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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Vapor pressures of substituted polycarboxylic acids are much lower than previously reported" *by* A. J. Huisman et al.

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The authors would like to thank Referee #1 for the careful review and valuable comments and queries. We address the reviewer's comments in our response given below. We will incorporate corresponding changes and clarifications in a revised version of the manuscript.

Comments and Responses

Referee #1: Vapour pressures are of great importance to our understanding of gas-to-particle partitioning and contributions to our understanding of these datasets

is to be welcomed. As the paper is directly critical of other work in the field there are several points which must be added to the work to avoid drawing any misleading conclusions.

Authors' response: We try to avoid misleading conclusions by the reader of our paper and the points raised by the reviewers will help us to further clarify our statements. We would also like to note that – regardless of whether a paper is directly critical of other work in the field or not – our philosophy is that each scientific paper should be critical about related work of others and about the validity of own procedures and statements.

Referee #1: It is stated that (ln300) that the physical state in bulk vapour pressure measurements may not be fully controlled and they refer to Soonsin (2010). I don't think that statement is valid; Riberio da Silva (1999;2001) re-crystallise their samples to ensure the measurement state is well defined, Booth (2009;2010) performed DSC measurements of samples to verify they were in a solid crystalline state. Additionally the fact that an odd-even effect for the vapour pressure also confirms that bulk techniques measure the crystalline solid phase. This should be added.

Authors' response: (Remark: ln300 refers to page 1147, line 10 of the discussion paper). The statement on that line reads: "As discussed in Soonsin et al. (2010), one possibility is that the physical state in other measurements was not fully controlled." and is not only referring to bulk measurements. We do suggest this lack of full control on the physical state as a possibility, because the comparison of the liquid- and solid-state data of Soonsin et al. (2010) for the straight-chain C_2 to C_5 dicarboxylic acids with data from the literature suggest that certain measurements of supposedly solid-state crystalline samples may actually have been performed on the liquid state or may have been altered partially by liquid, semi-solid, or amorphous solid material mixed with the crystalline sample. A striking example for such physical state related

effects on the pure solid / liquid vapor pressures is discussed for the case of succinic acid measurements by Soonsin et al. (2010).
The point here is that obtaining full control of the physical state and purity of solid-state samples is quite difficult, while measurements directly on pure liquid samples and aqueous solutions do not pose such a problem. While purification, re-crystallization and differential scanning calorimetry (DSC) are recommended for sample preparation and physical state characterization, such procedures are not necessarily sufficient to fully control the physical state of the whole sample material. For example, a DSC measurement will report the heat flow associated with melting / crystallization of the sample, therefore indicating the temperature (range) at which most of the sample underwent a phase transition, however, the typical crystallization of a liquid into a polycrystalline material does not exclude the possibility that there is a portion of amorphous solid or subcooled liquid remaining in the veins between the crystallites (aside from impurities, incl. hydrates, affecting the vapor pressure). This cannot be prevented completely by common re-crystallization nor detected by DSC measurements or the mentioned odd-even effect. Ideally, to maintain full control of the solid, crystalline state, a high-purity single crystal with very few defects would have to be grown under carefully controlled conditions. To our knowledge this is not done in the case of vapor pressure measurements on crystals reported in the literature. One thermodynamic consistency check that can be used to gain confidence in the validity and purity of the physical states of solid samples is to compare measured solid state vapor pressures with those of the corresponding saturated liquid solutions, as well as the measurement of vapor pressures over a sufficiently long time period (as demonstated by Soonsin et al., 2010). Therefore, we think that the statement in the manuscript is valid indeed.
Additionally, we note that we see this lack of full control of the physical state as one possibility out of several that may contribute to the discrepancy found among literature measurements of solid-state vapor pressures of low-volatility organic acids.

Referee #1: The authors mention that measurements generally agree where the

sample state is positively identified (ln27). It should be mentioned that the level of agreement between bulk sample measurements is as good as that between single particle measurements (e.g. Soonsin (2010) Zardini (2006) and Pope(2010)). It should be mentioned that good agreement between bulk measurements are shown for; Riberio da Silva (1999;2001), Davies and Thomas (1960), Booth(2009;2010) and Tao and McMurry (1989) for diacids and branched diacids in Oja and Suuberg (1999) and Booth (2011) for levoglucosan. Colomina (1978) and Booth (2012) for anisic acid.

