



Henry's law
constants of polyols

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Abstract

Henry's law constants (HLC) are derived for several polyols bearing between 2 and 6 hydroxyl groups, based on literature data for water activity, vapour pressure and/or solubility. Depending on the case, infinite dilution activity coefficients (IDACs), solid state pressures or activity coefficient ratios are obtained as intermediary results. For most compounds, these are the first values reported, while others compare favourably with literature data in most cases. Using these values and those from a previous work (Compernelle and Müller, 2014), an assessment is made on the partitioning of polyols, diacids and hydroxy acids to droplet and aqueous aerosol.

1 Introduction

Henry's law constant (HLC) describes the partitioning of a compound between the gas phase and a liquid, highly dilute solution. In the atmosphere, such dilute solutions, with water as the solvent, can be reached in cloud droplets. Aqueous aerosols are another example where liquid water is important, but in this case the solvent must be regarded as multicomponent, with significant inorganic and/or organic contributions. In a previous work (Compernelle and Müller, 2014) we determined additional HLC data for diacids and hydroxy polyacids, from water activities, solubilities and vapour pressures, employing thermodynamic relationships. We follow the same approach in this work, but with a focus on polyols: compounds with two or more hydroxyl groups, but no other functional group. Polyols such as 2-methyl tetrols were identified as important secondary organic aerosol (SOA) constituents (Claeys et al., 2004).

In Sect. 2, we first briefly review the thermodynamic relationships employed to derive HLC (k_h) and the associated enthalpy of gas phase dissolution ($\Delta H_{L \rightarrow aq}^\infty$). In Sect. 3 we derive intermediary results, namely infinite dilution activity coefficients (IDACs), solid state pressures and activity coefficient ratios, which are necessary components in deriving HLC but not as such available in the literature for all compounds. Next (Sect. 4),

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we present k_h and $\Delta H_{L \rightarrow aq}^{\infty}$ using the data from the previous Section and other literature data. In Sect. 5, we discuss the implications for partitioning to cloud droplets and aqueous ammonium sulfate aerosol, making use of the activity coefficient model AIOMFAC (Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients) (Zuend et al., 2011). We extend this also to dicarboxylic acids and hydroxy polyacids, making use of the model E-AIM (Extended AIM Aerosol Thermodynamics Model) to calculate the acid dissociation.

2 Thermodynamic relationships between HLC and other quantities

For HLC, several definitions exist. We will follow here the convention used by Sander (1999).

$$k_h \equiv \lim_{c_s, p_s \rightarrow 0} \frac{c_s}{p_s} \quad (1)$$

with c_s the solute molar concentration of the solution and p_s its partial pressure above it. Note that we assume ideal gas behaviour for the solute. With this convention, a larger k_h means a higher partitioning of the solute to the solution. At some point, we will employ also another definition of HLC, following again the notation of Sander (1999),

$$k_h^{px} \equiv \lim_{x_s, p_s \rightarrow 0} \frac{x_s}{p_s} \quad (2)$$

with x_s the solute mole fraction. The relation between both quantities is

$$k_h/k_h^{px} = c_{sol} \quad (3)$$

with c_{sol} the total molar concentration of the solution, (or solvent, since we assume that the solute is infinitely diluted). In case the solvent is pure water, we write $c_{sol} = c_w$.

If the solute is a liquid at the temperature of interest and the solvent is water, k_h can be obtained by Eq. (4)

$$k_h = \frac{c_w}{\gamma^\infty \rho_L^0} \quad (4)$$

5 with γ^∞ the infinite dilution activity coefficient (IDAC) of the solute (mole fraction based and with the symmetric convention $\gamma^\infty = 1$ for pure liquid solute) and ρ_L^0 its liquid vapour pressure. The corresponding enthalpy change (neglecting the small temperature dependence of c_w) is equal to

$$-\frac{d \ln k_h}{d(1/T)} = \Delta H_{g \rightarrow aq}^\infty$$

$$= \Delta H_{L \rightarrow aq}^\infty - \Delta H_{vap} \quad (5)$$

$$\Delta H_{L \rightarrow aq}^\infty = \frac{d \ln \gamma^\infty}{d(1/T)} \quad (6)$$

$$\Delta H_{vap} = -\frac{d \ln \rho_L^0}{d(1/T)} \quad (7)$$

15 with ΔH_{vap} the enthalpy of vaporisation and $\Delta H_{L \rightarrow aq}^\infty$ the enthalpy of solution of the liquid, at infinite dilution. If the solute is a solid at room temperature, as is generally the case for polyols with more than three hydroxyl groups, the following equation can be applied instead of Eq. (4).

$$k_h = \frac{\gamma^{sat} c_w X^{sat}}{\gamma^\infty \rho_{Cr}^0} \quad (8)$$

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with x^{sat} the solute mole fraction at the solubility limit and γ^{sat} the corresponding activity coefficient. In case the solubility is small, $\gamma^{\infty}/\gamma^{\text{sat}} \approx 1$ and Eq. (8) reduces to

$$k_h \approx c_w \frac{x^{\text{sat}}}{\rho_{\text{Cr}}^0} \quad (9)$$

5 The corresponding enthalpy change (again neglecting the temperature dependence of c_w) is equal to

$$\begin{aligned} \Delta H_{\text{g} \rightarrow \text{aq}}^{\infty} &= -R \frac{d \ln k_h}{d(1/T)} \\ &= \Delta H_{\text{Cr} \rightarrow \text{aq}}^{\infty} - \Delta H_{\text{sub}} \end{aligned} \quad (10)$$

$$\Delta H_{\text{Cr} \rightarrow \text{aq}}^{\infty} = - \frac{d \ln \frac{\gamma^{\text{sat}} x^{\text{sat}}}{\gamma^{\infty}}}{d(1/T)} \quad (11)$$

$$10 \quad \Delta H_{\text{sub}} = - \frac{d \ln \rho_{\text{Cr}}^0}{d(1/T)} \quad (12)$$

with ΔH_{sub} the sublimation enthalpy and $\Delta H_{\text{Cr} \rightarrow \text{aq}}^{\infty}$ the enthalpy of solution of the solid at infinite dilution. The data required for Eqs. (4), (5), (8) and (10) is not always available as such in the literature. In Sect. 3, data for IDACs, solid state pressures and activity coefficient ratios is derived.

3 Intermediary results

3.1 Infinite dilution activity coefficients

In case the compound is a liquid at room temperature, Eq. (4) applies and the IDAC is required. Estimation methods to calculate activity coefficients exist (e.g. Peng et al.,

2001; Marcolli and Peter, 2005; Compernelle et al., 2009; Zuend et al., 2011) but experimental data is preferred. Suleiman and Eckert (1994) provide IDAC data for diols, but only for compounds with up to four carbon atoms. For many other polyols, the IDAC of the solute is not reported, but instead data is available on the water activity a_w over the entire concentration range. In that case, γ_s^∞ can be obtained by the integral form of the Gibbs-Duhem relation (Prausnitz et al., 1999),

$$\ln \gamma_s^\infty = \int_0^1 \frac{\ln \gamma_w(t)}{(1-t)^2} dt \quad (13)$$

with $\gamma_w = a_w/x_w$ the activity coefficient of water and x_w the water mole fraction. Note that we added the subscript "s" to γ^∞ to distinguish clearly the activity coefficient of the solute and the activity coefficient of water. An activity coefficient expression f can be used, e.g. Margules, Van Laar, Wilson or UNIQUAC (Prausnitz et al., 1999; Carlson and Colburn, 1942), to fit the $\ln \gamma_w$ data of a binary system. Marcolli and Peter (2005) provide a_w data for 14 diols and two triols over the whole composition range, but the data is rather coarse grained. This is especially critical in the dilute region; from Eq. (13) it can be concluded that a small change in $\ln \gamma_w$ leads to a comparatively large change in $\ln \gamma_s$ (see Eq. 13). Therefore, where possible, we included also more fine grained data in the dilute region (Borghesani et al., 1989; Romero and Páez, 2006). Sometimes it was difficult to fit both types of data sets well with a single activity coefficient expression. In such a case, we applied the following

$$\ln \gamma_s^\infty = \int_0^{\bar{x}_w} \frac{f^{(1)}(t)}{(1-t)^2} dt + \int_{\bar{x}_w}^1 \frac{f^{(2)}(t)}{(1-t)^2} dt \quad (14)$$

with $f^{(1)}, f^{(2)}$ two $\ln \gamma(t)$ expressions, one fitted to the data of Marcolli and Peter (2005), the other to the data applicable to the dilute region $[\bar{x}_w, 1]$. Both for Eqs. (13) and (14),

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the activity coefficient expressions with the lowest standard deviation vs. experimental $\ln \gamma_w$ were chosen. The results are provided in Table 1. For the cases where Eq. (14) was applied, Eq. (13) was also applied to the data of Marcolli and Peter (2005); in most cases, the difference in the resulting IDAC is rather small. This indicates that even in those cases where only the coarse grained data of Marcolli and Peter (2005) is available, the derived γ_s^∞ are still quite reliable, at least for the smaller γ_s^∞ . However, for the more hydrophobic diols (1,2-pentane diol, 1,2-hexane diol, 1,7-heptane diol), where γ_s rises quickly in the dilute region and no fine grained a_w data is available, the uncertainty will be larger.

