Evaluation of the Peak Variance in Gradient Liquid Chromatography

Supplementary Information

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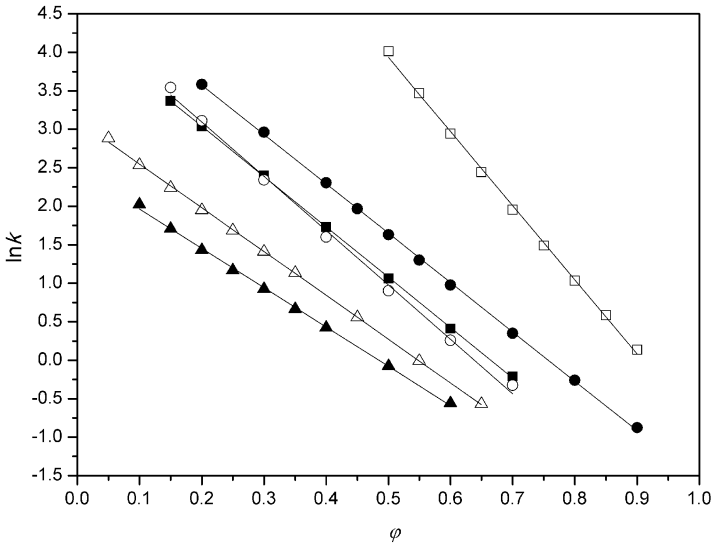
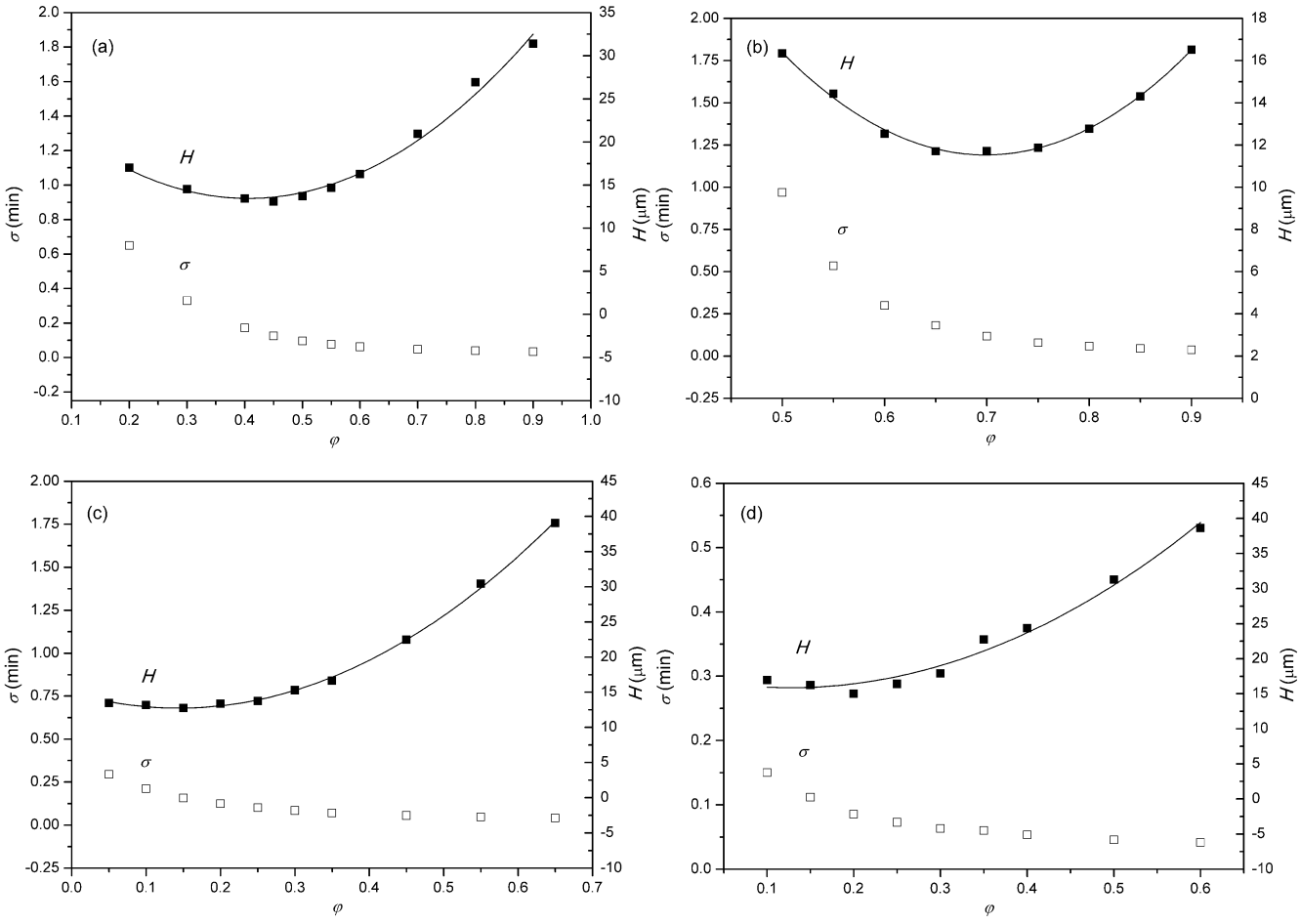