Authors' response: (Remark: ln27 refers to page 1135, line 5 of the discussion paper). Our statement refers to a comparison of different kinds of experimental techniques and the emphasis is on the control and knowledge of the sample state. As the Referee notes, there are a number of examples where good agreement is found among bulk measurements (Booth et al., 2012) and there are also a number of examples where good agreement is found among bulk sample techniques, single particle, and particle ensemble experiments (e.g. Booth et al., 2009; Soonsin et al., 2010, Booth et al., 2012; this study (2-Methylmalonic acid)). However, this is not a review article and we prefer to not report an extensive list of vapor pressure measurement comparisons where agreement was found among bulk techniques, since for a balanced discussion this would also require additional discussion on the reasons for agreements and disagreement in specific cases of low-volatility compounds and in addition a list of comparisons of single particle measurements, TDMA measurements, examples where the agreement is poor, etc. The focus of this paper is on the substances under study, the comparison and discussion of our measurements with related measurements of the same compounds and related consequences for liquid-state vapor pressure estimation models.

Referee #1: The paper makes comparisions with the methyl substituted diacid measurements of Mønster (2004) and assigns these as liquid phase measurements.

I believe these are solid phase measurements due to their result of a large leap in vp when adding an methyl group to an even carbon numbered acid and a small increase when adding to an odd acid, a result which arises from the crystal structre of diacids (this is discussed bottom of p 1462 of mønster et al). Also, a corrigendum to this paper (Volume 37, Issue 9, September 2006, Pages 1164) states the methyl-malonic acid vp is 9.1e-4 Pa. This should be changed.

Authors' response: We thank the Referee for noticing this. We will correct the vapor pressure for 2-methylmalonic acid by Mønster et al. (2004) accordingly in the text and in Fig. 2. Whether the measurements of Mønster et al. (2004) were in the pure solid or subcooled liquid state is not explicitly mentioned in their paper and could vary for the different substances they measured, depending on how easily these crystallize in their instrument and whether they potentially form hydrates or not. The argument of the reviewer regarding an odd-even effect is reasonable when assuming that the physical states were the same for all the compounds of the series of methylated dicarboxylic acids studied by Mønster et al. (2004). However, as discussed on page 1144, Section 4.1, our own measurements with 2-methylmalonic acid indicate that this compound does not readily crystallize and in fact did not crystallize in the EDB when dehydrating an aqueous 2-methylmalonic acid particle starting above deliquescence RH, even when holding the particle at RH $< 3\,\%$ for many days. An odd-even effect in vapor pressure can also appear in a measurement series of dicarboxylic acids if some (e.g., the even ones) of the compounds do crystallize while others (the odd ones) do not. We will further clarify the footnote (b) of Table 4 in this respect.

Manuscript revision: Correction of the 2-methylmalonic acid vapor pressure reported by Mønster et al. (2004) in Table 4 to $p^{\circ,\mathrm{L}}(298.15\,\mathrm{K}) = (9.1 \pm 3.2) \times 10^{-4}$ Pa. The same correction will be made in Fig. 2 and the text of section 4.1 will be updated to reflect the improved agreement between our measurement and this value.

Revision of footnote of Table 4 to: [b] Mønster et al. (2004), assumed liquid (physical

state is not specified in the reference), see Section 4.1.

Referee #1: Regarding the EDB measurements; Could the use of diethylene glycol as an anticrystallisation agent (ln 173) have any effect on the vp measurement?

Authors' response: (Remark: ln173 refers to page 1141, line 12 of the discussion paper)
A mixture of water and diethylene glycol is used as an injection solvent only for the EDB experiments with DL-tartaric acid. Diethylene glycol does readily evaporate into the humidified (organic-free) N_2 gas stream continuously flowing through the EDB glass chamber. Since our measurements are done on particles held over a long time period in the EDB (many hours to days), the initial, rapid evaporation of solvent is detected and not influencing the selected measurements of particle radius change used to determine the tartaric acid vapor pressure.