γ_s^∞ for pentane and hexane diols, derived from surface tension data, are reported by Romero et al. (2007); Páez et al. (2011). These are considerably higher than the data presented in Table 1. However, as explained by Brocos et al. (2007), very accurate surface tension data is a prerequisite to derive γ_s^∞ ; γ_s^∞ of diols, derived from surface tension data, are all overestimated compared to the literature data in their analysis. Moreover, it is not clear to us if the applied approximation (the Volmer surface equation of state, see Gracia-Fadrique et al., 2002) is valid in this case.

3.2 Solid state pressures

Liquid vapour pressure of organic compounds can be estimated (e.g. Pankow and Asher, 2008; Nannoolal et al., 2008; Compennolle et al., 2011), but for polyfunctional compounds the result is often not accurate. Solid state pressure is even more difficult to estimate, due to the crystal contribution. Therefore, experimental data is preferred. Solid state and/or liquid vapour pressure data for polyols with four or more hydroxyl groups is available (Barone et al., 1990; Bradley and Cotson, 1953; Nitta et al., 1950, 1951), but obtained at temperatures considerably above room temperature. The solid state pressure at $T_{\text{ref}} = 298.15\text{K}$ is given by

$$\ln p_{\text{Cr}}^0(T_{\text{ref}}) = 1/R \left(\Delta S_{\text{sub}}(T_{\text{ref}}) - \frac{1}{T_{\text{ref}}} \Delta H_{\text{sub}}(T_{\text{ref}}) \right) \quad (15)$$

If at the temperature of measurement T_{meas} , the compound is a solid, the following transformation is applied

$$\Delta S_{\text{sub}}(T_{\text{ref}}) = \Delta S_{\text{sub}}(T_{\text{meas}}) + \int_{T_{\text{meas}}}^{T_{\text{ref}}} \frac{C_{p,g} - C_{p,cr}}{T} dT \quad (16)$$

$$\Delta H_{\text{sub}}(T_{\text{ref}}) = \Delta H_{\text{sub}}(T_{\text{meas}}) + \int_{T_{\text{meas}}}^{T_{\text{ref}}} (C_{p,g} - C_{p,cr}) dT$$

If at T_{meas} the compound is a liquid, the transformation is

$$\Delta S_{\text{sub}}(T_{\text{ref}}) = \Delta S_{\text{vap}}(T_{\text{meas}}) + \int_{T_{\text{meas}}}^{T_{\text{fus}}} \frac{C_{p,g} - C_{p,L}}{T} dT + \Delta S_{\text{fus}}(T_{\text{fus}}) + \int_{T_{\text{fus}}}^{T_{\text{ref}}} \frac{C_{p,g} - C_{p,cr}}{T} dT \quad (17)$$

$$\Delta H_{\text{sub}}(T_{\text{ref}}) = \Delta H_{\text{vap}}(T_{\text{meas}}) + \int_{T_{\text{meas}}}^{T_{\text{fus}}} (C_{p,g} - C_{p,L}) dT + \Delta H_{\text{fus}}(T_{\text{fus}}) + \int_{T_{\text{fus}}}^{T_{\text{ref}}} (C_{p,g} - C_{p,cr}) dT$$

with $C_{p,g}$, $C_{p,L}$, $C_{p,cr}$ the constant pressure heat capacities for respectively gas, liquid and crystalline phase, T_{fus} the melting temperature, ΔS_{fus} , ΔH_{fus} the entropy and enthalpy of fusion, and ΔS_{vap} , ΔH_{vap} the entropy and enthalpy of vaporisation. Fusion data was taken from Barone et al. (1990); Tong et al. (2007, 2010a, 2009); Badea et al. (2014). Experimental heat capacity data for solid and liquid was taken from Tong et al. (2007, 2008, 2009, 2010a, b); Zhang and Yang (1989); Della Gatta et al. (1999), while for the gas it was calculated by the method of Benson (1976), available in the NIST Chemistry Webbook (Stein and Brown). In Table 2 the derived solid state pressures and sublimation enthalpies at room temperature are presented.

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There is a good agreement between the fusion data (T_{fus} and ΔH_{fus}) between different data sources. $C_{p,L}$ and $C_{p,Cr}$ were not always available. In that case, the data of a stereo-isomer was taken instead. For liquid phase heat capacities, this can be justified by (i) the similar $C_{p,L}$ of xylitol and adonitol, and (ii) the similar ΔS_{vap} and ΔH_{vap} of stereo isomers reported by Barone et al. (1990), indicating similar thermodynamic properties of the liquid phase. Neglecting the integrals involving the heat capacity differences in Eqs. (16) and (17) can lead to serious error: while for the tetrols the change is only minor, there is a factor 5 to 7 increase in $\rho_{Cr}^0(298.15\text{K})$ for the pentols and most hexols, and a factor 40 increase for sorbitol. Estimating $C_{p,g}$ with the method of Joback and Reid (1987) instead of the method of Benson (1976) led to changes in $\rho_{Cr}^0(298.15\text{K})$ smaller than a factor two. Note that these two methods do not take the intramolecular hydrogen bonding into account. The group contribution $C_{p,g}$ estimation method of Paraskevas et al. (2013); Sabbe et al. (2008), based on quantum chemical data, does include corrections for intramolecular hydrogen bonds. However, it is not clear how to apply these correction terms for species with 3 or more hydroxyl groups. Using one HOCCO term (NNI5 in the terminology of Paraskevas et al. (2013)) per hydroxyl group for the linear polyols, one obtains a factor 2 to 3 higher $\rho_{Cr}^0(298.15\text{K})$ for the pentols and hexols, compared to the case where this term is neglected.

In most cases the high temperature ρ_L^0 or ρ_{Cr}^0 data is obtained from a single reference (Barone et al., 1990); only for erythritol and pentaerythritol is a comparison possible between different data sources. The high temperature ρ_L^0 or ρ_{Cr}^0 data of erythritol and pentaerythritol is comparable among the different data sources (Barone et al., 1990; Bradley and Cotson, 1953; Nitta et al., 1951, 1950), but due to differences in ΔH_{vap} or ΔH_{sub} , the extrapolated $\rho_{Cr}^0(298.15\text{K})$ is a factor 7 to 50 higher if the data of Nitta et al. (1950, 1951) is used. In these latter cases the enthalpy is determined over a quite narrow temperature interval ($\sim 12\text{K}$). The data of Bradley and Cotson (1953); Barone et al. (1990) is determined over a 30 to 40 K interval and is therefore considered more reliable.

3.3 Activity coefficient ratios

The ratio $\gamma_s^\infty / \gamma_s^{\text{sat}}$ can be obtained from water activity data in the subsaturation range (Compernelle and Müller, 2014).

$$\ln \frac{\gamma_s^\infty}{\gamma_s^{\text{sat}}} = \frac{1 - x_s^{\text{sat}}}{x_s^{\text{sat}}} \ln \gamma_w(\tilde{x}_w) + \int_{\tilde{x}_w}^1 \frac{\ln \gamma_w(t)}{(1-t)^2} dt \quad (18)$$

$$\tilde{x}_w = 1 - x_s^{\text{sat}}$$

The polyols with more than three hydroxyl groups considered here are solid at room temperature. Their water activity is only measured up to the solubility limit, if measured at all. Similarly to our previous work (Compernelle and Müller, 2014), activity coefficient expressions (Margules, Van Laar, Wilson (see e.g. Prausnitz et al., 1999; Carlson and Colburn, 1942)) were fitted to a_w data in the subsaturation range, and the fitting parameters were used to obtain the solute activity coefficient ratio $\gamma_s^\infty / \gamma_s^{\text{sat}}$. This was done for erythritol, xylitol, sorbitol and mannitol (Fig. 1). The UNIFAC (UNIQUAC Functional-Group Activity Coefficient) method of Marcolli and Peter (2005) (UNIFAC-MP, identical to AIOMFAC for polyol-water systems) underestimates γ_w of these polyols.

For adonitol and arabinitol, we calculated $\gamma_s^\infty / \gamma_s^{\text{sat}}$ from the simple but successful one parameter Margules fittings of Chirife et al. (1984). The results are presented in Table 3. For nonane diol, decane diol, pentaerythritol and dulcitol, no a_w data was found, but reasonable assumptions for $\gamma_s^\infty / \gamma_s^{\text{sat}}$ could be made. As expected, the polyols with a lower solubility (erythritol, mannitol) have $\gamma_s^\infty / \gamma_s^{\text{sat}}$ close to unity. We included estimations of the activity coefficient ratio by UNIFAC-MP. This method gave lower $\gamma_s^\infty / \gamma_s^{\text{sat}}$ as compared to our results.

