Interactive comment on Atmos. Chem. Phys. Discuss., 11, 6957, 2011.
Reply to anonymous referee # 1
2011-05-02

1. Cis-Pinonic Acid (CPA) is categorized as belonging to the HULIS group (L8 P6959). Is there a reference for this? CPA has molecular weight < 200 g/mol. HULIS is commonly defined as being of considerably larger molecular weight and resembling terrestrial and aquatic humic and fulvic acids (Graber and Rudich, 2006). Furthermore, atmospheric Humic-like substances that play a role in CCN activation have been collected and extracted from biomass burning events or show a strong absorbance in UV/VIS spectra (e.g., but not limited to, Graham et al, 2002; Havers et al, 1998; Gysel et al, 2004; Kiss et al, 2005) . Particle phase CPA, PAD, and PAL are formed during the oxidation of biogenic terpene emissions such as alpha pinene (e.g., Gao et al, 2004). The ambient formation mechanisms of the organic acids and HULIS presented in this study are very different and hence are not expected to generate similar surface tension results. L8 P6959 suggests that the types of organics studied are closely related. Fig. 1 and 6 states that the PAL, CPA, PAD are HULIS compounds. What type evidence exists to suggest that PAL, CPA, and PAD can be classified as HULIS?

We agree that the term "HULIS" arises from the similarity to humic and fulvic acids, and that the HULIS compounds have much larger molecular weight than CPA, PAD and PAL in our study. In fact, these three organic compounds, CPA, PAD and PAL, could be the building block or repeating unit in real HULIS compound, and therefore could serve as model compounds to describe the properties of HULIS (Kiss, 2005). In our paper, the use of the term HULIS is somewhat unclear. The main objective is to investigate model compounds that usually are chosen to resemble HULIS in other similar experimental work. To clear out this point the following line are inserted to the introduction:

Humic acid differ somewhat from HULIS found in aerosol samples, but model compounds, like CPA, PAD and PAL are often used to describe the properties of HULIS (Kiss, 2005).

In the title and throughout the document, the term HULIS has been extended with the term model in order to emphasize that there is a difference between naturally occurring HULIS and the organic compounds that are used in this study.

2. The GROMACS simulation package is utilized but the specified input parameters for the organic acids are not given. What assumptions are made for the non-ideal organic interactions with water? The names of algorithms are provided but the key thermodynamic assumptions are not explicitly expressed. Atmospheric HULIS is a mixture of organics and even standards such as Suwanee River HULIS have differing properties. What average properties are assigned to the HULIS used in this study?

As we use a force field to describe the interactions between the atoms, we therefore assume that the non-ideal interactions of organic molecules with water consist only electrostatic and Van der Waals interactions. The SPC/E water model consists of three sites representing one oxygen and two hydrogen atoms, respectively, with the inter-molecular interactions optimized according to experimentally measured properties of liquid water. Similarly, in the OPLS force field, the inter-atomic interactions have been parameterized to fit experimental properties of liquids such as density and heat of vaporization, and a recent study has shown that the solvation free energy is nicely reproduced by the OPLS force field [Shivakumar et al., (2010) *J. Chem. Theory Comput.*, Vol. 6, pp. 1509–1519]. Although this force field is not specially tailored for the organic acids in this study, the parameterization protocol ensures the transferability of the parameters. Our previous paper [Li et al., (2010) *J. Phys. Chem. Lett.*, Vol. 1, pp. 769–773] also supported the use of the OPLS force field.

In molecular dynamics simulations, we employed the canonical (*NVT*) ensemble, with temperature maintained at 286 K by the Nosé-Hoover method. This method is developed as an extended-ensemble approach, in other words, the Hamiltonian of the system is extended by introducing a thermal reservoir and a friction term in the equations of motion. This approach has been shown to produce a correct canonical ensemble [Hoover, (1985) *Phys. Rev. A*, Vol. 31, pp. 1695–1697].

In this study, we aimed to simulate the structures of the organic acid-water clusters, for instance the formation of the aggregate driven by entropy effects. We also paid attention to the surface tension of the clusters, which provides insight into the indirect effect of the organic acids on climate. The algorithms and parameters mentioned above ensure reasonable description of these properties, such as the structures and the surface tension, of the systems, which have been proved through comparison with experimental data.

The above text has been added into the manuscript. Please see pages 4-5.

3. Several previous papers have provided surface tension data for atmospheric HULIS samples (e.g., Salma et al.,2010, and several more too long to list) How do the authors' MDS results and Szyszkowski Langmuir coefficients compare to previously published data from other groups? How do the authors' data compare to other group papers that measure the surface tension of CPA?

Thank you for this statement. We add the following data to table 3 for comparison:

Kiss et al. (2005) 3)	2408.3007	0.1457
Kiss et al. (2005) 4)	33680.9872	0.0704
Tuckermann and Cammenga (2004) 2)	315.3176	0.0981
Tuckermann (2007) 2)	41.3025	0.0813

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2) Experimental data

3) Experimental data, September 1999

4) Experimental data, April-May, 2000

The following sentence is added: The experimental data from Tuckermann (2007) are in accordance to this study.

