Atmospheric Chemistry and Physics Discussions

Interactive Comment

Interactive comment on "The role of surfactants in Köhler theory reconsidered" *by* R. Sorjamaa et al.

R. Sorjamaa et al.

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We would like to thank the Referee 3 for the comments.

General comments:

"It should be clarified in the manuscript why it is assumed that SDS molecules at the surface do not contribute to the solute term and, thus, are treated as undissolved species".

We make the assumption that SDS molecules at the surface do not contribute to the solute term because it is the assumption that is made in the Gibbsian model of surface thermodynamics. The Gibbs' model, as we point out in the manuscript, assumes two homogeneous phases, and a surface phase in between. All phases are in equilibrium with each other. Thus, the surface excess molecules are not treated as undissolved species: they just don't appear in the terms written for the homogeneous liquid phase ("the bulk"). The important thing is that the Gibbs' model gives us the correct solute concentrations in the bulk of the droplet (as depicted in our Fig. 1). The Raoult term

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describes the vapor pressure decrease of water due to dissolved species in the bulk of the droplet. Thus, we calculate the Raoult term from the bulk concentrations.

Also, one has to consider thermodynamic consistency: Why should the bulk concentration calculated using the surface/bulk partitioning apply to determination of one thermodynamic quantity (surface tension) but not to others (e.g. activities)? Thermodynamic quantities measured in the laboratory are always given as functions of bulk concentrations.

Note that the considerations in our paper is in fact nothing new (although the Referee states that our treatment "exceeds the idea of Li et al."). The equations of multicomponent classical gas-liquid nucleation theory (e.g. Wilemski, 1984, Laaksonen et al., 1999) are exactly similar as those applied in this study: the differences are that in nucleation theory, all species are taken to be volatile, and the bulk concentration is assumed known, whereas we take only water to be volatile, and assume the total numbers of molecules known. Furthermore, a similar treatment as presented in this paper applies for solution droplets created by dispersing a bulk surfactant solution (Bianco and Marmur, 1993; Laaksonen, 1993). Even in cloud physics, the effect of adsorption on the bulk concentrations has been known for decades: in their book, Dufour and Defay (1963) made calculations for inorganic salts in cloud droplets and noted that for such species, the effect is so small that it can be ignored.

Specific comments:

P. 2782: l. 7 "Clarify here in the abstract that the term partitioning is defined as surface/bulk partitioning in order to avoid any confusion with e.g. gas/particle partitioning"

We will clarify this in the revised paper.

P. 2785: l. 21/22 "There are approaches available which allow an estimate of the surface tension as a function of drop size. So, this statement should be made more carefully and it should be rather clarified under which conditions this curvature dependence

can be neglected."

There are several recent papers on the curvature dependence of fluids much simpler than water (e.g. Schmelzer et al., 1996; Laaksonen and McGraw, 1996; Tsekov et al., 2000), and even those do not always agree with each other. Estimates for the curvature dependence of water are not reliable (see e.g. Zakharov et al., 1997). With surfactant solutions, the situation is even worse as the curvature dependence also depends on the solution composition (see e.g. Laaksonen and Napari, 2001). Fortunately, it can be shown that for droplets in the size range we are considering, the curvature effect on surface tension is miniature. We will clarify this in the revised manuscript.

P. 2786: l. 18 "Give a reference for Equation (6) and explain the meaning of h."

The complete equation has been given by Laaksonen et al. (1988). The constant h is a product that depends on the degree of dissociation of the electrolyte, and on its Henry's constant and saturation vapour pressure. We will clarify this in the revised manuscript.

P. 2787: l. 7/8 "This statement requires some clarification. Why is only the bulk concentration important for the Raoult effect?"

The Raoult effect, by definition, describes the vapour pressure lowering of the solvent due to presence of solutes in the bulk of the liquid.

P. 2789: l. 15-18 "Equation (14) is not included in the paper by Shulman et al. (1996). So, clarify why their data were fitted to this equation. Does MOCW really represent the solubility in water or rather the dissolved fraction?"

In their paper Shulman et al. give data for the solubility of cis-pinonic acid in water and in aqueous ammonium sulphate solutions. As far as we know the original equations into which their data has been fitted have not been published. That is why we used the data published in Shulman's article and fitted it to the equation presented in our manuscript. MOCW does indeed represent the pinonic acid solubility in water (0.02 mol/l from Shulman et al. (1996)). In the revised manuscript, we will avoid the multiple

use of M for molarity, solubility and molar weight so that the reader will not be confused.

P. 2790: l. 19/20 "Replace solute effect by Raoult effect as it is applied throughout the rest of the manuscript"

This will be done in the final version of the paper.

P. 2791: l. 2 "Li et al. (1998) obtain a value of ns/nb = 13.9 under the assumption of the same conditions. What are the potential reasons for the deviation to the value from the current study (ns/nb = 10.9)?"

The calculated critical supersaturation (as well as critical size) depends on whether we consider the surfactant partitioning to affect only the Kelvin term (as in Li et al. (1998)) or both the Kelvin and the Raoult terms. In the latter case, the critical radius for an initially dry 50 nm radius SDS particle is smaller than in the former case (Fig 2.). So, the critical radius is smaller when partitioning is accounted for also in Raoult effect. The smaller the droplet the smaller the surface area, thus there is a smaller amount of SDS molecules on droplet surface and the value of ns/nb is therefore smaller when partitioning is accounted for in Raoult effect.

P. 2792/2793: "The CCN activity of pinonic acid has been investigated in a model study by Hegg et al., 2001. They have found a significant decrease in drop number concentration compared to inorganic compounds. Can an estimate be given to what extent the consideration of partitioning, i.e. the accelerated dissolution, might counteract this supression?"

We will give an estimate in the revised paper.

P. 2797: Table 2 "Explain briefly in the table caption Approaches 2 and 3"

The approaches 2 and 3 are explained in the text, but it is true that they have to be made more understandable also in the figure caption. This will be done in the revised paper.

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