Electronic Supplementary Information (ESI)

The Kinetics of Adsorption/Desorption of selected semivolatile Hydrocarbons and H_2O Vapor on two Mineral Dust Materials: a molecular View

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Table S1 : Master List of performed gas-solid Experiments for semivolatile hydrocarbons interacting with two mineral dust proxies

Sample ID	Mass/ mg[b]	Organics	Substrate	Uptake/#	Uptake/# cm^{-2}	Recovery /%	Uptake /ML	k_0/s^{-1}	k_{ss}/s^{-1d} remarks
FS10	161.8	Applinate	Kaolinite LO	$8.50\ 10^{17}$	$2.30\ 10^{13}$	60.3	0.096	(4.08)	
FS11	Reads.	Applinate	Kaolinite LO	$7.16\ 10^{17}$	$1.97\ 10^{13}$		0.081		
FS40	373.7	Applinate	ATD-C	$2.31\ 10^{18}$	$5.72\ 10^{13}$	10.0	0.244	(1.45)	
FS41	Reads.	Applinate	ATD-C	$8.0\ 10^{17}$	$1.98\ 10^{13}$		0.084	1.25	
FS60	59.7	Menthol	ATD-C	$1.69\ 10^{17}$	$2.62\ 10^{13}$	3.44	0.115	0.35	
FS61	Reads	Menthol	ATD-C	$2.08\ 10^{16}$	$3.23\ 10^{12}$		0.014		
FS70	54.1	Menthol	Kaolinite LO	$1.45\ 10^{17}$	$1.19\ 10^{13}$	26.8	0.052	0.49	
FS71	Reads	Menthol	Kaolinite LO	$9.26\ 10^{16}$	$1.58\ 10^{13}$		0.070		
FS90	100.4	Pipol acetate	ATD-C	$3.09\ 10^{18}$	$2.85\ 10^{14}$	13.4	1.168	0.23	
FS91	Reads	Pipol acetate	ATD-C	$7.62\ 10^{17}$	$7.03\ 10^{13}$		0.288	0.072	
FS100	40.3	Pipol acetate	Kaolinite LO	1.08 1018	$1.19\ 10^{14}$	24.6	0.488	1.07	
FS101	Reads	Pipol acetate	Kaolinite LO	6.70 1017	$7.39\ 10^{13}$		0.303		
S200	40.8	Benzylacetate	ATD-C	$1.94\ 10^{17}$	$4.40\ 10^{13}$	23.7	0.168	0.083	
S201[a]	25.6	Benzylacetate	Kaolinite LO	$2.11\ 10^{17}$	$3.67\ 10^{13}$	48.3	0.140	0.57	$7.36\ 10^{-4}$
S203	41.7	Benzylacetate	ATD-C	$2.17\ 10^{17}$	$4.81\ 10^{13}$	23.6	0.184	0.083	
S204	Reads.	do.	do.	$8.24\ 10^{16}$	$1.83\ 10^{13}$	52.0	0.070	0.021	
S205	33.2	Benzylacetate	Kaolinite LO	$2.92\ 10^{17}$	$3.91\ 10^{13}$	53.1	0.149	0.366	
S206	Reads.	do.	do.	$1.85\ 10^{18}$	$2.47\ 10^{14}$	72.5	0.094	0.0929	
S207	46.4	Limonene	ATD-C	$1.34\ 10^{17}$	$2.67\ 10^{13}$	0.0	0.102	0.120	$9.03\ 10^{-3}$ $3.72\ 10^{-3}$
S208	Reads.	do.	do.	$2.71\ 10^{16}$	$5.41\ 10^{12}$	0.0	0.022		$3.48\ 10^{-3}$
S209	20.1	Limonene	Kaolinite LO	$4.43\ 10^{17}$	$9.80\ 10^{13}$	0.0	0.410	0.270	$1.12\ 10^{-2}$
S210	Reads.	do.	do.	$1.29\ 10^{17}$	$2.85\ 10^{13}$	0.0	0.120	0.051	$8.98\ 10^{-3}$
S211	16.3	γ-Terpinene	Kaolinite LO	$9.23\ 10^{17}$	$2.52\ 10^{13}$	not det.	0.104	0.040	$1.34\ 10^{-3}$

