Supplement of Atmos. Chem. Phys., 20, 13131–13143, 2020
https://doi.org/10.5194/acp-20-13131-2020-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Technical note: Estimating aqueous solubilities and activity coefficients of mono- and α,ω-dicarboxylic acids using COSMO*therm*

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Table S1: Number of dicarboxylic acid conformers in the COSMO*base* and obtained using systematic sampling and COSMO*conf*. The number of conformers in the COSMO*base* is limited to 10.

Acid	COSMO*base*	Systematic sampling + COSMO*conf*
Oxalic	3	4
Malonic	8	6
Succinic	10	8
Glutaric	10	25
Adipic	10	44
Pimelic	10	75
Suberic	10	132

Conversion of experimental activity coefficients

Experimentally determined activity coefficients are commonly given in a molality basis using a 1 molal solution as the reference state (convention III[S1]). To switch from the molality basis to the mole fraction basis (used by COSMO*therm*) in convention III:

$$\gamma_i^{\mathrm{III}}(x_i) = \frac{x_i^\circ}{x_i}\gamma_i^{\mathrm{III}}(m_i)\frac{m_i}{m_i^\circ} \tag{1}$$

where x_i° is the mole fraction of compound i at the reference state ($x_i^\circ = 0.0177$ when $m_i^\circ = 1$ mol kg^{-1}). Molality m relates to the mole fraction x with:

$$m = \frac{x}{M_w(1-x)}, \tag{2}$$

where M_w is the molar mass of the solvent water. The reference state composition of convention III can be used in the COSMO*therm* calculation (as opposed to the pure compound reference state) to obtain directly comparable activity coefficients.

Clustering interaction parameters

We tested the COSMO-RS-DARE method implemented in COSMO*therm* and compared the activity coefficients of the water–acetic acid system with experimentally determined values. The activity coefficients calculated using different reaction products in the acetic acid–water system are shown in Figure S1. We added the acetic acid dimer formation, the acetic acid hydrate formation and the water dimer formation separately. Additionally, we tested adding the water dimer and the hydrated acid. Note that the water activity coefficient is calculated only up to 0.95 mole fraction of acetic acid.

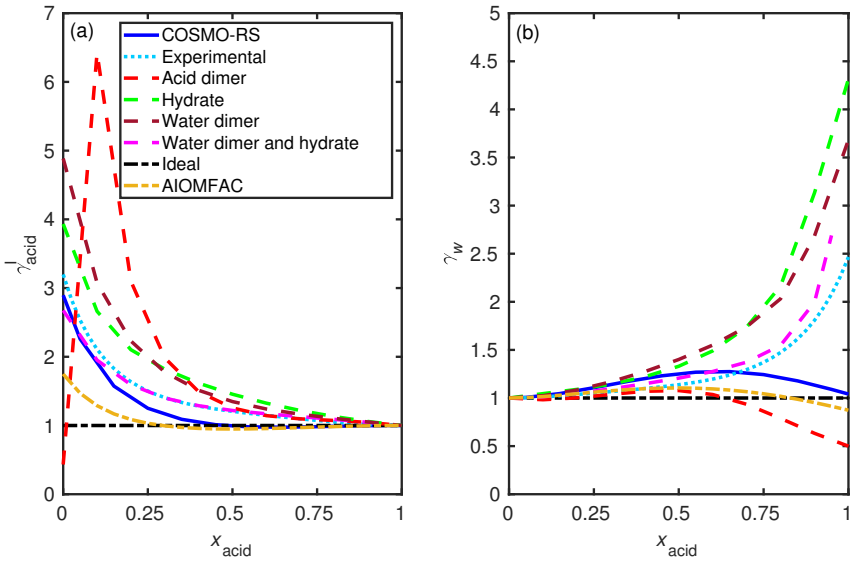

Figure S1: Activity coefficients of (a) acetic acid and (b) water in the binary acetic acid–water system, at 298.15K. The activity coefficients were estimated in COSMO*therm* using the monomers of both compounds (COSMO-RS) and COSMO-RS-DARE using different reaction products to describe acetic acid and water in the binary system. The experimental activity coefficients were derived by Hansen et al.[S2] and UNIFAC-predictions were calculated using AIOMFAC-web.[S3]

Based on the comparison with the experimental activity coefficients, the hydrated acid and water dimer are needed to describe the activity coefficient of water in the binary system. However, acetic acid activity coefficients are described quite well with COSMO-RS.

The enthalpic parameters used for each of the calculations of acetic, malonic, glutaric and succinic acid are shown in Table S2.

Table S2: The enthalpic parameters (c_H[kJ mol^{-1}]) of the clustering reactions used in the COSMO-RS-DARE calculation. A = acid dimer, H = acid hydrate and W = water dimer.

