INFLUENCE OF DENSITY DIFFERENCES BETWEEN DISPERSE AND CONTINUOUS PHASES ON COAGULATION

by

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ABSTRACT

Experimentally, a difference was found between coagulation rates of quartz in aqueous solutions, under μg conditions and under 1 g: at μg conditions, coagulation is faster than at 1g. This difference is contrary to theoretical expectations; however, at 1 g in dispersions in which there is no density difference between the disperse and continuous phases, coagulation rate is also higher than in dispersions in which there is such a density difference. Theoretically, a difference in coagulation rates is not expected from low Reynolds number hydrodynamics. Apparently the non-linear terms in the Navier-Stokes equation become important even for small (1-3 μm) particles, when they are close enough for the London-van der Waals forces to be important.

INTRODUCTION

The present work originated in the context of an investigation of orthokinetic (i.e. shear-induced) coagulation. The theory of orthokinetic coagulation [1,2,3] appears to show some discrepancies with experiments; in order to check this, experiments in a surveyable flow field are required. However, the flow fields [4,5] investigated invariably showed either a rather complicated flow pattern which makes application of the theory uncertain because of the uncertainties in the shear rates to be employed in the calculations, or were too small to effectively keep the solid particles used (quartz) suspended; in this case it is the experimental coagulation rate which is uncertain.

Typical values of density differences between the dispersed and continuous phases are of the order of 1.5 * 10^2 kg/m³. Shear-induced coagulation of particles larger than about 1 μm in such cases requires a certain minimum shear rate below which the dispersed
particles tend to settle. Large shear rates, however, lead to complicated flow patterns. In order to circumvent this limitation, we thought it worth while to perform coagulation experiments under μg-conditions.

A pronounced influence of gravity on coagulation of particles is not expected, since for particles in the typical colloid chemistry range (dimensions < 1 μm) gravity effects are thought to be negligible, while for particles beyond this range coagulation is thought to be negligible. However, near the upper end of the colloid chemical size range, for particles between 1 and 10 μm, say, both gravity and (orthokinetic) coagulation may be non-negligible processes. Shear-induced coagulation experiments with dispersed particles in this range and of irregular shape (as frequently encountered in practical cases) have been reported to show slower coagulation than theoretically expected [4,5].

Conclusions are uncertain, however, because theoretical calculations generally refer to spherical particles: differences in shape may result in differences in colloid chemical and hydrodynamical forces [4]. In addition, the experimental coagulation vessels used in practical circumstances (stirred vessels) have a rather complicated flow pattern [6,7] which gives an additional uncertainty to the theoretical predictions.

Nevertheless, the coagulation of such particles is of considerable practical importance, and the interplay of Brownian, shear- and sedimentation induced coagulation is interesting from a theoretical point of view as well.

In the μg-experiments reported here, quartz was used as dispersed phase, in spite of the generally very irregular shapes of the particles; its great advantage over other dispersed phases is the stability of its interface with aqueous solutions. In the lg coagulation-experiments, also reported here, polystyrene (PS) was used as dispersed phase, because the density of PS is close to that of water; therefore the density of the continuous phase can easily be matched, by addition of methanol, sucrose or D₂O. Sucrose and methanol were used because they do not induce surface charges, D₂O was used because in this case no correction needs to be applied for viscosity changes.

EXPERIMENTAL

a) μg-experiments

Quartz particles were prepared by grinding quartz (ex. Merck, pro analysi) in an agate
ball mill for 24 hours. After decanting and drying, the solid was dispersed in twice distilled water and fractionated by sedimentation. It was washed twice with concentrated nitric acid and then washed ten times with twice distilled water until the pH was constant. Washing was performed by centrifugation, decanting the supernatant and redispersing it in fresh liquid. After washing, the particles were dried in an oven at 600 °C for 24 hours. Coagulation was followed by light extinction, using a Philips CQ13A laser (λ<sub>vacuum</sub> = 0.820 μm), and a Philips HAD1100 detector. In front of the detector, a 0.1 mm slit was placed.

\[(X \times 10^{-3})\]

![Diameter vs. Frequency](image.png)

