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# Evaluation of the Uncertainties Caused by the Forward Scattering in Turbidity Measurement of the Coagulation Rate

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The forward scattering light (FSL) received by the detector can cause uncertainties in turbidity measurement of the coagulation rate of colloidal dispersion, and this effect becomes more significant for large particles. In this study, the effect of FSL is investigated on the basis of calculations using the *T*-matrix method, an exact technique for the computation of nonspherical scattering. The theoretical formulation and relevant numerical implementation for predicting the contribution of FSL in the turbidity measurement is presented. To quantitatively estimate the degree of the influence of FSL, an influence ratio comparing the contribution of FSL to the pure transmitted light in the turbidity measurement is introduced. The influence ratios evaluated under various parametric conditions and the relevant analyses provide a guideline for properly choosing particle size, measuring wavelength to minimize the effect of FSL in turbidity measurement of coagulation rate.

## I. Introduction

Turbidity measurement is a very useful tool in many types of routine chemical analyses because of its simplicity and easy implementation. As one of its important applications, the coagulation rate of suspensions can be assessed by the turbidity measurement.[1−6] Particularly, when the extinction cross section of doublets formed during aggregation is theoretically achievable, the absolute coagulation rate constants can be quantitatively determined.[2−4]

In previous studies,[4−6] we have shown that the *T*-matrix method[7−10] can be used to accurately calculate the extinction cross section of the doublet without size limitation. We further suggested that to reduce the measurement error, if possible, choosing larger particles would be more preferable.[4] That is because, for small particles, a high number concentration of particles is usually required in order to enhance the signal-to-noise ratio in the measurement. As is well-known, the scattering intensity decreases toward smaller particles approximately as the sixth power of the radius. In this case, dispersions of smaller particles at low number concentration become almost a transparent medium, and therefore, the change in its turbidity becomes very difficult to detect accurately. The turbidity of smaller particles can be increased by increasing the number concentration of particles. However, a high number concentration of particles will make the coagulation happen too quickly, and therefore, the linear portion of the turbidity−time curve becomes very short before it curves. In this case, the measurement usually needs to be done in only several seconds.[11,12] This causes large errors associated with the data fluctuations and the insufficient data collection time. As an effort to overcome the difficulty with small particles, Puertas et al.[3] used the RGD approximation to calculate the total light scattering cross section of the aggregate, taking into account the contributions from pairs of particles with zero, one, and two particles between them, and developed a technique for getting the coagulation rate constant from turbidity measurement by fitting the curve of turbidity change for longer time. In comparison with using smaller particles, proper turbidity can be reached for larger particles without resorting to a high number concentration of particles. Therefore, the linear portion of the turbidity−time curve can last much longer, making more accurate measurement possible. However, it does not mean that the larger the better for particle sizes used in the turbidity measurement. This is because, with the increase of particle size, the forward-scattering light (FSL) intensity increases significantly and detectors always have a certain acceptance angle.[13] In general, acceptance angles for a real turbidity measurement instrument or commercial spectrophotometers are in the range of a few degrees. In this case, some forward-scattered light may fall with the transmitted light onto the light detector to cause an error of the turbidity measurements,[14] and this effect becomes more serious for larger particles. When worrying about FSL effect for larger particles, one may hesitate to use large particles in the turbidity measurements if they lack necessary knowledge about how to reduce and control the FSL effect.

In this paper, we focus on assessing how the errors caused by FSL for the turbidity measurement related to particle size (size parameter) and acceptance angle of detector by calculating the portion of the FSL that falls on the detector in addition to the

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transmitted light in the aggregation process. We further deduce the allowed particle size for a given error tolerance and an acceptance angle of detector and discuss how to properly choose the measuring wavelength to reduce the effect of FSL on the turbidity measurement. In addition, we also discuss how to make a correction on the error caused by the effect of FSL when the geometrical parameters related to the detector, such as the acceptance angle, are available.

## II. Theory

The absolute coagulation rate for colloidal suspension is defined by:

$$\left.\frac{\mathrm{d}N_1}{\mathrm{d}t}\right|_{t=0} = -k_{11}N_1^2 \tag{1}$$

Theoretically, the turbidity $\tau$ is related to the extinction cross sections of dispersed particles, and can be expressed as

$$\tau = N_1C_1 + N_2C_2 + \cdots + N_iC_i + \cdots \tag{2}$$

where $N_i$ and $C_i$ are the number concentration and the extinction cross sections, respectively, for the aggregates of $i$ particles. At the initial stage of aggregation, there exist only single particles and the aggregates formed by two particles. Therefore,

$$\frac{\mathrm{d}\tau}{\mathrm{d}t} = C_1\frac{\mathrm{d}N_1}{\mathrm{d}t} + C_2\frac{\mathrm{d}N_2}{\mathrm{d}t} \tag{3}$$

In combination with eq 1 and noting that $\mathrm{d}N_1/\mathrm{d}t = -2\mathrm{d}N_2/\mathrm{d}t$ at the initial stage of aggregation, eq 3 can be rewritten as

$$\left.\frac{1}{\tau_0}\frac{\mathrm{d}\tau}{\mathrm{d}t}\right|_{t=0} = \frac{1}{N_1C_1}\left(\frac{C_2}{2} - C_1\right)k_{11}N_1^2 = \left(\frac{C_2}{2C_1} - 1\right)k_{11}N_1 \tag{4}$$

where $\tau_0 = N_1C_1|_{t=0}$ is the turbidity of the initial monodispersed colloidal suspension. Therefore, the coagulation rate $k_{11}$ can be determined when the left-hand side of eq 4 and the number concentration $N_1|_{t=0}$ are measured, and the so-called optical factor $F_o = C_2/2C_1 - 1$, which is the key factor for achieving the coagulation rate constant from the turbidity measurement, and has to be theoretically calculated. The $T$-matrix method[7−10] is an exact technique for the computation of nonspherical scattering based on a direct solution of Maxwell's equations, and therefore, it can be used to accurately evaluate the optical factor.[4,5] However, when the detector of turbidimeters or spectrophotometers receives not only the transmitted light, but also a portion of the forward-scattering light, the problem becomes not so straightforward.

In the turbidity measurement, the turbidity $\tau$ is related to the transmission intensity of light as

$$I = I_0 \exp(-\tau L) \tag{5}$$

where $I$ is the transmission intensity of light, $I_0$ is the intensity of the incident light, and $L$ is the length that the light passed through the colloidal suspension. Upon measuring the transmission rate $I/I_0$ and the length $L$, the turbidity $\tau$ can be measured. The left-hand side of eq 4 can then be evaluated after the turbidities at different time are measured in the initial stage of aggregation.

Equation 5 works only for the ideal condition that no forward light scattering would be received by the detector. When the detector accepts the light intensity $I$ containing some contribution from the forward scattering light (the so-called apparent transmitted light intensity), eq 5 should be modified. To do so, similarly to ref 14, eq 5 can be rewritten as

$$I = I_0 \exp(-\tau RL) \tag{6}$$

where $R$ is the factor for correction to $\tau$. In eq 6, $\tau$ is also the real turbidity that can be expressed by eq 2, while $\tau R$ is the actually measured turbidity that contains the contribution of FSL.

