Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Henry's law constants of diacids and hydroxypolyacids: recommended values" *by* S. Compernolle and J.-F. Müller

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Henry's law constants are of interest to predict the partitioning of volatile and semivolatile organic compounds to highly dilute (aqueous) solutions, such as cloud droplets. Compernolle and Müller focus on the Henry's law constants (HLC) of dicarboxylic acids and hydroxypolycarboxylic acids and present a new assessment of the range of recommended HLC values for pure water as a solvent. Substantial uncertainties regarding experimental pure component vapor pressures make their recommendation of HLC values critically dependent on the choice of the vapor pressure values.

This paper is interesting and the assessment of relevance for the community. I recommend the article for publication in ACP after consideration of my suggestions and comments given below.

General comments

- In the introduction (p. 25126) it is stated that: "The Henry's law constant is a fundamental molecular property regulating the partitioning between the gas and aqueous phase. In the atmosphere, this aqueous phase can be a cloud droplet or an aqueous aerosol." Further down on the same page it is also stated: "Of course, due to the presence of organic and inorganic molecules, an aqueous aerosol can hardly be regarded as a pure water phase, as is required for HLC.". I agree with the latter statement and think that there is a contradiction between the two sentences in the introduction. I suggest rephrasing the first sentence, because the HLC is not a "fundamental molecular property"; rather it is a property based on a limiting law that describes the partitioning of a compound between the gas phase and a specified highly dilute liquid phase (aqueous or any other solvent). An aqueous aerosol phase, unless very close to 100 % relative humidity, does not meet that criterion (as recognized by the authors) and the partitioning of an organic compound can be substantially influenced by other solutes. This is why gas-particle partitioning schemes should use activity coefficient models that depend on solution composition, rather than using HLC. I would therefore focus on cloud droplets when describing atmospheric applications of HLC.

- Effective and intrinsic HLC.
  The authors mention the distinction between effective and intrinsic HLC (Eq. 8), which is of importance for strong acids. However, it is not mentioned which definition they use in their tables, for Eq. (3), etc. I assume their data evaluation

approach and tabulated values should reflect intrinsic values. However, the experimental activity coefficient ratios obtained from water activities will yield effective HLC values unless corrected, which could present a source of uncertainty for the relatively strong diacids that tend to partially dissociate in highly dilute aqueous solutions. In that context, the availability and treatment of experimental data at very high dilution of the solute, including consideration of certain points as outliers, as done in the cases of malic and tartaric acid (in the Supplement), may influence considerably the final value taken and its interpretation as effective or intrinsic HLC (see also my Specific Comments to the Supplement below). I suggest to discuss this more clearly in the paper and to state what definition is used in Eq. (3) and where appropriate.

- Use of activity coefficient models for obtaining HLC.
  In Section 3 (p. 25131) the use of group-contribution activity coefficient models (UNIFAC-Peng, UNIFAC-Raatikainen, AIOMFAC) is discussed. In addition, for the actual data evaluation, fitted expressions for binary mixture's activity coefficients (Margules, Van Laar, Wilson) are used. For the readers less familiar with these models and their advantages and drawbacks, it may seem unclear why the group-contribution models are discussed at all. This should be pointed out more clearly.
  One could argue that a mixture-specific model that fulfills the Gibbs-Duhem relation, when fitted to a selection of experimental data, will always perform as good or better than a predictive group-contribution model. Zuend et al. (2008) (in their section 3.4) discuss some of the differences between group-contribution and system-specific activity coefficient models. Clegg and Seinfeld (2006) and Zuend et al. (2011) (in their section 4.1) also show the usefulness of specifically fitted models (Gibbs-Duhem-Margules parameterization) for binary mixtures, being superior to predictive group-contribution models for a specific system, but

limited to that system and by the available experimental data. A key advantage of group-contribution models is their versatility for predicting properties of various complex systems, including for systems containing organic compounds for which no experimental data is available. Hence, for systems where a Margules type model could not be fitted to experimental data for the purpose of retrieving activity coefficients. The UNIFAC-Peng model and models that inherited some of its interaction parameters, such as the AIOMFAC model, as well as the UNIFAC version by Raatikainen and Laaksonen, have been fitted to some experimental water activity data for dicarboxylic acids and hydroxypolycarboxylic acids by Peng et al. (2001) as stated by the authors. Therefore, in this case the models could be considered somewhat biased to represent the Peng et al. (2001) data well, which is probably why the authors use these models in a comparison in this study. Moreover, the AIOMFAC model is aimed at describing organic-inorganic interaction in solutions that also include dissolved electrolytes. Hence, AIOMFAC could be useful in estimating HLC of diacids in dilute aqueous systems containing salts, for which experimental data is very limited. Also, regarding the final values of the HLC listed in this study, given the uncertainty from the vapor pressure data, it would be of interest how much of a difference it would make when using UNIFAC-Peng or AIOMFAC instead of the Margules model for the activity coefficient ratios.
  I suggest to consider some of these aspects in the revised version of the paper.

- I agree with the comment of Rolf Sander regarding the Supplement. I would prefer the information from the Supplement to be presented in the main article, perhaps as an appendix.

