

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

### **Anonymous Referee #3**

Received and published: 18 June 2004

General Comments: This paper presents a modification of the Köhler theory with focus on the surface activity of organic species (sodium dodecyl sulfate (SDS), pinonic acid). Such explorative investigations of organic properties are of great importance in order to assess the role of organic aerosols in CCN activity and cloud formation. The particular focus of this study is the investigation of the effect of partitioning of soluble organic species between the bulk phase and a surface layer. This effect was already addressed by Li et al. (1998) who analyzed the influence of partitioning on surface tension, i.e., on the Kelvin term. The current study exceeds this idea by addressing the possible effect of bulk/surface partitioning on the reduction of the Raoult term.

My main concern on this idea is the thermodynamical assumption, which has been made about the nature of the surface layers. In a recent study, Decesari et al. (2003) have shown that SDS tends to form an expanded, soluble film on the drop surface. In addition, they point out that only insoluble, more compressed films (e.g. fatty acids)

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

cause a delay in water adsorption. However, the authors of the current study ascribe the reduction of the solute term to a reduced solute bulk concentration if partitioning is considered. But in general, water uptake is a function of the number of dissolved solute molecules. 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.

In the case of less soluble organics (pinonic acid) the formation of such surface layers leads to a smaller bulk concentration and thus, to an accelerated dissolution which in turn enhances the Raoult term. In this case, the consideration of partitioning of organics exhibits an important effect since the effect of partial solubility and gradual dissolution on the solute term has been discussed in several recent model studies.

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

p. 2785: l. 21/22 There are approaches available which allow an estimate of the surface tension as a function of drop size (e.g., Pruppacher and Klett, 1997, and references therein). So, this statement should be made more carefully and it should be rather clarified under which conditions this curvature dependence can be neglected.

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

p. 2787: l. 7/8 This statement requires some clarification. Why is only the bulk concentration important for the Raoult effect? (See my general comments above)

p.2789: l. 15-17 Eq.(14) is not included in the paper by Shulman et al. (1996). So, clarify why their data were fitted to this equation.

p.2789: l. 15 and 18: Does MOCW really represent the solubility in water or rather the dissolved fraction?

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

p.2789: The multiple use of M for both molarity, solubility and as dimension for Msalt is confusing in this context

p. 2790: l. 5 Replace "Solute effect" by "Raoult effect" as it is applied throughout the rest of the manuscript

p. 2790: l. 19/20 How do you treat the Raoult term? Point it out in a more detailed form the main difference between your study and this one by Li et al. (1998).

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

p. 2792/2793: The CCN activity if 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 suppression?

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

Technical corrections:

p. 2795: l. 13 replace higly by highly

p. 2804: Figure 7 I suggest using consistent colors (e.g., broken/solid lines) for each pair of bulk and total concentration of the individual compositions

#### References

Decesari, S., M. C. Facchini, M. Mircea, F. Cavalli, and S. Fuzzi, Solubility properties of surfactants in atmospheric aerosol and cloud/fog samples, *J. Geophys. Res.* 108, D21, 4865, doi: 10.129/2003JD003566, 2003.

Hegg, D. A., S. Gao, W. Hoppel, G. Frick, P. Caffrey, W. R. Leitch, N. Shantz, Am-

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

brusko, J., and Albrechtinski, T., Laboratory studies of the efficiency of selected organic aerosols as CCN, Atmos. Res. 58, 155-166, 2001.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 2781, 2004.

**ACPD**

4, S951–S954, 2004

---

Interactive  
Comment

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper