Evaluation of Monodispersion Silica for High Performance Liquid Chromatography using Van Deemter Plot

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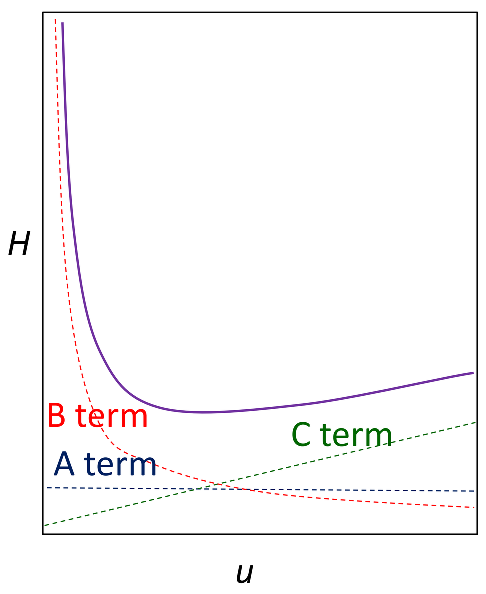
Abstract

The feature of a superficially porous (core shell) particle used as a highly efficient material is existence of a core, a thin porous layer and narrow particle size distribution, which lead to higher efficiency than a totally porous particle. On the other hand, recently a monodispersion silica gel has been presented to be the almost same particle size distribution as a superficially porous silica and to be higher performance materials than a conventional totally porous silica. In this study, a monodispersion totally porous silica and a superficially porous silica were compared regarding theoretical plate and Van Deemter plot. As a result of a plate measurement, a monodispersion silica showed 16% higher theoretical plate than a conventional totally porous silica, while a superficially porous silica indicated 47% higher. It was leaded by comparing with Van Deemter plot that only A term of Van Deemter Equation was decreased by effect of narrow particle distribution and both B and C terms were reduced by effect of a thickness of porous silica layer. It was elucidated that predominance of superficially porous silica over totally porous silica was leaded by not only low Eddy diffusion due to narrow particle size distribution but also both low longitudinal diffusion and short mass transfer path due to a thin porous layer.

$$H = Ad_p + B\frac{D_m}{u} + C\frac{d_p^2}{D_m}u$$



A term : Eddy diffusion(dp is particle diameter)

B term : Longitudinal diffusion (Dm is diffusion coefficient)

