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Colloids and Surfaces
A: Physicochemical and Engineering Aspects 111 (1996) 223–229

COLLOIDS AND SURFACES A

Rheo-optics of concentrated kaolinite suspensions

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Received 25 September 1995; accepted 24 November 1995

Abstract

A shear-optical method is described which uses multiply scattered light to investigate concentrated colloidal kaolinite suspensions. The shear-optical response derives from the orientation of floc fragments or discrete colloidal particles in the flowing suspension. The apparatus required is robust and inexpensive. The method is used to study the effect of pH, and an organic deflocculant, on the flocculation of kaolinite. The effect of pH on the shear-optical response of concentrated suspensions correlates inversely with the pH-dependence of the fractal dimension measured by Herrington and Midmore for kaolinite flocs in very dilute suspensions. The effect of deflocculant on the shear-optical response correlates closely with the effect of the same deflocculant on the suspension viscosity.

Keywords: Kaolinite suspensions; Rheo-optics

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1. Introduction

Rheo-optics (or optical rheometry) is the study of the structure of fluids in which flow causes some optically-measurable change in the structure. Various flows and optical responses may be combined to yield a large number of techniques. See for example the reviews of Fuller [1] and van de Ven [2]. These authors describe the application of rheo-optics to fluids in which the optical scattering centres are dilute, and only single scattering need be considered. Rheo-optical measurements on concentrated and multiply scattering fluids are less common. Multiply scattered light is largely incoherent, making unusable the single scattering techniques based on an angle — or polarisation — dependence of optical scattering or transmission. A remaining measurable optical property is the optical power (flux) of the multiply scattered light, and we describe a method in which shear alters the transmittance of such light.

Photons may be considered to diffuse through a multiple scattering medium, and their transport and density can be described by a diffusion equation [3]. However, only for some simple cases, such as spheres, can the diffusivity be related to the internal properties of a suspension. Despite this, multiply scattered light from concentrated turbid fluids carries enough information to form an image, and to make spectroscopic analyses [3]. Velocimetry using time-resolved (photon correlation) spectroscopy has been applied to both laminar [4] and turbulent [5] flow of concentrated and turbid fluids. The shear-behaviour of discrete kaolinite clay particles in dilute suspensions has been investigated by measuring the shear-

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SSDI 0927-7757(95)03496-X

dependence of the optical transmittance [6,7]. The clay volume fraction (v) was kept below about 0.001 to avoid multiple scattering. For $v < 0.001$, the transmitted light was found to be predominantly coherent. The experimental results were consistent with a single scattering model of shear-orientation of discrete plate-like clay particles, in competition with relaxation by rotary Brownian motion.

The diffuse and incoherent nature of multiply scattered light might suggest that light scattered from non-spherical particles in a concentrated suspension will not be sensitive to their state of orientation. However, the non-random orientation of particles will be shown to affect the multiply scattered light in highly turbid kaolinite suspensions with v up to about 0.3. The results correlate closely with the fractal dimension of kaolinite flocs measured by Herrington and Midmore [8] at a much lower concentration, and also with the rheology of concentrated kaolinite slurries. The rheo-optical method we describe can thus be used to measure the state flocculation of the suspension.

2. Method

Light was injected by means of an optical fibre into a suspension flowing between optically-absorbing walls. Other fibres, with an attached photodetector, were arranged to collect scattered light at different places in the flow. The diffuse transmittance direction could be parallel to either the streamlines, or to the velocity gradient, depending on the choice of injection and pickup fibres. See Fig. 1, and Section 2.1 below. This apparatus was used to investigate kaolinite suspensions, particularly the effects of shear rate, clay volume fraction (v), pH, and the dosage of a deflocculant. The clay particles were platelet-shaped, with face diameters in the order of 1 μm, and a thickness/diameter ratio of about 0.04.

2.1. Apparatus

2.1.1. Hydrodynamics

The slot-flow cell, made from optically-absorbing matt black plastic, is shown in Fig. 1.

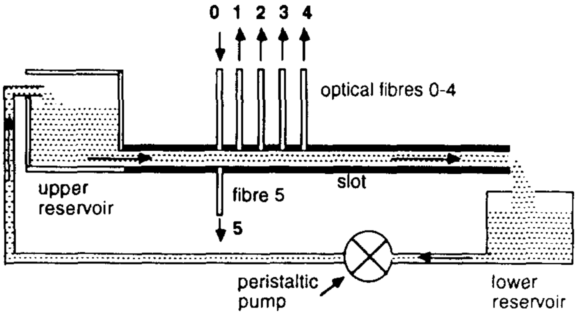

Fig. 1. Schematic diagram of slot-flow apparatus.

