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Atmospheric
Chemistry
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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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Responses to Referee 2:

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

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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.

R: While 99.2-99.9% is a limited range for RH, the concentration of an ideal solute would decrease by a factor eight (by dilution) over this range, and the droplet diameter increases by a factor of 2. Also, as pointed out in the Theory section, this is the only range below 100% in which the Kelvin effect is significant, and very little data is currently available for micron-sized droplets in this size range. We agree, however, that there are limitations on the information available at this range of RH, and have added text to the abstract and conclusions emphasizing that conclusions are only valid at high RH (99-100%). We feel that our main conclusions are justified: inorganic hygroscopicity is consistent with water activity measurements of macroscopic solutions and with insignificant surface activity, and organic hygroscopicity (particularly SDS) increases as droplet size increases, suggesting that surface activity reduces hygroscopicity under the experimental conditions.

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.

R: We agree that for multi-component particles, or for particles of unknown composition, activation measurements would be an important addition to this method. However, the CCN activity of each of the single components used here here is relatively well-known, and the corresponding values of kappa are consistent with the values measured here, at least as RH–>99.9%.

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

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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.

R: We have added the following definition to the beginning of the theory section: "Hygroscopicity is defined as the tendency of a substance to absorb water from the atmosphere. Therefore the more hygroscopic a particle, the more water it will absorb (and the greater its Dwet) at a given RH." We introduce both kappa and delta as single parameters representing hygroscopicity, and have made modifications to parts of the text where this distinction was blurred. For example, p15607, line 24 has been changed from "hygroscopicity (our experimental values of kappa and delta)" to "observed hygroscopicity (as expressed by the parameters kappa and delta)." Also, the italicized parenthetical phrase has been added p15610, line 15: "As expected, the high-RH hygroscopicity, expressed as kappa, of both inorganic compounds..." Furthermore, we have replaced the word "hygroscopicity" with either kappa or delta when approproate (e.g., p15613, line 10).

Section 2 requires mayor revisions with respect to motivation and reasoning behind the different approaches taken.

R: We have made extensive revisions to section 2, and believe that it is improved, especially with respect to its clarity. The Kohler Eq. has been included, repetitious language has been removed, and specific instances of potentially confusing language have been revised.

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.

R: We have reemphasized the statistical test applied to the trends in kappa vs. RH and delta vs. Dwet. Of the six compounds studied, only two had statistically significant ($p<0.05$) trends in kappa vs. RH: malonic acid and sucrose. We emphasize that the only conclusions drawn are that the variation in malonic acid aerosol hygroscopicity with RH is consistent with published water activity data, and that sucrose aerosol hygroscopicity at high-RH is slightly greater than predicted for an ideal solution droplet. We feel that these conclusions are supported by the data. Regarding delta vs. Dwet, again only two compounds (SDS and malonic acid) showed significant trends. The p-value for the SDS trend was ∼10ˆ-6, and we therefore feel confident that this trend is real, and it is the source of most of the discussion of trends in the manuscript. The malonic acid trend is in the same direction but much mild, and we conclude that all organic compounds showed this trend, although in most cases it was not significant, and that it was most significant for SDS.

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.

R: It has been moved to the theory section.

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

R: We have removed the word "chemical".

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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.)

R: We have added the reference, and mentioned the two main conclusions from Wex et al. (2008) with which our sensitivity analysis concurs: first, that hygroscopicity is insensitive to s.t. when RH<95%, and second, that the sensitivity of Dwet to the Raoult effect is greater for more hygroscopic particles.

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

R: Done.

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.

R: We have removed this sentence from the manuscript.

page 15601, line 17: Define Vw and Vs.

R: Done (this is actually on page 15602).

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

R: See next response - we assume you are referring to page 15602 here.

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

R: We have removed this sentence, and discuss the significance of picking a value for sigma later in the same paragraph.

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?

R: While kappa is better suited to probe the Raoult effect and delta the Kelvin effect, in reality both effects are always acting and cannot be completely isolated (since only one parameter in used at a time). It is therefore important, when using a single parameter, to keep in mind how this parameter might reflect both effects.

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

R: Done.

