN·m$^{-1}$) | 100·$u_r$ ($\sigma$) |
|-------|--------|-------------|-------------|-------------|-----------------|-------------------|-----------------|----------------|----------------|-----------------|-----------------|----------------|
| 423.30 | 3.42   | 20.05       | 60.40       | 19.55       | 711.5           | 0.30              | 45.05           | 20.94          | 1.002          | 1.8             | 15.89           | 2.4             |
| 473.35 | 4.01   | 20.07       | 60.46       | 19.47       | 675.9           | 0.30              | 46.60           | 23.08          | 0.650          | 2.0             | 13.55           | 2.3             |
| 523.42 | 4.50   | 20.05       | 60.40       | 19.55       | 636.2           | 0.80              | 46.71           | 25.11          | 0.445          | 2.9             | 10.90           | 2.0             |
| 572.46 | 4.84   | 20.03       | 60.34       | 19.63       | 593.5           | 1.5               | 45.80           | 26.97          | 0.3173         | 1.8             | 8.58            | 1.5             |
| 423.30 | 3.42   | 20.05       | 60.40       | 19.55       | 711.5           | 0.30              | 45.05           | 20.94          | 1.002          | 1.8             | 15.89           | 2.4             |
| 473.35 | 4.01   | 20.07       | 60.46       | 19.47       | 675.9           | 0.30              | 46.60           | 23.08          | 0.650          | 2.0             | 13.55           | 2.3             |
| 523.42 | 4.50   | 20.05       | 60.40       | 19.55       | 636.2           | 0.80              | 46.71           | 25.11          | 0.445          | 2.9             | 10.90           | 2.0             |
| 572.46 | 4.84   | 20.03       | 60.34       | 19.63       | 593.5           | 1.5               | 45.80           | 26.97          | 0.3173         | 1.8             | 8.58            | 1.5             |
| 373.17 | 2.85   | 40.93       | 40.99       | 18.08       | 736.9           | 0.30              | 43.45           | 18.70          | 1.440          | 1.7             | 18.00           | 2.3             |
| 398.17 | 3.18   | 41.08       | 41.14       | 17.77       | 720.8           | 0.30              | 44.90           | 19.83          | 1.082          | 2.6             | 17.09           | 2.4             |
| 423.16 | 3.55   | 41.05       | 41.11       | 17.84       | 703.8           | 0.30              | 46.37           | 20.94          | 0.829          | 1.9             | 15.18           | 2.0             |
| 473.16 | 4.11   | 40.79       | 40.85       | 18.35       | 667.1           | 0.30              | 48.28           | 23.07          | 0.5482         | 1.5             | 12.83           | 1.3             |
| 523.14 | 4.60   | 40.76       | 40.81       | 18.43       | 627.1           | 0.80              | 47.52           | 25.08          | 0.3767         | 2.1             | 10.06           | 2.7             |
| 572.65 | 4.58   | 41.27       | 41.33       | 17.40       | 584.0           | 1.5               | 43.32           | 26.90          | 0.278          | 6.4             | 7.83            | 5.1             |
| 373.18 | 2.93   | 63.53       | 21.38       | 15.09       | 727.7           | 0.30              | 44.60           | 18.70          | 1.080          | 1.0             | 17.43           | 1.8             |
| 398.21 | 3.28   | 63.29       | 21.30       | 15.41       | 711.6           | 0.30              | 46.59           | 19.84          | 0.8361         | 0.96            | 16.06           | 2.7             |
| 423.21 | 3.63   | 63.12       | 21.24       | 15.64       | 694.4           | 0.30              | 47.79           | 20.94          | 0.6480         | 1.2             | 14.62           | 1.1             |
| 473.20 | 4.17   | 62.78       | 21.13       | 16.10       | 656.8           | 0.30              | 48.41           | 23.07          | 0.4370         | 2.0             | 11.89           | 1.3             |
| 523.24 | 4.56   | 62.67       | 21.09       | 16.23       | 614.7           | 0.80              | 47.43           | 25.06          | 0.3092         | 2.5             | 8.98            | 3.7             |
| 573.35 | 4.83   | 62.57       | 21.06       | 16.37       | 568.1           | 1.5               | 45.45           | 26.87          | 0.2172         | 3.6             | 6.51            | 2.0             |
| 298.16 | 2.63   | 87.40       | 2.32        | 10.28       | 769.5           | 0.30              | 35.66           | 17.49          | 2.504          | 1.7             | 23.27           | 1.2             |
| 323.06 | 2.91   | 88.88       | 2.77        | 8.35        | 752.7           | 0.30              | 35.66           | 18.68          | 1.565          | 3.5             | 20.98           | 0.76            |
| 347.99 | 3.16   | 89.45       | 3.21        | 7.34        | 735.6           | 0.30              | 35.66           | 19.82          | 1.097          | 1.3             | 19.74           | 1.3             |
| 372.90 | 3.38   | 89.59       | 3.65        | 6.76        | 718.3           | 0.30              | 35.66           | 20.91          | 0.823          | 1.7             | 17.93           | 0.93            |
| 397.83 | 3.58   | 89.50       | 4.08        | 6.42        | 700.8           | 0.30              | 35.66           | 21.97          | 0.6318         | 1.6             | 16.33           | 2.1             |
Table 2 (continued)

| $T$ (K) | $p$ (MPa) | 100·($x_1$) | 100·($x_2$) | 100·($x_3$) | $\rho_L$ (kg·m$^{-3}$) | 100·$u_r$ ($\rho_L$) | $\rho_V$ (kg·m$^{-3}$) | 100·$u_r$ ($\rho_V$) | $\eta_V$ (μPa·s) | 100·$u_r$ ($\eta_V$) | $\eta_L$ (mPa·s) | 100·$u_r$ ($\eta_L$) | $\sigma$ (mN·m$^{-1}$) | 100·$u_r$ ($\sigma$) |
|---------|-----------|-------------|-------------|-------------|----------------------|----------------------|----------------------|----------------------|----------------|----------------------|----------------|----------------------|----------------|----------------------|
| 422.76  | 3.77      | 89.26       | 4.52        | 6.22        | 683.0                | 0.30                 | 35.67                | 22.98                | 0.5064         | 1.6                    | 14.84          | 0.87                 |
| 472.53  | 4.09      | 88.50       | 5.38        | 6.13        | 646.8                | 0.30                 | 35.71                | 24.91                | 0.3403         | 1.7                    | 11.84          | 0.91                 |
| 522.41  | 4.37      | 87.41       | 6.28        | 6.31        | 609.5                | 0.80                 | 35.85                | 26.70                | 0.2396         | 2.9                    | 8.84           | 1.7                  |
| 572.33  | 4.63      | 85.92       | 7.35        | 6.73        | 571.3                | 1.5                  | 36.20                | 28.27                | 0.1655         | 4.3                    | 5.97           | 1.9                  |
| 0.850 n-hexadecane (1) + 0.050 N$_2$ (2) + 0.100 CO$_2$ (3) |
| 298.14  | 5.06      | 83.57       | 5.27        | 11.15       | 770.6                | 0.30                 | 63.60                | 18.46                | 2.4260         | 0.77                   | 21.49          | 3.2                  |
| 323.11  | 5.45      | 84.85       | 6.08        | 9.07        | 752.9                | 0.30                 | 63.61                | 19.58                | 1.5470         | 4.3                    | 19.74          | 2.7                  |
| 348.12  | 5.62      | 85.39       | 6.63        | 7.98        | 735.2                | 0.30                 | 63.61                | 20.61                | 1.0770         | 2.3                    | 18.40          | 2.5                  |
| 373.08  | 5.70      | 85.60       | 7.06        | 7.35        | 717.6                | 0.30                 | 63.60                | 21.59                | 0.8060         | 2.3                    | 17.10          | 1.7                  |
| 398.04  | 5.81      | 85.49       | 7.54        | 6.98        | 700.1                | 0.30                 | 63.60                | 22.56                | 0.6320         | 2.1                    | 15.67          | 0.81                 |
| 422.99  | 6.07      | 84.94       | 8.30        | 6.77        | 682.6                | 0.30                 | 63.61                | 23.55                | 0.5010         | 2.9                    | 14.31          | 2.4                  |
| 0.775 n-hexadecane (1) + 0.025 N$_2$ (2) + 0.200 CO$_2$ (3) |
| 298.14  | 3.65      | 76.59       | 2.60        | 20.80       | 770.7                | 0.30                 | 54.28                | 17.52                | 2.1470         | 1.8                    | 20.95          | 2.3                  |
| 323.11  | 3.96      | 79.98       | 3.00        | 17.02       | 754.3                | 0.30                 | 54.28                | 18.69                | 1.4190         | 2.0                    | 19.43          | 1.7                  |
| 348.13  | 4.23      | 81.58       | 3.37        | 15.05       | 737.4                | 0.30                 | 54.28                | 19.81                | 1.0150         | 1.9                    | 18.04          | 1.4                  |
| 373.16  | 4.46      | 82.37       | 3.70        | 13.93       | 720.1                | 0.30                 | 54.28                | 20.88                | 0.7760         | 2.1                    | 16.56          | 2.1                  |
| 398.11  | 4.66      | 82.71       | 4.01        | 13.28       | 702.3                | 0.30                 | 54.28                | 21.92                | 0.6040         | 2.9                    | 15.21          | 1.2                  |
| 423.11  | 4.85      | 82.78       | 4.29        | 12.93       | 684.1                | 0.30                 | 54.28                | 22.92                | 0.4853         | 1.6                    | 14.05          | 1.8                  |
| 473.09  | 5.18      | 82.36       | 4.84        | 12.80       | 646.3                | 0.30                 | 54.32                | 24.85                | 0.3290         | 2.1                    | 11.07          | 1.1                  |
| 523.09  | 5.51      | 81.30       | 5.46        | 13.24       | 606.7                | 0.80                 | 54.46                | 26.67                | 0.2324         | 2.1                    | 8.33           | 1.7                  |
| 573.11  | 5.92      | 79.45       | 6.37        | 14.18       | 565.3                | 1.5                  | 54.78                | 28.35                | 0.1646         | 3.2                    | 5.53           | 2.4                  |
| 0.750 n-hexadecane (1)+ 0.050 N$_2$ (2)+ 0.200 CO$_2$ (3) |
| 298.14  | 5.50      | 74.75       | 4.96        | 20.29       | 772.0                | 0.30                 | 73.70                | 18.45                | 2.1320         | 3.0                    | 19.43          | 2.2                  |
| 323.15  | 5.72      | 77.99       | 5.42        | 16.59       | 754.6                | 0.30                 | 73.70                | 19.50                | 1.3700         | 2.6                    | 18.12          | 2.3                  |
Table 2 (continued)

| $T$ (K) | $p$ (MPa) | 100·($x_1$) | 100·($x_2$) | 100·($x_3$) | $\rho_L$ (kg·m$^{-3}$) | 100·$u_r(\rho_L)$ | $\rho_V$ (kg·m$^{-3}$) | 100·$u_r(\rho_V)$ | $\eta_V$ (μPa·s) | 100·$u_r(\eta_V)$ | $\eta_L$ (mPa·s) | 100·$u_r(\eta_L)$ | $\sigma$ (mN·m$^{-1}$) | 100·$u_r(\sigma)$ |
|--------|-----------|-------------|-------------|-------------|-------------------------|----------------------|-------------------------|----------------------|------------------|-----------------|------------------|-----------------|-----------------|-----------------|
| 348.15 | 5.94      | 79.44       | 5.88        | 14.68       | 737.1                    | 0.30                 | 73.70                   | 20.53                 | 1.001            | 1.5             | 17.32            | 2.2             |
| 373.15 | 6.15      | 80.06       | 6.36        | 13.58       | 719.4                    | 0.30                 | 73.70                   | 21.54                 | 0.777            | 1.7             | 16.31            | 1.8             |
| 398.15 | 6.37      | 80.20       | 6.86        | 12.94       | 701.5                    | 0.30                 | 73.70                   | 22.53                 | 0.599            | 1.8             | 14.83            | 1.4             |
| 423.16 | 6.60      | 80.01       | 7.40        | 12.60       | 683.4                    | 0.30                 | 73.70                   | 23.51                 | 0.4843           | 1.4             | 13.76            | 1.1             |
| 473.21 | 7.10      | 78.89       | 8.64        | 12.47       | 646.8                    | 0.30                 | 73.74                   | 25.41                 | 0.3239           | 1.3             | 10.68            | 1.4             |
| 523.21 | 7.69      | 76.81       | 10.30       | 12.89       | 609.6                    | 0.80                 | 73.87                   | 27.24                 | 0.2272           | 3.0             | 7.86             | 2.3             |

Directly measured values for frequency $\omega_q$ and damping $\Gamma$ at a defined wave vector $q$ of surface fluctuations were combined with reference data for $\rho_L$, $\rho_V$, and $\eta_V$ described in the text to determine $\eta_L$ and $\sigma$ by an exact numerical solution of the dispersion relation. [21, 22] The relative expanded uncertainties ($k=2$) for the employed properties are $u_r(\rho_V)=0.05$ and $u_r(\eta_V)=0.10$. For $\rho_L$, $\eta_L$, and $\sigma$, the relative expanded uncertainties $u_r(\rho_L)$, $u_r(\eta_L)$, and $u_r(\sigma)$, respectively, are given in the table. $u_r(\rho_L)$ is estimated to account for the unknown impact of the dissolved gas. The relative expanded uncertainty ($k=2$) for pressure is $u_r(\rho)=0.005$ for all investigations. The combined expanded uncertainty ($k=2$) for the temperature $u_C(T)$ is estimated to be 0.02 K at 298.15 K and 0.8 K at 573.15 K and can be extrapolated linearly in between. The partial pressures for N$_2$ and CO$_2$ during the filling procedure at $T=298.15$ K for the four mixtures consisting of n-hexadecane, N$_2$, and CO$_2$ are, in order of appearance in the table, (1.99 and 0.755) MPa, (4.45 and 0.821) MPa, (2.23 and 1.55) MPa, and (4.05 and 1.51) MPa. The uncertainty of the specified compositions $x_1$ and $x_2$ for the ternary mixture containing n-hexadecane and n-octacosane is estimated to be $u(x)=0.01$ based on the accuracy of the scale used in the sample preparation and the change of composition during measurements due to the transition of molecules from the liquid to the vapor phase.
All ten ternary mixtures in this work were investigated on the experimental SLS setup detailed in our previous publication for the binary mixtures containing He, N₂, H₂O, or CO₂ [9, 11]. The combined expanded uncertainty (\(k = 2\)) for \(T\) accounting for the difference of the two \(T\) probes is estimated to be \(U(T) = 0.02\) K at 298.15 K and \(U(T) = 0.8\) K at 573.15 K and can be extrapolated linearly in between. The overall relative uncertainty for the reported pressure, which includes the pressure stability during a measurement series, is \(u_r(p) = 0.005 (k = 2)\).

