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A Study of the Influence of Free Convection on Coagulation Process

It was assumed [1, 2] that gravity affects the coagulation process in two ways: free convection, which is hard to be avoided on the ground, and sedimentation, which can be greatly reduced by the density-matching method. We present a ground-based experiment set-up to study the influence of convection on the perikinetic coagulation for aqueous polystyrene (PS) dispersions. The turbidity measurement was used to evaluate the relative coagulation rate and convection-driven flows in the solution were checked with a visual-magnification system. The pattern of flow field, temperature profile in the sample cell is given. Our experiments show that there was no noticeable difference of coagulation rate observed no matter whether convection flows exist (with the flow speed up to 180 $\mu m/s$) or not.

1 Introduction

Profound gravitational influence on the coagulation is unexpected by general theoretical prediction [3–6] and common sense. However, *Folkersma et al.* [1] performed a series of experiments on perikinetic coagulation under the μg (microgravity conditions were created by a sounding rocket), 1-g, and high-g conditions, and found that the coagulation rate under μg is much higher than that under the $1g$. Their finding might serve as an example that it is possible for a tiny influence to lead to dramatic effects in the dynamic behaviour of a system. It was assumed [1, 2] that there are two aspects of gravity contributing to the difference: free convection, which is thought to be hard avoided on ground and sedimentation, which can be greatly reduced by the density-matching method for some cases. According to the data presented in [2], when free convection is not present the coagulation would be 420% faster than that when free convection exists. This assumed significant change in the coagulation process caused by convection flows initiated the present work.

From our practice, the key factors to cease the free-convection is to keep a steady ambient temperature and to make all experimental equipment and material have enough temperature pre-equilibrium time with the environment. The strength of convection was controlled by changing the temperature gradient applied to the sample cell. And therefore we can test how free convection, as a single factor, affects the coagulation process on the ground. There has been many research work devoted to the influence of strong convection flows on the coagulation process [7–9]. Our concern is not shear-dominated coagulation, so our study is limited only to very weak convections (with the maximum speed $< 180\ \mu m/s$), only those are reasonably thought to be inevitable in normal ground-based experiments.

2 Experimental

Monodispersed polystyrene (PS) lattices (product of *Duke Scientific Corporation*, USA) with diameters of $2.013 \pm 0.025\ \mu m$ were used in our experiment. The density of PS particles was $1.05\ g/cm^3$ at room temperature. NaCl was used as an electrolyte to induce rapid coagulation and after mixing with latex its concentration were 0.5 M. We used a $H_2O + D_2O$ mixture (including NaCl) as the liquid phase to make its density match the density of PS latex to reduce the effects of sedimentation and centrifugalization when convection flows exist. If PS latex volume fraction is $1.5 \cdot 10^{-4}$, its number concentration (N_0) is $3.4 \cdot 10^7\ cm^{-3}$. The theoretically estimated coagulation time ($T_{1/2} = 3\eta/8N_0KT$) is about 3,000 s. Since density match method can basically prevent dispersions from sedimentation, if convection flows can also be refrained a simulated microgravity condition (no sedimentation and no convection flows) can be reached.

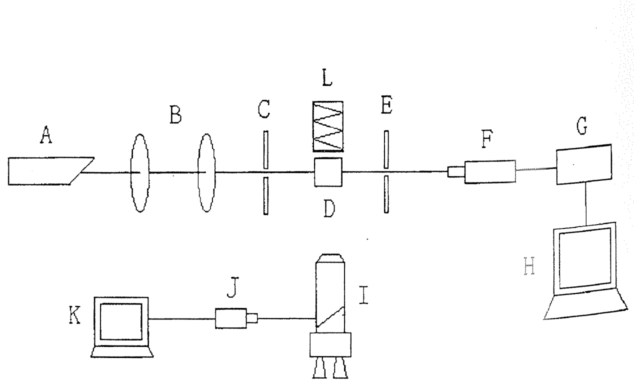

Fig. 1. Experimental set-up: A, stabilised He-Ne laser: B, lens group: C, aperture: D, sample cell: E, aperture: F, detector: G, data acquisition device and computer: H, monitor: I, microscope: J, CCD camera: K, monitor: L, thermostat

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Paper submitted: February 10, 2000
Submission of final revised version: April 29, 2000
Paper accepted: May 19, 2000

Turbidity (τ) versus time (t) was employed to monitor the electrolyte-induced coagulation process of PS dispersions with an initial number concentration N_0, according to:

$$\frac{1}{\tau_0}\left(\frac{d\tau}{dt}\right)_{t\to 0} = A\frac{1}{N_0}\left(\frac{dN}{dt}\right), \tag{1}$$

Where A is a constant (which depends 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. From data of the relative turbidity (τ/τ_0) versus time (t), relative coagulation rates can be obtained.