Figure S1. Plots of ln$k$ vs φ for anisole (●), *o*-cresol(■), biphenyl (□), phenol(Δ), aniline (▲) and acetophenone (○). The solid line is the linear fit to data.



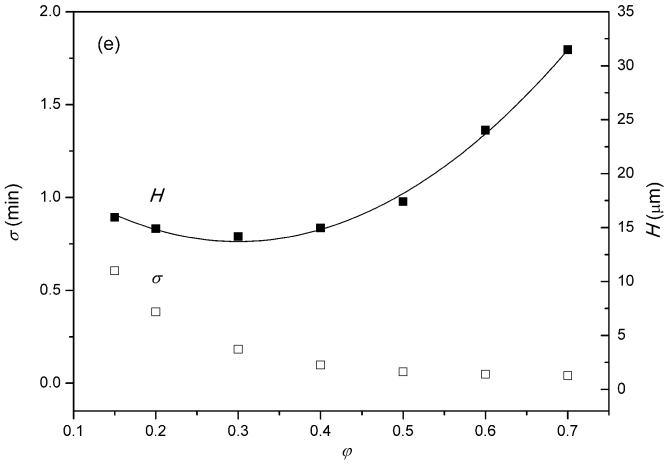
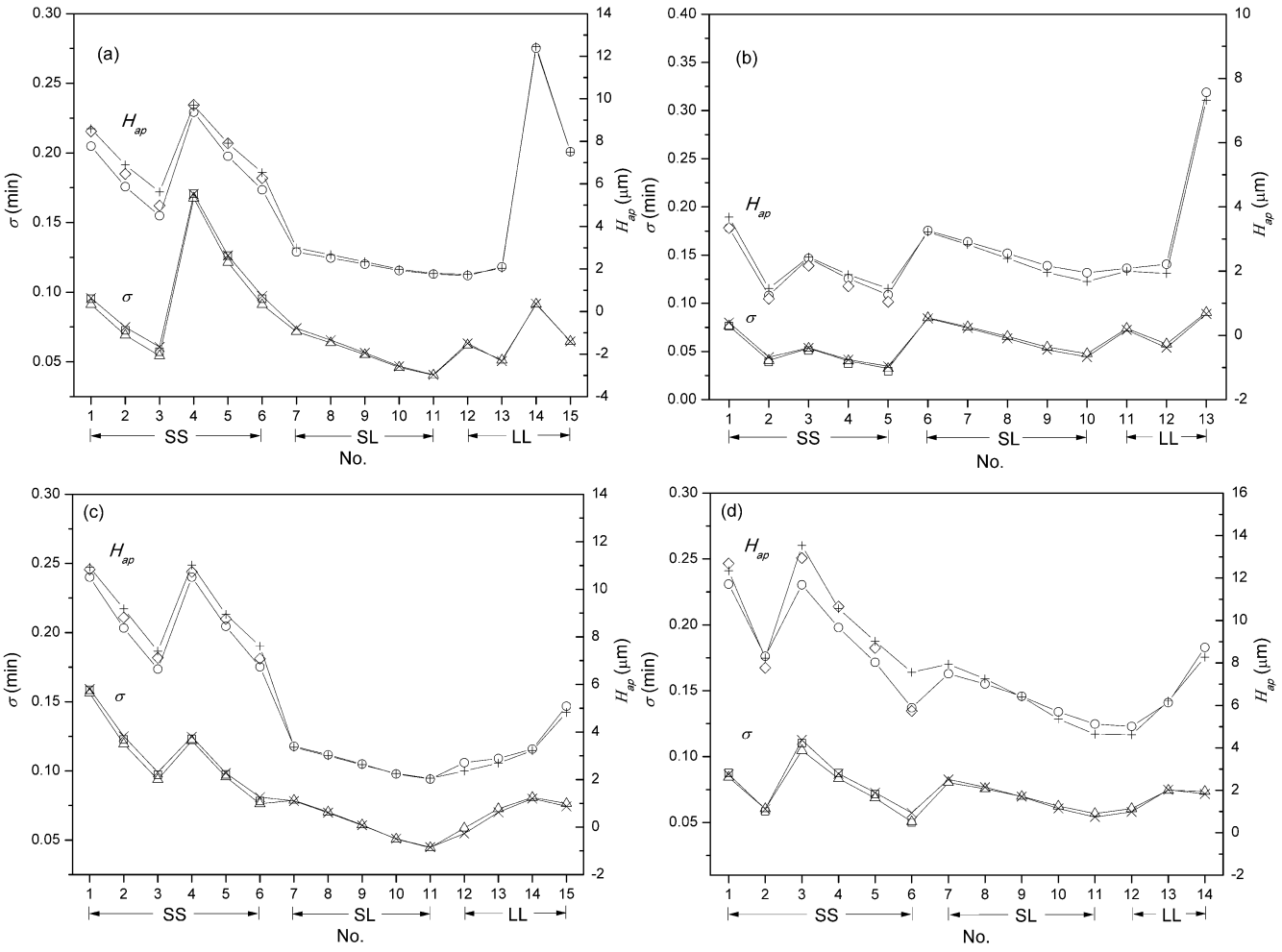


