Non-Gravitational Effects with Density-Matching in Evaluating the Influence of Sedimentation on Colloidal Coagulation *

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The method of density matching between the solid and liquid phases is often adopted to effectively eliminate the effect of sedimentation of suspensions in studies on dynamic behaviour of a colloidal system. However, the associated changes in the solvent composition may bring side effects to the properties investigated and therefore might lead to a faulty conclusion if the relevant correction is not made. To illustrate the importance of this side effect, we present an example of the sedimentation influence on the coagulation rate of suspensions of $2\,\mu m$ (diameter) polystyrene. The liquid mixtures, in the proper proportions of water (H_2O), deuterium oxide (D_2O) and methanol ($MeOH$) as the liquid phase, density-matched and unmatched experiments are performed. Besides the influence of viscosity, the presence of methanol in solvent media, used to enhance the sedimentation effect, causes significant changes (reduction) in rapid coagulation rates compared to that in pure water. Without the relevant corrections for those non-gravitational factors it seems that gravitational sedimentation would retard the coagulation. The magnitude of the contribution from the non-gravitational factor is quantitatively determined, making the relevant correction possible. After necessary corrections for all factors, our experiments show that the influence of the sedimentation on coagulation rates at the initial stage of the coagulation is not observable.

Coagulation of colloidal suspensions is important for fundamental research and industrial applications.[1−19] Dynamic behaviour of coagulation processes changes with various external factors. Great efforts have been made to study the influence of a gravitational field on the coagulation.[10−19] It is commonly understood that the influence of sedimentation on the coagulation appears only when differences among settling velocities of particles exist. From the equilibrium among gravitational force, buoyancy, and viscous drag, we can obtain the settling velocity of a spherical particle with radius a_0, i.e.

$$\nu = 2|\Delta\rho|ga_0^2/9\eta, \qquad (1)$$

where $\Delta\rho$ is the density difference between the liquid and solid phases, namely $\Delta\rho = \rho_l - \rho_s$ with ρ_l and ρ_s being the densities of the liquid-phase material and the polystyrene (PS) particles, respectively; and η is the viscosity of the suspending medium. The Stokes settling velocity of Eq. (1) holds only for an infinitely dilute sphere-like suspension. With the increasing particle concentration, the settling velocity of an individual particle fluctuates around a mean velocity which is noticeably smaller than that of Eq. (1) because of the presence of other particles in the fluid, as shown in Ref. [19]. However, because the volume fraction of particles, Φ, concerned in this study is very low (about 5×10^{-4} v/v), we suppose that at the very beginning of the coagulation, all particles in the monodispersed suspension have the same size and therefore should have the same settling velocity regardless of whether the density of particles is matched ($\Delta\rho = 0$) or not

($\Delta\rho \neq 0$) with that of the medium. With time, the formation of different-sized particles leads to additional collisions because larger particles settle faster than smaller ones and catch the smaller ones during sedimentation. Therefore, sedimentation should accelerate the coagulation, see for instance Refs. [3–7]. Since colloidal particles are small, gravity is usually of little importance for colloidal coagulation unless $\Delta\rho$ is large. However, based on experiments with density-matching for dispersion and liquid phase, Folkersma *et al.*[10−13] found that sedimentation has a pronounced influence on the coagulation rate of aqueous suspensions of $2\,\mu m$ (in diameter) PS even at the initial stage of the coagulation. According to their data, with a density difference between dispersions and liquid phase and with no density difference, the coagulation rate without sedimentation is significantly larger than that when sedimentation exists, i.e., when a difference between densities of the solid and liquid phases exists. This finding suggests that for the system studied, not only is the magnitude of the influence of sedimentation profound, but the direction of the influence is also contrary to expectations: sedimentation is found to retard rather than to accelerate coagulation. From their experiments, Folkersma *et al.*[11] further inferred that under microgravity conditions, the theoretical value of the rate constant according to von Smoluchowski[8] is best approached because the microgravity conditions best reflect the theoretical assumptions: hydrodynamic interactions and interparticle forces are ignored.

As a possible example that tiny influences may lead to dramatic effects in the dynamic behaviour of a sys-

tem, Folkersma's unusual finding has attracted our attention. However, our experiments and computer simulations[17,18] could not support their conclusion. As an alternative attempt to deal with this issue, it would be helpful to consider the factors that may affect the conclusion drawn from the density-matching and unmatched experiment. In this Letter, we show that changes of ingredients of the liquid phase may, to a certain extent, alter the characteristics of the coagulation process in consideration. In this case it is possible to reach the conclusion that sedimentation retards the coagulation, if the data of the density matching experiment are not properly corrected for the contribution from factors other than gravity. However, after necessary corrections for non-gravitational factors, our experiment still confirms the point of view that there is no observable influence of gravity on colloidal coagulation at the initial stage of the coagulation. Furthermore, we assume the effects of the non-gravitational factors originate from variation of the strength of van der Waals attractive forces against hydrodynamic resistance between approaching particles for coagulation. This assumption is verified by the calculations of Hamaker constants when the solvent composition is changed.

