

Interactive comment on “An analytical solution to calculate bulk mole fractions for any number of components in aerosol droplets after considering partitioning to a surface layer” by D. Topping

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1

I would like to thank referee3 for their constructive comments and suggestions. General and minor points are addressed in the following text with changes made in the original manuscript where required.

The authors of this paper present a model to account for the partitioning of solute to the surface layer of a droplet. The inputs require only surface tension

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parameters from binary systems. The approach is computationally efficient however the predictions have yet to be tested against measurements. The paper is well written and the concept is relevant to the cloud droplet and geoscientific modeling community. However the model is in its formative stages; logical ideas are proposed, idealistic assumptions are applied, key surface tension parameters must be prescribed (γ_i and Γ_i), but little conclusive evidence of the models validity is given. The reviewer has serious concerns that the theory and application has not been properly tested.

Response: It is true that the model derivation is based on some idealised assumptions which facilitate derivation, as recognised by all referees comments. The referee has suggested comparisons with alternative and more complicated modelling tools which can be applied for ternary systems, further down in this review. These have been carried out and added to the revised manuscript as discussed shortly. It was perhaps unclear that the main driver for this paper was to provide tools to enable theoretical considerations of bulk/surface partitioning in complex mixtures of any number of compounds. Following this, as stated in the original manuscript, it is then possible to assess sensitivities of aerosol properties to choice of predictive technique and complexity, eg (McFiggans et al 2010). Of course, it would be ideal to compare predictions with empirically observed behaviour for complex mixtures and models capable of including all postulated phenomena. However it is difficult to carry this out beyond 3 components. It will be extremely useful, if not essential, that future work includes comparison of laboratory studies on complex mixtures of known properties, but also an analysis of sensitivity within large scale models such that the level of complexity required, for even ternary systems, can be assessed.

The author is aware of many of these shortcomings. However the reviewer believes there are additional, quick, yet effective methods to evaluate the model. The authors could compare their simulations to additional already published data points where surface layer partitioning is evident (e.g., Sorjmaa et al., 2004). Currently the

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author compares his model to 3 pendant drop surface tension measurements. The author could also compare his model with other partitioning models to strengthen his arguments. How do these results compare with the numerical technique of Laaksonen (2006) and Kokkola et al (2006), Li et al, 2004?

Response: In the revised manuscript comparisons are made with the published datapoints in Sorjamaa et al 2004 in which the effect of common ions are assessed. This also follows recommendations of the other referees. Results are very interesting. In our approach we have not only assumed that idealised assumptions pertain at the bulk/surface interface, but also the mixed surface tension of the SDS-NaCl system can be described by the simple mixing rule of Li and Lu (2001) rather than using the parameterised form derived from the mixture. In other words, the surface tensions of the binary systems are combined to describe the behaviour of the mixture. We have already published comparisons for ternary and higher order systems which show that the ability of this approach to capture the measured behaviour tends to improve as more components are added to the mixture (Topping et al 2007). For a pure SDS system in water, our approach can replicate the predicted critical point on the kohler curve within 3 decimal places. With an 80% mass ratio of SDS within the multi-component system, our predictions give a difference in critical saturation ratio of 0.036, compared to the difference of -0.042 when the Li et al 1998 predictions are compared. At 50% mass ratio, the difference reduces to 0.01, the two predictions equal to within 3 decimal places at a 20% mass ratio. Thus, there is evidently a difference in approaches when the common ion effect is present. This is to be expected given the differing levels of complexity in both approaches. In this system, it is known that NaCl decreases surface tension of aqueous sodium dodecyl sulphate (SDS) solution. Thus the use of the Li and Lu (2001) model tends to over-predict the final surface tension even after partitioning has been taken into account, resulting in an additional forcing which increases the final critical saturation ratio. It is possible to include a separate empirically derived surface tension fit to calculate the equilibrium saturation ratio within the Kohler equation for a specific mixture within the framework

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Interactive Discussion

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presented here. However, for illustrative purposes the same model used to define the bulk/surface partitioning equations are used in the results presented in table (2) for consistency. It is difficult to extrapolate the deviations found here to other mixtures of atmospherically relevant compounds or multi-component mixtures of higher order. As the referee recognises, more experimental data is required.

The author states the changing concentration gradients approach the surface. Are those concentrations at equilibrium? If not, can assuming chemical equilibrium in the system be valid? Would it make more sense to apply pseudo-steady state assumptions to the system?

