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Atmospheric Chemistry and Physics Discussions

Interactive comment on “SIMPOL.1: A simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds” *by* J. F. Pankow and W. E. Asher

Anonymous Referee #1

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The authors present a group contribution method for estimating the liquid phase vapour pressures and vaporization enthalpies of organic compounds. This kind of data is crucially needed to investigate e.g. the role of atmospheric organics in secondary aerosol particle formation and growth. The method is simple and easy to use and is based on a large number of reference data points. The paper is well written and suited for publication in ACP. However, there are some issues that I think the authors should address more carefully in their article, particularly in regards of the possible atmospheric applications of the method:

1) Even though the number of compounds used in the basis and test sets is large, very few of them have vapour pressures that are low enough to (at least as pure compounds) partition in the condensed phase in the atmosphere. The lowest data points are at 1e-8 atm, whereas I would think that the condensable vapours in the atmosphere might have vapour pressures as low as 1e-14 atm. The authors should add some more discussion on this - whether the method is likely to work well also at these very small vapour pessures. I understand that there is very little data available, but I think this is very important point, particularly taken into account the increased uncertainty with decreasing vapour pressures shown in Fig. 12.

2) Also, from an atmospheric point of view it seems a little bit odd that most of the results (on e.g. the success of the prediction method) shown in the figures has been calculated at 333.15 K. I understand that this is about at the middle of the temperature range used in the optimization, but it is problematic, since the atmospheric temperatures correspond to the lower end of the studied range (similarly with the vapour pressures). Even though the increase in the uncertainty with decreasing temperature is demonstrated in Figs. 10 and 11, some more discussion on this would be appropriate, e.g. whether the only reason for the uncertainties is the ’experimental difficulties’.

3) On p. 11853 a comparison is made between literature data on measured vapour pressure of adipic acid and the SIMPOL.1 prediction. The solid state measurement of Tao and McMurry (1989) has been used together with the fusion enthalpy to get an estimate for the liquid phase vapour pressure. Are the authors aware of recent studies by Cappa et al. (2007) and Koponen et al. (2007)? The previous presents new measurements on the solid state vapour pressures of C4-C12 dicarboxylic acids and the latter reports vapour pressure values for subcooled liquid phase C3-C5 diacids. The results of these studies agree, i.e. using the fusion enthalpy, the solid phase values measured by Cappa et al. (2007) yield similar values for C3-C5 acids as observed by Koponen et al. (2007), so at least these studies seem consistent. However, the solid state values measured by Cappa et al. (2007) are about an order of magnitude lower

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than the values measured by Tao and McMurry (1989). Therefore, in the case of adipic acid, the results by Cappa et al. (2007) would yield a liquid phase vapour pressure of the order of 1e-9 atm, which again is an order of magnitude lower than predicted with SIMPOL. If a similar comparison is made with glutaric acid (C5 dicarboxylic acid), where measurement data on the liquid phase vapour pressure is available (Koponen et al., 2007), SIMPOL.1 predicts vapour pressure of the order of 1e-7 atm, whereas the values reported by Koponen et al. (2007) are again about an order of magnitude lower. Could the authors comment of this?

Minor comments:

3) It would be nice if the authors could comment shortly how the basis and test sets have been chosen

4) What about multicomponent mixtures? How relevant in the atmosphere do the authors think that these vapour pressures are?

5) I am not sure whether it is necessary to show all Eqs. 4-6 and 10-18. Even though it is on one hand nice to see all the steps, on the other hand they are quite straightforward and I think that it might be enough just to show the starting point and the result.

References:

Cappa, C.D., Lovejoy, E.R. and Ravishankara, A.R., J. Phys. Chem. A 2007, 111, 3099-3109.

Koponen I.K., Riipinen, I., Hienola, A., Kulmala, M. and Bilde, M., Environ. Sci. Technol. 2007, 41, 3926-3933.

Tao, Y. and McMurry, P.H. Environ. Sci. Technol., 1989, 23, 1519.

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