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Atmospheric
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Discussions

Interactive comment on "Aerosol hygroscopicity at high (99 to 100%) relative humidities" *by* C. R. Ruehl et al.

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In general, the text is quite long and somewhat difficult to follow. Especially introduction section is long and sometimes possibly too detailed. For example, authors list 11 papers as an example of studies using surface tension measurements from macroscopic solutions, and after that there is a detailed description of surface tension measurements from macroscopic solutions (page 15599, line 8). Introduction could be condensed and some parts (e.g. the Köhler equation) could be moved to other sections.

R: We have shortened the introduction. Specifically, we cut the number of examples of macroscopic s.t. measurements from 11 to 4, greatly shortened the description of s.t. measurement techniques, and moved the Köhler Eq. to the theory section.

Authors make the use of macroscopic surface tension measurements questionable in the case of submicron droplets (e.g. page 15599, line 23). However, surface tension should not depend on droplet size. Macroscopic surface tensions should be valid for droplets larger than a few tens of nanometers, but it is clear that bulk solution concentration changes due to surfactant partitioning and it must be taken into account.

Then the real question is, just as in page 15608 line 5, when the effect of surfactant partitioning can not be neglected.

R: Agreed, and we have added text to the introduction emphasizing that it is the overall hygroscopicity (not just the surface tension component) of submicron aerosols that we are exploring.

Instead of comparing model predictions (with different approximations or kappa and delta and values) to the experimental data, the authors compare kappa and delta values from models and experiments. In order to conclude that bulk solution data can not be used in predicting high-RH hygroscopicity, the authors should show that droplet growth can not be predicted well when accounting for surfactant partitioning, surface tension and non-ideality. Otherwise, the conclusion could be that kappa-Köhler theory, or these parametrization, is not valid for surfactants.

R: We show in Fig. 10a that SDS delta cannot be predicted using constant values of gamma (surface partitioning) and sigma (surface tension). Also, Fig. 7a demonstrates that using a macroscopic values of phi for SDS (i.e., assuming micellization) underpredicts hygroscopicity. However, Fig. 7a suggests that a constant value of phi (i.e., constant kappa) represents the SDS data reasonably well, because the hygroscopicity does not vary with RH. We therefore conclude that macroscopic values of phi, sigma, and gamma for SDS are not appropriate for micron-sized droplets, but we do not claim that kappa-Köhler theory is invalid for surfactants.

It seems quite strange that only droplet wet size, which depends greatly on dry size, is used in describing aerosol hygroscopicity. Growth factors are commonly used in the literature.

R: The single parameters used here (i.e., kappa and delta) take into account not only dry size, but RH as well, which is why we decided to use them instead of growth factors to express hygroscopicity. We include the droplet wet size because this is the measurement that is actually made in our lab, but our main conclusions are based on trends in kappa (with RH) and delta (with Dwet).

In spite of these few flaws, the topic is very interesting, so the paper deserves to be published after some corrections.

Specific comments/questions

Page 15596, line 15: The sentence starting from this line should be clarified.

R: We have rewritten the sentence: "The results suggest that, for a soluble, single-component surface-active aerosol at high RH, surface partitioning reduces hygroscopicity to a greater extent than surface tension reduction increases it."

Page 15597, line 13: It looks like the first half of this paragraph contains both theory and results. Why are these given in the introduction?

R: This has been moved to the theory section.

Page 15598, Eq. 2: How are the sensitivities calculated, because it is not possibly to solve Dwet from Eq. 1 analytically and aw is a function of Dwet? What are the reference values for surface tension, water activity and droplet diameter?

R: The reference value for surface tension is that of pure water, and this has been added to the text. The sensitivities are calculated as functions of RH and Dwet, and specification of these two variables leaves only one unknown (aw) in Eq. 1.

Page 15601, line 11: Why would molecules prefer surface instead of micelles in the case of curved surface?

R: We have removed this line from the manuscript.

Page15607, Eq. 14: How is this surfactant partitioning taken into account in practice? Total surfactant concentration can be calculated from Eq. 9, but surface concentration (Eq. 14) must be subtracted from that. Surface concentration depends on droplet area, but it is the unknown. Is droplet size solved iteratively?

R: Yes, all calculations of droplet size involving partitioning are solved iteratively, as now indicated in the text.

Page 15611, lines 9-16: First of all, osmotic coefficient should be one at infinite dilution. Then, according to Widera et al. (2003) osmotic coefficient is 0.622 at SDS concentration 0.01 mol/kg, and this concentration is already higher than the CMC (0.008 mol/kg). Osmotic coefficient is about 0.12 at 0.15 mol/kg solution.

R: We have corrected this, omitting the reference to phi at infinite dilution, and now state that "phi drops sharply to 0.12 once the CMC is exceeded, and is ~0.12 for all [SDS] observed in this study (>110 mol/m3)." This minimum concentration is equivalent to 0.11 mol/kg, and according to Widera (2003) phi is already lowered to 0.13 at 0.10 mol/kg.

Page 15611, line 13: If SDS concentration is always higher than CMC (or 0.15 mol/kg), even with accounting for surfactant partitioning, droplet surface tension is 0.30 mJ/m2, osmotic coefficient is 0.12 and there is a SDS monolayer in surface. Have you done any calculations how well droplet size is predicted by using these values? It seems that and can not be predicted correctly by using these values, but then the real problem is in the assumption made for calculating and values from the experimental data.

R: The red dash-dot line in Fig. 8a is the SDS kappa assuming phi=0.12, sigma=0, and no partitioning. This demonstrates that observed SDS droplet size (represented by kappa, which goes as Dwetˆ3) is much greater than that predicted assuming phi=0.12. If we included partitioning and/or raised sigma to 30 mJ/m2, these predicted values would decrease even further.

Technical corrections Page 15597, line 19: Vw is molar volume of water.

R: We have made this correction.

Page 15602, line 24: Should there be something like “If constant sigma is assumed: : :”?

R: We have removed this line from the text.

Page 15603, Eq. 4: Vw should be in the numerator

R: We have made this correction.

Page 15604, Eq. 10: Vs should be Vw

R: We have made this correction.

Page 15611, line 6: party should be partly

R: We have made this correction.

Page 15611, line 21: Extra space before comma

R: We have made this correction

Page 15614, line 18: varionation should be variation

R: We have made this correction.

Page 15624, line 5: Khler should be Köhler

R: We have made this correction.

Page 15625, line 23: There is an extra plus sign after the doi

R: We have removed it.

Page 15634, Fig. 7: Word “hygroscopicity” repeated

R: We have made this correction.

References Widera, B., Neueder, R., and Kunz, W.: Vapor pressures and osmotic coefficients of aqueous solutions of SDS, C(6)TAB, and C(8)TAB at 25 C, Langmuir, 19, 8226–8229, 2003.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15595, 2009.