The determination of \(\eta_L\) and \(\sigma\) is possible by solving the complete form of the dispersion equation \(D(\eta_L, \eta_V, \rho_L, \rho_V, \sigma, \Gamma, \omega q, q)\) for surface waves at the boundary between a liquid phase (subscript L) and a vapor phase (subscript V). Here, \(\rho\) and \(q\) refer to the density and the modulus of the wave vector, while \(\Gamma\) and \(\omega q\) describe the damping and the frequency of the surface wave of a specific \(q\) value. In this work, four to six measurements are performed at each thermodynamic state, where different \(q\) values corresponding to different external angles of incidence relative to the normal of the vapor–liquid interface \(\Theta_E\) between (2.5 and 3.2)° were adjusted. Literature data on \(\rho_L\) could not be found for the present mixtures. However, \(\rho_L\) is available for the binary mixtures \(n\)-hexadecane + \(n\)-octacosane at \(x_{n\text{-hexadecane}} = (0.25, 0.50, \) and 0.75) [13] and \(n\)-hexadecane + CO₂ at \(x_{CO_2} = (0.069, 0.59, \) and 0.73) [26] up to 473 K, and for \(n\)-hexadecane + N₂ up to 475 K at atmospheric pressure [27]. Here, the estimated amount of dissolved N₂ is less than 0.02% across the complete temperature range. Ashcroft et al. [28] measured \(n\)-hexadecane + CO₂ and \(n\)-hexadecane + N₂ at \(T = 298\) K and atmospheric \(p\) and found CO₂ to have a seven times stronger impact on \(\rho_L\) than N₂. Their estimated mole fraction of dissolved gas was \(1.34 \times 10^{-3}\) and \(1.39 \times 10^{-2}\) for N₂ and CO₂ [28]. For the present work, the impact of dissolved N₂ on \(\rho_L\) in the \(n\)-hexadecane + CO₂ + N₂ mixtures is neglected. For input into the dispersion equation, \(\rho_L\) is calculated with the estimated \(x_{CO_2}\) provided in Table 2. In the ternary mixture \(n\)-hexadecane + \(n\)-octacosane + CO₂, \(\rho_L\) for the binary liquid mixture \(n\)-hexadecane + \(n\)-octacosane are used with deviations between \(n\)-hexadecane + CO₂ and pure \(n\)-hexadecane applied to account for the influence of dissolved CO₂. In our previous publication, it is mentioned that a dissolved gas should have a relatively small impact on the mixture \(\rho_L\) when the molecular weight between components is large [11]. Therefore, the impact of CO₂ in \(n\)-octacosane is assumed negligible compared to that observed for \(n\)-hexadecane + CO₂. Should \(\rho_L\) data for these ternary mixtures become available, the values for \(\eta_L\) and \(\sigma\) reported in this work can be corrected using the expressions provided in the work of Klein et al. [9].

The vapor phase properties \(\eta_V\) and \(\rho_V\) were calculated via the Lucas model [29] and Dalton’s law using the aforementioned solubility data. The composition of the vapor phase was calculated with Raoult’s law, assuming that the partial pressure \(p_i\) in the vapor phase can be calculated by multiplying the liquid phase mole fraction \(x_i\) with the vapor pressure of the pure component under saturation conditions. The partial pressures in the vapor phase for the gases are calculated with the REFPROP software version 10.0 [30] from the recorded experimental pressures assuming isochoric conditions starting from the respective fill pressures for CO₂ and N₂ of (0.773 and 1.86, 0.837 and 4.22, 1.56 and 2.09, and 1.53 and
3.97) MPa. Estimated relative expanded uncertainties \((k=2)\) for \(\eta_V\) and \(\rho_V\) are assumed to be \(u_r = (0.10 \text{ and } 0.05)\) [29].

Reported uncertainties in \(\eta_L\) and \(\sigma\) were calculated via an error propagation scheme [4, 6] considering uncertainties introduced by the measured variables and adopted reference data or predictions. Total expanded relative measurement uncertainties \((k=2)\), averaged over all investigated systems and thermodynamic states, were determined to be \(u_r(\eta_L) = 0.021\) and \(u_r(\sigma) = 0.019\).

### 3 EMD Simulations

Using EMD simulations, multiple thermophysical properties are accessible by modeling the dynamics of molecules in a statistical ensemble under equilibrium conditions. These simulations are, however, highly sensitive to the inter- and intramolecular interactions described by the underlying force field (FF) using atomistic pair-wise potentials. The dynamics of the atoms and molecules can then be calculated using classical Newtonian equations of motion. For a detailed description of the underlying theory of EMD simulations, the reader is referred to the respective literature [31–33].

In this work, EMD simulations were performed using the GROMACS software package, version 5.1.2 [34] at \(T = (323.15, 348.15, 373.15, 423.15, 473.15 \text{ and } 573.15)\) K. The bonds between the lighter hydrogen atoms and the heavier carbon or oxygen atoms in the solvent molecules were constrained using the LINCS algorithm [35] and the simulation timestep was 2 fs. Dispersive and electrostatic interactions are calculated within a cutoff radius of 1.6 nm. Long-range electrostatic interactions beyond the cutoff radius are modeled via the particle-mesh Ewald (PME) algorithm [36]. For simulations in the slightly compressed liquid phase, standard dispersion corrections for energy and pressure are considered beyond the cutoff radius. For simulations in vapor–liquid equilibrium (VLE), long-range LJ interactions are considered using the LJ-PME algorithm [37].

For systems of two solvents mixed with one gas species, simulations were initialized by randomly inserting the solvent molecules into a cubic simulation box with periodic boundary conditions in all directions. The total number of solvent molecules of both species consist of approximately 30,000 atoms. This amount was selected to maintain comparable simulation effort between all simulations. Approximate atomic proximity is then estimated with a steepest-decent energy minimization of the binary mixture. After this, solute molecules are added to match the calculated solute mole fractions in the liquid phase according to the aforementioned solubility data. A further energy minimization for the ternary mixture is performed. Then, the desired \(T\) and \(p\) are realized in a 1 ns simulation run in the canonical ensemble \((NVT)\) followed by a 10 ns simulation run in the isothermal-isobaric ensemble \((NpT)\). To avoid a possible phase separation, the reference \(p\) in the latter equilibration run is set 0.2 MPa above the calculated saturation \(p\). The liquid density \(\rho_L\) is determined from this same simulation run in the \(NpT\) ensemble, neglecting the first 0.5 ns to account for the equilibration of \(T\) and \(p\). \(\eta_L\) is calculated from a subsequent simulation in the \(NVT\) ensemble. Here, simulation runtimes are approximately (40
to 60) ns long. The calculation of $\eta_L$ from these runs is based on the Green–Kubo method [38, 39] and the reader is referred to our previous publications for further detail [10, 14].

To calculate $\sigma$, the cubic simulation boxes are then extended in the $z$-direction to create two vapor–liquid interfaces and introduce VLE. For typical simulation boxes with a box length of (6.0 to 7.4) nm, previous studies have shown that an extension by a factor of three is sufficient to ensure that the long solvent molecules in the vapor phase only interact with one of the two interfaces at any given time [14]. To calculate the number of solute molecules for the vapor phase, the vapor densities of the solute at the required $p_i$ were obtained from the REFPROP database [30]. Afterwards, VLE simulations of about (15 to 20) ns in the $NVT$ ensemble were performed to calculate $\sigma$ from the diagonal elements of the pressure tensor, i.e. $p_{xx}$, $p_{yy}$, and $p_{zz}$ [33], neglecting the first 1 ns from calculations to account for equilibration.