In this case, the left-hand side of eq 4 can be modified to

$$\left.\frac{1}{\tau_0R_0}\frac{\mathrm{d}(\tau R)}{\mathrm{d}t}\right|_{t=0} = \left.\frac{1}{\tau_0}\frac{\mathrm{d}\tau}{\mathrm{d}t}\right|_{t=0} + \left.\frac{1}{R_0}\frac{\mathrm{d}R}{\mathrm{d}t}\right|_{t=0} \tag{7}$$

$\mathrm{d}r/\mathrm{d}t$ can be written as

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{\mathrm{d}R}{\mathrm{d}N_1}\frac{\mathrm{d}N_1}{\mathrm{d}t} = -\frac{\mathrm{d}R}{\mathrm{d}N_1}k_{11}N_1^2 \tag{8}$$

Combining eqs 7, 8, and 4, we can get

$$\left.\frac{1}{\tau_0R_0}\frac{\mathrm{d}(\tau R)}{\mathrm{d}t}\right|_{t=0} = \left[\left(\frac{C_2}{2C_1} - 1\right) - \left.\frac{N_1}{R_0}\frac{\mathrm{d}R}{\mathrm{d}N_1}\right|_{t=0}\right]k_{11}N_1 \tag{9}$$

This equation is quite similar as eq 4 except subtracting a term $(N_1/R_0)(\mathrm{d}R/\mathrm{d}N_1)|_{t=0}$ from the optical factor. The difference is that the optical factor in eq 4 needs a correction as shown in eq 9 after taking into account FSL. In order to assess the degree of the influence degree of FSL, the magnitude of the correction factor $F_c = (N_1/R_0)(\mathrm{d}R/\mathrm{d}N_1)|_{t=0}$ needs to be compared with the value of the optical factor $F_o$.

Wind and Szymanski[14] have deduced the expression of $R$, which can be written as

$$R = -\frac{1}{\tau L}\ln(I_r + \exp(-\tau L)) \tag{10}$$

where $I_r = I_s/I_0$ ($I_s$ is the FSL that can be received by the detector). $I_r$ was deduced by ref 14 to be

$$I_r = \frac{\tau_{sca}}{2}\int_{z=0}^{L}\int_{\theta=0}^{\psi(z)} p(\theta)\sin\theta \exp\left(-\tau_{ext}\frac{L}{\cos\theta}\right) \exp\left(-\tau_{ext}z\left(1 - \frac{1}{\cos\theta}\right)\right)\mathrm{d}\theta\,\mathrm{d}z \tag{11}$$

where $\tau_{sca}$ and $\tau_{ext}$ can be expressed as

$$\tau_{sca} = \sum N_iC_{sca,i} \tag{12}$$

$$\tau_{ext} = \sum N_iC_{ext,i} \tag{13}$$

where $C_{sca,i}$ and $C_{ext,i}$ are the scattering and extinction cross sections of aggregates of $i$ single particles. Two primary particles (singlets) aggregating to form one doublet is the only process involved at the very beginning of aggregation. Therefore, the values for $i$ in eqs 12 and 13 that need to be considered are only 1 and 2. $p(\theta)$ in eq 11 is equal to $4\pi\tau(\theta)/\tau_{sca}$, where $\tau(\theta)$ is the differential scattering efficiency at angle $\theta$.[14]

Mie theory is applicable to precise evaluation of the distribution of scattering intensity of a spherical particle (or singlet) to get

the values of $p(\theta)$ for a monodispersed colloidal suspension. However, in order to calculate the correction factor $F_c$, the distribution of scattering intensity from doublets should also be calculated, because the number concentration of doublets will increase with the decrease of $N_1$ during aggregation. Mie theory cannot handle the problem dealing with nonspherical particles. In this study, we use the $T$-matrix method to calculate the distribution of scattering of both single and doublet as well as the values of $p(\theta)$ for different $N_1$ and $N_2$.

In the $T$-matrix method,[4,5,7−10] both incident and scattered electric fields are expanded in a series of vector spherical wave functions as follows:

$$\mathbf{E}^{\mathrm{inc}}(\mathbf{r}) = \sum_{n=1}^{\infty}\sum_{m=-n}^{n}[a_{mn}Rg\mathbf{M}_{mn}(kr) + b_{mn}Rg\mathbf{N}_{mn}(kr)] \quad (14)$$

$$\mathbf{E}^{\mathrm{sca}}(\mathbf{r}) = \sum_{n=1}^{\infty}\sum_{m=-n}^{n}[p_{mn}\mathbf{M}_{mn}(kr) + q_{mn}\mathbf{N}_{mn}(kr)] \quad (15)$$

where $k = 2\pi/\lambda$, and $\lambda$ is the wavelength in the surrounding medium. The harmonics $Rg\mathbf{M}_{\mathrm{mn}}$ and $Rg\mathbf{N}_{\mathrm{mn}}$ have a Bessel-function radial dependence and are regular (finite) at the origin, whereas the functions $\mathbf{M}_{\mathrm{mn}}$ and $\mathbf{N}_{\mathrm{mn}}$ have a Hankel-function radial dependence and vanish at infinity. Due to the linearity of Maxwell's equations, the scattered field coefficients $\mathbf{p} = [p_{mn}, q_{mn}]$ are related to the incident field coefficients $\mathbf{a} = [a_{mn}, b_{mn}]$ by means of the so-called transition matrix (or $T$ matrix)

$$p_{mn} = \sum_{n'=1}^{\infty}\sum_{m'=-n'}^{n'}[T^{11}_{mnm'n'}a_{m'n'} + T^{12}_{mnm'n'}b_{m'n'}] \quad (16)$$

$$q_{mn} = \sum_{n'=1}^{\infty}\sum_{m'=-n'}^{n'}[T^{21}_{mnm'n'}a_{m'n'} + T^{22}_{mnm'n'}b_{m'n'}] \quad (17)$$

In compact matrix notation, eqs 16 and 17 can be rewritten as

$$\begin{bmatrix}\mathbf{p}\\ \mathbf{q}\end{bmatrix} = \mathbf{T}\begin{bmatrix}\mathbf{a}\\ \mathbf{b}\end{bmatrix} = \begin{bmatrix}\mathbf{T}^{11} & \mathbf{T}^{12}\\ \mathbf{T}^{21} & \mathbf{T}^{22}\end{bmatrix}\begin{bmatrix}\mathbf{a}\\ \mathbf{b}\end{bmatrix} \quad (18)$$

The $T$ matrix for a cluster consisting of $i$ spheres ($i = 1$ or 2 in this study) can be computed. The explicit expressions and calculations for the $T$ matrix can be found in ref 7. From the $T$ matrix, we can then calculate the extinction cross sections and the Stokes scattering matrix,[7] in which the scattering intensity at different scattering angle can be obtained. Thus, the values of $p(\theta)$ for different $N_1$ and $N_2$ can be calculated.

The scheme visualizing some geometric parameters used in eq 11 is shown in Figure.1. For the measurement of coagulation rate of colloidal suspension, the sample is at some distance away from the detector. Therefore, some parameters are not the same as in ref 14, where an aerosol system was discussed.

In Figure.1, the distance from $z = 0$ to $z = L$ is the optical path length of the sample cell of colloidal suspension. Before the transmitted and scattered light reaches the detector, they will be refracted at the interface between the wall of the sample cell and air or liquid phase so that the incident angle in the suspension is not the same as in the air, as is shown in Figure 1. Here, the interface at $z = L$ is considered to be between colloidal suspension and the air, and the refraction at the interface of glass wall of the sample cell is ignored. This simplification is appropriate because the refraction at two parallel glass interfaces has no influence on the light beam direction, and the thin glass wall could make little deviation of the beam.

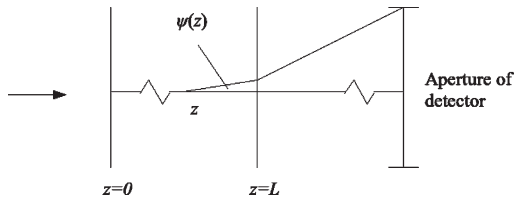


**Figure 1.** Scheme visualizing some geometric parameters in eq 11 for turbidity measurement.

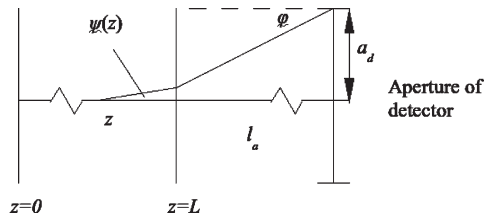


**Figure 2.** Schematic diagram for open detector system.

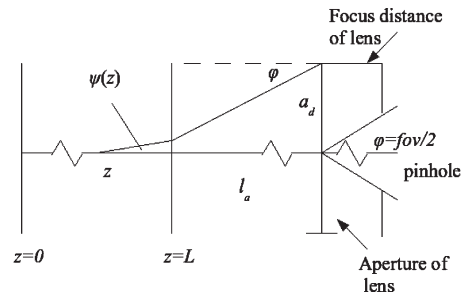


**Figure 3.** Schematic diagram for lp detector system.

As shown in Figure.1, suppose $\psi(z)$ is the largest angle (in the colloidal suspension) of forward scattering light from point $z$ that can be received by the detector. Then, the integration range of the polar angle at the point $z$ in eq 11 is from 0 to $\psi(z)$.

As introduced in ref 14, there are two kinds of configurations for the detector: "open detector system" and "lp detector system", which can be schematically shown in Figures 2 and 3, respectively. Similar to Figure 1, $z = 0$ and $z = L$ represent the positions of two walls of the sample cell, and the refraction of light at $z = L$ is considered.

For the two different configurations of detectors, the determination of $\psi(z)$ is a little different. As shown in Figure.2, geometrically we can get the formula

$$(L - z)\tan\psi(z) = a_d - l_a\tan\varphi \quad (19)$$

For commonly used spectroscopy, the angle $\psi(z)$ is small, so we can use the approximation that $\sin\psi(z) = \tan\psi(z) = \psi(z)$. This approximation does not cause much error even though the angle is exaggerated as larger as 15° (about 0.26 rad), which should be much larger than the common reception angle for a turbidity measurement system discussed in this study. Considering the refraction rule $\varphi = n_w\psi(z)$, we can get

$$\psi(z) = \frac{a_d}{L - z + l_a n_{\mathrm{w}}} \quad (20)$$

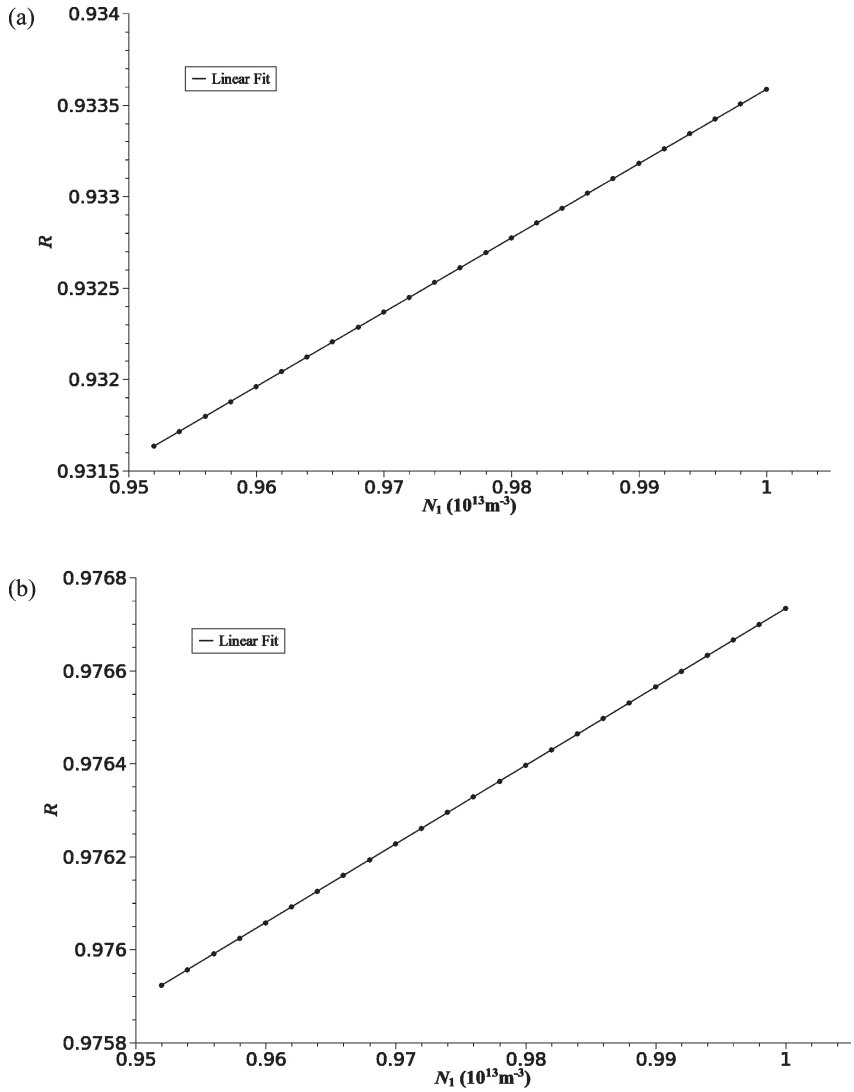


**Figure 4.** Values of $R$ for different $N_1$ during aggregation: (a) open detector system, (b) lp detector system.

where $n_w$ is the refractive index of water, and the refractive index of air is approximated as 1 in this study.

For lp detector configuration as shown in Figure 3, $\psi(z)$ should be a constant value $fov/2n_w$ if $z \geq L + l_d n_w - n_w a_d/(fov/2)$. Otherwise, it is the same as for the open detector system. Here, $fov$ is the aperture angle of the pinhole from the center of lens, as shown in Figure3.

$R$ at different $N_1$ for the above-mentioned two detector configurations is calculated with some typical parameters of $N_1|_{t=0}$, particle diameter $d$, and wavelength of incident light in the air $\lambda$. The results are shown in Figure 4. We can see that the $R - N_1$ curve can be linearly fitted perfectly at the initial stage of aggregation, that is, $R$ proportional to $N_1$ at the beginning of aggregation (our calculation showed, however, that this linear relationship no longer exists for a longer period). Therefore, we can even use two different pairs of $N_1$ and $R$ at the beginning of aggregation to get the correction factor $F_c$. By comparing the magnitudes of $F_c$ and corresponding optical factors $F_o$, relative errors caused by FLS in measuring the coagulation rate for different parameters can be evaluated quantitatively.

## III. Results and Discussion

**A. Influence of Particle Size and Incident Wavelength.** As a sample case, the influences of FSL for the colloidal suspension of polystyrene particles dispersed in water in a variety of conditions are calculated in this study. Our previous studies have shown that the refractive indices of the particle and medium should be corrected for different incident wavelengths when solving light scattering problems, especially when particles are large. An inverse method for determining the refractive indices of medium and dispersed particles simultaneously by turbidity measurement has been described.[15] However, for simplicity, the refractive indices of water and polystyrene particle and their values at different incident wavelengths are corrected according to the empirical formula[16−18] used in our previous studies.[4,5]

Figure 5 shows the comparison of optical factors $F_o$ and the correction factors $F_c$ for different-sized particles (diameters $d$ = 0.5, 0.6, 0.8, 1, 1.5, and 2 $\mu$m, respectively) and incident wavelengths. Figure 5a is for the open detector system, while Figure 5b is for the lp (lens and pinhole) detector system.