The gravity-driven flow rate could be varied by altering the inclination of the cell. The suspension discharged from the slot's lower end into a reservoir, from which a peristaltic pump returned it to another reservoir at the head of the slot. The slot dimensions were $2a = 3$ mm in the vertical plane and $2b = 30$ mm in the horizontal plane. The slot length was 300 mm. For a Newtonian fluid in laminar slot flow, taking $a \ll b$, the velocity $u(x)$ in the direction of the slot length is

$$u(x) = u_0\left(1 - \frac{x^2}{a^2}\right) \tag{1}$$

where x is measured from the central plane of the slot in the direction of the a-axis, and u_0 is the fluid velocity of the centre plane. The shear rate $\dot{\gamma} = \mathrm{d}u/\mathrm{d}x$, and in laminar flow the average shear rate over the slot area is

$$\dot{\gamma}_{\mathrm{av}} = \frac{u_0}{a} = \frac{3\dot{Q}}{8a^2b} \tag{2}$$

where $\dot{Q}$ is the volume flow rate in the slot. For slot flow the Reynolds number (Re) is approximately $u_0 b\rho/\eta$, where ρ is the density of the suspension. Thus $\dot{\gamma}_{\mathrm{av}} \approx \eta \mathrm{Re}/ab\rho$. Taking $\eta = 1$ mPa s for the least viscous suspension, $\rho = 1000\ \mathrm{kg\,m^{-3}}$ and a critical Reynolds number of 1000, then $\dot{\gamma}_{\mathrm{av}} \approx 50\ \mathrm{s^{-1}}$ is the upper laminar shear rate. Laminarity was confirmed by the linear paths of black particles added to a flowing white suspension and observed through a transparent wall temporarily attached to the wide side of the slot. For a given inclination of the slot the pump speed was adjusted to maintain a constant volume of suspension in the reservoir. A subsequent calibration of the pump then gave $\dot{Q}$ and $\dot{\gamma}_{av}$. A slow time-dependence of the detected photovoltage was attributed to sedimentation, and the suspension was periodically remixed by reversing the pump for a few minutes at the maximum rate.

2.1.2. Optics

The fibres were multimoded plastic (RS 368–047), of 1 mm diameter (see Fig. 1). The light input fibre (0) and four light pickup fibres (1–4) were embedded in the upper black wall of the slot, aligned with their centres 2.85 mm apart in the middle of the wall, and along the direction of the flow velocity u. A pickup fibre (5) was placed exactly opposite the input fibre. With a multiple-scattering fluid in the slot, the output fibres 1–4 collected light which had been transmitted along the flow direction, while the output fibre 5 collected light which had been transmitted across the 3 mm slot gap, parallel to the primary velocity gradient. The effect of replacing the scattering fluid with practically non-scattering water was to reduce the light power from fibres 1–4 by a factor of about 100. This showed that practically all the light detected from the turbid samples had been scattered by the sample itself, and had not reached the pickup fibre by some other route. Light, filtered to a mean wavelength of 589 nm and a half power bandwidth of 16 nm, was obtained from a quartz-halogen lamp and focused onto an optical diffuser placed over the input end of the input fibre. The various transmitted optical fluxes, from pickup fibres 1–5, were detected as a photovoltage V using a silicon photodiode photometer. Proportionality of the photovoltage V to the optical flux Φ was checked in a separate experiment by measuring V for light transmitted through two linear dichroic sheet polarisers, varying the angle α between their dichroic absorption axes. Experiment gave $V \propto \cos^2 \alpha$, and comparison with Malus' law ($\Phi \propto \cos^2 \alpha$) therefore shows that $V \propto \Phi$. To obtain a complete theoretical description of the received photosignals in terms of the suspension's multiple scattering properties will be difficult. Simple expressions exist only for the case of a laterally unbounded and parallel-sided sheet of multiple scattering material. For diffuse light incident on a scattering but non-absorbing sheet of thickness z, Kubelka [9] showed the diffuse reflectance R and transmittance T to be

$$R = \frac{Sz}{1 + Sz} \tag{3}$$

and

$$T = \frac{1}{1 + Sz}. \tag{4}$$

Here S is an inverse scattering distance which describes the propagation in a multiple scattering material. For spherical scatterers, S is related to their number density N, and the optical scattering cross-section per scatterer C_{sca}, by [10]

