Henry’s law constants of diacids and hydroxypolyacids: recommended values

S. Compernolle and J.-F. Müller

Belgian Institute for Space-Aeronomy, 1180 Brussels, Belgium

Received: 27 August 2013 – Accepted: 10 September 2013 – Published: 26 September 2013

Correspondence to: S. Compernolle (steven.compernolle@aeronomie.be)

Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

In spite of the importance of diacids and functionalised diacids for organic aerosol formation through aqueous-phase processes in droplets and aerosol water, there seems to be no reliable set of experimental values for their Henry’s law constants (HLC). We show that their estimation through the use of infinite dilution activity coefficients is also prone to error. Here we present HLC values for diacids and hydroxy polyacids determined from solubilities, water activities and vapour pressures of solids or solutions, by employing thermodynamic relationships. The vapour pressures are found to be the largest source of error, but the analysis of the obtained HLC points to inconsistencies among specific vapour pressure data sets. Although there is considerable uncertainty, the HLC of diacids appear to be higher than estimated by the often cited review work of Saxena and Hildemann (1996).

1 Introduction

The Henry’s law constant is a fundamental molecular property regulating the partitioning between the gas and aqueous phase. In the atmosphere, this aqueous phase can be a cloud droplet or an aqueous aerosol. Polyacids are important constituents in droplets and aerosols. An often-cited HLC compilation for atmospheric purposes is that of Sander (1999); these values are also available at the NIST Chemistry Webbook. This compilation contains HLCs for several diacids and functionalised diacids, but most of them are not experimental but rather estimated by group-contribution, taken from the review paper of Saxena and Hildemann (1996).

In any case, HLC of dicarboxylic acids are likely very high, such that they will be almost completely dissolved in aqueous droplets. However, for aqueous aerosols, the total water content of the aqueous phase is much lower and the gas phase fraction could be significant. Of course, due to the presence of organic and inorganic molecules, an aqueous aerosol can hardly be regarded as a pure water phase, as is required for...
HLC. Still, the availability of a reliable set of HLC is valuable as a reference point. Furthermore, HLC estimation methods also need reliable HLC to fit their parameters.

Through thermodynamics, vapour pressures of liquid or solid, solubilities and activity coefficients are all related. The focus in this work is on HLC, but we will need the other quantities as well. Therefore, we first briefly review their thermodynamic relationships. For HLC, several definitions exist. We will follow here the convention taken by Sander (1999)

\[ k_h \equiv \lim_{c_s, p_s \to 0} \frac{c_s}{p_s} = \lim_{x_s, p_s \to 0} \frac{x_s c_w}{p_s} \]  

(1)

with \( c_s \) the molar concentration of the solute in the aqueous solution, \( p_s \) its partial pressure above it, \( x_s \) the mole fraction in the aqueous phase and \( c_w \) the molar concentration of pure water (55.6 M). As expressed by Eq. (1), they should in principle be measured at the infinite dilution limit (IDL). For an ideal solution, where there is no difference in interaction between like or unlike molecules the partial pressure would equal \( p_s = x_s p_{L,s}^0 \) (Raoult’s law), with \( x_s \) the mole fraction of the solute and \( p_{L,s}^0 \) its liquid saturation vapour pressure. However, in general solutions are not ideal, the solute molecules behave differently in water than in a liquid of its own, and therefore an activity coefficient correction is needed.

\[ p_s = \gamma_s x_s p_{L,s}^0 \]  

(2)

The activity coefficient \( \gamma_s \) expresses the preference of the solute to the mixture, compared to a solvent of pure \( s \) itself. If the solvent is the same as the solute, \( \gamma_s = 1 \), while a value below (above) unity means that the solute prefers the mixture (solvent of pure \( s \)). Combination of Eqs. (1) and (2) leads to

\[ k_h = \frac{c_w}{\gamma_s^\infty p_{L,s}^0} \]  

(3)
with $\gamma_s^\infty$ the infinite dilution activity coefficient (IDAC). Suppose now that the solute is a crystalline solid in pure form. Above the solid, gas-phase molecules with a sublimation pressure $p_{\text{Cr,s}}^0$ will be present. Now if the solute is added to water above its saturation point, a solid phase will form in the water phase. If it can be assumed that this solid is the same as in the dry form (e.g. there is no incorporation of water in the crystal structure), one has

$$p_s^{\text{sat}} = p_{\text{Cr,s}}^0 = \gamma_s^{\text{sat}} x_s^{\text{sat}} p_{L,s}^0$$

(4)

with $x_s^{\text{sat}}$ the mole fraction solubility of the solid and $\gamma_s^{\text{sat}}$ the activity coefficient at this point. In principle, liquid and solid can only co-exist at the fusion point, where $p_{\text{Cr}}^0 = p_L^0$. Hence if the substance is solid at the temperature of interest, the vapour pressure of the subcooled liquid is inaccessible from a thermodynamic point of view, as $x_s$ cannot increase above $x_s^{\text{sat}}$. In practice, however, metastable, strongly supersaturated solutions might exist in small particles (Peng et al., 2001; Soonsin et al., 2010; Huisman et al., 2013), such that $p_s \rightarrow p_{L,s}^0$ can be approached. $p_{L,s}^0$ can also be related to $p_{\text{Cr,s}}^0$, as sublimation can be seen thermodynamically as first a fluidization of the solid, and then a vaporization of the resulting liquid. The fusion enthalpy and entropy have then to be taken into account:

$$p_{\text{Cr,s}}^0(T) = \exp \left( -\frac{\Delta H_{\text{fus}}(T)}{RT} + \frac{\Delta S_{\text{fus}}(T)}{R} \right) p_{L,s}^0(T)$$

