

**HULIS in
nanoaerosol clusters**

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HULIS in nanoaerosol clusters; investigations of surface tension and aggregate formation using molecular dynamics simulations

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Abstract

Cloud condensation nuclei act as cores for water vapor condensation, and their composition and chemical properties may enhance or depress the ability for droplet growth. In this study we use molecular dynamics simulations to show that humic-like substances of larger systems (8.6 nm in diameter) mimic experimental data well referring to reduction of surface tension. The structural properties examined show the ability for the humic-like substances to aggregate inside the nanoaerosol clusters.

1 Introduction

Understanding climate change is of utmost importance to mankind, since the effects of changes in the climate, both on regional and global scale, severely alter the conditions for life for a vast majority of the species on Earth. The Intergovernmental Panel on Climate Change (IPCC) states in the Forth Assessment Report (AR4) that a major uncertainty in the radiative forcing components of the atmosphere is due to clouds (IPCC, 2007). Therefore it is of interest to refine the representation of clouds in the climate models.

Clouds cannot form unless there is a high relative humidity and presence of cloud condensation nuclei (CCN), that is, the number of aerosol particles available for uptake or condensation of water vapor. The most widely used theory that describes a process in which water vapor condenses and forms liquid cloud drops was developed by the Swedish meteorologist Hilding Köhler in the beginning of the 20th century (Köhler, 1936) and is based on equilibrium thermodynamics. It combines the change in saturation vapor pressure due to a curved surface (the Kelvin effect), and to the solute (the Raoult's Law). At that time only soluble inorganic particles such as sea salt were thought to act as CCN. However, present knowledge concerning the aerosol multi-phase system has identified that its organic components contribute and play a crucial role in the formation of cloud droplets in their ability to lower the surface tension for the

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water uptake (Novakov and Penner, 1993; Shulman et al., 1996; Facchini et al., 1999b; Rodhe, 1999).

Observations of airborne aerosol organic mass in urban areas have identified several surface active compounds, where humic-like substances (HULIS) are found abundant (Cini et al., 1996; Decesari et al., 2001; Facchini et al., 1999a, 2000; O'Dowd et al., 2002; Samburova et al., 2005). Cis-pinonic acid (CPA), which is an oxidation product from terpene evaporating from trees, is an organic acid belonging to the group of HULIS. Surprisingly CPA has also been detected in polar regions, where there is little vegetation (Fu et al., 2009). This is either suggested to depend on long range transport or local/regional marine sources of terpenes. Closely related to CPA are two potentially surface active compounds; Pinic acid (PAD) and Pinonaldehyde (PAL). The surface tension reduction has however been determined experimentally only for one of the above identified HULIS acids, that is, CPA (Shulman et al., 1996; Varga et al., 2007; Kiss et al., 2005). The chemical structures of CPA, PAD, and PAL, are given in Fig. 1.

The underlying objective in this novel study is to use molecular dynamics (MD) simulations to investigate surface tension for clusters of water and surfactants (PAD and PAL) of atmospheric relevance, which to our knowledge have not been experimentally determined previously. In the case of CPA a direct comparison is made with the experimental data by Shulman et al. (1996). Previous work by Nijmeijer et al. (1992), Zakarov et al. (1998), and Chakraborty and Zachariah (2008), have used MD to determine surface tension for water clusters. However, these studies are limited to water and fatty acids. We believe that the HULIS compounds in this study make out a good model for other surfactants present in the troposphere.

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2 Theoretical background

2.1 MD simulations

MD-simulations describe the motion of atoms using Newtonian classical mechanics equations of motion (van der Spoel et al., 2005; Leach, 2001, pp. 303–406). In MD simulations, the Newton's equation of motion is solved numerically to evolve the atoms. The advantage of the MD simulation approach is that one can follow the motion of any atom based on the trajectory generated from the simulations, which is very hard for an experimental study to achieve. Therefore, MD simulations can provide us with detailed information about a system, such as the structure and dynamic properties. Furthermore, the effects of experimental conditions, such as pressure, temperature, on a system can also be studied through MD simulations.