Referee #1: If the walls of the trap got contaminated with the evaporating species, would this cause a lowering of vapour pressure measured? This may explain these EDB results and those previous work (Soonsin 2011) such as that of oxalic acid where the EDB results are several orders of magnitude lower than the collective results of de Witt (1983), de Kruif (1975), Booth(2009), Bradley and Cotson (1953) and Noyes and Wobbe (1923). Or succinic acid where the solid measurements agree with Davis and Thomas (1960), Riberio da Silva (2001), Bilde (2003), Cappa (2007)and Salo (2010) but disagree after they leave a particle in the trap for a day and a half. This should be discussed in the text.

Authors' response:
As described in the article (Section 2) and in more detail by Colberg (2001) and Zar-

dini et al. (2006): our EDB apparatus consists of a three wall temperature-controlled glass chamber containing a levitated charged particle (diameter 2 to 9 µm) held in place through applied electric AC and DC fields. A constant flow (typically 25 sccm) of a N_2/H_2O gas mixture with a controlled H_2O partial pressure is pumped continuously through the chamber at a constant total pressure adjustable between 200 and 1000 hPa. The temperature can be varied between 330 K and 160 K with a stability better than 0.1 K and an accuracy of ±0.5 K. The relative humidity in the chamber is set by automatic mass flow controllers regulating the N_2/H_2O mixing ratio. During an experiment, the temperature and the relative humidity are kept constant while measuring a particular evaporation rate. It is important to note that the N_2/H_2O gas flow is completely free of any evaporated organic molecules prior to entering the glass chamber as the gas flow is freshly generated from a purified liquid N_2 reservoir, part of which is flowing over an enclosed temperature-controlled liquid solution of purified, deionized water containing 2.5 wt-% of dissolved sulfuric acid to scrub any ammonia from laboratory air potentially leaking into the system (see also our reply to query 4 of Referee #2).The mean residence time of a gas molecule in the trap is $\sim$ 2 min. The continuous gas flow ensures that the evaporating organic and water molecules are relatively quickly transported out of the chamber with respect to the timescale of hours and days of an experiment.

Zhang and Davis (1987) studied the problem of contamination of an electrodynamic particle trap with the evaporating species in detail for a setup very similar to ours. They concluded that for flows of low Reynolds numbers the partial pressure of the organic species far from the particle, p_∞, can be calculated as:

$$p_\infty = \frac{p}{(1 + \frac{Q}{4\pi r D_v})}, a \tag{1}$$

where Q is the volumetric flow rate. Hence, the partial pressure can be maintained at a value less than 1% of the vapor pressure, if the flow rate satisfies the inequality

$$Q > 400\pi r D_v . b \tag{2}$$

The minimum flow rates used (20 sccm) always exceeded $2000\pi r D_v$.

Therefore, it is extremely unlikely that the walls of the trap (or a steady accumulation of organic molecules in the glass chamber) would be an issue in our instrument. A number of measurements with a variety of dicarboxylic acids, including 2-methylmalonic acid of this study, where good agreement is found in comparison to other experimental techniques, indicate also that a long term saturation of the trap does not occur.

Possible reasons for differences between some literature values for, e.g., the solid-state succinic acid and glutaric acid vapor pressures and the measurements of Soonsin et al. (2010) are clearly discussed in Soonsin et al. (2010). The fact that better agreement is found with some literature data for the derived vapor pressure of solid succinic acid, shortly after efflorescence of a particle, rather then when the particle is left for additional time (days) in the EDB, indicates that the solid formed after efflorescence from a solution droplet is not a perfect crystalline solid and may include amorphous solid material or a hydrated crystalline form that have a higher vapor pressure (thermodynamics theory entails that an amorphous solid has a higher vapor pressure than the stable crystalline structure at the same temperature and total pressure). While the experiment time in our EDB apparatus is on the order of hours to several days, time scales of many other vapor pressure measurement methods are much shorter (seconds to minutes) or material samples much larger. Therefore, those experiments may in some cases not measure the most stable crystalline form of an organic acid; rather amorphous material affecting the measured vapor pressure may be present besides a crystalline form. A longer measurement or smaller samples may be necessary to unmask the vapor pressure of the crystalline solid in such setups. Furthermore, we note that in case of the succinic acid experiments of Soonsin et al. (2010), the vapor pressure over the saturated solution is in agreement with the value of the solid after prolonged evaporation – with the saturated solution showing a constant evaporation rate over many hours of experiment (and not a change of slope as seen in the case of the solid).

