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Filtration Mechanism of Latex Spherical Particles
by Cylindrical Pores of Comparable Radius

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Abstract

Filtration mechanism of buoyant sphere suspension is analyzed by applying low Reynolds number hydrodynamics. Polystyrene latex particles are used for the sphere system, and pores of polycarbonate membrane filters provide the capillary system ; the pore size is well defined and comparable to the diameter of particles. The accordance between the analytical result and the experimental data is satisfactory, and thereby it gives a sound base for the turbidity measurements, which is convenient for measuring latex size in situ.

§ 1. Introduction

Latex is a suspension of polystyrene spheres in water ; the diameter of the particle is about 2,000 A, typically, and the size distribution has a sharp maximum. ⁽¹⁾ The particles are negatively charged on the surface, due to SO_4^- end groups which are generated by the chemical synthesis process, and every particle is surrounded by ionic double layer. ⁽²⁾

The particle size is usually measured by using electron microscope, which needs dried up samples. ⁽³⁾ In a series of latex experiments, we faced a problem to measure the particle size, hopefully in situ, and looked for a convenient method. Finally, we picked up the filtration method, which gave the particle size by measuring the optical turbidity of the filtrate, as reported in the preceding paper. ⁽⁴⁾ However, another question arose for employing the filtration method ; i.e., we must know the filtration mechanism of a particle through a cylindrical capillary. The point of the question is that the diameter of the capillary is larger than that of the particle. This question can be expressed another way ; why is it possible to filter such a semimacroscopic system as latex when the diameter of the pore is larger than that of the particle ?

It is an old problem to study the filtration mechanism itself. Ever since Ruth established the theory of the cake formation, ⁽⁵⁾ (layer formation of suspended

material on a filter base), it appears that the essence of filtration problem is a matter of solving a flow rate of the suspending fluid through the entangled capillary network in the cake. In our case, to the contrary, the cake formation can be neglected since the total particle number in the suspension is low enough that there will be only 10 particle layers left upon the membrane filter after the filtration. As a matter of fact, high fraction of the particles enter into the filtrate. Here in this work, we study the throughput of particles through the straight pores on the filter base, and this is a problem of hydrodynamics of low Reynolds number.⁽⁶⁾

§ 2. Experimental Conditions

Polystyrene latex suspensions are obtained from Dow Chemical Co., and diameters of which are 910, 1760, 2340, and 2550 Å, with $\pm 1\%$ standard deviation. Samples are diluted by deionized water down to 1.0×10^{-2} wt%, which correspond to particle densities of 2.41×10^{11} , 3.34×10^{10} , 1.42×10^{10} , and $1.10 \times 10^{10} \text{cm}^{-3}$, respectively. Ten milli-litre of each sample is filtered by using polycarbonate membrane filters of 4.5cm diameter of $10 \mu\text{m}$ thick. The membrane filter, supplied by Nuclepore Corporation, has well defined holes of 4000 Å diameter, and the area which opened by the holes is 15% of the surface. The actual shape of the hole is a cylindrical capillary of $\lambda = a/r_o = 1/2$ and $L/2a = 50$, typically, where a is the particle radius, r_o is the radius of the capillary and L is the capillary length; it is $10 \mu\text{m}$ for the present case. The constant pressure is applied across the membrane filter by using a suction pump. The velocity of the suspension through the capillary is controlled by changing the suction rate of the pump, and the mean fluid velocity in the capillary is estimated by measuring the time interval necessary for filtration of the 10 ml sample; typical fluid velocity is about $4.2 \times 10^{-2} \text{cm/sec}$. Estimated Reynolds number (R_e) at this fluid velocity is 1.7×10^{-6} , and the low Reynolds number condition is well satisfied; $D = 4000 \text{ Å}$, $V_m = 4.2 \times 10^{-2} \text{cm/sec}$, and $\mu = 1.002 \text{ cp}$ for $R_e = \rho V_m D / \mu$, where ρ is the density of fluid, V_m is the maximum velocity, D is the capillary diameter and μ is the viscosity.

§ 3. Theoretical Basis for Data Analysis

Theoretical basis for the analysis are obtained along the line shown in a Brenner's paper.⁽⁷⁾ Starting from eq.(2.38) in ref.(7), the flux density vector \mathbf{J} is expressed as,

$$\mathbf{J} = U C - \exp(-E) \mathcal{D} \cdot \nabla (C \exp E) , \quad \dots\dots(1)$$

where U is the velocity vector of neutrally buoyant sphere center ($\rho=1.05$ for polystyrene), C is the particle density function, E is the potential energy function due to an external force which acts on the particle, and \mathcal{D} is the diffusivity dyadic. The first term of eq.(1) represents the convective particle flux and the second term is for diffusion and external force.

