

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

Anonymous Referee #2

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I did not manage to get all the way through this ms. The work that is presented here is either simple, but rendered complex and hard to grasp by the authors' obscure description, or it is actually complex and made more so. It would be hard for anyone, except the authors, to make full use of the results valuable though they may be.

The abstract. This ought to offer a self-contained description of the results, that can be understood without reference to other papers or to other parts of the ms. (1) C_0 is known well enough by those familiar with the authors' work, but for those who are not it is insufficiently defined by only the words "saturation concentration". (2) The expression "mean field approximation" adds nothing here, and I'm not clear what the authors intend. (3) "we show that a linear structure activity relation (SAR)... is directly tied to ideal solution .. behaviour." I am almost certain that this sentence is meaningless.

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(4) "...slightly non-linear SAR emerge from off-diagonal (carbon-oxygen) interaction elements." Again, impossible to get any significant meaning from this. "Off-diagonal" is a piece of jargon related to the authors' use of a matrix for interactions later in the ms. (5) I doubt very much that an approximate treatment such as that being proposed here would be able to predict phase separation with any accuracy. (6) OA not defined.

Introduction (1) $\{\mu\text{m}\}^3$ is not a unit, but $\{\mu\text{m}\}^3 \text{ m}^{-3}$ is (space before "m"). This error is common. (2) An annoyance: don't invent your own terminology where one already exists. Writing $\log_{10}(C^*)$ as $/C^*$ is unnecessary and potentially confusing for reasons that are obvious. (3) The complexity of the organic portion of the aerosol, and our partial knowledge of its composition, is a difficulty that has helped determine the approach the authors (and others) have taken. However, it is not "the challenge we seek to confront". (4) "SAR" is not an accurate expression as the authors' approach does not seem to involve any explicit structural information. (5) nC, nH etc not defined. These would normally mean numbers of moles, but appear to mean numbers of atoms. (6) A contradiction: "a generalised prediction of activity coefficients for individual organics will fall out naturally and self-consistently from this formulation" is followed a few sentences later by: "We do not seek to accurately predict the phase partitioning of specific molecules. ...we seek to understand the bulk behaviour of OA." (7) More idiosyncratic jargon: "rich behaviour". (8) "...carbon-oxygen cross interaction (the hydrophobicity)". The word hydrophobic refers specifically to water whereas the interaction is general.

Theory

I have two general objections: first, the authors are attempting to develop an activity coefficient scheme within a system of mass-based concentrations. I won't say this is impossible, but it is a fundamental difficulty that is not explained. Consequently, I have to wonder whether the authors' exposition that includes "pseudo-Arrhenius", "Boltzmann term" and a division by the gas constant to "scale" energies that are used in expressions with quantities that have units of $\mu\text{g m}^{-3}$, is correct - or whether the use

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of these terms just lends the text an air of spurious thermodynamic respectability.

Second, there are very many activity models in existence, and of varying degrees of complexity and suitability for application to organic aerosols in general and to the problem the authors are trying to solve in particular. Beyond passing reference to UNIFAC there is no mention of any of them. I suspect that it would have been possible to adapt some of these to the present problem and to do so in a way much more easy to understand - and much more clearly related to existing theory and thermodynamic principles - than what the authors have developed.

In the remaining parts of the theory section, before I completely lost track of what the author's were trying to do, I noted:

(1) In eq (7) the introduction of a matrix - do they just mean a summation of the different interactions?"

(2) $i \rightarrow A$. I don't think "i" tends to "A" at all.

(3) "We shall assume that ... with the fractions of A and B in the solvent." This assumption comes completely out of the blue, and is not explained.

(4) "In a recurring theme...". I have no idea what the authors are alluding to.

(5) "..the non-ideality of the off-diagonal element". Another unnecessary obscurity.

(6) "f" in many equations. This is a fraction, but whether mole or mass fraction I don't think is explained, though the authors appear to decide that the "appropriate" one is close to a volume fraction (end of section 3.3, and a long time after it is first introduced).

I did not get all the way through the theory section. In my opinion the authors are so deeply involved in the development of their theory that they have been unable to explain it clearly, simply, and methodically to potential users. There are too many leaps of faith, and too much obscure language and unclear writing for me to be convinced. There may be a good paper here, but it will require substantial re-writing to produce it.

There is one other point about presentation: papers should be written so that diagrams, and their description, should be understandable from a black and white printout. The authors make rather indiscriminate (and unnecessary) use of colour, and refer to colours explicitly in the text.

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