4 Results and Discussion

The results from SLS experiments for $\eta_L$ and $\sigma$ are summarized in Table 2 along with their expanded experimental uncertainties, the liquid-phase mole fraction, and the input parameters for solving the dispersion relation at each indicated state point. Headers for the six mixtures consisting of $n$-hexadecane, $n$-octacosane, and CO$_2$ indicate the average mixture compositions. Due to the large variation in the liquid-phase compositions for the mixtures consisting of $n$-hexadecane, N$_2$, and CO$_2$, the desired composition is given in the headers. The data for $\eta_L$ and $\sigma$ calculated from EMD simulations, together with their thermodynamic states and statistical uncertainties, are reported in Table 3.

The data for $\eta_L$ and $\sigma$ of the ternary mixtures are shown and discussed in the following sections. First, both SLS and EMD results for the mixtures $n$-hexadecane + $n$-octacosane + CO$_2$ and the $n$-hexadecane + N$_2$ + CO$_2$ are directly compared to check the ability of the EMD simulations to predict the properties of the ternary mixtures. Initially in the form of a parity plot in Fig. 1 and later shown with previously reported correlations for the pure component $n$-hexadecane or the mixture’s binary subsystem.

The results in Fig. 1 show that EMD simulations tend to overpredict $\eta_L$ and $\sigma$ of the ternary mixtures in comparison to the experimental results. The average absolute relative deviation of $\eta_L$ and $\sigma$ between EMD and SLS results is (34 and 12)% for all ten mixtures where a direct comparison could be made. This agrees with all previous investigations within this series, where the L-OPLS-T FF was applied for the prediction of $\eta_L$ and $\sigma$ of the pure solvents [14, 40], binary liquid mixtures [13], as well as binary mixtures consisting of a liquid with a dissolved gas [9, 11, 12]. The results also show that by applying the $T$-dependent correction, the overprediction of both properties is $T$ independent. Therefore, the influence of the dissolved gas can still be investigated using EMD simulations by comparing the results for the ternary mixtures to the results for the pure solvents or binary subsystems which were also investigated by EMD simulations. Congruently, the reported SLS experimental results are compared to our previously reported SLS results for the corresponding
Table 3 Liquid density $\rho_L$, liquid dynamic viscosity $\eta_L$, and interfacial tension $\sigma$ with their expanded statistical uncertainties ($k=2$) of the ternary mixtures of $n$-hexadecane and $n$-octacosane with dissolved CO$_2$, of $n$-hexadecane with dissolved N$_2$ and CO$_2$, and of 1-hexadecanol and $n$-octacosane with dissolved CO$_2$ or H$_2$O obtained by EMD at or close to saturation conditions for each investigated temperature $T$ and pressure $p$

| $T$ (K) | $p$ (MPa) | $\rho_L$ (kg·m$^{-3}$) | $10^3\cdot u_r (\rho_L)$ | $\eta_L$ (mPa·s) | $10^3\cdot u_r (\eta_L)$ | $\sigma$ (mN·m$^{-1}$) | $10^3\cdot u_r (\sigma)$ |
|---------|-----------|-------------------------|--------------------------|----------------|------------------------|------------------------|------------------------|
| 373.16  | 1.54      | 751.01                  | 0.49                     | 2.59           | 12                     | 23.5                   | 5.2                    |
| 423.15  | 2.09      | 716.52                  | 0.20                     | 1.66           | 18                     | 20.0                   | 6.0                    |
| 473.15  | 2.31      | 682.76                  | 0.56                     | 1.01           | 18                     | 17.4                   | 7.5                    |
| 573.15  | 2.77      | 612.18                  | 0.75                     | 0.489          | 15                     | 10.67                  | 7.0                    |
| 373.15  | 1.79      | 742.79                  | 0.76                     | 2.01           | 19                     | 22.2                   | 12                     |
| 423.15  | 1.90      | 708.14                  | 0.62                     | 1.28           | 17                     | 18.9                   | 5.4                    |
| 473.15  | 2.28      | 673.45                  | 0.54                     | 0.82           | 14                     | 16.527                 | 0.15                   |
| 573.16  | 2.74      | 599.86                  | 0.91                     | 0.393          | 4.2                    | 9.42                   | 5.9                    |
| 373.15  | 1.78      | 732.72                  | 0.63                     | 1.70           | 29                     | 20.4                   | 4.9                    |
| 423.15  | 1.96      | 697.18                  | 0.41                     | 1.02           | 23                     | 17.7                   | 15                     |
| 473.16  | 2.33      | 661.52                  | 0.64                     | 0.68           | 18                     | 14.5                   | 11                     |
| 573.14  | 2.79      | 583.62                  | 1.2                      | 0.294          | 8.0                    | 8.5                    | 12                     |
| 373.15  | 2.99      | 752.51                  | 0.75                     | 2.34           | 27                     | 22.7                   | 7.8                    |
| 423.15  | 3.57      | 718.07                  | 0.53                     | 1.45           | 11                     | 19.4                   | 5.8                    |
| 473.16  | 4.23      | 683.95                  | 0.36                     | 0.98           | 11                     | 15.23                  | 5.7                    |
| 573.15  | 5.02      | 613.11                  | 0.46                     | 0.427          | 12                     | 10.0                   | 13                     |
| 373.14  | 3.08      | 744.84                  | 0.52                     | 1.93           | 22                     | 20.67                  | 2.7                    |
| 423.15  | 3.65      | 709.56                  | 0.35                     | 1.145          | 7.8                    | 17.5                   | 6.9                    |
| 473.15  | 4.11      | 674.92                  | 0.45                     | 0.764          | 7.0                    | 14.2                   | 7.4                    |
| 573.14  | 4.85      | 599.93                  | 0.47                     | 0.372          | 7.1                    | 8.726                  | 0.77                   |
| 373.15  | 3.14      | 734.82                  | 0.55                     | 1.40           | 21                     | 20.1                   | 6.3                    |
| 423.14  | 3.84      | 698.89                  | 0.43                     | 0.98           | 17                     | 15.9                   | 11                     |
| 473.16  | 4.53      | 662.48                  | 0.53                     | 0.612          | 13                     | 13.2                   | 7.9                    |
| 573.15  | 5.05      | 583.98                  | 0.83                     | 0.293          | 16                     | 7.27                   | 10                     |
| 323.15  | 3.15      | 756.47                  | 0.34                     | 2.15           | 16                     | 23.16                  | 4.0                    |
| 348.15  | 3.30      | 737.57                  | 0.62                     | 1.42           | 17                     | 20.7                   | 9.7                    |
| 373.15  | 3.47      | 719.36                  | 0.28                     | 1.17           | 12                     | 18.7                   | 7.4                    |
| 423.15  | 4.01      | 682.81                  | 0.56                     | 0.64           | 16                     | 16.3                   | 6.4                    |
| 473.14  | 4.41      | 645.54                  | 0.78                     | 0.423          | 11                     | 14.00                  | 5.2                    |
| 573.16  | 4.85      | 563.90                  | 0.48                     | 0.211          | 21                     | 7.245                  | 0.45                   |
| 323.15  | 3.06      | 755.46                  | 0.28                     | 2.18           | 18                     | 21.3                   | 15                     |
Table 3 (continued)

| T (K) | $p$ (MPa) | $\rho_L$ (kg·m$^{-3}$) | $10^3 u_r (\rho_L)$ | $\eta_L$ (mPa·s) | $100 u_r (\eta_L)$ | $\sigma$ (mN·m$^{-1}$) | $100 u_r (\sigma)$ |
|-------|-----------|------------------------|---------------------|------------------|-------------------|------------------|------------------|
| 348.15 | 3.47      | 736.21                 | 0.40                | 1.376            | 7.0               | 20.8             | 5.6              |
| 373.14 | 3.47      | 717.72                 | 0.41                | 1.09             | 16                | 18.7             | 6.7              |
| 423.15 | 3.96      | 680.85                 | 0.18                | 0.62             | 17                | 15.99            | 3.7              |
| 473.15 | 4.32      | 643.15                 | 0.38                | 0.41             | 27                | 12.14            | 7.4              |
| 573.15 | 4.96      | 559.74                 | 0.95                | 0.196            | 18                | 6.54             | 9.1              |