(5)

Unfortunately, $\Delta H_{\text{fus}}$ and $\Delta S_{\text{fus}}$ can only be measured at the fusion point, where $\Delta H_{\text{fus}} = T_{\text{fus}} \Delta S_{\text{fus}}$, which is in our case often far above the temperature of interest (around room temperature). Thus, extrapolation schemes are necessary, e.g. by assuming a constant heat capacity difference $\Delta C_{p,ls}$ between liquid and solid:

$$\frac{\Delta H_{\text{fus}}(T)}{RT} - \frac{\Delta S_{\text{fus}}(T)}{R} \approx -\frac{\Delta H_{\text{fus}}(T_{\text{fus}})}{R} \left( \frac{1}{T_{\text{fus}}} - \frac{1}{T} \right) + \frac{\Delta C_{p,ls}}{R} \left( 1 - \frac{T_{\text{fus}}}{T} - \ln \frac{T}{T_{\text{fus}}} \right)$$

(6)
ΔC_{p,ls} is generally not available and has to be estimated, e.g. by neglecting it or imposing $\Delta C_{p,ls} \approx \Delta S_{\text{fus}}(T_{\text{fus}})$. This is the approach taken by e.g. Booth et al. (2010).

If the solubility is low, such that $x_{s}^{\text{sat}}$ is close to the IDL, we have

$$k_{h} \approx \frac{c_{s}^{\text{sat}}}{p_{s}^{\text{sat}}} = \frac{c_{s}^{\text{sat}}}{p_{c,s}^{0}} \approx c_{w} \frac{x_{s}^{\text{sat}}}{p_{c,s}^{0}} \quad (7)$$

In this work, we will first investigate the reliability of HLC values of diacids present in the literature. Then we will evaluate the reliability of UNIFAC-type group contribution methods to obtain IDAC, as the IDAC is one ingredient, apart from the subcooled liquid vapour pressure $p_{L}^{0}$, to obtain HLC via Eq. (3). Next we will show how more reliable HLC values can be constructed using thermodynamic relationships and existing experimental data on sublimation pressures, solubilities and water activities. Vapour pressures of solids or solutions bear the largest uncertainty, with considerable disagreement between the results of different research groups (e.g. Booth et al., 2010; Soonsin et al., 2010; Cappa et al., 2007; Chattopadhyay and Ziemann, 2005). However, comparing the thus-derived HLC between different molecules will reveal clues as to the consistency of the vapour pressure data sets.

2 Case study on the reliability of compiled literature values for diacids

HLC estimation methods need of course experimental data to fit and/or test their models. Some studies (e.g. Raventos-Duran et al., 2010; Hilal et al., 2008; Modarresi et al., 2007) report also estimated vs. experimental HLC values for diacids. The origin and reliability of the experimental values is then of prime importance, as any estimation method can only be as good as the data on which it is based on. We choose here the data set compiled by Raventos-Duran et al. (2010) to fit the model GROMHE, but similar conclusions would be very likely drawn for other compilations. GROMHE is developed especially for atmospherically relevant compounds. It is based on a compilation
which includes data for five diacids: oxalic, malonic, succinic, glutaric and adipic acid. Their HLC values as used by Raventos-Duran et al. (2010) are presented in Table 1.

The HLC of oxalic acid was taken from Gaffney et al. (1987), but this article refers to a conference abstract (Gaffney and Senum, 1984) we could not obtain, and it is therefore unclear how the value was originally obtained. Furthermore, Gaffney et al. (1987) state that this HLC is an effective one at pH = 4, while the basis set of the GROMHE method should consist of intrinsic HLCs according to Raventos-Duran et al. (2010). For diacids, the relation between effective and intrinsic HLC is

\[ k_{h}^{\text{eff}} = k_{h}^{\text{intr}} \left( 1 + \frac{K_{a,1}}{[H^{+}]} + \frac{K_{a,1}K_{a,2}}{[H^{+}]^2} \right) \] (8)

Given that oxalic acid is a quite strong acid, with dissociation constants of \( K_{a,1} = 5.18 \times 10^{-2} \), \( K_{a,2} = 5.30 \times 10^{-5} \) (Apelblat, 2002), it will be mostly in ionized form at this pH, and \( k_{h}^{\text{eff}} / k_{h}^{\text{intr}} \approx 800 \).

The HLC of glutaric acid was taken from another compilation (Hilal et al., 2008). From there, one can follow the trace via the compilation of Modarresi et al. (2007) to the compilation of Sander (1999) and finally to the original source, Saxena and Hildemann (1996), which makes clear that this value is not experimental but rather estimated by a group-contribution method. This notion was explicitly mentioned in the compilation of Sander (1999), but was lost in the compilations of Modarresi et al. (2007); Hilal et al. (2008); Raventos-Duran et al. (2010) directly or indirectly referring to it. We emphasize here that these last three compilations were made explicitly to develop and/or test HLC estimation methods, hence it is required that the compiled HLC values are all experimental rather than estimated!