The relative refractive index $n_p/n_w$ ($n_p$ and $n_w$ are the refractive indices of polystyrene and water, respectively) and the size

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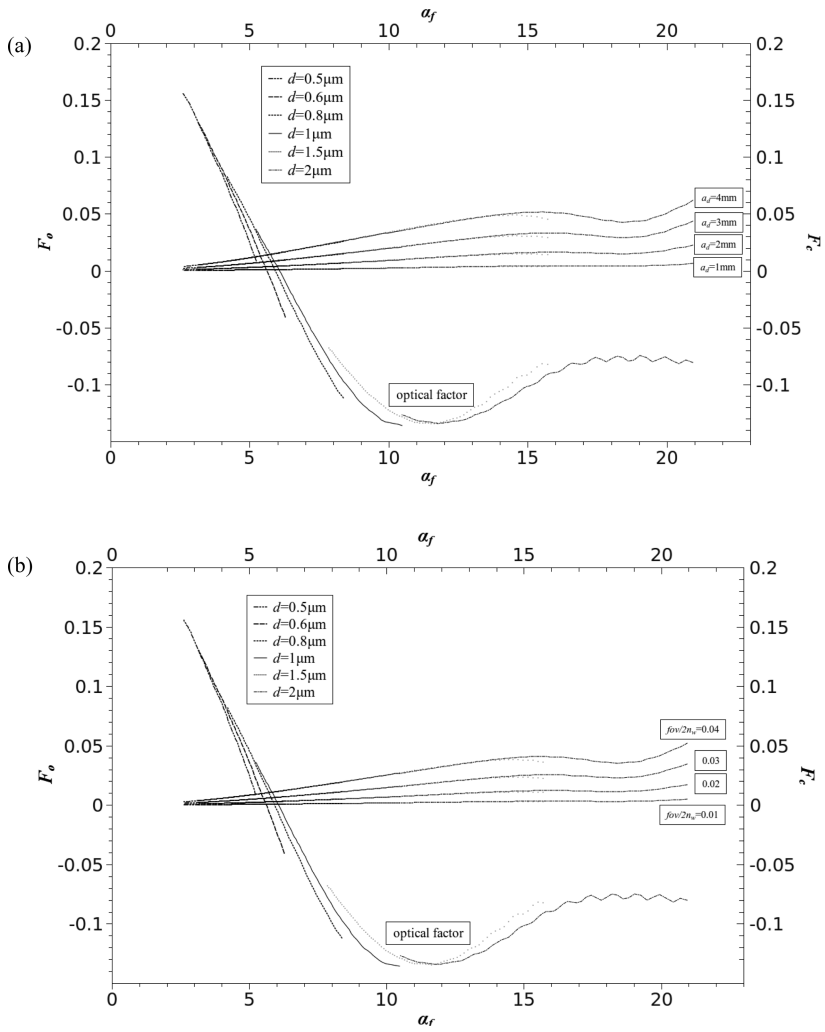


**Figure 5.** Optical factors $F_o$ and the correction factors $F_c$ for different $\alpha_f$. The particle diameters are 0.5, 0.6, 0.8, 1, 1.5, and 2 $\mu$m, respectively. The other parameters are $N_1|_{t=0} = 1 \times 10^{13}$ m$^{-3}$, $L = 1$ cm, $l_a = 6$ cm: (a) open detector system with $a_d = 1$, 2, 3, and 4 mm, respectively; (b) lp detector system with $fov/2n_w = 0.01$, 0.02, 0.03, and 0.04 rad, respectively.

parameter $\pi d/\lambda_w$ ($\lambda_w$ is the wavelength in water) are the two determinant parameters in the calculation of the optical factor. Therefore, the size parameter becomes the only determinant parameter for the optical factor if the refractive indices are independent of wavelength, as was commonly assumed in most literature (where only small particles are discussed). When the particles under consideration are smaller (as the size parameter $\alpha < 3$), the refractive indices have ignorable dependence on the wavelength. Only, in this situation, the same size parameter can give the same optical factor no matter what the particle size is. However, this is not the case when particles are large, as discussed in our previous study,[4] and the refractive indices have to be corrected for different wavelengths, as shown in Figure 5.

In Figure 5, the $x$-axis is $\alpha_f$, which is equal to $\pi d/(0.75\lambda)$, representing the size parameter if the refractive index of water is taken to be a constant 1.33. Figure 5 shows the change tendencies of the $F_o$ and $F_c$ with $\alpha_f$ and these tendencies are similar for different-sized particles. Here, we can see that, after the corrections of the refractive indices at different incident wavelengths are made, the optical factors are actually changing with particle size for a fixed $\alpha_f$.

In Figure 5, the number concentration of the monodispersed particles before aggregation is set to $1 \times 10^{13}$ m$^{-3}$ and $L$ to 1 cm. For the open detector system, the results with $l_a = 6$ cm and the results for radii of aperture of detector $a_d$ of 1, 2, 3, and 4 mm are compared. For lp detector system, $l_a$ satisfies the condition $L + l_a n_w - n_w a_d/(fov/2) \leq 0$ so that $\psi(z)$ is $fov/2n_w$ for $z$ from 0 to $L$. In addition, the results for forward angle in water $fov/2n_w$ of 0.01, 0.02, 0.03, and 0.04 rad are compared. Since commonly used light beam in turbidity measurements are visible, the wavelengths of the incident light in Figure 5 are in the range from 400 nm to 800 nm. We can see that these tendencies for both the open detector system and lp detector system are actually quite similar.

In previous studies,[4] we have pointed out that, at a certain wavelength, the change in turbidity completely loses its sensitivity to the coagulation process (the so-called blind point, where $F_o$ are actually equal to zero), which makes the measurement impossible. Therefore, we should avoid conducting turbidity measurement in the zone near the "blind point", or the so-called "blind zone". Figure 5 clearly shows that, with the increase of $\alpha_f$, the optical factors change from positive values to the negative values, crossing the "blind zone".

On the other hand, $F_c$ is always positive and increases with $\alpha_f$. A positive $F_c$ means that $R$ decreases during aggregation because $N_1$ decreases. From eq 6, it can be expected that smaller $R$ corresponds to more scattering light accepted by the detector. Comparatively, according to the definition of $F_o$, a negative value of $F_o$ means that the extinction cross section for a doublet is smaller than for two single particles. The smaller extinction cross section means that the light being scattered and absorbed is