Figure S2. Plots of H,σ vs φ for (a) anisole, (b) biphenyl, (c) phenol, (d) aniline and (e) acetophenone. The solid line is the fit to data by using the quadratic polynomial equation (Eq. (4)).



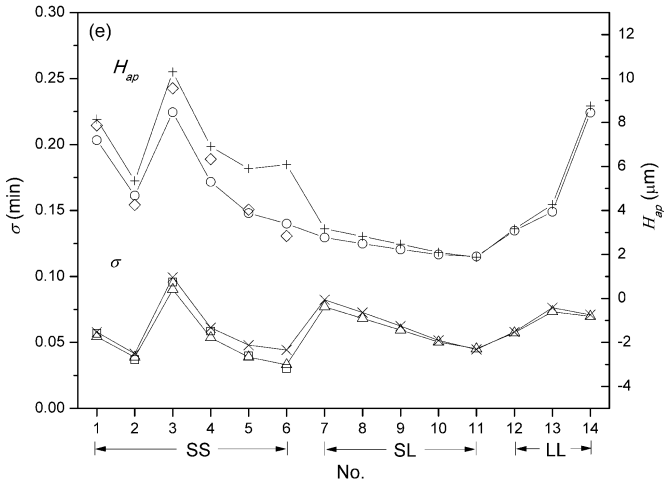


Figure S3. Comparisons of the experimental and predicted values of H_{ap} and σ for (a) anisole, (b) biphenyl, (c) phenol, (d) aniline and (e) acetophenone. Symbols: o and Δ, experimental values; + and ×, theoretical values calculated by using Eqs. (2), (6), (8) and (11); ◊ and □, theoretical values calculated by using Eqs. (2) and (12)-(14).