In our experiments, turbidity (τ) versus time t was employed[20−22] to monitor the salt-induced coagulation process of PS dispersions with an initial number concentration N_0, according to

$$(1/\tau_0)(d\tau/dt)_{t\to 0} = A(1/N_0)(dN/dt), \qquad (2)$$

where A is a constant depending on factors such as $d(\ln\tau/d\lambda)$ and $\tau = (1/L)(\ln T_0/T)$. T, λ, and L are the transmission, the wavelength, and the optical path of light, respectively. Since $(d\tau/dt) \propto (dN/dt)$ for the sake of simplicity and what we are concerned with, in this study we deal only with relative coagulation rates that are evaluated by performing the measurements of τ versus t. Turbidity change of suspensions with time was measured by a TU-1901 spectrometer (Beijing Purkinje General Instrument Co., Ltd.) at wavelength 600 nm, which is more favourable for a large slope of the line of τ versus t.

Monodispersed PS lattices (product 5200A of Duke Scientific Corporation, USA) with diameters 2 μm were used in the experiment. The PS microspheres have a density of 1.05 g/cm³ and a refractive index of 1.59 (at 589 nm). The standard deviation of the mean diameter expressed as a percentage of the mean diameter $\leq$ 4%. There are no detailed data about the characteristics of the lattices surfaces, such as surface charge density available from the particle provider. However, since we are dealing with only the rapid coagulation in which the electrical repulsion between particles is fully suppressed because of the high electrolyte concentrations used, the data of surface charge density should not be so essential. Zeta potential is a good index of the mag-

nitude of the repulsive interaction between colloidal particles. The Zeta potential for the PS particles measured with BI-ZetaPALS (Brookhaven Instrument Corp., USA) is −56 mV (in 1×10^{-4} M NaCl solution). The number concentration of particles in suspension is 6×10^7 p/cm³ in all experiments discussed here. To minimize the influence of adding electrolyte on viscosities of solvent media, $MgCl_2$, instead of NaCl, is used to induce rapid coagulation (after mixing with latex, the concentration of $MgCl_2$ in the final solution is 0.05 M higher than the critical coagulation concentration (CCC)). Our experiments show that the coagulation rates with 0.05 M $MgCl_2$ as the electrolyte are the same as those when 0.5 M NaCl are used.

Following Folkersma *et al.*, different buoyant levels for the sedimentation test can be reached by adjusting the density of the liquid phase composed of proper mixtures of H_2O, D_2O, and MeOH. To ensure that PS dispersions are mono-dispersed, for each experiment new PS samples are used. The densities of H_2O, PS particles, D_2O, and MeOH are 1.00 g/cm³, 1.05 g/cm³, 1.10 g/cm³, and 0.79 g/cm³, respectively, at room temperature (25°C). The density of a 50% H_2O plus 50% D_2O mixture as the liquid phase is just matched with the density of PS particles. For each mixing formula of solvent media, over five independent experiments of coagulation rates are performed to yield an average result.
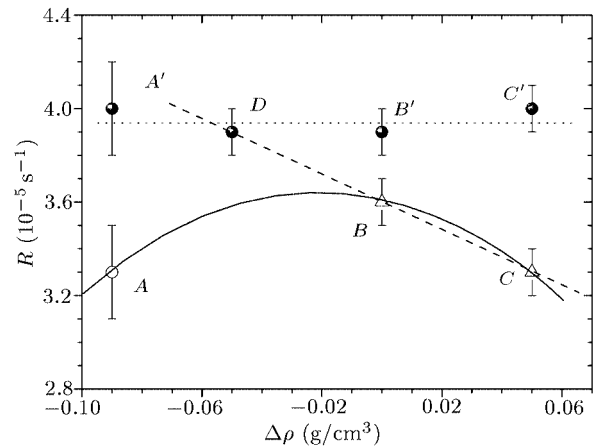
Fig. 1. Relative coagulation rates R of PS particles dispersed in different solvent media versus density difference $\Delta\rho$, with and without necessary corrections. Triangle: R without viscosity corrections (using D_2O as density-matching agent); open-circle: R with viscosity corrections (using MeOH as density-matching agent); closed-circle: R with all necessary corrections. Dotted line: R with all necessary corrections at various density differences; dashed line: R without viscosity corrections (using D_2O as density-matching agent); solid line: the imaginary tendency similar to that described in Ref. [11].

