

# Supplement to GMDD paper "Chemistry and deposition in the Model of Atmospheric composition at Global and Regional scales using Inversion Techniques for Trace gas Emissions (MAGRITTE v1.0). Part B. Dry deposition" by Müller et al.

## S1 Evaluation of HLC estimation methods

### 5 S1.1 Overview of methods

We consider direct HLC estimation methods as well as estimation methods for the liquid vapor pressure ( $p_0^L$ ) and the infinite dilution activity coefficient (IDAC). IDAC and  $p_0^L$  might be combined to estimate HLC (Eq. (6)). An overview of the methods is given in Table S1.

**Table S1.** Estimation methods considered in this work for the Henry's Law constant ( $k_h$ ), the liquid state saturation vapour pressure ( $p_0^L$ ), and the activity coefficient ( $\gamma$ ).

method	abbr.	property	remark
GROMHE	grom	$k_h$	a
Cabani	Cab	$k_h$	
EVAPORATION	evap	$p_0^L$	
Nannoolal	Nan	$p_0^L$	b
UNIFAC-Hansen	Hansen	$\gamma$	c
AIOMFAC	aiom	$\gamma$	d
AIOMFAC(m)	aiom(m)	$\gamma$	
UNIFAC-Raatikainen	Raat	$\gamma$	c
UNIFAC-Dortmund	dort	$\gamma$	c
AQUAFAC-Jain	aqua	$\gamma^\infty$	a

<sup>a</sup> Estimates only at 298.15 K.

<sup>b</sup> Vapour pressure estimation method of Nannoolal et al. (2008), using the boiling point estimation method of Nannoolal et al. (2004) as input.

<sup>c</sup> Estimates  $\gamma$  at any organic-water composition (not only at infinite dilution).

<sup>d</sup> Estimates  $\gamma$  at any organic-inorganic-water composition (not only at infinite dilution).

The methods considered here estimating HLC directly from molecular structure are the method of Cabani et al. (1981) and the more recent GROMHE (GROup contribution Method for Henry's law Estimate, Raventos-Duran et al., 2010), which was developed specifically for atmospherically relevant compounds. Raventos-Duran et al. (2010) showed that GROMHE performed better than two other HLC estimation methods: HENRYWIN (Meylan and Howard, 2000) and SPARC (Hilal et al., 2008). These latter two methods are therefore not considered here.

The estimation methods of  $p_0^L$  include the group-contribution method EVAPORATION (Estimation of VApour Pressure of Organics Compennolle et al., 2011) and the vapour pressure estimation method of Nannoolal et al. (2008), with normal boiling points estimated with the method of Nannoolal et al. (2004).

A popular group-contribution method to estimate activity coefficients is UNIFAC (UNIQUAC Functional-group Activity Coefficients) (Fredenslund et al., 1977). Although UNIFAC estimates activity coefficients for mixtures of organic molecules and water in any concentration range, we only consider here infinite dilution activity coefficients. Several UNIFAC parameterisations exist. The parameterisation of Hansen et al. (1991) (UNIFAC-Hansen) has a broad coverage of functional groups, but was not developed for atmospheric compounds. Nonetheless, UNIFAC-Hansen is a starting point on which several other reparameterisations are build. Raatikainen and Laaksonen (2005) introduced reparameterisations for acid and hydroxyl groups and water (UNIFAC-Raatikainen), while keeping UNIFAC-Hansen parameters for the other groups. UNIFAC-Dortmund (Gmehling et al., 2002) was developed as a successor of the original UNIFAC, and has a different mathematical

framework. AIOMFAC (Aerosol Inorganic Organic Mixtures Functional groups Activity Coefficients, Zuend, 2011) can be considered as a generalisation of UNIFAC as it also covers mixtures with inorganic components. Regarding the organic part, it combines features of the UNIFAC versions of Peng et al. (2001) and Marcolli and Peter (2005), both developed specifically for atmospherically relevant compounds. These latter two methods are therefore not separately discussed. Finally, AQUAFAC (Aqueous Functional Group Activity Coefficients, Jain et al., 2008) estimates an IDAC from molecular structure and is based on data for compounds of pharmaceutical and environmental interest. As opposed to UNIFAC and AIOMFAC, it only calculates the activity coefficient at infinite dilution of the solute.

## S1.2 Scope of the methods

The HLC estimation method of Cabani et al. (1981), GROMHE and the IDAC estimation method AQUAFAC are applicable only to infinitely dilute aqueous solutions. The UNIFAC-like estimation methods (including AIOMFAC) treat water-organic mixtures in any concentration range. In addition, AIOMFAC treats also water-organic-inorganic mixtures (Zuend, 2011). GROMHE and AQUAFAC are limited to 298.15 K, while the other methods allow for a temperature dependence. Very recently, the temperature range of AIOMFAC has been extended (Ganbavale et al., 2015) to deal also with the low temperatures of the upper troposphere. Not all methods are designed for all molecule types considered here. The method of Cabani et al. (1981) and UNIFAC-Dortmund cannot treat mono-nitrates, hydroperoxides, peracids and peroxy acyl nitrates. AQUAFAC applies to mono-nitrates but not to the other molecule types just mentioned.

## S1.3 Modifications to AIOMFAC

AIOMFAC (Zuend, 2011) inherited parameters of the acid-water and acid-hydroxyl interaction groups from the UNIFAC version of Peng et al. (2001). However, this made estimations for monofunctional acids worse compared to the original UNIFAC-Hansen (see Tables S6 and S7). Therefore, two COOH groups are now considered: (i) COOH<sup>Hansen</sup> with the original parameters of Hansen et al. (1991), and (ii) COOH<sup>Peng</sup> with the parameters of Peng et al. (2001). These two groups differ in their interaction with H<sub>2</sub>O and the OH group. The following criterion is chosen to discriminate between both groups: a COOH group of a molecule is evaluated as COOH<sup>Hansen</sup> if there are no other hydrogen-bonding groups (OH, COOH, OOH or COOOH) in the molecule, and as COOH<sup>Peng</sup> if there are. With this criterion, mono-functional acids have the COOH<sup>Hansen</sup> group, while diacids and hydroxy-acids (used by Peng et al. (2001) to derive the parameters) have the COOH<sup>Peng</sup> group. This modification can be compared to the one applied by Marcolli and Peter (2005), where several CH<sub>n</sub> group were considered instead of one, depending on the molecular structure.