Clusters	acetic	malonic	glutaric	succinic
A	0.0	0.0	0.0	
H	-16.7	-14.6	-33.8	
W	-16.7	0.0	0.0	0.0
W+H	0.0; 0.0			0.0; -14.6

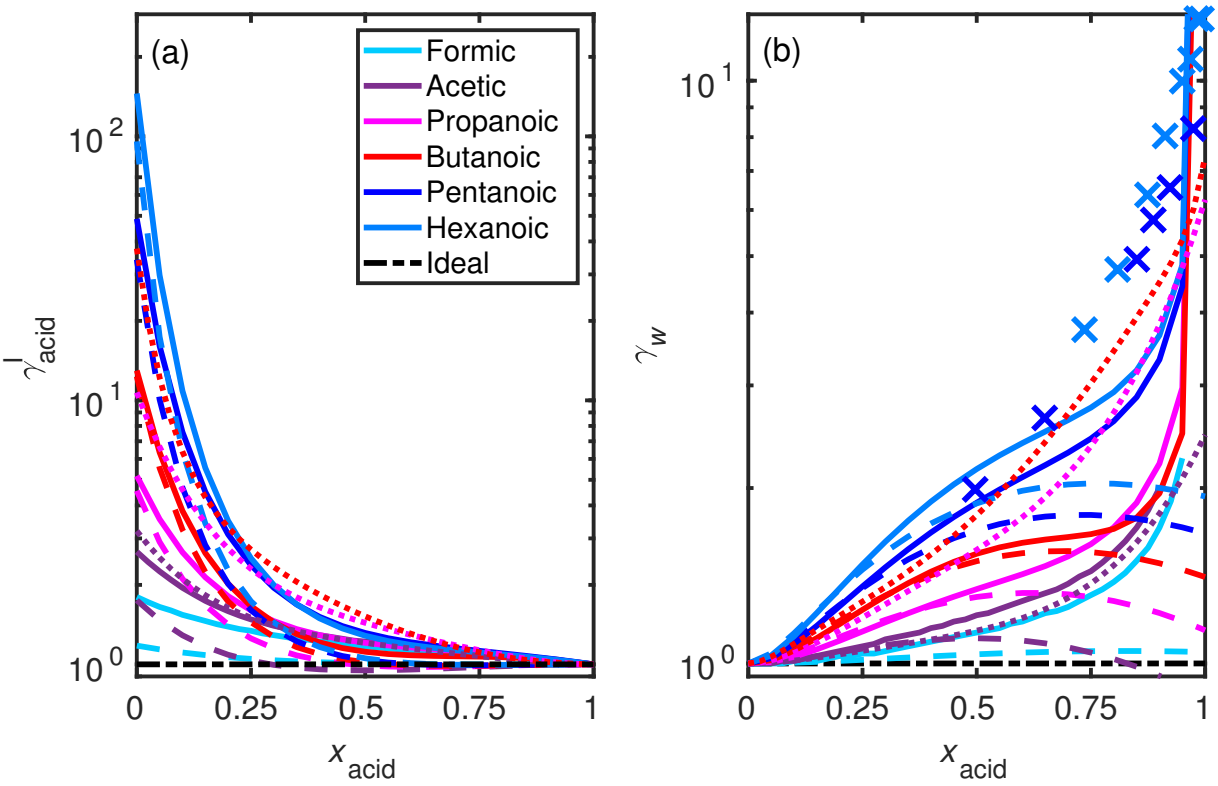

Figure S2: Activity coefficients (γ^{I}) of (a) monocarboxylic acids and (b) water in all mixing states of the binary aqueous solutions, at 298.15 K. The solid lines represent activity coefficient estimates using COSMO-RS-DARE ($c_H = 0$), dashed lines are UNIFAC estimates, dotted lines are calculated from the equations fitted to experiments by Hansen et al.,[S2] and the markers are the experimental points from the same study.

