

We thank reviewer 2 for the positive feedback and her/his thoughtful suggestions. Below, we answer the specific comments one by one, but start with question #2 as the answer to it provides the framework for answering question #1.

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?*

We thank the reviewer for raising this question. The enthalpy of evaporation is a function of temperature; the first question being how much this influences the values provided in Table 2 of the manuscript. Let us analyze the data of PEG3 following e.g. Chickos and Acree Jr. (2003). If the heat capacities of the liquid and gas phase are known, C_{pl} and C_{pg} , respectively, then the vaporization enthalpy, $\Delta H_{\text{vap}}(T^\ominus)$, at $T^\ominus = 298.15$ K can be related to the experimental measurements by using Eq. 1, generally referred to as Kirchhoff's equation.

$$\Delta H_{\text{vap}}(T^\ominus) = \Delta H_{\text{vap}}(\bar{T}) + \int_{T^\ominus}^{\bar{T}} (C_{pl} - C_{pg}) dT, \quad (1)$$

where \bar{T} refers to the mean temperature of all measurements, which is equal to 357 K for our PEG3 data when calculating the mean of the inverse temperature range covered by the data. If we estimate $(C_{pl} - C_{pg})$ by using the method suggested by Chickos and Acree Jr. (2003) (which should be accurate to about $\pm 30 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$):

$$(C_{pl} - C_{pg}) = (10.56 + 0.26C_{pl}), \quad (2)$$

it yields $101 \pm 30 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$ for the difference between heat capacity of the liquid and heat capacity of the gas phase, when we take the value for the heat capacities of the liquid phase, C_{pl} , from Stephens and Tamplin (1979). Using Eq. 1 with this average value for $(C_{pl} - C_{pg})$ yields an increase to the uncorrected enthalpy of vaporization of $6.0 \pm 1.8 \text{ kJ} \cdot \text{mol}^{-1}$ when using the temperature difference between mean temperature, \bar{T} , and 298.15 K. Therefore, the enthalpy at the mean temperature of the measurements obtained by the linear regression, which is $\Delta H_{\text{vap}}(\text{exp}, \bar{T}) = 78.3 \pm 0.7 \text{ kJ} \cdot \text{mol}^{-1}$, should be corrected to $\Delta H_{\text{vap}}^\ominus = 84.3 \pm 1.9 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K. This corresponds to a shift of 7.5 %, which is clearly non-negligible. The magnitude is somewhat smaller for the higher mass PEGs. In the revised manuscript we calculate the enthalpy for 298 K for all PEGs and will provide the additional data in an updated Table 2 as given below and correct the values plotted in Fig. 11 of the manuscript as shown in Fig. 1 and add a few sentences explaining how we calculated the correction.

To answer the question whether the temperature dependence of the enthalpy of evaporation can explain the deviations seen in the linear regression, we integrate the Clausius-Clapeyron equation, eq. (3) in a more general form, by including Kirchhoff's equation, eq. (1), in the same manner as above, namely assuming a constant, temperature independent, heat capacity difference

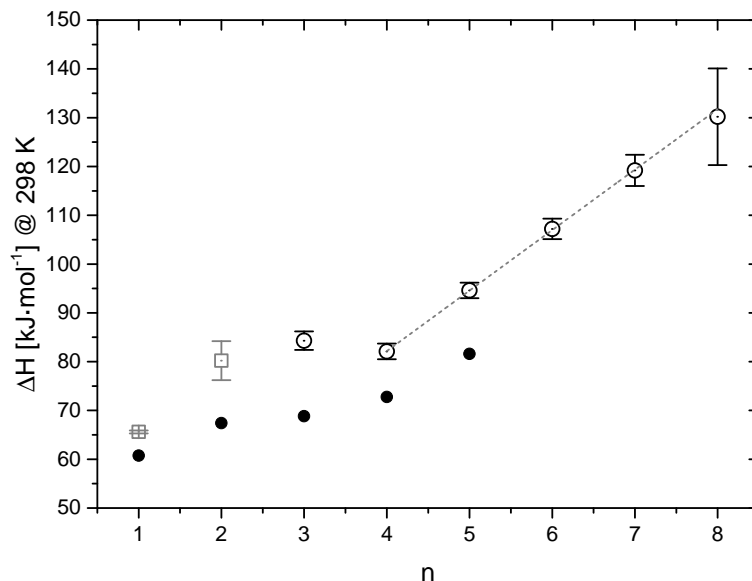


Figure 1. Enthalpies for all PEGs, open circles this study, open squares Chickos and Acree Jr. (2003). Filled circles: computational predictions from this study. Dashed line is a fit through the data of PEG4 to PEG8.

