

# Surface-Active *cis*-Pinonic Acid in Atmospheric Droplets: A Molecular Dynamics Study

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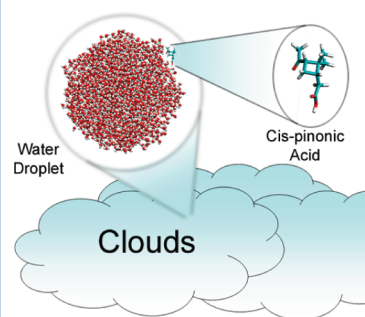
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**ABSTRACT** Water vapor in the atmosphere can condensate and form cloud droplets when there is a certain amount of humidity and a presence of cloud condensation nuclei, and organic solutes called surfactants can significantly lower the surface tension of water — one of the parameters determining cloud droplet population. We here present a molecular dynamics study of the behavior of *cis*-pinonic acid, a commonly found organic compound in cloud condensation nuclei, and its effect on the surface tension of water clusters. Specifically, the decrease in surface tension is found to depend on not only the concentration of the organic compound but also the droplet size due to the spontaneous assembly of the surfactant molecules on the droplet surface. This leads to the conclusion that the partitioning of the surfactant between the bulk and surface plays an important role in the behavior of atmospheric aerosol particles and thus in their availability for cloud formation.

**SECTION** Atmospheric, Environmental and Green Chemistry



The climate on Earth is changing, mainly because of man-made emissions of so-called greenhouse gases like carbon dioxide and methane.<sup>1</sup> In making a recommendation that greenhouse emissions should be reduced, scientists are in the unhappy situation of asking for commitments to reduce an effect whose magnitude they cannot accurately project. This is due to an imperfect knowledge of some components of the climate system. One of the largest uncertainties in climate model projections is the indirect effect of aerosol particles on climate through their effect on cloud reflectivity (albedo). Understanding the optical properties of clouds in the Earth's atmosphere is currently limited by difficulties at the fundamental level of adequately describing the chemical properties and size of atmospheric aerosol particles and their significant effect on the cloud albedo as well as precipitation.<sup>2–4</sup>

The Köhler theory<sup>5</sup> describes the ability of droplet nucleation (formation), called the Kelvin effect, and equilibrium growth of cloud droplets, called the Raoult effect. The Kelvin effect relates to the curvature of the droplet, which decreases the ability of droplet nucleation, a necessary step prior to further growth of the droplets. The Raoult effect increases the ability for droplet growth because of the solution of the aerosol constituents inside of the droplet. The critical supersaturation of water vapor at which the droplet nucleation happens can be lowered by the presence of surface-active organic compounds (SAOC) within the aerosol.<sup>6–8</sup> Facchini et al. have done a “back-of-the-envelope” calculation to estimate the effect of atmospheric surfactants in changing the Earth's climate.<sup>2</sup>

Although such a calculation is too ideal,<sup>3</sup> it has shown the importance of these SAOC. Also, Sorjamaa et al. have reconsidered the Köhler equation based on an empirical parameterization of the surface tension.<sup>7</sup> Their works allow atmospheric scientists to relate the surface tension to cloud droplet activation by means of the Köhler equation and to make estimations and predictions.

*cis*-Pinonic acid (CPA), one of the atmospheric organic compounds produced by oxidation of terpenes in organic vapors,<sup>9</sup> is found to depress the surface tension of water even at very low concentrations.<sup>10–13</sup> Several studies have addressed the effect of CPA, which is more prominent than any other studied organic acid, using the Szyszkowski equation to model the amount of decrease in surface tension.<sup>14</sup> However, the surfactant partitioning between the bulk and the surface was often neglected. As pointed out by Sorjamaa et al.,<sup>7</sup> the partitioning of the SAOC not only affects the Kelvin effect by decreasing the surface tension of the droplet but also influences the Raoult effect by altering the bulk concentration of the surfactant. Neglecting the partitioning effects of SAOC will result in an overestimation of the necessary critical supersaturation in cloud droplet activation. In altering cloud droplet activation, this in turn will play an important role in affecting the climate since it may result in an increase in the population

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**Table 1.** Effective Surface Tension Values for Pure Water Clusters and CPA/Water Mixtures<sup>a</sup>