In ref. (7), Brenner showed examples of handling the problem when there is no convective transport, and in our case for filtration problem, the convection term must be carried on. Equation(1) is solved by using the continuity equation,

$$\text{div } \mathbf{J} = 0. \quad \dots\dots(2)$$

Substituting eq. (1) into eq. (2), we obtain a differential equation for $C(r, z)$, written in a cylindrical coordinate. It is easily solved for $C(r, z)$ as shown in Appendix, and the result is as following ;

$$\overline{C}_f(z) = \overline{C}_0 \left(1 - \frac{a}{r_0}\right)^2 \left\{ 1 + \left(1 - \frac{\overline{C}_1}{\overline{C}_0}\right) \left(\frac{2V_m}{D_{II}} \cdot z\right) \right\} \quad \dots\dots(3)$$

The eq. (3) is the same to eq(A-16), as shown in the Appendix, and the meaning of the notations are as following ;

$\overline{C}_f(z)$: area-averaged particle concentration within the capillary.

$\overline{C}_0 = C(r, 0)$: particle concentration at the entrance of the capillary.

$\overline{C}_1 = C(r, -\infty)$: particle concentration in the reservoir

r_0 : radius of the capillary.

a : radius of the latex particle.

V_m : maximum fluid velocity at the center of the capillary. (We assumed the Hagen-Poiseuille flow for the fluid, and further assumed that the particle velocity is equal to the fluid velocity within the capillary. This assumption will be well justified, since the particle is well buoyant and the fluid velocity is very slow: Low Reynolds number.)

$D_{||}$: a component of the diffusivity dyadic. This component represents the parallel component to the capillary axis, and it is assumed to be a constant.

z : coordinate of the capillary axis. We take a cylindrical coordinate system.

If we simplify, in the eq.(3), that $\overline{C}_0 \doteq \overline{C}_1$, then we have,

$$\overline{C}_r(z) = \overline{C}_0 \left(1 - \frac{a}{r_0}\right)^2 \quad \dots\dots(4)$$

Physically speaking, this effect originates from the geometrical factor which limits the suspending sphere to enter into the capillary. This effect will be easily understood by the following modified form;

$$\overline{C}_r(z) = \frac{\overline{C}_0 \pi (r_0 - a)^2}{\pi r_0^2} \quad \dots\dots(5)$$

As mentioned above, there is a restriction for a buoyant particle to get through the capillary by the geometrical factor as shown in eq. (5). Meanwhile, there is no restriction for the host fluid to get into the capillary. This is the physical reason that the membrane filter can filtrate the suspension, even though the diameter of the capillary is larger than that of the sphere.

§ 4. Analysis of the Experimental Data and Discussions

Optical turbidity (T_{obs}) is defined as,

$$T_{obs} = -\log\left(\frac{I_{obs}}{I_0}\right), \quad \dots\dots(6)$$

where I_{obs} is the light intensity which is transmitted through the optical sample cell, and I_0 is the initial light intensity. If the "narrow beam condition" is well satisfied, as shown in Fig.1, i.e., any light will be lost out of the beam once it is

scattered, then the light intensity I_{obs} is represented by,

$$I_{obs} = I_0 \exp(-N\sigma x), \quad \dots\dots(7)$$

where N is the density of the light scattering particle, σ is its cross section, and x is the optical path length through the cell. In the present case, N , the particle density, is represented by $\overline{C}_f(z)$ in the eq.(3).

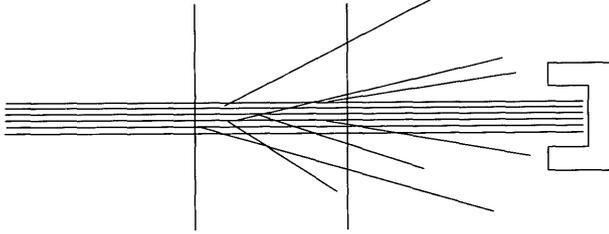


Fig. 1

Fig. 1 The “Narrow Beam” condition for the optical experiment. Any light quanta which were scattered by a latex particle will be lost out of the beam, and contributes to the reduction of the light intensity through the cell.

