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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Technical note: Estimating aqueous solubilities and activity coefficients of mono- and α, ω-dicarboxylic acids using COSMO-RS-DARE" *by* Noora Hyttinen et al.

Anonymous Referee #2

Received and published: 26 June 2020

General comment

This paper employs the recently developed COSMO-RS-DARE model to estimate activity coefficients and solubilities of carboxylic acids in water. COSMO-RS-DARE is an extension of COSMOtherm that takes dimerization and aggregation in solution explicitly into account. This technical note concludes that COSMO-RS-DARE leads to better agreement with experimental data than COSMOtherm for the investigated mixtures.

Although this paper is submitted as a technical note, the technical description of COSMOtherm and its extension COSMO-RS-DARE is lacking a proper derivation and explanation. Also, the benefit of COSMO-RS-DARE compared with COSMOtherm re-

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Discussion paper

mains unclear. As it seems, the new method relies on experimentally determined activity coefficients to calculate dimerization equilibria. Therefore, the benefit of COSMO-RS-DARE in the absence of experimental data is unclear. It is not clear whether COSMO-RS-DARE just performs better in predicting solubilities because of an additional degree of freedom introduced through potential dimerizations or a more accurate description of the system.

Major revisions of the manuscript are required before this technical note can be considered for publication. The different COSMO versions need to be explained better and the discussion of the results needs to be improved.

Specific comments

Lines 20 – 22: Here, acidity is mentioned as highly relevant. But the approach used in this technical note totally neglects deprotonation of acids.

Line 25: activity data of carboxylic acid-water systems is abundant as exemplified by the studies mentioned just below this sentence and there are even more. Please revise this sentence.

Lines 65 – 66: the meaning of a pseudo-chemical potential should be explained.

Line 79: activity should be replaced by the activity coefficient in this equation.

Line 81: This equation should be derived or a reference should be given.

Line 96: How is the dielectric energy calculated or defined?

Line 96: The difference between the chemical potential and the pseudo chemical potential is not clearly made and not explained. Here, the same symbol is used to refer to the chemical potential that was used before for the pseudo chemical potential.

Line 100: Equation (11) needs to be explained better.

Line 112: The derivation of Eq. (14) remains obscure. The equation rather seems to

be a definition of the effective equilibrium constant than a derived equation.

Line 116: How is the surface of a molecule defined? Either explain here or give a reference.

Line 125: what is a property calculation?

Line 125: what is the screening charge density? A scheme might help to explain it.

Line 128 – 129: Why are interaction sites of molecule B not treated the same way?

Line 133 – 134: Why is the entropic parameter kept zero? This seems arbitrary. Please justify.

Lines 150 – 158: This section is difficult to understand. A scheme might help.

Lines 225 – 227: This finding questions the benefit of the method.

Lines 234: I would not refer to dicarboxylic acids as being of low aqueous solubility. Some dicarboxylic acids have a high solubility. Moreover, data well into the supersaturated range is available (e.g. in Soonsin et al., 2010). This sentence needs to be revised accordingly.

Line 247: Figs S2 and S3 should be moved to the main manuscript.

Line 255: Fig. S4 should be moved to the main manuscript.

Line 264: The logarithmic plot is not very informative. Rather show the figures from the SI here.

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