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4 Henry's law constants and enthalpies of gas dissolution

Using Eqs. (4), (5), (9) and (10), the data provided in the previous Tables, as well as literature data, the Henry's law constants and gas dissolution enthalpies can be derived. The values are tabulated in Table 4.

The expected order hexols > pentols > tetrol > tritol > diol in k_h is generally followed. Diols have k_h between 10^5 and 10^7 M atm⁻¹. The diols with longer hydrophobic chains have considerably lower k_h than their α, ω counterparts (e.g. an order of magnitude difference between 1,2- and 1,5-pentanediol). For the linear polyols, k_h and $\Delta H_{g \rightarrow aq}^\infty$ are roughly comparable among the different stereo-isomers. Clearly, the large differences in x^{sat} and ρ_{Cr}^0 of the hexols are mainly due to their different crystal structure, which does not affect k_h . Although pentaerythritol has the same number of hydroxyl groups as erythritol, its k_h is 10 times larger. Probably the tetragonal arrangement of the hydroxyl groups of pentaerythritol facilitates bonding with the water molecules.

5 Impact on gas-particle partitioning

Similarly as for the diacids and hydroxy polyacids (Compernelle and Müller, 2014), we assess the importance of the partitioning to the particulate phase for polyols in clouds and aqueous aerosol, approximating the liquid phase as a dilute aqueous solvent. Moreover, we also perform a sensitivity test, aiming at determining the particulate fraction of polyols, diacids and hydroxy polyacids in the case of an aqueous ammonium sulfate aerosol.

5.1 Pure water as the solvent

For clouds, the liquid water content (LWC) varies between typically 0.1 and 1 g m⁻³, and for aqueous aerosols between 10⁻⁶ and 10⁻⁴ g m⁻³ (Ervens et al., 2011). The

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particulate fraction of organic solute is equal to

$$f_{p,s} \equiv \frac{n_{p,s}}{n_{p,s} + n_{g,s}} \quad (19)$$

with $n_{p,s}$, $n_{g,s}$ the moles of solute in particulate and gas phase respectively. If partitioning between gas and aqueous phase is governed solely by Henry's law, and the solvent is considered pure water, $f_{p,s}$ can be calculated from

$$f_{p,s} = \frac{1}{k^*/k_h + 1}, \text{ with } k^* = \frac{\rho_w}{LWC} \frac{1}{RT} \quad (20)$$

with ρ_w the density of pure water. For clouds, k^* varies between 4×10^4 and $4 \times 10^5 \text{ Matm}^{-1}$. From Table 4, it can be deduced that all polyols with three or more hydroxyl groups will be almost completely partitioned to the aqueous phase. Diols will be completely or partially in the aqueous phase, depending on the case. For aqueous aerosol, if one (falsely) assumes the aerosol phase to be pure water, k^* varies between 4×10^8 and $4 \times 10^{10} \text{ Matm}^{-1}$. With this assumption, diols will not partition appreciably to the aqueous phase, glycerol will partition to some extent, and only at the highest water content, while all polyols with four or more hydroxy groups should reside almost completely in the particulate phase.

5.2 Aqueous ammonium sulfate aerosol as the solvent

An aqueous aerosol is not a dilute aqueous solution, but is instead a concentrated mixture of organics and/or inorganics. HLC determined for a pure water solvent are less applicable to such mixtures. We present here a sensitivity test for a simple aerosol mixture of water and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, AS). It is more convenient to use

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here the alternative HLC definition k_h^{DX} instead (Eq. 2). k_h^{DX} can be equated to

$$k_h^{DX} = \lim_{n_{g,s}, n_{p,s} \rightarrow 0} \frac{n_{p,s}/n_{p,tot}}{\frac{n_{g,s}}{V_{air}} RT} = \frac{f_{p,s}}{1 - f_{p,s}} \frac{V_{air}}{n_{p,tot} RT} \quad (21)$$

with $n_{g,s}, n_{p,s}$ the number of moles of solute in gas and particulate phase respectively;
 5 $n_{p,tot}$ the total number of moles of the solution and V_{air} a unit volume of air. Conversely, the particulate fraction is equal to

$$f_{p,s} = \frac{1}{1 + \frac{1}{k_h^{DX}} \frac{V_{air}}{RT} n_{p,tot}} \quad (22)$$

Note that in the particular case of the AS–water system

$$10 \quad n_{p,tot} = n_{p,w} + 3n_{p,AS} + n_{p,s} = n_{p,w} + 3n_{p,AS} \quad (23)$$

as each molecule of AS dissociates in three ions, and the amount of solute is infinitesimally small.

The organic solutes considered are the polyols discussed in this work, and the
 15 diacids and hydroxy polyacids treated in our previous work (Compernelle and Müller, 2014). k_h^{DX} of a solute for a solvent consisting of water and a mole fraction x_{AS} of dissolved AS can be calculated from

$$k_h^{DX}(x_{AS}) = k_h^{DX}(x_{AS} = 0) \frac{\gamma_s^\infty(x_{AS} = 0)}{\gamma_s^\infty(x_{AS})} = k_h^{DX}(x_{AS} = 0) \frac{1}{\gamma_s^*} \quad (24)$$

20 with γ_s^* the activity coefficient of the organic solute using the asymmetric convention (i.e. $\gamma^* = 1$ if the solute is infinitely diluted in pure water). $k_h^{DX}(x_{AS} = 0)$ was taken from Table 4 or Table 3 of Compernelle and Müller (2014) (recommended values only), after the appropriate conversion $k_h^{DX} = c_w k_h \cdot \gamma_s^\infty(x_{AS})$ and $\gamma_s^\infty(x_{AS} = 0)$ were calculated with

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the model AIOMFAC (Zuend et al., 2011), available online (<http://www.aiomfac.caltech.edu>). This model calculates activity coefficients taking interactions between water, organics and inorganics into account. A very small organic mole fraction ($x_{\text{org}} = 10^{-10}$) was chosen to ensure that $\gamma_s^\infty(x_{\text{AS}})$ and $\gamma_s^\infty(x_{\text{AS}} = 0)$ represent IDACs. As a consequence, the impact of the organic solute on the activities of water and the ions is negligible. Although the activities are estimated and not measured, we note that activity data sets of several AS–water–organic mixtures (organic being a polyol, diacid or hydroxy polyacid) are used to determine AIOMFAC's parameters (Zuend et al., 2011).

Given a particular x_{AS} , the water activity and hence the relative humidity (RH) are fixed by the AIOMFAC model. Note that AS has a deliquescence RH (DRH) of 79.5 % and an efflorescence RH (ERH) of ~ 35 % (Martin, 2000). Below the ERH, only solid AS is present in the particulate phase.

The particulate fraction $f_{\text{p,s}}$ of the organic solute depends on the amount of solvent (water + AS) per volume of air. A fixed AS mass concentration of $4 \mu\text{g m}^{-3}$ was chosen, typical for inorganic aerosols at mid-latitudes over continents (<http://vista.cira.colostate.edu/improve/>). As a consequence, upon increasing RH from the ERH to 90 %, the LWC varies between 10^{-6} and 10^{-5}g m^{-3} , a typical range for aqueous aerosol.

Polyols. Due to their low k_h , diols do not partition significantly to aqueous aerosol and hence are not included in this analysis. Stereo isomers of xylitol and sorbitol were also not included, given their similar k_h and the fact that AIOMFAC does not distinguish between stereo isomers. For the polyols, AIOMFAC predicts an activity increase with lowering RH (or equivalently increasing the salt concentration) (Fig. 2a). The effect increases with the number of hydroxyl groups. However, this is more than compensated by the concomitant increase in $k_h(x_{\text{AS}} = 0)$ (Table 4). The particulate fraction of polyols decreases with decreasing RH both due to the increase in solute activity, and the decrease of total absorbing mass. Glycerol, with three hydroxyl groups, has left the particulate phase for 95 % already at RH = 90 % (Fig. 2b). On the other hand, sorbitol, with six hydroxyl groups, is still for 50 % in the particulate phase at RH = 44 %.

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Linear diacids. Diacids with two (oxalic) up to ten (sebacic) carbon atoms are considered. Let us neglect acid dissociation for the moment. AIOMFAC's interaction parameters are negative (stabilising) between the carboxylic acid group COOH on the one hand, and the ions NH_4^+ and SO_4^{2-} on the other hand. For the group CH_2 , these interaction parameters are positive (destabilising). As a consequence, the activity of the linear diacids with 4 carbon atoms or more increases with decreasing RH. The activity of oxalic acid, on the other hand, decreases with decreasing RH, while the activity of malonic acid stays roughly constant. Even without taking acid dissociation into account, it is clear that these diacids partition appreciably to the particulate phase (Fig. 2b). Note that for malonic acid, we chose the lower of the recommended k_h values from Table 3 of Compernelle and Müller (2014); the higher value would lead to f_p near unity even without acid dissociation.