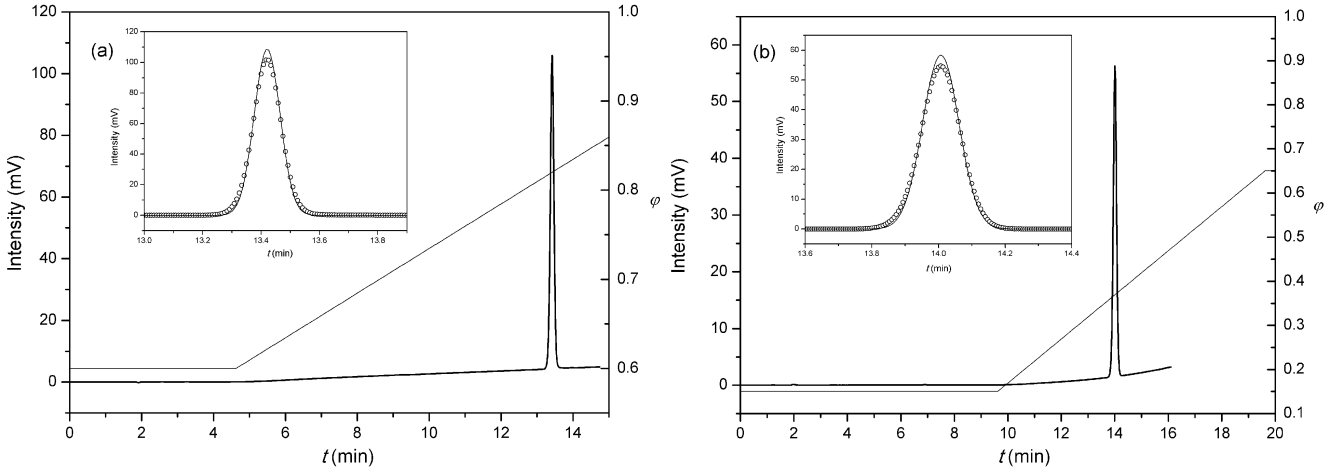


Figure S4. Chromatograms corresponding to (a) No. 10 in Fig. S3(b) (SL gradient) and (b) No. 12 in Fig. S3(c) (LL gradient), respectively. In the insets, the circle denotes the data obtained by subtracting the baseline from the experimental elution peak, and the solid line is the Gaussian curve calculated by using the corresponding predicted value of σ as shown in Fig. S3.

Table S1 Gradient conditions for biphenyl, phenol, aniline and acetophenone.

Biphenyl		
No	Type	Gradient profile ($t_{P,i}$,φ_i)
1	SS	0min, 0.60; 6min, 0.60; 6.01min, 0.75; 30min, 0.75
2	SS	0min, 0.60; 7min, 0.60; 7.01min, 0.85; 30min, 085
3	SS	0min, 0.65; 6min, 0.65;6.01min, 0.80; 30min, 0.80
4	SS	0min, 0.65; 5min, 0.65; 5.01min, 0.85; 30min, 0.85
5	SS	0min, 0.65; 5min, 0.65; 5.01min, 0.90; 30min, 0.90
6	SL	0min, 0.60; 30min, 0.90
7	SL	0min, 0.60; 25min, 0.90
8	SL	0min, 0.60; 20min, 0.90
9	SL	0min, 0.60; 15min, 0.90
10	SL	0min, 0.60; 12min, 0.90
11	LL	0min, 0.60; 5min, 0.60; 25min, 0.90; 30min, 0.90
12	LL	0min, 0.65; 5min, 0.65; 15min, 0.90; 30min, 0.90
13	LL	0min, 0.70; 5min, 0.70; 25min, 0.90; 30min, 0.90

Phenol		
No	Type	Gradient profile ($t_{P,i}$,φ_i)
1	SS	0min, 0.10; 3min, 0.10; 3.01min, 0.15; 30min, 0.15
2	SS	0min, 0.10; 3min, 0.10; 3.01min, 0.20; 30min, 0.20
3	SS	0min, 0.10; 3min, 0.10; 3.01min, 0.25; 30min, 0.25
4	SS	0min, 0.15; 2min, 0.15; 2.01min, 0.20; 30min, 0.20
5	SS	0min, 0.15; 2min, 0.15; 2.01min, 0.25; 30min, 0.25
6	SS	0min, 0.15; 2min, 0.15; 2.01min, 0.30; 30min, 0.30
7	SL	0min, 0.05; 30min, 0.65
8	SL	0min, 0.05; 25min, 0.65
9	SL	0min, 0.05; 20min, 0.65
10	SL	0min, 0.05;15min, 0.65
11	SL	0min, 0.05; 12min, 0.65
12	LL	0min, 0.15; 5min, 0.15; 15min, 0.65; 30min, 0.65
13	LL	0min, 0.10; 5min, 0.10; 20min, 0.55; 30min, 0.55
14	LL	0min, 0.05; 1min, 0.05; 21min, 0.45; 30min, 0.45
15	LL	0min, 0.15; 1min, 0.15; 21min, 0.55; 30min, 0.55

