

ACPD article:

## **Influence of Organic Compound Functionality on Aerosol Hygroscopicity: Dicarboxylic Acids, Alkyl-Substituents, Sugars and Amino Acids**

*Article by Aleksandra Marsh et al.*

Review by Andreas Zuend

Marsh et al. present new measurements and discussion of the hygroscopicity of 36 different organic compounds using a custom-built “comparative kinetics” electrodynamic balance (CK-EDB). This instrument was designed to allow for hygroscopicity measurements of super-micron aqueous solution droplets over a wide range in relative humidity (RH), including the range above 90 % RH, which was inaccessible with reasonable precision by past EDB designs. These new data sets are certainly of value as the CK-EDB enabled measurements into the supersaturated RH (or water activity) range inaccessible by most bulk techniques, yet important for the measurement of the liquid state hygroscopicity of organic compounds with low solubility in water. Furthermore, the authors point out that a relatively short time for a set of measurements on a sample droplet enables measurements involving semi-volatile organic compounds without significant organic evaporation effects affecting the particle composition.

Processed experimental data, including error estimates, are tabulated in a practical format in the Supplementary Information (SI) to the article, which is commendable. This promises to be useful for independent comparison with other measurements and for future improvements of thermodynamic model parameterisations, such as the UNIFAC. The authors discuss the agreement/disagreement of UNIFAC-predicted water activity vs. mass fraction of organic in comparison to the new data sets and available experimental data for a subset of the systems. In addition, the authors parameterised an isotherm-based model by Dutcher et al. with a subset of the new data, providing inter- and extrapolation of the binary systems to concentrations not considered experimentally.

I regard this work as a valuable research contribution well within the scope of the ACP journal. Overall, the article is concise and well structured. I am generally supportive of this article and the wealth of new experimental data reported. However, there are several points that should be clarified in a revision of the manuscript before publication is recommended. In particular, the comparison of the measurements to the group-contribution model UNIFAC requires further clarifications about model versions/parametrisations and the description of UNIFAC’s limited ability of accounting for slight differences in molecular structure, e.g. branching at constant molar mass and/or O:C ratio, need to be improved to avoid confusion and incorrect explanations. Addressing the issues raised should be relatively straightforward, see the general and specific comments below.

### **General comments**

- Section 2. Methods and Materials. While the reader is referred to Rovelli et al. (2016) and Davis et al. (2013) for a detailed description of the CK-EDB method, a general description of the chemicals used, their purities and solution preparation is missing. Some of that information is provided in the SI

only. I suggest that a brief description is also given in the main text and that the reader should be informed about additional information on this in the SI.

