Atmos. Chem. Phys. Discuss., 11, C14210–C14214, 2012
www.atmos-chem-phys-discuss.net/11/C14210/2012/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 14 January 2012

General comments:

This paper presents molecular dynamics (MD) simulations of aqueous solutions of six amino acids. In agreement with previous observational experiments, serine, glycine, and alanine were found to increase surface tension, while valine, methionine and phenylalanine reduced surface tension. The authors conclude that (1) including the increased surface tension slightly improves the agreement between Köhler theory and recent cloud condensation nuclei (CCN) observations of serine and glycine described by Kristensson et al. (2010), and (2) that the described dependence of surface tension on droplet curvature could help improve predictions of the CCN activity of atmospheric

aerosols.

MD simulations are an interesting tool that can help to explain the surface activity of hydrophobic organics in small aqueous droplets, which are difficult to investigate in the laboratory. Accordingly, the results of these simulations could be of interest to the readers of ACP. Unfortunately, I think there are major flaws with each of the conclusions mentioned above, especially the second one, and therefore I cannot recommend the manuscript as currently written for publication. The authors have not helped to explain the previous CCN experiments on amino acids in any significant way. Furthermore, the conditions of the MD simulations are very different from those of nucleating cloud droplets in the atmosphere, and thus are not relevant to the CCN activity of ambient aerosols.

Specific comments:

Kristensson et al. (2010) have already discussed the potential influence of surface tension on their CCN experiments. They state that "[s]ome amino acids can behave as inorganic salts and increase surface tension in aqueous solution compared to pure water", resulting"in an increase of predicted critical supersaturation from 0.763% to 0.775% for a 40 nm diameter [glycine] particle. This brings our predicted values closer to the experimental, although the change is almost negligible." Having essentially dismissed an increase in surface tension as an explanation, they then go on to discuss other possible reasons for the discrepancy between theory and observations. The results of these MD simulations are in agreement, and in fact predict an even smaller change in critical supersaturation ($< 0.01\%$). Although the authors admit that there is only a "slight" improvement, they still state in the abstract that their methodology "is used to improve the Köhler equation in predicting the critical water vapour supersaturation of the droplet activation." I do not think this conclusion is justified.

I disagree with this final statement in the conclusions: "[O]ur method provides the possibility of incorporating the curvature dependence of droplet surface tension in atmo-

ACPD
11, C14210–C14214, 2012

spheric studies, which could help to improve the accuracy of the Köhler equation in predicting the critical water vapour supersaturation of the activation process of cloud droplets." CCN in the atmosphere have dry diameters of at least several 10s of nm, and due to water vapor condensation are typically hundreds of nm in diameter at the point of activation. The MD simulations described here only simulate droplets with diameters less than 10 nm. Thus the curvature dependence described here is essentially irrelevant to CCN activation. In other words, it is not at all clear that the quadratic fit to such small droplets and flat surfaces can be used to interpolate to droplets that are 100s of nm in diameter; i.e., I am not convinced that the curves in Fig. 6 are accurate at values of R_e^{-1} near 0.01 nm^{-1}.

P30920 L5: I disagree that these simulations are "representative [of] the remote marine atmospheric aerosol-cloud system." The simulated particles are composed of single amino acids, and such particles do not exist in the ambient atmosphere. To be representative of the atmosphere, they would need to have more realistic compositions (namely, other organic compounds and well as inorganic matter).

P30922 L24: The laboratory experiments of Leck & Bigg (1999) demonstrated that the *oxidation products* of L-methionine could nucleate new particles.

P30925 L20-21: Mopper & Zika (1987) report maximum amino acid concentrations in rainwater of 15 μM; to claim that the concentration of 0.56 M used in this study is "a bit high compared with the typical values in marine rain" is misleading. It is higher by a factor of approximately 40,000. Regardless, it is not clear why marine rain concentrations are relevant here; it is the presumably higher concentration at the point of activation (long before raindrops form) that is relevant.

P30925 L23-24: "we therefore increased slightly the number of amino acids..." Increased slightly compared to what? As written this implies it is increased slightly compared to typical marine rain concentrations, but as noted above this is quite a bit more than a slight increase.

ACPD
11, C14210–C14214, 2012

P30930 L2: "[T]herefore VAL is expected to increase the surface tension of the droplet." Doesn't this contradict the results from Table 1, which show that VAL decreases the surface tension of the droplet relative to that of pure water? Please clarify.

Figure 2 – Why are the results at the two air-water surfaces (at ~ 3.5 and ~ 6.2 nm) different?

Figure 6 – Unfortunately the limitation of the MD simulations is on display here. The authors present results for a flat surface ($R_e^{-1} = 0$ nm), but the largest droplet presented has a diameter of $\sim$ 6 nm ($R_e^{-1} = 0.3$ nm). This is much too small to be relevant for atmospheric CCN activation, which typically occurs when droplets are at least several hundred nm in diameter. The most important question in my mind is, "at what maximum diameter is the surface tension of a droplet enhanced relative to a flat surface?" Unfortunately, the MD simulations described in this manuscript are not able to answer this question.

Figure 7 – This figure suggests that the influence of the surface activity of amino acids on their CCN properties is at most minor, and likely negligible.

Technical corrections:

P30920 L26: should be "*help* determine" – along with meteorological variables such as updraft speed.

P30921 L13: should be "making them *reflect*" (grammar)

P30923-4: Equations 1 and 2 use variables which are not defined.

References:

Kristensson, A., Rosenørn, T., and Bilde, M.: Cloud droplet activation of amino acid aerosol particles, J. Phys. Chem. A, 114, 379–386, 2010.

Leck, C. and Bigg, E. K.: Aerosol production over remote marine areas – a new route, J. Geophys. Res., 26, 3577–3580, doi:10.1029/1999GL010807, 1999.

ACPD

11, C14210–C14214, 2012

Interactive Comment

Mopper, K. and Zika, R. G.: Free amino acids in marine rains: evidence for oxidation and potential role in nitrogen cycling, Nature, 325, 246–249, 1987.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 30919, 2011.

ACPD

11, C14210–C14214, 2012