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Interactive comment on "Henry's law constants of polyols" *by* S. Compernolle and J.-F. Müller

Anonymous Referee #2

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Reviewer

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Interactive Comment on "Henry's law constants of polyols" by S. Compernolle and J.-F. Muller

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General Comments

The authors report the calculation of Henry's law constants (HLC) for several polyols from literature data for water activity and vapour pressure and calculated/ estimated data for infinite dilution activity coefficients (IDACs), sublimation vapour pressures and activity coefficient ratios. These HLC values and those from a previous work are used to assess the partitioning of polyols, diacids and hydroxyacids into aqueous aerosol. The paper would be improved by a more detailed description of how exactly the authors did their calculations and more analysis of the effect of errors in their input values on the HLC values they calculate. This reviewer recommends that this paper is published in Atmospheric Chemistry and Physics after the following issues have been resolved.

Specific Comments

Introduction:-In their previous paper (Compernolle and Muller 2014) the authors provide an excellent critique of the available 'experimental' HLC values for diacids and hydroxyl polyacids from the literature. Although the data for these polyols is much

more limited than that for the polyacids, it would be a useful addition to the introduction if the authors could summarise and critique the literature data for HLC values for polyols in this paper in a similar way.

p. 13531-line 6:- References needed for E-AIM

p. 13531-Eq. 2:- what is the significance of the superscript 'px'? What is its meaning?

p. 13531-line 23:- Might be helpful to remind the reader C_w=55.5 Moles/Litre.

p. 13532- Eq 5-7:- A reference for this use of the Van't Hoff equation is required.

p. 13532-Eq 5. An 'R' is missing from in front of the derivative.

p. 13532-Eq 8. A reference is required for the derivation of this equation?

p. 13533-Eq 10-12. A reference is required for the derivation of these equations.

p. 13534 line 1:- Methods to estimate activity coefficients considerably pre-date the references quoted here. The original paper defining UNIFAC (Fredenslund et al. 1975) should be included in this set of references.

p. 13534-Section 3.1:- lines 3 to end of page:- The authors need to clarify how exactly they derived their values for IDAC and the activity coefficient ratio as discussed in

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Section 3.3. In its present form this section is very confusing.

Eq. 13 is an integral form of the Gibbs-Duhem relationship which can provide an IDAC for the solute. Did the authors use Eq. 13 to get the IDAC values for any of their compounds (if the methods given in Appendix A in Compernolle and Muller 2014 were followed then probably not)? Activity coefficient expressions such as Margules, Van Laar, Wilson, or UNIQUAC obey the Gibbs-Duhem relationship (ie. Eq 13) and, once the relevant parameters have been fitted to the data, the IDAC value can be obtained directly. Is there an advantage to using Eq 13 to get the IDAC values rather than fitting the available a_w data to (say) the Margules equation and obtaining the IDAC values from the Margules equation directly? Do the authors combine an activity coefficient expression with Eq. 13 in some way to get the IDAC values? In which case they should explain in more detail how they do this. If the authors do not use Eq. 13 to calculate IDAC values then perhaps it should be removed to avoid confusion. Either way the authors should make it much clearer how they calculated their IDAC values. If Eq. 13 is retained then Mansoori 1980 should be quoted as a reference (as this provides the derivation) and the authors should provide an explanation of what 't' is.

If an activity coefficient expression was used to calculate the IDAC values then which equation was used for each compound should be provided either in this section or in Table 1. Also Table 1 should include some information about the composition range of the data that was fitting to the activity coefficient expression.