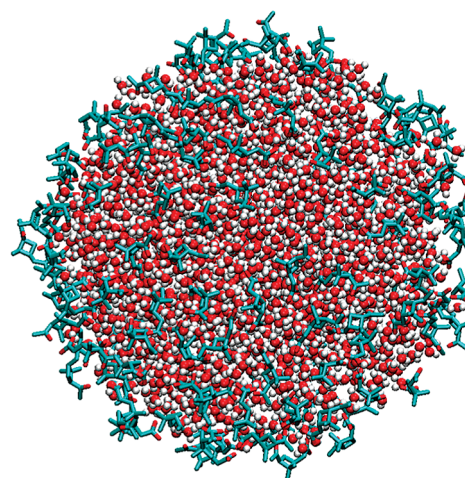
$N_C$	$N_W$	$R_e$	$C$	$\gamma_e$
0	1000	1.91	0.00	52.6
10	1000	1.92	0.56	51.3
20	1000	1.92	1.11	49.2
30	1000	1.94	1.63	44.8
60	1000	1.95	3.19	39.5
90	1000	1.97	4.68	36.8
0	2000	2.41	0.00	54.8
16	2000	2.42	0.45	50.6
32	2000	2.43	0.89	47.2
48	2000	2.43	1.32	45.3
96	2000	2.45	2.59	38.2
144	2000	2.47	3.80	34.2
0	5000	3.28	0.00	57.1
27	5000	3.29	0.30	48.6
54	5000	3.29	0.60	44.6
81	5000	3.30	0.90	42.4
162	5000	3.31	1.76	37.9
243	5000	3.33	2.61	30.8

<sup>a</sup>  $N_C$  and  $N_W$  represent the number of CPA and water molecules, respectively.  $R_e$  is the radius of the cluster (in nm),  $C$  is the concentration of CPA molecules (in mol/L), and  $\gamma_e$  is the calculated effective surface tension (in mN/m).

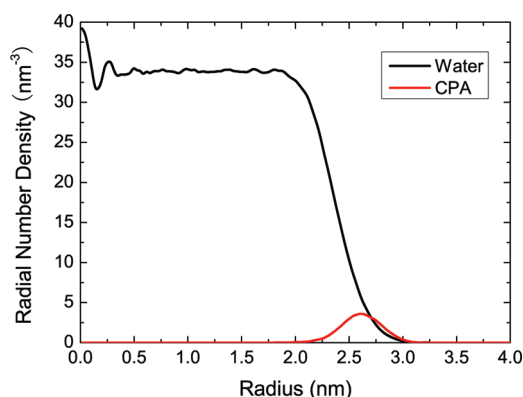
of droplets with smaller size and thus an effect on cloud optical properties or their albedo and the formation of precipitation.

In this Letter, we report on a molecular dynamics (MD) study of the surface-active CPA molecules in small water clusters under atmospheric temperature and show that the amount of decrease in surface tension of a droplet is not only related to the concentration of the surfactant (as in the Szyszkowski equation) but is also dependent on the size of the droplet. In particular, CPA molecules are remarkably concentrated on the droplet surface. Furthermore, with the increase of the size of the droplet, a lower concentration of CPA molecules is needed to reduce the surface tension by a certain amount.

A series of water clusters with different sizes and CPA concentrations were simulated (see Table 1), and the OPLS force field<sup>15</sup> and the SPC/E model<sup>16</sup> were used to describe the CPA molecules and water molecules, respectively. During the simulations, it was found that the CPA molecules spontaneously accumulate on the surface of the clusters due to their surfactant-like structure, as shown in Figure 1. By dividing the whole cluster into successive spherical shells with a constant thickness of 0.3 Å, the radial number densities for individual components (i.e., water and CPA) were calculated with respect to the radius from the center of mass of the cluster. A typical radial number density distribution is shown in Figure 2, in which it can be seen that all CPA molecules are partitioned to the surface. It is such kind of “coating” that results in the reduction of the surface tension since the CPA molecules are expected to diminish the hydrogen bonds in water clusters. Similarly, the insoluble fatty acids have also been reported to



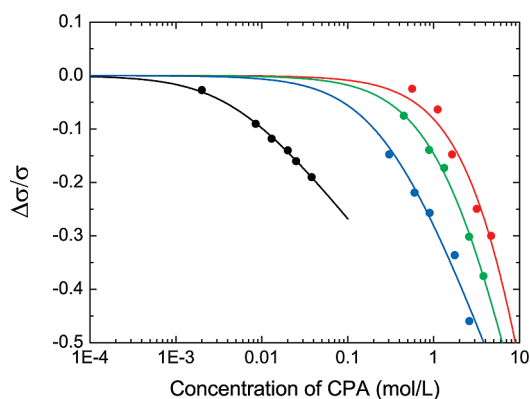
**Figure 1.** Snapshots of the droplet consisting of 144 CPA molecules and 2000 water molecules. Hydrogen atoms in the organic molecules are omitted for clarity.