0.775 n-hexadecane + 0.200 CO$_2$ + 0.025 N$_2$

| 323.15 | 4.12      | 759.70                 | 0.45                | 1.95             | 11                | 21.48            | 2.2              |
| 348.15 | 4.46      | 740.41                 | 0.36                | 1.45             | 18                | 19.977           | 0.41             |
| 373.15 | 4.59      | 721.50                 | 0.34                | 0.96             | 14                | 17.95            | 3.7              |
| 423.15 | 5.04      | 683.63                 | 0.36                | 0.612            | 9.6               | 15.42            | 4.2              |
| 473.15 | 5.40      | 644.73                 | 0.30                | 0.391            | 7.8               | 12.31            | 5.5              |
| 573.14 | 6.06      | 558.87                 | 0.87                | 0.192            | 17                | 5.97             | 14               |

0.750 n-hexadecane + 0.200 CO$_2$ + 0.050 N$_2$

| 323.15 | 5.98      | 760.06                 | 0.42                | 1.66             | 20                | 21.5             | 8.7              |
| 348.15 | 6.22      | 740.72                 | 0.49                | 1.39             | 10                | 18.8             | 7.2              |
| 373.15 | 6.25      | 721.84                 | 0.51                | 1.02             | 27                | 17.5             | 9.6              |
| 423.15 | 6.83      | 683.94                 | 0.80                | 0.602            | 3.8               | 14.2             | 7.1              |
| 473.15 | 7.28      | 645.35                 | 0.82                | 0.389            | 20                | 11.66            | 4.4              |
| 573.15 | 8.68      | 562.94                 | 0.42                | 0.203            | 12                | 5.88             | 4.5              |

0.450 n-octacosane + 0.450 1-hexadecanol + 0.100 CO$_2$

| 373.15 | 1.68      | 760.330                | 0.11                | 2.71             | 25                | 24.2             | 5.6              |
| 423.15 | 1.88      | 724.68                 | 0.19                | 1.49             | 13                | 20.09            | 1.5              |
| 473.15 | -0.40     | 685.89                 | 0.25                | 0.821            | 6.6               | 16.58            | 2.1              |
| 573.15 | 0.76      | 610.56                 | 0.55                | 0.367            | 7.8               | 10.49            | 5.3              |

0.400 n-octacosane + 0.400 1-hexadecanol + 0.200 CO$_2$

| 373.15 | 3.07      | 762.44                 | 0.91                | 2.22             | 25                | 21.90            | 3.4              |
| 423.15 | 3.33      | 726.12                 | 0.58                | 1.31             | 15                | 18.31            | 4.5              |
| 473.15 | 1.53      | 686.99                 | 1.1                 | 0.74             | 17                | 15.47            | 3.8              |
| 573.15 | 3.25      | 611.35                 | 1.4                 | 0.3619           | 1.5               | 9.27             | 6.6              |

0.478 n-octacosane + 0.478 1-hexadecanol + 0.044 H$_2$O

| 373.15 | -0.15     | 758.33                 | 0.23                | 2.91             | 26                | 24.6             | 6.0              |
| 423.15 | 0.15      | 722.62                 | 0.51                | 1.456            | 6.4               | 21.69            | 4.2              |
| 473.15 | -2.30     | 683.40                 | 0.67                | 0.79             | 30                | 17.90            | 3.4              |
| 573.15 | -1.25     | 606.93                 | 0.49                | 0.399            | 10                | 11.49            | 2.0              |

0.455 n-octacosane + 0.455 1-hexadecanol + 0.090 H$_2$O

| 373.15 | -0.14     | 758.72                 | 0.79                | 3.03             | 10                | 25.30            | 1.3              |
| 423.15 | 0.09      | 722.52                 | 0.50                | 1.44             | 11                | 21.38            | 4.3              |
| 473.15 | -2.39     | 682.31                 | 0.32                | 0.973            | 8.3               | 17.95            | 1.6              |
| 573.15 | -0.70     | 605.15                 | 0.46                | 0.383            | 8.8               | 11.40            | 1.8              |

The reported pressures are obtained from the simulation in the compressed liquid phase in a canonical ensemble.
pure solvents or binary mixtures [13, 14]. Since no data are available in the literature for $\eta_L$ and $\sigma$ of the ternary mixtures investigated in this work, a literature review was not possible.

4.1 Viscosity

The results for $\eta_L$ of the ternary mixtures consisting of $n$-octacosane, $n$-hexadecane, and CO$_2$ from SLS experiments (left) and EMD simulations (right) are shown in the upper part of Fig. 2. In addition, the results for $\eta_L$ of the binary solvent mixtures, i.e. binary mixtures of $n$-octacosane and $n$-hexadecane, investigated by SLS and EMD simulations [13] and represented by corresponding $T$-dependent correlations are shown in Fig. 2. While the $T$-dependent correlations for $\eta_L$ of the binary solvent mixtures investigated by SLS can be found in our previous publication [13] the corresponding correlations for $\eta_L$ from EMD simulations were obtained by fitting $\eta_L$ data reported in the same publication with respect to $T$ using a Vogel-type equation according to

$$\eta_{L,\text{calc}}(T)/\text{mPa} \cdot \text{s} = \exp \left( \sum_{i=0}^{n} \frac{\eta_{L,i}}{T^i} \right).$$

Here, all simulated data had the same statistical weight in the fitting and $\eta_{L,i}$ were the mixture-specific fit coefficients. To study the influence of the dissolved CO$_2$ in more detail, the relative deviation between $\eta_L$ of the ternary mixtures and that of the binary solvent mixtures is given in the lower part of Fig. 2, which will be discussed in the following.

The results in Fig. 2 obtained by SLS show that $\eta_L$ tends to decrease when CO$_2$ is dissolved in the solvent mixtures. This reduction increases with increasing amount of dissolved CO$_2$. The influence of the dissolved CO$_2$ here is more pronounced at low $T$ with a maximum deviation of 18% at $T=373$ K and reduces with increasing $T$.
This $T$-dependent trend for $\eta_L$ was already observed for binary mixtures of CO$_2$ dissolved in linear and branched alkanes and alcohols [9, 11]. The results for the three different binary solvent mixtures at a given $x_{\text{CO}_2}$, however, are mostly within combined uncertainty which suggests that the composition of the solvent mixture seems to have a negligible influence on $\eta_L$ of the ternary mixtures. This is surprising given the fact that dissolving CO$_2$ leads to a relative reduction of 21% when dissolved in $n$-hexadecane [9] and 10% when dissolved in $n$-octacosane [11] at $T=373$ K. An investigation of the influence of dissolved CO$_2$ on $\eta_L$ of the binary solvent mixtures by EMD simulations is difficult due to the large relative expanded statistical uncertainties ($k=2$) averaging about $u_r(\eta_L)=0.15$. The results for $\eta_L$ of a given ternary mixture always fall within combined uncertainties with that of the respective binary solvent mixture. For the ternary mixture with $x_{\text{CO}_2}=0.20$, however, the EMD simulations seem to predict the qualitative influence of the dissolved CO$_2$ correctly with larger relative deviations from the binary solvent mixture of about $-10\%$ at $T\leq473$ K and smaller deviations of up to $-6\%$ at $T=573.15$ K. For the ternary mixture with $x_{\text{CO}_2}=0.10$, the results for $\eta_L$ scatter around the values of