- Temperature range and droplet temperatures. In the first paragraph of page 4 it is highlighted that the temperature in the EDB trapping region can be controlled well over a  $\sim 75$  K range, however, throughout the main text information about the actual temperature used is missing (including tables and figures). As far as I can tell from the temperature information given in the SI, all experiments and model calculations were carried out at 293.15 K. Were hygroscopicity measurements at other temperatures considered (which would be useful, e.g. for improved, temperature-dependent thermodynamic model parameterisations given the temperatures were sufficiently different)? Hence, a discussion on the EDB temperature range used and the actual droplet surface temperature during the evaporation experiments will require some discussion. From Rovelli et al. (2016) it seems clear that the time scale of the evaporation will lead to deviations between droplet and surrounding gas phase temperature. Moreover, given that the evaporation rate from a relatively concentrated solution droplet is different from the evaporation rate of the probe droplet, a discussion of such temperature related issues with respect to the retrieval of the sample droplet's water activity at a particular temperature seems appropriate.
- In contrast to the inorganic solutes used in Rovelli et al. (2016), the present study involves organic solutes, some of which may cause a significant increase in mixture viscosity with decreasing droplet water content during evaporation in the EDB. In this context, the time scale of 10 s for the evaporation from the droplets may become an issue for droplets  $> 10$   $\mu\text{m}$  radius, potentially impeding the droplet-gas mass transfer (e.g. Koop et al., 2011) and potentially violating assumptions about a homogeneous, concentration-gradient-free mixing of water and organic compound within sample droplets aside from a developing temperature gradient within a rapidly evaporating droplet. The authors discuss the viscosity concern in Section 3.3, where it is mentioned that for many compounds measurements unimpeded by kinetic limitations were not possible below 80 % RH. Because this consideration may not only apply to sugars and alcohols, but to many of the multifunctional organics of higher molar mass, a more general discussion of kinetic limitations and consequences for the CK-EDB data processing should be provided in Section 2 where the method is described. If a relatively viscous binary aqueous droplet is exposed to low RH and evaporates water quickly, there may be insufficient time for homogeneous mixing in the droplet bulk compared to the near-surface volume of the droplet, which could lead to a concentration gradient and a higher solute concentration in the surface region of the droplet, affecting the local water activity there. Under such conditions, an organic solute may appear as more hygroscopic than it would be under actual gas-particle equilibrium conditions. Did the authors consider such effects in their method and the data processing? It is also not clear whether the authors considered a longer measurement time scale with slower evaporation settings for systems where substantial kinetic limitations may occur (and for which organic evaporation may not be a concern). Please discuss.
- UNIFAC models – three general comments and clarifications:
  1. The authors compare many of the measurements to predictions by “the” UNIFAC model, however, the information about the specific model version used and its parameterisation for some of the compounds is incomplete in the manuscript. While the original UNIFAC model theory by Fredenslund et al. (1975) is mentioned on page 2, several UNIFAC modifications

(changes to model equations, e.g. UNIFAC-Dortmund, UNIFAC-Lyngby, etc.) and several revisions of UNIFAC parameter tables applicable to certain UNIFAC versions have been published in the past 40 years. For example, the AIOMFAC model (Zuend et al., 2008; 2011), which includes a UNIFAC model based on the original theory of Fredenslund et al. (1975), relies mostly on the revised parameter set by Hansen et al. (1991). However, Zuend et al. (2011) discuss several modifications of the parameter database, including the use of improved interaction parameters determined by Marcolli and Peter (2005) for alcohols and multifunctional compounds containing hydroxyl groups, as well as modified interaction parameters by Peng et al. (2001) for a subset of interactions involving carboxylic acid groups. These modifications are detailed in Zuend et al. (2011) and are used in the online version of the AIOMFAC model (which was used for several comparisons with measurements in the present paper; see also [www.aiomfac.caltech.edu/about.html](http://www.aiomfac.caltech.edu/about.html)). Similarly, the online UNIFAC versions in UManSysProp (<http://umansysprop.seaes.manchester.ac.uk>; Topping et al., 2016), which includes AIOMFAC and a UNIFAC version, and the E-AIM website's UNIFAC ([www.aim.env.uea.ac.uk/aim/aim.php](http://www.aim.env.uea.ac.uk/aim/aim.php)) contain modified parameter sets from Peng et al. (2001) and from other sources of UNIFAC parameter revisions (see also [http://www.aim.env.uea.ac.uk/aim/phpmain/edit\\_help.php#section100](http://www.aim.env.uea.ac.uk/aim/phpmain/edit_help.php#section100) for details on UNIFAC in E-AIM). While some of these newer parameterisations lead to only slight changes to predicted water activities compared to the original UNIFAC by Fredenslund et al. (1975) with the Hansen et al. (1991) parameters, others are significant – and e.g. in the case of AIOMFAC, the description of alcohols and sugars is substantially modified by the introduction of specific subgroups and main groups in the model for these compounds (of relevance for the comparisons with CK-EDB data made in this study). Therefore, to provide sufficient detail for clarity and reproducibility, it is necessary to specify which models and parameterisations were actually applied (e.g. in the Methods section).

