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On the evolution of sub- and super-saturated water uptake of secondary organic aerosol in chamber experiments from mixed precursors

Yu Wang et al.

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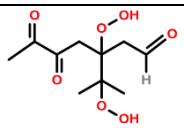
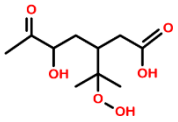
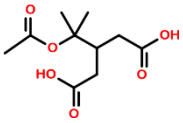
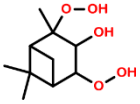
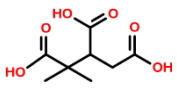
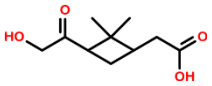
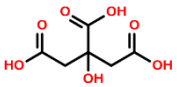
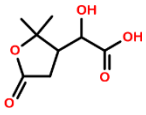
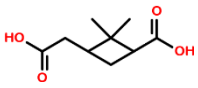
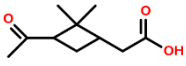
Table S1: Properties of the model compounds: O:C ratio, molecular weight MW, molecular weight of the artificial dimer (MW Dimer), SMILES code, sub-cooled liquid density, reference stating the compound as α-pinene oxidation product and molecular structure. The sub-cooled liquid density of the organic substances was calculated with UManSysProp based on the given SMILES codes (http://umansysprop.seaes.manchester.ac.uk/tool/sub_cooled_density, last access: 27/01/2022) and using the predictive technique by Girolami (1994) and Nannoolal et al. (2004) for the density and for the critical properties, respectively. For ammonium sulphate, the density of the crystalline solid based on data from Clegg and Wexler (2011) was used.

Name	O:C	MW (g/mol)	MW Dimer (g/mol)	SMILES code	Density (kg/m3)	Reference	Molecular structure
ValT4N10	0.70	248	496	CC(=O)C(=O)CC(CC=O)(OO)C(C)(C)OO	1192	(Valorso et al., 2011)	
ValT4N9	0.60	234	468	CC(=O)C(O)CC(CC(=O)O)C(C)(C)OO	1218	(Valorso et al., 2011)	
Diaterpenylic acid acetate	0.60	232	464	CC(=O)OC(C)(C)C(CC(=O)O)CC(=O)O	1161	(Eddingsaas et al., 2012)	
ValT4N3	0.50	218	436	CC1(C)C2CC1C(C)(OO)C(O)C2OO	1182	(Valorso et al., 2011)	
3-MBTCA	0.75	204	408	CC(C(CC(=O)O)C(=O)O)(C)C(=O)O	1327	(Eddingsaas et al., 2012)	
Hopinonic acid	0.40	200	400	CC1(C)C(CC(=O)O)CC1C(=O)CO	1183	(Eddingsaas et al., 2012)	
Citric acid	1.17	192	384	C(CC(O)(C(=O)O)CC(=O)O)(=O)O	1469	-	
2-hydroxy-terpenylic acid	0.63	188	376	CC1(C)OC(=O)CC1C(O)C(=O)O	1288	(Eddingsaas et al., 2012)	
Pinic acid	0.44	186	372	CC1(C)C(CC(=O)O)CC1C(=O)O	1210	(Eddingsaas et al., 2012)	
Pinonic acid	0.30	184	368	CC(=O)C1CC(CC(=O)O)C1(C)C	1053	(Eddingsaas et al., 2012)	
Norpinic acid	0.50	172	344	CC1(C)C(C(=O)O)CC1C(=O)O	1244	(Jaoui and Kamens, 2001)	

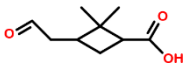
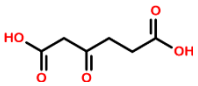
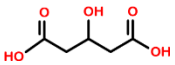
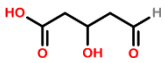
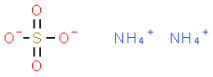
Pinalic acid	0.33	170	340	CC1(C)C(CC=O)CC1C(=O)O	1075	(Jaoui and Kamens, 2001)	
3-oxoadipic acid	0.83	160	320	O=C(CC(=O)O)CCC(=O)O	1281	-	
3-hydroxy-glutaric acid	1.00	148	296	OC(CC(=O)O)CC(=O)O	1375	(Kleindienst et al., 2007)	
5-COOH-3-OH-pentanal	0.80	132	264	O=CCC(O)CC(=O)O	1220	-	
Ammonium sulphate	-	132	-	-	1769	-	

Table S2: Composition and properties of the model mixtures: mass fraction of each substance in the organic mixture, average O:C ratio, average molecular weight and resulting κ_{HTDMA} and κ_{CCN} from the model calculations including non-ideality and phase-separation at an organic mass fraction $MR_{SOA/PM}$ = 0.8. The mean experimental κ at $MR_{SOA/PM}$ = 0.8 was 0.14 ± 0.03 and 0.09 ± 0.01 for HTDMA and CCN counter, respectively.