**Figure 2.** Radial number densities (in nm<sup>-3</sup>) of individual components in the droplet consisting of 144 CPA molecules and 2000 water molecules.

adsorb on the surface of the water droplet and to form a hydrophobic coating which results in an effective negative surface tension.<sup>17,18</sup> However, different from the insoluble fatty acids that “stand” perpendicularly to the surface with long hydrophobic tails pointing outside, the CPA molecules can only creep on the surface of a water cluster with the carbonyl and carboxylic groups pointing to the inside due to the quasi-planar structure. Therefore, the decrease in surface tension induced by CPA is relatively limited, and the surface tension of the coated water cluster does not go negative.

We followed the procedure described by Zakharova et al.<sup>19</sup> to calculate the so-called effective surface tension (denoted by  $\gamma_e$ ) of the clusters. As listed in Table 1, the effective surface tensions of pure water clusters consisting of 1000, 2000, and 5000 water molecules were 52.6, 54.8, and 57.1 mN/m, respectively, in agreement with the values computed by Bahadur et al.<sup>20</sup> This indicates that the effective surface tension  $\gamma_e$  serves as a good approximation to the exact surface tension  $\sigma$ . The reduction of the surface tension induced by the existence of CPA molecules is also listed in Table 1, and we can



**Figure 3.** Surface tension reduction induced by CPA molecules in (red line and dots) the cluster containing 1000 water molecules, (green line and dots) the cluster containing 2000 water molecules, (blue line and dots) the cluster containing 5000 water molecules, and (black line and dots) the experimental data reported by Shulman et al.<sup>10</sup> Dots represent the calculated or measured values, while lines show the fitted curve according to the Szyszkowski equation.

see that as the concentration increases, the surface tension goes much lower than that for a pure water cluster. To compare the calculated surface tension values between water clusters with different sizes, we here use  $\Delta\sigma/\sigma$ , that is, the percentage of the decrease in the surface tension to characterize the effect of CPA molecules. For all clusters, the dependence of  $\Delta\sigma/\sigma$  on the concentration of CPA molecules is shown in Figure 3 as a logarithm function according to the Szyszkowski equation.<sup>14</sup> In the calculations, the error is estimated as the difference between the surface tension obtained from the first and the second halves of the saved trajectory. Typical error estimations are of the magnitude of 1–2 mN/m, and therefore, the estimated error for  $\Delta\sigma/\sigma$  is around 0.02–0.04.

The calculated curves in Figure 3 have a similar trend as the experimental data reported by Shulman et al.,<sup>10</sup> although the organic carbon concentration in our study is much higher than that in reality. This is due to the smaller size of the clusters studied in this work. It is here relevant to point out that the reduction of the surface tension depends on both the droplet size and concentration of the organic compound. It can be seen from Figure 3 that the curve for the cluster containing 2000 water molecules is shifted leftwards compared with the cluster containing 1000 water molecules, and the curve for the cluster containing 5000 water molecules is shifted even further, indicating that a lower concentration of CPA molecules is needed to give rise to the same amount of decrease in the surface tension in a larger droplet. The experimentally measured curve is much more shifted than the three curves from MD simulations in that the droplet sizes are much larger than the ones in this study. By fitting to the Szyszkowski equation  $\Delta\sigma/\sigma = -B \times \ln(1 + A \times C)$ , where  $C$  denotes the concentration of CPA molecules in mol/L, the coefficients  $B$  and  $A$  are derived for the three water clusters in this study as well as the experimental results reported by Shulman et al.,<sup>10</sup> as listed in Table 2. It can be seen that with the increase of a droplet size, the coefficient  $B$  becomes smaller, while  $A$  becomes much larger.