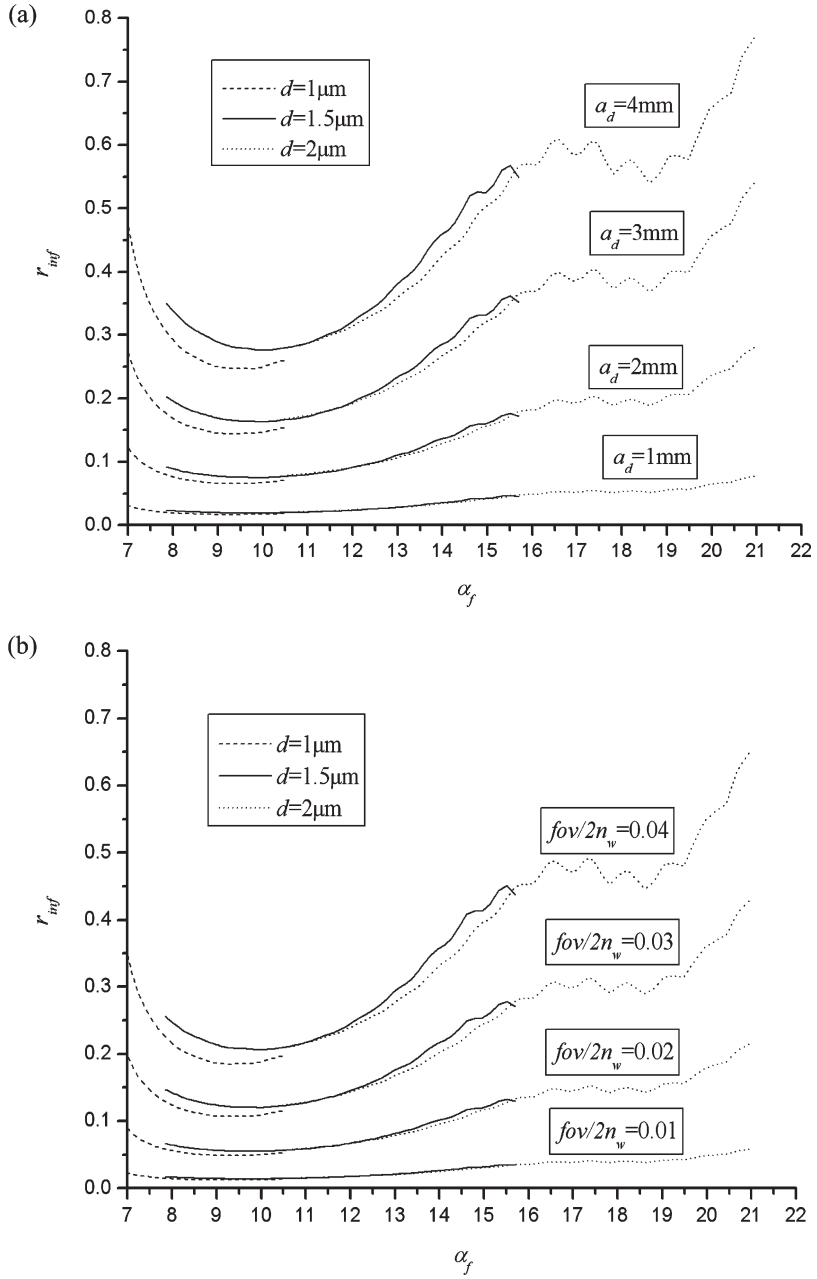


**Figure 6.** Values of $r_{\mathrm{inf}}$ for different $\alpha_f$. The particle diameters are 1, 1.5, and 2 $\mu$m, respectively. The other parameters are $N_1|_{t=0} = 1 \times 10^{13}\ \mathrm{m}^{-3}$, $L = 1$ cm, $l_a = 6$ cm. (a) Open detector system with $a_d = 1$, 2, 3, and 4 mm, respectively. (b) lp detector system with $fov/2n_{\mathrm{w}} = 0.01$, 0.02, 0.03, and 0.04 rad, respectively.

weaker. If there is no absorption, the above result means that the total scattering intensity is smaller for a doublet than that for two single particles.

Combining the above two consequences, it can be inferred that the scattering light distributed more in the low-angle region for a doublet than that for two single particles. For large $\alpha_f$, although the total scattering intensity is smaller, the scattering intensity accepted in the low-angle region is still larger for a doublet, because more scattering light is distributed in low-angle region for doublet. This is the reason why $R$ is positive and the optical factor is negative for large $\alpha_f$.

For the convenience of discussion of the influence of FSL, we define the FSL influence ratio as

$$r_{\mathrm{inf}} = \left| \left( \frac{N_1}{R_0} \frac{\mathrm{d}R}{\mathrm{d}N_1} \right)_{t=0} \Big/ \left( \frac{C_2}{2C_1} - 1 \right) \right| = |F_{\mathrm{c}}/F_{\mathrm{o}}| \qquad (21)$$

which is the absolute value of the ratio of the correction factor to the optical factor. The larger $r_{\mathrm{inf}}$ means that the forward scattering has stronger influence on the turbidity measurement of coagulation rate and causes a larger error for $k_{11}$ evaluated according to eq 4.

The influence ratio $r_{\mathrm{inf}}$ can be reduced by properly choosing measuring parameters to make the magnitude of $F_{\mathrm{c}}$ (the numerator) smaller and the magnitude of $F_{\mathrm{o}}$ (the denominator) larger. Apparently, the "blind zone" (where approximately $4 < \alpha_f < 7$; see Figure 5) should be avoided for turbidity measurements because the optical factor is close to zero there. Therefore, we only need to consider two ranges: either where $\alpha_f < 4$ or where $\alpha_f > 7$. In the first range ($\alpha_f < 4$), the optical factors are positive and degressive function of $\alpha_f$, while the correction factor is positive and increases with $\alpha_f$. Obviously, in this region choosing smaller $\alpha_f$ (namely, smaller particles and larger light wavelengths)

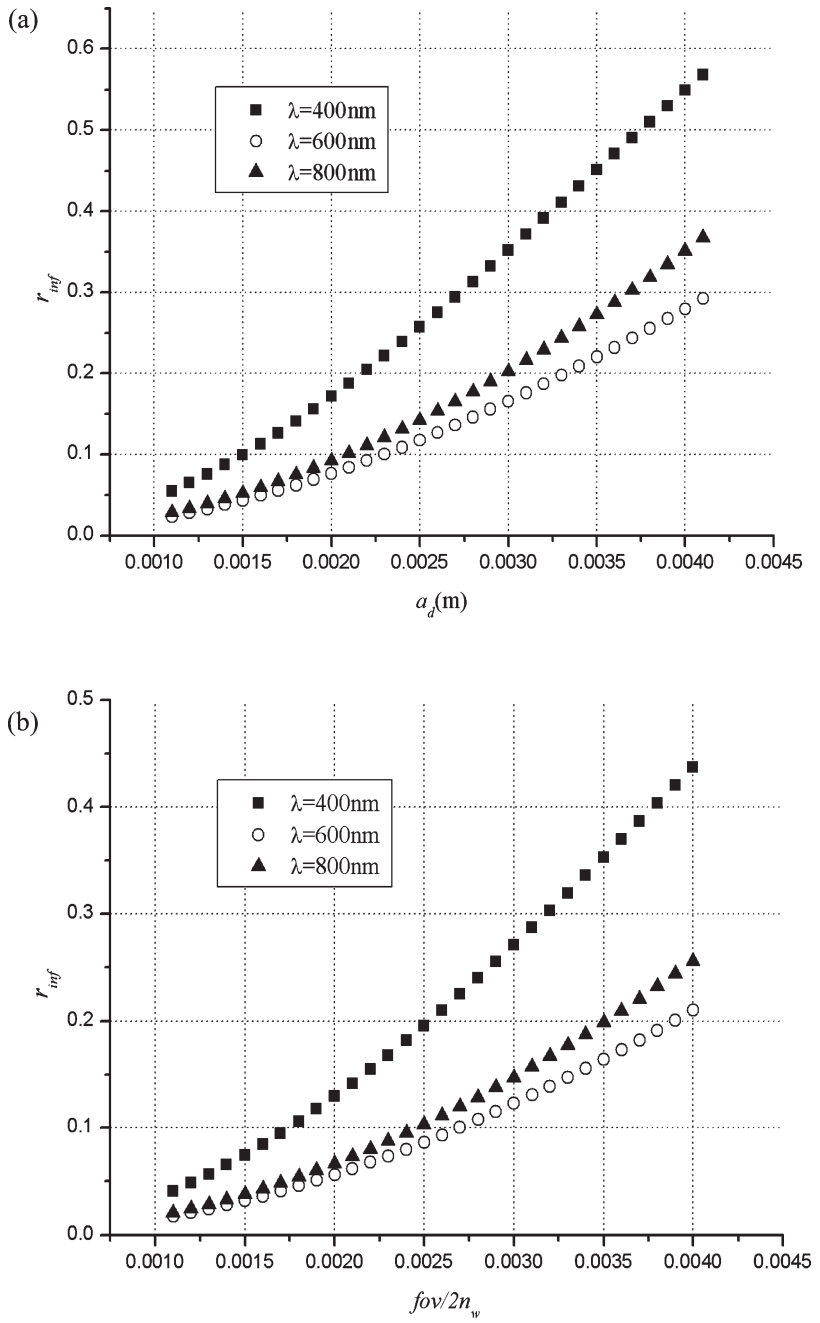


**Figure 7.** Values of $r_{\mathrm{inf}}$ for different $a_d$ or $fov/2n_{\mathrm{w}}$. The particle diameter is 1.5 $\mu$m. $N_1|_{t=0} = 1 \times 10^{13}$ m$^{-3}$, $L = 1$ cm, $l_a = 6$ cm. (a) Open detector system. (b) lp detector system.

for turbidity measurements will be preferable if we do not consider the difficulty in measuring the change in the turbidity as mentioned in the Introduction. In the second region, the problem is not straightforward, because the absolute value of optical factor increases first and then decreases with $\alpha_f$, although the magnitude of the correction factor keeps increasing. How to choose the values of $\alpha_f$ to reduce the influence ratio will be discussed in detail later.