Mixture number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Monomer/Dimer	**M**	**M**	**M**	**M**	**M**	**D**	**D**	**M**	**D**	**M**	**D**	**M**	**D**	**M**	**D**	**D**	**D**
ValT4N10					0.087	0.087	0.126	0.126		0.600	0.600	0.043	0.043			0.500	0.470
ValT4N9							0.205	0.205		0.240	0.240					0.300	
Diaterpenylic acid acetate	0.189	0.418		0.418	0.094	0.094	0.205	0.205				0.256	0.256			0.100	
ValT4N3	0.087	0.193		0.193			0.158	0.158				0.096	0.096	0.107	0.107	0.100	
3-MBTCA			0.418		0.094	0.094	0.274	0.274	0.418			0.047	0.047				
Hopinonic acid	0.176	0.389		0.389								0.194	0.194	0.216	0.216		
Citric acid										0.160	0.160						0.530
2-hydroxy-terpenylic acid					0.244	0.244						0.122	0.122				
Pinic acid					0.176	0.176						0.088	0.088				
Pinonic acid														0.301	0.301		
Norpinic acid	0.244																
Pinalic acid	0.305													0.376	0.376		
3-oxoadipic acid			0.389						0.389								
3-hydroxy-glutaric acid			0.193				0.032	0.032	0.193								
5-COOH-3-OH-pentanal					0.305	0.305						0.152	0.152				
Average O:C	0.45	0.50	0.83	0.50	0.66	0.66	0.65	0.65	0.83	0.75	0.75	0.58	0.58	0.36	0.36	0.64	0.95
Average MW	189	216	173	432	173	347	440	220	346	234	468	192	385	185	369	478	430
κ_{HTDMA} 0.8	0.097	0.098	0.190	0.095	0.140	0.119	0.107	0.114	0.157	0.113	0.107	0.116	0.107	0.085	0.083	0.093	0.140
κ_{CCN} 0.8	0.184	0.176	0.215	0.088	0.202	0.134	0.107	0.177	0.154	0.174	0.101	0.187	0.109	0.138	0.079	0.088	0.132