Hydroxy polyacids. Citric and tartaric acid exhibit a modest activity increase upon decrease of the RH. On the other hand, they have extremely high $k_h(x_{\text{AS}} = 0)$ values (Compernelle and Müller, 2014). Therefore, they will reside almost completely in the particulate phase from RH = 100 % to the ERH.

Impact of acid dissociation. The effective HLC, $k_h^{\text{px,eff}}$, of a polyacid is larger than k_h^{px} due to acid dissociation. For a diacid one has

$$k_h^{\text{px,eff}} = \frac{x_{\text{H}_2\text{A}} + x_{\text{HA}^-} + x_{\text{A}^{2-}}}{\rho_{\text{H}_2\text{A}}} \quad (25)$$

with $x_{\text{H}_2\text{A}}$, x_{HA^-} and $x_{\text{A}^{2-}}$ the mole fractions of the undissociated acid, monodissociated acid and twice dissociated acid respectively. Acid dissociation is governed by the acid dissociation constants

$$K_{\text{a},1} = \frac{\gamma_{\text{H}^+} x_{\text{H}^+} \gamma_{\text{HA}^-} x_{\text{HA}^-}}{\gamma_{\text{H}_2\text{A}} x_{\text{H}_2\text{A}}} \quad (26)$$

$$K_{\text{a},2} = \frac{\gamma_{\text{H}^+} x_{\text{H}^+} \gamma_{\text{A}^{2-}} x_{\text{A}^{2-}}}{\gamma_{\text{HA}^-} x_{\text{HA}^-}}$$

with $K_{a,j}$ mole fraction based acid dissociation constants, and γ^* mole fraction based activity coefficients, with the asymmetric convention (i.e. becoming unity at infinite dilution in pure water). Combining Eqs. (25) and (26) leads to

$$K_h^{px,eff} = K_h^{px} \left(1 + K_{a,1} \frac{\gamma_{H_2A}^*}{\gamma_{HA^-}^* \gamma_{H^+}^* x_{H^+}} + K_{a,1} K_{a,2} \frac{\gamma_{H_2A}^*}{\gamma_{A^{2-}}^*} \left(\frac{1}{\gamma_{H^+}^* x_{H^+}} \right)^2 \right) \quad (27)$$

AIOMFAC does not calculate activity coefficients of ionised organic acids. To describe the ionisation in the water–AS–diacid system, we used the models provided at the site of E-AIM (<http://www.aim.env.uea.ac.uk/aim/aim.php>). Specifically, model IV was used, which is an implementation of the parameterisations of Friese and Ebel (2010) and (for the diacids) of Clegg and Seinfeld (2006). Solid formation was prevented, and the dissociation equilibria H_2O/OH^- , NH_4^+/NH_3 , HSO_4^-/SO_4^{2-} were taken into account. At the vanishingly small acid concentration used, E-AIM calculates the same $\gamma_{H_2A}^*$, $\gamma_{HA^-}^*$ and $\gamma_{A^{2-}}^*$ regardless of the identity of the diacid. This is not realistic; one expects a larger γ^* value for a diacid with more CH_2 groups. Therefore, $\gamma_{H_2A}^*$, equal to γ_s^* in Eq. (24), is still calculated by AIOMFAC, to take into account the destabilising CH_2 -ion interaction. $\gamma_{H^+}^* x_{H^+}$, $\frac{\gamma_{H_2A}^*}{\gamma_{HA^-}^*}$ and $\frac{\gamma_{H_2A}^*}{\gamma_{A^{2-}}^*}$ in Eq. (27) are determined by the E-AIM calculation. Note that due to the vanishingly small acid concentration, $\gamma_{H^+}^* x_{H^+}$ is determined by the amounts of water and AS only. Acid dissociation constants were taken from E-AIM or Apelblat (2002). Oxalic and malonic acid are predicted to be completely in the aqueous phase from RH = 100 % to the ERH, while the particulate fraction of the other diacids are clearly enhanced (Fig. 2c), compared to the calculation without acid dissociation (Fig. 2b).

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6 Discussion and conclusions

6.1 Assessing main uncertainties

HLC of polyols with 2–6 hydroxy groups are derived in this work, using experimental data and thermodynamic relationships. This study complements a previous work (Compernelle and Müller, 2014) where the focus was on diacids and hydroxy polyacids. For the polyols with four or more hydroxy groups, the largest source of uncertainty is probably the use of solid state pressures extrapolated over a large temperature interval. Room temperature measurements of solid state pressure will lead to more precise k_h values. Alternatively, improvement is possible by using $C_{p,g}$ derived from experiment or from ab initio calculations in Eqs. (16) and (17), rather than using a group contribution method. For some more hydrophobic diols studied here (1,2-pentane diol, 1,2-hexane diol, 1,7-heptane diol), the largest uncertainty probably lies in the derived γ_s^∞ . More fine grained a_w data in the dilute region could accommodate for this. For nonane diol and decane diol, only solubilities from a secondary reference (Merck Millipore) could be retrieved; new solubility measurements are desirable to obtain a better k_h estimate.

6.2 Comparison with literature

HLC compilations of polyols are provided by e.g. Sander (1999) and Saxena and Hildemann (1996). However, most values in these studies are estimated. Bone et al. (1983) provide HLC measurements for 1,2-ethane diol and 1,3-propane diol (Table 4). Their values are lower but reasonably close (within a factor of 2) to ours. While the majority of HLC values of polyols provided by Saxena and Hildemann (1996) are estimated, a few are derived from vapour-liquid equilibrium data. For 1,2-propane diol, 2,3-butane diol and glycerol, their HLC values are within a factor 3, but for 1,4-butane diol the difference is more than an order of magnitude. The estimated values presented by Saxena and Hildemann (1996) are obtained by a group-contribution method (Suzuki et al., 1992) (values not reproduced in Table 4). For the diols, overestimations by ~ 1 order

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of magnitude compared to our values are common. For the compounds with three or more hydroxyl groups, the overestimation ranges between 3 (glycerol) and 8 (mannitol) orders of magnitude, showing the limitations of such an estimation method.

6.3 Atmospheric implications

5 According to the HLC derived in this and the previous work (Compernelle and Müller, 2014), diols will be partially or completely in the aqueous phase in clouds, while polyols with three or more hydroxyl groups, diacids and hydroxy polyacids will be completely in the aqueous phase. Regarding aqueous aerosol, the sensitivity test performed here using aqueous AS aerosol indicates that polyols with four or more hydroxyl groups
10 are significantly or totally in the particulate phase, depending on the RH. The same holds for the longer linear diacids (succinic and higher). The shorter linear diacids (oxalic and malonic), and the hydroxy polyacids (citric and tartaric) are completely in the particulate phase both at lower and higher RH, due to (i) their relatively high acid dissociation constants and/or (ii) stabilizing or only mildly destabilizing interactions with
15 AS and/or (iii) very high k_h values.

Bao et al. (2012) measured gas particle partitioning of diacids at a site in Japan in different seasons. According to this study, both particulate and gaseous fractions are significant, and RH influences the partitioning. Xie et al. (2014) measured gas particle partitioning of 2-methyl tetrols at a site in Denver and found about equal particulate and
20 gaseous fractions. Our sensitivity test, based on a simple AS–water aerosol system, cannot be quantitatively compared with these studies, but does show that partitioning to the particulate phase is important for diacids and tetrols.