One of the CH<sub>n</sub> groups considered by AIOMFAC and inherited from Marcolli and Peter (2005) is the hydrophobic tail group CH<sub>n</sub><sup>tail</sup> (noted CH<sub>n</sub><sup>alc-tail</sup> in Zuend, 2011). This group was inserted to account for the tendency of alcohols with hydrophobic alkyl chains to form micelles (Marcolli and Peter, 2005). In AIOMFAC, it is only applied for molecules that contain OH groups and no other functionalities. Here, we also apply it to any molecules with hydrogen bonding groups. The exact procedure to identify CH<sub>n</sub> as CH<sub>n</sub><sup>tail</sup> is given by Marcolli and Peter (2005). Applying this group for monofunctional acids gives a further improvement for both  $k_h$  and  $\gamma^\infty$ .

The AIOMFAC interaction parameters for nitrates, hydroperoxides, peroxides, peracids and peroxy acyl nitrates were derived in the study of Compernelle et al. (2009) and are based on fittings to activity coefficients generated by SPARC 4.2. In that study, a procedure was followed to generate parameters independent of other UNIFAC-versions. However, we noticed that this leads to relatively bad parameters especially for the nitrate group and the PAN group. Essentially, we repeated the procedure of Compernelle et al. (2009), with the difference that instead of the interaction parameters of Table 5 in that study, parameters of UNIFAC-Hansen are used instead. The resulting parameters are given in Table S2.

## 40 S1.4 Extension of AQUAFAC

We extended the AQUAFAC method (Jain et al., 2008), such that it can also treat PANs, hydroperoxides, peracids and peroxides. HLC data (Sander, 2015) and  $p_L^0$  data (Egerton et al., 1951; Bruckmann and Willner, 1983) were first combined to obtain  $\gamma^\infty$  data, and group contributions were derived following a least square optimization of calculated vs. experimental  $\log_{10} \gamma^\infty$  data. These are presented in Table S3.

**Table S2.** Values of coefficients  $a_{mk}, a_{km}$  replacing those of Table 6 of Compornolle et al. (2009). They are derived by replacing first the parameters of Table 5 in the same study by experimental parameters of Hansen et al. (1991). The parameters of Table 7 of Compornolle et al. (2009) are unchanged.

$m \backslash k$	CH <sub>n</sub> ONO <sub>2</sub>	CH <sub>n</sub> OOH	COOOH	CH <sub>n</sub> OOCH <sub>n</sub>	PAN
C=C	1.1E4, -323	467, -58	743, 780	753, -269	461, 60
OH	-63, 843	-295, 144	1650, -465	-3, 834	-91, 577
H <sub>2</sub> O	309, 619	58, 102	137, -4	51, 437	211, 275
CHO	349, -157	-386, 405	1.2E4, -514	-11, 511	286, -173
CH <sub>n</sub> CO	-125, 113	-349, 433	723, -369	-174, 443	53, 16.6
COOH	-64, 1.14E4	-378, 1.2E4	-413, 1.1E4	-56, 1160	-282, 1.2E4
CH <sub>n</sub> O	1.1E4, -356	-423, 661	1.2E4, -578	49, 55	1.E4, -316
CCOO	2036, -400	1100, -425	646, -193	-74, 207	949, -342

**Table S3.** Newly derived AQUAFAC group contributions for hydroperoxides, peracids, peroxyacynitrates and peroxides.

group	contribution
-OOH	-1.041
-C(=O)OOH	-0.505
-C(=O)OONO	1.666
COOC	-0.85

### S1.5 Experimental data used for HLC evaluation

The methods are tested on monofunctional and polyfunctional compounds. For monofunctional compounds the following classes are considered: aldehydes, ketones, ethers, esters (non-formates), formates, alcohols, acids, nitrates, per-group members (either hydroperoxide or peracid) and peroxy acyl nitrates (PANs) (see Tables S6 and S7). A few polyfunctional classes are also tested: diols, dicarbonyls, diacids, polyols and functionalized diacids. The group 'others' in Table S6) includes various molecule types (e.g. dinitrates, hydroxynitrates, carbonyl nitrates, hydroxy hydroperoxides, hydroxy ethers).

We test two physical properties: HLC and IDAC, as they are both relevant to the aqueous phase. Methods that estimate one property can be combined with a vapour pressure estimation method (EVAPORATION or the Nannoolal method) to estimate the other property. A large part of the HLC data are retrieved from the compilation of Sander (2015), but regarding the polyfunctional compounds, we use also the HLC values derived recently (Compornolle et al., 2014a, b). The IDAC data originate to a large extent from Kojima et al. (1997). The HLC and IDAC experimental data are tabulated in Table S4 and Table S5 respectively, together with their assignment to a specific molecule class.

As some methods (GROMHE and AQUAFAC) provide estimations only at 298.15 K, we only use data within  $298.15 \pm 20$  K. For GROMHE, a fixed enthalpy of gas phase dissolution of 50 kJ/mol was used to correct for deviations from 298.15 K. A similar procedure was also applied by Raventos-Duran et al. (2010) to correct for small deviations from 298.15 K.

Table S4: Experimental HLC data used to test the methods.

name	reference	$T/K$	$k_h \frac{\text{atm}}{\text{M}}$
<i>mono-aldehydes</i>			
ethanal	Sander_Buttery1969	298.15	15
propanal	Sander_Buttery1969	298.15	13
butanal	Sander_Buttery1969	298.15	8.7
pentanal	Sander_Buttery1969	298.15	6.8
hexanal	Sander_Buttery1969	298.15	4.7
heptanal	Sander_Buttery1969	298.15	3.7

Table S4: (Continued)

