Supporting Information

Stationary-Phase Contributions to Surface Diffusion in Reversed-Phase Liquid Chromatography: Chain Length vs Ligand Density

*Julia Rybka, Alexandra Höltzel, Nicole Trebel, and Ulrich Tallarek**

Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35032 Marburg, Germany

* Corresponding author.

Phone: +49-(0)6421-28-25727; Fax: +49-(0)6421-28-27065;

E-mail: tallarek@staff.uni-marburg.de.

Table S1. Number of W and ACN molecules for productive simulations in the slit-pore model.

bonded phase	W/ACN (v/v)	N_W	N_{ACN}
C_{18}	70/30	23975	4902
	20/80	6647	10842
C_8	70/30	27400	5727
	20/80	7820	12512
hd-C_8	70/30	26637	5486
	20/80	7331	12241

Table S2. Number of W and ACN molecules for simulations of bulk diffusion coefficients.

W/ACN (v/v)	N_W	N_{ACN}
48/52	7278	2722
40/60	6588	3412
39/61	6493	3507
16/84	3555	6445
11/89	2636	7364
10/90	2370	7630

Table S3. Average number of *gauche* defects per chain.

bonded phase	W/ACN (v/v)	upright[a] N_{gauche}	tilted[a] N_{gauche}	bent[b] N_{gauche}	stretched[b] N_{gauche}	backfolded[b] N_{gauche}
C_{18}	70/30	3.96	3.70	3.87	1.26	4.03
	20/80	3.92	3.65	3.84	1.40	4.06
C_8	70/30	1.46	1.16	1.57	0.35	1.87
	20/80	1.40	1.15	1.58	0.40	1.95
hd-C_8	70/30	1.37	1.09	1.56	0.39	1.87
	20/80	1.29	1.09	1.55	0.40	1.88

[a] According to the angle between the surface normal and the vector pointing from the chain's grafting position to $CH_2(1)$.

[b] According to the position of the terminal methyl group in a chain.

Table S4. Locations of the limits of bonded-phase region ($z_{I/II}$) and interfacial region ($z_{II/III}$), and resulting interfacial width (w_{II}).

bonded phase	W/ACN (v/v)	$z_{I/II}$ (nm)	$z_{II/III}$ (nm)	w_{II} (nm)
C_{18}	70/30	1.26	2.19	0.93
	20/80	1.03	2.23	1.20
C_8	70/30	0.73	1.64	0.91
	20/80	n.d.[a]	1.55	n.d.
hd-C_8	70/30	0.89	1.73	0.84
	20/80	n.d.[a]	1.63	n.d.

[a] Not defined as total solvent density does not fall below 10% of its bulk value.

Table S5. Analyte-specific locations of the stationary-phase limit (z_{SP}).

bonded phase	W/ACN (v/v)	benzene z_{SP} (nm)	ethylbenzene z_{SP} (nm)	acetophenone z_{SP} (nm)	benzyl alcohol z_{SP} (nm)
C_{18}	70/30	2.43	2.51	2.43	2.37
	20/80	2.49	2.61	2.45	2.43
C_8	70/30	1.75	1.81	1.75	1.75
	20/80	1.75	1.77	1.77	1.77
hd-C_8	70/30	1.81	1.85	1.81	1.81
	20/80	1.81	1.81	1.81	1.81

Table S6. Parallel diffusion coefficients of **bonded-phase groups**.

