Supplement for 'Henry's law constants of diacids and hydroxypolyacids: recommended values'

Steven Compernolle

1 Obtaining the activity coefficient ratios $\gamma^{\infty}/\gamma^{\text{sat}}$

1.1 Procedure

Water activity data was collected from Peng et al. (2001); Velezmoro and Meirelles (1998). Peng et al. (2001) provides the water activity data graphically, both from their own measurements and from other sources, hence we obtained their bulk data with a plot digitizer program. For citric acid, due to the dense population of the points in the plot of Peng et al. (2001), we could not separate the data among the different references Levien (1955); Apelblat et al. (1995a,b); Peng et al. (2001), hence we treated it as one data set. For malic and tartaric acid, we obtained the bulk data measured by Peng et al. (2001) from the plots, while we took the data from Velezmoro and Meirelles (1998); Apelblat et al. (1995a) directly from the original works. For malonic and glutaric acid, we obtained water activity data at saturation from Wise (2003).

Activity coefficient ratios of the acid were calculated from the water activity coefficient data points using

$$\begin{aligned}\ln\frac{\gamma_s'}{\gamma_s^{\text{sat}}} =& -\frac{x_w'}{1-x_w'}\ln\gamma_w\left(x_w'\right)+\frac{\tilde{x}_w}{1-\tilde{x}_w}\ln\gamma_w\left(\tilde{x}_w\right)+\int_{\tilde{x}_w}^{x_w'}\frac{\ln\gamma_w(t)}{(1-t)^2}\mathrm{d}t \qquad (1)\\ \tilde{x}_w =& 1-x_s^{\text{sat}}\end{aligned}$$

with x_w' corresponding to the data points from the bulk measurements in the subsaturation range, hence $x_w' > \tilde{x}_w$ (or $x_s' < x_s^{\text{sat}}$). The water activity data at saturation was taken from Apelblat et al. (1995a); Wise (2003). The integration was performed with the Simpons rule integration technique available within the python package scipy. To extrapolate to $x_s = 0$, the resulting data points $\left(x_s', \ln\frac{\gamma_s'}{\gamma_s^{\text{sat}}}\right)$ were then fit to the following function

$$f\left(x_s, A_{12}, A_{21}\right) - f\left(x_s^{\text{sat}}, A_{12}, A_{21}\right) \qquad (2)$$

with x_s^{sat} taken from Apelblat and Manzurola (1987, 1989), A_{12}, A_{21} the parameters to optimize, and f corresponding to the following $\ln\gamma$ functional expressions

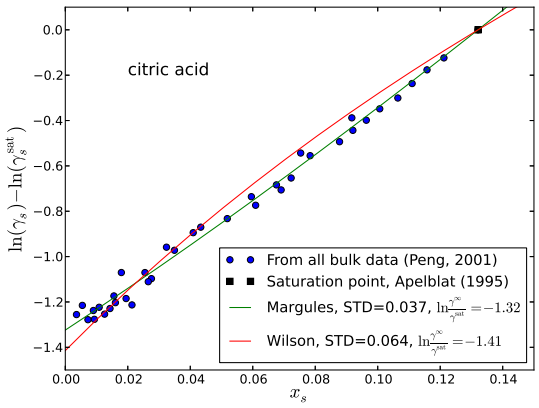

Figure 1: Subsaturation $\ln\frac{\gamma_s}{\gamma_s^{\mathrm{sat}}}$ data for citric acid, obtained by applying (1) to the water activity data obtained from Peng et al. (2001), and the fittings using formula (2)-(5).The Van Laar fitting is indistinguishable from the Margules fitting and is therefore not shown.

(see e.g. Prausnitz et al., 1999)

$$\text{Margules:} f(x_1, A_{12}, A_{21}) = (A_{12} + 2(A_{21} - A_{12})x_1)\, x_2^2 \tag{3}$$

$$\text{Van Laar:} f(x_1, A_{12}, A_{21}) = A_{12}\left(\frac{A_{21}x_2}{A_{12}x_1 + A_{21}x_2}\right)^2 \tag{4}$$

$$\text{Wilson:} f(x_1, A_{12}, A_{21}) = -\ln(x_1 + A_{12}x_2) + x_2\left(\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right) \tag{5}$$

The curve fitting function in the python package scipy was used for this purpose.

Given the sensivity to the choice of fitting function, we rounded finally all results to one significant figure.

1.2 Hydroxy-polyacids

For citric acid, fitting the data with the Margules or Van Laar formula gave nearly identical results, at least in the subsaturation range, and returned a lower STD than the Wilson formula. Therefore the Margules/Van Laar result $\frac{\gamma_s^\infty}{\gamma_s^{\mathrm{sat}}} = 0.27$ was chosen.

For malic acid, we distinguished between the data obtained from Peng et al. (2001) and from Velezmoro and Meirelles (1998), as the Peng et al. (2001) data is systematically lower. From the Peng et al. (2001) data, we find $\frac{\gamma_s^\infty}{\gamma_s^{\mathrm{sat}}} = 0.38$, while from the Velezmoro and Meirelles (1998) data, we find $\frac{\gamma_s^\infty}{\gamma_s^{\mathrm{sat}}} = 0.49$. As final result we took the geometric mean 0.43.