Sample ID	Mass/ mg[b]	Organics	Substrate	Uptake/#	Uptake/# cm^{-2}	Recovery /%	Uptake /ML	k_0/s^{-1}	k_{ss}/s^{-1d} remarks
S212	Reads.	do.	do.	$2.36\ 10^{17}$	$6.43\ 10^{12}$	not det.	0.0265	0.0102	$9.66\ 10^{-4}$
S213	22.1	γ-Terpinene	ATD-C	$3.50\ 10^{16}$	$1.46\ 10^{13}$	not det.	0.0604	0.0129	$4.38\ 10^{-4}$
S214	16.1	γ-Terpinene	ATD-C	$3.16\ 10^{16}$	$1.81\ 10^{13}$	8.73	0.0750	0.0067	
S215	Reads.	do.	do.	$6.96\ 10^{15}$	$4.00\ 10^{12}$	6.97	0.0165	0.0027	
S216	15.7	γ-Terpinene	Kaolinite LO	$1.05\ 10^{17}$	$2.96\ 10^{13}$	not det.	0.122	0.027	$8.76\ 10^{-4}$
S217	Reads.	do.	do.	$2.78\ 10^{16}$	$7.87\ 10^{12}$	not det.	0.265	0.0082	$6.70\ 10^{-4}$
S218	24.3	Toluene	ATD-C	$9.31\ 10^{16}$	$3.55\ 10^{13}$	50.8	0.112	0.0254	
S219	Reads.	do.	do.	$6.05\ 10^{16}$	$2.31\ 10^{13}$	80.8	0.073	0.0151	
S220	30.6	Toluene	Kaolinite LO	not det.	not det.	[c]	not det.		
S221	30.8	Toluene	Kaolinite LO	$7.38\ 10^{16}$	$1.06\ 10^{13}$	57.9	0.0334	0.0201	
S222	Reads.	do.	do.	$9.67\ 10^{16}$	$1.39\ 10^{13}$	54.7	0.0438	0.0188	
S223	Reads.	do.	do.	$6.46\ 10^{16}$	$9.32\ 10^{12}$	81.8	0.0293	0.0180	
S224	11.4	Limonene	Kaolinite LO	$4.83\ 10^{16}$	$1.88\ 10^{13}$	0.0	0.0782[h]	0.224[h]	
S225	40.8	Toluene	Kaolinite LO	$5.21\ 10^{16}$	$5.68\ 10^{12}$	103.7	0.0179[h]	0.200[h]	
S226	91.0	Toluene	ATD-C	$2.09\ 10^{17}$	$2.13\ 10^{13}$	71.3	0.0670[h]	0.366[h]	
S227	54.3	γ-Terpinene	Kaolinite LO	$1.08\ 10^{17}$	$8.84\ 10^{12}$	6.94	0.0278[h]	1.44[h]	
S228	Reads.	do.	do.	$2.71\ 10^{16}$	$2.22\ 10^{12}$	not det.	0.0070[h]	0.039[h]	
S230	73.2	Limonene	ATD-C					0.181[h]	
S231	36.6	Limonene	Kaolinite LO					2.11[h]	
S232	52.9	γ-Terpinene	ATD-C					1.00[h]	
S233	55.5	Applinate	ATD-C					2.10[h]	
S234	45.1	Applinate	Kaolinite LO					2.48[h]	
S235	52.4	Benzylacetate	Kaolinite LO					2.16[h]	
S236	58.0	Benzylacetate	ATD-C	$2.53\ 10^{17}$	$4.04\ 10^{13}$	7.8	0.1540	0.164	$1.53\ 10^{-3}$
S237	52.4	Benzylacetate	ATD-C					1.15[h]	
S238	51.9	Benzylacetate	ATD-C	$2.79\ 10^{17}$	$5.0\ 10^{13}$	31.6	0.1910	0.19	$1.23\ 10^{-3}$

Sample ID	Mass/ mg[b]	Organics	Substrate	Uptake/#	Uptake/# cm^{-2}	Recovery /%	Uptake /ML	k_0/s^{-1}	k_{ss}/s^{-1d} remarks
S239	55.3	Benzylacetate	Kaolinite LO	$2.57\ 10^{17}$	$2.07\ 10^{13}$	47.1	0.0789	> 2.0	
S240	51.2	Toluene	Kaolinite LO	$9.15\ 10^{16}$	$7.95\ 10^{12}$	64.8	0.0250	0.057	
S241	66.2	Toluene	ATD-C	$2.41\ 10^{17}$	$3.37\ 10^{13}$	55.8	0.1061	0.080	
S242[j]	62.4	H_2O	Kaolinite LO	$5.95\ 10^{17}$	$4.23\ 10^{13}$	123.8[j]	0.042	1.42	90' pumped
S243[k]	72.1	H_2O	Kaolinite LO	$1.28\ 10^{18}$	$7.91\ 10^{13}$	51.4	0.079	0.465	
S243	72.1	H_2O	Kaolinite LO	$1.26\ 10^{18}$	$7.80\ 10^{13}$	not det.	0.078	0.480	pumped overn.
S243	72.1	Applinate[i]	Kaolinite LO	$4.74\ 10^{17}$	$2.92\ 10^{13}$	15.0	0.124	0.172	
S244[k]	53.0	H_2O	Kaolinite LO	$8.91\ 10^{17}$	$7.48\ 10^{13}$	not det.	0.0745	2.11	Pumped overn.
S244	53.0	Applinate[i]	Kaolinite LO	$8.16\ 10^{17}$	$6.84\ 10^{13}$	41.1	0.291	large	
S245[k]	93.1	H_2O	ATD-C	$2.23\ 10^{18}$	$2.21\ 10^{14}$	not det.	0.221	1.170	$1.07\ 10^{-3}$ Pumped overn.
S245	93.1	Applinate[i]	ATD-C	$7.02\ 10^{17}$	$7.0\ 10^{13}$	10.74	0.297	0.298	
S246	88.6	H_2O	ATD-C	$1.92\ 10^{18}$	$2.01\ 10^{14}$	79.0	0.201	1.08	Pumped 2.5 d
S247	Reads	H_2O	ATD-C	$2.11\ 10^{18}$	$2.21\ 10^{14}$	70.0	0.221	0.880	Pumped 21 h
R248	MT SC	Applinate	-	$1.30\ 10^{16}$		112.0			
R249	MT SC	Toluene	-	$2.79\ 10^{15}$		100.0			