United-atom group number	C_{18}		C_8		hd-C_8	
	70/30 (v/v) W/ACN	20/80 (v/v) W/ACN	70/30 (v/v) W/ACN	20/80 (v/v) W/ACN	70/30 (v/v) W/ACN	20/80 (v/v) W/ACN
	$D_{\|\|}$ (10^{-9} m^2 s^{-1})		$D_{\|\|}$ (10^{-9} m^2 s^{-1})		$D_{\|\|}$ (10^{-9} m^2 s^{-1})	
1	0.010±0.003	0.012±0.004	0.013±0.005	0.013±0.005	0.013±0.005	0.012±0.005
2	0.033±0.018	0.035±0.020	0.043±0.015	0.044±0.023	0.043±0.017	0.040±0.007
3	0.049±0.015	0.051±0.015	0.075±0.025	0.079±0.024	0.077±0.022	0.070±0.021
4	0.081±0.032	0.095±0.033	0.16±0.03	0.18±0.06	0.16±0.06	0.16±0.06
5	0.13±0.03	0.14±0.03	0.28±0.10	0.29±0.11	0.26±0.10	0.26±0.11
6	0.19±0.05	0.20±0.05	0.51±0.11	0.52±0.12	0.46±0.11	0.47±0.12
7	0.24±0.07	0.24±0.08	0.76±0.14	0.78±0.14	0.71±0.13	0.72±0.14
8	0.30±0.07	0.32±0.08	1.07±0.19	1.14±0.20	1.02±0.19	1.07±0.19
9	0.39±0.11	0.40±0.11	–	–	–	–
10	0.49±0.15	0.51±0.11	–	–	–	–
11	0.58±0.15	0.59±0.15	–	–	–	–
12	0.68±0.15	0.69±0.15	–	–	–	–
13	0.81±0.19	0.81±0.19	–	–	–	–
14	0.94±0.22	0.93±0.23	–	–	–	–
15	1.10±0.22	1.10±0.25	–	–	–	–
16	1.29±0.26	1.32±0.27	–	–	–	–
17	1.50±0.33	1.62±0.35	–	–	–	–
18	1.78±0.37	1.98±0.47	–	–	–	–

Table S7. Diffusive mobility data for **benzene**.

	W/ACN (v/v)	$D_{\|\|,max}$ (10^{-9} m^2 s^{-1})	$D_{\|\|,bulk}$ (10^{-9} m^2 s^{-1})	$D_{\|\|,max}/D_{\|\|,bulk}$	$D_{m,analyte\_max}$ (10^{-9} m^2 s^{-1})
C_{18}	70/30	2.05 ± 0.07	1.44 ± 0.02	1.42 ± 0.05	1.74 ± 0.08
	20/80	2.61 ± 0.05	2.33 ± 0.02	1.12 ± 0.02	2.55 ± 0.06
C_8	70/30	1.93 ± 0.05	1.43 ± 0.04	1.35 ± 0.05	1.67 ± 0.05
	20/80	2.45 ± 0.05	2.30 ± 0.03	1.07 ± 0.04	2.63 ± 0.07
hd-C_8	70/30	2.14 ± 0.06	1.44 ± 0.05	1.49 ± 0.05	1.86 ± 0.09
	20/80	2.53 ± 0.04	2.31 ± 0.05	1.10 ± 0.04	2.72 ± 0.10

Table S8. Diffusive mobility data for **ethylbenzene**.

	W/ACN (v/v)	$D_{\|\|,max}$ (10^{-9} m^2 s^{-1})	$D_{\|\|,bulk}$ (10^{-9} m^2 s^{-1})	$D_{\|\|,max}/D_{\|\|,bulk}$	$D_{m,analyte\_max}$ (10^{-9} m^2 s^{-1})
C_{18}	70/30	1.64 ± 0.05	1.20 ± 0.04	1.37 ± 0.06	1.46 ± 0.10
	20/80	2.09 ± 0.08	1.91 ± 0.03	1.09 ± 0.05	2.03 ± 0.04
C_8	70/30	1.56 ± 0.12	1.21 ± 0.07	1.29 ± 0.05	1.37 ± 0.06
	20/80	1.97 ± 0.04	1.90 ± 0.03	1.04 ± 0.05	2.13 ± 0.08
hd-C_8	70/30	1.73 ± 0.04	1.24 ± 0.07	1.40 ± 0.05	1.53 ± 0.10
	20/80	2.04 ± 0.09	1.91 ± 0.03	1.07 ± 0.05	2.22 ± 0.12

Table S9. Diffusive mobility data for **acetophenone**.

	W/ACN (v/v)	$D_{\|\|,max}$ (10^{-9} m^2 s^{-1})	$D_{\|\|,bulk}$ (10^{-9} m^2 s^{-1})	$D_{\|\|,max}/D_{\|\|,bulk}$	$D_{m,analyte\_max}$ (10^{-9} m^2 s^{-1})
C_{18}	70/30	1.31 ± 0.02	1.08 ± 0.02	1.21 ± 0.03	1.20 ± 0.06
	20/80	1.68 ± 0.02	1.54 ± 0.02	1.09 ± 0.02	1.70 ± 0.12
C_8	70/30	1.24 ± 0.02	1.09 ± 0.04	1.14 ± 0.03	1.13 ± 0.06
	20/80	1.62 ± 0.02	1.54 ± 0.03	1.05 ± 0.03	1.75 ± 0.14
hd-C_8	70/30	1.33 ± 0.02	1.09 ± 0.03	1.22 ± 0.03	1.20 ± 0.11
	20/80	1.67 ± 0.05	1.55 ± 0.03	1.08 ± 0.03	1.79 ± 0.09

Table S10. Diffusive mobility data for **benzyl alcohol**.