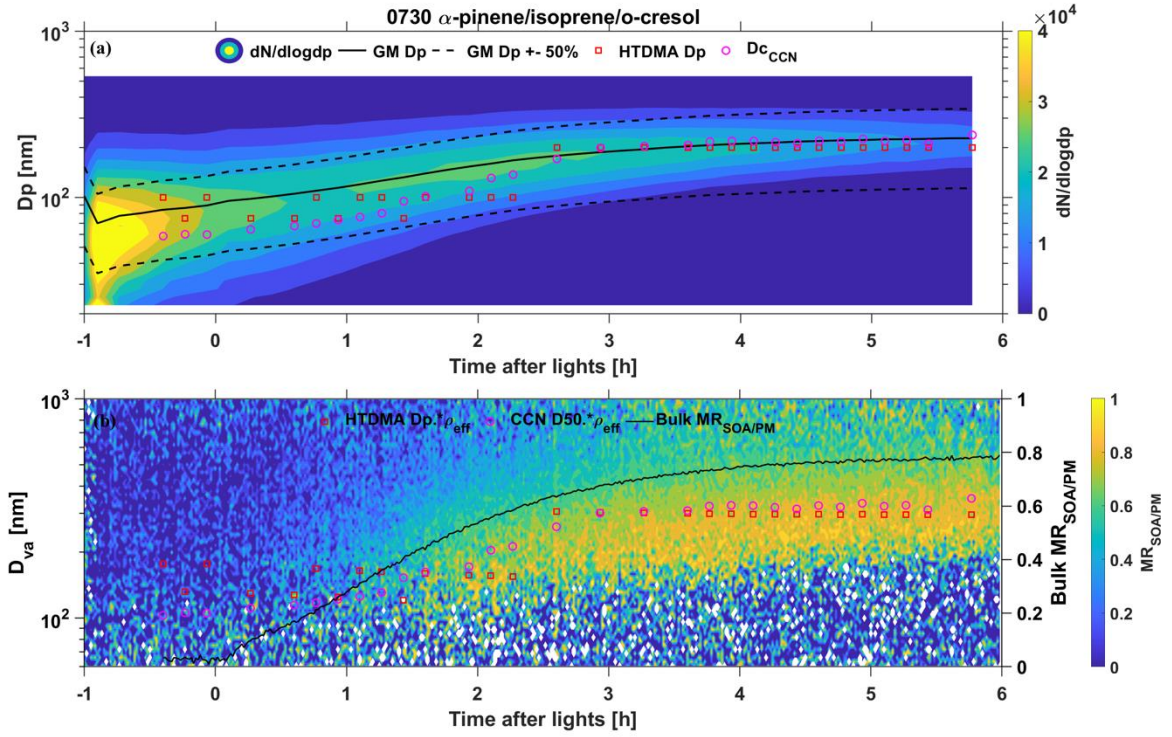


Figure S1. Time series of (a) particle number size distribution, HTDMA measured Dp and critical diameter measured by CCN counter (Dc_{CCN}). (b) Bulk and size-resolved $MR_{SOA/PM}$ in the ~~α-pinene/isoprene/*o*-cresol~~ system as an example. Here, the data points were selected when the 10-min moving average of $MR_{SOA/PM}$ between HTDMA dp and CCN Dc_{CCN} are within 5%.