Table 1. Saturation vapor pressures at 298.15 K and enthalpies of vaporization of the polyethylene glycols measured in this study as well as estimated enthalpies of vaporization at 298.15 K, together with the results of the quantum chemistry calculations, In addition we provide experimental data from the literature for ethylene glycol and diethylene glycol.

| | n | p(exp) [Pa] | $\Delta H_{\text{vap}}(\text{exp}, \bar{T})$ [kJ · mol ⁻¹] | \bar{T} [K] | $\Delta H_{\text{vap}}(\text{exp}, 298 \text{ K})$ [kJ · mol ⁻¹] | p(calc) [Pa] | $\Delta H_{\text{vap}}(\text{calc}, 298 \text{ K})$ [kJ · mol ⁻¹] |
|----------------------|---|--|---|------------------|---|----------------------|--|
| triethylene glycol | 3 | $(6.68^{+1.10}_{-0.95}) \cdot 10^{-2}$ | 78.3±0.7 | 349 | 84.3±1.9 | $2.65 \cdot 10^0$ | 68.81 |
| tetraethylene glycol | 4 | $(1.69^{+0.11}_{-0.10}) \cdot 10^{-2}$ | 77.1±0.4 | 345 | 82.1±1.6 | $1.82 \cdot 10^{-1}$ | 72.78 |
| pentaethylene glycol | 5 | $(5.38^{+0.71}_{-0.63}) \cdot 10^{-4}$ | 90.6±1.1 | 339 | 94.6±1.6 | $2.10 \cdot 10^{-2}$ | 81.60 |
| hexaethylene glycol | 6 | $(3.15^{+0.58}_{-0.49}) \cdot 10^{-5}$ | 102.1±1.5 | 351 | 107.2±2.1 | – | – |
| heptaethylene glycol | 7 | $(1.38^{+0.47}_{-0.35}) \cdot 10^{-6}$ | 113.7±2.7 | 357 | 119.2±3.2 | – | – |
| octaethylene glycol | 8 | $(9.2^{+20.4}_{-6.4}) \cdot 10^{-8}$ | 124.2±9.7 | 363 | 130.2±9.9 | – | – |
| ethylene glycol | 1 | 11.7±0.6 ^a | – | – | 65.6±0.3 ^b | $3.98 \cdot 10^1$ | 60.75 |
| diethylene glycol | 2 | 0.6±0.03 ^a | 66.9±0.3 ^b | 420 | 80.2±4.0 ^b | $3.80 \cdot 10^0$ | 67.41 |

^a ?, ^b Chickos and Acree Jr. (2003)

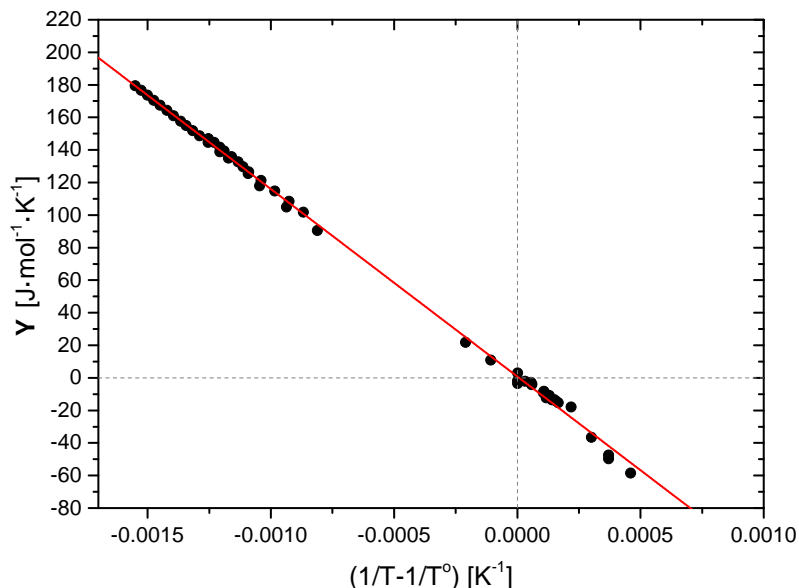


Figure 2. Ψ versus inverse temperature difference, $(\frac{1}{T} - \frac{1}{T^\ominus})$, filled circles: all data but Wise et al. (1950), red line: linear regression

between liquid and gas phase.