$$S = \frac{3}{4} N C_{sca} (1 - \overline{\cos\theta}). \tag{5}$$

Here θ is the usual polar scattering angle made by the scattered light with the unscattered incident light, and $\overline{\cos\theta}$ is the average of $\cos\theta$ weighted by the magnitude of the scattered intensity. We are unaware of expressions similar to Eq. (5) which describe S for non-spherical particles, whether randomly or non-randomly orientated. In general, both C_{sca} and $\overline{\cos\theta}$ will vary with the orientation of a non-spherical particle. Thus compared with single scattering measurements, where only C_{sca} varies with particle orientation, multiple scattering measurements are less straightforward to analyse.

Although some flux injected by fibre 0 will return to that fibre, most propagates into the fluid within the slot. Light incident on a black wall will be absorbed, so that the light flux will propagate predominantly parallel to the walls, and therefore parallel to the streamlines. This flux directionality will enable anisotropy in S to be detected.

3. Results

3.1. Polystyrene latex

Stable suspensions of 0.18 μm diameter polystyrene latex were used at various concentrations. These scattered strongly, with negligible absorption, at the wavelength used of 589 nm. The scattering parameter S was varied by changing the latex volume fraction. In a separate experiment (see [10]) the diffuse reflectance of a parallel-sided sheet of the suspension was measured as a function of its thickness, and Eq. (3) was used to analyse the data and to obtain S. Measurements were made of the photovoltage from light picked up by fibres 1–5 as a function of S, with light of wavelength 589 nm as input flux to fibre 0. The photovoltage data are plotted as $\log_{10}V$ vs. S in Fig. 2. The largely monotonic decrease of V with increasing S follows from the general prediction of Eq. (4), which describes an attenuation of the transmitted radiance by scattering. Apart from the factor of approximately 10^5, the dependence of the photovoltage on S shown by fibres 4 and 5 is similar. This is attributed to the approximately rectilinear transmission of flux to both fibres. Propagation between fibres 0–4 is approximately rectilinear because the interfibre distance is appreciably larger than the slot width, while propagation between fibres 0–5 is approximately rectilinear because the input and pickup fibres face each other across the 3-mm slot width. Thus by choice of pick-up fibres, it was possible to investigate the scattering of light which had travelled either approximately parallel to the streamlines, or approximately parallel to the velocity gradient. For any fibre-pair, the polymer latex suspensions showed no measurable flow-optical effects up to the maximum latex volume fraction ($v = 0.025$), and maximum shear rate ($\dot{\gamma}_{av} = 50\ \mathrm{s}^{-1}$).

3.2. Kaolinite suspensions

3.2.1. Effect of shear

The effect of shear was investigated for a commercial grade of kaolinite (ECC SPS grade). Optimally deflocculated suspensions of clay volume fraction $v = 0.02$ were prepared as follows. The clay (SG = 2.6) was added to deionised water and the pH adjusted to 8.5 using NaOH. A sodium polyacrylate deflocculant (Allied Colloids Dispex) was added at 2.1 mg per g dry wt. of the clay, and the suspensions mixed with a magnetic stirrer for about 24 h, checking and adjusting the pH as necessary. The SPS grade has 80 wt.% of clay platelets with an equivalent spherical diameter (ESD) less than 2 μm, and a (thickness)/(face diameter) ratio of about 0.04. Fig. 3 shows the effect on V of shearing the kaolinite suspension. The percentage change F in the photovoltage V depends on the position of the receiving fibre and on the average shear rate $\dot{\gamma}_{av}$. Fig. 3 shows the transmittance to increase for light propagated along the streamlines (fibres 1–4), and to decrease for propagation parallel to the velocity gradient (fibre 5). These data suggest the existence of orientatable and possibly deformable non-spherical entities in the suspension. Assuming a relation similar to Eq. (4) to determine the transmittance, and expecting that the entities' longest axes will preferentially orientate to be parallel to the streamlines, then the data of Figure 3 are consistent with light being

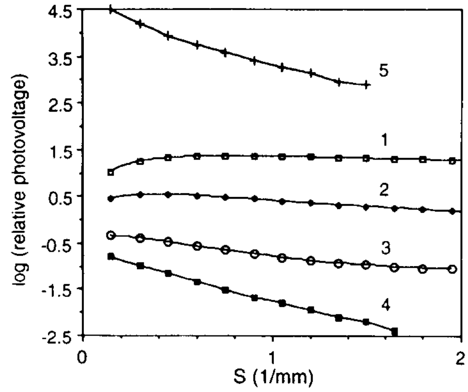

Fig. 2. Logarithm (base 10) of relative photovoltage for fibres 1 and 5, versus inverse scattering length S of polymer latex suspensions.

