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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 #2

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General

The manuscript deals with the determination of the hygroscopicity of aerosol particles consisting of different organic and inorganic substances at relative humidities (r.h.) larger than 99%.

The hygroscopicity of aerosol particles is a key issue in quantifying both, the aerosol direct and indirect effects. Investigations of hygroscopicity in the high r.h. range are of special interest as, in this range, a) particle optical properties are highly sensitive to small changes in r.h., and b) hygroscopicity is strongly related to the activation behaviour of the aerosol particles. Therefore the paper deals with a topic highly relevant to the field of atmospheric research and is consequently suitable for publication in ACP.

The main problem I personally have with this paper is that trying to understand the influences of both the Raoult and the Kelvin term in the Koehler equation with just hygroscopic growth measurements in such a limited r.h. range is at least challenging and often impossible. Performing both hygroscopic growth and activation measurements, as here could have been done even in the same instrument, seems to be the more appropriate and promising method to me. The main reason for my concern is discussed by the authors themselves, i.e., the respective sensitivities of the Koehler-equation to kappa and surface tension. As a consequence, partly also because of the narrow r.h. range considered, varying either kappa or delta becomes somewhat arbitrary.

Furthermore, the paper lacks a clear definition and a consistent use of ''hygroscopicity". Both kappa and delta are called hygroscopicity which is imprecise and confusing. Section 2 requires mayor revisions with respect to motivation and reasoning behind the different approaches taken.

Furthermore, the results given in figures 6 to 13 should be reviewed more critically. The significance, of some of the trends depicted in these figures needs to be discussed in view of both the experimental uncertainties and their general importance. As mentioned before, data collected in such a limited r.h. range might not sufficient to retrieve information about trends in hygroscopicity, let alone trends in the variables used to parameterize the Raoult and the Kelvin terms. In my opinion, these issues have to be addressed more thoroughly.

Earlier work is adequately recognized and credited and to my knowledge no portions of the manuscript have been previously published.

In summary, certain parts of the manuscript (e.g. the results concerning the influences of micelles) represent a significant contribution to the field of atmospheric science and should be published. However, the paper at present has to undergo mayor revisions!

Specific

The Koehler equation should be removed from the introduction.

page 15597, line 13: I don't consider the ability to reduce activity or surface tension a chemical property.

page 15598, line 10 ff: Wex et al, JAS (2008) performed a somewhat similar sensitivity analysis. Results should be referenced and briefly discussed. (Wex, H., F. Stratmann, D. Topping, and G. McFiggans (2008), The Kelvin versus the Raoult term in the Köhler equation, J. Atmos. Sci., 65, 4004-4016, doi:4010.1175/2008JAS2720.4001.)

page 15599, line 5: Close the bracket after 25°C.

page 15601, line 11: It should be explained how curvature of the surface can increase the tendency of free molecules to partition to the surface.

page 15601, line 17: Define Vw and Vs.

page 15601, line 24: The last sentence needs additional explanations.

page 15602, line 24: ''If sigma is assumed . . .'' Something seems to be missing here.

page 15603, line 10 ff: I find this reasoning confusing and somewhat symptomatic for the subsequent discussion: Kappa is a measure for the Raoult term and why should it matter for the Kelvin term which is parameterized by delta?

page 15603, line 11/12: "..., kappa is a more useful of indicator of the ..." – remove the first "of"

page 15603, equations (4) and (6): Check the definition of delta again. Inserting Eq. (6) in Eq. (7) differs from Eq. (4).

page 15603, line 24: "because delta proportional to sigma, as hygroscopicity increases, delta decreases" Again we are facing the definition issue.

page 15604, line 5: Again, kappa is a measure for the Raoult term.page 15605, line 1 ff: "... phi as a function of ns/nw is well known" – Is it really? I presume only for the

systems examined here?

page 15605, line 16: Isn't kappa anyhow constant for ideal solutions ?

page 15605, line 20: It should be explained why it is desirable that the increase in kappa is insensitive to dry.

page 15605, line 25: Again, delta is a measure for the Kelvin term

page 15606, line 1-10: Here the reasoning is confusing. Why is e.g. a phi required?

page 15606, line 15: Why should the Kelvin effect be evaluated? Rewording required.

page 15607, line 17 ff: Confusing, clarification needed.

page 15611, line 6: ''party" should be partly

page 15611, line 26: ''several studies" Please give references.

page 15612, line 5: I suspect circular reasoning here!?

page 15612, line 21: Despite the reduced proportion of SDS found in micelles, shouldn't the concentration in the solution stay constant as long as micelles exist? Clarification needed.

page 15613, line 1 ff: I recommend to give values for the CMC (critical micelle concentrations), together with the concentrations in droplets investigated here.

page 15614, line 23-25: In my opinion, this is a highly confusing statement. Clarification needed.

page 15615, line 5-7: According to my understanding delta does not account for non-ideality!? I think we still suffer from the deficiencies of section two.

page 15632, figure 5: I personally find this figure a little confusing. The colour code is impossible to decipher, there is no legend. A different kind of plot is needed.

page 15633, figure 6 and corresponding text: Two questions: a) why is there so much

spread in the data and b) isn't it a little optimistic do determine a trend in kappa from the data in the lower panel? Clarification needed. Here, in the following figures, and in the corresponding text, a clear definition of hygroscopicity is needed. What is the meaning of the different colours in this plot and in the following ones?

page 15634, figure 7 and corresponding text: Isn't the behaviour depicted in the lower panel trivial, i.e. a variation in kappa is compensated by a variation in delta, and vice versa? This again reflects my mayor concern with the results presented here. In the caption, ''hygroscopicity" should be erased.

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