2. Contrary to the statements on page 2, lines 30 – 32 and on page 8, lines 20-21, UNIFAC (and AIOMFAC) actually account for the molecular structure and for certain differences between branched and straight-chain dicarboxylic molecules of the same molar mass – albeit in a limited way. For example, via the differing number in hydrogen atoms on CH<sub>2</sub>, CH, and C subgroups, which leads to different values of the relative Van der Waals volume and surface area terms in the combinatorial part of the UNIFAC model for these alkyl subgroups (affecting predicted activity coefficients). For this reason, the UNIFAC subgroup assignments, as listed in Table S0 of the SI, are incomplete/incorrect in the case of the dicarboxylic acids. For example, CH<sub>n</sub> is not a UNIFAC/AIOMFAC *subgroup* and as such does not sufficiently characterise the compound; instead the appropriate subgroups need to be stated. For example, correct subgroup assignments show that the three distinct C<sub>7</sub>-dicarboxylic acids (see also Table 3 of Zuend et al. (2011): 3-methyl adipic acid, (CH<sub>3</sub>)(CH)(CH<sub>2</sub>)<sub>3</sub>(COOH)<sub>2</sub>, 3,3-dimethylglutaric acid, (CH<sub>3</sub>)<sub>2</sub>C(CH<sub>2</sub>)<sub>2</sub>(COOH)<sub>2</sub>, and pimelic acid, (CH<sub>2</sub>)<sub>5</sub>(COOH)<sub>2</sub>, have slightly different subgroup formulas in UNIFAC/AIOMFAC and consequently there should be distinct model curves in Fig. 5b and UNIFAC structure formulas in Table S0 of the SI. Although, this reviewer agrees that the differences between UNIFAC predictions for such similar dicarboxylic acids are likely small.

3. The UNIFAC group-contribution method also offers another way to account for proximity effects by neighboring subgroups in organic molecules: specific subgroups can be assigned to larger sections of a molecular structure and that has been proposed for modified UNIFAC parameterisations in the case of amino acids. For example, Gupta and Heidemann (1990) introduced a specific “proline” UNIFAC subgroup (including a subset of determined interaction parameters for aqueous solutions of amino acids). Kuramochi et al. (1997) introduced a series of new functional groups and determined UNIFAC parameters for the description of most amino acids, including histidine, for a modified UNIFAC version based on “Larsen’s UNIFAC”. Thus, statements like (page 10, line 15): “*UNIFAC predictions cannot be performed for all amino acids examined here; in particular, the ring structures found in proline and histidine, cannot be represented as subgroups in the current version of UNIFAC.*” are not generally correct – the UNIFAC parameterisation by Kuramochi et al. covers most amino acids studied experimentally in this work. However, it is correct that those “specialized” UNIFAC modifications are not implemented in the online versions of AIOMFAC and UNIFAC in E-AIM (see point (1) above), so they are not conveniently available for calculations, which is likely what is meant by the authors’ statement. Such general statements should therefore be revised accordingly and the work by Gupta and Heidemann (1990), Kuramochi et al. (1997) and others mentioned. Consider also that parameter sets that were determined for different UNIFAC model versions are typically not compatible and the use of specific subgroups with only a limited set of interaction parameters determined, e.g. for aqueous mixtures of amino acid solutions only, disqualifies the applicability of such models for predictions of complex, multi-component and multi-functional mixtures of interest in atmospheric aerosol chemistry (as discussed in Section 5.4 of Zuend et al., 2011).

### Specific comments and technical corrections

- Abstract, first sentence and page 4, line 9: “Hygroscopic data” should be “Hygroscopicity data” (the data itself is likely not hygroscopic).
- P3, line 7: correct spelling of “Köhler”
- P3, l. 11 – 13: “Values are typically determined from sub-saturated hygroscopic growth measurements and reported at the highest accessible RH (Pajunoja et al., 2015). The value of  $\kappa$  can also be inferred from measurements of the critical supersaturation required for CCN activation, a measurement in a super-saturated regime (Carrico et al., 2008).” It would be appropriate to state that  $\kappa$  values determined at different RH and, to a lesser extent temperature, can vary substantially, especially when comparing  $\kappa$  determined from CCN activation data at water super-saturation compared to sub-saturation conditions, as, e.g., discussed by Hodas et al. (2016) and references mentioned therein.
- P3, l. 33: correct “(approaching [values] very close to 1)”
- P4, l. 25: clarify the accuracy statement: “with a greater accuracy ( $< \pm 0.2$  % at water activities  $> 0.8$ ...” do you mean  $< \pm 0.2$  % error in water activity or in hygroscopic growth factor or MFS?