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- Apelblat, A.: Dissociation constants and limiting conductances of organic acids in water, *J. Mol. Liq.*, 95, 99–145, 2002. 13544
- 5 Badea, E., Nowicka, B., and Della Gatta, G.: Thermodynamics of fusion and sublimation for a homologous series of eleven alkane- α , ω -diols HO-(CH₂)_n-OH: structure-related odd-even effect, *J. Chem. Thermodyn.*, 68, 90–97, 2014. 13536, 13555
- Bao, L., Matsumoto, M., Kubota, T., Sekiguchi, K., Wang, Q., and Sakamoto, K.: Gas/particle partitioning of low-molecular-weight dicarboxylic acids at a suburban site in Saitama, Japan, *Atmos. Environ.*, 47, 546–553, 2012. 13546
- 10 Barone, G., Gatta, G. D., Ferro, D., and Piacente, V.: Enthalpies and entropies of sublimation, vaporization and fusion of nine polyhydric alcohols, *J. Chem. Soc. Faraday T.*, 86, 75–79, 1990. 13535, 13536, 13537, 13555
- Bastos, M., Nilsson, S.-O., Ribeiro da Silva, M. D., Ribeiro da Silva, M. A., and Wadsö, I.: Thermodynamic properties of glycerol enthalpies of combustion and vaporization and the heat capacity at 298.15 K. Enthalpies of solution in water at 288.15, 298.15, and 308.15 K, *J. Chem. Thermodyn.*, 20, 1353–1359, 1988. 13557
- 15 Benson, S. W.: *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, John Wiley & Sons, New York, 1976. 13536, 13537, 13555, 13557
- Bone, R., Cullis, P., and Wolfenden, R.: Solvent effects on equilibria of addition of nucleophiles to acetaldehyde and the hydrophilic character of diols, *J. Am. Chem. Soc.*, 105, 1339–1343, doi:10.1021/ja00343a044, 1983. 13545, 13557
- 20 Bonner, O. D. and Breazeale, W. H.: Osmotic and activity coefficients of some nonelectrolytes, *J. Chem. Eng. Data*, 10, 325–327, doi:10.1021/je60027a007, 1965. 13556
- Borghesani, G., Pedriali, R., and Pulidori, F.: Solute-solute-solvent interactions in dilute aqueous solutions of aliphatic diols. Excess enthalpies and gibbs free energies, *J. Solution Chem.*, 18, 289–300, 1989. 13534, 13554
- 25 Bower, V. E. and Robinson, R. A.: Isopiestic vapor pressure measurements of the ternary system: sorbitol-sodium chloride-water at 25 °C, *J. Phys. Chem.*, 67, 1540–1541, doi:10.1021/j100801a033, 1963. 13556
- 30 Bradley, R. S. and Cotson, S.: The vapour pressure and lattice energy of hydrogen-bonded crystals. Part II. α - and β -anhydrous oxalic acid and tetragonal pentaerythritol, *J. Chem. Soc.*, 1684–1688, doi:10.1039/JR9530001684, 1953. 13535, 13537, 13555

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- Brocos, P., Piñeiro, Á., Amigo, A., and Gracia-Fadrique, J.: A proposal for the estimation of binary mixture activity coefficients from surface tension measurements throughout the entire concentration range, *Fluid Phase Equilib.*, 260, 343–353, 2007. 13535
- Cammenga, H. K., Schulze, F. W., and Theuerl, W.: Vapor pressure and evaporation coefficient of glycerol, *J. Chem. Eng. Data*, 22, 131–134, 1977. 13557
- Carlson, H. C. and Colburn, A. P.: Vapor-liquid equilibria of nonideal solutions, *Ind. Eng. Chem.*, 34, 581–589, doi:10.1021/ie50389a013, 1942. 13534, 13538
- Cheon, Y.-H., Kim, K.-J., and Kim, S.-H.: A study on crystallization kinetics of pentaerythritol in a batch cooling crystallizer, *Chem. Eng. Sci.*, 60, 4791–4802, 2005. 13556
- Chirife, J., Favetto, G., and Fontán, C. F.: Microbial growth at reduced water activities: some physicochemical properties of compatible solutes, *J. Appl. Bacteriol.*, 56, 259–268, doi:10.1111/j.1365-2672.1984.tb01346.x, 1984. 13538, 13556
- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, 303, 1173–1176, doi:10.1126/science.1092805, 2004. 13530
- Clegg, S. L. and Seinfeld, J. H.: Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic acids at 298.15 K. 2. Systems including dissociation equilibria, *J. Phys. Chem. A*, 110, 5718–5734, doi:10.1021/jp056150j, 2006. 13544
- Cohen, S., Marcus, Y., Migron, Y., Dikstein, S., and Shafran, A.: Water sorption, binding and solubility of polyols, *J. Chem. Soc. Faraday T.*, 89, 3271, doi:10.1039/ft9938903271, 1993. 13556
- Comesaña, J. F., Correa, A., and Sereno, A. M.: Water activity in sorbitol or xylitol + water and sorbitol or xylitol + sodium chloride + water systems at 20 °C and 35 °C, *J. Chem. Eng. Data*, 46, 716–719, doi:10.1021/je0003187, 2001. 13556, 13558
- Compernelle, S., Ceulemans, K., and Müller, J.-F.: Influence of non-ideality on condensation to aerosol, *Atmos. Chem. Phys.*, 9, 1325–1337, doi:10.5194/acp-9-1325-2009, 2009. 13534
- Compernelle, S., Ceulemans, K., and Müller, J.-F.: EVAPORATION: a new vapour pressure estimation method for organic molecules including non-additivity and intramolecular interactions, *Atmos. Chem. Phys.*, 11, 9431–9450, doi:10.5194/acp-11-9431-2011, 2011. 13535
- Compernelle, S. and Müller, J.-F.: Henry's law constants of diacids and hydroxy polyacids: recommended values, *Atmos. Chem. Phys.*, 14, 2699–2712, doi:10.5194/acp-14-2699-2014, 2014. 13530, 13538, 13539, 13541, 13543, 13545, 13546

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- Della Gatta, G., Jóźwiak, M., and Ferloni, P.: Heat capacities near room temperature of ten solid alkane- α , ω -diols HO-(CH₂)_n-OH where $n = 6$ and 8–16, *J. Chem. Thermodyn.*, 31, 537–546, 1999. 13536, 13555
- Domalski, E. S. and Hearing, E. D.: Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K, *J. Phys. Chem. Ref. Data*, 22, 805–1159, 1993. 13555
- Engineering Sciences Data Unit Ltd: Vapour Pressures and Critical Points of Liquids. Glycols and Cyclic Diols, Item No 95002, vol. 2d(ii), ESDU International, London, 1995. 13557
- Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11, 11069–11102, doi:10.5194/acp-11-11069-2011, 2011. 13539
- Friese, E. and Ebel, A.: Temperature dependent thermodynamic model of the system H⁺-NH₄⁺-Na⁺-SO₄²⁻-NO₃⁻-Cl⁻-H₂O, *J. Phys. Chem. A*, 114, 11595–11631, doi:10.1021/jp101041j, 2010. 13544
- Góralski, P. and Tkaczyk, M.: Heat capacities of some liquid α , ω -Alkanediols within the Temperature Range between (293.15 and 353.15) K, *J. Chem. Eng. Data*, 53, 1932–1934, doi:10.1021/je800356x, 2008. 13555, 13557
- Gracia-Fadrique, J., Brocos, P., Piñeiro, A., and Amigo, A.: Activity coefficients at infinite dilution from surface tension data, *Langmuir*, 18, 3604–3608, doi:10.1021/la011761y, 2002. 13535
- Hao, H.-X., Hou, B.-H., Wang, J.-K., and Zhang, M.-J.: Solubility of erythritol in different solvents, *J. Chem. Eng. Data*, 50, 1454–1456, doi:10.1021/je0501033, 2005. 13556
- Jasra, R. and Ahluwalia, J.: Enthalpies of solution, partial molal heat capacities and apparent molal volumes of sugars and polyols in water, *J. Solution Chem.*, 11, 325–338, doi:10.1007/2BF00649291, 1982. 13557
- Joback, K. and Reid, R.: Estimation of pure-component properties from group-contributions, *Chem. Eng. Commun.*, 57, 233–243, 1987. 13537
- Knauth, P. and Sabbah, R.: Energetics of intra- and intermolecular bonds in o-alkanediols. III. Thermochemical study of 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, and 1,10-decanediol at 298.15 K, *Can. J. Chem.*, 68, 731–734, 1990. 13555, 13557
- Lopes Jesus, A., Ermelinda Eusébio, M., Redinha, J., and Leitão, M.: Enthalpy of solvation of butanediols in different solvents, *Thermochim. Ac.*, 344, 3–8, 2000. 13557
- Marculli, C. and Peter, Th.: Water activity in polyol/water systems: new UNIFAC parameterization, *Atmos. Chem. Phys.*, 5, 1545–1555, doi:10.5194/acp-5-1545-2005, 2005. 13534, 13535, 13538, 13554