	W/ACN (v/v)	$D_{\|\|,max}$ (10^{-9} m^2 s^{-1})	$D_{\|\|,bulk}$ (10^{-9} m^2 s^{-1})	$D_{\|\|,max}/D_{\|\|,bulk}$	$D_{m,analyte\_max}$ (10^{-9} m^2 s^{-1})
C_{18}	70/30	1.30 ± 0.03	1.11 ± 0.02	1.17 ± 0.03	1.22 ± 0.06
	20/80	1.67 ± 0.03	1.53 ± 0.02	1.09 ± 0.02	1.63 ± 0.09
C_8	70/30	1.22 ± 0.02	1.09 ± 0.03	1.12 ± 0.02	1.14 ± 0.02
	20/80	1.55 ± 0.02	1.47 ± 0.02	1.05 ± 0.03	1.68 ± 0.12
hd-C_8	70/30	1.30 ± 0.02	1.12 ± 0.03	1.16 ± 0.02	1.21 ± 0.04
	20/80	1.57 ± 0.03	1.49 ± 0.02	1.05 ± 0.02	1.74 ± 0.07

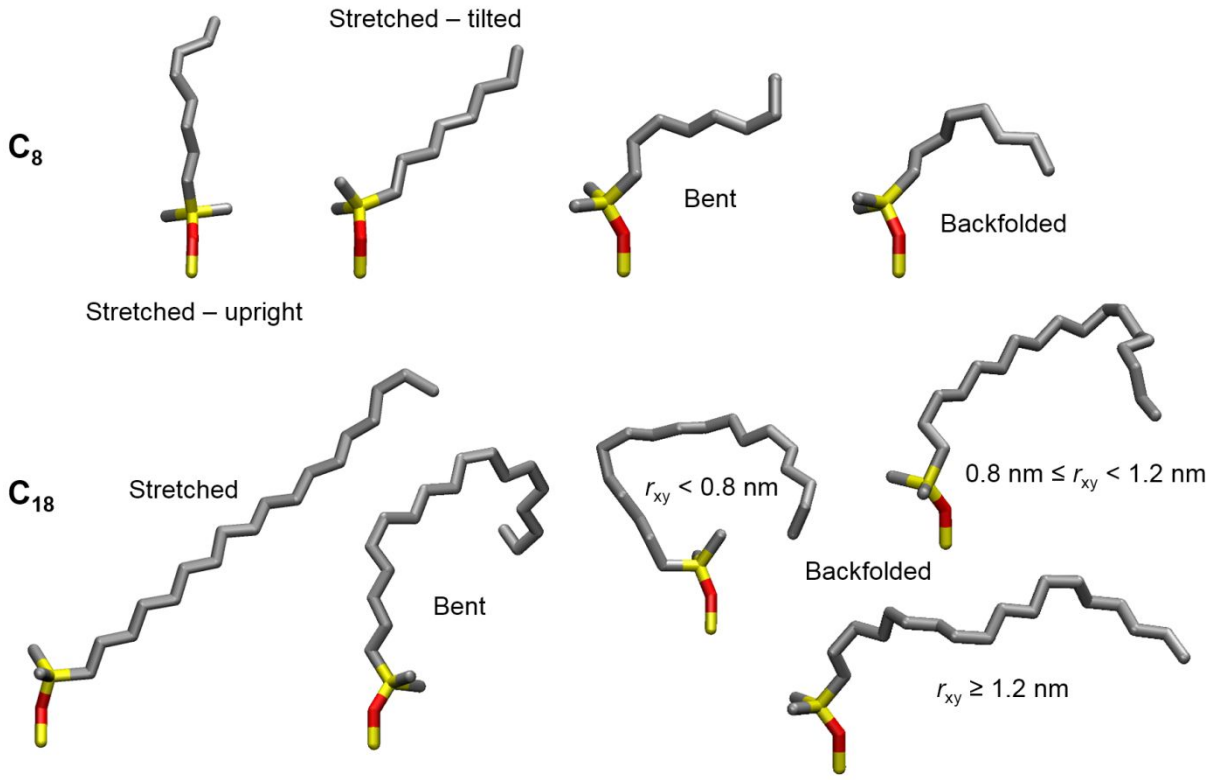

Figure S1.