$$\frac{dp}{p} = \frac{\Delta H_{\text{vap}}(T)}{R} \frac{dT}{T^2}, \text{ with } \Delta H_{\text{vap}}(T) = \Delta H_{\text{vap}}(T^\ominus) - (C_{p_l} - C_{p_g})(T^\ominus - T) \quad (3)$$

Integration of eq. (3) leads to:

$$\ln \frac{p}{p^\ominus} = -\frac{\Delta H_{\text{vap}}(T^\ominus) - T^\ominus(C_{p_l} - C_{p_g})}{R} \left(\frac{1}{T} - \frac{1}{T^\ominus} \right) + \frac{(C_{p_l} - C_{p_g})}{R} \ln \left(\frac{T}{T^\ominus} \right). \quad (4)$$

- 5 If we now plot $\Psi := \left\{ R \ln \left(\frac{p}{p^\ominus} \right) - (C_{p_l} - C_{p_g}) \ln \frac{T}{T^\ominus} \right\}$ versus $1/T - 1/T^\ominus$, we expect a straight line with $\Psi(0) = 0$. In Fig. 2 we show such a plot for the PEG3 data.

Clearly, considering the temperature dependence of the enthalpy of evaporation helps to reconcile the high temperature data with those taken by us at roughly room temperatures. However, its effect close to 298 K is minimal by default, see eq. 4. In particular, it does not significantly reduce the differences between our individual measurements. Hence, we prefer to not
10 include this detailed discussion in the main part of the revised manuscript, but we will put it into an appendix.

However, we will use this approach to estimate the vapor pressures at 298.15 K from the literature data at high temperatures without taking our new data into account. This will answer question # 1 of the reviewer:

1) Extrapolation from higher temperatures. *The first conclusion for the paper is that at least for the compounds studied*

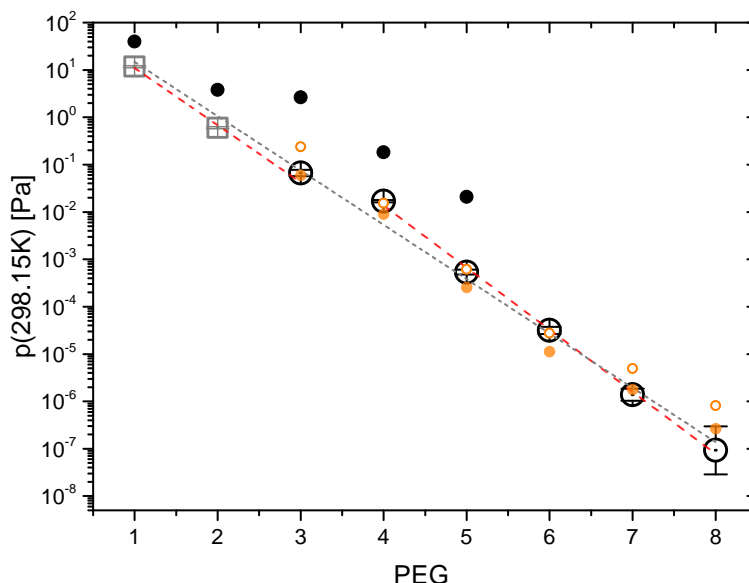


Figure 3. Saturation vapor pressure at 298.15 K plotted for all PEGs. Open black circles with error bars: results of this study. Filled orange circles: extrapolation of high temperature literature data to 298.15 K using an estimation of the temperature dependence of the enthalpy of evaporation as detailed in appendix B. Open orange circles: extrapolation of high temperature literature data to 298.15 K assuming a constant enthalpy of evaporation. Filled black circles: computational predictions from this study. Open squares with error bars: Ambrose and Hall (1981). Dashed gray line is a linear regression to all the experimental data, dashed red lines are separate linear regressions for $n=1$ to $n=3$ and $n=4$ to $n=8$.

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.