As a predictable results shown in Figure 5, $F_{\mathrm{c}}$ increases with the increase of aperture of detector for open detector configurations (or acceptance angle for lp detector configurations). When $a_d$ = 1 mm or $fov/2n_{\mathrm{w}} = 0.01$ rad, the correction factors are close to 0 in both (the first and second) regions of $\alpha_f$ up to 20, so that the influence of FSL on the measurement of coagulation rate constant is ignorable.

Now, we are focusing on the effect of FSL in the second region in Figure 5. The curves of $r_{\mathrm{inf}}$ vs $\alpha_f$ for "open detector configuration" and "lp detector configuration" are shown in Figure 6. Because there are minimum values for the optical factors around $\alpha_f = 10$, we can expect the minimum for $r_{\mathrm{inf}}$ to appear around $\alpha_f$ a little smaller than 10, considering that $F_{\mathrm{c}}$ is increasing with $\alpha_f$. From Figure 6, we can see that for $a_d = 2$ mm or $fov/2n_{\mathrm{w}} = 0.02$ rad, without considering the correction of FSL effect only when $7.3 < \alpha_f < 12.4$, $r_{\mathrm{inf}}$ is less than 10%, which might be acceptable for some experiments. When $a_d \geq 3$ mm or $fov/2n_{\mathrm{w}} \geq 0.03$ rad, the results of turbidity measurement without necessary correction for FSL effect would be beyond the acceptable range because $r_{\mathrm{inf}} > 10\%$.

**B. Influence of Aperture of Detector or Acceptance angle.** For open detector configuration, the FSL received by

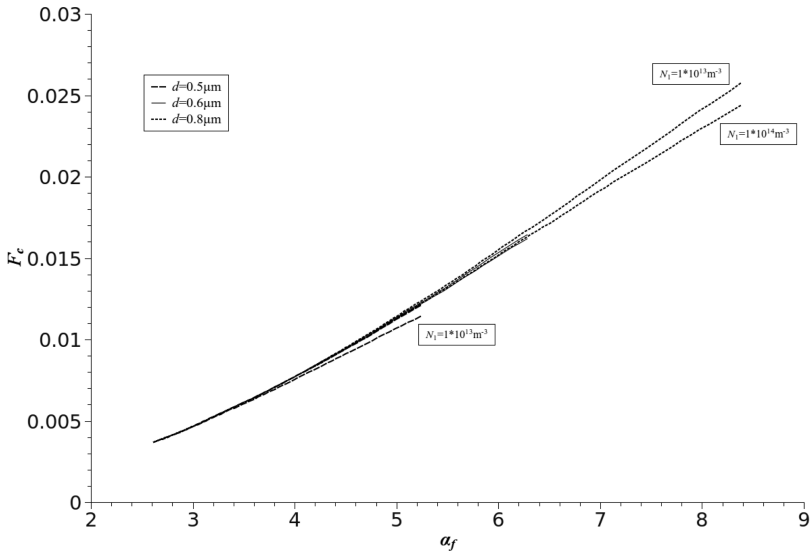


**Figure 8.** Correction factors for different number concentrations for open detector system with $a_d = 4$ mm. The particle diameters are 0.5, 0.6, and 0.8 $\mu$m.

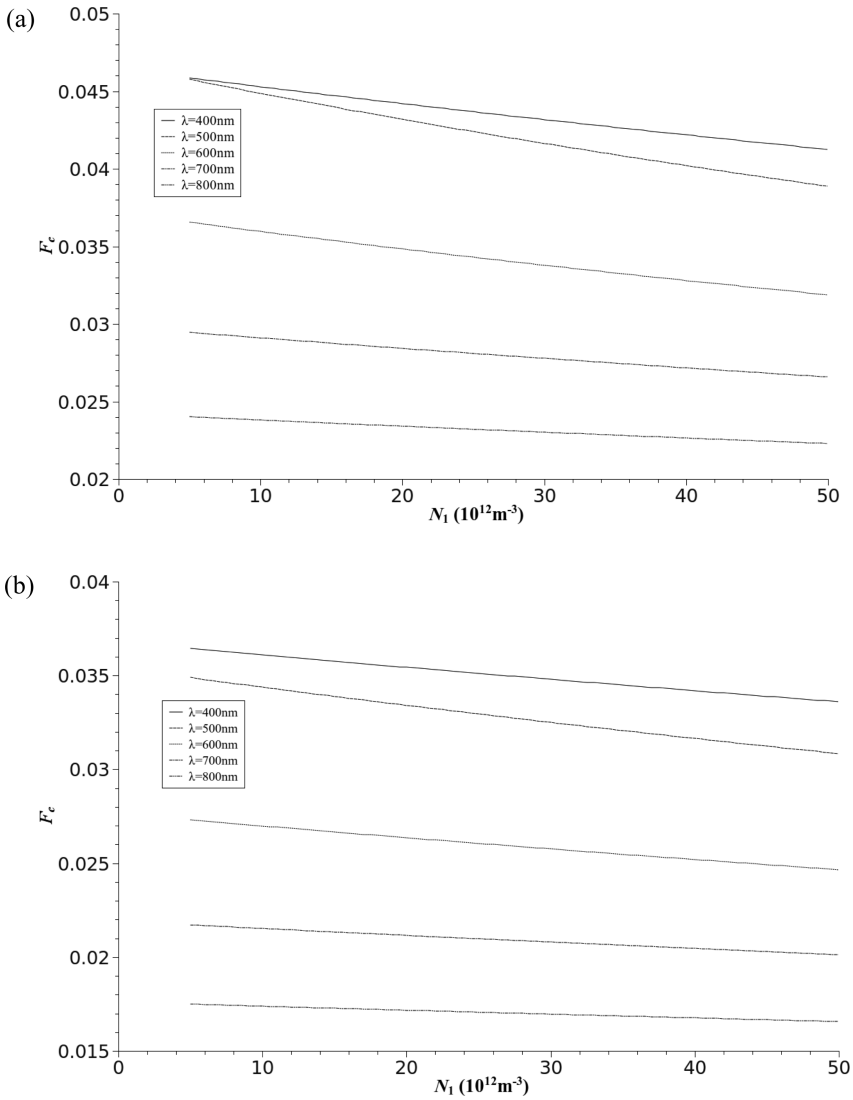


**Figure 9.** Correction factors vs number concentrations for particle diameter 1.5 $\mu$m. The wavelengths are 400, 500, 600, 700, and 800 nm, respectively. (a) Open detector system with $a_d = 4$ mm. (b) lp detector system with $fov/2n_w = 0.04$ rad.