A schematic diagram of our experimental set-up is shown in fig. 1. A microscope with a CCD camera and a monitor (the visual-magnification power for the whole system was over 1000 times) was employed. This system makes it possible to efficiently monitor small motions of particles.

A typical image of coagulated particles observed by means of our visual-magnification system is shown in fig. 2. The temperature gradient applied to the sample cell can be changed by adjusting the temperature of the thermostat shown in fig. 1.

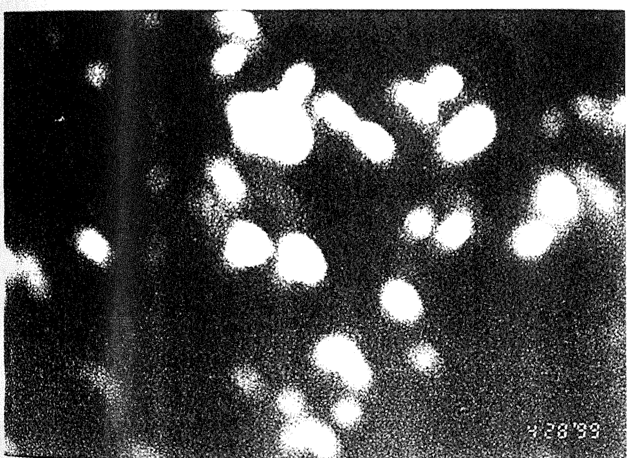

Fig. 2. A typical image of coagulated particles observed by means of our visual-magnification system

Fig. 3 shows the progression of the temperature difference (ΔT) versus time (t) across the sample cell, both of which were measured with thermoelectric couples from inside the sample cell. Since a tiny but steady temperature difference can be maintained, the flow field was rather steady during an experimental period. The temperature profile on the surface of the sample cell, measured by an IR imaging radiometer, is shown in fig. 4. A typical flow field obtained by PIV (particle image velocimeter) equipment is given in fig. 5 (to produce clear velocity vectors larger temperature difference than what we need for our test was imposed to the sample cell). We can see that the maximum speed of the convection flow occurs not far from the sidewall. The CCD was focused on this maximum speed zone. Indeed, to induce the convection flows is much easier than to avoid them on a ground-based experiment. We found that even a 0.2°C temperature difference may induce particles' motion with the maximum speeds

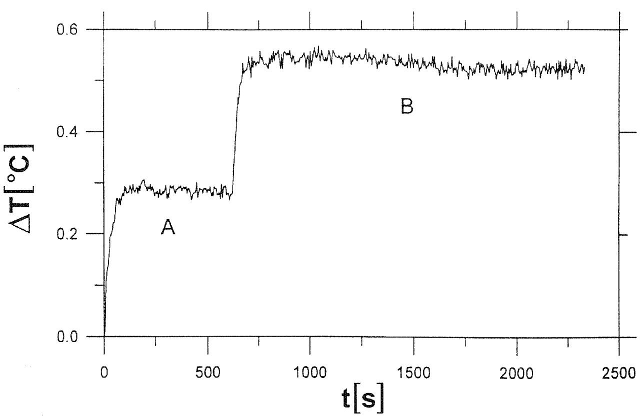

Fig. 3. The temperature difference versus time across the cell (portion A and B corresponding to a different temperature of the thermostat respectively)

of up to 20 µm/s. The probe laser beam was passing through the sample center and the centrifugal force may move particles away from the center and therefore leads to an unexpected change in turbidity measurement when convection going on. So the density match between PS particle and liquid phase is an essential step in our experiment here.

To make sure that our experimental set-up is valid to determine a relative coagulation-rate by using turbidity versus time (as discussed above) process, we did a blank test (only PS particles dispersed in liquid phase with no electrolytes added). From a slope of zero of 'τ/τ_0 vs. t' curve for the blank test, see fig. 6, we can conclude that the coagulation rate is zero. And also we confirmed that when NaCl was added, the slope of the linear fitting of 'τ/τ_0 vs. t' is no longer zero and its slope is basically proportional to the initial PS particle concentration. Therefore our experiment set-up and 'τ/τ_0 vs. t' measurement is valid to evaluate the relative coagulation rate.