name	reference	T/K	$k_h \frac{\text{atm}}{\text{M}}$
octanal	Sander_Buttery1969	298.15	1.9
nonanal	Sander_Buttery1969	298.15	1.3
trans-2-butenal	Sander_Buttery1971	298.15	52
2-methyl-2-propenal	Sander_Iraci1998	298.15	6.5
trans-2-hexenal	Sander_Buttery1971	298.15	20
trans,trans-2,4-hexadienal	Sander_Buttery1971	298.15	10
trans-2-octenal	Sander_Buttery1971	298.15	13
ethanal	Sander_Snider1985	298.15	13
ethanal	Sander_Betterton1988	298.15	11
ethanal	Sander_Zhou1990	298.15	17
ethanal	Sander_Benkelberg1995	298.15	13
propanal	Sander_Zhou1990	298.15	13
butanal	Sander_Zhou1990	298.15	9.6
pentanal	Sander_Zhou1990	298.15	6.4
hexanal	Sander_Zhou1990	298.15	4.9
heptanal	Sander_Zhou1990	298.15	3.3
octanal	Sander_Zhou1990	298.15	2.1
nonanal	Sander_Zhou1990	298.15	1
decanal	Sander_Zhou1990	298.15	0.61
2-propenal	Sander_Snider1985	298.15	7.4
<i>mono-ketones</i>			
propanone	Sander_Burnett1963	298.15	28
propanone	Sander_Buttery1969	298.15	25
propanone	Sander_Vitenberg1975	298.15	25
propanone	Sander_Hoff1993	298.15	27
butanone	Sander_Buttery1969	298.15	21
butanone	Sander_Vitenberg1975	298.15	18
butanone	Sander_Friant1979	303	10
2-pentanone	Sander_Buttery1969	298.15	16
2-heptanone	Sander_Buttery1969	298.15	7
2-octanone	Sander_Buttery1969	298.15	5.4
2-nonanone	Sander_Buttery1969	298.15	2.7
2-undecanone	Sander_Buttery1969	298.15	1.6
3-buten-2-one	Sander_Iraci1998	298.15	41
propanone	Sander_Snider1985	298.15	26
propanone	Sander_Zhou1990	298.15	35
propanone	Sander_Betterton1991	298.15	32
propanone	Sander_Benkelberg1995	298.15	27
butanone	Sander_Snider1985	298.15	18
butanone	Sander_Zhou1990	298.15	20
<i>mono-ethers</i>			
ethoxyethane	Sander_Signer1969	298.15	0.8
diisopropylether	Sander_Nielsen1994	298.15	0.49
tetrahydrofuran	Sander_Signer1969	298.15	22
2-methoxy-2-methylpropane	Sander_Robbins1993	298.15	1.6
2-methoxy-2-methylpropane	Callender and Davis (2001)	298.15	1.2

Table S4: (Continued)

name	reference	T/K	$k_h \frac{\text{atm}}{\text{M}}$
1-propoxypropane	Sander_Hartkopf1973	298.15	0.23
tetrahydrofuran	Sander_Cabani1971	298.15	14
tetrahydropyran	Sander_Cabani1971	298.15	8
2-methyltetrahydrofuran	Sander_Cabani1971	298.15	11
2,5-dimethyltetrahydrofuran	Sander_Cabani1971	298.15	5.7
2-methoxy-2-methylpropane	Bierwagen and Keller (2001)	298.15	0.73
<i>mono-formates</i>			
methylformate	Sander_Hoff1993	298.15	4.1
methylformate	Sander_Hartkopf1973	298.15	4.1
methylformate	Kutsuna et al. (2005)	298.15	4.2
ethylformate	Kutsuna et al. (2005)	298.15	3.4
propylformate	Kutsuna et al. (2005)	298.15	2.6
<i>mono-esters</i>			
methylacetate	Sander_Butler1935	298.15	11
methylacetate	Sander_Buttery1969	298.15	8.7
ethylacetate	Sander_Butler1935	298.15	7.6
methylpropanoate	Sander_Buttery1969	298.15	5.8
methylbutanoate	Sander_Buttery1969	298.15	4.8
methylpentanoate	Sander_Buttery1969	298.15	3.1
methylhexanoate	Sander_Buttery1969	298.15	2.7
methyloctanoate	Sander_Buttery1969	298.15	1.3
methylacetate	Sander_Kieckbusch1979	298.15	7.8
ethylacetate	Sander_Kieckbusch1979	298.15	5.9
propylacetate	Sander_Kieckbusch1979	298.15	4.6
butylacetate	Sander_Kieckbusch1979	298.15	3.6
pentylacetate	Sander_Kieckbusch1979	298.15	2.8
ethylacetate	Kutsuna et al. (2005)	298.15	6
<i>mono-acids</i>			
ethanoicacid	Sander_Khan1995	298.15	5500
propanoicacid	Sander_Butler1935	298.15	2300
propanoicacid	Sander_Servant1991	298.15	6200
propanoicacid	Sander_Khan1995	298.15	5700
butanoicacid	Sander_Butler1935	298.15	1900
butanoicacid	Sander_Khan1995	298.15	4700
pentanoicacid	Sander_Khan1995	298.15	2200
2-methylpropanoicacid	Sander_Servant1991	298.15	5700
2-methylpropanoicacid	Sander_Khan1995	298.15	1100
3-methylbutanoicacid	Sander_Khan1995	298.15	1200
trimethylaceticacid	Sander_Khan1995	298.15	350
2-methylpropenoicacid	Sander_Khan1995	298.15	2400
ethanoicacid	Sander_Johnson1996	298.15	4100
hexanoicacid	Sander_Khan1995	298.15	1400
<i>mono-alcohols</i>			
ethanol	Sander_Butler1935	298.15	190
ethanol	Sander_Burnett1963	298.15	220
ethanol	Sander_Rohrschneider1973	298.15	230

Table S4: (Continued)

name	reference	T/K	$k_h \frac{\text{atm}}{\text{M}}$
1-propanol	Sander_Butler1935	298.15	140
1-propanol	Sander_Burnett1963	298.15	160
1-butanol	Sander_Butler1935	298.15	120
1-butanol	Sander_Buttery1969	298.15	110
1-butanol	Sander_Burnett1963	298.15	140
1-butanol	Sander_Friant1979	303	54
1-pentanol	Sander_Butler1935	298.15	77
1-hexanol	Sander_Butler1935	298.15	65
1-hexanol	Sander_Buttery1969	298.15	59
1-octanol	Sander_Buttery1969	298.15	40
2-methyl-1-propanol	Sander_Butler1935	298.15	84
2-methyl-1-propanol	Sander_Snider1985	298.15	100
2-methyl-1-butanol	Sander_Butler1935	298.15	71
2-pentanol	Sander_Butler1935	298.15	68
2-methyl-2-propanol	Sander_Butler1935	298.15	84
2-methyl-2-butanol	Sander_Butler1935	298.15	73
2-methyl-3-buten-2-ol	Sander_Butler1935	303.15	65
ethanol	Sander_Snider1985	298.15	190
1-propanol	Sander_Snider1985	298.15	150
1-butanol	Sander_Snider1985	298.15	130
2-propanol	Sander_Snider1985	298.15	130
2-butanol	Sander_Snider1985	298.15	110
2-methyl-2-propanol	Sander_Snider1985	298.15	70
<i>mono-nitrates</i>			
1-propylnitrate	Sander_Hauff1998	298.15	0.79
2-propylnitrate	Sander_Hauff1998	298.15	0.62
1-butylnitrate	Sander_Hauff1998	298.15	0.65
2-butylnitrate	Sander_Hauff1998	298.15	0.44
1-pentylnitrate	Sander_Kames1992	293	1.2
1-pentylnitrate	Sander_Hauff1998	298.15	0.6
2-pentylnitrate	Sander_Hauff1998	298.15	0.34
3-pentylnitrate	Sander_Hauff1998	298.15	0.37
3-methylbutylnitrate	Sander_Hauff1998	298.15	0.45
1-hexylnitrate	Sander_Hauff1998	298.15	0.67
methylnitrate	Sander_Kames1992	298.15	2
ethylnitrate	Sander_Kames1992	298.15	1.6
1-propylnitrate	Sander_Kames1992	298.15	1.1
2-propylnitrate	Sander_Kames1992	298.15	0.79
1-butylnitrate	Sander_Kames1992	298.15	1
1-butylnitrate	Sander_Luke1989	298.15	1
2-butylnitrate	Sander_Kames1992	298.15	0.65
2-butylnitrate	Sander_Luke1989	298.15	0.65
2-methylpropylnitrate	Sander_Kames1992	298.15	0.7
2-pentylnitrate	Sander_Kames1992	298.15	0.37
<i>mono-peroxyacylnitrates</i>			
peroxyacetylnitrate	Sander_Holdren1984	283	5

