**Atmospheric
Chemistry
and Physics
Discussions**

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

Anonymous Referee #1

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Ruehl et al. have calculated hygroscopicity parameters from measured particle hygroscopicity and those have been compared with predicted hygroscopicity parameters. They have studied the effect of surface tension, surface activity and non-ideal solution behavior on hygroscopicity parameters. The topic is interesting, because hygroscopicity parameters are commonly used in modeling of cloud activation and hygroscopic growth. Also, more information is needed from organics in general and especially from surface active species. Selected RH range is interesting, because it is between that of most other hygroscopic growth and cloud activation studies.

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.

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.

Instead of comparing model predictions (with different approximations or κ and δ values) to the experimental data, the authors compare κ and δ 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 κ-Köhler theory, or these parametrization, is not valid 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.

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.

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?

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

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

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?

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.

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/m^2, 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 κ and δ can not be predicted correctly by using these values, but then the real problem is in the assumption made for calculating κ and δ values from the experimental data.

Technical corrections

Page 15597, line 19: V_w is molar volume of water.

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

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

Page 15604, Eq. 10: V_s should be V_w

Page 15611, line 6: party should be partly

Page 15611, line 21: Extra space before comma

Page 15614, line 18: varionation should be variation

Page 15624, line 5: Khler should be Köhler

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

Page 15634, Fig. 7: Word "hygroscopicity" repeated

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.