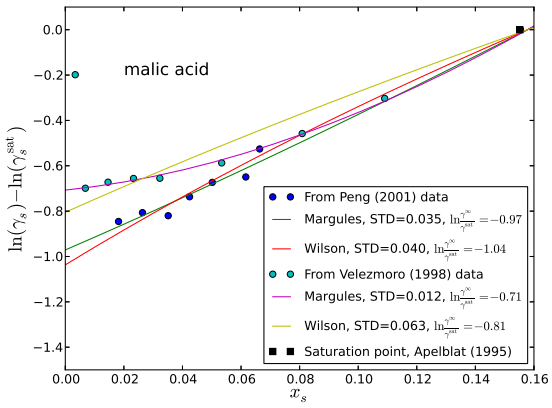

Figure 2: Similar as Fig. 1 but for malic acid. The point at the lowest x_s from the Velezmoro data is considered an outlier and was therefore not included in the fit. For the Peng data, the Van Laar fitting gave a nearly identical result as the Margules fitting in the subsaturation range, while for the Velezmoro data, the Van Laar fitting failed.

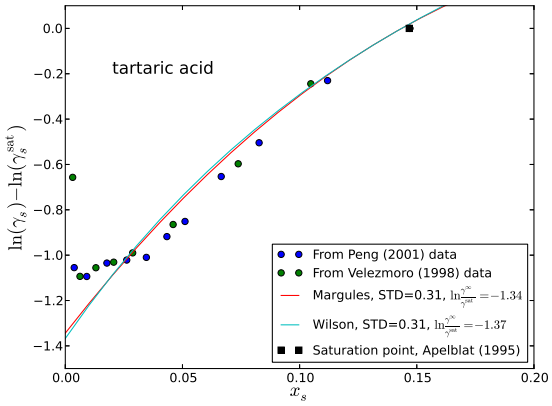

Figure 3: Similar as Fig. 1 but for tartaric acid. The point at the lowest x_s from the Velezmoro data is considered an outlier and was therefore not included in the fit.

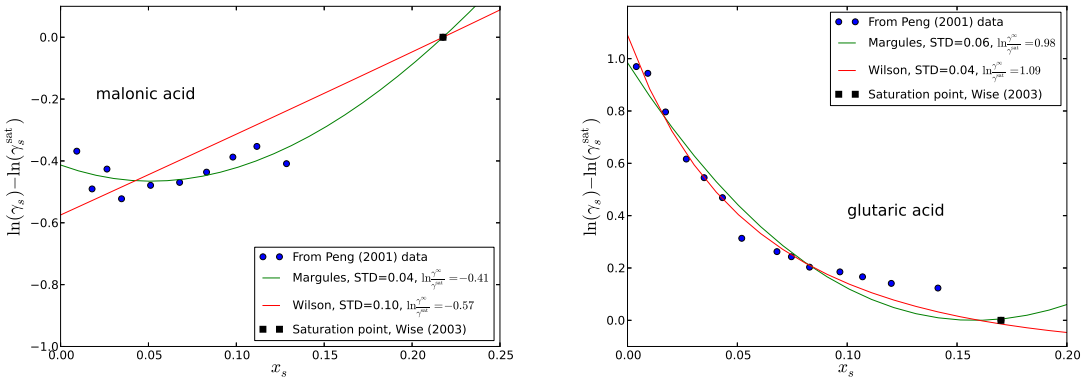

Figure 4: Similar as Fig. 1 but for malonic and glutaric acid.

For tartaric acid, the data from Peng et al. (2001) and Velezmoro and Meirelles (1998) agreed well, therefore the parameter fittings were applied to both data sets together. However, the fitting functions were not able to capture well the behaviour close to IDL. Therefore, we chose after inspection of the plot $\ln \frac{\gamma_s^\infty}{\gamma_s^{\mathrm{sat}}} = -1.08$, corresponding to $\frac{\gamma_s^\infty}{\gamma_s^{\mathrm{sat}}} = 0.34$.

1.3 Linear diacids

The most successfull fittings resulted in $\frac{\gamma_s^\infty}{\gamma_s^{\mathrm{sat}}} = 0.66$ for malonic acid and 2.97 for glutaric acid. For oxalic and succinic acid, as the water activity coefficients are close to unity and x_s^{sat} is low, no fitting was performed and $\frac{\gamma_s^\infty}{\gamma_s^{\mathrm{sat}}} = 1.0$ was assumed.

References

Apelblat, A. and Manzurola, E.: Solubility of oxalic, malonic, succinic, adipic, maleic, malic, citric, and tartaric acids in water from 278.15 to 338.15 K, J. Chem. Thermodyn., 19, 317–320, 1987.

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 ascorbic, glutaric, and pimelic acids in water at 298.15 K, J. Chem. Thermodyn., 21, 1005–1008, 1989.

Apelblat, A., Dov, M., Wisniak, J., and Zabicky, J.: The vapour pressure of water over saturated aqueous solutions of malic, tartaric, and citric acids, at temperatures from 288 K to 323 K, J. Chem. Thermodyn., 27, 35–41, 1995a.

Apelblat, A., Dov, M., Wisniak, J., and Zabicky, J.: Osmotic and activity coefficients of HO2CCH2C(OH)(CO2H)CH2CO2H (citric acid) in concentrated aqueous solutions at temperatures from 298.15 K to 318.15 K, J. Chem. Thermodyn., 27, 347–353, 1995b.

Levien, B. J.: A Physicochemical Study of Aqueous Citric Acid Solutions., J. Phys. Chem., 59, 640–644, doi:10.1021/j150529a016, 1955.

Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions, Environ. Sci. Technol., 35, 4495–4501, 2001.

Prausnitz, J. M., Lichtenthaler, R. N., and de Azevedo, E. G.: Molecular thermodynamics of fluid-phase equilibria, Prentice-Hall PTR, Upper Saddle River, New Jersey 07458, third edn., 1999.

Velezmoro, C. E. and Meirelles, A. J. A.: Water activity in solutions containing organic acids, Drying Technology, 16, 1789–1805, doi: 10.1080/07373939808917496, 1998.

Wise, M. E.: Hygroscopic growth of ammonium sulfate/dicarboxylic acids, J. Geophys. Res., 108, 4638, doi:10.1029/2003JD003775, 2003.