Also the use and validity of Eq. 14 is unclear. Do the authors have a reference or any other evidence that this equation is valid? The whole point of using something like the Margules equation (or Eq. 13) is that the same equation (with the same fitted parameters) is used across the whole composition range to ensure that Gibbs-Duhem is obeyed. If the authors use one equation for part of the composition range and a

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different equation for the rest then Gibbs-Duhem will not be satisfied. However fitting one set of data to one equation and a second set to a different equation would be fine (using different Margules parameters which would give two different IDAC values- as seen in Table 1) so is Eq 14 really describing the method used by the authors to fit two or more sets of data for the same organic solute?

p. 13535 line 5-9:- Using two sets of data to get two different IDAC values for the smaller diols gives an idea of the sensitivity of the IDAC values to errors in the a_w data. However, as the authors correctly point out, as the IDAC values increase for the more hydrophobic diols the uncertainty will be larger and for some of these diols there is only one value for IDAC because there is a single set of a_w data. It might be suspected for (say) 1,7 heptane diol or 1,2 hexane diol, that any fitted parameters in an activity coefficient expression may be poorly constrained and consequently the IDAC values sensitive to small errors in a_w. Could the authors do a sensitivity analysis using one of the above compounds and applying- 1) a small random error (do the authors providing the experimental data quote an error for their a_w values?), and 2) a small systematic error to the a_w data to see what effect this has on the calculated IDAC value.

p. 13535 line 25 to p. 13536 line 10:- Equations 15-17 need a reference. Also it might help to make your nomenclature in these equations clearer if you state that ΔS_{sub} and ΔH_{sub} are weak functions of temperature.

p. 13537:- Discussion of the results for sublimation pressures.

p. 13537 lines 1-2:- The authors should provide some figures about the agreement for fusion data between different data sources (were they all within 5% of each other or 3% or 1%?).

The authors make a convincing case that the integrals involving the heat capacity integrals are important to the calculation of P^o_{Cr} but they have nothing to say about the effect of error in the heat capacity values and the $\Delta H/\Delta$ S values in Eq. 16 and 17 on the calculation of P^o_{Cr}. The authors should do a sensitivity calculation for some of the compounds in Table 2 (in particular for sorbitol or mannitol where the extrapolation is large) where the effect of (say) a 5% error (or if the data suggests a more representative estimate of the error use that) in heat capacity values and the $\Delta H/\Delta$ S values and its impact on P^o_{Cr} can be evaluated. From this the authors should be able to draw some conclusions about the relative importance of errors in these quantities and how this varies with the temperature difference (T_{meas}-T_{ref}).

The authors should include T_{fus} values in Table 2 and also, rather than a single point for T_{meas}, they should indicate the temperature range of the data which they have used to derive their ΔH_{sub} and ΔH_{vap} at T_{meas}.

p. 13537 line 21-22:- 'The high temperature P^o_L and P^o_{Cr} data of erythritol and pentaerythritol is comparable among the data sources...' this is too vague. In what way are these three sets of data comparable and if they are so similar why do they give different ΔH_{Vap} or ΔH_{Sub} and different estimates for P^o_{Cr} at 298.15K? Doesn't this highlight one of the difficulties with this method (as defined by equations 15-17) of deriving sublimation pressures at 298.15K from high temperature vapour pressure data. The high temperature data needs to be very accurate and over a substantial temperature range to provide an accurate slope of the vapour (or sublimation) pressure. The authors should discuss the limitations and advantages of their method against alternative methods for calculating values for P^o_{Cr}. For example it is known that for some vapour pressure estimation methods that require normal boiling point (T_b) as an input (eg. Nannoolal et al. 2008) the vapour pressure correlation is relatively accurate and most of the error (for low volatility compounds) comes from the estimation of T_b.

Hence an alternative method to obtain P^o_{Cr} would be to use one of the standard vapour pressure estimation methods; fix the boiling point to give the experimental vapour pressure or sublimation pressure at T_{meas}; and estimate the subcooled liquid vapour pressure at 298.15K which can then be converted to the crystal sublimation pressure using the equation for the ratio of the solid/supercooled liquid fugacities (Prausnitz et al 1986), with the simplification that the gas phase is ideal and T_{fus} is a good approximation to the triple point temperature). This is the same equation as Eq. 1 in Compernolle et al., 2011.

p. 13538:- Section 3.3:- Similar issues to those raised in Section 3.1. Do the authors need to quote Eq. 18? Was it used to calculate the ratio of the activity coefficients? If not should it be removed it to avoid confusion to the reader? From figure 1 and the text in this section it is clear that the a_w data was correlated using the Margules equation. The form of the Margules equation should be provided, either in this section, or in Section 3.1. If Eq. 18 is to be retained can the derivation of Eq. 18 from Eq. 10 in Compernolle and Muller 2014 be provided (perhaps in an Appendix).