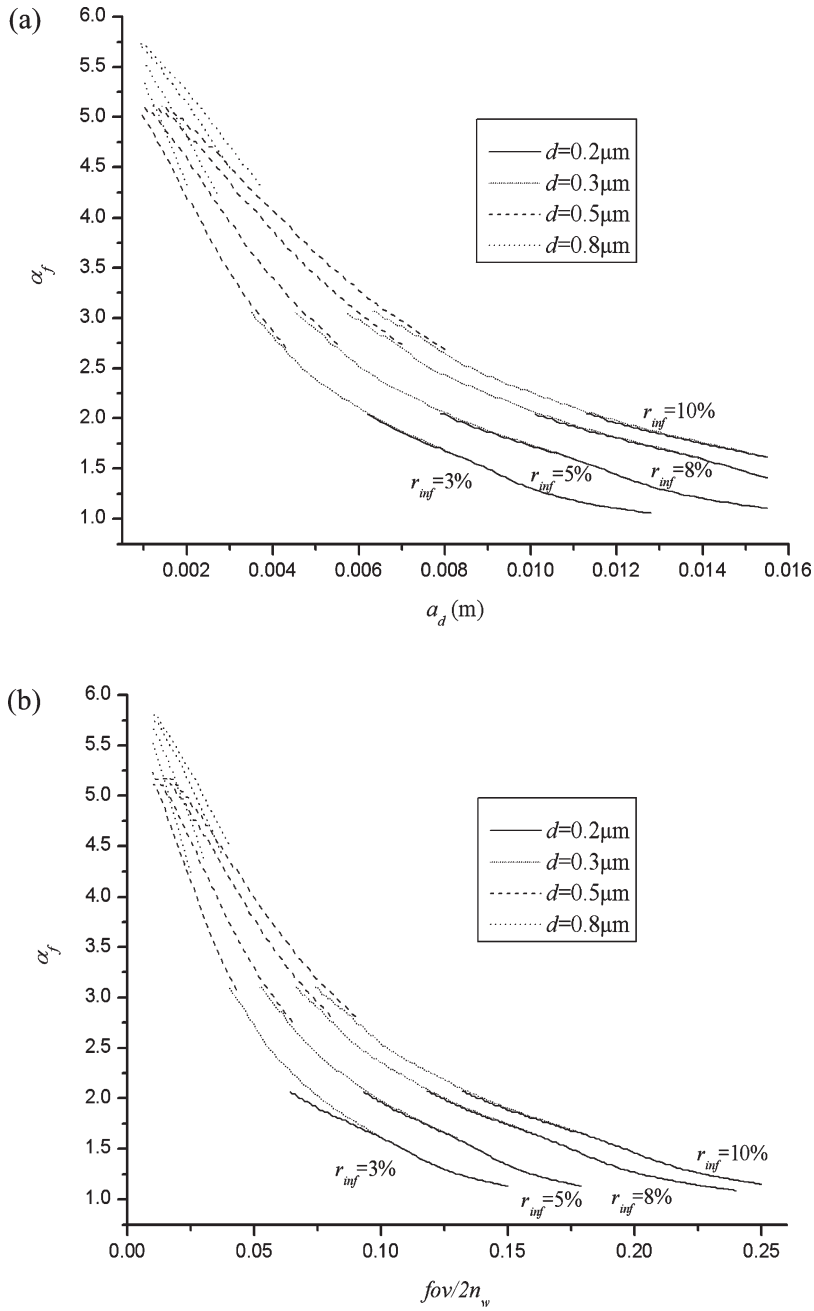


**Figure 10.** Values $\alpha_f$ and $a_d$ or $fov/2n_w$ that make $r_{inf}$ 3%, 5%, 8%, and 10%, respectively. The particle diameters are $d = 0.2$, 0.3, 0.5, and 0.8 $\mu$m. (a) Open detector system. (b) lp detector system.

the detector is related to $a_d$, while for lp detector configuration, it is related to $fov/2n_w$. Figures 5 and 6 clearly show that the correction factors and $r_{inf}$ increases with the increase of forward scattering angle accepted by the detector.

Taking particles of diameter of 1.5 $\mu$m as a sample, Figure 7 shows how $r_{inf}$ changes with $a_d$ at three different measuring wavelengths.

Three curves show that the effect of FLS increases rapidly with the accepted angle ($a_d$ or $fov/2n_w$). For $a_d > 2.3$ mm or $fov/2n_w > 0.027$ rad, all $r_{inf}$ will be larger than 10% for the three wavelengths shown in Figure.7. In these cases, to ensure that the relative error is not too large the correction of effect of FLS has to be made, namely, using eq 9 instead of eq 4 for coagulation rate evaluations. Otherwise, to ensure $r_{inf} < 10\%$ while using eq 4 for three wavelengths, we have to choose measuring parameters to have $a_d < 1.5$ mm or $fov/2n_w < 0.017$ rad.

**C. Influence of Number Concentration.** In previous discussions, the number concentrations for different-sized particles are considered all the same as $1 \times 10^{13}$ m$^{-3}$. At this number concentration, the transmission rate $I/I_0$ may be too large for small particles. To adjust the measured turbidity, we need to change the number concentration. Therefore, it would be necessary to study the influence of number concentration on the effect of FSL. By comparing the results of different number concentrations for $a_d = 4$ mm for open detector configuration as shown in Figure 8, we can see that, when the number concentration increases, the correction factor decreases. However, this decreasing tendency is insignificant. The results for number concentration $1 \times 10^{15}$ m$^{-3}$ for particles of $d = 0.6$ and 0.8 $\mu$m are not presented here, because their transmission rates for such number concentrations are too small (high turbidity), making the turbidity measurement difficult.

Figure 8 shows that the increase of number concentration can help to decrease the correction factor to some extent, but not much. Comparatively, Figure 9 shows the correction factors for $N_1|_{t=0}$ from $0.5 \times 10^{13}$ m$^{-3}$ to $5 \times 10^{13}$ m$^{-3}$ with $a_d = 4$ mm or $fov/2n_w = 0.04$ rad, in which $d = 1.5$ $\mu$m particle is used as an example of large particles in the turbidity measurement. The number concentration, $N_1|_{t=0}$, in this range makes the transmission rate $I/I_0$ in the range from 10% to 90% that is suitable for the turbidity measurement. Combining Figure 8 and Figure 9, we can infer that the number concentration has little influence on the correction factor and $r_{inf}$, although the increase of number concentration can decrease $F_c$ to some extent.

**D. How to Choose $\alpha_f$ in Turbidity Measurement.** When $r_{inf}$ is larger than a certain error tolerance, we have to make the correction for the effect of FSL and use eq 9 instead of eq 4 to evaluate coagulation rate. However, to calculate the correction factor $F_c = (N_1/R_0)(dR/dN_1)|_{t=0}$ we need to know some relevant geometrical parameters that are usually difficult to measure with necessary accuracy. To still use eq 4, we should discuss how to properly choose particle size and incident wavelengths to minimize $r_{inf}$.

Figures 10 and 11 show for different $a_d$ or $fov/2n_w$ how to choose $\alpha_f$ to make $r_{inf}$ smaller than 3%, 5%, 8%, and 10%, respectively. Figure 10 is for the first region (where $F_o > 0$) and particle diameters for the curves are $d = 0.2, 0.3, 0.5$, and $0.8$ $\mu$m, while Figure 11 is for the second region (where $F_o < 0$) and particle diameters for the curves are $d = 1, 1.5$, and $2$ $\mu$m. Since the number concentration has a rather limited effect, $N_1|_{t=0}$ is kept to a value of $1 \times 10^{13}$ m$^{-3}$. All the rest of the parameters are the same as in previous sections.

In Figure 10, associated with the situation of the first region ($F_o > 0$), the values of $\alpha_f$ and $a_d$ (or $fov/2n_w$) for points below each curve can make the corresponding $r_{inf}$ smaller than the values indicated on the curve. When $\alpha_f < 2.5$, we can have the $r_{inf} < 3\%$ even when $a_d$ is as large as 4.5 mm (or $fov/2n_w$ is as large as 0.05 rad). When $\alpha_f < 4$, the $r_{inf}$ can be smaller than 5% when $a_d <$ 3 mm (or $fov/2n_w < 0.035$ rad) and it can be smaller than 10% when $a_d < 4$ mm (or $fov/2n_w < 0.05$ rad). Therefore, the effect of FSL is negligibly small for $\alpha_f < 4$ if the allowanced error is 10%. Furthermore, in the first region, shown in Figure 10, the particles with diameter $d > 800$ nm should not be used for measuring coagulation rate because $\alpha_f$ would be larger than 4 for measuring wavelengths available in the range of visible light.

