



AN EXPERIMENTAL STUDY ON COAGULATION OF POLYSTYRENE SPHERES DISPERSED IN DENSITY-MATCHED LIQUID

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ABSTRACT

To simulate a low gravity (microgravity) environment to some extent for aqueous polystyrene (PS) dispersions, buoyancy by gravity is offset through a density-matching method. Either the light scattering method or turbidimetry measurement was employed to monitor the salt-induced coagulation process. In contrast to the distinct effect of gravity reported on 2 μm PS particles (Folkersma *et al*, 1997), only a weak influence of gravity was observed for 1 μm particles and no influence was found for 0.1 μm ones. The possible mechanism behind is discussed.

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INTRODUCTION

Advances of space technique have motivated the scientific exploration and investigation of the possible industrial applications of microgravity environment. Progress in some fields such as material sciences and biology, which make use of microgravity, has brought dispersions and colloidal systems to public attention (Sprenger and Marquardt, 1994; Sprenger, 1993).

Coagulation experiments under microgravity have been carried out and new phenomena were observed. Krutzer *et al* (1993) and Folkersma *et al* (1994) reported that under microgravity conditions, either created by sounding rocket flight or simulated by the density-matching method, a significantly increased coagulation rate was unexpectedly observed for 2 μm PS spheres in both orthokinetic and perikinetic coagulation regimes. Usually for particles in the colloidal size range ($\leq 1 \mu\text{m}$) gravitational influences are thought to be less important compared to Brownian motion. Thus, it is worth performing coagulation experiments on uniform spheres of *colloidal size* to examine how the gravity influence on the coagulation rate is related to the particle size. To simulate the reduced gravity environment to a certain extent, we used the density-matching method in which gravity is balanced by buoyancy. In the present study non-invasive optical techniques including the light scattering method and turbidity measurement were applied to determine the rate of the rapid coagulation of aqueous polystyrene dispersions.

EXPERIMENTAL

Method

The classical theory describing rapid coagulation was developed by Smoluchowski (see for example,

Zeichner and Schowalter, 1979). For the Brownian coagulation of initially monodisperse spheres with number concentration N_0 , the temporal evolution of the number concentration for aggregate containing i initial particles is given by

$$n_i(t) = N_0 (t/t_c)^{i-1} / [1 + (t/t_c)^{i+1}], \quad (1)$$

where $t_c = 3\eta/4k_bTN_0$ is the half-time of coagulation, at which the total number of particles is reduced to $N_0/2$, with η , k_b and T being the viscosity of the continuous phase, Boltzman constant, and temperature, respectively.

The light scattering technique can be used to evaluate the coagulation rate. In the low angle limit, the scattering intensity as a function of coagulation time t follows the relation (Zeichner and Schowalter, 1979):

$$I(t) = (1 + 2t/t_c) I_0, \quad (2)$$

where I_0 is the scattering intensity at time zero. From Eq. (2) we can see that the low-angle scattering intensity, $I(t)$, increases linearly with time. Importantly, the slope is proportional to the coagulation rate. As far as small dispersed spheres ($d = 96\text{nm}$) are concerned, it has been experimentally established that at the initial stage of coagulation the scattering intensity measured at a scattering angle even as large as 20° shows a linear increase with time (see Figure 1). Therefore, the low scattering angle restriction can be largely released for small PS spheres.

The measurement of change in turbidity τ versus time can also be used to evaluate the coagulation rate according to:

$$(1/\tau_0)(d\tau/dt)_{t \rightarrow 0} = A(1/N_0)(dN/dt), \quad (3)$$

where A is a constant (actually, it depends on other factors such as $d \ln \tau / d \lambda$), $\tau = (1/L) (\ln T_0/T)$, and T , λ and L are the transmission, the wavelength in the medium, and the optical path, respectively. The wavelength and the concentration used were carefully chosen to yield a T vs t curve for which the initial linear portion is long enough and the slope is noticeable.