Response: The section this is referring to was aimed at introducing the concept of altering concentrations as a function of distance from the centre of a droplet, manifest in a surface tension and thus bulk/surface partitioning effect. The detail of this phenomena is discussed succinctly in Sorjamaa et al (2004), and should have perhaps been more clear in the present document. To avoid conclusion regarding the assumptions used within the derivations and the overall theory, the following sentence has replaced the original: 'Briefly, accounting for this process is based on the concept that different concentrations in a bulk and surface layer impact the number of moles of a compound defining both the Raoult and Kelvin terms within the Kohler equation'.

The author assumes that the activity of the droplet can be represented by the mole fraction of material. This is true under ideal conditions, but is of greater concern for non-ideal systems where partitioning of bulk material occurs. This is an example of an assumption that will only be validated with comparison to actual measurements.

Response: I agree, there has to be experimental validation through measurements of CCN behaviour but also, fundamental thermodynamic validation of activity models, or

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assumed frameworks used within non-ideal partitioning models. The latter point remains a challenge for the atmospheric community as a whole, not only for bulk/surface partitioning calculations, despite recent evaluations of interaction parameters within available models (e.g. Zeund et al 2008). Whilst methods are available to calculate activities within multi-component droplets, there is no guarantee predictions remain highly accurate for particular chemical structures or concentration regimes, nor that the dependence on such models causes artificially correctly predicted behaviour (e.g. analogous to artificial condensed SOA mass predictions caused by choice of erroneous vapour pressure method).

Validated using bulk empirical data. This phrase seems to negate the importance of this study, if bulk data works well and is relevant. Can all bulk empirical data be used? That is pendant drop surface tension measurements appear to agree, how about other methods (e.g. De Nuoy ring?)

Response: This reference was referring to the fact that the simple surface tension mixing rules, on which the derivation provided in this study were based, have been validated using bulk data. Unfortunately I cannot comment fully on the comparable accuracy of the many experimental surface tension measurement techniques for a broad range of compounds, nor is it, unfortunately, within the scope of the current manuscript to do so. I completely agree that the referee has raised a valid point and it should form the focus of a future study (e.g. a compilation of surface tension data of atmospherically relevant compounds using multiple methods..and the impact on model sensitivity). It would be then possible to propogate the sensitivity of derived model parameters from choice of surface tension measurement. We have chosen to use the pendant drop surface tension method in previous studies for, as the referee states, there appears to be less variability. In addition, there are some broad observations regarding applicability. Manufacturers will cite, for example, the advantage of the Wilhelmy Plate method over the du Nouy Ring method, as being the ability to monitor

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time dependent surface tension variations and deformation of the du Nouy ring upon use, thus biased measurements. The pendent drop method is widely used within the atmospheric community (e.g. Kiss et al 2005). Using image processing software, and capability of a range of pressures and temperatures, the accuracy of the pendent drop techniques is impressive, with values as low as ± 0.001 mN/m often quoted. This technique also tends to require a smaller sample size which makes it useful for studying, for example, chamber extract or ambient samples. In all, the question is an important one and falls within the same remit as most of the criticisms/suggestions put forward. That is, the level of accuracy required for a broad range of organic functionality AND complexity should be answered using empirical data on the CCN behaviour of a broad range of aerosol and sensitivity studies within large scale prognostic models. Using this 'top down' assessment of the required accuracy of the partitioning method, one could then make an informed judgement on the required accuracy of the surface tension measurement technique.

P1095, L14. LiLu? Or Li and Lu 2001 model? Equations 18 and 19 are redundant. Equations 15 and 16 are redundant.

Response: It is the Li and Lu 2001 model and the manuscript has been updated accordingly. A complete derivation of the equations leading to the analytical expression was given to avoid any confusion of an already complex topic. However these have been removed in the revised manuscript.

Figure 1. Please specify if data points are actual measurements or derived in models. If measurements (provide the source in caption or figure).

Response: The data points in figure 1 are model predictions using parameters derived from experimental data.

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What is the meaning of the positive solution? Is it possible to have imaginary solutions to the quadratic equation? If so, under what circumstances.

Response: The positive solution gives negative mole fractions for the range of parameters displayed in figure 1b. The discriminant is positive with two distinct real roots.

References

- Kiss, G., Tombacz, Hansson H-C.,: Surface tension effects of humic-like substances in the aqueous extract of tropospheric fine aerosol, *J Atmos Chem*, 50: 279-294, 2005.
- Zuend, A., Marcolli, C., Luo, B,P., Peter, T.: A thermodynamic model of mixed organic-inorganic aerosols to predict activity coefficients, *Atmos. Chem. Phys.*, 8, 4559-4593, 2008

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