Table S4: (Continued)

name	reference	T/K	$k_h \frac{\text{atm}}{\text{M}}$
peroxyacetylnitrate	Sander_Kames1995	293	4.1
peroxypropionylnitrate	Sander_Kames1995	293	2.9
peroxybutylnitrate	Sander_Kames1995	293	2.3
peroxyisobutylnitrate	Sander_Kames1995	293	1
peroxy-2-propenoylnitrate	Sander_Kames1995	293	1.7
peroxyacetylnitrate	Sander_Kames1991	298.15	2.8
<i>mono-pergroup</i>			
hydroperoxymethane	Sander_Lind1994	298.15	300
hydroperoxymethane	Sander_OSullivan1996	298.15	310
hydroperoxyethane	Sander_OSullivan1996	298.15	340
aceticperoxyacid	Sander_Lind1994	298.15	670
aceticperoxyacid	Sander_OSullivan1996	298.15	840
<i>dicarbonyls</i>			
2,3-butadione	Sander_Snider1985	298.15	57
glyoxal	Sander_Zhou1990	298.15	360000
methylglyoxal	Sander_Zhou1990	298.15	32000
2,3-butadione	Sander_Betterton1991	298.15	74
methylglyoxal	Sander_Betterton1988	298.15	3700
<i>diols</i>			
1,2-ethanediol	Sander_Bone1983	293	410000
1,3-propanediol	Sander_Bone1983	293	920000
1,4-pentanediol	Compernolle et al. (2014b)	298.15	2.3e+06
1,2-pentanediol	Compernolle et al. (2014b)	298.15	140000
1,7-heptanediol	Compernolle et al. (2014b)	298.15	6.2e+06
1,2-hexanediol	Compernolle et al. (2014b)	298.15	170000
1,10-decanediol	Compernolle et al. (2014b)	298.15	2.7e+06
2,5-hexanediol	Compernolle et al. (2014b)	298.15	1.4e+06
2,4-pentanediol	Compernolle et al. (2014b)	298.15	390000
1,9-nonanediol	Compernolle et al. (2014b)	298.15	3.1e+06
1,2-propanediol	Compernolle et al. (2014b)	298.15	270000
1,3-butanediol	Compernolle et al. (2014b)	298.15	710000
1,2-ethanediol	Compernolle et al. (2014b)	298.15	660000
1,5-pentanediol	Compernolle et al. (2014b)	298.15	7.1e+06
1,2-butanediol	Compernolle et al. (2014b)	298.15	210000
1,3-propanediol	Compernolle et al. (2014b)	298.15	1.6e+06
2,3-butanediol	Compernolle et al. (2014b)	298.15	110000
1,4-butanediol	Compernolle et al. (2014b)	298.15	3.5e+06
<i>diacids</i>			
decanoicdiacid	Compernolle et al. (2014a)	298.15	7.7e+09
ethanoicdiacid	Compernolle et al. (2014a)	298.15	6.2e+08
octanoicdiacid	Compernolle et al. (2014a)	298.15	7.8e+09
butanoicdiacid	Compernolle et al. (2014a)	298.15	4.2e+09
propanoicdiacid	Compernolle et al. (2014a)	298.15	3.9e+10
heptanoicdiacid	Compernolle et al. (2014a)	298.15	8.2e+09
nonanoicdiacid	Compernolle et al. (2014a)	298.15	9e+09
pentanoicdiacid	Compernolle et al. (2014a)	298.15	5.2e+09

Table S4: (Continued)

name	reference	$T/K$	$k_h \frac{\text{atm}}{\text{M}}$
hexanoicdiacid	Compernolle et al. (2014a)	298.15	6.7e+09
propanoicdiacid	Compernolle et al. (2014a)	298.15	9.4e+09
pentanoicdiacid	Compernolle et al. (2014a)	298.15	2.4e+09
butanoicdiacid	Compernolle et al. (2014a)	298.15	2e+09
<i>polyols (&gt; 2 OH)</i>			
1,2,3-propanetriol	Compernolle et al. (2014b)	298.15	4.8e+08
meso-erythritol	Compernolle et al. (2014b)	298.15	1.1e+12
pentaerythritol	Compernolle et al. (2014b)	298.15	7.4e+12
D-mannitol	Compernolle et al. (2014b)	298.15	1.8e+17
adonitol	Compernolle et al. (2014b)	298.15	4.7e+13
D-arabinitol	Compernolle et al. (2014b)	298.15	6.8e+13
xylitol	Compernolle et al. (2014b)	298.15	4e+13
galacticol	Compernolle et al. (2014b)	298.15	9.1e+16
sorbitol	Compernolle et al. (2014b)	298.15	6.7e+16
<i>func. diacids</i>			
3-carboxylic-3-hydroxypentanoicdiacid	Compernolle et al. (2014a)	298.15	1.1e+17
2,3-dihydroxybutanoicdiacid	Compernolle et al. (2014a)	298.15	2.6e+17
<i>others</i>			
1,4-dioxane	Sander_Rohrschneider1973	298.15	220
1,4-dioxane	Sander_Friant1979	303	140
2-oxopropanoicacid	Sander_Khan1991	298.15	310000
1,2-ethylenedinitrate	Sander_Kames1992	293	640
1,2-propylenedinitrate	Sander_Kames1992	293	180
2-nitrooxyethanol	Sander_Kames1992	293	40000
1-nitrooxy-2-propanol	Sander_Kames1992	293	7300
2-nitrooxy-1-propanol	Sander_Kames1992	293	6700
nitrooxyacetone	Sander_Kames1992	293	1000
2-hydroxyethanal	Sander_Betterton1988	298.15	41000
1,3-dioxolane	Sander_Cabani1971	298.15	40
1,4-dioxane	Sander_Cabani1971	298.15	200
2-oxopropanoicacid	Sander_Khan1995	298.15	310000
2-nitrooxyethanol	Sander_Shepson1996	298.15	39000
1-nitrooxy-2-propanol	Sander_Shepson1996	298.15	11000
2-nitrooxy-1-propanol	Sander_Shepson1996	298.15	4500
1-nitrooxy-2-butanol	Sander_Shepson1996	298.15	5800
2-nitrooxy-1-butanol	Sander_Shepson1996	298.15	6000
3-nitrooxy-2-butanol	Sander_Shepson1996	298.15	10000
hydroxymethylhydroperoxide	Sander_OSullivan1996	298.15	1.7e+06
hydroxymethylhydroperoxide	Sander_Staffelbach1993	298.15	1.6e+06
hydroxymethylhydroperoxide	Sander_Zhou1992	298.15	480000
bis(hydroxymethyl)peroxide	Sander_Zhou1992	298.15	450000