Manuscript revision:
On page 1137, line 6 we replace: "Briefly, a single charged particle was generated and trapped using a combination of AC and DC electric fields in the EDB." by: "The EDB apparatus consists of a three wall temperature-controlled glass chamber containing a levitated charged particle held in place through applied electric AC and DC fields. A constant flow (typically 25 sccm) of a N_2/H_2O gas mixture with a controlled H_2O partial pressure is pumped continuously through the chamber at a constant total pressure adjustable between 200 and 1000 hPa. The temperature can be varied between 330 K and 160 K with a stability better than 0.1 K and an accuracy of $\pm$0.5 K. The relative humidity in the chamber is set by automatic mass flow controllers regulating the N_2/H_2O mixing ratio. During an experiment, the temperature and the relative humidity are kept constant while measuring a particular evaporation rate. Note that the N_2/H_2O gas flow is completely free of any evaporated organic molecules prior to entering the glass chamber as the gas flow is freshly generated from a purified liquid N_2 reservoir, part of which is flowing over an enclosed temperature-controlled liquid solution of purified, deionized water containing 2.5 wt-% of dissolved sulfuric acid to scrub any ammonia from laboratory air potentially leaking into the system."

On page 1138, line 8 we add: "Strictly, Eq. (1) is valid for stagnant conditions. However, the geometry of our EDB together with the flows used keeps the enhancement in evaporation rate due to the gas flow below $0.1\,\%$ (Zhang and Davis, 1987). On the other hand, the flow needs to be sufficiently large to avoid any significant contamination of the gas phase by the organic vapor evaporating from the particle. The partial pressure of the organic substance far from the particle, p_∞, (i.e. here close to the walls of the trap) has to be only a small fraction of the vapor pressure p. Our flows are sufficient to keep the ratio p_∞/p below $1\,\%$, cf. (Zhang and Davis, 1987)."

Referee #1: There has been a lot of recent interest in glassy state aerosols. Could

this cause any effects in the strongly saturated/subcooled samples measured in the trap?

Authors' response: Most of the organic compounds studied have a glass transition temperature that is lower than 280 K. Having a substantial amount of water in the binary solutions does further decrease the glass transition temperature (see, e.g., Lienhard et al., 2012). Citric acid is one of the substances with a relatively high glass transition temperature (~ 282 K), however, for this substance experiments were conducted at higher temperatures. Therefore, the pure melts or aqueous solution particles did not undergo a glass transition in the studied temperature range.

In general, a glassy particle may form when a (subcooled) liquid particle is cooled sufficiently fast to lower temperatures (or dried to lower water contents), to the point where the viscosity becomes very high and a glass transition occurs. The vapor pressure over a pure component glass is therefore closely related to the extrapolation of the subcooled (liquid) vapor pressure to lower temperatures. This is why an amorphous solid has a vapor pressure that is higher than the corresponding thermodynamically stable crystalline state and may therefore mask solid-state vapor pressure measurements of polycrystalline samples containing amorphous material. Unlike multicomponent organic aerosols, the pure melts or binary aqueous solutions at given RH are homogeneously mixed and of fixed stoichiometry, such that formation of a glassy shell or particle bulk-to-surface mass transfer limitations could not impose any hindrance for the evaporation of the organic compound under study.

Referee #1: The agreement (or lack thereof) between single particle and bulk measurements seems to range from very good to 5 orders of magnitude for the worst case. This is however not a unique situation for the ultra-low vapour pressures we are trying to measure. For example, reported P298 for the C7 to C12 diacids typically vary by 2 orders of magnitude and can reach more than 4 orders of magnitude for some

measurements (e.g Salo (2010) and Cappa (2007) for Azelaic acid). I think when a discrepancy of this size occurs, more independent measurements are needed before we can side with certain values.