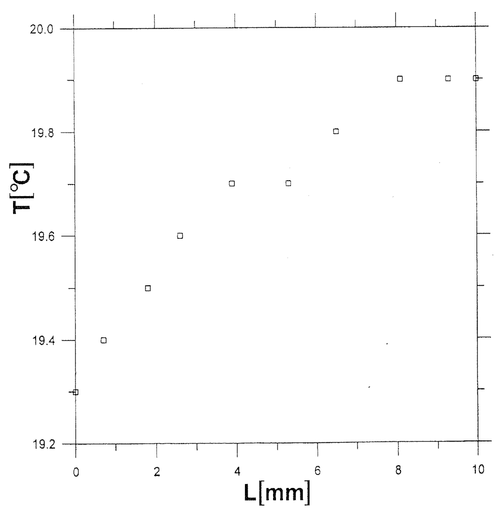

Fig. 4. The temperate profile on the surface of the sample cell, measured by an IR imaging radiometer

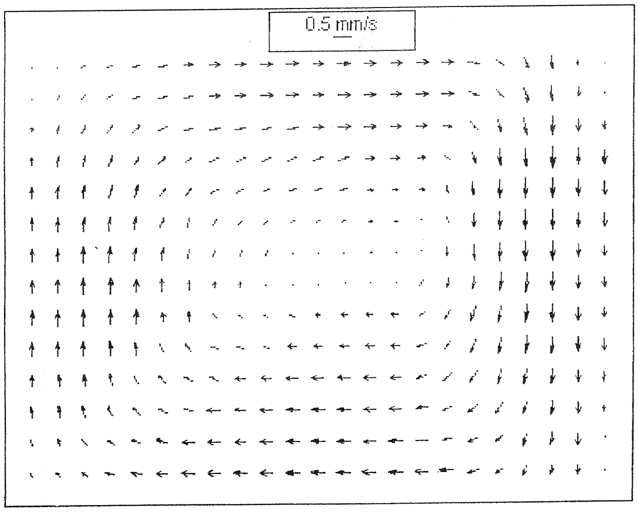

Fig. 5. A typical flow field in the sample cell obtained by PIV (particle image velocimeter)

3 Results and Discussion

A number of groups of coagulation experiments were performed under the same initial conditions: PS latex volume fraction $1.5 \cdot 10^{-4}$, and NaCl 0.5 M in the final solution. For each test group, 2 parallel coagulation experiments were proceeded: one of them is coagulation process without convection flows and the other one with convection flows "turned on" with a different maximum speed. When the maximum speeds of convection flows were 15, 60 and 180 μm/s, respectively, the difference of slopes (which are proportional to the coagulation rates) of two fitted lines is not significant in all cases. A rough estimation of the maximum shear rate in the sample cell with the maximum speed of 180 μm/s is $0.15\ s^{-1}$.

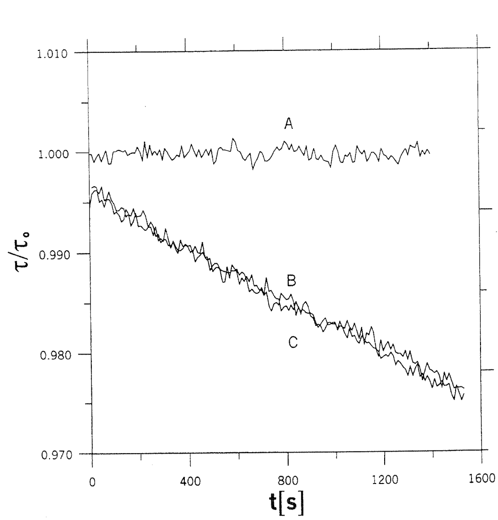

Fig. 6. Relative turbidity (τ/τ_0) versus time (t) for solutions with convection flows with the maximum speed of 180 μm/s (B) and without convection flows (C). (A) represents a process without NaCl added (no coagulation happening)

In fig. 6 we present the typical (τ/τ_0 vs. t) coagulation process (curve B) when we imposed the convection flows (with the maximum speed of approximately 180 μm/s and the maximum shear rate of $0.15\ s^{-1}$) in the solution. Curve C is its contrast experiment in which no convection flow existed. Curve A corresponds to the case when there was no NaCl added. We can see that both curves B and C do not show noticeable difference.