Fig. 2 (Top) Liquid dynamic viscosity $\eta_L$ of the ternary mixtures of $n$-hexadecane, $n$-octacosane, and CO$_2$ by SLS (left) and EMD simulations (right) as a function of $T$ and solute mole fraction (open and closed symbols). For comparison, the correlations for $\eta_L$ of the binary mixtures of $n$-hexadecane+$n$-octacosane from SLS and EMD simulations [13] are shown (lines). (Bottom) Relative deviations of $\eta_L$ of the ternary mixtures from $\eta_L$ of the binary mixtures of $n$-hexadecane and $n$-octacosane. The dash-dotted lines mark the average expanded uncertainty ($k=2$) of the data for the binary mixtures. Error bars are shown only exemplarily for the mixtures containing 20% CO$_2$ for clarity. The mole fractions of CO$_2$ and $n$-hexadecane given in the legend are approximate values. The real composition at each $T$ can be taken from Tables 2 and 3.
the binary solvent mixtures with relative deviations between (−6 and 12)%. This indicates that the L-OPLS-T FF might not be able to accurately predict the amount of free volume in the fluid mixture, which was already discussed in our previous publications [9, 11, 14].

The results for $\eta_L$ for the ternary mixtures consisting of $n$-hexadecane, CO$_2$, and N$_2$ from SLS experiments (left) and EMD simulations (right) are shown in the upper part of Fig. 3. Additionally, corresponding $T$-dependent correlations of the results for $\eta_L$ of pure $n$-hexadecane investigated by SLS [25] and EMD simulations [14] are shown in Fig. 3. The correlation for data from SLS can be found in our previous publication [25]. For EMD simulations, the results for $\eta_L$ of pure $n$-hexadecane were correlated with respect to $T$ using Eq. 1. In the present work, the influence of the dissolved gases is studied by calculating the relative deviation between $\eta_L$ of the ternary mixtures and that of pure $n$-hexadecane. This is shown in the lower part of Fig. 3.

The results in Fig. 3 show that $\eta_L$ for the mixtures with $x_{N_2}$=(0.025 and 0.050) at a given $x_{CO_2}$ are always within 3% of each other. The influence of dissolved CO$_2$, on the other hand, is much more pronounced, especially at low $T$. At $T=298$ K, for example, the relative reduction in $\eta_L$ in comparison to pure $n$-hexadecane is

![Fig. 3](image_url)
approximately 20% for $x_{CO_2} = 0.10$ and 30% for $x_{CO_2} = 0.20$. These values agree well with the finding for the binary mixture of CO$_2$ dissolved in n-hexadecane, where a relative reduction in comparison to pure n-hexadecane was found in $\eta_L$ to be approximately 19% for $x_{CO_2} = 0.10$ and 30% for $x_{CO_2} = 0.20$ [9]. Also, the $T$-dependent trend of the deviations between $\eta_L$ of the ternary mixtures and that of pure n-hexadecane, which shows a reducing influence of the dissolved gases with increasing $T$, agrees well with the observations made for the binary subsystem consisting of CO$_2$ dissolved in n-hexadecane [9]. This suggests that the influence of the dissolved N$_2$ is much smaller than the influence of the dissolved CO$_2$ and can be neglected in the case of the studied ternary mixture. This is also in agreement with our previous investigation of the subsystems consisting of N$_2$ dissolved in n-hexadecane, where $\eta_L$ of the binary mixtures was found to be mostly within combined uncertainties with that of pure n-hexadecane [9].

The results for $\eta_L$ for the ternary mixtures from EMD simulations, which are shown on the right side of Fig. 3, have a large relative expanded statistical uncertainty ($k=2$) of $\sigma(\eta_L) = 0.15$. Similar to the case for the ternary mixture of n-hexadecane, n-octacosane, and CO$_2$, only a qualitative evaluation of the influence of the dissolved gas is possible, since $\eta_L$ of all ternary mixtures are within combined uncertainties of pure n-hexadecane. For the mixtures with $x_{CO_2} = 0.20$, the EMD simulations predict a reduction in $\eta_L$ with respect to pure n-hexadecane with relative deviations up to $-31\%$ at the lowest investigated $T = 323$ K. Additionally, the influence of the dissolved gases decreases with increasing $T$, which is qualitatively in agreement with the SLS results. For $x_{CO_2} = 0.10$, the predicted reduction in $\eta_L$ of about $-(10 \text{ to } 15)\%$ at low $T$ and the convergence of $\eta_L$ with increasing $T$ to that of pure n-hexadecane seem to agree with the SLS results. For a quantitative analysis of the influence of the dissolved gases, however, the statistical uncertainties of the EMD simulations must be reduced, which would require either more independent simulation runs or longer simulation runtimes and, therefore, higher computational costs.

Finally, the ternary mixtures consisting of an equimolar mixture of n-octacosane and 1-hexadecanol and the solutes CO$_2$ or H$_2$O were studied using EMD simulations to investigate whether the presence of a polar solvent, in this case the primary alcohol 1-hexadecanol, has an influence on the thermophysical properties of mixtures. The results for $\eta_L$ from EMD simulations are shown in the upper part of Fig. 4. Additionally, also $\eta_L$ of the pure solvents n-octacosane and 1-hexadecanol [14] are shown in the form of a $T$-dependent correlation according to Eq. 1 as well as $\eta_L$ for the equimolar mixture based on the EMD results for the pure solvents and the mixing rule $\ln(\eta_{L,mix}(T)) = \sum_i w_i \cdot \ln(\eta_{L,i}(T))$. To study the influence of the solutes in more detail, the relative deviation between $\eta_L$ of the ternary mixtures and that of the binary solvent mixture according to the aforementioned mixing rule is given in the lower part of Fig. 4.

For the solvent H$_2$O, the EMD simulations of the ternary mixtures predict smaller $\eta_L$ which are within combined uncertainties with $\eta_{L,mix}$ and have an average deviation from $\eta_{L,mix}$ of $-11\%$. These results can be compared to the previous work of Klein et al. [11] who reported results for $\eta_L$ and $\sigma$ of the binary
subsystems consisting of H$_2$O dissolved in the solvents n-octacosane or 1-hexadecanol obtained from SLS and EMD simulations. Both methods showed agreement between $\eta_L$ of the binary mixture and that of the pure solvent. While the results in the present work agree with these findings for the n-octacosane + H$_2$O mixture, the SLS results of Klein et al., compared to their EMD results, have shown up to 37% larger values for the mixtures consisting of H$_2$O in 1-hexadecanol [11]. This was related to the inability of the applied FFs to accurately describe the relatively strong hydrogen bonding between H$_2$O and 1-hexadecanol. Since the same FFs are used in this work, the same outcome is expected for the present results for $\eta_L$ of the ternary mixtures. However, no experimental data are available for the ternary mixtures shown here, so a failure of the EMD simulations to predict larger $\eta_L$ of the ternary mixtures in comparison to $\eta_{L,mix}$ cannot be validated. Regardless, since the applied SPC/E FF [41] for the H$_2$O molecules does not consider a $T$-dependency in its FF parameters, it is strongly suggested that the hydrogen bonds are also not accurately represented in the ternary mixture. Also for the ternary mixtures containing 1-hexadecanol, n-octacosane, and CO$_2$, the results for $\eta_L$ of the ternary mixture are within combined uncertainty with $\eta_{L,mix}$ due to the large statistical uncertainty in determining $\eta_L$ by EMD simulations. Here, however, we can find the typical $T$-dependent trend for $\eta_L$ caused by dissolved CO$_2$.