- P6, l. 5: “with most solutes instead”, better: “with most pure organic compounds instead” since this is not about a solution but about the pure components.
- P6, title 2.3: Replace “hygroscopic” by hygroscopicity
- P7, l. 2: “In this equation, the gradient in water partial pressure is the difference between the RH and  $a_w$ , the instantaneous water activity at the droplet surface.” First, given the evaporation setup with an RH profile dependent on the distance from the droplet, it needs to be stated which RH (and measured where) is meant, i.e. is it the RH at the droplet surface or the RH (sufficiently) far away from the droplet. Second, the difference (RH -  $a_w$ ) or rather saturation ratio  $S - a_w$  (as in Rovelli et al., 2016) alone does not constitute a “gradient”. Also, since the component subscript “i” in Eq. (5) denotes water (i.e. subscript “w” as in  $a_w$ ), it would seem better to use “w” instead of “i”.
- P7, l. 9: “is the latent heat of vaporization”; add “of water” at temperature  $T_\infty$  (?).
- P8, l. 10: “using Peng corrections” the meaning of this is unclear. Also, as detailed above, the UNIFAC models likely used by the authors actually include further modifications in terms of the used parameter sets and/or subgroup assignments.
- P8, l. 20: “In addition, the UNIFAC predictions become less accurate as the added substituent becomes larger, a consequence of representing all CH, CH<sub>2</sub>, and CH<sub>3</sub> substituents by CH<sub>n</sub> (Zuend et al., 2008).” There seems to be a misunderstanding about the UNIFAC (AIOMFAC) way of group-contribution calculations, see the general comment above. Only group-group interactions in the residual UNIFAC expressions are common for all CH<sub>n</sub> subgroups (with n = 0,1,2,3), but the volume and surface area terms (combinatorial part) are not. This is the case in all variants of UNIFAC.
- P9, l. 20 and l. 17: There are actually more than two distinct UNIFAC group formulas for the different C<sub>7</sub>-dicarboxylic acids, see the general comment above. Also, given that the UNIFAC (AIOMFAC) model predictions of water activity show a deviation from the CK-EDB data for the straight-chain pimelic acid, the model-measurement deviations shown in Fig. 5b are expected and at least consistent in that sense. Related to the statement on line 17, the observed similarity in hygroscopicity of the different C<sub>7</sub>-dicarboxylic acids suggests that the degree of branching and/or lengths of alkyl substituents may not always play a substantial role, in particular above a water activity of 0.8. This seems to be a counter-example to the trends observed for the smaller dicarboxylic acids with alkyl substitutions (and a hint for a general underestimation of the hygroscopicity-contribution by the CH<sub>n</sub> groups as represented in UNIFAC/AIOMFAC).
- P10, l. 15: The sentence should be revised as certain nitrogen containing compounds are available in most UNIFAC models (including in AIOMFAC for organics + water systems) since the parameter set by Hansen et al. (1991) includes amine, amid, nitro, nitrile and pyridine groups and some version include organonitrate groups (Compernelle et al., 2009; Zuend and Seinfeld, 2012) and proline and histidine groups Kuramochi et al. (1997).
- P10, l. 18: clarify which model for activity coefficients was used in E-AIM for the amino acids.
- P10, l. 22: “except for L-valine”; According to Fig. 8, L-Threonine behaves similar to L-valine even though it contains a hydroxyl group instead of a methyl group. So it seems that L-valine is not an exception or not the only one. Also, the UNIFAC prediction for glycine is missing in Fig. 8a.