The HLCs of the other three diacids (malonic, succinic, adipic acid) are all taken from the compilation of Meylan and Howard (2000). Checking this compilation, it turns out that in all cases, the HLC does not refer to a directly measured value, but rather to an estimation obtained by combining solubility \( c_{s}^{\text{sat}} \) of the solid diacid and sublimation pressure \( p_{Cr}^{0} \), using Eq. (7). This is not necessarily a problem; Eq. (7) is correct provided...
the solubility is low, such that one is close to the IDL. Of course both $c_s^{\text{sat}}$ and $p^{0}_{\text{Cr}}$ should be reliable to obtain a reliable $k_h$. The solubilities $c_s^{\text{sat}}$ are all from the AQUASOL database (Yalkowsky and Dannenfelser, 1992) and they reasonably agree with the values from primary references (Apelblat and Manzurola, 1987, 1989; Marcolli et al., 2004). However, the solubility mole fraction $x^{\text{sat}}$ of malonic acid is about 0.16 (Apelblat and Manzurola, 1987), which is far from IDL, hence Eq. (7) does not hold. The $x^{\text{sat}}$ of succinic and adipic acid are much lower (0.013 and 0.003 respectively), hence Eq. (7) should be reasonably valid.

But for all these three diacids, the values for $p^{0}_{\text{Cr}}$ are questionable. The values for succinic and adipic acid are from the Handbook of Yaws (1994). In this compilation, the vapour pressures of these two acids refer to the liquid phase; the vapour pressures at 25°C present in the compilation of Meylan and Howard (2000) are obtained by first extrapolating liquid vapour pressures over 157 and 128 K below their melting points respectively, and then converting to sublimation pressures. The exact procedure of this conversion is not clear to us, but the reported values $p^{0}_{\text{Cr}}$ seem consistent with a simple approximate procedure like that of Yalkowsky (1979) where only the fusion temperature is from experiment, rather than the more precise procedure where both fusion temperature and enthalpy are taken from experiment. Finally, for malonic acid, the vapour pressure originates from the Handbook of Jordan (1954). The cited vapour pressure (0.2 Pa) is however orders of magnitude higher than the ones from recent experiments ($10^{-4}–10^{-3}$ Pa, see e.g. the overview table of Soonsin et al., 2010).

Given that strong reservations can be made for each of the HLC values in Table 1, the need for a reliable HLC set for diacids is clear.

3 Infinite dilution activity coefficients: usefulness in obtaining HLC

Following Eq. (3), HLC can be obtained by knowledge of the liquid vapour pressure $p^{0}_{L}$ and the IDAC $\gamma^{\infty}_{s}$. Note that diacids and hydroxy-polyacids are solid at room tem-
temperature, whereas $p_L^0$ and $\gamma_s^\infty$ are required for the subcooled liquid. Let us disregard the problem of obtaining a subcooled vapour pressure, and focus here on obtaining a reliable value of $\gamma_s^\infty$.

UNIFAC (Fredenslund et al., 1975; Hansen et al., 1991) is arguably the most popular activity coefficient method based on the group-contribution concept. Peng et al. (2001) and Raatikainen and Laaksonen (2005) provided new UNIFAC-parameterisations (called UNIFAC-Peng and UNIFAC-Raatikainen hereafter) using activity and/or solubility data of mixtures with water and diacids or functionalised diacids. A close relative of UNIFAC-Peng is AIOMFAC (Zuend et al., 2011), as it inherited some of its parameters, while other parameters were inherited from the UNIFAC parameterisation of Marcolli and Peter (2005) (UNIFAC-MP). UNIFAC-MP was adapted to better describe mono-alcohols and polyols. One would expect that these three models (UNIFAC-Peng, UNIFAC-Raatikainen, AIOMFAC) would give similar IDACs for diacids and hydroxy-polyacids, as they were based on experimental data for these molecules. The estimated IDACs are compared in Fig. 1.

### 3.1 Hydroxy-polyacids

Unexpectedly, large discrepancies, up to one order of magnitude, show up for the IDAC of malic, tartaric and citric acid as calculated by the various methods. AIOMFAC predicts a higher IDAC than UNIFAC-Peng for all three molecules. UNIFAC-Raatikainen gives IDAC values quite close to UNIFAC-Peng for malic and citric acid, but for tartaric acid it predicts an IDAC an order of magnitude lower.

Peng et al. (2001) developed their parameterisation solely based on water activity data $a_w$; activity data of the solute was not included. In principle, this is not a problem, as it follows from the Gibbs–Duhem relation that for a binary mixture, knowledge of the activity coefficient of one component results in knowledge of the activity coefficient of the other component. The Gibbs–Duhem relation in its derivative and integral form is
expressed as (see e.g. Mansoori, 1980)

\[ x_w \left( \frac{\partial \ln \gamma_w}{\partial x_w} \right)_{T,P} = x_s \left( \frac{\partial \ln \gamma_s}{\partial x_s} \right)_{T,P} \]  \hspace{1cm} (9)

\[ \ln \gamma_s = -\frac{x_w}{x_s} \ln \gamma_w + \int_0^{x_w} \frac{\ln \gamma_w(t)}{(1 - t)^2} dt \]  \hspace{1cm} (10)

where \( x_w, x_s \) denote the mole fraction of water and solute respectively, and \( \gamma_w, \gamma_s \) the corresponding activity coefficients. If the IDAC \( \gamma_s^{\infty} \) is desired, Eq. (10) reduces to

\[ \ln \gamma_s^{\infty} = \int_0^1 \frac{\ln \gamma_w(t)}{(1 - t)^2} dt \]  \hspace{1cm} (11)

hence to obtain the IDAC of the solute, any functional form of \( \gamma_w(t) \) should match the experimental water activity coefficients over the entire concentration range.