- 5 We have two options for this analysis now: first, assuming a temperature independent enthalpy of vaporization (shown as open orange circles in the revised figure of all vapor pressures, i.e. Fig. 3). Second, taking the difference in heat capacity between the two phases temperature independent, i.e. using eq. (4) (shown as filled orange circles in Fig. 3. Extrapolation using the high temperature data to room temperature taking into account the temperature dependence of the enthalpy of evaporation yields very consistent data with the new measurements: both agree within uncertainty estimates for PEG3, PEG7 and PEG8
- 10 and agree better than a factor of two for PEG4, PEG5 and PEG6. Taking a constant enthalpy of vaporization yields very good agreement for PEG4, PEG5 and PEG6, but substantial deviation - up to a factor of 10 - for PEG3, PEG7 and PEG8. We conclude that extrapolation to lower temperatures of high temperature data should take Kirchhoff's law into account.

We will add extrapolated values to Fig. 10 of the manuscript as shown in Fig. 3 here. Also, we will add the following paragraph to page 15 line 10 of the manuscript: Very satisfyingly, extrapolation of the high temperature literature data to 298.15 K incorporating the temperature dependence of the enthalpy of vaporization as detailed in Appendix B (orange filled circles in Fig. 3) yields values agreeing well within error with the newly derived saturation vapor pressures for PEG3, PEG7 and PEG8 of this study and agree better than within a factor of two for PEG4, PEG5 and PEG6. In contrast, using a constant enthalpy of vaporization for the extrapolation yields very good agreement for PEG4, PEG5 and PEG6, but substantial deviation - up to a factor of 10 - for PEG3, PEG7 and PEG8. We conclude that extrapolation to lower temperatures of high temperature data should take the temperature dependence of the enthalpy of vaporization (Kirchhoff's law) into account.

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.*

As reviewer 1 raised the same question we refer to our answer to this question of reviewer 1.

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.*

We thank reviewer 2 for the suggestion. We reanalyzed all FT-TDMA data by fixing the surface tension to the values provided by Gallagher (1932), taking the vapor pressures of Table 1 as reference pressure and varying the accommodation coefficient, α , until the calculated vapor pressure of an FT-TDMA experiment including its error exceeds the reference pressure confidence interval at the temperature of the FT-TDMA experiment. This yields a lower limit for α for each FT-TDMA experiment, with a mean value for α of all experiments equal to 0.5 and no discernible difference between the different PEGs. We will add the following sentences at line 5 page 15 in the revised manuscript:

To retrieve a lower limit for the accommodation coefficient, we analyzed the FT-TDMA experiments varying the accommodation coefficient until the calculated vapor pressure including its error exceeds the reference pressure confidence interval given in Table 1 at the temperature of each FT-TDMA experiment. The mean value of these accommodation coefficients for all experiments is equal to 0.5 and there is no discernible difference between the experiments for different PEGs. We conclude that the mass accommodation coefficient of the PEGs based on our study is greater than 0.5.

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.*

When taking the data at temperatures close to the melting point with the EDB setup there was no indication for any crystallization happening. The light scattering data in the EDB setup are very sensitive to phase transitions, see e.g. (Braun and

Krieger, 2001). In addition, crystallization should yield lower apparent vapor pressures, but the temperature data with the KEMS setup show a reverse temperature trend.

- 5 **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?*

For the analysis of the FT-TDMA data, surface tensions are needed to take into account the Kelvin effect. The data shown in the manuscript used surface tensions derived from the FT-TDMA experiments. However, as precise surface tension data are available (Gallagher and Hibbert, 1937; Gallagher, 1932), now we use those for the analysis of the FT-TDMA experiments
10 in the revised version and include them in the revised version of Table 2. (Since those are approximately - within 5%- the same for PEG5 to PEG7, we used the one for PEG7 in our calculations.) The figures and tables are revised accordingly (Table 1 and Fig. 3 show already the revised data.) Switching to the surface tensions reported in literature changes the values of the estimated vapor pressures by a very small amount.

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- 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
20 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.*

We will follow the advice and put the cut-outs into two-part figures. We tried filled symbols, however, then it became even more difficult to clearly relate the symbols to a specific data set as they tended to cover each other. We will increase the symbol
25 edge thickness to make the distinction between our data and literature data more clear. We re-size the symbols for Fig. 11.

References

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