

Interactive comment on “Amino acids in atmospheric droplets: perturbation of surface tension and critical supersaturation predicted by computer simulations” by X. Li et al.

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Author Comments (Manuscript ID: acp-2010-732) We thank Anonymous Referee #2 for the constructive and helpful comments. We here respond to the comments and revise our manuscript accordingly.

Referee #2 Interactive comment on “Amino acids in atmospheric droplets: perturbation of surface tension and critical supersaturation predicted by computer simulations” by X. Li et al.

Comment: This paper should not be accepted in ACP. My main objection is that the results show vanishingly small surface tension effects on critical supersaturations of
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particles large enough to act as CCN in the atmosphere. The effects are so small that they are not testable using CCN instruments as the signal would be overwhelmed by instrumental noise. Secondly, the size dependence correction used by the authors is not new as they have already introduced it in Li et al. (2010). Overall, it has been shown in recent years that surface tension effects on critical supersaturations are small even when the solutes are strong surfactants (see papers by Sorjamaa et al., Prisle et al., Topping et al.) I would suggest that the authors rewrite the paper and send it to a general physical chemistry journal as the subject of surface tension size dependence is one that is interesting per se, if not from the atmospheric viewpoint. Regarding the size dependence, I would note that Fig. 6 may be somewhat misleading in that the behavior of the surface tension as a function of radius might not be purely a size effect but partially a composition effect also. As shown in the above mentioned papers, the bulk mole fraction (i.e. the mole fraction in the center of the droplet) of the solute depends on droplet size, and the surface tension of course is a function of bulk mole fraction (rather than total mole fraction) of solute in the droplet.

Our response: We thank the referee for these comments. First, we agree with the referee that our predicted surface tension effects on critical supersaturations are very small and cannot fully explain the discrepancy between experimental observation and Köhler theory. In our revised manuscript, we are not drawing quantitative conclusion on supersaturation, instead, the curvature dependence of surface tension is estimated to gain insight into the size-effect of the water droplets. We aim to demonstrate the detailed mechanism of surface tension perturbation induced by the presence of amino acid molecules, and to show that such effect is closely dependent on the curvature of the surface.

What is new in our manuscript (compared with our previous work, Li et al., 2011) is that the differences in the behavior of hydrophobic and hydrophilic amino acids are addressed and that the different effects of amino acids on planar and spherical interfaces are discussed. The presence of surface-concentrated hydrophobic amino acids gives

rise to enhanced van der Waals repulsion near the liquid-gas interface, and we emphasize that such a repulsive effect results in different variation in surface tension of planar and spherical interfaces. In the planar interface, the repulsive effect contributes positively to the tangential component of pressure tensor P_T , leading to decreased surface tension, while in the spherical interface such effect contributes more to normal component of pressure tensor P_N and less to P_T , therefore the surface tension is enhanced. Naturally, the direction of the surface tension change is highly dependent on the curvature of the droplet, which determines the balance between P_N and P_T .

In the revised manuscript we also put more emphasis on the distribution and molecular orientation of the amino acids in water droplets, since surface-active components can undergo further chemical reactions with the surrounding air. This is related to the fact that they can more easily migrate to the surface and by this become relatively more available to chemical oxidation. Therefore the structural and chemical properties of individual DFAAs require a better understanding on the molecular orientation and affinity to the surface of the nanoaerosol droplet; we employ MD simulation to show that the hydrophobic amino acid molecules are concentrated on the droplet surface, with their zwitterionic backbones immersed on the surface and hydrophobic side-chain pointing outward.

Finally, we have modified Figure 6 (now Figure 8 in revised manuscript) to avoid possible ambiguity. It is our future goal to establish a unified expression for the prediction of surface tension of atmospheric droplets containing amino acids.

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