Figures 5–7 of Peng et al. (2001) display water activity vs. solute mass fraction plots for these three acids, for both experimental values and UNIFAC-Peng. The experimental data from zero up to saturation concentration (subsaturation range) was from several data sources, including Peng et al. (2001), while the data in the supersaturation range was only from Peng et al. (2001). Some observations that can be made from these plots are:

- UNIFAC-Peng fits the experimental data well in the subsaturation range.
- For malic and tartaric acid, UNIFAC-Peng slightly overestimates the water activity data in the supersaturation region.
- For citric acid, UNIFAC-Peng fits well the water activity data over the entire range.
Figure 2 presents similar plots for malic, tartaric and citric acid, where water activity is calculated with UNIFAC-Peng, AIOMFAC and UNIFAC-Raatikainen. Experimental data from Maffia and Meirelles (2001) and Apelblat et al. (1995) is also included. The data of Maffia and Meirelles (2001) was not included by Peng et al. (2001), but the agreement with UNIFAC-Peng is satisfactory. The data point from Apelblat et al. (1995) was included to show the saturation point.

AIOMFAC matches UNIFAC-Peng quite well in the subsaturation range, but returns a considerably higher $a_w$ in the supersaturation range. Given that Eq. (11) involves integration over the entire concentration range, this explains the systematically higher IDAC predicted by AIOMFAC compared to UNIFAC-Peng. As UNIFAC-Peng matches $a_w$ well for citric acid over the entire concentration range, and already overestimates $a_w$ in the supersaturation range for malic and tartaric acid, it follows that the IDAC of UNIFAC-Peng should be more reliable than those of AIOMFAC. The reason for the discrepancy between UNIFAC-Peng and AIOMFAC can be attributed to the fact that AIOMFAC is actually a hybrid method; its parameters describing the hydroxy-water interaction are not taken from UNIFAC-Peng, but rather from UNIFAC-MP, which was developed for mono-alcohols and polyols but not for hydroxy-acids. This combination was done to widen the scope method, but clearly this comes at a prize.

For citric acid, UNIFAC-Raatikainen matches UNIFAC-Peng closely, but for malic and tartaric acid, it gives a significantly lower water activity. This is reflected in the discrepancies of estimated IDAC in Fig. 1. Particularly for tartaric acid, the poor agreement of UNIFAC-Raatikainen with the water activity data of Maffia and Meirelles (2001) is clear in Fig. 2. This is surprising, as this data set was used in the development of UNIFAC-Raatikainen (Raatikainen and Laaksonen, 2005).

Although UNIFAC-Peng comes out as the most reliable method for the three acids, it overestimates the water activity data in the supersaturation region for malic and tartaric acid. Hence direct analysis of these data could result in a more precise IDAC of the solute. We converted the experimental water activity data from the plots of Peng et al. (2001) to water activity coefficient data and tried to fit it with the commonly used Mar-
gules, Van Laar and Wilson activity coefficient expressions (e.g. Prausnitz et al., 1999; Carlson and Colburn, 1942) (see Fig. 3). The resulting parameter set is then used to obtain the solute IDAC $\gamma_s^\infty$. All fittings extrapolate to a lower $\gamma_w^\infty$ than UNIFAC-Peng, and different solute IDACs are obtained. For malic acid, all fittings result in the same standard deviation, however, the Wilson model extrapolates to a much lower value of $\gamma_w^\infty$ than the other models. We conclude therefore that as long as no data near zero mole fraction water is included, IDACs of the solute obtained via water activity data are not well constrained. Therefore, they are not a good basis to derive HLCs, even if reliable subcooled liquid vapour pressures were available.

3.2 Linear diacids

For linear diacids, UNIFAC-Peng and AIOMFAC become identical (Fig. 1). UNIFAC-Raatikainen gives an only slightly higher IDAC for the longer chain diacids. However, this does not guarantee that they agree with experiment. Before proceeding further, let us first consider the peculiarities of linear diacid solubilities in more detail.

It is well known that several properties of linear diacids, such as melting point, fusion enthalpy, solubility and sublimation pressure, follow an even-odd alternation pattern with the number of carbon atoms in the chain. This is caused by the more stable crystal structure of linear diacids with an even number of carbon atoms (Thalladi et al., 2000). In the case of solubility, this leads to a lower solubility of the diacids with an even number of carbon atoms (Fig. 4). On top of the even-odd alternation pattern, the solubility decreases with the number of carbon atoms. One can view the dissolution of a solute in a solvent as first a fluidization process and second a mixing process.

\[
\ln x_s^{sat} = \frac{\Delta S_{fus}(T)}{R} \frac{\Delta H_{fus}(T)}{RT} + \frac{\Delta S_{mix}(T)}{R} - \frac{\Delta H_{mix}(T)}{RT} \tag{12}
\]
The ideal solubility model (Yalkowsky and Wu, 2010) assumes ideal mixing, such that the finite solubility is only caused by the fluidization process:

\[
\ln x_{\text{sat},\text{id}} = \frac{\Delta S_{\text{fus}}(T)}{R} - \frac{\Delta H_{\text{fus}}(T)}{R} \approx \frac{\Delta S_{\text{fus}}(T_{\text{fus}})}{R} - \frac{\Delta H_{\text{fus}}(T_{\text{fus}})}{R}
\]

(13)

where we used approximation (Eq. 6) and assumed a zero \( \Delta C_p \). The fusion data was obtained from Booth et al. (2010); Roux et al. (2005), and (if applicable) the sum over different solid-solid transition points was taken. From Fig. 4, it is clear that apart from the even-odd alternation pattern, there is only a small dependence of the ideal solubility with chain length. Therefore, the lowering of solubility with chain length must be due to a more difficult mixing, or equivalently an increase in activity coefficient. We showed previously (Compernolle et al., 2011) that for the longer chain diacids (starting from C7) UNIFAC-Peng and UNIFAC-Raatikainen underestimate \( \gamma_{\text{sat}}^s \), which should be close to \( \gamma_{\infty}^s \) for these low-soluble acids. These longer chain molecules were not in the data set used to develop UNIFAC-Peng or UNIFAC-Raatikainen. Therefore we conclude that they cannot be used as a tool to estimate their IDAC, or finally the HLC.