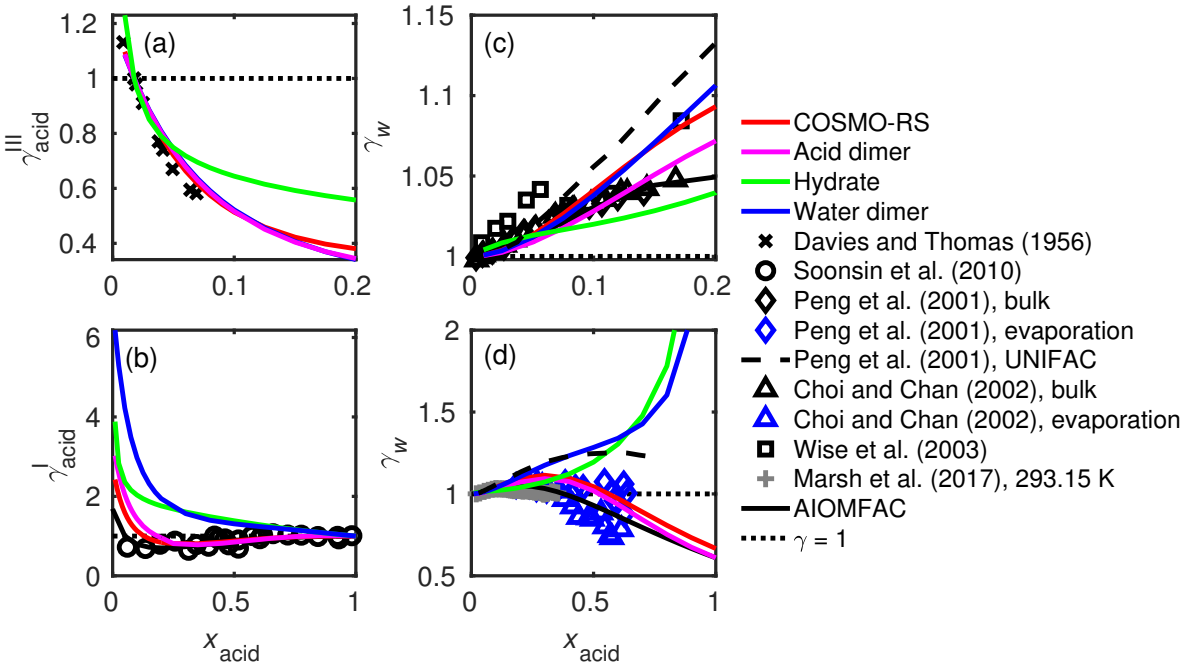

Figure S3: Activity coefficients of (a-b) glutaric acid and (c-d) water in the binary mixtures at 298.15 K calculated using different clustering reactions in COSMO*therm* calculation. As a comparison are experimentally determined activity coefficients of malonic acid by Davies and Thomas[S4] (at 298.15 K given in convention III) and Soonsin et al.[S5] (particle measurements at various temperatures given in convention I) and of water by Peng et al.,[S6] Choi and Chan,[S7] Marsh et al.,[S8] Wise et al.[S9] and AIOMFAC-web.[S3]

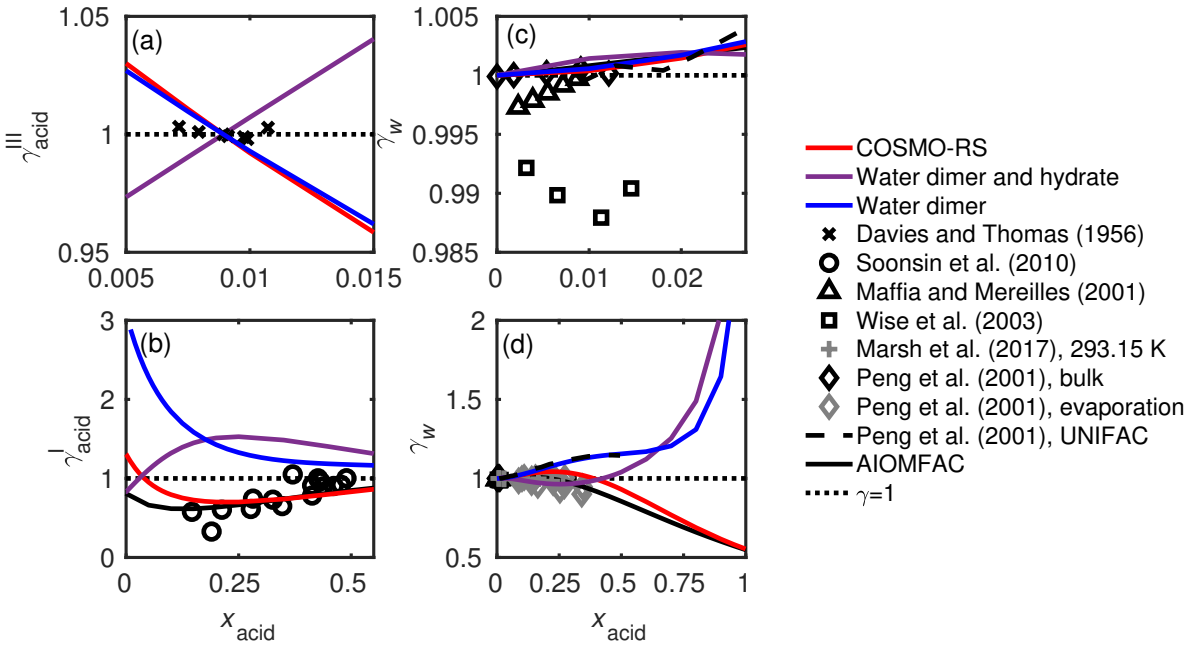

Figure S4: Activity coefficients of (a-b) succinic acid and (c-d) water in binary mixtures at 298.15 K calculated using different clustering reactions in COSMO*therm* calculations. As a comparison are experimentally determined activity coefficients of malonic acid by Davies and Thomas[S4] (at 298.15 K given in convention III) and Soonsin et al.[S5] (particle measurements at various temperatures given in convention I) and of water by Peng et al.,[S6] Marsh et al.,[S8] Wise et al.,[S9] Maffia and Meirelles[S10] and AIOMFAC-web.[S3]

