

Supporting Information
For
Retention modeling in combined pH/organic solvent gradient
reversed-phase HPLC

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The present section includes the Tables S1 to S7 with the adjustable parameters derived by fitting all the experimental retention data to different models.

Table S1. Values of adjustable parameters of eqn (3) obtained by fitting to this equation retention data recorded by gradient experiment Nos. 1-27 of Table 1.

solutes	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈
Arg	10.7	0.006	-19.2	0.12	21.4	0.011	0.126	-0.005	-0.56
Asn	13.1	0.030	-26.5	0.29	23.4	-0.037	0.038	0.001	0.22
Gln	16.2	0.058	-37.1	0.30	32.5	-0.044	0.021	0.001	0.35
Ser	17.2	0.062	-39.6	0.35	34.0	-0.060	0.008	0.003	0.52
Asp	29.3	0.179	-80.5	-0.41	70.8	-0.058	-0.160	0.006	1.77
Glu	29.0	0.272	-81.1	0.06	68.8	-0.135	-0.367	0.016	2.28
Thr	29.2	0.275	-84.5	0.21	73.9	-0.138	-0.361	0.015	2.09
Dopa	36.6	0.565	-116.6	0.15	96.6	-0.235	-0.787	0.016	4.43
Ala	38.7	0.863	-134.0	0.80	99.7	-0.409	-1.052	0.005	7.34
Tyr	43.3	1.156	-161.4	0.79	120.6	-0.438	-1.267	-0.018	8.84
Gaba	82.1	0.735	-261.6	-2.44	188.8	-0.419	-0.945	0.025	13.40
Met	69.0	1.455	-229.4	-1.64	172.8	-0.294	-0.921	-0.066	10.16
Val	110.0	1.411	-315.3	-7.91	236.4	0.028	-0.687	-0.069	13.98
Trp	162.6	1.400	-468.5	-13.17	377.4	0.322	-0.659	-0.065	17.07
Phe	180.5	1.347	-521.2	-14.98	432.3	0.456	-0.574	-0.062	17.27
Ile	253.3	1.295	-655.2	-27.38	515.5	1.085	-0.336	-0.066	25.38
Leu	292.1	1.259	-746.4	-32.70	588.7	1.363	-0.305	-0.061	28.72

Table S2. Values of adjustable parameters of eqn (4) obtained by fitting to this equation retention data recorded by gradient experiment Nos. 1-9 of Table 1.

solutes	a_0	a_1	a_2	a_3	a_4
Arg	9.55	0.006	-12.7	11.4	0.042
Asn	11.71	0.046	-19.2	17.9	0.015
Gln	14.27	0.088	-28.5	27.5	-0.026
Ser	13.92	0.118	-26.4	25.6	-0.058
Asp	16.33	0.278	-40.1	43.0	-0.272
Glu	13.80	0.507	-34.5	42.5	-0.622
Thr	16.87	0.471	-46.6	54.3	-0.547
Dopa	14.81	0.716	-44.2	55.7	-0.849
Ala	14.80	0.682	-44.0	51.7	-0.537
Tyr	19.11	0.643	-59.6	64.6	-0.407
Gaba	20.81	0.681	-67.2	73.1	-0.374
Met	40.58	0.661	-145.6	152.0	-0.327
Val	39.46	0.707	-142.6	150.2	-0.386
Trp	53.63	0.836	-202.5	214.7	-0.616
Phe	57.21	0.941	-219.4	236.1	-0.858
Ile	56.21	0.900	-214.2	228.9	-0.730
Leu	60.81	0.940	-233.8	249.4	-0.794

Table S3. Values of adjustable parameters of eqn (4) obtained by fitting to this equation retention data recorded by gradient experiment Nos. 10-18 of Table 1.

solutes	a_0	a_1	a_2	a_3	a_4
Arg	11.77	0.020	-22.4	22.2	0.013
Asn	15.71	0.045	-35.0	34.2	0.006
Gln	19.31	0.080	-47.9	46.8	-0.020
Ser	20.20	0.086	-49.5	48.0	-0.011
Asp	25.50	0.210	-71.4	71.2	-0.159
Glu	30.32	0.321	-89.1	88.6	-0.284
Thr	30.39	0.343	-90.7	92.2	-0.342
Dopa	34.00	0.682	-109.9	116.8	-0.869
Ala	28.00	1.103	-91.6	107.0	-1.531
Tyr	27.33	1.361	-95.3	115.0	-1.949
Gaba	43.91	1.354	-158.4	179.6	-1.966
Met	21.82	1.399	-63.8	69.4	-1.521
Val	27.96	1.336	-92.3	99.7	-1.217
Trp	54.88	1.253	-203.5	214.0	-0.992
Phe	62.65	1.163	-235.6	246.0	-0.777
Ile	75.26	1.046	-288.6	301.1	-0.407
Leu	85.57	1.008	-330.7	343.3	-0.302

Table S4. Values of adjustable parameters of eqn (4) obtained by fitting to this equation retention data recorded by gradient experiment Nos. 19-27 of Table 1.