The quality of an MD simulation is determined by the inter-atomic interactions, which can be modeled by incorporating a quantum chemistry calculation code into an MD simulation program, or simply by a predetermined molecular mechanical force field. With the currently available super computers, the quantum chemistry calculation may cover around a hundred atoms and the corresponding MD simulation may be carried out at a time scale of a few hundred picoseconds. However, an MD simulation can be used to simulate a system involving as large as $\sim 10^5$ atoms and at a time scale as long as $\sim 10^2$ nanoseconds when a force field is used to describe the interaction between the atoms.

In order to reach lower concentrations of the HULIS representative for atmospheric conditions, it is necessary that the inter-atomic interactions be described by a force field and the corresponding MD simulations be run on super computers. Since the development of computer science is very fast, the opportunity to go from nuclei mode (0.005 to 0.025 μm diameter) to accumulation mode (0.1 to 2.5 μm diameter) is within reach.

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2.2 Köhler theory

Köhler theory (1936) is as mentioned in the introduction used to predict the water vapor supersaturation of the air needed to condensate water vapor on existing CCN of various diameters according to Eqs. (1)–(4)

$$S = \frac{A}{d} - \frac{B}{d^3} \quad (1)$$

where $\frac{A}{d}$ is the Kelvin effect that depends on the curvature of the droplet and $\frac{B}{d^3}$ is the Raoult effect which is dependent on the solution of compounds in the droplet.

$$A = \frac{4\sigma M_W}{\rho_W RT} \quad (2)$$

where σ is the surface tension. For pure water the experimental value is 72.8 m Nm^{-1} . M_W is the molar weight of water. ρ_W is the density of water. R is the general gas constant ($= 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the temperature.

$$B = \frac{6m_S M_W}{\pi \rho_W m_S} \quad (3)$$

Here, m_S is the mass of the solute, and M_S is the molar weight of the solute. Sometimes the van't Hoff factor i is multiplied with B .

$$B' = Bi \quad (4)$$

Then $i \sim \nu\phi$, where ν is the number of ions produced from one solute molecule and ϕ is the molal osmotic coefficient of the solute in solution. However, the van't Hoff factor is often set to unity (Sorjamaa et al., 2004).

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2.3 Szyszkowski equation

The Köhler Eq. (1) uses a constant value of surface tension independent of droplet diameter. This means that the effect of dissolution during droplet growth is not considered. To make the Köhler theory as relevant as possible for atmospheric conditions, the effect of the concentration of the dissolved organic surfactant on cloud drop activation and growth has to be taken into account. An attempt to account for this is to introduce the empirical relationship developed by Szyszkowski (1908) which has later been improved (Meissner and Michaels, 1949; Facchini, 1999):

$$\frac{\Delta\sigma}{\sigma} = -D\ln(1 + C \cdot E) \quad (5)$$

Here, C is the concentration of the dissolved surfactant, D is a constant, and E is a constant specific for each compound. The constants D and E have been chosen to distinguish them from the constants in the Köhler equation.

3 Calculation details

Water clusters containing different organic molecules (Table 1) were considered. The SPC/E water model (Berendsen, 1987) and the OPLS force field (Jorgensen, 1996) were used to describe the water molecules and the organic molecules, respectively. For each cluster, the initial structure was generated using the GROMACS (Hess et al., 2005; Spoel et al., 2008) utility genbox. First, organic molecules were randomly inserted into a simulation box of $6.8 \times 6.8 \times 6.8 \text{ nm}^3$ and then 10 000 water molecules were added into the box. Thereafter, the box size was increased by 6.0 nm along each axis to minimize the interaction between the cluster and its periodic images so that the artifact caused by the use of the periodic boundary condition was minimized. The initial structure thus obtained was further optimized using the steepest descent and conjugate gradient methods.

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MD simulations were conducted using the GROMACS simulation package. For further reading concerning details in this section, we refer to GROMACS User Manual version 4.0 (Spoel et al., 2005). For all the simulations, the NVT ensemble was used with the temperature maintained at 286 K by the nosé–Hoover thermostat. For the organic molecules, the bonds containing hydrogen atoms were constrained by the LINCS algorithm (Hess, 1997, 2007) and for water molecules, they were kept rigid by the SETTLE algorithm (Miyamoto, 1992). The time step used was 2 fs. A cutoff distance of 10 Å was used to truncate the inter-atomic interactions and the Coulomb interaction beyond the cutoff distance was recovered by the particle mesh Ewald method (Darden, 1993; Essmann, 1995).