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- Martin, S. T.: Phase transitions of aqueous atmospheric particles, *Chem. Rev.*, 100, 3403–3454, 2000. 13542
- Matsumoto, Y., Touhara, H., Nakanishi, K., and Watanabe, N.: Molar excess enthalpies for water + ethanediol, + 1,2-propanediol, and + 1,3-propanediol at 298.15 K, *J. Chem. Thermodyn.*, 9, 801–805, 1977. 13557
- Mullin, J. W.: *Crystallization*, 4th edn., Butterworth-Heinemann, Linacre House, Jordan Hill, Oxford OX2 8DP, 2001. 13556
- Nannoolal, Y., Rarey, J., and Ramjugernath, D.: Estimation of pure component properties: Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions, *Fluid Phase Equilibr.*, 269, 117–133, doi:10.1016/j.fluid.2006.11.014, 2008. 13535
- Nichols, N., Sköld, R., Spink, C., and Wadsö, I.: Thermochemistry of solutions of biochemical model compounds 6. α , ω -dicarboxylic acids, -diamines, and -diols in aqueous solution, *J. Chem. Thermodyn.*, 8, 993–999, 1976. 13557
- Ninni, L., Camargo, M. S., and Meirelles, A. J. A.: Water activity in polyol systems, *J. Chem. Eng. Data*, 45, 654–660, doi:10.1021/je990303c, 2000. 13554, 13556
- Nitta, I., Seki, S., Momotani, M., Suzuki, K., and Nakagawa, S.: On the phase transition in pentaerythritol (II), *P. Jpn Acad.*, 26, 11–18, 1950. 13535, 13537, 13555
- Nitta, I., Seki, S., and Suzuki, K.: Energy of hydrogen bond in tetragonal pentaerythritol, *B. Chem. Soc. Jpn.*, 24, 63–69, 1951. 13535, 13537, 13555
- Páez, M. S., Alvis, A., and Arrazola, G.: Comportamiento superficial e interfacial de soluciones acuosas diluidas de isómeros de pentanodiol a 288.15 K, *Inf. Tecnol.*, 22, 65–70, doi:10.4067/s0718-07642011000100009, 2011. 13535
- Pankow, J. F. and Asher, W. E.: SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds, *Atmos. Chem. Phys.*, 8, 2773–2796, doi:10.5194/acp-8-2773-2008, 2008. 13535
- Paraskevas, P. D., Sabbe, M. K., Reyniers, M.-F., Papayannakos, N., and Marin, G. B.: Group additive values for the gas-phase standard enthalpy of formation, entropy and heat capacity of oxygenates, *Chem. Eur. J.*, 19, 16431–16452, doi:10.1002/chem.201301381, 2013. 13537
- Parks, G. S. and Huffman, H. M.: Thermal data on organic compounds. iv. the heat capacities, entropies and free energies of normal propyl alcohol, ethyl ether and dulcitol, *J. Am. Chem. Soc.*, 48, 2788–2793, doi:10.1021/ja01690a004, 1926. 13555

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Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multi-functional acids: measurements and UNIFAC predictions, *Environ. Sci. Technol.*, 35, 4495–4501, 2001. 13533

Piacente, V., Ferro, D., and Della Gatta, G.: Vaporization enthalpies of a series of α , ω -alkanediols from vapour pressure measurements, *Thermochim. Ac.*, 223, 65–73, 1993. 13555, 13557

Piacente, V., Ferro, D., and Della Gatta, G.: Vaporization enthalpies of five odd-numbered (C7 to C15) α , ω -alkanediols, *Thermochim. Ac.*, 232, 317–321, 1994. 13555, 13557

Prausnitz, J. M., Lichtenthaler, R. N., and de Azevedo, E. G.: *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd edn., Prentice-Hall PTR, Upper Saddle River, New Jersey 07458, 1999. 13534, 13538

Robinson, R. A. and Stokes, R. H.: Activity coefficients in aqueous solutions of sucrose, mannitol and their mixtures at 25 °C, *J. Phys. Chem.*, 65, 1954–1958, doi:10.1021/j100828a010, 1961. 13556

Romero, C. M. and Páez, M. S.: Isopiestic determination of osmotic and activity coefficients of aqueous solutions of aliphatic polyols at 298.15 K, *Fluid Phase Equilibr.*, 240, 140–143, 2006. 13534, 13554, 13556

Romero, C. M., Páez, M. S., Miranda, J. A., Hernández, D. J., and Oviedo, L. E.: Effect of temperature on the surface tension of diluted aqueous solutions of 1,2-hexanediol, 1,5-hexanediol, 1,6-hexanediol and 2,5-hexanediol, *Fluid Phase Equilibr.*, 258, 67–72, 2007. 13535

Sabbe, M. K., De Vleeschouwer, F., Reyniers, M.-F., Waroquier, M., and Marin, G. B.: First principles based group additive values for the gas phase standard entropy and heat capacity of hydrocarbons and hydrocarbon radicals, *J. Phys. Chem. A*, 112, 12235–12251, doi:10.1021/jp807526n, 2008. 13537

Sander, R.: *Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3)*, Public Report, available at: <http://www.henrys-law.org/> (last access: 1 May 2014), 1999. 13531, 13545

Saxena, P. and Hildemann, L. M.: Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, 24, 57–109, 1996. 13545, 13557

Scatchard, G., Hamer, W. J., and Wood, S. E.: Isotonic solutions. I. The chemical potential of water in aqueous solutions of sodium chloride, potassium chloride, sulfuric acid, sucrose,

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urea and glycerol at 25 °C, *J. Am. Chem. Soc.*, 60, 3061–3070, doi:10.1021/ja01279a066, 1938. 13554

Seidell, A.: Solubilities of Organic Compounds, D. Van Nostrand Co., 3rd Edn., 250 Fourth Avenue, New York, 1941. 13556

Stein, S. and Brown, R.: NIST Chemistry WebBook, NIST Standard Reference Database Number 69, chap. Structures and Properties Group Additivity Model, National Institute of Standards and Technology, Gaithersburg MD, 20899, available at: <http://webbook.nist.gov>, last access: 1 May 2014. 13536

Suleiman, D. and Eckert, C. A.: Limiting activity coefficients of diols in water by a dew point technique, *J. Chem. Eng. Data*, 39, 692–696, doi:10.1021/je00016a011, 1994. 13534, 13554

Suzuki, T., Ohtaguchi, K., and Koide, K.: Application of principal components analysis to calculate Henry's constant from molecular structure, *Comput. Chem.*, 16, 41–52, 1992. 13545

Toktonov, A. V.: Thermochemical insight into “green chemistry” processes: experiment and ab initio calculations, Ph.D. thesis, Rostock University, available at: http://rosdok.uni-rostock.de/resolve/id/rosdok_disshab_000000000219 (last access: 1 May 2014), 2009. 13557

Tong, B., Tan, Z.-C., Shi, Q., Li, Y.-S., Yue, D.-T., and Wang, S.-X.: Thermodynamic investigation of several natural polyols (I): heat capacities and thermodynamic properties of xylitol, *Thermochim. Ac.*, 457, 20–26, doi:10.1016/j.tca.2007.02.022, 2007. 13536, 13555

Tong, B., Tan, Z., Shi, Q., Li, Y., and Wang, S.: Thermodynamic investigation of several natural polyols (II), *J. Therm. Anal. Calorim.*, 91, 463–469, doi:10.1007/s10973-007-8361-8, 2008. 13536, 13555

Tong, B., Tan, Z., Zhang, J., and Wang, S.: Thermodynamic investigation of several natural polyols, *J. Therm. Anal. Calorim.*, 95, 469–475, doi:10.1007/s10973-008-9268-8, 2009. 13536, 13555

Tong, B., Liu, R.-B., Meng, C.-G., Yu, F.-Y., Ji, S.-H., and Tan, Z.-C.: Heat capacities and non-isothermal thermal decomposition reaction kinetics of d-mannitol, *J. Chem. Eng. Data*, 55, 119–124, doi:10.1021/je900285w, 2010a. 13536, 13555

Tong, B., Yu, Y., Tan, Z.-C., Meng, C.-G., Cui, L.-J., Xiao, G., and Liu, R.-B.: Thermodynamic investigation of several natural polyols (IV): heat capacities and thermodynamic properties of adonitol, *Thermochim. Ac.*, 499, 117–122, doi:10.1016/j.tca.2009.11.011, 2010b. 13536, 13555

Verevkin, S. P.: Determination of vapor pressures and enthalpies of vaporization of 1,2-alkanediols, *Fluid Phase Equilib.*, 224, 23–29, 2004. 13557

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- Verevkin, S. P.: Vapor pressures and enthalpies of vaporization of a series of the 1,3-alkanediols, *J. Chem. Eng. Data*, 52, 301–308, doi:10.1021/je060419q, 2007. 13557
- Verevkin, S. P., Emel'yanenko, V. N., and Nell, G.: 1,2-propanediol. Comprehensive experimental and theoretical study, *J. Chem. Thermodyn.*, 41, 1125–1131, 2009. 13557
- 5 Wang, Z., Wang, Q., Liu, X., Fang, W., Li, Y., and Xiao, H.: Measurement and correlation of solubility of xylitol in binary water+ethanol solvent mixtures between 278.00 K and 323.00 K, *Korean J. Chem. Eng.*, 30, 931–936, doi:10.1007/s11814-012-0225-7, 2013. 13556
- Xie, M., Hannigan, M. P., and Barsanti, K. C.: Gas/particle partitioning of 2-methyltetrols and levoglucosan at an urban site in Denver, *Environ. Sci. Technol.*, 48, 2835–2842, doi:10.1021/es405356n, 2014. 13546
- 10 Zhang, Z. Y. and Yang, M. L.: Heat capacities and phase transitions of 1,1,1-trihydroxymethylpropane and pentaerythritol over the superambient temperature range, *Thermochim. Ac.*, 156, 157–161, 1989. 13536, 13555
- Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O., McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups, *Atmos. Chem. Phys.*, 11, 9155–9206, doi:10.5194/acp-11-9155-2011, 2011. 13531, 13534, 13542
- 15