**Table 2.** Fitted Coefficients and Calculated Quantities in the Szyszkowski Equation<sup>a</sup>

$N_W$	$R_e$	$B$	$A$	$\Gamma_{\max}$	$a_{\text{mol}}$
1000	1.91	0.6007	0.1454	13.287	0.125
2000	2.41	0.3348	0.5484	7.716	0.215
5000	3.28	0.1884	3.4499	4.523	0.367
expt.		0.0864	212.4109	2.511	0.661

<sup>a</sup>  $B$  is dimensionless, while  $A$  is in L/mol.  $N_W$  is the number of water molecules,  $R_e$  is the radius of the pure water cluster (in nm),  $\Gamma_{\max}$  is the maximal surface excess concentration of the surfactant molecules (in  $10^{-6}$  mol/m<sup>2</sup>), and  $a_{\text{mol}}$  is the area per molecule (in nm<sup>2</sup>).

According to the Langmuir isotherm and the Gibbs adsorption isotherm, the Szyszkowski equation can be rewritten as

$$\Delta\sigma/\sigma = -\frac{\Gamma_{\max}}{\sigma} RT \ln(1 + KC)$$

where  $\Gamma_{\max}$  is the maximal surface excess concentration of the surfactant,  $\sigma$  is the surface tension of the pure water cluster, and  $K$  is the Langmuir equilibrium constant. Therefore, the empirical parameter  $B$  is equal to the quantity  $\Gamma_{\max}RT/\sigma$ , and  $A$  is equal to the equilibrium constant  $K$ .  $\Gamma_{\max}$  can then be calculated from the fitted values of  $B$ , and the area per molecule can also be determined as the invert of  $\Gamma_{\max}$ , as shown in Table 2. The experimental  $\Gamma_{\max}$  and  $a_{\text{mol}}$  values are calculated under  $T = 298$  K and  $\sigma = 72$  mN/m. However, the above equation is derived based on the assumption that the solute molecules do not interact with each other. This is not the case in small clusters where the adsorbed surfactant molecules definitely “see” each other due to the limited size of the cluster. As the cluster gets larger and the concentration goes lower, the area per molecule becomes larger, as shown in Table 2. The value of parameter  $B$  may also be affected by the inherent deficiency of the SPC/E water model since this model is known to underestimate the surface tension of bulk water.<sup>21</sup> Nevertheless, the SPC/E is computationally efficient and gives better surface tension values compared with other three-site water models.<sup>21</sup> The large increase in the equilibrium constant  $K$  (and also the empirical parameter  $A$ ) can be attributed to the size-dependent nature of SAOC-induced surface tension reduction and also reflect the fact that the CPA molecules become more effective in decreasing the surface tension of larger water droplets due to the coating effect of such surface-active organic compounds.

This work concerns the study of systems with water and surfactants in a droplet-like form. The main focus is to explore if it is possible to measure an effect of surface tension in such droplet-like systems, that is, for a surfactant in a nanoaerosol droplet. Although we at present are confined to particle sizes that do not perfectly mimic atmospheric conditions, using concentrations that by far exceed those reported by other studies,<sup>10,11</sup> we consider it as a starting point for more detailed studies concerning the effect of surface tension. We report that the surface tension is not only concentration-dependent but also varies with size. A change of diameter size changes the surface area to volume ratio in a nonlinear manner, and bearing in mind that a vast majority of the CPA molecules reside on the surface, this is highly relevant for the effect of



CPA for surface tension reduction in relation to surface and bulk concentrations.

An aerosol is not homogeneous in its composition but can consist of a variety of particles of different composition and content. O'Dowd et al. have detected newly formed particles of CPA in the atmosphere over forested areas that are in the size range of 3–5 nm in diameter.<sup>9</sup> They argue that these particles can act as cloud condensation nuclei and thereby form such clusters of water and a CPA mixture. It is therefore of interest to see how the surface tension reduction affects the ability for water condensation and further growth of the droplet. Köhler theory is generally accepted for predictions of particle growth under supersaturation conditions and thereby cloud droplet formation. However, it is mainly a theory applied to inorganic particles, while a high percentage of a typical aerosol particle is made up by organic materials.<sup>10</sup> In this context, we have conducted a study of surfactant properties of a common organic molecule, CPA, in order to determine whether it is possible to measure surface tension in small clusters (nanoaerosols). Surface tension is an important property of the droplet since it reduces the amount of supersaturation of the water vapor available for condensation and droplet growth. Köhler theory deals with the surface tension term as being constant. We show in this study that this is not a reasonable assumption and that, according to the Szyzkowski equation, the surface tension varies for both concentration and size. This could imply that Köhler theory could be better adjusted by taking these findings of a variable surface tension into account. We also show that a vast majority of the CPA molecules reside on the surface of the water cluster, which clearly indicates that a bulk concentration (as measured in laboratory studies) is not suitable to use as the concentration on the surface is much higher. On the other hand, the number of solute molecules is far less than what a bulk concentration would suggest. This has an effect on the so-called Raoult term in the Köhler theory. These findings will be the subject of our upcoming detailed studies.