For each cluster, the equilibration was done during an MD simulation of 8 ns. Thereafter, a 1 ns production simulation was carried out. During the simulations, the trajectories were recorded at every 1 ps (500 steps). The trajectories were later used to study the structures of the clusters and to evaluate the surface tension of the clusters. The trajectories and their graphical representation could be followed using the VMD package (Humphrey et al., 1996). For details on the method to calculate the surface tension, we refer to Li et al. (2010).

4 Results and discussion

4.1 Aggregate formation

As reported in previous work (Li et al., 2010), CPA could easily move from the interior of a droplet to reside on the surface (Li et al., 2010), since CPA is an amphiphilic molecule. This behavior was expected in this study. However, during the equilibration of the systems described in Table 1, we found that not all the CPA molecules moved to the surface. In fact, there was an accumulation of molecules in the inside of the cluster so that a formation of an aggregate appeared. Table 1 shows when aggregation appeared in the simulations that we refer to as systems of various content of HULIS.

However, none of the systems containing 13 or 27 molecules of surfactant showed a real tendency for aggregation formation. This indicates a micelle type of dynamics (Tanford, 1973) with critical micelle concentration (cmc) as a threshold for formation of such aggregates.

The behavior of aggregate formation is different from what was reported in a previous study by Li et al. (2010) where all CPA molecules moved to the surface in clusters consisting of 1000, 2000 and 5000 water molecules. The low solubility of CPA, 3.7 g L^{-1} (Tuckermann, 2007) indicates that CPA molecules may not dissolve in water, but rather aggregate when there are a large number of CPA molecules in a cluster. The HULIS molecules aggregate as a result of the so called hydrophobic effect (Tanford, 1973), where the “shell” of water molecules around the HULIS molecules is reduced when hydrophobic parts of the molecule are “hidden” and packed together, as well as hydrophilic parts are creating hydrogen bonds on the surface of the aggregate. The hydrophobic effect is mainly driven by an increase of entropy in the system. In a larger water cluster there is enough space (volume) to form such a solvation shell.

Figure 3a shows the radial number density of the system with 162 PAL and 10 000 water molecules. Figure 3b is a corresponding snapshot for the system taken at 6 ns. From the figures, we can see that the aggregate is not entirely centered in the clusters, but rather near the surface, contributing to the radial number density peak at the radius of the cluster at 4.2 nm. So far, aggregates that accumulate on the surface are found to be stable and could remain on the surface. The water molecules are not shown in Fig. 3 and the cluster is shown in cross-section view. The value for radial number density is determined as a mean over the time from the production simulation.

Figure 4a shows the radial number density of the system with 162 CPA and 10 000 water molecules. From the figure, we can find that the accumulation of CPA molecules in the volume element is between 1 and 3 nm and in the region of the bell-shaped peak at 4.2 nm. This means that for this system, the aggregation can be found even in the inner part of the cluster. Figure 4b shows a snapshot of the cluster taken at 6 ns, where the water molecules are removed for clarity.

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The findings of aggregates in the water clusters may be of importance both for the dynamics of the droplets and for their growth. Similar results have been reported by Virtanen et al. (2010) for plant chamber experiments, where Volatile Organic Compounds are found to be in an amorphous solid state.

4.2 Surface tension calculations

The surface tension is the computed effective surface tension γ_e from the procedure described by Zakharov et al. (1997). The diameter of the clusters varies between 8.28 nm and 8.6 nm.

For pure water, the surface tensions for liquid/gas interface calculated using the SPC/E water model are lower in comparison with the experimental data. This is also common for water models, as no force field model could reproduce the experimental surface tensions accurately (Chen and Smith, 2007). The general behavior of the system, however, is not affected. Among the water models available, the SPC/E model is able to give the surface tensions which are closest to the experimental values.