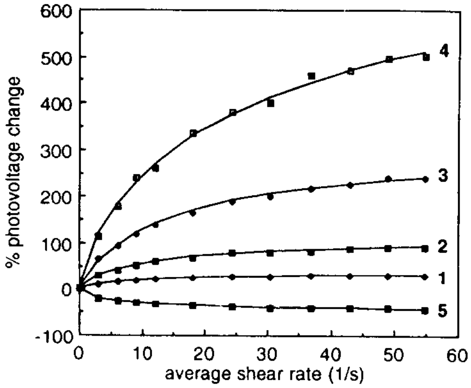

Fig. 3. Shear-induced % photovoltage change versus average shear rate for fibres 1–5. Clay volume fraction 0.02; pH 8.5; 2.1 mg Dispex added per g of dry clay.

multiply scattered most strongly when it is incident onto the greater projected area of the entity. Using very dilute ($v \approx 4.10^{-4}$) size-fractionated kaolinite suspensions where the orientating entities were discrete particles, and at a closely similar wavelength of 546 nm, Champion and co-workers [6,7] found a contrary result except for particle sizes large enough to fall within the 2–3 μm ESD range, in which case the measured turbidity increased on shearing. In our unfractionated suspensions, the proportion of such particles is small. Thus a clear distinction between very dilute and more concentrated suspensions is evident, which may arise from the difference between single and multiple scattering. Fig. 3 shows that most of the transmittance change on flow occurs for $\dot{\gamma}_{av} < 50\ s^{-1}$. A lower limit for the size of the orientating entity may be estimated by assuming that the orientation results from competition between alignment due to flow, and the randomising disorientation of rotary Brownian motion. The rotational Peclet number $Pe = \dot{\gamma}_{av}/D_r$ then determines the degree of orientation, where D_r is the rotary diffusion coefficient of the orientated entity. If $Pe \gg 1$ describes nearly complete orientation at $\dot{\gamma}_{av} \approx 50\ s^{-1}$, then $D_r \ll 50\ s^{-1}$. For an entity of diameter d then we expect

$$D_r \approx \frac{k_B T}{\eta d^3} \tag{6}$$

where k_B is the Boltzmann constant, T is the Kelvin temperature, and η is the viscosity of the suspending medium. Taking $\eta = 1$ mPa s for water at $T = 293$ K then $d > 0.4$ μm. Compared with the known particle size (80% less than 2 μm) this suggests that the orientating entities could be mostly discrete kaolinite particles, as expected [7] for an optimally deflocculated suspension, but it does not exclude the possibility of flocs.

Fig. 3 shows F to be greater for the most-separated input and receiving fibres, which can be understood as follows. From Eq. (4) we assume $T = (1 + Sz)^{-1}$ for a separation z of the injection and the pick-up fibres. If the scattering parameter changes from a quiescent value S_0, to S in shear, then the fractional change in V is

$$F = \frac{V - V_0}{V_0} = \frac{(S_0 - S)z}{1 + Sz} \tag{7}$$

which increases with z to reach a limiting value of $(S_0 - S)/S$. Thus the sensitivity to shear-induced changes of S is greatest for the most-separated fibres.

3.2.2. Concentration

Fig. 4 shows the effect of clay volume fraction v on F for light of $\lambda = 589$ nm, transmitted from fibre 0 to fibres 1 and 5, at a mean shear rate of $\dot{\gamma}_{av} = 50\ s^{-1}$, at which complete particle orientation can be assumed. The suspension was prepared for optimal deflocculation as described in Section 3.2.1. The results are qualitatively explicable via Eq. (7). For small v, and hence small S, then $Sz \ll 1$, giving $F = (S_0 - S)z$. The initial increase and decrease in the fractional change shown in Figure 4 thus correspond to the expectation that both S_0 and S increase with increasing clay volume fraction v. Fibre 1 receives light transmitted parallel to the streamlines, and here $F > 0$ shows that $S < S_0$ for light incident onto mostly the edges of particles. Fibre 5 receives light transmitted parallel to the velocity gradient, and here $F < 0$ shows that $S > S_0$ for light incident onto mostly the faces of particles.