A deeper insight in the driving factors behind the solubility of linear diacids can be achieved by comparing fusion enthalpies and entropies with solution enthalpies and entropies close to IDL, as done in Fig. 5. The solution enthalpy and entropy for the low-solubility diacids succinic, adipic, suberic and azelaic acid was derived by fitting Van’t Hoff equations to the temperature-dependent solubility data of Apelblat and Manzurola (1987); Yu et al. (2012); Apelblat and Manzurola (1990). Note that for suberic acid, we chose the data of Yu et al. (2012) over that of Apelblat and Manzurola (1990) as the solubility varied more continuously with temperature. Solubility data for pimelic acid is also available (Apelblat and Manzurola, 1989) but the solubility vs. temperature curve is quite irregular; this could mean that several solid-solid transitions take place (e.g. due to uptake of water in the crystal). We therefore omitted the pimelic acid data. Malonic and
glutaric are highly soluble in water, hence their solution enthalpy and entropy derived from solubility would be far from IDL. Instead, we took the solution enthalpies derived from caloric measurements at low concentrations (Taniewska-Osinska et al., 1990).

Given that the $\Delta H_{\text{fus}}$, $\Delta S_{\text{fus}}$ are obtained at a higher temperature than $\Delta H_{\text{sol}}$, $\Delta S_{\text{sol}}$, it is not fully justified to simply take their differences to obtain $\Delta H_{\text{mix}}$, $\Delta S_{\text{mix}}$, but for qualitative purposes it will probably suffice. One notices that from glutaric acid on, $\Delta H_{\text{sol}} - \Delta H_{\text{fus}} \approx \Delta H_{\text{mix}}$ gradually increases, meaning that the energetic interactions acid–water become less strong compared to the acid–acid interactions in the pure melt. This is unfavourable for the solution process and is one reason why $x_{\text{sat}}$ decreases with chain length. Furthermore, one notices that the entropy of mixing $\Delta S_{\text{sol}} - \Delta S_{\text{fus}} \approx \Delta S_{\text{mix}}$ decreases, especially for the longer chain molecules, again causing $x_{\text{sat}}$ to decrease. For azelaic acid, this entropic effect has become the dominant contribution to the low solubility.

Such a strongly negative $\Delta S_{\text{mix}}$ is typical for dissolution of hydrophobic molecules in water. The presence of the hydrophobic chain causes the water molecules to re-order themselves, resulting in an entropy decrease. There are many examples of this effect in the HLC compilation of Abraham et al. (1990), for example for the series of linear 1-alkanols. For linear $\alpha, \omega$-diacids, and presumably also for linear $\alpha, \omega$-diols, with both tails hydrogen-bonding, it takes only a longer chain before this hydrophobic effect becomes important.

4 HLC data: results

From Eq. (7) it follows that HLC can be derived from solubility and sublimation pressure data, provided the solubility is low enough such that the IDL is a good approximation. But even if the compounds are quite water soluble, as is the case for the short-chained linear diacids and the hydroxy-polyacids, one can still derive the HLC. Indeed, combi-
nation of Eqs. (3) and (4) leads to
\[ k_h = \frac{\gamma_s^{\text{sat}} c_s x_s^{\text{sat}}}{\gamma_s^{\infty} p_{\text{Cr},s}} \] (14)

The ratio \( \gamma_s^{\text{sat}} / \gamma_s^{\infty} \) can be retrieved if sufficient water activity data is available in the concentration range \( x_s = [0, x_s^{\text{sat}}] \). From Eq. (10) one derives
\[
\ln \frac{\gamma_s^{\infty}}{\gamma_s^{\text{sat}}} = \frac{1 - x_s^{\text{sat}}}{x_s^{\text{sat}}} \ln \gamma_w(\tilde{x}_w) + \frac{1}{\tilde{x}_w} \int_{\tilde{x}_w}^{1} \ln \gamma_w(t) (1 - t)^2 \, dt
\] (15)
\[ \tilde{x}_w = 1 - x_s^{\text{sat}} \]

The important point is that the integral no longer involves the supersaturation region, where data is typically less precise or scarce. Applying Eq. (15) on the subsaturation data leads to the \( \gamma_s^{\infty} / \gamma_s^{\text{sat}} \) data given in Table 2. Their detailed derivation is outlined in the Supplement. For the longer linear chain diacids (C6 and higher), we did not find water activity data in the subsaturation range in the literature. However, their solubility is low, such that \( \gamma_s^{\infty} / \gamma_s^{\text{sat}} \approx 1 \) can be assumed. In Table 3, the HLC data at 25 °C derived from Eq. (15) or Eq. (7) are presented.