Table S5: Experimental IDAC data used to test the methods.

name	reference	$T/K$	$\gamma^\infty$
<i>mono-aldehydes</i>			



Table S5: (Continued)

name	reference	$T/K$	$\gamma^\infty$
octanal	Kojima_Abraham1990	298.15	8920
propanal	Kojima_Dallas1993	298.15	13.03
butanal	Kojima_Dallas1993	298.15	48.6
pentanal	Kojima_Dallas1993	298.15	220.2
hexanal	Kojima_Dallas1993	298.15	813.4
octanal	Kojima_Li1992	298.15	8243
ethanal	Kojima_Mash1980	298.15	3.94
ethanal	Kojima_Pecsar1966	293.15	3.59
ethanal	Kojima_Pecsar1966	303.15	4.36
ethanal	Kojima_Pecsar1966	313.15	3.71
propanal	Kojima_Pecsar1966	293.15	14.7
propanal	Kojima_Pecsar1966	303.15	17.6
propanal	Kojima_Pecsar1966	313.15	15.4
butanal	Kojima_Pecsar1966	293.15	63
butanal	Kojima_Pecsar1966	303.15	73
butanal	Kojima_Pecsar1966	313.15	61
heptanal	Kojima_Sorensen1979	303.15	4178
octanal	Kojima_Sorensen1979	303.15	19230
nonanal	Kojima_Sorensen1979	303.15	75188
<i>mono-ketones</i>			
2-nonanone	Kojima_Abraham1990	298.15	24800
propanone	Kojima_Bao1993	298.15	7.69
butanone	Kojima_Bao1993	298.15	26.4
3-pentanone	Kojima_Bao1993	298.15	106
propanone	Kojima_Dallas1993	298.15	7.01
butanone	Kojima_Dallas1993	298.15	25.6
2-pentanone	Kojima_Dallas1993	298.15	93.4
2-hexanone	Kojima_Dallas1993	298.15	355.7
2-heptanone	Kojima_Dallas1993	298.15	1397
3-pentanone	Kojima_Dallas1993	298.15	107.4
3-methyl-2-butanone	Kojima_Dallas1993	298.15	84
cyclopentanone	Kojima_Dallas1993	298.15	29.2
propanone	Kojima_Landau1991	298.15	7.31
butanone	Kojima_Landau1991	298.15	27.6
2-pentanone	Kojima_Landau1991	298.15	102
3-pentanone	Kojima_Landau1991	298.15	113
propanone	Kojima_Lee1963	288.15	5.85
propanone	Kojima_Lee1963	288.15	5.83
propanone	Kojima_Lee1963	303.15	7.65
propanone	Kojima_Lee1963	303.15	7.42
2-nonanone	Kojima_LiCar1993	298.15	16290
5-methyl-2-hexanone	Kojima_Macedo1979	298.15	1520
propanone	Kojima_Mash1980	298.15	7.56
butanone	Kojima_Mash1980	298.15	27.8
2-pentanone	Kojima_Mash1980	298.15	98.9
3-pentanone	Kojima_Mash1980	298.15	113

Table S5: (Continued)

name	reference	$T/K$	$\gamma^\infty$
3-hexanone	Kojima_Mash1980	298.15	412
butanone	Kojima_Othmer1947	298.15	25.98
propanone	Kojima_Richon1985	303.15	7.69
2-heptanone	Kojima_Sorensen1979	293.15	1435
2-heptanone	Kojima_Sorensen1979	298.15	1468
4-heptanone	Kojima_Sorensen1979	303.15	1653
5-nonanone	Kojima_Sorensen1979	303.15	21700
3-methyl-2-pentanone	Kojima_Sorensen1979	298.15	261
4-methyl-2-pentanone	Kojima_Sorensen1979	298.15	292
3,3-dimethyl-2-butanone	Kojima_Sorensen1979	298.15	288
2-methyl-3-pentanone	Kojima_Sorensen1979	298.15	361
2,4-dimethyl-3-pentanone	Kojima_Sorensen1979	298.15	1107
2,6-dimethyl-4-heptanone	Kojima_Sorensen1979	298.15	8760
cyclohexanone	Kojima_Sorensen1979	298.15	54.1
propanone	Kojima_Sorrentino1986	303.15	7.7
butanone	Kojima_Sorrentino1986	303.15	29.5
butanone	Kojima_Zhang1995	298.15	25.3
<i>mono-ethers</i>			
1-propoxypropane	Kojima_Abraham1990	298.15	2330
1-butoxybutane	Kojima_Abraham1990	298.15	37500
2-methoxy-2-methylpropane	Kojima_Dallas1993	298.15	112.5
1-propoxypropane	Kojima_Dallas1993	298.15	1560
diisopropylether	Kojima_Dallas1993	298.15	496.1
tetrahydrofuran	Kojima_Dallas1993	298.15	17
tetrahydropyran	Kojima_Dallas1993	298.15	78.6
ethoxyethane	Kojima_Kohn1988	298.15	109.6
1-propoxypropane	Kojima_Li1993	298.15	2315
1-butoxybutane	Kojima_Li1993	298.15	47180
diisopropylether	Kojima_Li1993	298.15	628
diisopropylether	Kojima_LiCar1993	298.15	667
1-propoxypropane	Kojima_LiCarr1993	298.15	2210
1-butoxybutane	Kojima_LiCarr1993	298.15	28100
ethoxyethane	Kojima_Nielsen1994	296.15	72
diisopropylether	Kojima_Nielsen1994	296.15	639
tetrahydrofuran	Kojima_Pividal1992	293.15	16.6
tetrahydrofuran	Kojima_Pividal1992	308.15	23.5
1-methoxypropane	Kojima_Sorensen1979	298.15	132
1-methoxybutane	Kojima_Sorensen1979	298.15	546
2-methoxybutane	Kojima_Sorensen1979	298.15	302
1-methoxy-2-methylpropane	Kojima_Sorensen1979	298.15	442
1-ethoxypropane	Kojima_Sorensen1979	298.15	257
1-propoxypropane	Kojima_Sorensen1979	298.15	1444
2-ethoxypropane	Kojima_Sorensen1979	298.15	200
2-propoxypropane	Kojima_Sorensen1979	298.15	1202
ethoxyethane	Kojima_Zhang1995	298.15	69.7
tetrahydrofuran	Kojima_Zhang1995	313.15	20.8