When v is large, $Sz \gg 1$, and Eq. (6) gives $F = (S_0 - S)/S$. The found independence of F on v suggests that when $v > 0.05$, both S and S_0 depend on v in a similar way.

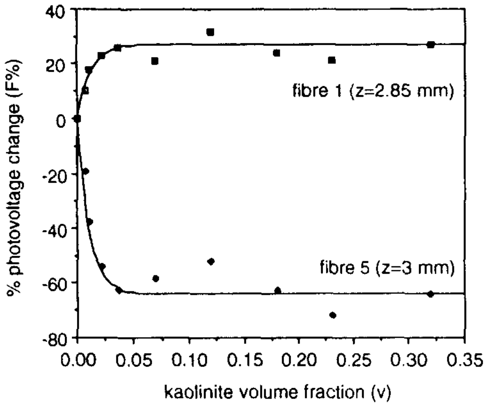

Fig. 4. Shear-induced % photovoltage change versus kaolinite volume fraction for fibres 1 and 5. Suspension pH 8.5; 2.1 mg Dispex added per g of dry clay.

3.2.3. pH and flocculation

SPS grade kaolinite was made into an aqueous suspension of volume fraction $v = 0.01$, using 2.1 mg of the deflocculant Dispex per gram of dry clay, and adding NaOH to obtain a pH = 8.5, as in Section 3.2.1. Measurements made of the static ($\dot{\gamma}_{av} = 0$) scattering parameter S_0, using a single optical fibre bundle [10], showed that S_0 was unchanged by pH, remaining at 2.65 mm^{-1}. This suspension was used in the slot-flow cell, the photovoltage at $\lambda = 589$ nm being measured for fibre 3. The inter-fibre separation was 8.55 mm, thus $S_0 z \approx 23$, showing that the experiment occurred well into the multiple scattering regime. The photovoltage measured as $\dot{\gamma}_{av}$ was changed from 0 to 50 s^{-1}. The suspension was well-mixed and divided into two parts. The pH of one part of the suspension was incrementally decreased by successive additions of 1 M HCl. The pH of the other part was increased by successive additions of 1 M NaOH. Fig. 5 shows the effect of pH on F for a shear rate change from 0 to 50 s^{-1}, showing that F decreases rapidly for pH < 4. The behaviour with pH shown in Fig. 5 may be compared with the pH-dependence of the fractal dimension d_f of kaolinite flocs found by Herrington and Midmore [8], where the behaviour of their d_f data for 1mM KCl closely resembles our data. These workers used a quasi-elastic light scattering method to investigate a different kaolinite (ECC Supreme) in suspensions dilute enough ($v = 8.5 \times 10^{-5}$) to avoid multiple scattering. The difference between the clays is not significant in this case; SPS has 80% less than 2 μm ESD, whereas for Supreme 95% is less than 2 μm. Herrington and Midmore [8] found a rapid transition from a tenuous floc structure for pH > 4.5 to a dense floc structure for pH < 4. The relative floc tenuosity was obtained from measurements of d_f in suspensions. Our results at high concentration (Fig. 5), and those of Herrington and Midmore [8] (their Fig. 2) at much smaller concentration, show a closely similar pH behaviour in which d_f and F appear to be inversely related, with a rapid change in both quantities at pH ≈ 4. Thus the flow-optical technique at high concentration appears to reflect the pH-behaviour of the fractal properties measured at a much smaller concentration. It is possible that the rapid increase in F for pH > 4 results from the increased tenuosity of the flocs in this pH range, particularly if floc tenuosity may be associated with floc fragility or deformability in shear flow.

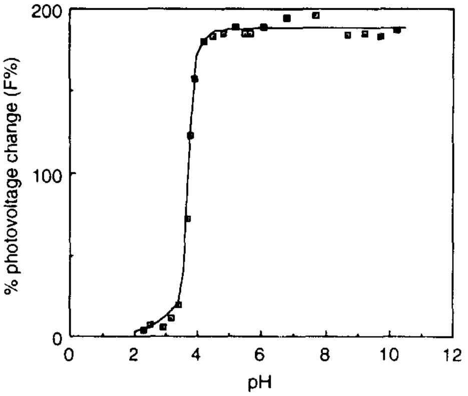

Fig. 5. Effect of pH on shear-induced % photovoltage change at fibre 3 for kaolinite suspension of volume fraction 0.01, with 2.1 mg added Dispex per g of dry clay.