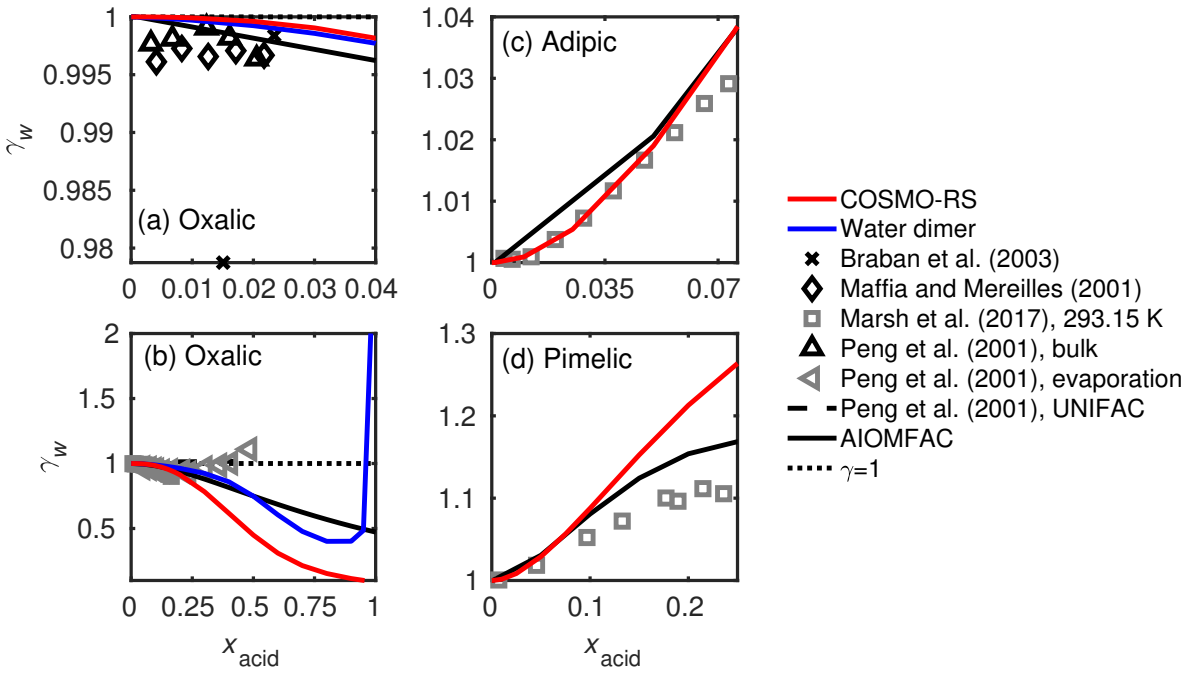

Figure S5: COSMO*therm*-estimated water activity coefficients in aqueous (a-b) oxalic acid, (c) adipic acid and (d) pimelic acid solutions at 298.15 K. The experimental and model activity coefficients are by Peng et al.,[S6] Marsh et al.,[S8] Maffia and Mereilles,[S10] Braban et al.[S11] and AIOMFAC-web.[S3]

Dissociation correction

Dissociation of an acid HA in water can be described using an equilibrium reaction

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{A^-} + \mathrm{H_3O^+} \tag{3}$$

where the degree of dissociation is given according to the dissociation constants ($\mathrm{p}K_\mathrm{a}$). The mole fractions of the ionic compounds are calculated using the dissociation correction at different mole fractions of the undissociated acid (x_acid). First, the acid mole fraction is converted to molar concentration (mol l^{-1}):

$$c_\mathrm{acid}^\mathrm{HA} = x_\mathrm{acid} \frac{\rho}{M_\mathrm{solution}} \tag{4}$$

For the conversion, the density of the aqueous acid solution is needed, and is calculated using the molar volume ($\widetilde{V}_\mathrm{solution}(T)$) of the acid estimated by COSMO*therm* and of water estimated from the experimental pure water density.

$$\widetilde{V}_\mathrm{solution}(T) = \sum_i x_i \widetilde{V}_i(T) \tag{5}$$

$$\rho_i = \frac{M_i}{\widetilde{V}_i(T) N_A}, \tag{6}$$

where N_A is the Avogadro constant. In addition, the molar mass of the solution is calculated as the mole fraction weighted molar masses of the individual compounds i:

$$M_\mathrm{solution} = \sum_i x_i M_i \tag{7}$$

The dissociated molar concentration is estimated using the undissociated concentration, $\mathrm{p}K_\mathrm{a}$ (1.25 for oxalic acid[S12]) and pH of water (7.0).