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

R: Eq. (7) is the Kohler Eq. with delta, Eq. (4) is the Kohler Eq. with kappa. Only one parameter is used at a time, and so combining Eq. (7) with Eq. (6) (the definition of delta) yields the original Kohler Eq. (1). To get to Eq (4), one has to combine the definition of kappa (Eq. 3) with Eq (1). The confusion here no doubt results from a lack of clarity in the Theory section, and we have extensively revised it accordingly, e.g., emphasizing that only one parameter can be used at a time.

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

R: Hygroscopicity has now been defined (i.e., Dwet at a given Ddry and RH), and because a larger Dwet at a given Ddry and RH causes delta to decrease, it is inversely related to hygroscopicity.

page 15604, line 5: Again, kappa is a measure for the Raoult term.

R: We believe our use of the terms "Raoult effect" and "Kelvin effect" have led to some confusion. We have thus in many instances replaced the terms with more appropriate language. For example, the subsection title referred to here has been changed from "Influence of the Raoult effect on kappa" to "Predicted values of kappa".

page 15605, line1 ff: "... phi as a function of ns/nw is well known" – Is it really? I presume only for the systems examined here?

R: We have changed the preceding phrase from "For most solutes,..." to "For most common solutes, including the ones examined here,

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

R: This is true if the surface tension is known, and we have made the correction.

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

R: We have removed this text from the manuscript.

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

R: See response above - we see that the previous wording ("The influence of the Kelvin effect on delta") caused some confusion, as it implies that the Kelvin effect is a secondary influence on hygroscopicity. We have changes the subsection title to "Predicted values of delta".

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

R: Because hygroscopicity is influenced both by phi and sigma, if one uses a single parameter for hygroscopicity, one must choose whether to parametrize the Kelvin (sigma) or the Raoult (phi) term, and an assumption must be made regarding the other term. In this case, since delta is a parametrization of the Kelvin term, use of Eq. (7) to calculate delta given requires that water activity (expressed here as phi) be known or assumed. This is analogous to an assumption of surface tension being required to use Eq. (5) to solve for kappa.

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

R: We have removed this sentence. We now more specifically state that the goal is not just to "evaluate the Kelvin effect," but more specifically, to look for variation in hygroscopicity as expressed by delta with Dwet.

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

R: We have revised this line, which now reads: "For a soluble surfactant, the excess surface concentration is not expected to reside exclusively at the interface (e.g., in a self-assembled monolayer), but rather as a concentration gradient between the bulk and surface phases." We have also added a reference to Moroi (2004), which describes the difference between soluble and insoluble surfactants in more detail.

page 15611, line 6: ‘’party” should be partly

R: The correction has been made.

page 15611, line 26: ‘’several studies” Please give references.

R: We have added citations to Prenni et al. (2001) and Sjogren et al. (2007)

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

R: We have removed this line.

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.

R: Any SDS that transferred from micelle to solution would increase particle hygroscopicity because water would need to be absorbed to keep SDS concentration constant. We now refer to "the hygroscopicity of an SDS particle" instead of SDS hygroscopicity to make this more clear.

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

R: We have added this.

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

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tion needed.

R: We have added the paranthetical phrase: ...expect delta to be a more conservative metric of Kelvin effects (i.e., to be less likely to exhibit a trend with D_wet than if phi were held constant)

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.

R: Delta can account for nonideality, it all depends on the assumption chosen for the Raoult term. We think the revisions of Section 2 will make this more clear.

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.

R: We have omitted this figure, which included all data from this study, and was only obliquely referred to in the text. We instead refer to Table 1 when summarizing all data, or comparing one compound to another.

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?

R: As discussed in the experimental section, much of the scatter is probably due to uncertainty in the RH at the point the Dwet measurement is made. If the temperature in the view volume fluctuates by $\sim$0.01K, this changes RH by $\sim$0.1% (absolute), with a resulting uncertainty in kappa depicited by the error bars. In the lower panel, we report the significance of the trend in AS kappa (p=0.068), and although this trend is not particularly strong or significant, it does match very well with macroscopic observations, which is the only conclusion drawn regarding AS. We have clarified our definition of hygroscopicity in the text, and added colorbars indicating that color represents RH.

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.

R: This is done just to illustrate that whether hygroscopicity is parametrized as kappa or delta, a strong trend in SDS hyg. with Dwet is present. We hope that it helps illustrate the difference between the two parameters. The extra word has been removed.

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