Apparently, the plots in Figure 10 show that smaller $\alpha_f$ is preferred to reduce trim down the effect of FSL. However, to produce moderate turbidity for an efficient measurement, particles should not be too small.[4] Therefore, the choice of particle size and wavelength should make $\alpha_f$ smaller than 4, yet not too small in this region.

Comparatively, Figure 11 shows the results of the second region ($F_o < 0$). The curves have the same meanings as in Figure 10. However, in this figure, only the values of $\alpha_f$ and $a_d$ (or $fov/2n_w$) for points between the top and the bottom curves can make $r_{inf}$ smaller than the values indicated on curves. For each value of $r_{inf}$, the top curves are calculated by using $d = 1.5$ and $2$ $\mu$m particles, while the bottom curve are calculated by using $d =$ 1 $\mu$m particles. We can see that when $a_d = 2.3$ mm or $fov/2n_w =$ 0.027 rad the range of $\alpha_f$ for $r_{inf} < 10\%$ is already limited. When $a_d = 2$ mm or $fov/2n_w = 0.024$ rad, there exists a range of $\alpha_f$ making $r_{inf} < 8\%$, but no $\alpha_f$ can make $r_{inf} < 5\%$. For $a_d <$ 1.6 mm or $fov/2n_w < 0.014$ rad, there exists a range of $\alpha_f$ for $r_{inf} <$ 5%, while for $a_d < 1.2$ mm or $fov/2n_w < 0.014$ rad, there exists a range of $\alpha_f$ for $r_{inf} < 3\%$. Therefore, the requirement of smaller $a_d$ or $fov/2n_w$ in the second region is much stricter than in the first region. For $a_d > 2.3$ mm or $fov/2n_w > 0.027$ rad, $r_{inf}$ will be larger than 10% for most $\alpha_f$ so that $F_c$ for the effect of FSL have to be made in the calculations of $k_{11}$.

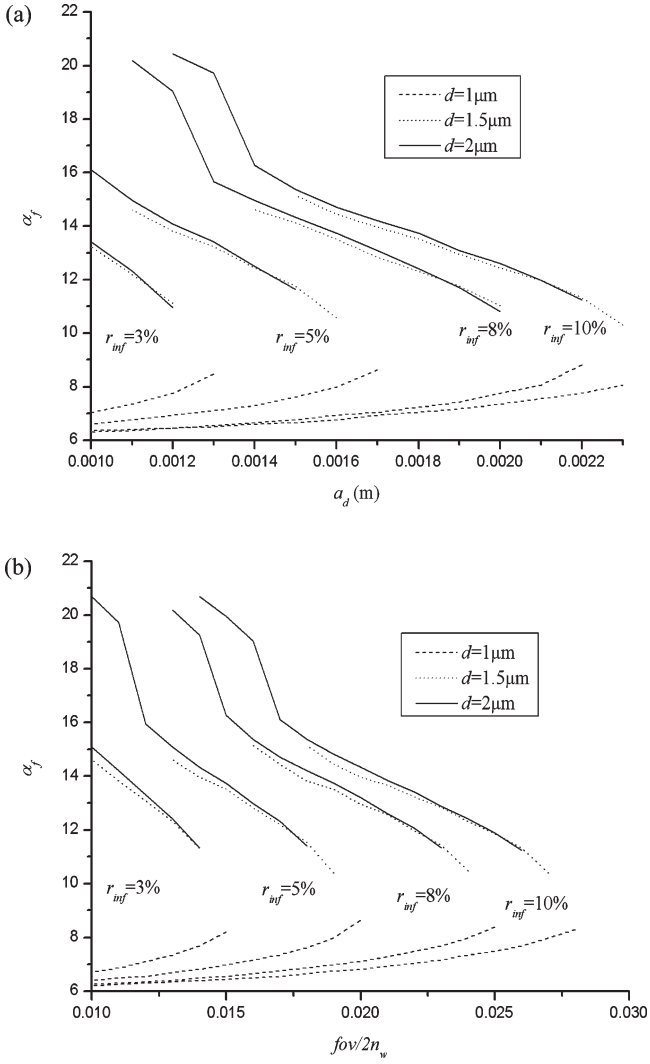


**Figure 11.** Values $\alpha_f$ and $a_d$ or $fov/2n_w$ that make $r_{inf}$ 3%, 5%, 8%, and 10%, respectively. The diameters are $d = 1, 1.5$, and $2$ $\mu$m. (a) Open detector system (b) lp detector system.

Besides, Figure 11 shows that $\alpha_f$ in the range from 9 to 10 corresponds to a minimum valley of $r_{inf}$ no matter what the value of $a_d$ is, which provides a clue on how to choose the particle size and wavelength to reduce $r_{inf}$ in the second region.

## IV. Conclusion

In this study, the effect of FSL on measuring the coagulation rate by turbidity measurement, especially for larger particles, was investigated based on calculations using the *T*-matrix method. The relevant modified formula including the contribution of FSL in the turbidity measurement was deduced. To evaluate the effect of FSL, the errors contributed by FSL were calculated and compared with the pure transmitted light in the turbidity measurement of the coagulation rate for two different detector configurations under various conditions. To quantitatively estimate the degree of the influence of FSL, we defined a FSL influence ratio, and its value was computed in different situations. The main results of this study can be summarized as follows:

(1) Characteristics and performance of the turbidity measurement depends on the wavelength used and the magnitude of

optical factor $F_o$ to a great extent. According to the value of $F_o$ and the measuring wavelength, the measurement range can be divided into three regions: $F_o > 0$, $F_o \sim 0$, and $F_o < 0$, corresponding to the above-named "first region", "blind zone", and "second region", respectively.

(2) Turbidity measurement should not be conducted near the "blind zone".

(3) In the first region, reducing the effect of FSL is very straightforward: choosing particle size and measuring wavelength to make $\alpha_f$ small, namely, smaller particles and large wavelength. However, since moderate turbidity would be more appropriate for the turbidity measurement, we need to properly increase the particle size used.

(4) In the second region, there is a minimum valley of $r_{inf}$ for $\alpha_f$ in the range from 9 to 10, so around the value we can have a relatively small effect of FSL, as long as $a_d$ or $fov/2n_w$ is not large.

(5) To remove the error caused by FSL in the coagulation rate evaluation, the modified eq 9 should replace the original eq 4 if the relevant parameters are available.

(6) The particle number concentration has only a weak influence on the effect of FSL, implying that we do not need to worry much about whether adjusting the number concentration would worsen the effect of FSL. However, too large a number concentration will cause remarkable multiple scattering, which will also affect the accuracy of turbidity measurement. In our previous study,[19] we have evaluated the influence of multiple scattering and showed how to choose volume fractions or number concentrations to avoid the possible effect of multiple scattering. Therefore, for $\alpha_f$ corresponding to a small FSL effect, the number concentration should also be appropriately restricted. It should also be pointed out here that the forward scattering intensity is affected by the interparticle interactions through the structure factor. However, the volume fractions used in the turbidity measurement are mostly very low (less than $10^{-4}$) in order to ensure a moderate turbidity. Therefore, the effects of the structure factor are ignorable.

(7) The most important measure to reduce the error caused by FSL should be making the acceptance angle small in the experimental setup of the turbidity measurement, although this issue is beyond the scope of this paper. Special efforts have been made[20] towards this target, and for the best result, the acceptance angle can be reduced to close to 0.

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