$$c_\mathrm{acid}^\mathrm{A^-} = -0.5 \times 10^{-\mathrm{pH}} + \sqrt{0.25 \times 10^{-2\mathrm{pH}} + c_\mathrm{acid}^\mathrm{HA} 10^{-\mathrm{p}K_\mathrm{a}}} \tag{8}$$

This approximation assumes that there is only a small concentration of the acid in water so the pH of the solution is close to that of pure water. This assumption is made because the pK_a value of the acid is only given for pure water, not acid water solutions. The predicted dissociation correction is therefore less accurate at high concentrations of acid than in low acid concentrations. The total mole fraction of the acid in the solution is calculated as the sum of the undissociated and dissociated acid:

$$x_{\text{acid}}^{\text{DC}} = (c_{\text{acid}}^{\text{HA}} + c_{\text{acid}}^{\text{A}^-}) \frac{M_{\text{solution}}}{\rho} \tag{9}$$

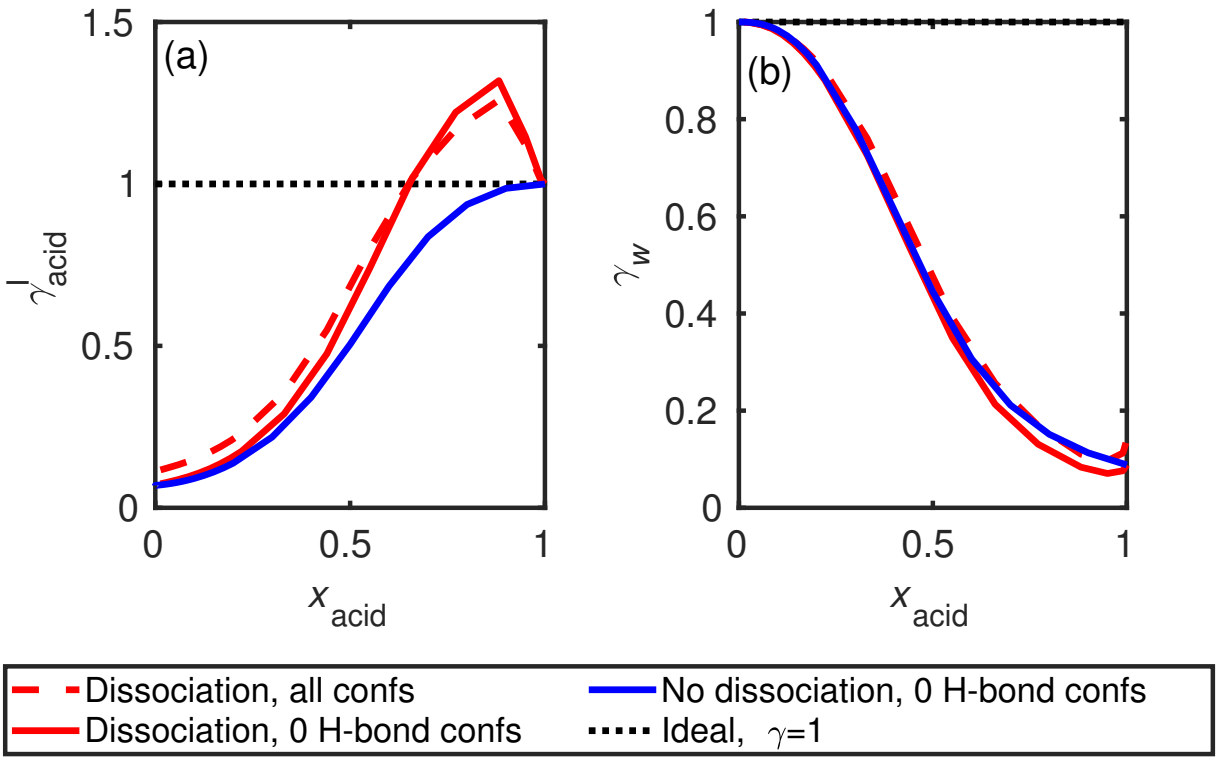

Figure S6: Activity coefficients of (a) oxalic acid and (b) water at 298.15 K calculated for systems where dissociation of oxalic acid was (red) and was not (blue) accounted for. Activity coefficients were calculated using either the full set of acid conformers (all confs) or only conformers containing no intramolecular H-bonds (0 H-bond confs). On the x-axis, the mole fraction is for the total oxalic acid, meaning $x_{\text{acid}}^{\text{DC}}$ in the systems where dissociation is included and x_{acid} in the system where dissociation is not taken into account. In both systems, the reference state for oxalic acid is the pure neutral acid and for water pure neutral water.