Solubility data was taken from Apelblat and Manzurola (1987, 1989, 1990); Bretti et al. (2006), and was consistent with other solubility data (Marcolli et al., 2004). As especially the sublimation pressures disagree between different sources, we grouped the data in Table 3 per sublimation pressure reference. Where possible, also the enthalpy of gas-phase dissolution is given, calculated as \( \Delta H_{g \rightarrow aq} = \Delta H_{\text{sol}} - \Delta H_{\text{sub}} \).
5 Discussion and conclusions

5.1 Consistency of sublimation pressure data

If other homologous series (linear alkanes, acids, 1-alkanols, 2-ketones, etc.) are any guide (Sander, 1999), one would expect a rather slow variation of the HLC of linear diacids with chain length compared to e.g. liquid vapour pressure $p^0_L$. For example, when going from acetic to hexanoic acid, HLC at 25°C is lowered by a factor 4, while $p^0_L$ is lowered roughly by a factor 400. Also, no even-odd alternation of $k_h$ or gas dissolution enthalpy $\Delta H_{g\rightarrow aq}$ with chain length is expected, as this is a peculiarity for properties involving the crystalline phase. Figure 6 presents the HLC and $\Delta H_{g\rightarrow aq}$ of the linear diacids vs. carbon number, grouped per reference of sublimation pressure. The large variation in $k_h$ reflects the variation in $p^0_{Cr}$ from different data sources. Some of the lowest $k_h$ and, in absolute value, $\Delta H_{g\rightarrow aq}$ are found for Salo et al. (2010), especially for the longer chains C8–C10 where $k_h$ lowers rapidly with chain length. This is likely due to samples that are not purely crystalline, a possibility acknowledged by these authors. For pimelic acid Salo et al. (2010) could distinguish two modes and they attributed the one with the lowest $p^0_{Cr}$ to the crystalline phase. This is probably correct, as for this acid the derived HLC and $\Delta H_{g\rightarrow aq}$ are more comparable to these derived from $p^0_{Cr}$ data of other authors. The HLC data derived from Ribeiro da Silva et al. (1999, 2001) exhibits the smallest variation with chain length, more in line with the expectation. The dissolution enthalpies derived from the data of Booth et al. (2010) and of Bilde et al. (2003) exhibit a strong even-odd alternation – although in reverse directions – and contrary to expectation. This could be an indication of experimental artefacts in the measurement of $\Delta H_{sub}$ in these works.

Apart from diacids, Booth et al. (2010) also presented $p^0_{Cr}$ data on hydroxy-polyacids (malic, tartaric and citric acid). Using fusion enthalpy data, these data was then converted to subcooled liquid $p^0_L$. From these data, it followed that $p^0_L$(tartaric) > $p^0_L$(succinic), and $p^0_L$(citric) > $p^0_L$(adipic), which is counter-intuitive, as one expects gen-
eraly a lower $p_L^0$ with increasing number of polar groups. On the other hand, one could argue that for molecules with many functional groups, it is difficult for the molecules to get optimal intermolecular bonding for all functional groups at once. Comparing $k_h$ instead of $p_L^0$ can provide a more stringent test; the small water molecules should more easily interact with all functional groups at once. From Table 3, one finds that $k_h$(tartaric) > $k_h$(succinic) and $k_h$(citric) > $k_h$(adipic), which seems to be at least qualitatively correct. We note however, that Huisman et al. (2013) found a much lower $p_L^0$ than Booth et al. (2010) for these acids. These $p_L^0$ data were derived from $p_L$ measurements above water mixtures and by extrapolating the solute mole fraction to $x_s \rightarrow 1$; if on the other hand the extrapolation $x_s \rightarrow 0$ was performed, HLC data could be derived, and they would be likely orders of magnitude higher than those of Booth et al. (2010).

5.2 Atmospheric implications

Notwithstanding the high variations in the derived HLC of the linear diacids, they are most often higher than the estimations provided by the review work of Saxena and Hildemann (1996). For clouds, the liquid water content (LWC) varies between 0.1–1 gm$^{-3}$, and for aqueous aerosols $10^{-6}$–$10^{-4}$ gm$^{-3}$ (Ervens et al., 2011). If partitioning between gas and aqueous phase is governed solely by Henry’s law, the aqueous phase fraction $f_{aq}$ of a species can be calculated from

$$f_{aq} = \frac{1}{k^*/k_h + 1}, \text{ with } k^* = \frac{\rho_w}{LWC \ RT}$$

(16)

with $\rho_w$ the water density. For clouds, $k^*$ is between $4 \times 10^4$–$4 \times 10^5$ Matm$^{-1}$. For oxalic acid, the lowest $k_h$ value from Table 3 is $6.0 \times 10^6$ Matm$^{-1}$, leading to $f_{aq}$ between 0.94 and 0.993. Taking also the acid dissociation of oxalic acid into account at a typical pH of 4 (Eq. 8), $f_{aq}$ is above 0.9999. The other $k_h$ values for oxalic acid from Table 3 are about two orders of magnitude higher, leading to an even more complete dissolution. For the other species in Table 3, $k_h$ varies between $10^8$–$10^{11}$ Matm$^{-1}$ (provided one
dismisses the lowest values from Salo et al. (2010) corresponding probably to non-purely crystalline samples), orders of magnitude higher than $k^*$. Hence for clouds, the diacids and hydroxy-polyacids should reside almost completely in the aqueous phase.

For aqueous aerosols, $k^*$ is typically between $4 \times 10^8$–$4 \times 10^{10}$ M atm$^{-1}$, which is in the range of $k_h$ values from Table 3. Hence significant partitioning to the aqueous phase or the gas-phase are both possible, depending on the species and the LWC. The HLC values reported here are applicable for partitioning to dilute aqueous solutions, so they can only serve as a first guide to obtain the partitioning to aqueous aerosol, which is a concentrated solution containing both organics and inorganics.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/13/25125/2013/acpd-13-25125-2013-supplement.pdf.

Acknowledgements. This work was supported by the project BIOSOA (SD/CS/05A, 2011–2014) funded by the Belgian Science Policy Office.