Table 1. Infinite dilution activity coefficients derived in this work, the sources of water activity they are based on, and comparison with literature.

molecule	γ_s^∞	a_w source	γ_s^∞ (lit.) ^f
1,2-ethane diol	0.75, 0.69 ^g	a,b	0.8
1,2-propane diol	1.25, 1.08 ^g	a,b	1.0
1,3-propane diol	1.23, 1.25 ^g	a,b	1.2
1,2-butane diol	3.00, 3.74 ^g	a,b,c	2.0
1,3-butane diol	2.14, 1.97 ^g	a,b,c	2.2
1,4-butane diol	2.27, 2.12 ^g	a,b,c	2.8
2,3-butane diol	2.10, 1.77 ^g	a,b,c	1.6
1,5-pentane diol	5.99, 5.26 ^g	a,b	
1,2-pentane diol	11.9	a	
1,4-pentane diol	3.8	a	
2,4-pentane diol	2.8	a	
1,2-hexane diol	26.3	a	
2,5-hexane diol	5.7	a	
1,7-heptane diol	27.9	a	
glycerol	0.52	a,d,e	
1,2,4-butanetriol	0.45	a,d	

^a Marcolli and Peter (2005)^b Borgesani et al. (1989)^c Romero and Páez (2006)^d Ninni et al. (2000)^e Scatchard et al. (1938)^f Suleiman and Eckert (1994)^g The second value is obtained by applying Eq. (13) to the data of Marcolli and Peter (2005) only.

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**Table 2.** Solid state pressure and enthalpy of sublimation of polyols, obtained from Eqs. (15), (16) and/or (17), at $T_{\text{ref}} = 298.15\text{K}$, and reference to the data used to obtain them. $C_{p,g}$ is estimated by the method of Benson (1976).

molecule	# OH	$p_{\text{Cr}}^0(T_{\text{ref}})$ atm	$\Delta H_{\text{sub}}(T_{\text{ref}})$ kJ mol ⁻¹	Data source for Eqs. (15), (16) and/or (17).			
				$p_{\text{L}}^0, \Delta H_{\text{vap}}(\text{L})^{\text{a}}$ or $p_{\text{Cr}}^0, \Delta H_{\text{sub}}(\text{Cr})$	T_{meas} K	$T_{\text{fus}},$ ΔH_{fus}	$C_{p,\text{L}}(\text{L})^{\text{a}}$ or $C_{p,\text{Cr}}(\text{Cr})$
nonane- diol	2	1.4×10^{-8}	148	L ^b	323	g	Cr ^k , L ⁱ
		2.3×10^{-8}	148	L ^c	360	g	Cr ^k , L ^o
decane- diol	2	1.4×10^{-9}	151	Cr ^b	342		Cr ^k
		1.7×10^{-9}	161	L ^c	364	g	Cr ^k , L ^o
erythritol	4	4.6×10^{-12}	155	L ^d	412	h	L, Cr ^h
		3.5×10^{-11}	136	Cr ^e	386		Cr ^h
penta- erythritol	4	7.1×10^{-14}	166	Cr ^d	436		Cr ^j
		3.4×10^{-12}	135	Cr ^e	404		Cr ^j
		9.2×10^{-14}	147	Cr ^f	394		Cr ^j
xylitol	5	7.4×10^{-13}	162	L ^d	433	h	L, Cr ^h
adonitol ^{p,r}	5	2.7×10^{-13}	166	L ^d	443	h	L, Cr ^h
arabinitol ^{q,r}	5	2.1×10^{-13}	166	L ^d	440	d	L, Cr ^m
sorbitol	6	3.6×10^{-16}	198	L ^d	477	h	L, Cr ^h
mannitol ^t	6	6.6×10^{-18}	206	L ^d	477	h	Cr ⁿ , L ^m
dulcitol ^{s,t}	6	1.9×10^{-18}	210	L ^d	482	d	Cr ⁿ , L ^m

^a "L" (liquid) and "Cr" (crystalline) are used as shorthand to describe the phase state of the non-gaseous phase. ^b Knauth and Sabbah (1990), ^c Piacente et al. (1993, 1994), ^d Barone et al. (1990), ^e Nitta et al. (1950, 1951), ^f Bradley and Cotson (1953), ^g Badea et al. (2014), ^h Tong et al. (2007, 2008, 2009, 2010b, a), ⁱ Góralski and Tkaczyk (2008), ^j Zhang and Yang (1989), ^k Della Gatta et al. (1999).

^l No $C_{p,\text{Cr}}, C_{p,\text{L}}$ data was found for arabinitol. The data for adonitol was taken instead.

^m No $C_{p,\text{L}}$ data was found for mannitol and dulcitol in the literature; the $C_{p,\text{L}}$ data for sorbitol was taken instead.

ⁿ No $C_{p,\text{Cr}}$ data was found for dulcitol in the desired temperature range. Low temperature ($\leq 292.8\text{K}$) data (Parks and Huffman, 1926) is comparable to that of mannitol, therefore, $C_{p,\text{Cr}}$ of mannitol was taken instead.

^o No $C_{p,\text{L}}$ data for decane diol was found in the literature. It was estimated by the method of Domalski and Hearing (1993).

^p also named ribitol, ^q also named arabitol, ^r stereo isomer of xylitol, ^s also named galacticol, ^t stereo isomer of sorbitol.

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**Table 3.** Mole fraction solubilities x_s^{sat} and activity coefficient ratios $\gamma_s^\infty/\gamma_s^{\text{sat}}$ derived from a_w data. Estimations of $\gamma_s^\infty/\gamma_s^{\text{sat}}$ by UNIFAC-MP are also given.

molecule	x_s^{sat}	$\gamma_s^\infty/\gamma_s^{\text{sat}}$	a_w data source	$\gamma_s^\infty/\gamma_s^{\text{sat}}$ MP
nonane diol	1×10^{-3a}	1.0 ^q	–	1.06
decane diol	7.6×10^{-5a}	1.0 ^q	–	1.01
erythritol	0.074 ^b	0.84	h, k, i	0.75
pentaerythritol	0.067 ^c	0.8 ⁿ	–	0.70
xylitol	0.18 ^e	0.56	h, j	0.32
adonitol	0.15 ^d	0.66 ^l	l	0.37
arabinitol	0.20 ^d	0.60 ^l	l	0.30
sorbitol	0.196 ^g	0.45 ^p	h, j, m	0.18
mannitol	0.0209 ^f	0.96 ^o	h, m	0.80
dulcitol	0.0031 ^d	1.0 ^q	–	0.97

Solubilities: ^a Merck Millipore (<http://www.merckmillipore.com/>), at 20 °C, ^b Hao et al. (2005), ^c Cheon et al. (2005), ^d Cohen et al. (1993), ^e Wang et al. (2013), ^f Seidell (1941), ^g Mullin (2001).

Water activities: ^h Ninni et al. (2000), ⁱ Bonner and Breazeale (1965), ^j Comesaña et al. (2001), ^k Romero and Páez (2006), ^l Chirife et al. (1984) (one parameter fittings), ^m Robinson and Stokes (1961); Bower and Robinson (1963).

ⁿ No a_w data was found in the literature. The current value was assigned in analogy to erythritol, which has the same number of hydroxyl groups, a similar x_s^{sat} and a similar $\gamma_s^\infty/\gamma_s^{\text{sat}}$ as predicted by UNIFAC-MP.

^o For mannitol, only the a_w data of Robinson and Stokes (1961) was used, as the data of Ninni et al. (2000) led to $\gamma_w > 1$, which is probably wrong.

^p Due to the extrapolation involved (no a_w data at x_{sat}), this value is more uncertain.

^q No a_w data was found. $\gamma_s^\infty/\gamma_s^{\text{sat}} = 1$ was assumed because of the low solubility, i.e. Eq. (9) is considered valid.