Table S3: Natural logarithm of COSMO*therm* (COSMO-RS-DARE) estimated acid activity coefficients ($\ln \gamma^{\mathrm{I}}_{\mathrm{acid}}$) in binary acid–water solutions, at 298.15 K.

x_{acid}	formic	acetic	propanoic	butanoic	pentanoic	hexanoic
1.00E-06	0.58711339	0.98392293	2.31317841	3.42829066	4.05194158	5.16411499
0.025	0.54306177	0.89236732	1.90249404	2.68958718	3.45079596	4.31954159
0.05	0.50332373	0.8096863	1.64934125	2.30607734	2.97255997	3.65850591
0.075	0.46731327	0.73534001	1.46094509	2.02958375	2.58562041	3.13281444
0.1	0.434569	0.66867114	1.31152646	1.81252307	2.26829997	2.70863213
0.125	0.4047397	0.60900203	1.18891182	1.63463471	2.00493149	2.36173115
0.15	0.37749182	0.5556545	1.08591572	1.48469703	1.78389375	2.07454091
0.175	0.35259059	0.50797919	0.9977602	1.35565429	1.5964182	1.83408597
0.2	0.32977124	0.46539521	0.9210704	1.24278385	1.43584441	1.63069033
0.225	0.30884161	0.42738104	0.85338982	1.14273196	1.29703622	1.45701288
0.25	0.28963087	0.39343659	0.79288278	1.0530592	1.17599883	1.30739072
0.275	0.27196141	0.36311586	0.73816836	0.97197488	1.06960048	1.17748078
0.3	0.25566778	0.3360208	0.68818099	0.89810215	0.97537331	1.0638511
0.325	0.24056269	0.31178433	0.6421236	0.83038045	0.89132991	0.96376444
0.35	0.22653098	0.29006508	0.59937391	0.76797473	0.81587872	0.87503351
0.375	0.2133948	0.27057018	0.55944627	0.7102203	0.74773737	0.79589953
0.4	0.20107795	0.25302578	0.52196564	0.65657718	0.68586123	0.72493063
0.425	0.18948401	0.23718293	0.4866354	0.60660369	0.62940233	0.66095305
0.45	0.17853837	0.2228179	0.45321946	0.55993203	0.57765162	0.60299791
0.475	0.1682009	0.20971166	0.42153494	0.51623973	0.5300164	0.55026302
0.5	0.15843619	0.19767164	0.39142472	0.47526402	0.4859993	0.50206269
0.525	0.14922683	0.18653103	0.36275696	0.43677485	0.44518533	0.45783904
0.55	0.14054248	0.17613174	0.33542649	0.40056219	0.40722672	0.41711193
0.575	0.13233649	0.16631693	0.30933932	0.3664547	0.37182437	0.37948709
0.6	0.12459371	0.15694515	0.28441342	0.33429643	0.33871859	0.34461105
0.625	0.11725594	0.14789019	0.26057911	0.30394537	0.30768746	0.31218399
0.65	0.11026062	0.1390434	0.2377726	0.2752809	0.2785398	0.28195327
0.675	0.10351528	0.13030554	0.21594159	0.24818717	0.25110952	0.25368934
0.7	0.09694731	0.12159215	0.19503017	0.22255982	0.22524549	0.22719742
0.725	0.0904611	0.11282353	0.17498985	0.19830468	0.20082069	0.20230645
0.75	0.0839854	0.10393196	0.15577502	0.17533129	0.17771128	0.17886555
0.775	0.07742878	0.09486058	0.13734462	0.15355996	0.15582024	0.15675354
0.8	0.0706814	0.08556259	0.11965481	0.13291147	0.13505208	0.13581851
0.825	0.06364838	0.07600082	0.1026639	0.11331201	0.11531497	0.11596991
0.85	0.05624226	0.06615389	0.0863318	0.09469547	0.09653572	0.09710858
0.875	0.04838156	0.0559908	0.0706215	0.07699158	0.07863617	0.07915037
0.9	0.04000893	0.04549554	0.05549405	0.06013436	0.06154661	0.06200374
0.925	0.03104436	0.03466039	0.04090928	0.04406603	0.04520168	0.04559182
0.95	0.02142662	0.02348012	0.0268257	0.02872479	0.02953624	0.02983746
0.975	0.01109837	0.011936	0.01320409	0.01405402	0.01449056	0.01466692
1	4.6E-07	4.9E-07	5.2E-07	5.5E-07	5.7E-07	5.8E-07

Table S4: Natural logarithm of COSMO*therm* (COSMO-RS-DARE) estimated water activity coefficients ($\ln \gamma_w$) in binary acid–water solutions, at 298.15 K.