References


Apelblat, A. and Manzurola, E.: Solubility of ascorbic, 2-furancarboxylic, glutaric, pimelic, salicylic, and o-phthalic acids in water from 279.15 to 342.15 K, and apparent molar volumes of


Chattopadhyay, S. and Ziemann, P. J.: Vapor pressures of substituted and unsubstituted monocarboxylic and dicarboxylic acids measured using an improved thermal Desorp-
Henry’s law constants of multifunctional acids

S. Compernolle and J.-F. Müller

ACPD 13, 25125–25156, 2013

Abstract

Introduction

Conclusions

References

Tables

Figures

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion


Linstrom, P. J. and Mallard, W. G. (Eds.): NIST Chemistry Webbook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899.


Table 1. HLC of diacids from the compilation of Raventos-Duran et al. (2010).

<table>
<thead>
<tr>
<th>Acids</th>
<th>HLC/M atm$^{-1}$</th>
<th>Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxalic</td>
<td>$10^{6.8}$ a</td>
<td>Origin not clear. Effective instead of intrinsic</td>
</tr>
<tr>
<td>malonic</td>
<td>$10^{6.6}$ b</td>
<td>Invalid application of Eq. (7). Too high $p_0^0$</td>
</tr>
<tr>
<td>succinic</td>
<td>$10^{8.4}$ b</td>
<td>Gross extrapolation of $p_0^0$ from high $T$</td>
</tr>
<tr>
<td>glutaric</td>
<td>$10^{8.3}$ c</td>
<td>HLC not experimental</td>
</tr>
<tr>
<td>adipic</td>
<td>$10^{8.3}$ b</td>
<td>Gross extrapolation of $p_0^0$ from high $T$</td>
</tr>
</tbody>
</table>

Obtained from:

- a Gaffney et al. (1987)
- b Meylan and Howard (2000)
- c Hilal et al. (2008)
Table 2. \( \frac{\gamma_s^\infty}{\gamma_s^{\text{sat}}} \) data at 25 °C, derived from the water activity data of Peng et al. (2001); Velezmoro and Meirelles (1998); Apelblat et al. (1995); Wise (2003).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \frac{\gamma_s^\infty}{\gamma_s^{\text{sat}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxalic</td>
<td>1.0(^a)</td>
</tr>
<tr>
<td>malonic</td>
<td>0.7</td>
</tr>
<tr>
<td>succinic</td>
<td>1.0</td>
</tr>
<tr>
<td>glutaric</td>
<td>3.0</td>
</tr>
<tr>
<td>malic</td>
<td>0.4</td>
</tr>
<tr>
<td>tartaric</td>
<td>0.3</td>
</tr>
<tr>
<td>citric</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\(^a\) The effective water activity coefficient of oxalic acid \( a_w/x_w \) is very close to unity and shows little variation in the measured concentration range. Therefore \( \frac{\gamma_s^\infty}{\gamma_s^{\text{sat}}} \approx 1 \) was assumed. Note however that a more elaborate treatment should take into account the acid dissociation, which is significant in the subsaturation concentration range.
Table 3. HLC data at 25°C and dissolution enthalpies. The last column provides the source of the sublimation pressure.

<table>
<thead>
<tr>
<th>molecule</th>
<th>$k_L$ (\frac{M}{atm\cdot m^2})</th>
<th>$\Delta H_{\text{g}\rightarrow\text{aq}}$ (kJ/mol^2)</th>
<th>source for $P^0_{\text{Cr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>linear diacids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oxalic</td>
<td>$6.0 \times 10^6$</td>
<td>73</td>
<td>Booth et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>$5.2 \times 10^6$</td>
<td>88</td>
<td>Soonsin et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>$6.2 \times 10^6$</td>
<td>92</td>
<td>Soonsin et al. (2010)$^a$</td>
</tr>
<tr>
<td>malonic</td>
<td>$3.1 \times 10^9$</td>
<td></td>
<td>Booth et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>$2.2 \times 10^9$</td>
<td>113</td>
<td>Cappa et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>$3.3 \times 10^9$</td>
<td></td>
<td>Supply and Ziemann (2005)</td>
</tr>
<tr>
<td>succinic</td>
<td>$6.7 \times 10^8$</td>
<td>62</td>
<td>Booth et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>$1.3 \times 10^9$</td>
<td>94</td>
<td>Soonsin et al. (2010)$^a$</td>
</tr>
<tr>
<td></td>
<td>$2.4 \times 10^9$</td>
<td>97</td>
<td>Cappa et al. (2007)$^b$</td>
</tr>
<tr>
<td>glutaric</td>
<td>$7.1 \times 10^8$</td>
<td>98</td>
<td>Booth et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>$6.3 \times 10^9$</td>
<td>94</td>
<td>Soonsin et al. (2010)$^a$</td>
</tr>
<tr>
<td></td>
<td>$5.4 \times 10^9$</td>
<td>97</td>
<td>Soonsin et al. (2010)$^a$</td>
</tr>
<tr>
<td></td>
<td>$2.5 \times 10^9$</td>
<td>109</td>
<td>Cappa et al. (2007)$^b$</td>
</tr>
<tr>
<td>adipic</td>
<td>$2.9 \times 10^9$</td>
<td>79</td>
<td>Booth et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>$6.7 \times 10^9$</td>
<td>106</td>
<td>Cappa et al. (2007)$^b$</td>
</tr>
<tr>
<td></td>
<td>$5.7 \times 10^8$</td>
<td>114</td>
<td>Bilde et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>$3.0 \times 10^9$</td>
<td>57</td>
<td>Salo et al. (2010)</td>
</tr>
<tr>
<td>pimelic</td>
<td>$1.1 \times 10^9$</td>
<td>121</td>
<td>Cappa et al. (2007)$^b$</td>
</tr>
<tr>
<td></td>
<td>$1.7 \times 10^9$</td>
<td>92</td>
<td>Bilde et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>$8.4 \times 10^8$</td>
<td>115</td>
<td>Salo et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>$2.4 \times 10^9$</td>
<td>129</td>
<td>Salo et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>$3.4 \times 10^9$</td>
<td>105</td>
<td>Ribeiro da Silva et al. (1999)$^c$</td>
</tr>
</tbody>
</table>
### Table 3. Continued.