Aniline		
No	Type	Gradient profile ($t_{P,i}$,φ_i)
1	SS	0min, 0.15; 1min, 0.15; 1.01min, 0.20; 30min, 0.20
2	SS	0min, 0.15; 1min, 0.15; 1.01min, 0.30; 30min, 0.30
3	SS	0min, 0.10; 1min, 0.10; 1.01min, 0.15; 30min, 0.15
4	SS	0min, 0.10; 1min, 0.10; 1.01min, 0.20; 30min, 0.20
5	SS	0min, 0.10; 1min, 0.10; 1.01min, 0.25; 30min, 0.25
6	SS	0min, 0.10; 1min, 0.10; 1.01min, 0.35; 30min, 0.35
7	SL	0min, 0.10; 30min, 0.60
8	SL	0min, 0.10; 25min, 0.60
9	SL	0min, 0.10; 20min, 0.60
10	SL	0min, 0.10; 15min, 0.60
11	SL	0min, 0.10; 12min, 0.60
12	LL	0min, 0.10; 1min, 0.10; 11min, 0.50; 30min, 0.50
13	LL	0min, 0.10; 2min, 0.10; 17min, 0.50; 30min, 0.50
14	LL	0min, 0.15; 1min, 0.15; 16min, 0.50; 30min, 0.50

acetophenone		
No	Type	Gradient profile ($t_{P,i}$,φ_i)
1	SS	0min, 0.40; 1min, 0.40; 1.01min, 0.50; 30min, 0.50
2	SS	0min, 0.40; 1min, 0.40; 1.01min, 0.60; 30min, 0.60
3	SS	0min, 0.40; 1min, 0.30; 1.01min, 0.40; 30min, 0.40
4	SS	0min, 0.30; 1min, 0.30; 1.01min, 0.50; 30min, 0.50
5	SS	0min, 0.30; 1min, 0.30; 1.01min, 0.60; 30min, 0.60
6	SS	0min, 0.30; 1min, 0.30; 1.01min, 0.70; 30min, 0.70
7	SL	0min, 0.20; 30min, 0.70
8	SL	0min, 0.20; 25min, 0.70
9	SL	0min, 0.20; 20min, 0.70
10	SL	0min, 0.20; 15min, 0.70
11	SL	0min, 0.20; 12min, 0.70
12	LL	0min, 0.30; 2min, 0.30; 12min, 0.60; 30min, 0.60
13	LL	0min, 0.30; 3min, 0.30; 18min, 0.60; 30min, 0.60
14	LL	0min, 0.40; 2min, 0.40; 17min, 0.70; 30min, 0.70

Table S2 Relative errors between the experimental and theoretical values of σ and H_{ap} for anisole.

No.	Type	σ (min)					H_{ap} (μm)				
		Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]	Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]
1	SS	0.091	0.096	-5.1	0.095	-4.4	7.77	8.59	-10.5	8.47	-9.0
2	SS	0.069	0.075	-8.4	0.073	-5.0	5.87	6.89	-17.4	6.47	-10.2
3	SS	0.054	0.061	-11.7	0.057	-5.1	4.50	5.62	-24.8	4.97	-10.5
4	SS	0.168	0.170	-1.7	0.171	-1.8	9.37	9.69	-3.5	9.71	-3.7
5	SS	0.121	0.126	-4.1	0.126	-4.0	7.30	7.91	-8.3	7.90	-8.2
6	SS	0.091	0.097	-6.9	0.095	-4.6	5.72	6.53	-14.2	6.26	-9.5
7	SL	0.072	0.074	-3.4			2.80	2.99	-6.9		
8	SL	0.064	0.066	-3.0			2.52	2.67	-6.1		
9	SL	0.055	0.056	-2.4			2.23	2.34	-5.0		
10	SL	0.046	0.047	-1.6			1.93	1.99	-3.1		
11	SL	0.040	0.041	-0.6			1.76	1.79	-1.5		
12	LL	0.062	0.063	-1.9			1.69	1.75	-3.6		
13	LL	0.051	0.051	1.3			2.10	2.04	2.8		
14	LL	0.091	0.092	-0.3			12.38	12.45	-0.6		
15	LL	0.065	0.065	0.1			7.51	7.50	0.1		

a) Experimental value.

b) Theoretical values calculated by using Eqs. (2), (6), (8) and (11).

c) Relative error, (exp-theo)/exp×100%.

d) Theoretical values calculated by using Eqs. (2) and (12)-(14).

Table S3 Relative errors between the experimental and theoretical values of σ and H_{ap} for *o*-cresol.