Authors' response: It is a bit surprising indeed that for the same substances such large deviations in vapor pressures are found among different measurements and experimental techniques – yet as the Referee states, this is not new. As mentioned in Section 5.2, we would welcome additional, independent measurements of the compounds where the largest deviations were found. Previous studies as well as this study clearly show that measuring low vapor pressures of organic acids is a difficult task and requires sophisticated instruments as well as appropriate sample preparation and uncertainty analysis. It therefore is clear that future measurements with bulk, single particle, and TDMA setups should put special rigor on sample preparation and employ a careful instrument calibration and error analysis. Although a method not used by many other groups, we believe that EDB measurements are particularly useful and reliable as this method allows measuring liquid-state vapor pressures directly, including measurements of saturated solutions related to vapor pressures of crystalline solids. Furthermore, long measurement times (days) are possible with micrometer-sized samples in the EDB and seem to be key to understand certain physical state (impurity) effects when measuring evaporation rates of solids. It would certainly be of interest to see long-time evaporation experiments with other measurement methods too (if technically possible).

Referee #1: The authors mention that increased functionalisation of the carbon backbone is a counter intuitive result (ln41). We might naively think this is the case but there is a wealth of evidence and a suitable reason to suppose this is the case. The work of Chattopadhyah and Zieman (2005) suggested intra-molecular bonding as a physical mechanism to explain these results, they observed this phenomena for oxo-

diacids as did Froesch (2010). It's quite hard to find a wide range aliphatic compounds where we can just add extra groups on in any position to probe this behaviour, the only relevant examples I can think of are butane-2-ol and DL-butane-2,3-diol (P298 2.4 and 32 Pa respectively (TRC Thermodynamic tables)) and b-keto esters and 1,3-dicarbonyl compounds (Nannoolal 2008). The idea of extra groups raising vapour pressure has been seen for a variety of aromatic compounds; e.g. Benzophenone, oxybenzophenone and dioxybenzophenone (Merck). The idea that this comes from intramolecular bonding is backed up by results showing an increased volatility when polar groups are adjacent e.g. OH groups adjacent to acid groups in hydroxbenzoic acids(Perlovich 2006), OH groups next to OH groups (Verevkin and Kozolva 2008) in catechols. They also state that and that Compernolle (2011) was unable to rationalise these measurements (ln59). Nannoolal (2008) acknowledges these effects but has to exclude them from his method as it was too difficult to incorporate. To my knowledge Compernolle (2011) is the first attempt to include this phenomena. The dangers of overfitting to a small dataset are correctly identified by the authors, but in this case it could be avoided by using some of the other suggested examples of intramolecular bonding. It must be emphasised in the text that the idea of intramolecular bonding is not dependant on a single set of measurements.

Authors' response: (Remark: ln41 refers to page 1135, line 23 of the discussion paper; ln59 is page 1136, line 16).
Note: a similar point concerning functionalization of dicarboxylic acids, effects of intramolecular bonds, and the correction in the EVAPORATION model has been discussed in detail in a recent ACP publication by one of us (Zuend and Seinfeld, 2012; see discussion in: http://www.atmos-chem-phys-discuss.net/12/C1107/2012/acpd-12-C1107-2012.pdf).

We will extend and clarify this discussion point in the revised version of the paper.
We agree with the Referee that there are some examples where an increase in vapor

pressure is found for a compound that is further functionalized with respect to its parent compound. Hence, counter to the typical finding that additional functionalization by oxygen-bearing groups leads to a lowering in vapor pressure, the opposite is possible in certain cases and has been observed – but only for samples in the crystalline state and not subcooled liquids, about which the statement on page 1135, line 23 is.

