Interactive comment on “A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics” by N. M. Donahue et al.

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In the present paper the authors present a highly simplified and potentially useful treatment of non-ideality which is wrapped up into an effective volatility basis set. The authors then propose this simplified model can be used as a diagnostic tool. It would be useful if the authors could clarify their treatment of activity coefficients so that their work can be repeated and compared with existing treatments. It would appear, based on figures 2 and 9 that only positive deviations from non-ideality are considered/predicted across the entire C*, O:C ratio composition space. Specifically, activity coefficients are always shown to be greater than 1, suggesting non-ideality always increases the volatility of all condensates to varying degrees. Isn’t this missing half of the story? i.e., negative deviations from non-ideality? There are numerous sources in the literature
which present both positive and negative deviations from [non] ideality [e.g. Vladimir A. Durov and Oleg G. Tereshin, Fluid Phase Equilibria, Volume 210, Issue 1, 30 July 2003, Pages 91-104]. Since the direct equations for the activity coefficient are not given it is difficult to formulate a more detailed comment.

The equations were presented, but we did not combine the penultimate equations to give $\gamma_{i,s}$ itself, which we now do explicitly in Eq. 13. It is certainly true that positive and negative excursions from ideality occur, and we are making the simplifying assumption that the dominant behavior for the great majority of atmospheric organics is positive (positive activity coefficients and thus increased partial pressures.

Our greatest interest is to be able to predict or explain phase separation for condensed-phase organics, which is associated with positive deviations from ideality.

Similarly, since it is claimed that the parameters required for predictive purposes can be constrained from ambient data, essentially fitting the model to the system which you would like to follow, does this not already implicitly include the effect of nonideality? It would be useful if the authors could clarify this point.

We have argued something like this in the past. When we invert SOA formation data from $\alpha$-pinene + O$_3$ for example we obtain a volatility distribution of the products, and this empirical distribution does indeed contain $\gamma$ (i.e., we are inverting for $C^*$ and not $C^o$). The challenge is extending to very different compositions than those encountered during a given experiment. For example, if the question is whether POA will act as a good SOA seed, and what the quantitative effect will be on SOA yields (or even whether that question is well posed), we need to be able to extrapolate. That requires a model for activity coefficients, and that is what we seek to address in the second half of this paper.

It is probable that, if this framework proves to be useful, we will need to tune the non-ideality term based on experimental results. It is empirical after all. However, there is a difference between inserting totally *ad hoc* tuners into an empirical expression and
basing the tuners on a theoretical foundation. We are attempting to take the second pathway.

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