Specific comments

- p. 25127, Eq. (2), line 19: Here activity coefficients on mole fraction basis are in-

troduced. The basis should be mentioned since there are other scales for activity coefficients (molality, mass fraction, molarity, etc.). And "compared to a solvent of pure s itself" would be the pure component reference state at the same temperature and pressure. Eq. (2) also implies ideal gas behavior of the organic compound (the "solute"), which should be stated, because certain organic acids tend to form dimers in the gas phase (this is probably not an issue at the low partial pressures the HLC refer to).

- p. 25127, Eq.(3): Define the symbol $p_{L,s}^0$.

- p. 25128, line 3: Revise the sentence "Now if the solute is added to water above its saturation point, a solid phase will form in the water phase." ("water above its saturation point" = beyond its solubility limit in water?, "water phase" = aqueous phase?

- p. 25128, line 9: Correct the statement:"In principle, liquid and solid can only co-exist at the fusion point,"; there is not just a fusion "point" in the (p, T) phase diagram, unless restricted to a single temperature or pressure (there is a melting curve). For correctness also state: "In principle, a compound's pure liquid and solid state can only...".

- p. 25128, line 15 (and at other occurrences): Replace "fluidization" by "melting" or "dissolution"; fluidization is a different process unrelated to what the authors mean here.

- p. 25134, line 10: It is stated: "As UNIFAC-Peng matches a_w well for citric acid over the entire concentration range, and already overestimates a_w in the supersaturation range for malic and tartaric acid, it follows that the IDAC of UNIFAC-Peng should be more reliable than those of AIOMFAC.". As a developer of AIOMFAC, I may be a bit biased on this point, but I would suggest some changes

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regarding a few statements about AIOMFAC and UNIFAC-Peng. First, UNIFAC-Peng matches the experimental water activity data of citric acid better over the concentration range *where data is available*. Second, "and already overestimates a_w in the supersaturation range for malic and tartaric acid": if it overestimates, how can you be sure that it is more reliable than AIOMFAC? It seems to me from Fig. 2 that AIOMFAC actually matches the a_w data of tartaric acid better than UNIFAC-Peng. I also assume that the infinite dilution activity coefficients from these models were actually directly calculated for a finite, tiny solute concentration, it therefore would be of interest to see a model-experiment comparison figure for the dilute range, to see which model better matches the data at the very dilute conditions (not implying to say that AIOMFAC would do better there). In principle, a model that fulfills Gibbs-Duhem relation may match the true infinite dilution activity coefficient value perfectly while deviating from experimental data at higher concentrations. As long as Eq. (3) would be used for HLC values and not Eq. (14), that would not be a problem.

- p. 25134, line 17: Sentence needs rewording."This combination was done to widen the scope method, but clearly this comes at a prize." I suggest to delete the "but clearly this comes at a prize" part, because (1) the combination of UNIFAC parameters within AIOMFAC does also lead to reasonable descriptions for other systems (see tartaric acid), perhaps as good or better then UNIFAC-Peng; (2) all of these UNIFAC versions are actually hybrid methods because they include parameters from several sources (UNIFAC-Peng contributes just a small subset of refitted parameters (as stated on page 25132); (3) to judge whether the approach taken in AIOMFAC comes at a prize or not, given the predictive and broad scope of all UNIFAC-based models, this would need to be evaluated on a much wider data basis.

- p. 25136, line 15: Statement: "Therefore we conclude that they cannot be used as a tool to estimate their IDAC, or finally the HLC." is somewhat misleading, as

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in fact, UNIFAC models could be used for exactly that, an estimation based on its predictive capability. Of course, it is less reliable than using a specifically fitted model based on actual activity coefficient data.

- p. 25140, line 7-11: To my knowledge, it should be possible to *estimate* a HLC value from vapor pressures measured by Huisman et al. (2013) using Eq. (3) and the IDAC from the fitted Margules or Van Laar model. I suggest to include the data from such a derivation in Table 3.

- Supplement, page 1: A comment: the water activity data from the measurements of Peng et al. (2001) is available in tabulated form online (http://ihome.ust.hk/ keckchan/hygroscopic.html).
  Same page: It is unclear to me how the experimental data points shown in the figures (Supplement) were obtained from Eq. (1). What functional form for $\ln \gamma_w(t)$ was used in the integral term?

- Supplement, Figures 1-4: The experimental data points at very high dilution ($x_s \rightarrow 0$) seem to indicate a relative increase or "upward curvature" in the activity coefficient ratio ($\gamma_s / \gamma_s^{sat}$) and two experimental points at the lowest x_s were considered outliers by the authors. Could it be that the data points are actually showing the correct behavior due to acid dissociation at very high dilution, which is not considered in the model fit curves? Such dissociation effects on activity coefficients are known for inorganic salts and acid at high dilution in water (see, e.g., Fig. 3 - 5 of Zuend et al., 2008). Especially for tartaric acid (Fig. 3), the trend seems not to be captured by any of the fitted models. This raises the question of effective vs. intrinsic HLC extracted from such data and model fits. I suggest that the authors briefly comment on this.

Technical corrections

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- p. 25128, line 2 (and at other occurrences): I suggest to replace the expression "sublimation pressure" by "solid state vapor pressure" because sublimation is a phase transition process not a physical state.

- p. 25137, line 19: delete "only".

References

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