No.	Type	σ (min)					H_{ap} (μm)				
		Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]	Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]
1	SS	0.061	0.063	-2.5	0.059	4.4	6.98	7.34	-5.2	6.39	8.5
2	SS	0.039	0.045	-13.6	0.038	3.8	3.60	4.65	-29.1	3.33	7.5
3	SS	0.100	0.103	-3.0	0.100	0.4	8.19	8.70	-6.2	8.14	0.7
4	SS	0.059	0.066	-12.1	0.061	-2.7	4.88	6.13	-25.6	5.15	-5.5
5	SS	0.039	0.051	-31.7	0.041	-6.1	2.92	5.07	-73.6	3.29	-12.5
6	SS	0.033	0.046	-38.5	0.031	5.6	2.55	4.90	-92.2	2.28	10.7
7	SL	0.082	0.081	1.3			2.99	2.91	2.7		
8	SL	0.073	0.072	0.8			2.67	2.63	1.5		
9	SL	0.063	0.063	1.1			2.39	2.34	2.1		
10	SL	0.054	0.052	2.3			2.14	2.04	4.7		
11	SL	0.047	0.046	2.0			1.95	1.87	4.1		
12	LL	0.060	0.058	2.6			3.06	2.90	5.2		
13	LL	0.077	0.075	2.4			3.96	3.77	4.8		
14	LL	0.072	0.070	2.6			7.57	7.18	5.2		

a) Experimental value.

b) Theoretical values calculated by using Eqs. (2), (6), (8) and (11).

c) Relative error, (exp-theo)/exp×100%.

d) Theoretical values calculated by using Eqs. (2) and (12)-(14).

Table S4 Relative errors between the experimental and theoretical values of σ and H_{ap} for biphenyl.

No.	Type	σ (min)					H_{ap} (μm)				
		Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]	Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]
1	SS	0.076	0.080	-4.9	0.076	0.0	3.34	3.68	-10.0	3.34	0.1
2	SS	0.041	0.044	-8.4	0.039	4.2	1.24	1.46	-17.3	1.14	8.2
3	SS	0.053	0.054	-0.8	0.051	4.8	2.40	2.44	-1.7	2.17	9.4
4	SS	0.040	0.042	-3.3	0.037	6.9	1.77	1.89	-6.8	1.53	13.4
5	SS	0.032	0.035	-7.4	0.029	9.2	1.27	1.46	-15.3	1.04	17.5
6	SL	0.085	0.084	0.7			3.26	3.22	1.4		
7	SL	0.076	0.074	1.5			2.91	2.83	2.9		
8	SL	0.066	0.064	3.0			2.55	2.40	6.0		
9	SL	0.055	0.052	5.0			2.17	1.96	9.6		
10	SL	0.048	0.044	7.1			1.95	1.68	13.9		
11	LL	0.074	0.072	2.1			2.09	2.00	4.3		
12	LL	0.058	0.054	6.7			2.22	1.93	12.9		
13	LL	0.090	0.089	1.6			7.57	7.32	3.3		

a) Experimental value.

b) Theoretical values calculated by using Eqs. (2), (6), (8) and (11).

c) Relative error, (exp-theo)/exp×100%.

d) Theoretical values calculated by using Eqs. (2) and (12)-(14).

Table S5 Relative errors between the experimental and theoretical values of σ and H_{ap} for phenol.

No.	Type	σ (min)					H_{ap} (μm)				
		Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]	Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]
1	SS	0.156	0.159	-2.0	0.159	-1.5	10.51	10.93	-4.0	10.84	-3.1
2	SS	0.120	0.125	-4.7	0.123	-2.6	8.37	9.18	-9.6	8.81	-5.3
3	SS	0.094	0.099	-5.5	0.097	-3.5	6.64	7.40	-11.4	7.12	-7.1
4	SS	0.122	0.125	-2.4	0.123	-1.0	10.51	11.02	-4.8	10.73	-2.1
5	SS	0.096	0.098	-2.9	0.097	-1.8	8.44	8.95	-6.0	8.76	-3.7
6	SS	0.076	0.081	-6.2	0.078	-2.5	6.74	7.61	-13.0	7.08	-5.1
7	SL	0.079	0.078	0.6			3.40	3.36	1.2		
8	SL	0.070	0.070	0.8			3.04	3.00	1.4		
9	SL	0.061	0.061	0.5			2.65	2.62	1.2		
10	SL	0.051	0.051	-0.4			2.23	2.25	-0.7		
11	SL	0.045	0.045	-0.7			2.02	2.05	-1.6		
12	LL	0.059	0.055	6.7			2.71	2.36	13.0		
13	LL	0.073	0.070	3.5			2.89	2.69	6.9		
14	LL	0.081	0.080	1.0			3.28	3.22	1.9		
15	LL	0.076	0.074	2.7			5.09	4.82	5.3		

a) Experimental value.