Figure 1

Size distribution of the quartz sample 1: number average distribution 2: volume average distribution

The initial size distribution of the quartz particles is shown in figure 1. The number-averaged diameter of the particles was 1.48 μm; the volume averaged diameter was 2.07 μm; the density of the quartz, as determined with a Quantachrome stereo pycnometer, was 2.77*10^3 kg/m^3. μg-experiments were performed in two sounding rockets launched as part of the TEXUS series from a base in Kiruna (Sweden). The module available could accommodate 9 experimental units of the type depicted in figure 2. Such coagulation units could be filled without leaving a gas bubble at the top of the vessel; this
is important because the boundary conditions for flow under \( \mu g \) should be equal, for comparisons' sake, to those at 1 g.

Of these experimental units, one was used as a check on differences in flow patterns between 1g- and \( \mu g \)-conditions (although no such difference was expected, in view of the equality of boundary conditions for the flow); these flow patterns were made visible by adding 0.68 g of aluminium powder to 100 ml of a 0.05 M sodium dodecyl sulphate solution and the flows were recorded by a film camera.

Coagulation was performed in the other 8 experimental units available, containing 0.01% (v/v) quartz dispersions in a 0.5 M NaCl solution. In the NaCl solutions concerned, the quartz-particles showed pronounced coagulation; but they could be redispersed again by ultrasonic vibration (37 kHz) and stirring (320 rpm). Completeness of redispersion was checked by light transmission. Such homogenization procedures lasted about 20 seconds and were repeated several times.

In a rocket flight experiment, ultrasonics (US) and 320 rpm stirring were switched on during lift-off, to prevent sedimentation and aggregation. US vibrations and stirring were switched off a few seconds after \( \mu g \)-conditions had been reached.

The coagulation experiments were performed at 4 different stirring speeds: 0, 50, 100 and 220 rpm., respectively. Every experiment was performed in duplicate (A and B, resp.). In experiments of the A series, the laser was switched on 5 seconds after the lift-off homogenization had been turned off; light extinction was then continuously recorded as a function of time. 5 seconds later, the stirring at the speed prescribed for each experiment started. In experiments of the B series, both the switching on of the laser and the start of the stirring started 90 seconds later.

On each experimental unit, shortly (10 min.) before (and in one case also shortly after) the \( \mu g \) flight a 1g reference experiment was performed.

Since rocket flight requirements frequently necessitate a stay of several days in the rocket module before the rocket can be launched, we performed experiments in which a dispersion was homogenized every 24 hours, after which a coagulation-experiment was performed.

After filling the vessels for the \( \mu g \)-experiments, they were closed and vacuum tests were made to check for leakage and air bubbles. Such bubbles may perturb the experiments by positioning themselves, at \( \mu g \)-conditions, between the laser and the detector.
If their presence was suspected, the filling and closing procedure was repeated until all the vessels were free of air bubbles.

Figure 2

Experimental set up: (1) vessel; (2) cap; (3) slave-magnet; (4) master magnets; (5) laser; (6) detector

b) 1 g experiments

The polystyrene (PS) latex used for these coagulation experiments had a number averaged diameter of 1.897 μm. Their volume averaged diameter was 2.030 μm. Its density, as measured by means of a Paar DM A-10 densitometer, was found to be 1.050*10³ kg/m³.

Densities between PS and aqueous solutions were matched (resp. nearly matched) by addition of sucrose (ex Janssen Chimica, pro analyti), methanol (ex Merck, "pro analyti", nr. 5868), or deuterium oxide (ex Merck nr. 2919).

Of all solutions used, densities and viscosities were measured.
Registration of detection signal. US vibrations were operated during the time interval bb and during the start of time interval dd.

The coagulation apparatus employed was the same as used in the μg experiments (fig.2).

Coagulation experiments were performed at a volume fraction of $1 \times 10^{-4}$. Suspensions with twice that concentration were prepared by diluting a concentrated PS latex with twice distilled water, using ultrasonic vibrations for dispersing (by means of a Branson 1200 Ultrasound Bath). A typical light transmission ($T$) vs. time ($t$) curve is shown in fig. 3. The value of $d(\ln E)/dt$ (where $E = - \log(T)$) was calculated from the slope of the line in the time interval cc, switched in between periods during which US vibrations were generated (bb and the first part of dd, respectively).