The calculated surface tensions are listed in Table 2. As we can see from the table, the surface tension decreases significantly when HULIS molecules are involved. CPA is more effective than PAD or PAL molecules in reducing the surface tension. With a CPA concentration of 0.07 mol L^{-1} , the surface tension of the cluster becomes 46.2 mN m^{-1} , corresponding to a reduction of the surface tension by about 19%. For the cluster with highest CPA concentration (0.81 mol L^{-1}), a reduction of 38% of the surface tension was found.

4.2.1 Szyszkowski parameters

Table 3 shows the Szyszkowski equation parameters E and D (see Eq. 5) for the HULIS of CPA. The data was determined through least squares fit of the Langmuir-Gibbs relation, described in Li et al. (2010). The constant D is dimensionless.

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It can be seen that there is a significant increase in the constant E compared to Li et al. (2010) and also an almost 50% reduction of D , giving the graph of the 10 000 water system (Fig. 5) a much better resemblance to the experimental data by Shulman (1996). A part of the deviation from the ideal Szyszkowski graph may be explained by the aggregation formation in the nanoaerosol clusters. Therefore it may lead to an uncertainty in determining the surface tension of droplets containing these HULIS compounds.

In Table 4, we list the Szyszkowski parameters E and D for the three compounds CPA, PAD and PAL. The latter two have not been experimentally determined previously under atmospheric conditions.

In Fig. 6 the graphs of the Szyszkowski equation for the three compounds are shown. It should be noted that there are two anomalies in the data points of 54 PAL and of 162 PAD, the latter affecting the graph in such a way that the slope is diminished severely. These anomalies reflect the difficulties in computing the surface tensions in clusters with HULIS aggregates. However, it can still be observed that CPA shows a larger effect on surface tension reduction with lower concentrations. At higher concentrations, all the HULIS compounds can reduce greatly the surface tensions.

4.2.2 Köhler curves

In Fig. 7, the calculated Köhler curves are displayed for a 0.1 μm diameter dry CPA CCN. The green curve shows the calculated Köhler curve when using the value of 0.073 N m^{-1} for pure water. The red and cyan curves are using 0.05 and 0.03, respectively, as examples of reduced surface tension due to the CPA activity. Blue curve shows the calculated Köhler curve under same conditions stated above, with the difference that the value for surface tension is not a constant, but is calculated from the Szyszkowski equation (Eq. 5). The values for the Szyszkowski parameters D and E , assumed to be for larger droplets, are taken from this study.

As can be seen from Fig. 7, the Köhler curve in the case of variable surface tension shows that a lower supersaturation is needed for cloud droplet formation and growth,

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indicating that a greater number of cloud droplets may form and thereby the albedo will increase. On the other hand, it can be seen that the critical supersaturation is shifted towards larger diameters.

The concentrations in this work are about 1–2 order of magnitude higher than observed experimentally (Shulman et al., 1996). However, we have shown that the increase of the Szyszkowski parameter E for larger systems, which is more approaching the experimental value (Shulman et al., 1996), is a convincing indication that the method of MD simulations is valid. For larger systems it may work even better, and that may be a future task. Preliminary results show that the Aitken mode particles with larger sizes could be covered and the Köhler equation could be improved by incorporating surface tension corrections (Li et al., 2011).

5 Concluding remarks

In this study we have shown that MD simulation is an effective tool for investigating the properties of nanoaerosols such as surface tension, surface to bulk distribution and aggregation formation for HULIS compounds. The advantage of MD simulations is that they could provide us the microscopic details which are often hard to observe experimentally, such as the structures and aggregation formation of nano-sized aerosol clusters.

By comparison to experimental studies (Shulman et al., 1996) parameters of an expanded Köhler equation that takes a variable value for surface tension from the Szyszkowski equation (Eq. 5) into account could be used even for previously undetermined HULIS compounds PAD and PAL. The MD method gives us a tool for deriving the Szyszkowski parameters for almost any surface active compound.

This study further reveals, for larger particles of pure CPA, a reduction of critical supersaturation. This may result in the formation of more activated cloud droplets and an increased albedo (Facchini et al., 1999b; Rodhe, 1999). It may even be so that the cloudiness and type of cloud formation over highly vegetated areas are misjudged

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in climate models as a result of the effect of lowering the surface tension of cloud droplets. There may also be other surface active compounds that affect cloud formation in various types of settings that are worth examining.