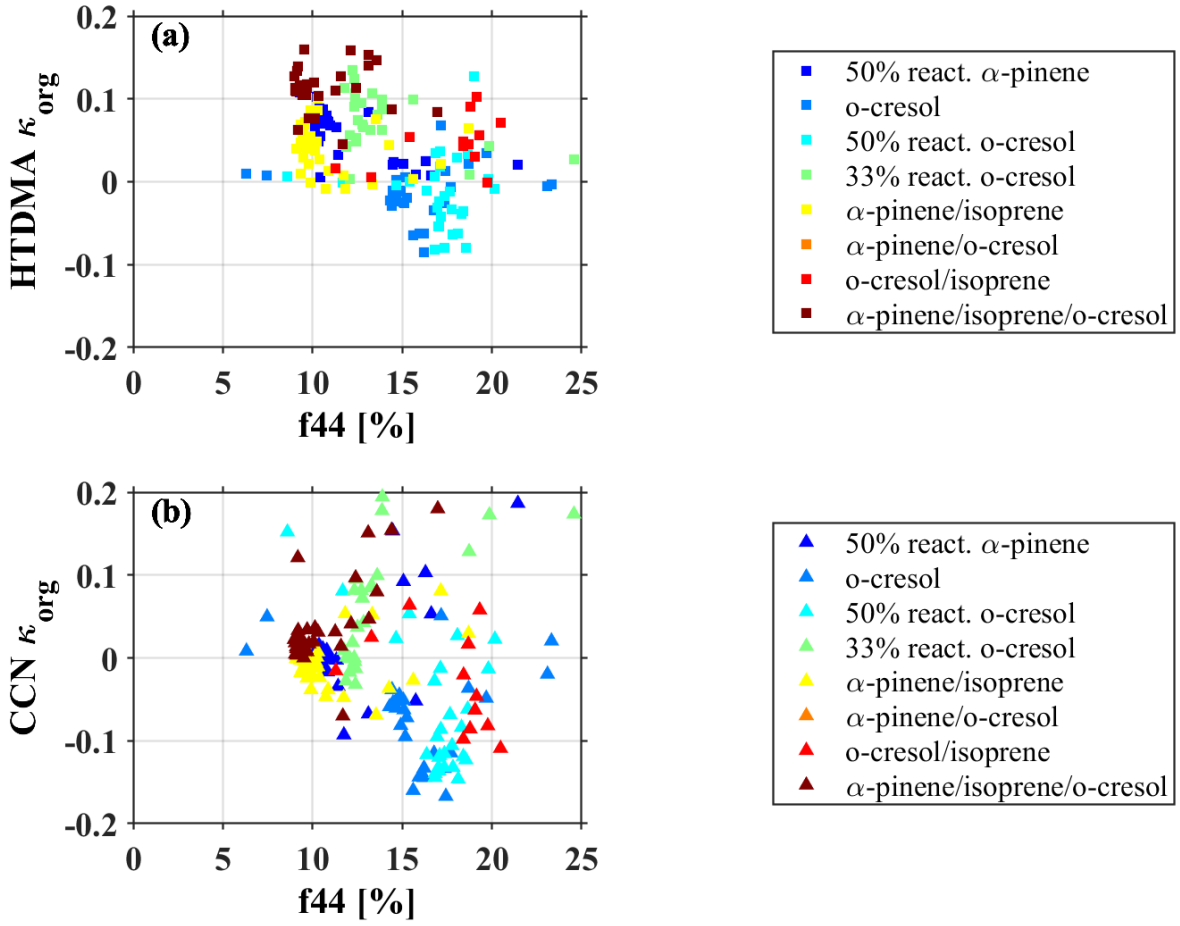


Figure S2. (a) relation between κ_{org} calculated from HTDMA and the fraction of m/z 44 in total organic signal, f_{44}. (b) relation between κ_{org} calculated from CCN counter and f_{44} in all investigated VOC systems.