- P10, l. 30: “is fitted to molality experimental data”; molality of what? The last part of that sentence needs to be rephrased as well.
- P11, l. 13: Statement needs to be revised given the above clarification about specific UNIFAC parameterisations for aqueous solutions of amino acids.
- P11, l. 15: “This is a consequence of the current reliance of the UNIFAC parameterisation on the data of Chan et al. (2005).” This statement is incorrect, because the UNIFAC models used by the authors do in fact not contain the modified parameters by Chan et al. (2005); rather, they are based on Hansen et al. (1991) and Peng et al. (2001) parameters for the amino acids. Also, as is clearly shown in Chan et al. (2005), their modified UNIFAC parameterisation yields similar results to the Peng et al. version in many cases and the Peng et al. parameterisation is in reasonable agreement with their own experimental data (e.g. for threonine). Therefore, the discrepancies between the new CK-EDB data and the UNIFAC model curves shown indicate clear discrepancies among different experimental data sets, as is discussed by the authors in the first paragraph of page 11.
- P11, l. 27: “Molecular structures presented in Fig. 10 are the open chain form, which must be used during modelling using UNIFAC.”; Why “must”? AIOMFAC also allows you to use the cyclic structure of sugars in aqueous solution, e.g. glucopyranose instead of glucose, if desired.
- P12, l. 10: and Fig. 11 & 12: replace the compound class labelled “organic acids” by a more appropriate label, e.g. “dicarboxylic acids”, since amino acids are also organic acids but not part of that class.
- P12, l. 32: Statement is incorrect, see comment to P11, l. 15.
- P13, first paragraph. With respect to the applicability of the determined component-kappa values from binary data with a simple mixing rule for a complex mixture’s total hygroscopicity parameter kappa, I suggest the authors consider in this section that it remains rather uncertain whether the kappa values determined based on binary water + amino acid data apply in multicomponent mixtures of relevance for atmospheric aerosol. This is because the substantial hygroscopicity exhibited by many of the amino acids, due to their zwitterionic nature in aqueous solution, may be affected substantially by the presence of inorganic acids and dissolved salts in aerosol mixtures, altering the partial water uptake contribution by the amino acids in a non-linear manner. This may motivate further experimental investigations for organic-inorganic mixtures with the CK-EDB and other setups.
- Table 1: State the temperature (range) for the measurements. Also the caption text and table header concerning SMILES needs revision.
- Fig. 1: Lower panel, at around 0.9 water activity, the red triangles-up and black triangles-down symbols suggest a larger scatter in experimental data than the binned data and error bars account for. It is unclear why if it is assumed that the different drying rates have similar measurement uncertainty? A brief discussion may be useful.
- Fig. 2: state the UNIFAC parameterisation used, if AIOMFAC-web was used, then stating that would be sufficiently specific.
- Fig. 6: the y-axis label “ $n(\text{water})/n(\text{solute})$ ” would be better written as in Fig. 7 or perhaps in abbreviated form, such as  $n_w/n_s$ .

- Figs. 8 and 9: The UNIFAC (Peng et al. parameterisation) model curve for Glycine is missing.
- Fig. 9: Comparing this figure to Fig. 1 of Chan et al. (2005), it is clear that many experimental data points from Na et al. are missing, as well as bulk data by Kuramochi et al. (1997) to higher MFS/lower  $a_w$  than shown and data by Ninni and Mereilles (2001) in Fig. 9b. Including all these measurements in Fig. 9 will provide a better comparison for the discussion concerning the substantial discrepancies found among the experimental data sets and in comparison to model predictions.
- Supplementary Information: It would be useful to briefly state at the end of the main text what information is provided in the SI.
- SI, Table S0: the page numbers for different systems are listed, but the pages in the SI were not numbered. Also, the AIOMFAC subgroups stated for the dicarboxylic acids with  $\text{CH}_n$  groups should be revised, see general comment. The “ $\text{CH}_n(\text{OH})$ ” groups stated for citric acid, tartaric acid and other compounds should be stated with OH preferentially in superscript (e.g.  $\text{CH}_2^{\text{[OH]}}$  for a  $\text{CH}_2$  subgroup bonded to an OH group, which is specified separately) to avoid confusion about the number of OH groups present in the molecular structure (see also Table 3 of Zuend et al., 2011).
- SI, Fig. S8.1: Check the caption text and symbols in the figure. I do not see any coloured curves for data at different temperatures stated in the caption.
- SI, S26 and S27: For aqueous PEG mixtures, much improved interaction parameters have been determined for a PEG-specific version of AIOMFAC, but these are not yet included in AIOMFAC-web (see also Hodas et al., 2016).