The finding that HULIS compounds may aggregate inside nanoaerosol clusters could have implications of various aspects when describing and parameterizing CCN and cloud droplets containing HULIS compounds. Even physical and chemical properties of CCN and cloud droplets could be affected by the ability for HULIS compounds to aggregate. Therefore, aggregation formation in aerosols is probably also a key factor in cloud microphysics.

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Table 1. Aggregation formation in the simulations of nanoaerosol systems.

| System simulated | Aggregate formation |
|------------------------|-------------------------------------|
| 13 CPA + 10 000 water | No |
| 27 CPA + 10 000 water | No |
| 54 CPA + 10 000 water | Yes |
| 81 CPA + 10 000 water | Yes |
| 162 CPA + 10 000 water | Yes |
| 13 PAD + 10 000 water | No |
| 27 PAD + 10 000 water | Yes, not so pronounced ¹ |
| 54 PAD + 10 000 water | Yes |
| 81 PAD + 10 000 water | Yes |
| 162 PAD + 10 000 water | Yes, near surface |
| 13 PAL + 10 000 water | No |
| 27 PAL + 10 000 water | No |
| 54 PAL + 10 000 water | No |
| 81 PAL + 10 000 water | Yes, not so pronounced ¹ |
| 162 PAL + 10 000 water | Yes, near surface |

¹ Less than 10 molecules in the aggregate.

Table 2. Surface tension for the systems simulated.

| System simulated | Concentration (mol L ⁻¹) | Surface tension (mN m ⁻¹) | Surface tension (%) |
|------------------------|---|---|---------------------------|
| 10 000 water | 0.00 | 57.0 ¹ | 100.0 |
| 13 CPA + 10 000 water | 0.07 | 46.2 | 81.1 |
| 27 CPA + 10 000 water | 0.15 | 45.0 | 78.9 |
| 54 CPA + 10 000 water | 0.27 | 42.4 | 74.4 |
| 81 CPA + 10 000 water | 0.40 | 38.7 | 67.9 |
| 162 CPA + 10 000 water | 0.81 | 35.3 | 61.9 |
| 13 PAD + 10 000 water | 0.07 | 52.2 | 91.6 |
| 27 PAD + 10 000 water | 0.15 | 48.2 | 84.6 |
| 54 PAD + 10 000 water | 0.29 | 45.1 | 79.1 |
| 81 PAD + 10 000 water | 0.43 | 40.6 | 71.2 |
| 162 PAD + 10 000 water | 0.86 | 40.1 | 70.4 |
| 13 PAL + 10 000 water | 0.07 | 49.8 | 87.4 |
| 27 PAL + 10 000 water | 0.15 | 45.7 | 80.2 |
| 54 PAL + 10 000 water | 0.30 | 44.2 | 77.5 |
| 81 PAL + 10 000 water | 0.45 | 40.6 | 71.2 |
| 162 PAL + 10 000 water | 0.88 | 34.0 | 59.6 |

¹ Value taken from Bahadur and Russel (2008).[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Table 3.** Szyszkowski parameters E and D from three different studies.

| Number of water molecules | E (L mol ⁻¹) | D |
|---------------------------|----------------------------|--------|
| 1000 ¹ | 0.1454 | 0.6007 |
| 2000 ¹ | 0.5484 | 0.3348 |
| 5000 ¹ | 3.4499 | 0.1884 |
| This study, CPA | 75.1282 | 0.0905 |
| Expt. ² | 212.4109 | 0.0864 |

¹ Data from Li et al. (2010).² Experimental data from Shulman et al. (1996).