x_w	formic	acetic	propanoic	butanoic	pentanoic	hexanoic
1	0	-5E-08	1.7E-07	2.8E-07	2.1E-07	2.1E-07
0.975	0.00019972	-7.392E-05	0.00847335	0.01381594	0.01200194	0.014972
0.95	0.00147804	0.00217264	0.02158323	0.03350339	0.03446216	0.04438665
0.925	0.00368102	0.00638856	0.03710701	0.05593732	0.06357085	0.08256988
0.9	0.00668606	0.01225051	0.05407727	0.07998413	0.09683614	0.12594266
0.875	0.01039222	0.01947113	0.07193617	0.10507107	0.13263293	0.17225418
0.85	0.01471747	0.02780006	0.09035854	0.13091114	0.16991068	0.22008405
0.825	0.0195955	0.03702253	0.10917322	0.15738393	0.20800891	0.26855251
0.8	0.02497682	0.04695596	0.12831939	0.18444308	0.24652012	0.31711846
0.775	0.03080987	0.05744642	0.14780159	0.21211272	0.28521225	0.36546483
0.75	0.03705543	0.06836862	0.16766966	0.24044703	0.32397327	0.41344492
0.725	0.04368744	0.0796164	0.18800211	0.26949323	0.36276201	0.46098104
0.7	0.05068866	0.09110543	0.20889734	0.29931689	0.4015883	0.5080698
0.675	0.05805941	0.10277171	0.23045247	0.3299853	0.44050528	0.55475684
0.65	0.06579615	0.1145722	0.25277235	0.3615663	0.47959089	0.60112139
0.625	0.0739233	0.12647749	0.27596512	0.39412395	0.51893249	0.64725614
0.6	0.08245107	0.13847875	0.30013231	0.42772737	0.55862787	0.69327117
0.575	0.09139246	0.1505833	0.32537733	0.46244295	0.59878266	0.7392832
0.55	0.10076756	0.16281585	0.35180603	0.49833879	0.63950824	0.78542266
0.525	0.11059325	0.17522915	0.37951643	0.53550894	0.6809327	0.8318258
0.5	0.12088797	0.18789156	0.40862535	0.5740386	0.72319431	0.8786577
0.475	0.13166451	0.20089586	0.43925515	0.61403017	0.76643969	0.92607043
0.45	0.14295802	0.21436386	0.47154549	0.65561727	0.81082333	0.97424313
0.425	0.15482644	0.2284508	0.50565166	0.69893124	0.85652184	1.02335857
0.4	0.16733277	0.24335175	0.54175093	0.7441356	0.90374532	1.07364085
0.375	0.18060018	0.2593055	0.58005241	0.79143454	0.95273103	1.12533813
0.35	0.19479999	0.27660253	0.62081019	0.84106044	1.00374062	1.17874354
0.325	0.21018319	0.29560159	0.66432233	0.89331643	1.057102	1.23420316
0.3	0.22707471	0.31674589	0.71097728	0.94857781	1.1132397	1.2921322
0.275	0.24596267	0.3405945	0.76125276	1.00732473	1.17264919	1.35305112
0.25	0.26745595	0.3678594	0.81579887	1.07018006	1.23600175	1.41762407
0.225	0.29239808	0.3994669	0.87546045	1.13797741	1.30413792	1.48667799
0.2	0.32199823	0.43665748	0.94138704	1.2118609	1.3782254	1.56148125
0.175	0.35794539	0.48115331	1.01520312	1.29344976	1.45991644	1.64363407
0.15	0.40271088	0.5354436	1.09930642	1.38514025	1.55161844	1.73555565
0.125	0.46012377	0.60336201	1.1974348	1.49066134	1.6570733	1.8409844
0.1	0.53656974	0.69129094	1.31586668	1.61629194	1.78257075	1.96623056
0.075	0.64398355	0.81113089	1.46642437	1.77384717	1.9399234	2.123098
0.05	0.80906523	0.98952938	1.67566726	1.98989995	2.15568352	2.33817684
0.025	1.11685083	1.31146564	2.02844528	2.34935174	2.5147199	2.69633977
1.00E-06	6.14037385	6.34972347	7.09744323	7.42506865	7.58978369	7.77038825

Table S5: Natural logarithm of COSMO*therm* (COSMO-RS) estimated acid activity coefficients ($\ln \gamma^{\mathrm{I}}_{\mathrm{acid}}$) in binary acid–water mixtures at 298.15 K calculated using conformers containing no intramolecular H-bonds.