Figure 5, including the text to the figure, is changed to include experimental values from Kiss (2005) and Tuckermann and Cammenga (2004)

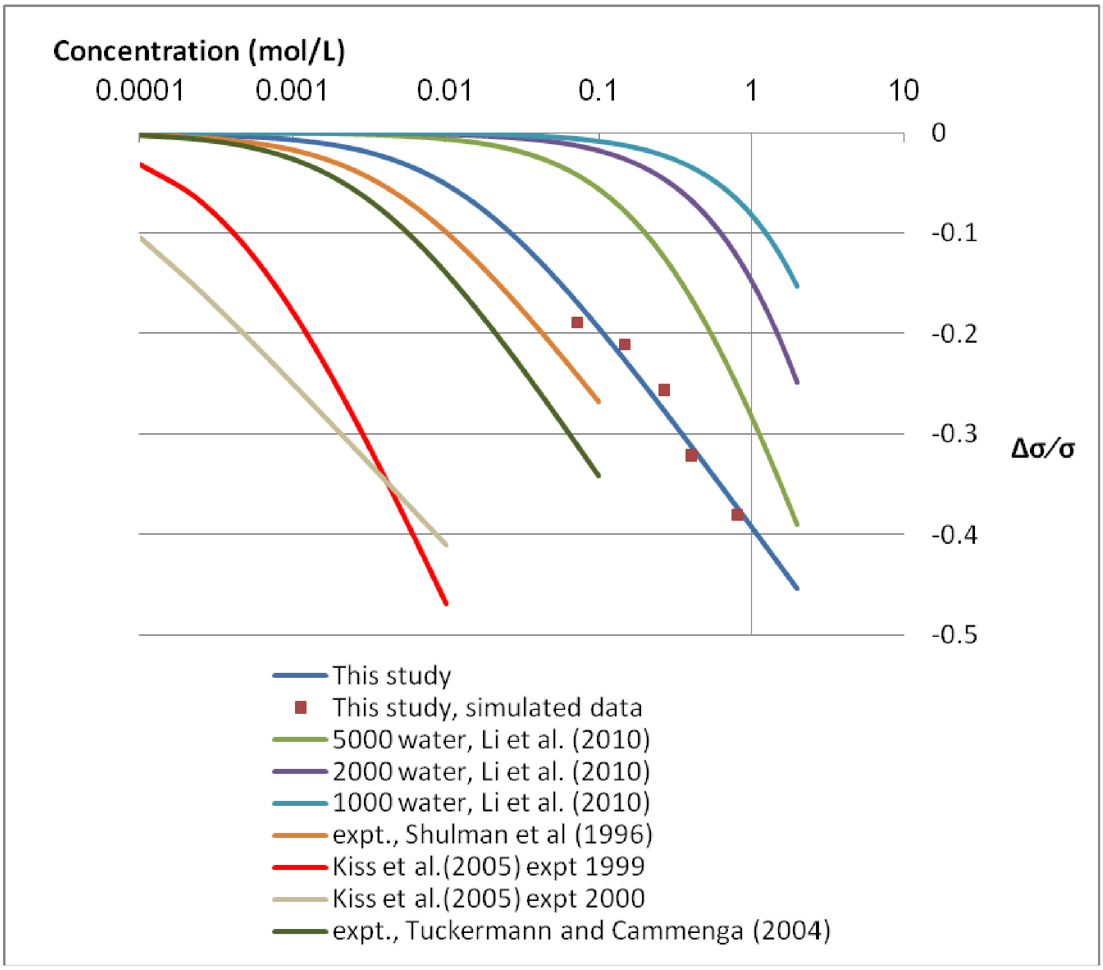

Fig. 5. Fitted Szyszkowski curves from four different studies.

The following sentence is added: The deviation by Kiss et al. from the other experimental data is due to that real aerosol particles with HULIS were examined that have even stronger amphiphilic properties than model HULIS compounds (Kiss et al. 2005).

The following reference is added:

Tuckermann, R., Cammenga, H. K.: The surface tension of aqueous solutions of some atmospheric water-soluble organic compounds, Atmos. Env. 38, 6135-6138, 2004

4. Why was 10,000 water molecules chosen? Is this a relevant amount of water to induce activation of the organic acid solute? When the authors discuss aggregation, how does it relate to activation? The CCN effects of CPA, PAL, and PAD have been previously published. Is the amount of water provided for activation similar to those reported in experiments?

From previous work (Li et al, 2010) we found that the surface tension reduction of CPA is dependent not only on its concentration, but also on the system size. The latter is related to the curvature of the water clusters. The more water molecules used to simulate a droplet, the better the agreement will be with the experimental values obtained by Shulman (1996). In order to determine and establish this trend and to come closer to the experimental values, we therefore simulated the systems of 10000 water molecules. Computer simulations of such systems are already very time-consuming and it is still hard to simulate even larger systems in practice with the currently available resources. Since aggregation appeared, it seems like an evidence for processes of real importance to occur at this system size and larger.

5. Futhermore the effects of solute dissolution and limitation of solubility for surface tension and CCN have been discussed (e.g, Shulman et al 1996, Topping et al,). How will this effect Kohler curves in Fig. 7. Is the impact of limited solubility accounted for?

This is an important question, and we will try to clarify the text by inserting the following paragraph into section 4.1.

The impact of limited solubility is indirectly accounted for, since the values for surface tension are computed with aggregation of a large part of surfactants. The surfactants in the aggregate do not contribute to the lowering of the surface tension, and the reason for aggregation is partly due to the low solubility.

In the section where the Köhler curve is discussed, the following sentence is added:
The low solubility of CPA is taken into account by the fact that not all CPA molecules contribute to lowering of the surface tension, but aggregate instead of concentrating at the surface.