The light intensity, which is measured before filtration, is represented by,

$$I_{ref} = I_0 \exp(-\overline{C}_1 \sigma x), \quad \dots\dots(8)$$

and the turbidity for the reference sample becomes,

$$T_{ref} = -\log\left(\frac{I_{ref}}{I_0}\right) = \overline{C}_1 \sigma x. \quad \dots\dots(9)$$

Therefore, the “relative turbidity”, which is defined by T_{obs}/T_{ref} becomes,

$$\frac{T_{obs}}{T_{ref}} = \frac{\overline{C}_f}{\overline{C}_1} \quad \dots\dots(10)$$

This is expressed explicitly,

$$\frac{\overline{C}_f}{\overline{C}_1} = \left(\frac{\overline{C}_0}{\overline{C}_1}\right) \left(1 - \frac{a}{r_0}\right)^2 \left\{1 + \left(1 - \frac{\overline{C}_1}{\overline{C}_0}\right) \left(\frac{2V_m \cdot Z}{D_{II}}\right)\right\} \quad \dots\dots(11)$$

Figure 2 shows the particle size dependence of the relative turbidity ; line A is the experimental result shown in Fig. 6 in ref.(4), and curve(a) is the plot of eq. (4), where $r_0 = 2000\text{\AA}$.

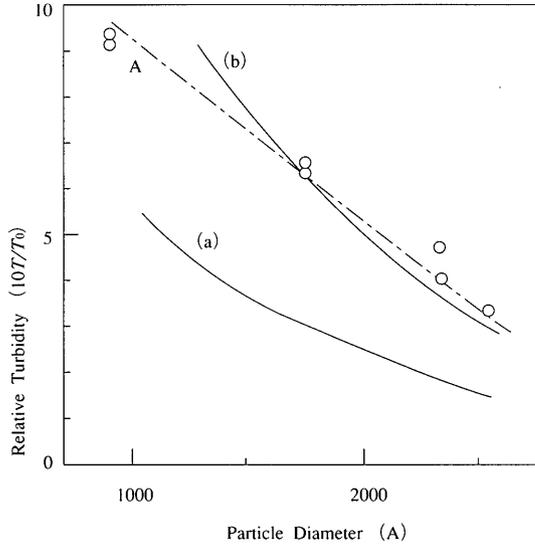


Fig. 2

Fig. 2 Particle size dependence of the relative turbidity ($10T_{obs}/T_{ref}$); open circles are the experimental data shown in Fig. 6 of ref. 4. Curve (a) is calculated by using eq. (4), where $r_o=2000$ Å is used for pore radius. Curve (b) is the normalized result of curve (a) to the experimental datum at $d=1760$ Å. The normalization factor of curve (a) to (b), about 2, is justified by the velocity dependence of the relative turbidity, as shown in Fig. 3.

We obtain curve (b) by normalizing the curve (a) at 1760 Å, and it fits well to the experimental data from $2a=1500$ Å to 2500 Å. Justification for the normalization is that eq. (4) is the result for $V_m=0$, and the experimental data shown by the line A in Fig. 2 is taken with a constant velocity of 3.4×10^{-2} cm/sec.

As a matter of fact, relative turbidity of filtrate depends on the fluid velocity as shown in Fig. 3. If we pick up the datum at $V_m=1.7 \times 10^{-2}$ cm/sec in Fig. 3 as an approximation for the $V_m=0$ datum, then the value at $V_m=3.4 \times 10^{-2}$ cm/sec is higher than that of at $V_m=1.7 \times 10^{-2}$ cm/sec by about a factor of 2. This is the same magnitude used for the normalization of the curve (a) to curve (b) in the Fig. 2.