Shih *et al.* [11] considered a gelled network as a collection of close-packed, linked fractal flocs, with Euclidean dimension E. From their expressions for the yield strain and the elastic modulus, the yield stress = (modulus) × (yield strain), can be written $v^{(E-1)/(E-d_f)}$, independently of the link strength between the flocs. Thus the yield stress is expected to depend on pH through d_f. However, for kaolinite concentrations similar to ours, neither the Bingham yield stress (τ_B) data of Herrington and Midmore [8], nor those of Williams and Williams [12], show any effect of pH in the region of pH ≈ 4. The unexpected absence of a pH effect on τ_B was explained by Herrington and Midmore [8] by supposing that in concentrated kaolinite suspension a floc structure exists to a lower pH than in dilute suspension. Our flow-optical results do not support their supposition. An alternative explanation may be that the correct rheological measure of structure or flocculation is the shear stress τ extrapolated to zero shear rate, τ_0, rather than the Bingham yield stress τ_B. For a true Bingham fluid $\tau = \tau_B + \eta_B \dot{\gamma}$, where η_B is a Bingham plastic viscosity, and $\tau_B = \tau_0$. However, the rheological data of Williams and Williams [12] show that kaolinite suspensions are shear-thinning, and deviate significantly from the Bingham model particularly at low shear rates ($< 100\ \mathrm{s}^{-1}$) which define τ_0. Thus although τ_B is a measure of the shear-thinning behaviour of a suspension, it is unlikely to be a measure of structure or flocculation.

3.2.4. Effect of deflocculant

An SPS grade kaolinite suspension of $v = 0.15$ was prepared without Dispex, and the pH adjusted to 8.5 as described in Section 3.2.1. This sample was studied in the slot-flow apparatus, using fibre 3, $\lambda = 589$ nm, and measuring F as the Dispex concentration was increased. At zero shear rate the quiescent photovoltage drifted owing to sedimentation, and F was therefore measured from the change in photovoltage between the mean shear rates of 3 and $50\ \mathrm{s}^{-1}$. Fig. 6 shows the effect of the sodium polyacrylate dispersant (Dispex) on F. From the behaviour of F with pH (Section 3.2.2), where a decrease of F is associated with deflocculation, the maximum in F over the range 0 to 0.2% wgt Dispex suggests a maximum deflocculation. Viscosity (η) data is also shown also in Fig. 6, taken from the data of Beazley [13]. The minimum in η as a function of Dispex concentration coincides closely with the maximum of F at about 0.17 wt.% of Dispex, supporting the flow-optical result. Above 0.17 wt.% of Dispex the decrease of F and the increase in η with extra added Dispex suggests that reflocculation is occuring, possibly owing to extra ions contributed by the Dispex.

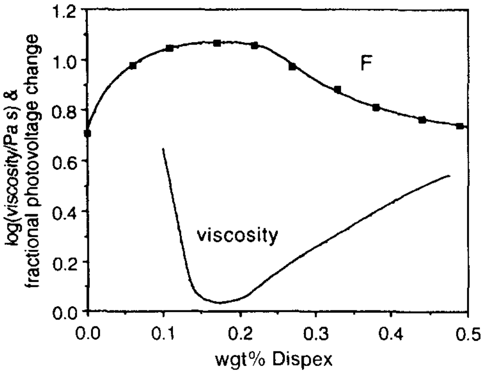

Fig. 6. Effect of Dispex added to a clay suspension of pH 8.5 on the viscosity (line) and the shear-induced fractional photovoltage change (marked line).

4. Conclusion

The diffuse optical transmittance through a concentrated kaolinite suspension has been shown to depend on the shear rate. The proposed origin of this optical effect is an orientation of kaolinite particles or flocs. The changes of transmittance (F) on shear are shown to correlate closely with other measures of flocculation, such as the floc fractal dimension d_f, and the suspension viscosity when a chemical deflocculant is added. The present technique, although using multiply scattered light, has been shown to give useful results at a concentration much greater than allowed by optical measurements in the single scattering regime. We have not attempted a theoretical description of the flow-induced anisotropy of optical transmission in the multiple scattering regime.

This work has been carried out in part within the DTI Colloid Technology Project (GHM). One of us (PRW) thanks the London Guildhall University for receipt of a Research Assistantship.

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