Salt-induced Coagulation

Two kinds of monodisperse polystyrene latices (Duke Scientific Corp.) with diameters of $0.993 \mu\text{m}$ and 96 nm were used as supplied. The density of PS is 1.05 g/cm^3 at room temperature. MgCl_2 was used to induce fast coagulation at final concentrations of 0.16 mol/l and 0.05 mol/l for 96-nm and $0.993 \mu\text{m}$ spheres, respectively. To adjust the density difference between particle and medium, three kinds of liquid with different proportions of H_2O and D_2O were used: liquid I - $100\% \text{ H}_2\text{O}$ (with density $\sim 1 \text{ g/cm}^3$); liquid II - $50\% \text{ H}_2\text{O} + 50\% \text{ D}_2\text{O}$ ($\cong 1.05 \text{ g/cm}^3$) and liquid III - $100\% \text{ D}_2\text{O}$ ($\cong 1.105 \text{ g/cm}^3$).

RESULTS AND DISCUSSION

Figure 1 shows the change in relative scattering intensity (I/I_0) with time (second) for PS (diameter of 96 nm , the volume fraction is 5.6×10^{-6}) dispersed in liquid phase with different densities (liquid I, II). Apparently the slope of liquid I (0.013 /s) is larger than that of liquid II (0.012 /s). However, to compare the coagulation rate and considering Stokes Law, the slope of liquid II should be multiplied by the ratio of the viscosity of liquid II and I ($\eta/\eta_0 = 1.125$). After this correction, the difference between these two coagulation rates is not distinguishable within our experimental accuracy ($\pm 4\%$). We repeated this experiment for different PS concentrations, as shown in table 1, and a similar conclusion can be reached: a gravitative influence on such small particle dispersions is negligible.

Table 1. Slopes of $(I/I_0) \sim t$ at different concentrations for liquid I and II.

Volume fraction ($\times 10^6$)	4.3		5.6		7.4	
Composition	H_2O	$\text{H}_2\text{O} + \text{D}_2\text{O}$	H_2O	$\text{H}_2\text{O} + \text{D}_2\text{O}$	H_2O	$\text{H}_2\text{O} + \text{D}_2\text{O}$
Slope of $(I/I_0) \sim t (\times 10^2/\text{s})$	1.1	0.96	1.3	1.2	1.6	1.4

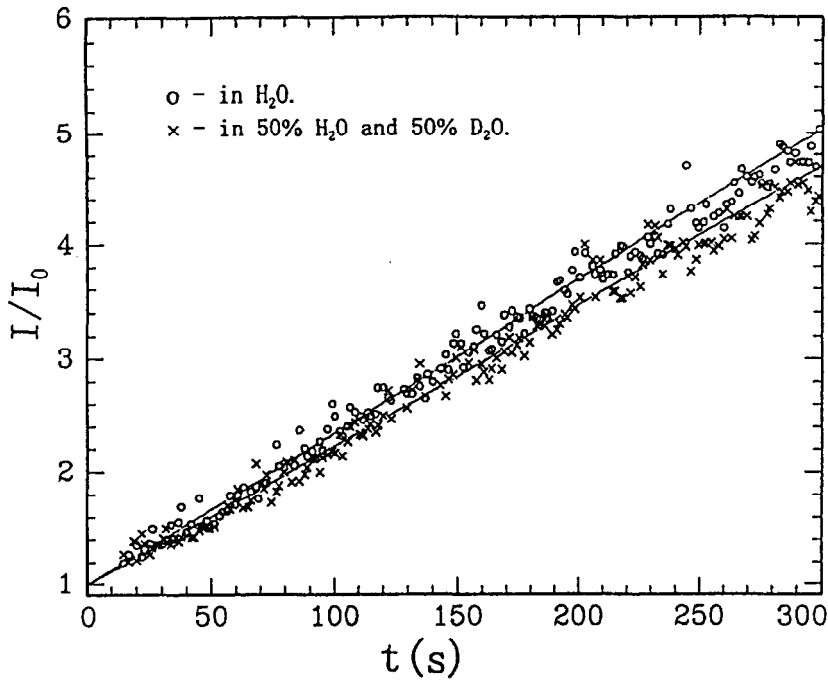


FIG.1. Relative intensity of scattering light (I/I_0)-Time for 96 nm particles, the wavelength of the light in vacuum $\lambda_0=633$ nm .