10 ml of this dispersion was mixed with an equal volume of a 1 M NaCl solution, with the chemical added for (nearly) matching densities.

All experiments were performed at $22 \pm 1 \, ^\circ C$. 
RESULTS

a) $\mu$g-experiments

The time necessary for visible movement in a $\mu$g experimental unit, to die out after stirring at some definite values of the stirring rate, is shown in fig.4. This was measured in the experimental unit followed by a camera, containing a dispersion of aluminum particles, both for horizontally placed and for vertically placed vessels. In neither case the time required for the fluid to come to rest does exceed a period of 22 seconds. No change of coagulation characteristics was noted during the experiments performed during 1 week before the flight. Neither were differences noted between the A and B series experiments. This rules out the possibility of disturbance by residual motion of the rocket after attainment of $\mu$g conditions, and by a gradual change of the quartz/water interface during the period preceding the rocket flight. Neither was the homogenization procedure influenced by accelerations (up to 20 g). No differences in flow pattern could be detected at $\mu$g- and 1g-conditions, in agreement with expectations since the boundary conditions for the flow were identical in both cases because of the absence of detectable air bubbles.

1g-experiments performed before and after the $\mu$g-experiment were in complete mutual agreement.

During flight, the temperature increased slightly from 29 to 35 °C.

A typical result of a light transmission vs. time curve is shown in fig.5. When stirring was started, first a slight increase in transmittance was observed (as shown by a slight increase in the output voltage of the detector). This effect was the same at 1g and $\mu$g, and it can be ascribed to alignment of the non-spherical particles in the flow. Light transmission changes due to coagulation were taken to start after the initial sudden light transmission jump. These data showed a very good reproducibility.

Typical results are shown in figure 6.

The observations indicate that the light transmission of the experimental units with the lower stirring rates increased faster under $\mu$g- than under 1g-conditions; whereas at the higher stirring speeds no significant difference between them was noted. Thus, at low stirring speeds (0 and 100 rpm.) coagulation appears to be faster under $\mu$g- than under 1g-conditions.
Time for visible motion to die out, after stirring at the rates concerned.

- Vessel placed horizontally
- Vessel placed vertically

Figure 4

The difference of the initial transmission vs. time curves for spherical glass particles (G) and non-spherical quartz particles (Q) for two different stirring speeds.

Figure 5
Figure 6
Typical light transmission vs. time curves, at a) 0 rpm and b) 100 rpm stirring rates, resp. Dispersions of quartz (volume fraction $1 \times 10^{-4}$) in 0.5 M NaCl solution.

b) 1g-experiments

Values of the densities, viscosities and coagulation rates for each dispersion are presented in tabel 1.

Figure 7 shows the coagulation rate as a function of the density difference, after correction had been made for viscosity differences. Thus, in fig.7 $\nu \cdot d(lnE)/dt$ (with $\nu$ = the kinematic viscosity of the dispersion medium; $E$ = light extinction; $t$ = time) is plotted; the coagulation rate is thought to be, other conditions being equal, inversely proportional to $\nu$. Going from a small density difference to a density difference of zero, one can see an increase in coagulation rate by a factor $\approx 2.5$. There is no significant difference in this respect, between experiments with a continuous phase with lower density than that of the disperse phase, and experiments in which the density of the continuous phase is higher than that of the dispersed phase.
### Table 1