C term : Mass transfer

1. F. D. Antia and C. Horvath, *J. Chromatogr.,* 435 (1988) 1-15.

Figure 1. Van Deemter equation

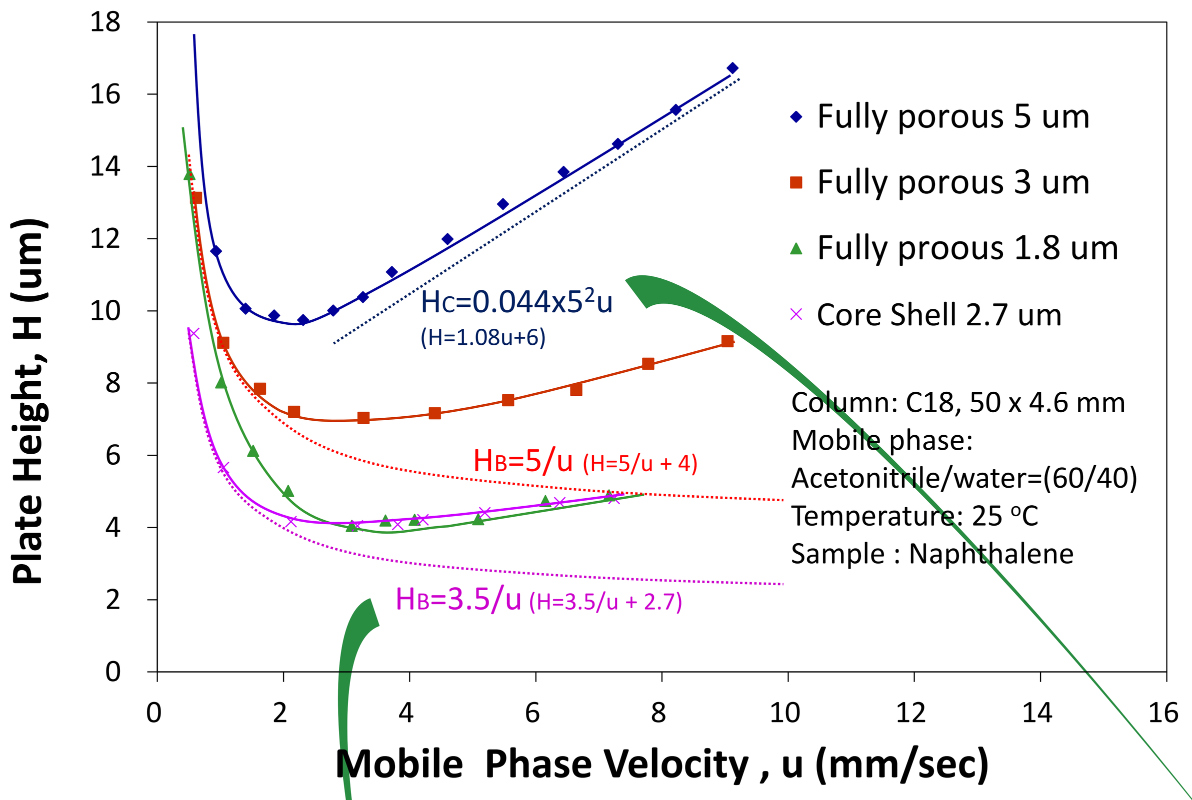


Figure 2. Comparison of plate height plots

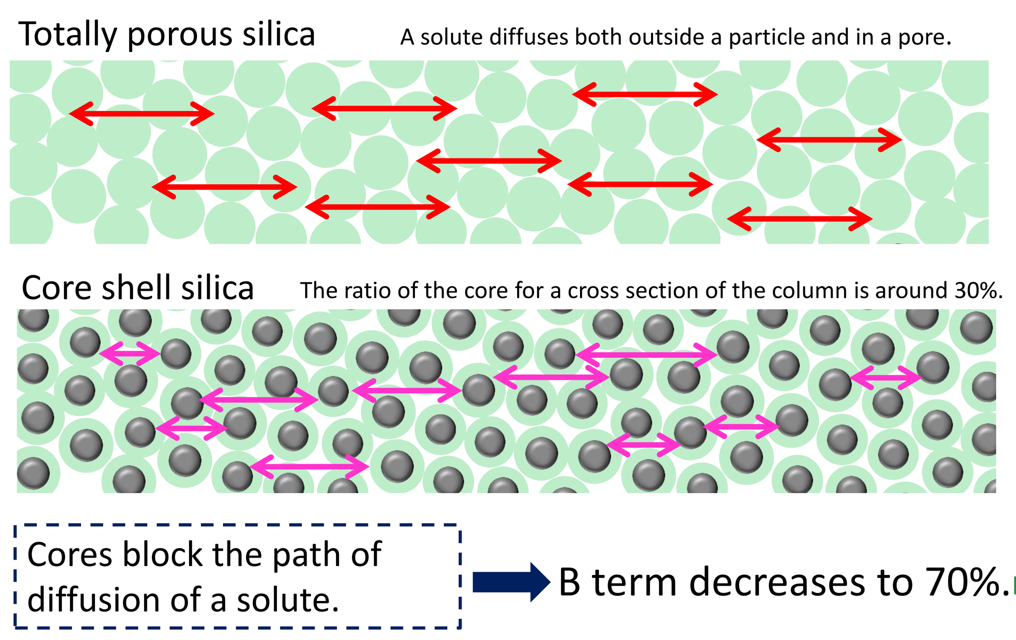


Figure 3. Difference of diffusion in column Longitudinal direction

Table 1. Parameter of each particle $H = Ad_p + B\frac{D_m}{u} + C\frac{d_p^2}{D_m}u$

Particle	A·dp	B·Dm	(C/Dm)·dp²
Totally porous Conventional particle size distribution 1.8 µm	1.33x1.8=2.4 (Conventional distribution)	5 (Totally porous)	$0.044 \times 1.8^2 = 0.14$
Totally porous Narrow particle size distribution 2.7 µm	1.00x2.7=2.7 (Narrow distribution)	5 (Totally porous)	$0.044 \times 2.7^2 = 0.32$
Core shell Narrow particle size distribution 2.7 µm	1.00x2.7=2.7 (Narrow distribution)	3.5 (Core shell)	0.14 same as 1.8um particle (Core shell)
Totally porous Conventional particle size distribution 2.7 µm	1.33x2.7=3.6 (Conventional distribution)	5 (Totally porous)	$0.044 \times 2.7^2 = 0.32$