Figure 1 shows the relative coagulation rates, with and without necessary corrections for the side effects of the mixing formula of media, of PS particles dispersed in different media versus $\Delta\rho$.

With regard to corrections for the effect of density-matching media, it is mentioned in Ref. [11] that "sucrose and methanol were used because they do not induce surface charges, but a disadvantage is that the viscosity of the continuous phase is changed. Therefore deuterium oxide was also used because in this case no correction needs to be applied for the viscosity change."

Table 1. Relative coagulation rates before and after the viscosity corrections for dispersions with different density differences between the solid and liquid phases. Here R_1 and R_2 are the relative coagulation rates before and after the viscosity corrections, respectively. All viscosities are measured with capillary viscometers.

Medium	$\Delta\rho$ (g/cm^3)	R_1 ($\times 10^{-5}$)	R_2 (10^{-5})
D$_2$O	0.05	3.3 (± 0.1)	4.0 (± 0.1)
H$_2$O+D$_2$O	0	3.6 (± 0.1)	3.9 (± 0.1)
H$_2$O	-0.05	3.9 (± 0.1)	3.9 (± 0.1)
20%MeOH + D$_2$O + H$_2$O	-0.05	1.8 (± 0.1)	3.2 (± 0.2)
20% MeOH+ H$_2$O	-0.09	2.0 (± 0.1)	3.3 (± 0.2)

Based on the above consideration, our experiments show the trend that sedimentation retards the coagulation, which is similar to that described in Ref. [11] although there are differences in the magnitude. This trend can be clearly seen from the solid line in Fig. 1 going through the points: (A) $\Delta\rho = -0.09\,\text{g/cm}^3$ for the mixture of (80% H$_2$O + 20% MeOH) with a viscosity correction; (B) $\Delta\rho = 0\,\text{g/cm}^3$ for the mixture of (50% H$_2$O + 50% D$_2$O) without a viscosity correction; (C) $\Delta\rho = 0.05\,\text{g/cm}^3$ for the 100% D$_2$O without a viscosity correction. There is a maximum value for the coagulation rate when sedimentation vanishes ($\Delta\rho = 0\,\text{g/cm}^3$).

Because the coagulation rate depends directly on the viscosity of the media, for the purpose of comparing coagulation rates in different liquid mixtures it is an essential step to make corrections for the difference between the viscosities of the media when dealing with the data from density-matching experiments. Although deuterium oxide and water do share the same chemical properties, physical properties of deuterium oxide, such as viscosity and boiling point, are rather different from that of water. In particular, the viscosity of deuterium oxide is 1.2 times larger than that of water at room temperature. Therefore, corrections for the differences of viscosities have to be carried out for points B and C. After these corrections, points B and C move up to points B' and C' in Fig. 1. Therefore within the error limits there is actually no apparent difference between the cases of $\Delta\rho = 0\,\text{g/cm}^3$ and $\Delta\rho = 0.05\,\text{g/cm}^3$ after the viscosity corrections. This fact implies that as long as the relevant correction for the change in viscosity is made, D$_2$O can be used as a substitute for H$_2$O without observable side effects in density-matching experiments on the coagulation process.

To understand what happen to point A in Fig. 1, we work out a way to examine whether there is any non-gravitational factor involved for a reduction in the coagulation rate when methanol is added in the liquid phase. We prepare ternary liquid mixtures comprised of 20 wt.% MeOH and a certain amount of D$_2$O and H$_2$O to make the final density of the liquid phase equal to that of pure water (namely, $\Delta\rho = -0.05\,\text{g/cm}^3$ for the mixtures). If there is no factor other than gravity involves in the ternary, with the correction made for the viscosity difference the mixtures should have had a coagulation rate equal to that of pure water because both of them have the same density. However, this was not the case: our experiment shows that the coagulation rate of the ternary mixtures $[3.2(\pm 0.2) \times 10^{-5}]$ is about 18% lower than that for pure water $[3.9(\pm 0.1) \times 10^{-5}]$ (both with viscosity corrections, shown in the column R_2 of Table 1). We attribute this deduction in the coagulation rate for the mixtures to non-gravitational factors. The fact that the coagulation rate of the ternary mixtures is, within the error limits, nearly the same as that of the mixtures of (80% H$_2$O + 20% MeOH), $[3.3(\pm 0.2) \times 10^{-5}]$, with the above conclusion that D$_2$O can be used as a substitute for H$_2$O without any side effect, made us reasonably assume that it is the presence of methanol which slows down the coagulation process. In other words, the difference, amounted to 0.7×10^{-5}, between the coagulation rates of the ternary mixtures and water should be caused by the non-gravitational influence contributed from 20% MeOH. Thus this difference is the correction required for the side effect of methanol. Therefore, the correction has to be taken into account when estimating the coagulation rate of the mixtures of (80% H$_2$O + 20% MeOH). With this correction, we should move the position of its representing point from A to A' in Fig. 1. After all the necessary corrections, points A', D, C' and B' in Fig. 1 are on the same level within error limits, as denoted by the dotted line in Fig. 1. Therefore, at the initial stage of the coagulation process, our density-matched and unmatched experiments basically provide us with the same coagulation rates within error limits. The errors of the data shown in Fig. 1 are caused not only by fluctuations in the turbidity measurements but also associated with the uncertainty of the viscosity measurements in our experiments.