Zuend and Seinfeld (2012) mention the finding of Chattopadhyay and Ziemann (2005): "In case of vapor pressure measurements referring to the solid state, Chattopadhyay and Ziemann (2005) found that keto substitutions in α-position of a carboxyl group can raise the solid state vapor pressure of dicarboxylic acids with respect to the unsubstituted parent dicarboxylic acid, while keto substitutions at a β-position or further away from the carboxyl group, lower the solid state vapor pressure. For example, in case of glutaric acid (pentanedioic acid) they found an increase of the vapor pressure by less then an order of magnitude for 2-oxopentanedioic acid at 298 K, yet a decrease in vapor pressure by more than one order of magnitude for 3-oxopentanedioic acid. Chattopadhyay and Ziemann (2005) suggest that a keto group in the α-position may hydrogenbond with the carboxyl group. Hence, an internal hydrogen bond may reduce the intermolecular bonding and may lead to an increase in vapor pressure relative to the value of the unsubstituted parent dicarboxylic acid."

As mentioned by the Referee, there are some additional examples for other classes of compounds (mostly functionalized aromatic compounds). However, contrary to the statement of the Referee, Frosch et al. (2010) did not find this phenomenon for oxo-diacids, they actually report a lowering in vapor pressures for all further functionalized compounds. This is also summarized in Table 3 of Booth et al. (2010). Furthermore, while Chattopadhyay and Ziemann (2005) found a slight increase in vapor pressure for 2-ketoglutaric acid relative to glutaric acid, the measurements of Booth et al. (2010) show a slight decrease. So these results are not consistent among different measurements and certainly when an increase in vapor pressure is found, it is typically of less than an order of magnitude.

There are two important points to note: (1) such vapor pressure increases due to intramolecular bonds have been measured only for solid-state samples and so far never for samples in the liquid state. (2) There are many examples where an effect of neighboring functional groups is found on vapor pressure, e.g., for carboxyl and ketone groups in α-position to each other (e.g., Nannoolal et al., 2008; Compernolle et al., 2011), but these intramolecular interactions lead typically to a decrease in vapor pressure with respect to the parent, less functionalized compound – only that the decrease in vapor pressure is less than what would be expected from a simple group-additive model (i.e., when the functional groups would not interact within the molecule). This is an important point because such effects are indeed considered in the EVAPORATION model of Compernolle et al. (2011) and do not need an additional, empirical correction term. Such group-association effects are also considered in the model of Nannoolal et al. (2008). In contrast to these expected effects, Booth et al. (2010) report for certain functionalized dicarboxylic acids an increase in the liquid-state vapor pressure of nearly two orders of magnitude (in the case of tartaric acid vs. succinic acid) that clearly exceed our expectation and the predictions of all current liquid-state vapor pressure estimation models (when not forced to reproduce the reported data). Other examples are not as extreme. The effects of intramolecular interactions of oxygen-bearing functional groups are likely amplified in crystalline solids as compared to liquids since the regular arrangement of the molecules in a crystal may enhance the existence of *intra*molecular hydrogen bonds when *inter*molecular hydrogen bonds are less available or sterically hindered. In a disordered liquid or amorphous solid state, the intramolecular hydrogen bonds have more competition from intermolecular hydrogen bonds, thereby reducing the relative vapor pressure increase due to the intramolecular bonds.

The Referee suggests to use "some other suggested examples of intramolecular bonding" to avoid overfitting of the EVAPORATION model (or other such models). However, the point is that EVAPORATION predicts the vapor pressure of the liquid state, consequently requires liquid-state vapor pressure data for its parametrization. Thus, most other data sets suggested above by the Referee would not be of any direct

use, because they report on an intramolecular effect in the solid state that may be less pronounced in the liquid state (and not lead to a relative vapor pressure increase). Conversions from solid to liquid state vapor pressures are possible with the use of thermochemical data (see, e.g., Booth et al., 2010), but in the specific cases, where the intermolecular interactions among functional groups may differ substantially, such conversions are subject to additional uncertainties which are difficult to quantify. Additionally, the current empirical correction term in the EVAPORATION model is tailored to apply only to aliphatic compounds containing at least two carboxyl groups and at least one additional carbonyl-like or hydrogen-bonding functional group, regardless of their relative positions in the molecules. Thus, the functionalized aromatic compounds mentioned by the Referee are not part of the compounds represented by the EVAPORATION model and would not be of use to re-parametrize the model correction term, at least not in the current form. Besides, our vapor pressure measurements for the liquid state clearly question the necessity for such an additional, empirical correction term in the EVAPORATION model (or other liquid-state vapor pressure estimation models).