Table S5: (Continued)

name	reference	$T/K$	$\gamma^\infty$
<i>mono-formates</i>			
methylformate	Kojima_Dallas1993	298.15	15.5
ethylformate	Kojima_Dallas1993	298.15	47.3
propylformate	Kojima_Dallas1993	298.15	169
methylformate	Kojima_Pescar1966	293.15	16.1
methylformate	Kojima_Pescar1966	303.15	17.4
methylformate	Kojima_Pescar1966	313.15	14.2
ethylformate	Kojima_Pescar1966	293.15	46
ethylformate	Kojima_Pescar1966	303.15	51
ethylformate	Kojima_Pescar1966	313.15	41
propylformate	Kojima_Pescar1966	293.15	150
propylformate	Kojima_Pescar1966	303.15	168
propylformate	Kojima_Pescar1966	313.15	131
methylacetate	Kojima_Dallas1993	298.15	22.6
<i>mono-esters (non-formates)</i>			
ethylacetate	Kojima_Dallas1993	298.15	65.3
propylacetate	Kojima_Dallas1993	298.15	242
butylacetate	Kojima_Dallas1993	298.15	814
pentylacetate	Kojima_Dallas1993	298.15	3233
hexylacetate	Kojima_Dallas1993	298.15	12490
isopropylacetate	Kojima_Dallas1993	298.15	195.5
isobutylacetate	Kojima_Dallas1993	298.15	844.4
isopentylacetate	Kojima_Dallas1993	298.15	2977
ethylpropanoate	Kojima_Dallas1993	298.15	256
ethylbutanoate	Kojima_Dallas1993	298.15	730
methylpropanoate	Kojima_Melder1978	293.15	87.1
methylbutanoate	Kojima_Melder1978	293.15	331
methylpentanoate	Kojima_Melder1978	293.15	1259
methylhexanoate	Kojima_Melder1978	293.15	3981
ethylacetate	Kojima_Pividal1992	288.15	63.9
butylacetate	Kojima_Sorensen1979	298.15	799.5
isopentylacetate	Kojima_Sorensen1979	303.15	3146
cyclohexylacetate	Kojima_Sorensen1979	298.15	2720
methylbutanoate	Kojima_Sorensen1979	294.15	358.9
ethylpropanoate	Kojima_Sorensen1979	298.15	260
ethylbutanoate	Kojima_Sorensen1979	295.15	1041
propylpropanoate	Kojima_Sorensen1979	298.15	1019
ethylpentanoate	Kojima_Sorensen1979	298.15	2880
propylbutanoate	Kojima_Sorensen1979	290.15	4454
butylpentanoate	Kojima_Sorensen1979	298.15	19400
isopropylbutanoate	Kojima_Sorensen1979	298.15	3077
ethylacrylate	Kojima_Sorensen1979	293.15	257
vinylacetate	Kojima_Sorensen1979	293.15	416
methylacetate	Kojima_Zhang1995	313.15	27.2
ethylacetate	Kojima_Zhang1995	313.15	84.5
<i>mono-acids</i>			

Table S5: (Continued)

name	reference	$T/K$	$\gamma^\infty$
ethanoicacid	Kojima_Hwang1992	298.15	2.9
hexanoicacid	Kojima_Hwang1992	298.15	468
pentanoicacid	Kojima_Sorensen1979	298.15	127
hexanoicacid	Kojima_Sorensen1979	298.15	470.5
heptanoicacid	Kojima_Sorensen1979	303.15	2523
butanoicacid	Kojima_Tochigi1977	298.15	52.9
<i>mono-alcohols</i>			
ethanol	Kojima_Abraham1990	298.15	3.73
1-propanol	Kojima_Abraham1990	298.15	13.5
1-butanol	Kojima_Abraham1990	298.15	52.24
1-pentanol	Kojima_Abraham1990	298.15	208.9
1-hexanol	Kojima_Abraham1990	298.15	738.9
2-methyl-1-propanol	Kojima_Altsybeeva1964	298.15	48.4
2-methyl-2-propanol	Kojima_Altsybeeva1964	298.15	12.2
2-propanol	Kojima_Bergmann1991	317.85	8.8
ethanol	Kojima_Dallas1993	298.15	3.74
ethanol	Kojima_Dallas1993	298.15	3.69
1-propanol	Kojima_Dallas1993	298.15	13.36
1-butanol	Kojima_Dallas1993	298.15	50.2
1-pentanol	Kojima_Dallas1993	298.15	198.1
1-hexanol	Kojima_Dallas1993	298.15	799
2-methyl-1-propanol	Kojima_Dallas1993	298.15	49
3-methyl-1-butanol	Kojima_Dallas1993	298.15	208
2-propanol	Kojima_Dallas1993	298.15	7.47
2-methyl-2-propanol	Kojima_Dallas1993	298.15	11.9
cyclohexanol	Kojima_Dallas1993	298.15	157
1-hexanol	Kojima_Djerki1988	298.15	645
1-butanol	Kojima_Hofstee1960	313.15	49.5
ethanol	Kojima_Landau1991	298.15	4.03
1-propanol	Kojima_Landau1991	298.15	15
1-butanol	Kojima_Landau1991	298.15	53.7
2-propanol	Kojima_Landau1991	298.15	7.75
2-butanol	Kojima_Landau1991	298.15	22.4
1-pentanol	Kojima_Larkin1973	298.15	197.5
1-pentanol	Kojima_Lebert1984	298.15	192
ethanol	Kojima_LiCar1993	298.15	3.8
1-propanol	Kojima_LiCar1993	298.15	14.17
1-butanol	Kojima_LiCar1993	298.15	53.33
1-hexanol	Kojima_LiCar1993	298.15	791.8
1-pentanol	Kojima_LiCarr1993	298.15	225.4
1-butanol	Kojima_Mash1980	298.15	51.6
1-pentanol	Kojima_Mash1980	298.15	197
1-heptanol	Kojima_Mash1980	298.15	3270
2-propanol	Kojima_Mash1980	298.15	8.13
2-butanol	Kojima_Mash1980	298.15	26.2
2-pentanol	Kojima_Mash1980	298.15	97