Folkersmas' assume that it is convection flows, which is hard to prevent on a ground-based experiment, to profoundly slow down the perikinetic coagulation process due to the disruption of aggregates by convection-driven flows. According to the data in [1], the coagulation rate constant k_{11} ($p^{-1}\,cm^{-3}\,s^{-1}$) for the 1g (density matched) is $2.046.10^{-12}$ and k_{11} for the μg is $8.616.10^{-12}$, so convection flows would reduce the coagulation rate by a factor 4 if *Folkersmas*' assumption holds. Our experiments did not seem to be in the range of this assumption. To make more reasonable comparison, now we consider the differences of the experimental conditions between our study and those of *Folkersma* et al.

In both cases the same sized PS particles (2 μm) and the same concentration of NaCl were used. However, we used PS latex volume fraction $1.5 \cdot 10^{-4}$ instead of $1.0 \cdot 10^{-4}$ [1], because higher concentration of PS particles can make ($d\tau/dt$) larger (compared with fluctuations in τ measurement) and therefore more reliable evaluation of (dN/dt) becomes possible. Since the PS latex particles used in *Folkersmas*' experiment and ours came from different sources, particle's characteristics is a possibility to account for the different results in both cases.

There was difference between *Folkersmas*' experimental procedure and ours although the turbidity measurement for coagulation rates were used in both cases. For one thing, we used fresh dispersion's sample for each individual experiment but the same sample was used repeatedly in *Folkersmas*' procedure with formed aggregates being redispersed by magnetic stirring and ultrasonic vibration. The heating effect of stirring and ultrasonic vibration would raise the temperature of dispersion's solution and therefore cause stronger convection flows. According to their calculation the maximum flow speed and shear rate are 780 μm/s and $1.3\ s^{-1}$, respectively. Our investigation was limited only to very weak convection because convection flows stronger than what we imposed during the experiment should not be a problem to prevent on the ground, and therefore not generally happen for ground-based experiments.

4 Conclusion

An experimental set-up was constructed to make it possible to test, in a ground-based experiment, how convection-driven flows, as a single factor, contribute to the perikinetic coagulation process. Our experiment shows that weak free convection-driven flows do not markedly affect perikinetic coagulation for 2-μm particles' dispersion. Our observations provide a direct experimental evidence that free convection, as a main cause, profoundly slowing the perikinetic coagulation process is, at least, not the general case. We assume that different characteristics of the different PS particles and experimental methods used in *Folkersma*'s experiment and ours might account for the different results.

Acknowledgements

The work was partially supported by the grant '95-Yu-34' of the Ministry of Science and Technology and the grant 19789201 of the National Natural Science Foundation of China.

References

1 *Folkersma, R., van Diemen, A. J. G., Stein, H. N.*: Influence of Gravity on Perikinetic Coagulation (Experimental). J. Colloid Interface Sci., vol. 206, p. 482 (1998)
2 *Folkersma, R., Stein, H. N.*: Influence of Gravity on Perikinetic Coagulation (Theoretical). J. Colloid Interface Sci., vol. 206, p. 494 (1998)
3 *Melik, D. H., Fogler, H. S.*: Effect of Gravity on Brownian Flocculation. J. Colloid Interface Sci., vol. 101, p. 84 (1984)
4 *Wang, Y. G., Wen, C. S.*: The Effect of Weak Gravitational Force on Brownian Coagulation of Small Particles. J. Fluid Mech., vol. 214, p. 599 (1990)
5 *Zinchenko, A. Z., Davis, R. H.*: Gravity-Induced Coalescence of Drops at Arbitrary Peclet Numbers. J. Fluid Mech., vol. 280, p. 119 (1994)
6 *Qiao, R. L., Wen, C. S.*: The Coagulation Rate of Small Particles in a Sedimenting Dispersion. J. Colloid Interface Sci., vol. 178, p. 364 (1996)
7 *Feke, D. L., Schowalter, W. R.*: The Influence of Brownian Diffusion on Binery Flow-induced Collision Rates in Colloidal Dispersions. J. Colloid Interface Sci. vol. 106, p. 203 (1985)
8 *van de Ven, T. G. M., Mason, S. G.*: The Microrheology of Colloidal Dispersions. VIII. The Effect of Shear on Perikinetic Doublet Formation. Colloid Poly. Sci. Vol. 255, p. 794 (1977)
9 *Hunt, J. R.*: Seld-similar Particle Size Distributions during Coagulation: Theory and Experiment Verification. J. Fluid Mech., vol. 122, p. 169 (1982)