## References

- Compernelle, S., Ceulemans, K., and Müller, J.-F.: Influence of non-ideality on condensation to aerosol, *Atmos. Chem. Phys.*, 9, 1325-1337, doi:10.5194/acp-9-1325-2009, 2009.
- Davies, J. F., Haddrell, A. E., Rickards, A. M. J., and Reid, J. P.: Simultaneous Analysis of the Equilibrium Hygroscopicity and Water Transport Kinetics of Liquid Aerosol, *Anal. Chem.*, 85, 5819-5826, doi:10.1012/ac4005502, 2013.
- Fredenslund, A., Jones, R. L., and Prausnitz, J. M.: Group-contribution estimation of activity coefficients in nonideal liquid mixtures, *AIChE Journal*, 21, 1086-1099, doi:10.1002/aic.690210607, 1975.
- Gupta, R. B. and Heidemann, R. A.: Solubility models for amino acids and antibiotics, *AIChE Journal*, 36, 333-341, 1990.
- Hansen, H. K., Rasmussen, P., Fredenslund, A., Schiller, M., and Gmehling, J.: Vapor-liquid-equilibria by UNIFAC group contribution. 5. Revision and extension, *Ind. Eng. Chem. Res.*, 30, 2352–2355, 1991.
- Hodas, N., Zuend, A., Schilling, K., Berkemeier, T., Shiraiwa, M., Flagan, R. C., and Seinfeld, J. H.: Discontinuities in hygroscopic growth below and above water saturation for laboratory surrogates of oligomers in organic atmospheric aerosols, *Atmos. Chem. Phys.*, 16, 12767-12792, doi:10.5194/acp-16-12767-2016, 2016.

- Koop, T., Bookhold, J., Shiraiwa, M., and Poschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, *Phys. Chem. Chem. Phys.*, 13, 19238–19255, doi:10.1039/c1cp22617g, 2011.
- Kuramochi, H., Noritomi, H., Hoshino, D., and Nagahama, K.: Representation of activity coefficients of fundamental biochemicals in water by the UNIFAC model, *Fluid phase equilibria*, 130, 117-132, 1997.
- Marculli, C. and Peter, T.: Water activity in polyol/water systems: new UNIFAC parameterization, *Atmos. Chem. Phys.*, 5, 1545–1555, doi:10.5194/acp-5-1545-2005, 2005.
- Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions, *Environ. Sci. Technol.*, 35, 4495–4501, doi:10.1021/es0107531, 2001.
- Rovelli, G., Miles, R. E. H., Reid, J. P., and Clegg, S. L.: Accurate Measurements of Aerosol Hygroscopic Growth over a Wide Range in Relative Humidity, *J. Phys. Chem. A*, 120, 4376–4388, doi:10.1021/acs.jpca.6b04194, 2016.
- Zuend, A. and Seinfeld, J. H.: Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation, *Atmos. Chem. Phys.*, 12, 3857-3882, doi:10.5194/acp-12-3857-2012, 2012.
- Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O., McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups, *Atmos. Chem. Phys.*, 11, 9155–9206, doi:10.5194/acp-11-9155-2011, 2011.