The authors need to comment on the impact of likely errors in their input data on the activity coefficient ratio. How sensitive is the activity coefficient ratio to errors in the solubility limit? How reliable are the solubility limits provided with the a_w data? Would small errors in the a_w data have a significant impact upon the calculated activity coefficient ratio?

p. 13538 line16-17:- 'For adonitol and arabinitol ∴... the simple but successful one parameter Margules fittings of Chirife et al.' This is a bit subjective (on what basis is it successful?). Can the authors please delete 'simple but successful'.

p. 13538 line19 '...but reasonable assumptions [for the activity coefficient ratio] could be made.' This demands more explanation, which you provide in Table 3, so suggest you insert '(see Table 3)' after 'made'.

p. 13539 line1:- The first line should read "Using Eqs. (4), (5), (8) and (9)...?

p. 13540 Eq. 20:- need a reference for the derivation of this equation.

p. 13540 line 10:- need a reference for the range of k* in clouds. Also for the calculation of k* for clouds and aerosol- what temperature is used?

p. 13541 Eq. 21/22:- Need references for the derivation of these equations (or provide their derivation in an Appendix). Also the form of Eq 21 should be made clearer by putting brackets around $f_{p,s}/(1-f_{p,s})$.

p. 13542 line9-10:- What is the range of X_{AS} used and what were the corresponding RH values?

p. 13542 line 26-28:- Sentence beginning:- 'Glycerol...' needs to be reworded... Suggest:- 'At RH=90% glycerol, with three hydroxyl groups, is 95% in the gas phase while sorbitol, with six hydroxyl groups, is still 50% in the particulate phase at RH=44%.' The authors should comment that this may be due to glycerol being much more volatile than sorbitol.

p. 13545:- Section 6.1:- in this section the authors discuss some of the uncertainties in their HLC values. However they really need to have discussed in the earlier part of

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the work the expected uncertainties in key inputs to HLC values such as solid state pressures and IDAC values to make this meaningful. Once they have provided some information on the sources and magnitude of likely errors for their $P_C^o r$ values and IDAC then the authors should be able to comment authoritatively on the impact on their HLC of different sources of error for different compounds. In its present form without the error estimates to back up the statements in this section are quite devoid of meaning.

Tables:-

The authors should provide the chemical structures for the compounds in Tables 2 and 3.

Technical Corrections

p. 13532-line15:- insert 'solute' after 'liquid' to improve clarity.

p. 13533-line 2:- The sentence should read 'In the case that the solubility is small. . .'

p. 13536 line 2 and line 6:- The authors might consider using 'temperature correction' rather than 'transformation' to improve clarity.

p. 13538 line 15:- suggest 'underestimates γ_w of these polyol/water mixtures.'

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p. 13541 line 12:- to improve clarity insert 'polyol' so that it reads '...the amount of polyol solute is infinitesimally small.'

References

Compernolle, S., Ceulemans, K., and Muller, J.-F.:- EVAPORATION: a new vapour pressure estimation method for organic molecules including non-additivity and intramolecular interactions, Atmos. Chem. Phys. 11, 9431-9450(2011)

Fredenslund, A., Jones, L. J., and Prausnitz, J. M.: Group-Contribution Estimation of Activity Coefficients in nonideal liquid mixtures, AIChE Journal, 21, 1086-1099(1975).

Mansoori, G. A.: Classical thermodynamic basis of activity coefficients: predictive and consistency rules for binary and ternary mixtures based on the relation between excess Gibbs free energy of (c)- and (c-l)-component mixtures, Fluid Phase Equilib., 4,197-209, 1980.

Prausnitz, J. M., Litchenthaler, L. J., and de Azevedo, E. M. : Molecular Thermodynamics of Fluid-Phase Equilibria, 2nd edition, Prentice Hall, NJ, USA, 1986, Section 9.2