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Atmospheric Measurement Techniques Discussions

Interactive comment on "A reference data set for validating vapor pressure measurement techniques: Homologous series of polyethylene glycols" *by* Ulrich K. Krieger et al.

Anonymous Referee #2

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This is a well-written paper focusing on the measurement, with well-characterized uncertainty, of the vapor pressures of a homologous series of 6 polyethylene glycols. The paper provides a useful dataset for future volatility measurement studies but also draws a number of important conclusions about the conditions under which these studies should be performed. The combination of measurement techniques and the wide range of vapor pressures covered are strengths of the work. A couple of aspects of the study and the presentation of some results could be further improved. These are discussed below. I recommend publication after these issues are addressed.

(1) Extrapolation from higher temperatures

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Discussion paper

The first conclusion for the paper is that at least for the compounds studied extrapolation from higher temperatures can be used instead of the challenging measurements at the lower temperatures. However, the authors miss the opportunity of providing some additional guidance given the availability of data from other studies. Could one obtain accurate estimates for PEG3 extrapolating from the 400-550 K range to room temperature? How about PEG4? Some additional analysis without using the new data would be helpful.

(2) Change in evaporation enthalpy with temperature

One of the issues (related to the previous comments) that the authors avoid discussing in any detail is the change in evaporation enthalpy with temperature. This change depends on the difference of the heat capacities of the liquid and vapor and of course the temperature change. Reasonable estimates of this effect can be obtained. How important are these effects for the 260-550 K temperature range and the compounds discussed here? Could these effects explain the tendency of the linear regressions used here to exceed the measured values in a number of cases?

(3) Measurements at higher relative humidity

It is not quite clear which measurements were performed at higher RH and how they were analyzed. Figure 1 should be the key here, but it is too early in the manuscript and is not well connected to the corresponding results.

(4) Mass accommodation coefficient

How close to unity can the mass accommodation coefficients be based on this data set? More than 0.9, 0.5, 0.1, something else? This is a nice result of the study and a little extra analysis could be helpful.

(5) PEG8 melting point

The PEG8 melting point is quite close to some of the measurements in Fig. 9. Could this be one more factor contributing to the variability of these data points.

(6) Surface free energies

The authors measured the surface free energies in some of the systems but these measurements are not included in Table 2. Were these estimates compared to literature values for these compounds?

(7) Presentation of results

I do like the idea of having cut-outs of the figures but I was confused by the fact that these were different figures in different pages. It is probably better to combine Figures 2 and 3 into a two-part Figure 2, Figures 4 and 5 into a two-part Figure 3. This will also allow the addition of cut-outs of the rest of the figures and help the discussion of the results. It took me some effort to see the difference of a factor of 2 mentioned in the text.

It would also be helpful if the authors used filled color symbols to separate the measurements performed in the present work with those existing in the literature.

The use of large symbols together with the small uncertainties in Figure 11 result in confusion. It appears that there are different symbols in the first 4 cases.

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