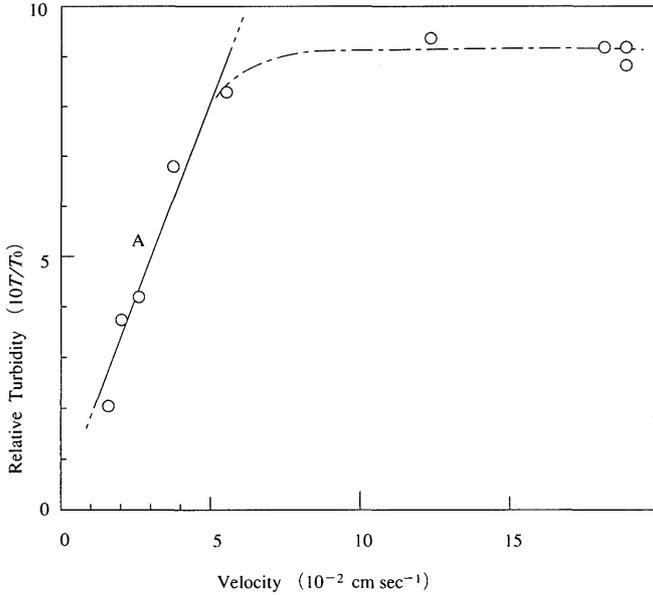


Fig. 3

Fig. 3 Velocity dependence of the relative turbidity ; open circles are the experimental data shown in Fig. 8 in ref. 4. The straight line A represents the linear part of V_m in eq. (3). The broken line shows the saturation effect of the relative turbidity, *i.e.*, when the velocity becomes higher and higher, all the particles will go through the pores. Experimentally, it is 90%

Linear increase of the relative turbidity as a function of the fluid velocity, as shown in Fig. 3, is well explained by eq.(3). It should start from the value given by $(1-a/r_0)^2$, which is 0.172 for $2a=2340 \text{ \AA}$ for example, and should go up to $T_{obs}/T_{ref}=1.0$; experimentally this is 0.9. Beyond that velocity higher, T_{obs}/T_{ref} must show level off and should be independent to the fluid velocity ; which is true as shown by the experimental data in Fig. 3.

Difusivity value for D_l is estimated by the gradient of the straight line A in Fig.

3, and it turned out that $D_{II}=2.1\times 10^{-5}\text{cm}^2/\text{sec}$, which sounds like a reasonable value.

§ 5. Conclusions

- (1) Theoretical base for the turbidity measurements is established by employing the hydrodynamics of low Reynolds number. It turned out that the turbidity method is quite useful, when the parameter a/r_0 and the particle density are properly chosen, for measuring the latex particle size in situ.
- (2) Dominating factor of the filtration mechanism of semimacroscopic suspension, such as latex, is the geometric factor. This factor limits a sphere to flow through a capillary when the pore size is comparable to that of the sphere.
- (3) The potential effect does not show up in the simplified approximation formula.
- (4) Diffusivity of latex particles of 2340 Å diameter is estimated as $2.1\times 10^{-5}\text{cm}^2/\text{sec}$, at $1.4\times 10^{10}/\text{cm}^3$ particle concentration.

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Appendix

We consider to obtain an analytical formula, to calculate the latex particle density in a filtrate.(c.f. Fig. A-1)

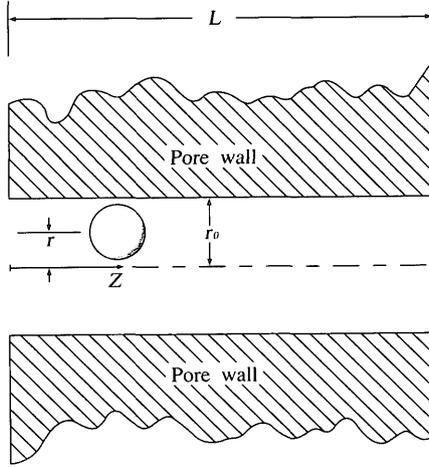


Fig. A-1

Fig. A-1 Schematic layout of a capillary and a sphere system. The diameters of the system are the same order of magnitude.

We start from the flux density vector, which is given by eq.(2.38)in ref.(7), i.e. ;

$$\mathbf{J} = UC - \exp(-E) \mathbf{D} \cdot \nabla (C \exp E), \quad \dots\dots (A-1)$$

and the continuity condition,

$$\text{div } \mathbf{J} = 0, \quad \dots\dots (A-2)$$

where,

$$\text{div } \mathbf{J} = \frac{\partial J_r}{\partial r} + \frac{J_r}{r} + \frac{\partial J_\varphi}{r \partial \varphi} + \frac{\partial J_z}{\partial z}, \quad \dots\dots (A-3)$$

$$\mathbf{U} = U_r \mathbf{i}_r + U_\varphi \mathbf{i}_\varphi + U_z \mathbf{i}_z, \quad \dots\dots (A-4)$$

$$\mathbf{D} = \mathbf{i}_x \mathbf{i}_x D_\perp(r) + \mathbf{i}_\varphi \mathbf{i}_\varphi D_\varphi(r) + \mathbf{i}_z \mathbf{i}_z D_\parallel(r) \quad \dots\dots (A-5)$$

∇ is the gradient operator in the cylindrical coordinate.