In summary, the behavior of CPA molecules has been studied for different droplet sizes and different concentrations. Molecular dynamics simulations show that the CPA molecules spontaneously accumulate on the surface of small water clusters and therefore considerably decrease the surface tension of the cluster. Moreover, it was found that the decrease in surface tension not only depends on the concentration of the organic compound but that it is also sensitive to the size of the droplet. As the size of a droplet increases, a lower concentration of CPA molecules is needed to reduce the surface tension by a certain amount since the surfactant molecules become more “effective” in reducing the surface tension when they are concentrated on the droplet surface. Therefore, the partitioning of the surfactant between the bulk and the surface is an important factor that influences the available number fraction of water-soluble aerosol particles and thus cloud optical properties or cloud albedo.

## METHODS SECTION

Molecular dynamics simulations were performed by the GROMACS program package,<sup>22,23</sup> employing the NVT ensemble with the temperature maintained at 286 K by the

Nosé–Hoover thermostat<sup>24,25</sup> to mimic the temperature in the atmosphere. Three types of water clusters were constructed, consisting of 1000, 2000, and 5000 water molecules. For each water cluster, different numbers of CPA molecules were added to give rise to a series of concentration levels. The OPLS force field<sup>15</sup> was used for the CPA molecules, in combination with the SPC/E water model.<sup>16</sup> In CPA molecule, the bonds containing hydrogen atoms were constrained by the LINCS algorithm,<sup>26,27</sup> while water molecules were kept rigid by the SETTLE algorithm.<sup>28</sup> Each cluster was inserted into a cubic simulation cell with an edge length equal to the cluster diameter plus 6.0 nm in order to minimize the interaction between the cluster and its periodic images so that the periodic artifact could be neglected. During the simulations, all short-range interatomic interactions were truncated at a cutoff distance of 1.0 nm, with Coulombic long-range interactions treated by the particle mesh Ewald method<sup>29,30</sup> and dispersion corrections taken into account by the GROMACS program.<sup>23</sup> All simulations were carried out with a time step of 2 fs. Each system was first energy-minimized and subjected to a 2 ns simulation to reach equilibrium, after which, a production simulation of 1 ns was carried out with trajectories saved every 0.1 ps. By analyzing the saved trajectories, the normal component of the Irving–Kirkwood pressure tensor<sup>31</sup> was calculated according to the formula given by Thompson et al.<sup>32</sup>

$$P_N(r) = P_K(r) + P_U(r) = k_B T \rho(r) + S^{-1} \sum_k f_k$$

where  $k_B$  is Boltzmann constant,  $T$  is temperature,  $S$  is the area of the spherical surface of radius  $r$ , and  $f_k$  is the normal component of the force between an pair of molecules acting across the surface  $S$ . Knowing  $P_N(r)$ , the work of formation  $W$  can be calculated as described by Zakharova et al.<sup>19</sup>

$$W = 2\pi \int_0^{R_\beta} P_N(r) r^2 dr - 2\pi P^\beta R_\beta^3 / 3$$

where  $P_\beta$  is the vapor pressure and  $R_\beta$  is the radius of a sphere in the vapor region, that is,  $P_N(R_\beta) = P_\beta$ . With the radius of the equimolar dividing surface  $R_e$  obtained from the density profile

$$R_e^3 = -\frac{1}{\rho_\alpha - \rho_\beta} \int_0^\infty r^3 \frac{d\rho(r)}{dr} dr$$

it is convenient to evaluate the so-called effective surface tension  $\tilde{\gamma}_e$  as an approximation to the exact surface tension  $\sigma$

$$\sigma \approx \tilde{\gamma}_e = \frac{3W}{4\pi R_e^2}$$

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