The Referee claims that there is a wealth of evidence of increasing vapor pressure with increasing number of substitutions. However, the examples that are mentioned do not withstand closer inspection: the example of butane-2-ol and DL-butane-2,3-diol is actually supporting our argument that the functionalization by an additional oxygen-bearing group lowers the liquid-state vapor pressure of an organic compound. The Referee states: "It's quite hard to find a wide range aliphatic compounds where we can just add extra groups on in any position to probe this behaviour, the only relevant examples I can think of are butane-2-ol and DL-butane-2,3-diol (P298 2.4 and 32 Pa respectively (TRC Thermodynamic tables)) ...", however, the stated values are incorrect: the first value should be in units of kPa. A look at the normal boiling points T_b (at $p^{\circ,\mathsf{L}} = 101.325$ kPa) of the two compounds already indicates that DL-2,3-butanediol ($T_b = 453.85$ K) will very likely have a lower vapor pressure at $T = 298$ K than

2-butanol ($T_b = 372.7$ K). Using the Antoine equation with the parameters listed in the Landolt-Börnstein Database (Dykyj et al., 2000; data tables available online: http://www.springermaterials.com/docs/info/10688583_3.html), the liquid-state vapor pressures are: $p^{\circ,\mathsf{L}}(298.15\,\mathrm{K}) = 2.44 \times 10^3$ Pa for 2-butanol and $p^{\circ,\mathsf{L}}(298.15\,\mathrm{K}) \approx 24$ Pa for DL-2,3-butanediol. The value for DL-2,3-butanediol is an estimation obtained by extrapolation to lower temperatures beyond the stated temperature range for the given Antoine equation parameters (because the normal boiling point is much higher than room temperature). Hence, here the vapor pressure of the diol is approximately two orders of magnitude lower than the one of the corresponding secondary alcohol, clearly supporting our argument.

We could not find experimental data on subcooled liquid vapor pressures of oxybenzophenones and dioxybenzophenones at room temperature. However, using again the Antoine equation with parameters from the Landolt-Börnstein Database (Dykyj et al., 2000) with slight extrapolation from the verified temperature ranges yields the following liquid-state vapor pressures at 385 K: 128.81 Pa for benzophenone, 8.81 Pa for 2-hydroxy-4-methoxy-benzophenone, and 1.19 Pa for 2,4-dihydroxy-benzophenone. Further extrapolation to 298.15 K yields: 0.136 Pa for benzophenone, 0.00988 Pa for 2-hydroxy-4-methoxy-benzophenone, and 0.00043 Pa for 2,4-dihydroxy-benzophenone. Hence, also in the case of benzophenone, functionalization with additional oxygen-bearing groups clearly lowers the liquid-state vapor pressure.

Manuscript revision: On page 1135, line 23 (after "a counterintuitive result.") we add the following statements: "There have been a few specific cases reported in the literature where addition of an oxygen-bearing functional group to a parent structure can lead to an increase of the solid-state vapor pressure. As discussed in Zuend and Seinfeld (2012), such effects have been reported, e.g., by Chattopadhyay and Ziemann (2005) for substitutions where a ketone group is added in α-position to a carboxyl group. While keto substitutions in α-position of a carboxyl group can raise

the solid-state vapor pressure of a dicarboxylic acid with respect to the unsubstituted parent structure, keto substitutions at a β-position or further away from the carboxyl group always results in decreased solid-state vapor pressure. Chattopadhyay and Ziemann (2005) suggest that a ketone group in α-position may form an internal hydrogen bond with the carboxyl group. Such an internal hydrogen bond may reduce the level of intermolecular hydrogen bonding and may lead to an increase in vapor pressure relative to the unsubstituted parent carboxylic acid. However, such effects on the pure compound vapor pressure have been observed only for samples measured in the solid state. Although the presence of intermolecular group interactions may lessen the reduction in vapor pressure as compared to the prediction of a simple 'additive' group-contribution model, the typical behavior observed is that addition of an oxygen-bearing functional group to an organic structure lowers the pure compound vapor pressure."

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