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**Table 4.** Henry's law constants and gas dissolution enthalpies for the polyols considered in this work, from Eqs. (4), (5), (9), (10). γ_s^∞ is taken from Table 1, ρ_{Cr}^0 , ΔH_{sub} from Table 2 and $\gamma_s^\infty/\gamma_s^{sat}$ from Table 3.

molecule	k_h	$\Delta H_{g \rightarrow aq}^\infty$	Data source for Eqs. (4) and (5).		k_h
	Matm ⁻¹	kJ mol ⁻¹	ρ_{Cr}^0 ΔH_{vap}	$\Delta H_{L \rightarrow aq}^\infty$ (L) or $\Delta H_{Cr \rightarrow aq}^\infty$ (Cr)	Matm ⁻¹ (lit.)
1,2-ethane diol	6.6×10^5	-72.9	a	L ^e	4.1×10^{5j}
1,2-propane diol	2.7×10^5	-78.8	a	L ^f	1×10^{5k}
1,3-propane diol	1.6×10^6	-79.1	a	L ^e	9.2×10^{5j}
1,2-butane diol	2.1×10^5	-82.1	a	L ^g	
1,3-butane diol	7.1×10^5	-84.5	a	L ^g	
1,4-butane diol	3.5×10^6	-89.6	a	L ^g	1×10^{5k}
2,3-butane diol	1.1×10^5	-82.2	b	L ^g	4×10^{4k}
1,2-pentane diol	1.4×10^5		a		
1,4-pentane diol	2.3×10^6		b		
1,5-pentane diol	7.1×10^6	-103.5	b	L ^e	
2,4-pentane diol	3.9×10^5				
1,2-hexane diol	1.7×10^5		a		
2,5-hexane diol	1.4×10^6		b		
1,7-heptane diol	4.6×10^6 – 8.4×10^6		c		
1,9-nonane diol	2.4×10^9 – 4.0×10^9				
1,10-decane diol	2.5×10^6 – 3.0×10^6				
glycerol	4.8×10^9	-92.6	d	L ^h	6×10^{8k}
erythritol	1.1×10^{12}	-133		Cr ⁱ	
pentaerythritol	6.7×10^{13}	-133		Cr ^j	
xylitol	4.0×10^{13}	-140		Cr ^j	
adonitol	4.7×10^{13}	-147		Cr ^j	
arabinitol	6.8×10^{13}	-147		Cr ^j	
sorbitol	6.7×10^{16}	-181		Cr ^j	
mannitol	1.8×10^{17}	-184		Cr ^j	
dulcitol	9.1×10^{16}	-181		Cr ^j	

^a Verevkin (2004), Verevkin (2007), Toktonov (2009). For 1,2-propanediol: Verevkin et al. (2009). ^b Engineering Sciences Data Unit Ltd (1995).

^c ρ_L^0 from either Piacente et al. (1994, 1993) (giving rise to the lower k_h) or Knauth and Sabbah (1990) (giving rise to the higher k_h). ρ_L^0 is corrected to 298.15 K using $C_{p,L}$ data from Góralski and Tkaczyk (2008) and $C_{p,g}$ estimated with the method of Benson (1976), but the effect is small. ^d Cammenga et al. (1977).

^e Nichols et al. (1976). ^f Matsumoto et al. (1977). ^g Lopes Jesus et al. (2000). ^h Bastos et al. (1988). ⁱ Jasra and Ahluwalia (1982).

^j Bone et al. (1983), value at 293 K. ^k Saxena and Hildemann (1996), value obtained from vapour-liquid equilibrium data.

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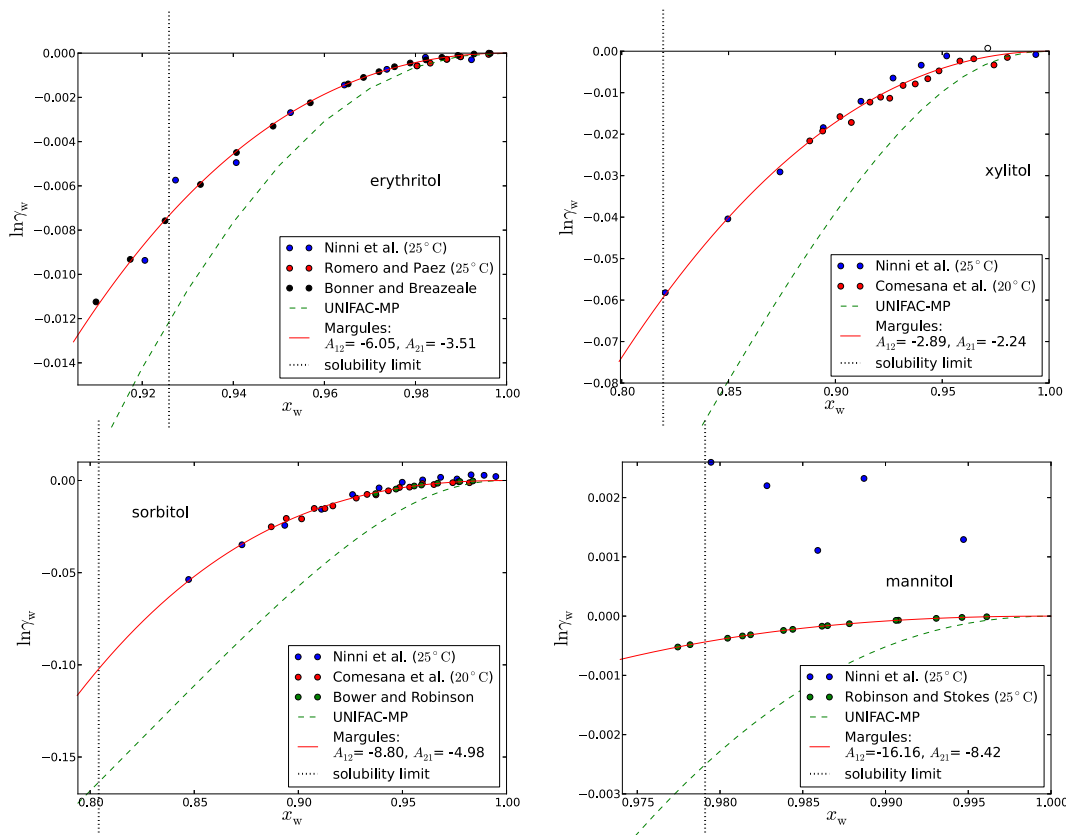
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Figure 1. The $\ln\gamma_w$ data for erythritol, xylitol, mannitol and sorbitol, compared with the fitting using the Margules formula, and UNIFAC-MP results. Note that the data of Comesaña et al. (2001) is at 20 °C rather than 25 °C, but from their data at 35 °C, it can be deduced that the temperature dependence of $\ln\gamma_w$ is small.

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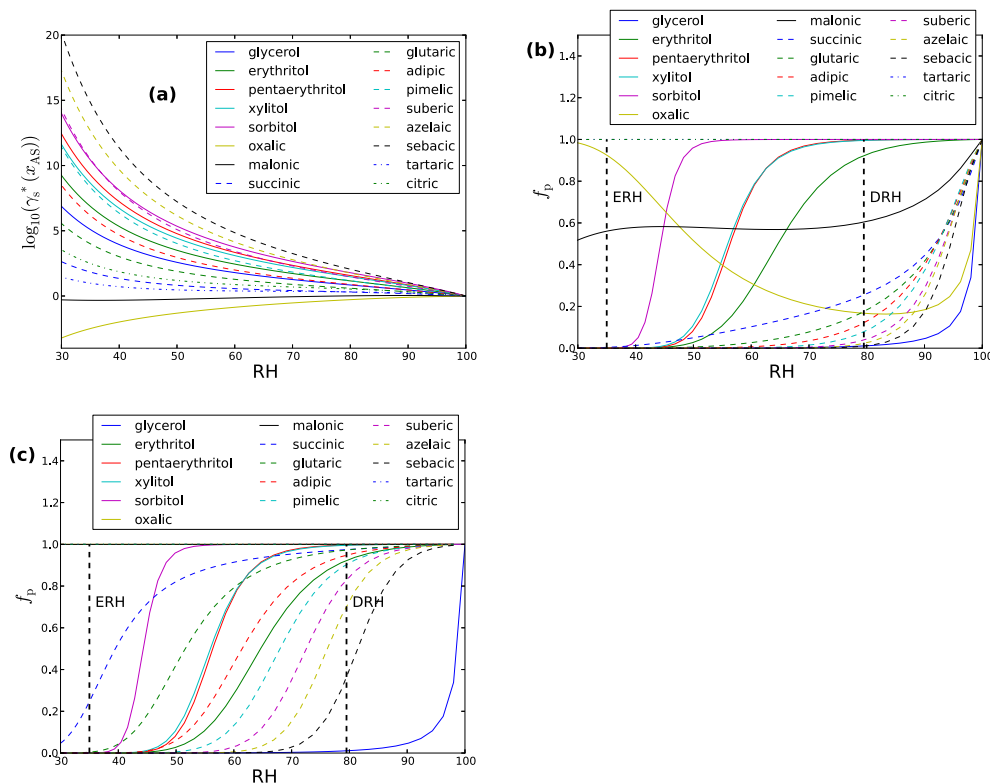
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Figure 2. (a) Activity coefficient correction ($\log_{10} \gamma_s^*$) of the organic solute vs. RH for an AS–water particle, as calculated by AIOMFAC. (b) Particulate fraction of the organic solute vs. RH. Acid dissociation is not taken into account. Tartaric and citric acid have $f_p = 1$ over the entire presented range. (c), as (b), but taking acid dissociation into account using the on-line model of E-AIM (see text for more details). Oxalic, malonic, tartaric and citric acid have $f_p = 1$ over the entire presented range.