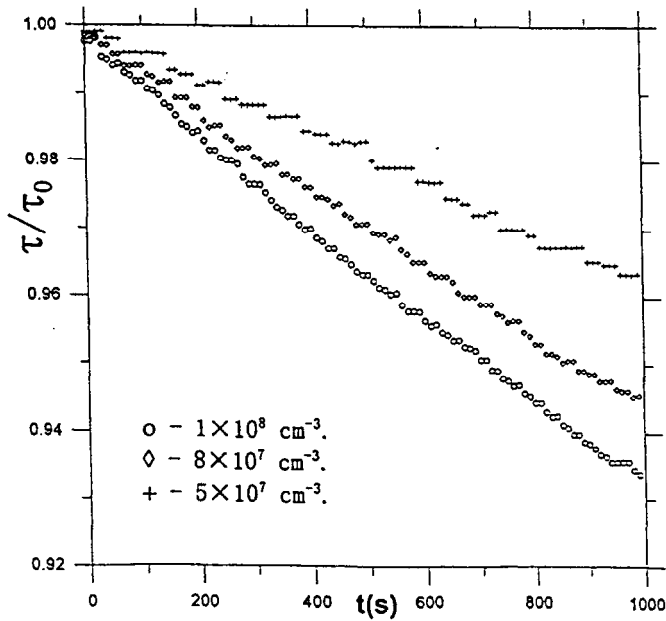


FIG.2. Relative turbidity (τ/τ_0)-Time (t) curves for 993 μ m particles of different concentration, the wavelength of the light in vacuum $\lambda_0=450$ nm .

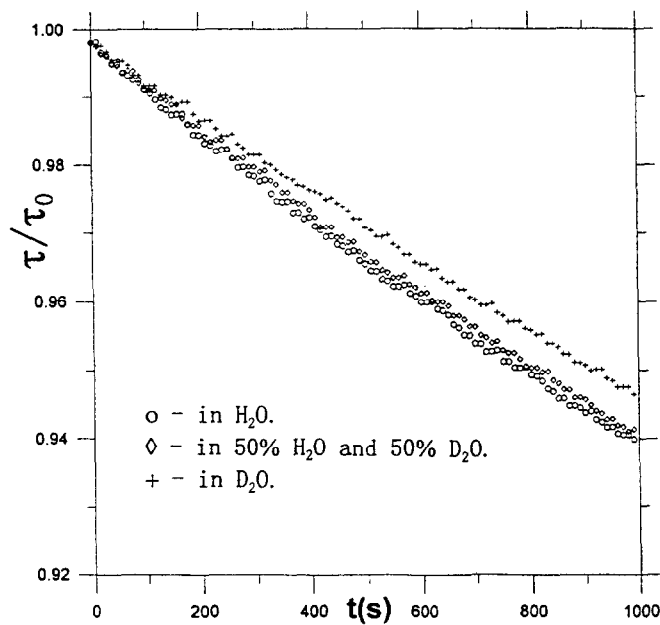


FIG. 3. Relative turbidity (τ/τ_0) ~ Time(t) curves for 0.993 μm particles in different solution, the wavelength of the light in vacuum $\lambda_0 = 450$ nm, volume fraction of solid 5×10^{-5} .

For 0.993- μm particles, we tested first the validity of the coagulation-rate approach by the light transmission versus time as discussed above. Figure 2 shows relative turbidity-time curves for samples of a ratio of particle concentration of 1 : 0.8 : 0.5, respectively. From the slopes of these curves the ratio of the coagulation rates for these samples can be calculated to be 1 : 0.81 : 0.53, which is quite reasonable to represent the ratio of the coagulation rates being supposed for these samples. And, when there was no MgCl_2 added to the solution, the transmission-time curve is flat (slope is zero) for a quite long period (over an hour) so we confirmed that the change in transmission with time is caused by the particles' coagulation, not their sedimentation.