**Fig. 4** (Top) Liquid dynamic viscosity $\eta_L$ of the ternary mixtures consisting of n-octacosane and 1-hexadecanol with dissolved CO$_2$ or H$_2$O investigated by EMD simulations as a function of $T$ and solute mole fraction (open and closed symbols). For comparison, $\eta_L$ of the pure solvents n-octacosane and 1-hexadecanol investigated by EMD simulations [14] are shown (dashed and dotted lines). Additionally, $\eta_{L,mix}$ calculated via a mass-based logarithmic mixing rule described in the work of Lenahan et al. [13] for an equimolar binary mixture of n-octacosane and 1-hexadecanol is shown (solid line). (Bottom) Relative deviations of $\eta_L$ of the ternary mixtures from $\eta_{L,mix}$. The dash-dotted lines mark the average expanded statistical uncertainty ($k = 2$) of the pure solvents.
This is a reduction of $\eta_L$ which is more pronounced at low $T$. The relative reduction, which is between $- (30$ and $17)\%$ for $x_{CO_2}=0.20$, is larger than the one seen by SLS and EMD simulations for the binary mixture of CO$_2$ dissolved in $n$-octacosane and closer to the ones observed by EMD simulations for CO$_2$ dissolved in the primary alcohol 1-dodecanol [12]. This can be explained by stronger interactions between CO$_2$ and the polar alcohol in comparison to the non-polar $n$-alkane and was also found when comparing binary mixtures of CO$_2$ dissolved in $n$-dodecane with mixtures of CO$_2$ dissolved in 1-dodecanol by EMD simulations. Here, a stronger reduction of $-44\%$ for the 1-dodecanol-based mixture was observed in comparison to $-22\%$ for the $n$-dodecane-based mixture at $T=323.15$ K and $x_{CO_2}=0.20$ [12].

### 4.2 Interfacial Tension

The results for $\sigma$ of the ternary mixtures consisting of $n$-octacosane, $n$-hexadecane, and CO$_2$ from SLS experiments (left) and EMD simulations (right) are shown in the upper part of Fig. 5. Additionally, the results for $\sigma$ of the binary solvent mixtures investigated by SLS and EMD simulations [13] and represented by corresponding $T$-dependent correlations are shown in Fig. 5. While the $T$-dependent correlations for $\sigma$ of the binary solvent mixtures investigated by SLS can be found in our previous publication [13], the corresponding correlations for $\sigma$ from EMD simulations were obtained by fitting $\sigma$ reported in the aforementioned publication with respect to $T$ using a second-order polynomial function, which considers all simulated data with the same statistical weight. As was done for $\eta_L$, the influence of dissolved CO$_2$ is investigated by calculating the relative deviation between $\sigma$ of the ternary mixtures and that of the binary solvent mixtures, which is given in the lower part of Fig. 5.

The results in Fig. 5 obtained by SLS show a reduction in $\sigma$ when CO$_2$ is dissolved in the solvent mixtures in all cases. This reduction increases with increasing $x_{CO_2}$. The influence of the dissolved CO$_2$ is more pronounced at large $T$ with a maximum deviation of 22% at $T=573$ K and $x_{CO_2}=0.20$. Similar to $\eta_L$, the composition of the binary solvent mixture seems to have a negligible influence on $\sigma$ of the ternary mixture, which is expressed by a very similar relative reduction in $\sigma$ for the three different solvent compositions at a given $T$ and $x_{CO_2}$. The $T$-dependent trend of the reduction in $\sigma$ due to the dissolved CO$_2$ agrees well with the one observed for the binary subsystems of CO$_2$ dissolved in $n$-hexadecane [9] or $n$-octacosane [11].

In contrast to $\eta_L$, where the influence of the dissolved CO$_2$ could only be investigated qualitatively due to the large uncertainties, the smaller statistical uncertainty related to the determination of $\sigma$ allows a better investigation of the influence of the dissolved gas by EMD simulations. By comparing the relative deviation between $\sigma$ of the ternary mixture and the binary solvent mixtures from SLS and EMD simulations, we can observe that EMD simulations are able to predict the reduction in $\sigma$ by dissolving CO$_2$ correctly over the entire $T$ range. The simulations can predict the $T$-dependent trend of this reduction, its absolute value, as well as the influence of $x_{CO_2}$. This shows that EMD simulations are still able to correctly predict the relative influence of the dissolved gas on $\sigma$, even though they overpredict the absolute values.
for $\sigma$ of the pure solvents and the mixtures in comparison to the experimental results from SLS [9, 11, 13, 14].

The results for $\sigma$ for the ternary mixtures consisting of $n$-hexadecane, CO$_2$, and N$_2$ from SLS experiments (left) and EMD simulations (right) are shown in the upper part of Fig. 6. Additionally, the results for $\sigma$ of pure $n$-hexadecane investigated by SLS [25] and EMD simulations [14] and represented by corresponding $T$-dependent correlations are shown here. The $T$-dependent correlation for $\sigma$ of pure $n$-hexadecane investigated by SLS can be found in our previous publication [25]. The results for $\sigma$ of pure $n$-hexadecane investigated by EMD simulations [14] were correlated with respect to $T$ using a second-order polynomial function. The influence of the dissolved gases was studied by calculating the relative deviation between $\sigma$ of the ternary mixtures and that of pure $n$-hexadecane. This is given in the lower part of Fig. 6.

The results in Fig. 6 show a reduction in $\sigma$ caused by the dissolved gas mixture over the entire $T$ range for all four investigated ternary mixtures. Deviations from $\sigma$ of pure $n$-hexadecane are in the range of $-\,(9.4\text{ to } 27\%)$. An increase of $x_{CO_2}$ and $x_{N_2}$.

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**Fig. 5** (Top) Interfacial tension $\sigma$ of the ternary mixtures of $n$-hexadecane, $n$-octacosane, and CO$_2$ by SLS (left) and EMD simulations (right) as a function of $T$ and solute mole fraction (open and closed symbols). For comparison, the correlations for $\sigma$ of the binary mixtures of $n$-hexadecane and $n$-octacosane from SLS [ref] and EMD simulations [ref] are shown (lines). (Bottom) Relative deviations of $\sigma$ of the ternary mixtures from $\sigma$ of the binary mixtures of $n$-hexadecane and $n$-octacosane. The dash-dotted lines mark the average expanded uncertainty ($k=2$) of the data for the binary mixtures. Error bars are shown only exemplarily for the mixtures containing 20% CO$_2$ for clarity. The mole fractions of CO$_2$ and $n$-hexadecane given in the legend are approximate values. The real composition at each $T$ can be taken from Tables 2 and 3.
leads to a decrease in $\sigma$ and, therefore, an increased reduction. When compared to the binary sub-systems consisting of $n$-hexadecane with dissolved CO$_2$ or N$_2$ [9], it seems that the influence of the different solutes add up in the ternary mixture. For example, the relative reduction in $\sigma$ from that of pure $n$-hexadecane for the ternary mixture with $x_{\text{CO}_2} = 0.10$ and $x_{\text{N}_2} = 0.05$ is $-20\%$. For the binary sub-systems this value is $-(10$ and $11)\%$ for $x_{\text{CO}_2} = 0.10$ and $x_{\text{N}_2} = 0.05$ [9]. The $T$-dependent trend of the reduction decreases with increasing $T$ up to $T = 473$ K. At larger $T$, the reduction increases, resembling that observed for the binary sub-systems. These observations suggest that the influence of multiple different solutes on $\sigma$ can be approximated using the assumption that the influence of the solute can be transferred from binary mixtures to multicomponent mixtures provided no strong interactions between the solute molecules are possible. Whether such an assumption also holds true for systems where strong interactions between the components are possible, e.g. polar solutes in an alcohol, cannot be answered here and must be further investigated.