Table S5: (Continued)

name	reference	$T/K$	$\gamma^\infty$
2-hexanol	Kojima_Mash1980	298.15	282
1-propanol	Kojima_Pecsar1966	293.15	24
1-propanol	Kojima_Pecsar1966	303.15	26
1-propanol	Kojima_Pecsar1966	313.15	22
ethanol	Kojima_Pecsar1996	293.15	6.51
ethanol	Kojima_Pecsar1996	303.15	6.15
ethanol	Kojima_Pecsar1996	313.15	5.5
ethanol	Kojima_Pividal1992	283.15	4.38
ethanol	Kojima_Pividal1992	293.15	4.81
ethanol	Kojima_Pividal1992	313.15	5.17
2-propanol	Kojima_Pividal1992	298.15	12.9
ethanol	Kojima_Prausnitz1992	298.15	3.83
ethanol	Kojima_Prausnitz1992	298.15	3.88
ethanol	Kojima_Prausnitz1992	303.15	4.12
2-methyl-1-propanol	Kojima_Sagert1986	293.15	44.4
2-butanol	Kojima_Sagert1986	293.15	20.8
2-methyl-2-propanol	Kojima_Sagert1986	293.15	11.4
1-pentanol	Kojima_Sorensen1979	298.15	270
1-octanol	Kojima_Sorensen1979	298.15	11605
1-nonanol	Kojima_Sorensen1979	298.15	46260
1-decanol	Kojima_Sorensen1979	298.15	176500
1-dodecanol	Kojima_Sorensen1979	298.15	3.876e+06
1-tetradecanol	Kojima_Sorensen1979	298.15	3.97e+07
2-methyl-1-butanol	Kojima_Sorensen1979	298.15	161
2,2-dimethyl-1-propanol	Kojima_Sorensen1979	298.15	136
2,2-dimethyl-1-butanol	Kojima_Sorensen1979	298.15	742
3-hexanol	Kojima_Sorensen1979	298.15	348
3-methyl-2-pentanol	Kojima_Sorensen1979	298.15	288
4-methyl-2-pentanol	Kojima_Sorensen1979	298.15	350
3,3-dimethyl-2-butanol	Kojima_Sorensen1979	298.15	229
2-methyl-3-pentanol	Kojima_Sorensen1979	298.15	278
2,2-dimethyl-3-pentanol	Kojima_Sorensen1979	298.15	781
2,4-dimethyl-3-pentanol	Kojima_Sorensen1979	298.15	916
1-hexene-3-ol	Kojima_Sorensen1979	298.15	216
4-hexene-3-ol	Kojima_Sorensen1979	298.15	141
2-methyl-4-penten-3-ol	Kojima_Sorensen1979	298.15	177
2-methyl-2-pentanol	Kojima_Sorensen1979	298.15	170
3-methyl-3-pentanol	Kojima_Sorensen1979	298.15	128
2,3-dimethyl-2-butanol	Kojima_Sorensen1979	298.15	131
2-methyl-2-hexanol	Kojima_Sorensen1979	298.15	660
3-methyl-3-hexanol	Kojima_Sorensen1979	298.15	537
2,3-dimethyl-2-pentanol	Kojima_Sorensen1979	298.15	413
2,4-dimethyl-2-pentanol	Kojima_Sorensen1979	298.15	476
2,3-dimethyl-3-pentanol	Kojima_Sorensen1979	298.15	388
3-ethyl-3-pentanol	Kojima_Sorensen1979	298.15	379
2,2,3-trimethyl-3-pentanol	Kojima_Sorensen1979	298.15	1040

Table S5: (Continued)

name	reference	$T/K$	$\gamma^\infty$
<i>diols</i>			
1,3-nonanediol	Kojima_Macedo1979	298.15	610
2,4-dimethyl-2,4-nonanediol	Kojima_Macedo1979	298.15	2480
2-propyl-1,3-heptanediol	Kojima_Macedo1979	298.15	940
1,2-ethanediol	Suleiman and Eckert (1994)	297.45	0.8
1,2-ethanediol	Suleiman and Eckert (1994)	308.15	0.8
1,2-ethanediol	Suleiman and Eckert (1994)	317.85	1
1,3-propanediol	Suleiman and Eckert (1994)	297.95	1.2
1,3-propanediol	Suleiman and Eckert (1994)	307.85	1.2
1,4-butanediol	Suleiman and Eckert (1994)	299.35	2.8
1,4-butanediol	Suleiman and Eckert (1994)	309.05	2.8
2,3-butanediol	Suleiman and Eckert (1994)	298.95	1.6
2,3-butanediol	Suleiman and Eckert (1994)	308.85	1.7
1,2-propanediol	Suleiman and Eckert (1994)	296.75	1
1,2-propanediol	Suleiman and Eckert (1994)	308.25	1.1
1,2-butanediol	Suleiman and Eckert (1994)	299.15	2
1,2-butanediol	Suleiman and Eckert (1994)	308.35	2.1
1,2-butanediol	Suleiman and Eckert (1994)	318.05	2.2
1,3-butanediol	Suleiman and Eckert (1994)	299.05	2.2
1,3-butanediol	Suleiman and Eckert (1994)	308.75	2.3

### S1.6 Results of HLC evaluation

The standard deviation of an estimation method vs. experimental values is calculated as

$$SD = 1/\sqrt{N} \sqrt{\sum_{i=1}^N (U_{\text{est}} - U_{\text{exp}})^2} \quad (1)$$

with  $U$  either  $\log_{10}(k_h)$  or  $\log_{10}(\gamma^\infty)$ , and  $i$  running over the molecules of the specific molecule class. In Tables S6 and S7, the SD is given per method and per molecule class. Colours green ( $SD < 0.5$ ), orange ( $0.5 < SD < 1.0$ ) and red ( $SD > 1.0$ ) are used to indicate the performance.

In general, the methods perform worse for polyfunctional molecules compared to monofunctional molecules. The direct HLC estimation method of Cabani et al. (1981) performs well for monofunctional compounds (except for nitrates, which are not covered by this method). However, for polyfunctional compounds large errors are found, and for the polyol class (more than 2 hydroxyl groups) the method largely fails. The recently developed HLC estimation method GROMHE (Raventos-Duran et al., 2010) performs clearly better for the diols, but for the other polyfunctional classes errors are also large.

The performance of UNIFAC-Raatikainen is the worst among all UNIFAC-like methods. This is mainly due to the reparameterisation of the  $\text{CH}_n\text{-H}_2\text{O}$  based on data for some polyfunctional molecules (diacids and functionalized diacids), which makes the method less suitable for other molecule types. This method is not recommended.