Snapshots illustrating typical conformations of C_8 and C_{18} chains. Color-code: Si, yellow; O, red; CH_2 and CH_3 united-atom groups, gray.

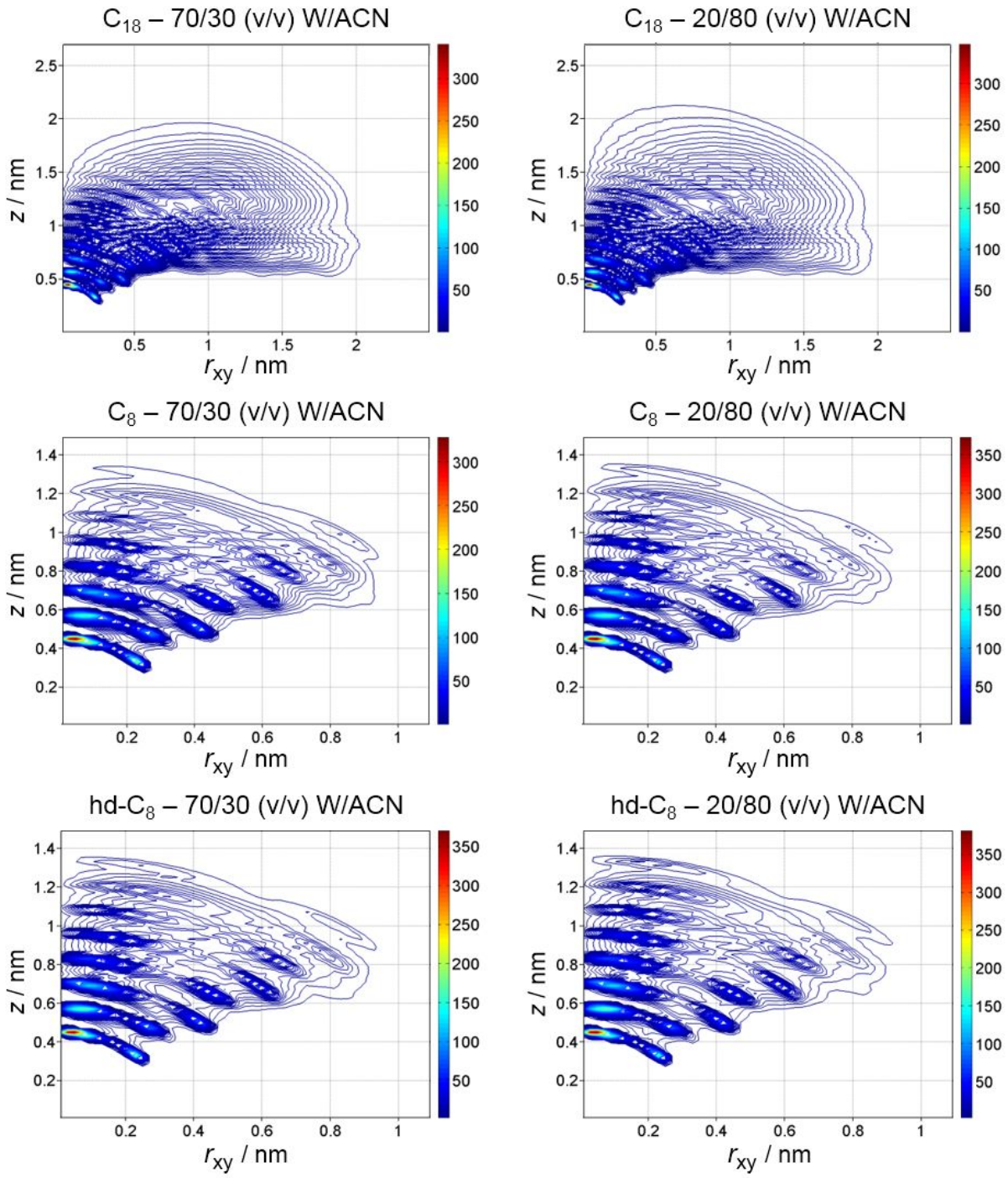

Figure S2.

Spatial distribution of the alkyl groups in a chain. Shown is the probability for a given united-atom group of a chain to be found at a certain horizontal distance r_{xy} from the chain grafting position and vertical distance z from the silica surface.