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Atmospheric Chemistry and Physics Discussions

Interactive comment on "HULIS in nanoaerosol clusters; investigations of surface tension and aggregate formation using molecular dynamics simulations" *by* T. Hede et al.

Anonymous Referee #2

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The authors use molecular dynamics simulations (MDS) to explore the properties of partially soluble organics as droplet surfactants. High molecular weight Humic-like Subtances (HULIS) form aggregations in simulated droplet simulations and agree with experimental data.

The subject matter is relevant and of interest to the larger scientific community. The authors have applied similar MDS for CCN activation to other organic components (Li et al 2010; 2011), and now apply their technique to "HULIS" represented by 3 organic acids. The results may add to the existing knowledge on surface active organics and their role in cloud condensation nucleation. The document is succinct. The reviewer

has a few concerns that once addressed will clarify key points in the paper.

MAJOR CONCERNS

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?

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?

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?

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? 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?

Additional References.

Surface Tension of CPA (Hyvärinen et al, 2006) The work of Sorjmaa et al 2004 is pivotal in describing the effects of significant surface tension depression and its relation to Kohler Theory.

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