| nr  | \( \rho \) (g/cm\(^3\)) | \( \Delta \rho \times 10^{-2} \) (g/cm\(^3\)) | \( \nu \) (mm\(^3\)/s) | \( |v \times d(Ln E)/dt| \times 10^{-4} \) (mm\(^2\)/s) |
|-----|----------------|----------------|----------------|--------------------------------------------------|
| 1   | 1.112          | 6.2            | 2.09           | 3.03                                             |
| 2   | 1.061          | 3.1            | 1.54           | 3.48                                             |
| 3   | 1.066          | 1.6            | 1.37           | 5.49                                             |
| 4   | 1.060          | 1.0            | 1.31           | 6.34                                             |
| 5   | 1.049          | 0.1            | 1.23           | 7.55                                             |
| 6   | 1.040          | -1.0           | 1.14           | 6.14                                             |
| 7   | 1.035          | -1.5           | 1.10           | 5.19                                             |
| 8   | 1.029          | -2.1           | 1.07           | 4.25                                             |
| 9   | 1.019          | -3.1           | 1.02           | 3.43                                             |
| 10  | 0.988          | -6.2           | 1.65           | 3.17                                             |
| 11  | 0.972          | -7.8           | 1.78           | 3.13                                             |
| 12  | 1.050          | 0              | 1.02           | 6.39                                             |
| 13  | 1.098          | -4.8           | 1.02           | 3.49                                             |

1-9 sucrose  10-11 methanol  12-13 \( D_2O \)

**Figure 7**

Coagulation rate of polystyrene in solutions of different densities.
These results confirm the results of the \( \mu g \)-experiments, in which at low stirring speeds, coagulation appeared to be faster under \( \mu g \)-conditions.

DISCUSSION

The influence on coagulation rate of either the absence of a gravity field (when there is a density difference between the disperse and continuous phases), or of the absence of a density difference (when there is a gravity field), is unexpected. Theories on orthokinetic coagulation usually assume the absence of such an influence; and if any such influence is found, the evidence concerned should be checked as to whether the experiments are disturbed by incomplete fulfillment of assumptions made either explicitly or not, in calculating the coagulation rate from the data.

The data obtained in the present investigation all go back to light transmission vs. time measurements.

It should be noted that experimental coagulation rates as reported here increase with vanishing density difference between disperse and continuous phase; while disturbances of the interpretation of light transmission increases as measure of coagulation rate, by the presence of a gravity field or of a density difference, would act in the reverse direction:

a) Different settling rates bring particles into each other's vicinity which would remain apart in the absence of a gravity field (when Brownian motion can be neglected); this would increase the coagulation rate;

b) such different settling rates induce additional shear which superimposes a shear-induced coagulation on the Brownian coagulation;

c) in the presence of a gravity field, coagulation measurements by light transmission in quartz dispersions might be disturbed by sedimentation. Part of the suspended solids may be removed by sedimentation from that part of the coagulation vessel which is passed through by the light beam; thus light transmission would increase faster than when this effect would be absent. This also would increase the apparent coagulation rate rather than decrease it.
Nevertheless, the present investigation shows that the reverse is found. While at present no definitive conclusion can be offered, two alternatives are considered as most acceptable explanations:

a) At 1 g, newly formed pairs may be disrupted by the flow of the surrounding liquid on sedimentation. This would especially be expected for pairs in the secondary minimum of the potential energy vs. distance curves [8]. Against that alternative the remark should be made that for spherical particles at the electrolyte concentration concerned no secondary minimum of any importance is expected. In this case, the irregular shape of the quartz particles could be important; however, the effect is found for polystyrene particles as well, which have a degree of sphericity which is seldom (if ever) surpassed.

b) Sedimenting particles which are close together but not yet touching, may experience a repulsive pressure by the additional flow between them compared with the situation in the absence of sedimentation.

Against that alternative it should be remarked that no such repulsive pressure is expected on the basis of low Reynolds number hydrodynamics [9,10]. The only way out left at present appears to be, that for particles which are close enough for the London-van der Waals forces to be important, the non-linear terms in the Navier-Stokes equation become important.

CONCLUSION

In the absence of a gravity field, or (when a gravity field is present) in the absence of a density difference between disperse and continuous phases, coagulation is faster than in the presence of these items. This has been found:

a) for dispersions of quartz in aqueous 0.5 M NaCl solutions under μg conditions;

b) for dispersions of polystyrene in aqueous 0.5 M NaCl solutions with density matching between disperse and continuous phases.

The only explanation which appears to be available for this observation is that settling particles which are close together but do not yet touch, experience a repulsive pressure due to the flow between them. If this explanation holds, this additional pressure should be ascribed to the non-linear terms in the Navier-Stokes equation.
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