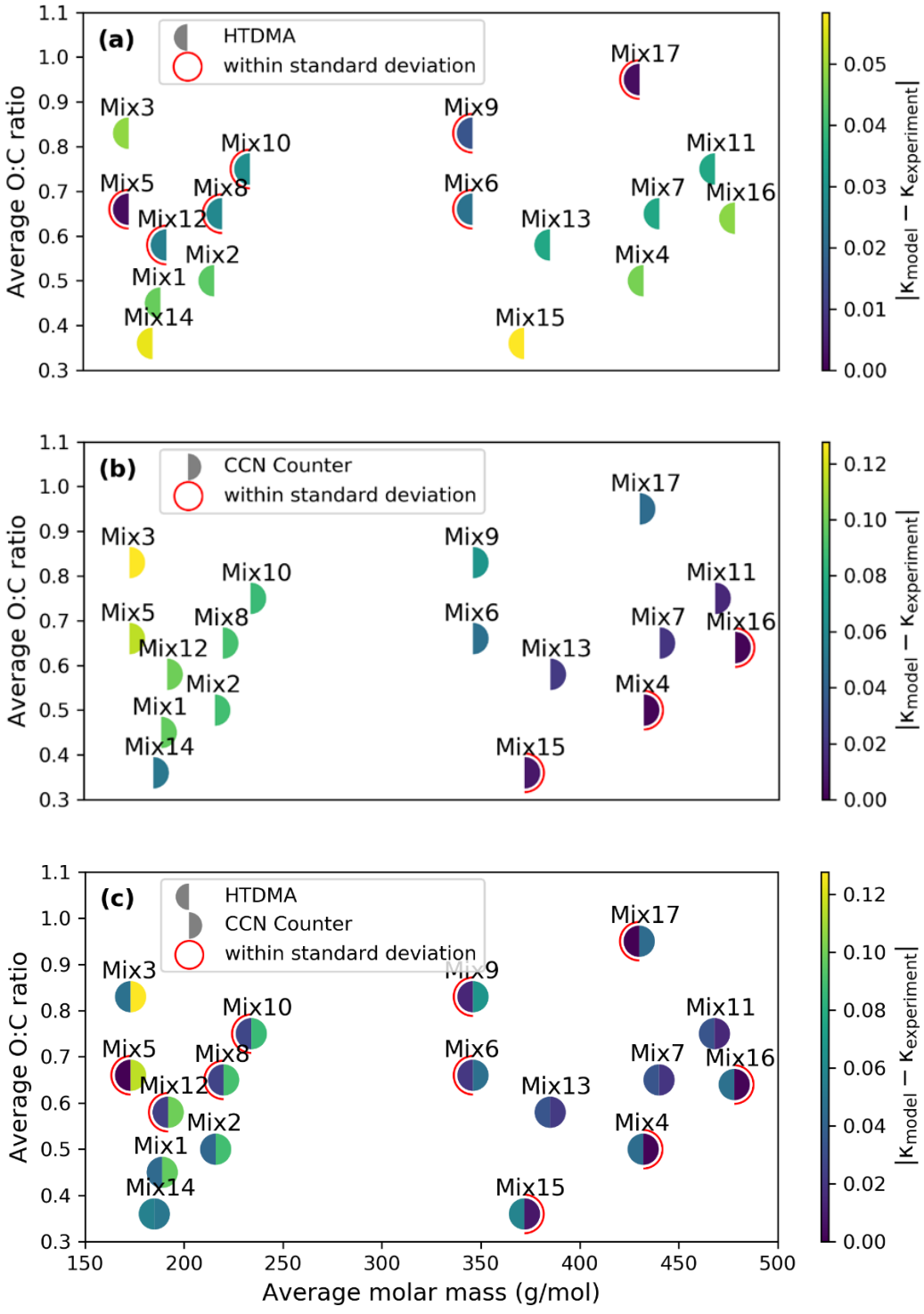

(a)
HTDMA
within standard deviation
(b)
CCN Counter
within standard deviation
(c)
HTDMA
CCN Counter
within standard deviation
Mix1
Mix2
Mix3
Mix4
Mix5
Mix6
Mix7
Mix8
Mix9
Mix10
Mix11
Mix12
Mix13
Mix14
Mix15
Mix16
Mix17
Average O:C ratio
Average molar mass (g/mol)
|Kmodel − Kexperiment|

Figure S3: Discrepancy between model and experiment at an organic mass fraction MRSOA/PM = 0.8 for all model compound mixtures: the mixtures are placed in the figure according to their average molecular weight MW (x-axis) and average O:C ratio (y-axis) and color-coded according to the difference between the modelled and mean experimental κ at $MR_{SOA/PM}$ = 0.8. The calculation of κ is based on the growth factor at (a) $RH = 90\%$ (HTDMA) and (b) the critical supersaturation Sc (CCN counter). Panel (c) shows a comparison of (a) and (b). The red border marks mixtures, where the discrepancy is smaller than the experimental standard deviation for either κ_{HTDMA} (left side) or κ_{CCN} (right side). The mean experimental κ at $MR_{SOA/PM}$ = 0.8 was 0.14 ± 0.03 and 0.09 ± 0.01 for HTDMA and CCN counter, respectively.

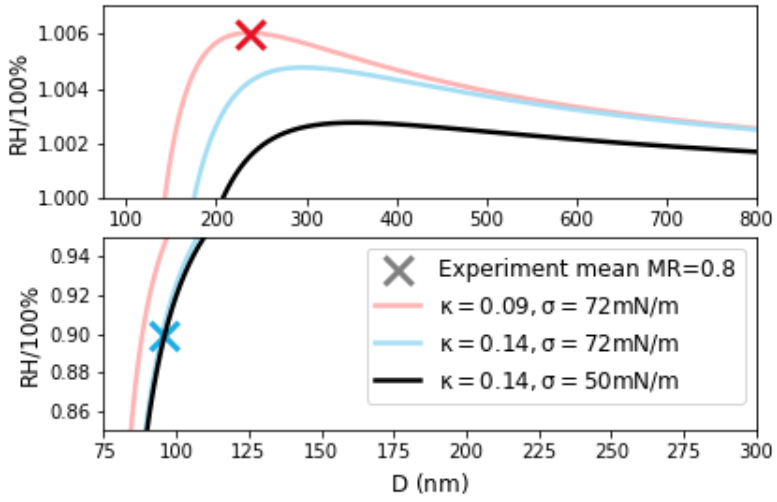


Figure S4: Köhler curves showing the influence of a lowered surface tension on hygroscopic growth and the critical supersaturation for the example of SOA with the experimentally determined mean κ-values at $MR_{SOA/PM}$ = 0.8. From the S_c measured in the CNN counter (red cross), a κ of 0.09 was derived by assuming the surface tension of water ($\sigma = 72$ mN/m) (light red line). From the wet diameter measured in the HTDMA (blue cross), a κ of 0.14 was derived. Assuming $\sigma = 72$ mN/m for a particle with $\kappa = 0.14$ (light blue line) leads to a higher *S*c than for the same particle having a lower surface tension of $\sigma = 50$ mN/m (black line).

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