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**Table 4.** Szyszkowski parameters E and D for the three HULIS compounds.

| Compound | E (L mol^{-1}) | D |
|----------|-----------------------------|--------|
| CPA | 75.1282 | 0.0905 |
| PAD | 21.8899 | 0.1066 |
| PAL | 24.3134 | 0.1292 |

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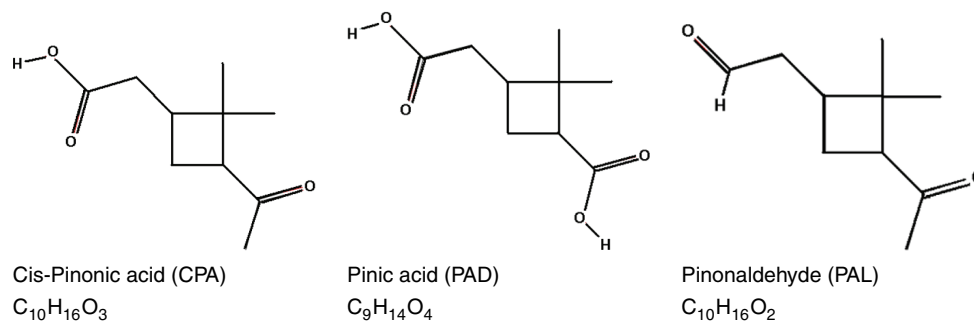


Fig. 1. HULIS molecular structures of the three compounds simulated in this study.

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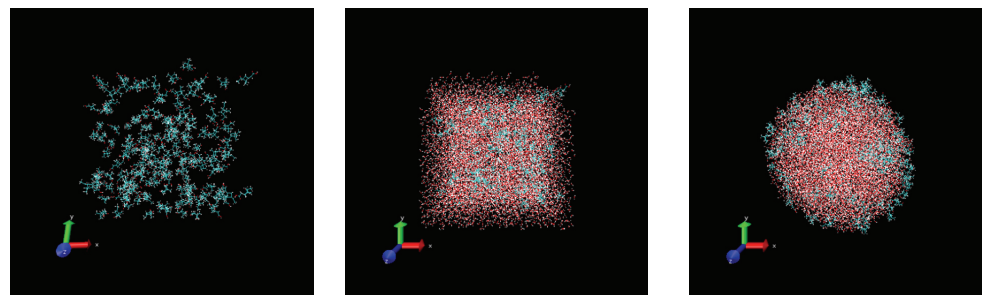
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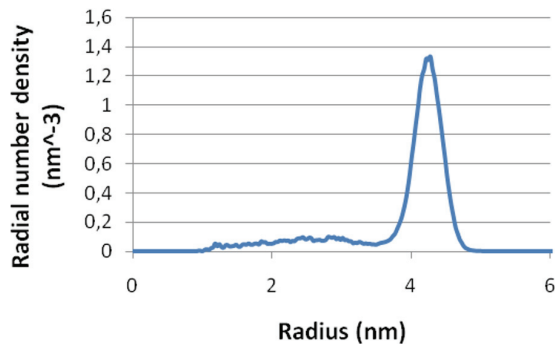
(a) Molecules randomly distributed in a cubic box.

(b) 10 000 water molecules added.

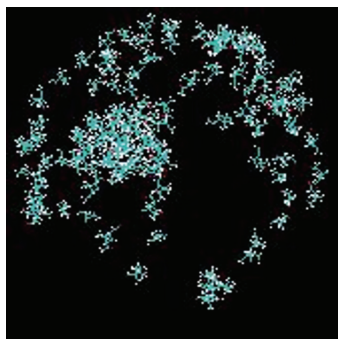
(c) The system adapts to a sphere with surfactants on the surface after 8 ns of simulation.

Fig. 2. How a cluster (162 CPA + 10 000 water molecules) is formed. At first, CPA 162 molecules were inserted into the simulation box in which the molecules are randomly distributed **(a)**. Then 10 000 water molecules were inserted into the box as well. As we can see, the cluster thus generated is of the cubic form **(b)**. However, during the simulation, the molecules inside the box gradually form a nano-sized droplet – a spherical cluster. **(c)** Illustrates the structure of the cluster after 8 ns of simulation.

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(a)



(b)

Fig. 3. (a) 162 PAL system with aggregate near inner surface showing a large peak for radial number density at 4.2 nm. (b) 162 PAL system; cross-section picture.