<table>
<thead>
<tr>
<th>molecule</th>
<th>$k_h$ $\text{M atm}^{-1}$</th>
<th>$-\Delta H_{\text{eq}}$ $\text{kJ mol}^{-1}$</th>
<th>source for $p_{Cr}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>suberic</td>
<td>7.8 x 10^9</td>
<td>134</td>
<td>Cappa et al. (2007)^b</td>
</tr>
<tr>
<td></td>
<td>4.3 x 10^8</td>
<td>114</td>
<td>Chattopadhyay and Ziemann (2005)</td>
</tr>
<tr>
<td></td>
<td>1.2 x 10^6</td>
<td>150</td>
<td>Bilde et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>1.0 x 10^6</td>
<td>67</td>
<td>Salo et al. (2010)</td>
</tr>
<tr>
<td>azelaic</td>
<td>9.6 x 10^10</td>
<td>140</td>
<td>Cappa et al. (2007)^b</td>
</tr>
<tr>
<td></td>
<td>1.3 x 10^8</td>
<td>100</td>
<td>Chattopadhyay and Ziemann (2005)</td>
</tr>
<tr>
<td></td>
<td>1.6 x 10^8</td>
<td>115</td>
<td>Bilde et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>2.0 x 10^7</td>
<td>58</td>
<td>Salo et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>1.5 x 10^9</td>
<td>118</td>
<td>Ribeiro da Silva et al. (1999)^c</td>
</tr>
<tr>
<td>sebacic</td>
<td>7.7 x 10^9</td>
<td>140</td>
<td>Cappa et al. (2007)^b</td>
</tr>
<tr>
<td></td>
<td>8.4 x 10^7</td>
<td>100</td>
<td>Chattopadhyay and Ziemann (2005)</td>
</tr>
<tr>
<td></td>
<td>1.4 x 10^7</td>
<td>58</td>
<td>Salo et al. (2010)</td>
</tr>
<tr>
<td>hydroxy-polyacids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>malic</td>
<td>3.5 x 10^10</td>
<td></td>
<td>Booth et al. (2010)</td>
</tr>
<tr>
<td>tartaric</td>
<td>1.5 x 10^10</td>
<td></td>
<td>Booth et al. (2010)</td>
</tr>
<tr>
<td>citric</td>
<td>6.5 x 10^10</td>
<td></td>
<td>Booth et al. (2010)</td>
</tr>
</tbody>
</table>

^a Results using $p_{Cr}^0$ from a saturated solution.  
^b $p_{Cr}^0$ data measured at relatively high $T$: from 318–358 K for succinic acid to 353–385 K for sebacic acid.  
^c $p_{Cr}^0$ data measured at relatively high $T$: from 339–357 K for malonic acid to 367–377 K for azelaic acid.
Henry’s law constants of multifunctional acids

S. Compernolle and J.-F. Müller

Fig. 1. Comparing $\log_{10} \gamma^\infty$ at 298.15 K as estimated by different methods: AIOMFAC and UNIFAC-Raatikainen, vs. UNIFAC-Peng. For the linear diacids, AIOMFAC and UNIFAC-Peng are identical.

\[
\log_{10} \gamma^\infty = \hat{\gamma} \ln \gamma^w(t) (1 - \frac{2}{t^2})
\]
Fig. 2. Water activity at 25 °C in function of mass fraction solute, as predicted by UNIFAC-Peng, AIOMFAC and UNIFAC-Raatikainen, for malic, tartaric and citric acid. Experimental data from Maffia and Meirelles (2001) and Apelblat et al. (1995) is also included.
**Fig. 3.** Water activity coefficient data vs. water mole fraction for malic and tartaric acid. Experimental data was taken from the figures of Peng et al. (2001), and fitted with Margules, Van Laar or Wilson expressions for the activity coefficient. The solute IDAC $\gamma_s^\infty$ resulting from the different fittings is given in the legend. In the case of tartaric acid, the fitting with the Wilson expression was not successful. For a reference, the UNIFAC-Peng estimation is also included.
Fig. 4. Logarithm of the solubility mole fraction at 298.15 K of linear diacids, and of the ideal solubility mole fraction, as calculated by Eq. (13). Solubility data was taken from Apelblat and Manzurola (1987, 1989, 1990); Bretty et al. (2006), fusion data from Booth et al. (2010); Roux et al. (2005).
Fig. 5. Enthalpies and entropies of fusion and solution for linear diacids, and their differences. Note that for the enthalpies $\Delta H/(R T_{\text{ref}})$, $T_{\text{ref}} = 298.15 \text{K}$ is plotted, and for the entropies $\Delta S/R$. 

The graph shows the trend of $\Delta H_{\text{fus}}$, $\Delta S_{\text{sol}}$, $\Delta H_{\text{sol}}$, $\Delta S_{\text{sol}} - \Delta S_{\text{fus}}$, $\Delta H_{\text{sol}} - \Delta H_{\text{fus}}$, and $\Delta S_{\text{sol}} - \Delta S_{\text{fus}}$ against the number of carbon atoms from 2 to 10.
Fig. 6. $\log_{10} k_H$ (a) and $\Delta H_{g \rightarrow aq}$ (b) of linear diacids, grouped per data source of sublimation pressure.