Of all tested methods, the combination EVAPORATION-AIOMFAC has the best performance, giving also reasonable values for polyols, diacids and functionalized diacids. However, its performance regarding mono-acids, mono-nitrates, mono-PANs and dicarbonyls is relatively poor. Therefore, a slightly modified AIOMFAC version has also been devised and tested (AIOMFAC(m), see Subsection S1.3). These changes are found to reduce the errors for mono-acids, mono-nitrates, mono-PANS and dicarbonyls, at the expense of a slight worsening for mono-aldehydes.

GROMHE has the largest number of molecule classes with 'low' (green in Tables S6 and S7) standard deviations, mostly for monofunctional molecules. AIOMFAC(m) combined with EVAPORATION (ev/aiom(m) in Tables S6 and S7) has the

**Table S6.** Standard deviation estimation methods vs. experimental values in  $\log_{10}$  units for HLCs.  $N$  is the number of measurements for evaluation.

scope	$N$	grom	evap Han	evap aiom	evap aiom(m)	evap Raat	evap dort	evap aqua
all	216	0.9	0.8	0.7	0.6	1.7	nan†	0.9
filtered**	161	1.0	0.8	0.7	0.5	1.8	1.1	1.0
monoaldehydes	26	0.3	0.5	0.5	0.6	0.9	0.5	0.4
monoketones	19	0.2	0.4	0.4	0.4	0.7	0.4	0.7
monoethers	11	0.5	0.6	0.6	0.6	0.4	0.3	0.8
monoesters	14	0.1	0.2	0.2	0.2	0.5	0.2	0.3
monoformates	5	0.0	0.2	0.2	0.2	0.2	0.1	0.4
monoalcohols	26	0.2	0.5	0.4	0.4	1.2	0.4	0.8
monoacids	14	0.4	0.4	0.6	0.3	0.5	0.4	0.3
mononitrates*	20	0.2	0.8	0.8	0.4	1.2	nan	0.2
monopans*	7	0.3	1.3	1.3	0.9	1.5	nan	0.2
monoper*	5	0.1	0.3	0.2	0.3	1.5	nan	0.7
dicarbonyls	5	1.0	2.4	2.4	0.0	2.4	2.4	2.5
diols	18	0.4	0.9	0.5	0.5	2.0	1.1	0.7
diacids	12	1.7	0.9	0.5	0.5	0.5	1.3	0.5
polyols	9	1.5	1.0	0.6	0.6	6.1	2.9	2.6
func. diacids	2	6.7	2.8	2.1	2.1	0.8	3.7	1.5
others*	23	0.7	0.7	0.6	0.8	1.2	nan	0.8
scope	$N$	grom	evap Han	evap aiom	evap aiom(m)	evap Raat	evap dort	evap aqua
all	216	nan	1.3	1.2	1.3	2.0	nan	1.5
filtered**	161	3.5	0.9	0.7	0.7	2.0	1.1	1.3
monoaldehydes	26	0.32	0.5	0.5	0.5	0.9	0.5	0.5
monoketones	19	0.1	0.5	0.5	0.5	0.7	0.3	0.7
monoethers	11	0.3	0.6	0.6	0.6	0.4	0.3	0.8
monoesters	14	0.1	0.3	0.3	0.3	0.5	0.2	0.4
monoformates	5	0.2	0.1	0.1	0.1	0.2	0.1	0.3
monoalcohols	26	0.1	0.7	0.5	0.5	1.0	0.5	1.0
monoacids	14	0.3	0.5	0.4	0.5	0.4	0.5	0.6
mononitrates*	20	nan	0.9	0.9	0.5	1.3	nan	0.2
monopans*	7	nan	2.8	2.8	3.2	2.5	nan	3.9
monoper*	5	nan	3.4	3.4	3.1	2.2	nan	3.6
dicarbonyls	5	2.4	1.7	1.7	1.7	1.7	1.7	1.9
diols	18	1.1	1.1	0.7	0.7	1.9	1.4	1.0
diacids	12	0.8	2.0	1.4	1.4	1.5	2.4	1.4
polyols	9	14.5	0.9	1.2	1.2	7.5	1.7	4.0
func. diacids	2	2.5	2.3	1.7	1.7	0.7	3.2	1.8
others*	23	nan	2.0	2.0	2.3	1.8	nan	1.7

Method abbreviations are defined in Table S1.

\* Some methods cannot do estimations for these molecule classes.

\*\* Molecule classes marked with \* are not taken into account in this group. In this way, all methods can be compared.

† nan ('not a number'): some or all molecules in this class could not be treated by the method, therefore no SD could be calculated.

**Table S7.** Standard deviation of estimation methods vs. experimental values in  $\log_{10}$  units regarding IDACs. The same convention for the colours is used as in Table S6.

scope	$N$	evap grom	evap Cab	aqua	aiom	aiom(m)
all	243	0.43	0.39	0.45	0.32	0.30
mono-aldehydes	19	0.38	0.11	0.28	0.32	0.32
mono-ketones	43	0.24	0.13	0.55	0.25	0.25
mono-ethers	28	0.34	0.21	0.48	0.47	0.47
mono-esters	31	0.33	0.30	0.22	0.16	0.16
mono-formates	12	0.38	0.23	0.28	0.06	0.06
mono-alcohols	85	0.37	0.25	0.53	0.31	0.32
mono-acids	6	0.38	0.27	0.10	0.67	0.18
diols	19	0.98	1.17	0.27	0.30	0.30
scope	$N$	Nan/grom	Nan/Cab	dort	Han	Raat
all	243	0.46	0.44	0.35	0.36	1.12
mono-aldehydes	19	0.45	0.18	0.27	0.32	0.73
mono-ketones	43	0.23	0.13	0.15	0.25	0.50
mono-ethers	28	0.38	0.26	0.34	0.47	0.58
mono-esters	31	0.36	0.32	0.33	0.16	0.48
mono-formates	12	0.36	0.18	0.06	0.06	0.26
mono-alcohols	85	0.49	0.41	0.28	0.37	1.45
mono-acids	6	0.21	0.24	0.31	0.40	0.65
diols	19	0.90	1.17	0.85	0.60	2.12

Method abbreviations are defined in Table S1.

lowest overall SD compared to the other methods, and the lowest number of molecule classes with 'large' (red in Tables S6 and S7) SDs (only one, for the functionalized acids, which are difficult for most methods). When focussing on the polyfunctional molecule classes, it remains the best method, as all other methods have at least two, and frequently more, molecule classes with 'large' SDs.



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