The coagulation rate depends on two basic factors: particles' motion and the collision efficiency. The fact that further enhancing the concentration of the electrolyte does not result in any further increase of the coagulation rate for the liquid mixtures of (80% H$_2$O + 20% MeOH) indicates that electrostatic repulsion vanishes. To exclude the possibility of the presence of steric repulsion, a microscopic approach described in Refs. [23,24] is used to check the collision efficiency for PS particles dispersed in the above mixtures. It is found that every collision is effective to make a colliding particle pair stick together, implying that there is no steric repulsion involved. Therefore, the coag-

ulation processes discussed above are in a diffusion-limited regime, i.e., rapid coagulation.

According to Smoluchowski's theory,[8] the rapid coagulation rate constant depends only on the temperature and viscosity of the suspending medium. However, this theory does not take account of hydrodynamic effects[25,26] on the collision of particles. The influence of the hydrodynamic interaction on particle diffusion is calculated by Honig *et al.*[26] The hydrodynamic resistance would prevent approaching particles from collision and therefore retard the coagulation process. This is a possible explanation for a much lower experimental value of the rapid coagulation rate constant, compared to the theoretical prediction. In practice, van der Waals attractive forces play a role in helping approaching particles to overcome the hydrodynamic resistance for coagulation. As a possible explanation for the origin of the effect of the non-gravitational factor discussed above, the changes in the composition of the suspending media may cause a change in the Hamaker constant and therefore the strength of van der Waals attractive forces, and eventually lead to variation in the coagulation rate.

With regard to coagulation behaviour of PS particles dispersed in n-alkanol/water mixtures, Vincent *et al.*[27] showed that a certain amount of alcoholic content in the mixtures may cause a reduction in the rapid coagulation rate compared with that in pure water. They supposed that the preferential absorption of n-alkanols on latex particles may lead to an increase in the hydrodynamic radius of the particles and slow down the coagulation, although this effect is not significant. In addition, they assumed that the absorption and wetting characteristic of PS particles in n-alkanol/water mixtures would significantly affect the characteristic of electrostatic interactions. Apparently, since the size of latex particles (mean particle radius 110 nm) used in their experiments are much smaller than that discussed above, the influence of sedimentation on the coagulation should be negligible. Therefore, the influence of an absorbed layer MeOH on the hydrodynamic radius is certainly negligible for $2\,\mu m$ particles, as in our case.

Changes of composition of the liquid medium for density-matching experiments on the dynamic behaviour of colloidal systems may contribute to changes of the characteristics investigated, but the literature concerning this issue is scarce. In this study, we present an example of a study on the influence of sedimentation on the coagulation rate of suspensions of $2\,\mu m$ (in diameter) polystyrene using the density-matching method to address the importance of this problem.

Using solvent media composed of proper mixtures of H_2O, D_2O, and MeOH, we perform density-matched and unmatched experiments to test the influence of sedimentation on the coagulation process of PS dispersions. We demonstrate that the presence of methanol in solvent media can cause a significant reduction in the rapid coagulation rate, compared with that of pure water. Omitting the necessary correction for this non-gravitational factor associated with the presence of methanol and the correction for the difference in viscosities between water and deuterium oxide may lead to a faulty conclusion that sedimentation retards the coagulation process even at the beginning of coagulation process. We quantitatively evaluate the magnitude of the contribution from the non-gravitational factor and make the relevant correction possible. After necessary corrections, our experimental data confirm that there is no observable influence of sedimentation on the coagulation rates at the initial stage of the coagulation.

Although the example with density-matching presented here is only related to the influence of sedimentation on the coagulation process, the side effects associated with density-matching may exist in studies on other dynamic behaviour of a colloidal system and, accordingly, caution is advised.

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