solutes	a_0	a_1	a_2	a_3	a_4
Arg	14.3	-0.095	-32.6	30.6	0.323
Asn	12.8	0.011	-21.3	18.1	0.094
Gln	15.3	0.029	-28.4	23.3	0.108
Ser	16.8	0.044	-33.2	28.5	0.094
Asp	31.6	0.167	-97.3	98.3	-0.049
Glu	28.1	0.280	-77.8	75.4	-0.193
Thr	28.1	0.280	-77.8	75.4	-0.193
Dopa	36.1	0.584	-114.4	117.4	-0.645
Ala	39.6	0.893	-131.4	140.5	-1.089
Tyr	46.2	1.127	-166.5	182.0	-1.445
Gaba	87.3	0.639	-312.6	313.6	-0.494
Met	79.6	1.094	-291.8	296.8	-0.913
Val	120.3	0.929	-453.8	459.1	-0.459
Trp	175.0	0.915	-685.3	703.4	-0.369
Phe	199.8	0.792	-791.0	814.7	-0.087
Ile	252.7	0.724	-995.7	1017	0.128
Leu	289.1	0.700	-1146	1173	0.182

Table S5. Values of adjustable parameters of eqn (5) obtained by fitting to this equation retention data recorded by gradient experiment Nos. 1-3, 10-12 and 19-21 of Table 1.

solutes	b_0	b_1	b_2	b_3	b_4
Arg	4.38	0.034	0.71	-0.058	-0.001
Asn	4.17	0.045	1.17	-0.102	0.001
Gln	4.14	0.061	1.43	-0.127	0.003
Ser	4.64	0.057	1.49	-0.140	0.006
Asp	8.88	0.109	0.57	-0.096	0.010
Glu	4.62	0.097	2.46	-0.278	0.025
Thr	4.55	0.120	2.40	-0.264	0.021
Dopa	1.03	0.303	3.83	-0.407	0.016
Ala	-4.94	0.631	5.87	-0.580	-0.015
Tyr	-8.25	0.925	6.44	-0.595	-0.050
Gaba	8.87	0.466	3.75	-0.536	0.017
Met	24.5	1.178	-3.00	0.101	-0.074
Val	60.6	1.159	-13.36	0.829	-0.067
Trp	88.8	1.108	-21.21	1.390	-0.055
Phe	102.3	1.027	-25.13	1.676	-0.043
Ile	161.3	1.064	-42.12	2.882	-0.047
Leu	187.6	1.025	-49.62	3.414	-0.040

Table S6. Values of adjustable parameters of eqn (5) obtained by fitting to this equation retention data recorded by gradient experiment Nos. 4-6, 13-15 and 22-24 of Table 1.

solutes	b_0	b_1	b_2	b_3	b_4
Arg	6.23	0.025	0.09	-0.008	-0.001
Asn	6.94	0.027	0.23	-0.028	0.002
Gln	7.52	0.047	0.22	-0.030	0.003
Ser	7.69	0.045	0.36	-0.047	0.005
Asp	7.89	0.088	0.56	-0.078	0.009
Glu	8.08	0.096	0.92	-0.130	0.018
Thr	8.08	0.096	0.92	-0.130	0.018
Dopa	5.93	0.189	1.96	-0.242	0.022
Ala	-0.11	0.386	4.27	-0.453	0.010
Tyr	-4.62	0.598	5.33	-0.515	-0.014
Gaba	2.51	0.349	4.46	-0.520	0.024
Met	-4.58	1.181	5.08	-0.471	-0.080
Val	11.49	1.200	0.53	-0.161	-0.078
Trp	23.23	1.192	-2.90	0.099	-0.074
Phe	27.71	1.137	-4.22	0.198	-0.066
Ile	61.08	1.144	-13.71	0.862	-0.064
Leu	73.03	1.112	-17.11	1.102	-0.059

Table S7. Values of adjustable parameters of eqn (5) obtained by fitting to this equation retention data recorded by gradient experiment Nos. 7-9, 16-18 and 25-27 of Table 1.

solutes	b_0	b_1	b_2	b_3	b_4
Arg	8.92	0.117	-1.13	0.099	-0.012
Asn	7.43	0.066	-0.24	0.017	-0.002
Gln	7.95	0.093	-0.33	0.025	-0.002
Ser	7.97	0.095	-0.17	0.007	-0.001
Asp	8.26	0.141	-0.15	-0.001	0.000
Glu	9.53	0.165	-0.34	0.004	0.005
Thr	8.79	0.159	-0.07	-0.019	0.005
Dopa	8.52	0.219	0.20	-0.055	0.009
Ala	6.59	0.256	1.44	-0.195	0.019
Tyr	5.14	0.362	1.66	-0.204	0.009
Gaba	8.38	0.209	1.23	-0.201	0.035
Met	-7.88	0.854	5.72	-0.512	-0.043
Val	-10.48	1.016	6.59	-0.584	-0.060
Trp	-8.91	1.075	5.95	-0.524	-0.066
Phe	-9.84	1.158	5.99	-0.507	-0.078
Ile	-6.79	1.255	5.41	-0.489	-0.087
Leu	-3.77	1.258	4.51	-0.425	-0.086