Figure 3 gives relative turbidity τ/τ_0 vs t measurements for 0.993- μm particles dispersed in liquid I, II and III. From the slopes of a linear fit of these data, we obtained $(\eta/\eta_0) \left| (1/\tau_0)(d\tau/dt)_{t \rightarrow 0} \right|$, which describes coagulation rates (see Table 2). Apparently, coagulation in liquid II (for the simulated microgravity case) has the fastest rate and slower coagulation rates happen in both liquid I (where buoyancy is negative - smaller than gravity) and liquid III (where buoyancy is positive). This result is consistent with previously reported observations (Folkersma *et al.*, 1994). Folkersma *et al.* (1994) in their sounding-rocket experiment found that in a gravity field, perikinetic coagulation proceeds slower than under microgravity conditions and their density-matching experiment supports this conclusion. In fact, some other experiments, including orthokinetic (i.e. shear-induced) coagulation, also show a similar behaviour.

Table 2. $\tau \sim t$ measurement for 0.993- μm particles in solutions of different densities.

Composition	$(\eta/\eta_0) \left (1/\tau_0)(d\tau/dt)_{t \rightarrow 0} \right $	$\Delta\rho$ (g/cm^3)
Liquid I (H_2O)	6.82×10^{-5}	~ -0.05
Liquid II ($\text{H}_2\text{O} + \text{D}_2\text{O}$)	7.30×10^{-5}	0
Liquid III (D_2O)	6.89×10^{-5}	~ 0.05

η_0 is viscosity of H_2O , $\Delta\rho = \rho - \rho_{\text{PS}}$, where ρ_{PS} is the density of dispersed particles PS.

When examining the results of coagulation kinetics obtained from light transmission measurements, the errors of the experimental data should be carefully considered. Lichtenbelt et al (1974) reported a standard deviation of ~5% for their results on PS spheres ($d \sim 91 - 357$ nm). The situation became even worse with $2 \mu\text{m}$ particles (Folkersma et al 1977). Keeping this in mind, our results seem to show that there is essentially no influence of gravity on Brownian coagulation at least for submicron size particles. At this moment, however, we can not exclude the possibility that when the size starts to reach the upper limit of colloid domains (i.e. $\sim 1 \mu\text{m}$ in diameter), a weak but noticeable accelerating effect would appear. Nevertheless, our observation can be understood based on the arguments below:

1. As predicted by the Smoluchowski theory, the rate constant of rapid coagulation is independent of particle size. This is still valid when hydrodynamic interaction is considered.
2. For particles of identical sizes, the ratio for the rates of coagulation without and with shear (or forced convection) is $J_{\text{shear}}/J_{\text{Brownian}} = \eta\gamma d^3/2K_bT$, where γ is the shear rate. Thus, in contrast to Brownian coagulation, shear coagulation depends strongly on particle size. For water at room temperature and at $\gamma = 1 \text{ s}^{-1}$, as compared with Brownian coagulation, shear-induced coagulation goes from negligible to comparable, and finally dominant, when the particle size increases from $0.1 \mu\text{m}$ to $1 \mu\text{m}$ and $10 \mu\text{m}$, respectively. In the case of irreversible coagulation occurring at the deep, primary minimum, the presence of shear (including simple shear flow, convection, sedimentation, etc) would increase the coagulation rate but remarkably only for large particles ($>1 \mu\text{m}$).
3. Shear can disrupt aggregates as well as bring particles together, particularly when the primary particles in aggregates are loosely bonded as a result of reversible aggregation occurring at the second minimum. This minimum is shallow, giving a depth proportional to particle size. Thus, the second minimum is important for coarse colloids ($>1 \mu\text{m}$), making both the formation and disintegration of particle pairs/clusters (particles adhere upon contact, but without uniting) feasible. This might partly account for the observation that a profound increase in coagulation rate was traced for $2\text{-}\mu\text{m}$ particles in sounding rocket flight.

CONCLUSION

The present study shows that there is essentially no gravitative influence on Brownian coagulation for submicro size particles. The concept of reversible aggregation arising from the existence of the second minimum may account for the profound effect of gravity reported on $2\text{-}\mu\text{m}$ particles (Folkersma, 1997). Apparently, both theoretical treatment and experimental evidence of high quality are required to get a deep insight into this problem.

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