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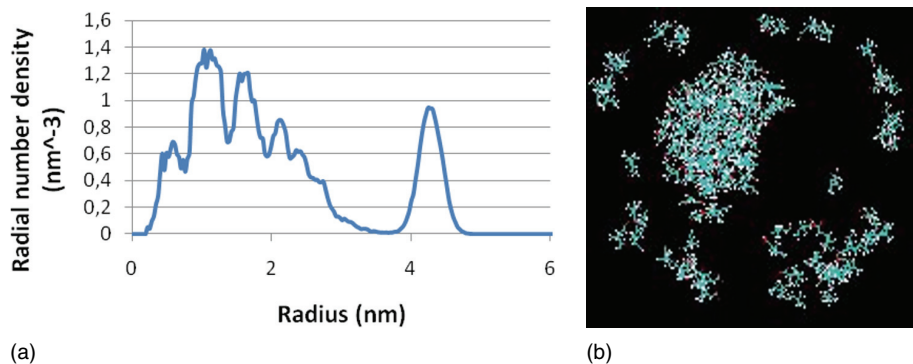


Fig. 4. (a) radial number density showing two main peaks at 1.8 and 4.2 nm. (b) 162 CPA system; cross-section picture.

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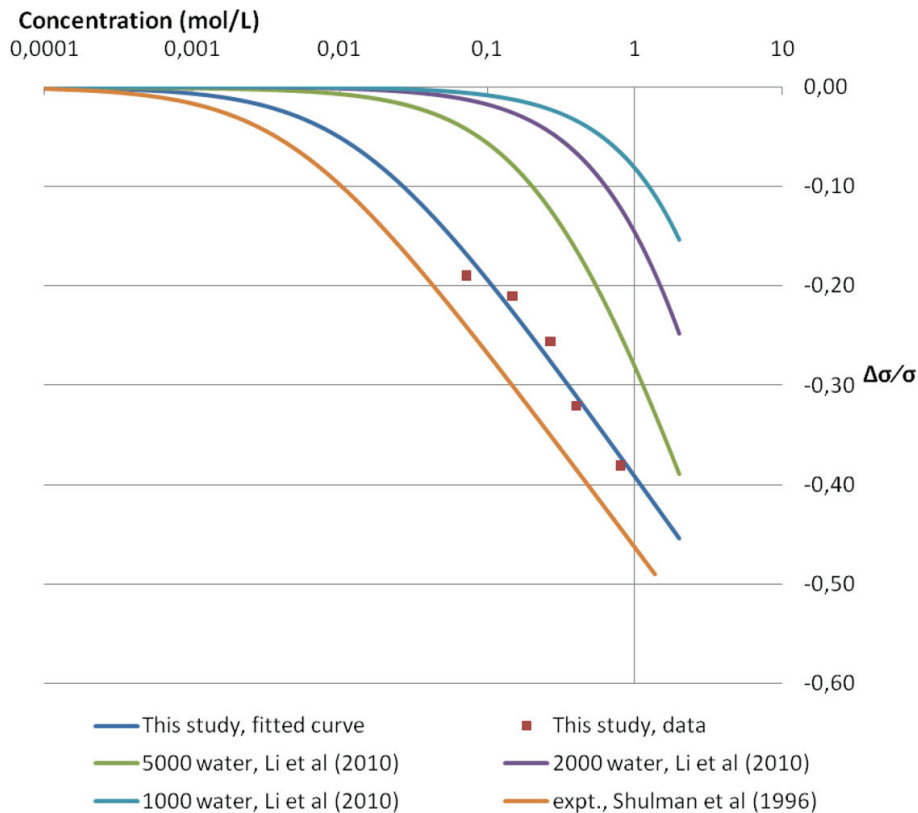


Fig. 5. Fitted Szyszkowski curves from three different studies.