The results for $\sigma$ for the ternary mixtures from EMD simulations, which are shown on the right side of Fig. 6, predict a similar influence of the solutes. Due to the larger uncertainties related to $\sigma$ of the ternary mixtures from EMD simulations in comparison to those from SLS, $\sigma$ of the four different ternary systems are always within uncertainties. Nevertheless, the relative reduction in $\sigma$ in comparison to the pure $n$-hexadecane predicted by EMD simulations are of the same magnitude and

Fig. 6 (Top) Interfacial tension $\sigma$ of the ternary mixtures of $n$-hexadecane, N$_2$, and CO$_2$ by SLS (left) and EMD simulations (right) as a function of $T$. Symbol fill (open or closed) and shape (diamond or triangle) refer to mole fraction N$_2$ and CO$_2$. For comparison, the correlations for $\sigma$ of pure $n$-hexadecane from SLS [25] and EMD simulations [14] are shown (solid lines). (Bottom) Relative deviations between $\sigma$ of the ternary mixtures from that of pure $n$-hexadecane. The dash-dotted lines mark the average expanded uncertainty ($k=2$) of the data for pure $n$-hexadecane. Error bars are shown only exemplarily for the mixtures containing $x_{\text{CO}_2}=0.20$ for clarity. The mole fractions of the dissolved gas given in the legend are approximate values. The real composition at each $T$ can be taken from Tables 2 and 3.

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show a similar $T$-dependent trend to those from SLS. This suggests that, also for such ternary mixtures, EMD simulations are able to accurately predict the influence of multiple dissolved gases on $\sigma$.

Finally, the results for $\sigma$ of the ternary mixtures consisting of an equimolar mixture of $n$-octacosane and 1-hexadecanol and the solutes CO$_2$ or H$_2$O, which were studied only by EMD simulations, are shown in the upper part of Fig. 7. Also here, $\sigma$ of the pure solvents $n$-octacosane and 1-hexadecanol [14] as well as $\sigma$ for the equimolar mixture based on the EMD results for the pure solvents [14] and the mixing rule $\sigma_{\text{mix}}(T) = \sum_i w_i \cdot \sigma_i(T)$ are shown in the form of a $T$-dependent correlation using a second-order polynomial function. To study the influence of the solutes in more detail, the relative deviation between $\sigma$ of the ternary mixtures and that of the binary solvent mixture according to the aforementioned mixing rule is given in the lower part of Fig. 7.

For the solvent H$_2$O, the EMD simulations predict smaller values within combined uncertainties for $\sigma$ of the ternary mixtures in comparison to $\sigma_{\text{mix}}$ at $T \leq 423.15$ K. This reduction in $\sigma$ increases with increasing $T$ with a maximum deviation of $-10\%$ for $x_{\text{H}_2\text{O}}=0.090$ and $T=573.15$ K. The influence of H$_2$O is very small, so $\sigma$ of the ternary mixtures with $x_{\text{H}_2\text{O}}=(0.045$ and 0.090) are within
combined uncertainties over the entire $T$ range. Since SLS experiments have shown $\sigma$ of the binary mixture consisting of 1-hexadecanol and $H_2O$ to be larger than that of the pure solvent [11], it is suggested that EMD simulations fail to predict that also $\sigma$ of the ternary mixture is larger than that of the binary solvent mixture. The reason for this failure is most probably due to a failure of the FF combination to accurately predict the hydrogen bonds at large $T$. This was already discussed in connection with $\eta_L$ in this work as well as in our previous publications [11, 12].

Also for the ternary mixtures containing 1-hexadecanol, $n$-octacosane, and CO$_2$, the results for $\sigma$ predict a reduction in $\sigma$ by dissolving CO$_2$ with respect to the binary solvent mixture with relative deviations of $- (7.1$ and $16\%)$ for $x_{CO_2} = (0.10$ and $0.20)$ at $T = 373.15$ K. With increasing $T$, the relative deviations increase and are $- (16$ and $26\%)$ for $x_{CO_2} = (0.10$ and $0.20)$ at $T = 573.15$ K. The relative deviations and the $T$-dependent trend are in agreement with the ones found for the binary mixture of $n$-octacosane and CO$_2$ [11]. In order to estimate the influence of the polar alcohol, the results for the binary mixture of 1-dodecanol and CO$_2$ from our previous publication is used [12]. Here, results are compared to those of a mixture based on the non-polar $n$-octacosane with dissolved CO$_2$. A stronger reduction of $\sigma$ by approximately $5\%$ for a given $x_{CO_2}$ over the entire $T$-range was found for the alcohol-based mixture. Given the statistical uncertainty of $\sigma$, it seems that the presence of the polar 1-hexadecanol has only a negligible impact. Therefore, the influence of CO$_2$ in the ternary mixture can be estimated based on the binary sub-system consisting of $n$-octacosane and CO$_2$. This is not surprising, since such long primary alcohols tend to orient themselves with their alkane tail towards the vapor–liquid interface [10, 13, 42].

5 Conclusions

SLS and EMD simulations were used to characterize ternary gas–liquid mixtures through the determination of $\eta_L$ and $\sigma$ in the $T$ range between $(298$ and $573)$ K and solute mole fractions up to about 0.20. The mixtures consisting of $n$-hexadecane, $n$-octacosane, and CO$_2$ as well as $n$-hexadecane, $N_2$, and CO$_2$ were investigated with both SLS and EMD simulations, while the ternary mixtures consisting of 1-hexadecanol, $n$-octacosane, and CO$_2$ as well as 1-hexadecanol, $n$-octacosane, and $H_2O$ are investigated by EMD simulations only. The average relative expanded uncertainties for SLS experiments and EMD simulations are $u_r(\eta_L) = (0.021$ and $0.15)$ and $u_r(\sigma) = (0.019$ and $0.061)$, considering all investigated systems. By comparing the thermophysical properties of the ternary mixtures with the ones of the pure solvents as well as binary subsystems, i.e. binary liquid mixture or binary mixtures consisting of a liquid with a dissolved gas, the influence of the dissolved gas on $\eta_L$ and $\sigma$ could be analyzed. Due to the large uncertainties for $\eta_L$ from EMD simulations, the results for ternary mixtures are often within combined uncertainties with the ones for the pure solvents or binary subsystems, which allowed only a qualitative comparison. The results for the ternary mixture consisting of $n$-hexadecane, $n$-octacosane, and CO$_2$, which include a variation of the composition of the binary sub-system, i.e. the solvent mixture, have shown the reduction of both properties due to
dissolving CO₂ to be independent of the solvent composition. This suggests that the influence of the dissolved gases can be estimated using the results of the binary subsystems, i.e. CO₂ dissolved in n-hexadecane or n-octacosane, and treating the binary solvent subsystem as a pseudo-pure liquid. Also for the ternary mixture consisting of n-hexadecane, N₂, and CO₂, a reduction in both properties due to the dissolved gases was determined using both SLS and EMD simulations. Here, this reduction can be estimated by adding up the reduction determined for the binary subsystem, i.e. n-hexadecane with dissolved N₂ or CO₂. This means that for such ternary mixtures the influence of the dissolved gases can also be estimated only with the help of the binary subsystems.

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Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

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