Assuming that, $\{U_r = U_\varphi = 0, D_\varphi = D_\perp = 0\}$,

eq. (A-1) reduces to as following ;

$$\begin{aligned}
\mathbf{J} &= U_z \mathbf{i}_z C(r, z) - \exp(-E(r)) (\mathbf{i}_z \mathbf{i}_z D_{II}(r)) \cdot \\
&\quad \left(\mathbf{i}_r \frac{\partial}{\partial r} + \mathbf{i}_z \frac{\partial}{\partial z} \right) (C(r, z) \exp E(r)), \\
&= U_z \mathbf{i}_z C(r, z) - \exp(-E(r)) \\
&\quad \left(\mathbf{i}_z D_{II}(r) \frac{\partial}{\partial z} C(r, z) \cdot \exp E(r) \right). \quad \dots\dots (A-6)
\end{aligned}$$

Therefore,

$$\operatorname{div} \mathbf{J} = -\frac{\partial}{\partial z} \left\{ U_z C(r, z) - D_{II}(r) \frac{\partial}{\partial z} C(r, z) \right\} = 0 \quad \dots\dots (A-7)$$

Assuming further, $\{U_z(r, z) = U(r)\}$, we obtain.

$$\frac{\partial}{\partial z} C(r, z) - \frac{U(r) C(r, z)}{D_{II}(r)} = -\frac{C_0(r)}{D_{II}(r)} \quad \dots\dots (A-8)$$

where $C_0(r)$ is an arbitrary function of r . Equation (A-8) is easily solved for z , and the result is.

$$C(r, z) = C_1(r) \exp \left\{ \frac{U(r)z}{D_{II}(r)} \right\} - \frac{C_0(r)}{U(r)} \quad \dots\dots (A-9)$$

where $C_1(r)$ is again an arbitrary function of r . We consider the boundary conditions as following ;

at $z = 0$, (at the entrance of a pore), we put,

$$C(r, 0) = \bar{C}_0 = C_1(r) - \frac{C_0(r)}{U(r)} \quad \dots\dots (A-10)$$

at $z = -\infty$, (at the reservoir), we put,

$$C(r, -\infty) = \bar{C}_1 = -\frac{C_0(r)}{U(r)} \quad \dots\dots (A-11)$$

therefore, $C_1(r) = \bar{C}_0 - \bar{C}_1$. \dots\dots (A-12)

We obtain,

$$C(r, z) = (\bar{C}_0 - \bar{C}_1) \exp \left\{ \frac{U(r)z}{D_{II}(r)} \right\} + \bar{C}_1 \quad \dots\dots (A-13)$$

We consider, nextly, the "Area-averaged concentration" of the particles, which is defined by as follows ;

$$\bar{C}_A(z) = \left(\frac{1}{\pi r_0^2} \right) \int_0^{r_0-a} C(r, z) 2\pi r \cdot dr \quad \dots\dots (A-14)$$

where the upper limit for the integration, $r_0 - a$, is due to the assumption of hard

-wall potential, which prohibits the sphere center to get closer to the wall than $r_o - a$ position.

By assuming, $\{D_{II}(r) = D_{II}$, constant, and $U(r) = 2V_m\{1 - (r/r_o)^2\}$, Hagen-Poiseuille flow, and \bar{C}_0, \bar{C}_1 ; constant $\}$,

we obtain, after a straight forward calculation,

$$\bar{C}_{\mathcal{A}}(z) = \left(\frac{1}{\pi r_o^2}\right) \{(\bar{C}_0 - \bar{C}_1) \exp\left(\frac{2V_m z}{D_{II}}\right) (-1) \pi r_o^2 D_{II} \{ \exp\left(\left(\frac{-1}{D_{II}}\right) \left(1 - \frac{a}{r_o}\right)^2\right) - 1 \} + \bar{C}_1 \pi (r_o - a)^2 \} \quad \dots (A-15)$$

After expanding the two exponential functions into the power series of the argument, and taking only the first term, we obtain, finally,

$$\bar{C}_{\mathcal{A}}(z) = \bar{C}_0 \left(1 - \frac{a}{r_o}\right)^2 \left\{ 1 + \left(1 - \frac{\bar{C}_1}{\bar{C}_0}\right) \left(\frac{2V_m \cdot z}{D_{II}}\right) \right\} \quad \dots (A-16)$$

which is shown as eq.(3), in the text.

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