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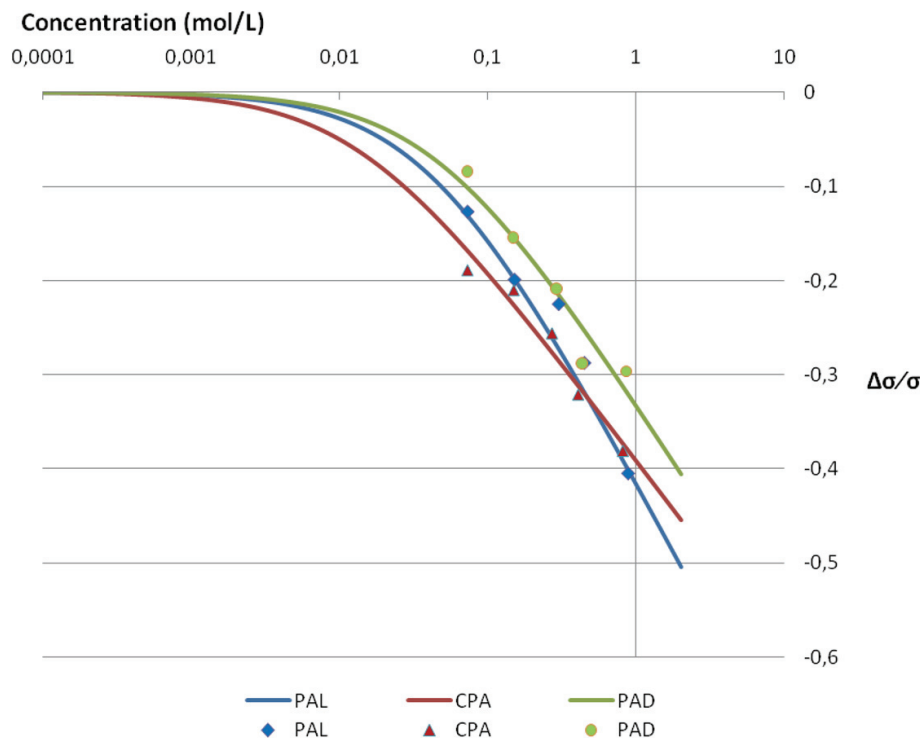
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Fig. 6. Szyszkowski graph – comparison between the three HULIS compounds.

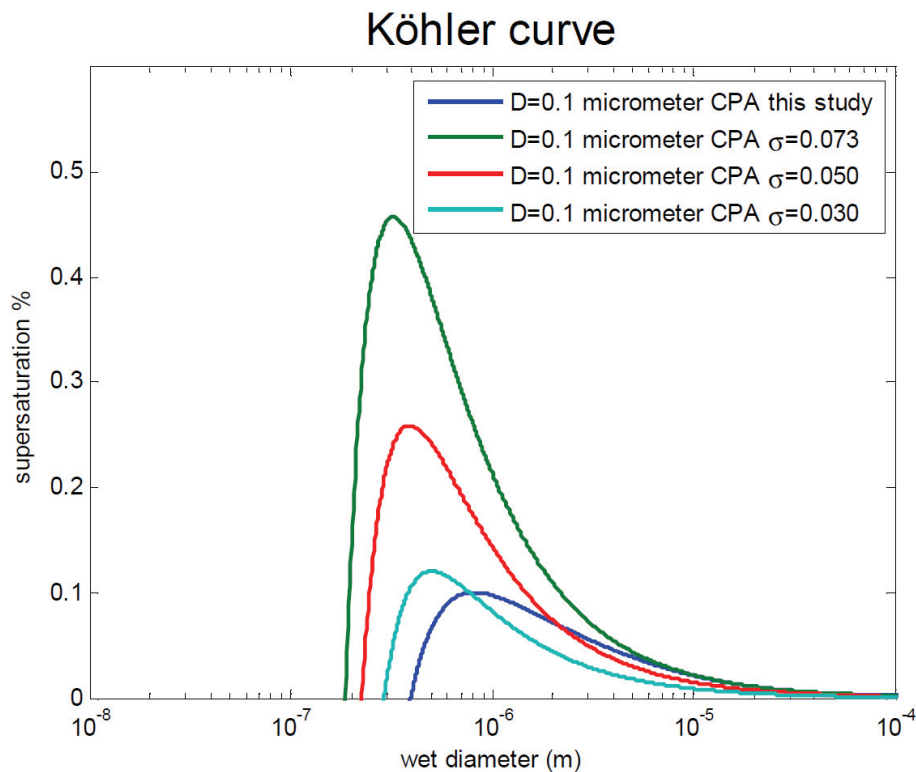


Fig. 7. Köhler curves with and without compensation for variable values for surface tension, determined by the Szyszkowski equation, using values for parameters D and E from this study. Dry diameters are in the four curves $0.1 \mu\text{m}$.

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