b) Theoretical values calculated by using Eqs. (2), (6), (8) and (11).

c) Relative error, (exp-theo)/exp×100%.

d) Theoretical values calculated by using Eqs. (2) and (12)-(14).

Table S6 Relative errors between the experimental and theoretical values of σ and H_{ap} for aniline.

No.	Type	σ (min)					H_{ap} (μm)				
		Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]	Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]
1	SS	0.084	0.087	-2.7	0.088	-4.1	11.71	12.34	-5.4	12.68	-8.3
2	SS	0.060	0.060	0.5	0.058	3.3	8.31	8.23	1.0	7.77	6.5
3	SS	0.105	0.113	-7.6	0.110	-5.2	11.68	13.53	-15.8	12.94	-10.8
4	SS	0.083	0.087	-4.5	0.087	-5.0	9.67	10.56	-9.2	10.65	-10.2
5	SS	0.069	0.073	-6.0	0.071	-4.2	8.03	9.02	-12.3	8.71	-8.5
6	SS	0.051	0.057	-13.3	0.050	1.3	5.89	7.56	-28.4	5.74	2.6
7	SL	0.080	0.083	-3.0			7.49	7.94	-6.0		
8	SL	0.076	0.077	-1.6			7.01	7.25	-3.4		
9	SL	0.070	0.070	0.2			6.43	6.40	0.5		
10	SL	0.063	0.061	2.9			5.70	5.36	6.0		
11	SL	0.057	0.054	4.8			5.12	4.64	9.4		
12	LL	0.061	0.058	4.0			5.01	4.62	7.8		
13	LL	0.074	0.075	-0.6			6.13	6.20	-1.1		
14	LL	0.074	0.072	2.7			8.73	8.27	5.3		

a) Experimental value.

b) Theoretical values calculated by using Eqs. (2), (6), (8) and (11).

c) Relative error, (exp-theo)/exp×100%.

d) Theoretical values calculated by using Eqs. (2) and (12)-(14).

Table S7 Relative errors between the experimental and theoretical values of σ and H_{ap} for acetophenone.

No.	Type	σ (min)					H_{ap} (μm)				
		Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]	Exp [a]	Theo1 [b]	RE(%) [c]	Theo2 [d]	RE(%) [c]
1	SS	0.054	0.058	-6.4	0.057	-4.5	7.20	8.15	-13.2	7.87	-9.3
2	SS	0.039	0.041	-7.0	0.037	4.6	4.68	5.35	-14.3	4.26	9.1
3	SS	0.090	0.099	-10.2	0.096	-6.2	8.47	10.30	-21.6	9.55	-12.8
4	SS	0.054	0.061	-14.2	0.059	-9.3	5.30	6.91	-30.4	6.34	-19.5
5	SS	0.039	0.048	-23.3	0.040	-2.0	3.88	5.90	-52.1	4.04	-4.1
6	SS	0.033	0.044	-33.7	0.030	8.6	3.40	6.09	-79.1	2.84	16.4
7	SL	0.077	0.082	-6.9			2.77	3.17	-14.4		
8	SL	0.068	0.073	-6.5			2.49	2.82	-13.3		
9	SL	0.059	0.062	-5.2			2.23	2.47	-10.8		
10	SL	0.050	0.052	-2.3			2.00	2.10	-5.0		
11	SL	0.045	0.045	1.1			1.91	1.87	2.1		
12	LL	0.057	0.058	-1.2			3.08	3.16	-2.6		
13	LL	0.073	0.076	-4.1			3.94	4.27	-8.4		
14	LL	0.070	0.071	-1.7			8.45	8.75	-3.6		

a) Experimental value.

b) Theoretical values calculated by using Eqs. (2), (6), (8) and (11).

c) Relative error, (exp-theo)/exp×100%.

d) Theoretical values calculated by using Eqs. (2) and (12)-(14).