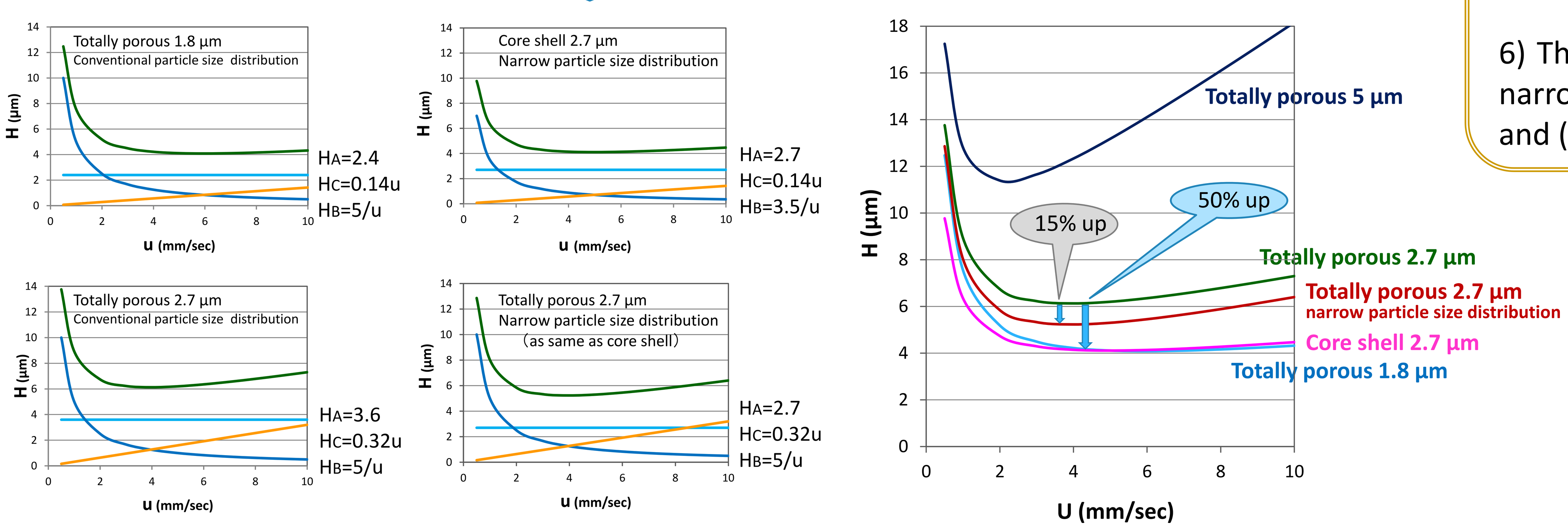
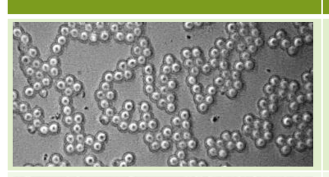
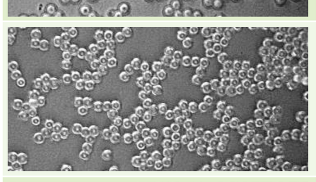
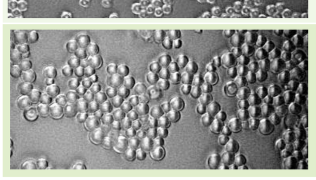


Figure 4. Van Deemter Plot

Table 2. Property and chromatographic data

Photo	Particle type	Average particle size	Particle size distribution	Pore diameter	Efficiency[a], Reduced HETP[a]	Retention time[b]
	Core shell particle	2.78 µm	$D_{90}/D_{10}=1.11$	9 nm	N=20,500 h=1.75	7.8 min
	Monodispersion totally porous particle	2.81 µm	$D_{90}/D_{10}=1.09$	10 nm	N=16,000 h=2.22	9.6 min
	Conventional totally porous particle	3.19 µm	$D_{90}/D_{10}=1.48$	12 nm	N=12,200 h=2.57	9.8 min

47% up

16% up

a: Stationary phase, C18; column dimension, 100 x 2.1 mm; mobile phase, acetonitrile/water (60/40); flow rate, 0.3 mL/min; column temperature, 25 °C; sample, butylbenzene.

b: Retention time of butylbenzene

Some assumptions and the definition of Van Deemter Equation

1) It is assumed by Plots in figure 3 that the ratio of B/Dm value of B term between core shell and totally porous particles is 7/10.

2) The particle size distribution is narrowed , a coefficient (A) of A term decreases. The coefficient (A) is also the same value in the case of the particle size distribution is the same.

3) C term value is in proportional to a particle size (dp) squared.

4) B·Dm is assumed to be 5 for a totally porous particle and 3.5 for a core shell particle by plots in figure 2 and above (1) .

5) C/Dm of totally porous particle is assumed to be 0.044 by plots in figure 2. The C term value of 1.8 µm totally porous particle is assumed to be as same as that of 2.7 µm core shell particle.

6) The coefficient A is assumed to be 1.33 and 1.00 for a conventional particle and a narrow particle size distribution particle respectively by plots in figure 2 and above (4) and (5).

Conclusion

- A monodispersion totally porous silica showed a narrow particle size distribution as same as superficially porous silica.
- A narrow particle size distribution made A term of Van Deemter Equation decrease 25% to compare with a conventional particle size distribution particle. The coefficient (A) became from 1.33 to 1.00. As the result, an efficiency increased 15% to 16%.
- Measurement value was almost corresponded the theoretically calculated value including some assumptions.
- A core shell silica showed ca. 50% higher theoretical plates than a conventional totally porous silica because reducing of both B and C term values of Van Deemter Equation was added due to a thin porous layer of the particle.