x_{acid}	oxalic	malonic	succinic	glutaric	adipic	pimelic	suberic
1.00E-05	-2.65907112	-0.76147623	0.26956113	1.01517117	1.77214707	2.83075064	3.92539504
1.00E-04	-2.65892982	-0.76178584	0.26884385	1.01395355	1.77037092	2.82786365	3.92120304
1.00E-03	-2.65750693	-0.76486483	0.26169778	1.00182523	1.75269587	2.79917832	3.87960096
1.00E-02	-2.64221592	-0.7938567	0.19299076	0.88526282	1.58416664	2.52952052	3.4927708
0.025	-2.61206024	-0.83441859	0.09004869	0.70945083	1.33324291	2.13956815	2.94581096
0.05	-2.54908715	-0.88063349	-0.04975587	0.4644688	0.98618239	1.61878275	2.23490472
0.075	-2.47256734	-0.90377939	-0.15431781	0.27282139	0.71367735	1.22157138	1.70512202
0.1	-2.38526103	-0.90892985	-0.23034661	0.12551488	0.50169746	0.91756566	1.30535724
0.15	-2.18731153	-0.88131486	-0.32007332	-0.06960104	0.2123435	0.50484233	0.76722482
0.2	-1.96950543	-0.82132369	-0.35431422	-0.17456567	0.04415175	0.25993824	0.44645608
0.25	-1.74191509	-0.74318077	-0.35466149	-0.22353327	-0.04936231	0.11500619	0.25200558
0.3	-1.51199257	-0.65623925	-0.3344778	-0.23758124	-0.09657739	0.03115844	0.13384835
0.35	-1.28604596	-0.56672077	-0.30252623	-0.23008487	-0.11503286	-0.01466767	0.06313905
0.4	-1.06967546	-0.47881434	-0.2645289	-0.20986537	-0.11596915	-0.03685903	0.02229626
0.45	-0.86726019	-0.39533995	-0.22437369	-0.18284385	-0.1067091	-0.04451807	0.0003384
0.5	-0.68225809	-0.31824726	-0.18469068	-0.15309123	-0.09210985	-0.04359607	-0.00983824
0.6	-0.37938855	-0.18839239	-0.11344128	-0.09554906	-0.058627	-0.03031156	-0.01196509
0.7	-0.17888564	-0.095186	-0.05888095	-0.04966094	-0.02973163	-0.01465444	-0.0055371
0.8	-0.06609544	-0.03719637	-0.02308128	-0.01922334	-0.01035333	-0.00351574	0.00036882
0.9	-0.01378992	-0.00800164	-0.00451074	-0.00351731	-0.00090247	0.00126736	0.00243884
1	0	0	0	0	0	0	0

Table S6: Natural logarithm of COSMO*therm* (COSMO-RS) estimated water activity coefficients ($\ln \gamma_w$) in binary acid–water mixtures at 298.15 K calculated using acid conformers containing no intramolecular H-bonds.

x_w	oxalic	malonic	succinic	glutaric	adipic	pimelic	suberic
0.99999	0	5E-08	4E-08	5E-08	7E-08	7E-08	7E-08
0.9999	0	7E-08	8E-08	1.2E-07	1.7E-07	2.3E-07	3E-07
0.999	-7.5E-07	1.79E-06	4.04E-06	6.81E-06	9.95E-06	1.608E-05	2.324E-05
0.99	-8.675E-05	0.00016148	0.00038243	0.00064773	0.00093858	0.00149573	0.00213602
0.975	-0.0006317	0.00087917	0.0022061	0.0037623	0.00539738	0.00840891	0.01179699
0.95	-0.00311576	0.00264485	0.00758855	0.01321616	0.01882883	0.0285457	0.03918605
0.925	-0.00824177	0.00416371	0.01449792	0.02591371	0.03690973	0.05494839	0.07429935
0.9	-0.01663632	0.00463725	0.02172558	0.03996773	0.05711788	0.08403243	0.1124331
0.85	-0.04510044	0.00047402	0.0341477	0.06728896	0.09750067	0.14197834	0.18772929
0.8	-0.09144363	-0.01244287	0.04108786	0.08911293	0.13215122	0.19295923	0.25427517
0.75	-0.15762448	-0.03532545	0.04090863	0.10294284	0.15814961	0.23396581	0.30912802
0.7	-0.24491619	-0.06853397	0.03300228	0.10789121	0.17474883	0.26451502	0.35214834
0.65	-0.35375308	-0.11192481	0.01737471	0.10388175	0.18215049	0.28507525	0.38412777
0.6	-0.48359634	-0.16503733	-0.00567036	0.09129719	0.18103421	0.29657654	0.40624308
0.55	-0.633206	-0.22719333	-0.03562267	0.07079153	0.17228952	0.30006252	0.41969759
0.5	-0.80053395	-0.2974949	-0.07184496	0.04322058	0.15692459	0.29662636	0.42567848
0.4	-1.16926895	-0.4573851	-0.15991292	-0.02909342	0.11046245	0.27322615	0.41961895
0.3	-1.53855188	-0.63160192	-0.26275954	-0.11714034	0.04961544	0.23421506	0.39596262
0.2	-1.8730348	-0.8065898	-0.37295939	-0.21298265	-0.01883421	0.18600459	0.3611006
0.1	-2.16430647	-0.97295678	-0.48425563	-0.31054967	-0.09001356	0.1333231	0.31974399
0	-2.41450073	-1.12458694	-0.59206637	-0.40585256	-0.16066295	0.07937015	0.27524831

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