Unless otherwise noted the rate coefficient for uptake k_0 is given for the 1 mm Ø orifice (however, see footnote h). k_0 values in brackets are lower limiting values because they were measured in 1 mm Ø uptake experiments. BET surface areas for Kaolinite LO and ATD-C are 22.5 and 10.8 m^2/g, respectively. Experiments under footnote h have been performed using a geometric surface area of 1.131 cm^2 (exception S224 with 0.292 cm^2), all others at 10.6 cm^2

[a] Reference sample S202: Benzylacetate in empty sample compartment: Uptake of $1.33\ 10^{15}$ molecule cm^{-2} with desorption of $3.28\ 10^{17}$ molecule

[b] Readsorption (Reads.) using identical sample of previous run after overnight pumping of typically 15-21 hours at 14 mm diameter exit orifice. Uptake rate coefficient k_0 always measured at 1 mm Ø exit orifice

[c] Desorption yield of $1.93\ 10^{16}$ molecule

[d] Interpreted as mass transfer (solid diffusion) coefficient except for limonene where it may correspond to chemisorption (see text)

[e] "Irreversible" and estimated "total" uptake on column 5 (from left)
[g] Next morning values w/o *in situ* overnight pumping of sample
[h] (Initial) kinetic values as well as uptake listed for the 14 mm orifice Ø
[i] Semivolatile uptake measured under condition of concurrent H_2O flow at saturation of substrate. Desorption of H_2O and semivolatile organic is concurrent, but only semivolatile desorption is systematically recorded
[j] Sample pumped for 90 minutes at 14 mm Ø KFR before first H_2O exposure. Note the amount of spontaneous desorption exceeding 100% which indicates only partial dehydration during restricted pumping period
[k] Sample pumped overnight (15-19 hrs.) at 14 mm Ø KFR before first H_2O exposure. Note the difference in H_2O uptake to S242

Table S2 : List of used semivolatile organics and some important molecular properties[a]

Semivolatile organic compound	**Sum formula**	**MW/g**	**Density ρ of pure liquid/g cm^{-3}**	**#/cm^2 Molecule/ML**
Menthol	$C_{10}H_{20}O$	156.3	0.890	2.28 10^{14}
2-Methyl-pentanoate ethyl ester ethyl applinate	$C_8H_{16}O_2$	144.2	0.860	2.35 10^{14}
cis-3-Hexenylacetate (pipol acetate)	$C_8H_{14}O_2$	142.2	0.876	2.40 10^{14}
Benzylacetate	$C_9H_{10}O_2$	150.2	1.054	2.62 10^{14}
Toluene	C_7H_8	92.1	0.865	3.18 10^{14}
Limonene	$C_{10}H_{16}$	136.2	0.841	2.40 10^{14}
γ-Terpinene	$C_{10}H_{16}$	136.2	0.850	2.43 10^{14}

[a] A rough approximation to the number of molecules cm^{-2} to form a molecular monolayer is $(\rho\ N_A/MW)^{2/3}$ where ρ, N_A and MW are the molecular density at ambient temperature, Avogadro's number and molecular weight, respectively, and represents a limiting value to the true coverage in number of molecules cm^{-2}.

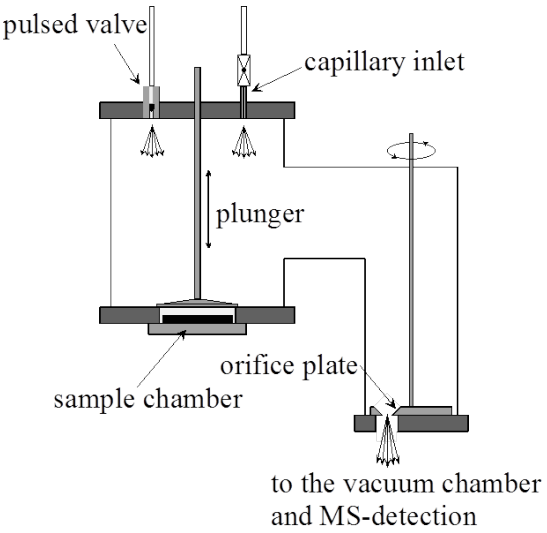

Figure S1: Essential Construction Elements of the two-chamber Knudsen Flow Reactor (KFR) used in the present study. Relevant geometric and kinetic parameters are listed in Table 1.