On the role of stress-induced migration
on time-dependent terminal velocities of falling spheres

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Abstract: There is experimental evidence to suggest that even under steady-state conditions the velocity of solid spheres or bubbles moving through viscoelastic fluids can become time dependent. One of the possible explanations offered for interpreting this phenomenon has been the generation of a polymer depleted layer in the line of passage of the particles, which disappears due to the counterbalancing effect of molecular diffusion in the long range. We have done some careful experiments and measured these concentrations to show that no such depletion layers are formed. Alternative explanations of the phenomenon have been examined and the importance of the possible effects of microstructures generated through temporary associations has been emphasised.

Key words: Falling spheres; viscoelastic fluids; stress-induced migration

1. Introduction

The subject of migration of macromolecules has attracted the attention of researchers for some time now. The speculation that macromolecules migrate under a variety of conditions has been put forward by many investigators. The validity of this speculation itself is open to some question and diverse views on this approach have been expressed. This paper addresses itself to the question of providing an answer by obtaining an experimental verification of such an assertion. Before we do this, however, it is important to address the question of macromolecular migration in some detail.

1.1 Theoretical framework on macromolecular migration

The suggestion that migration of macromolecules was possible in tube flows was made in the 1950s. For instance, Garner et al. [1] and Busse [2] speculated that the random coils of high-molecular-weight polymer will get distorted to a higher degree near the tube wall; thus, they will have reduced conformational entropies. The entropic driven force arising out of this was postulated to lead to a macromolecular migration away from the wall region. Garner and Nissan [1] suggested that such molecular migration

may be responsible for the slip phenomena in capillary tubes. An approximate analysis of macromolecular migration was reported by Schreiber et al. [3].

Metzner et al. [4] and Tirrell and Malone [5] based their arguments on the observation that, in deforming fluids, macromolecules stretch and align themselves, thereby changing the free energy levels, in any nonhomogeneous flow field where there is a spatial variation of strain rate. Consequently the molecular extension and orientation and, therefore, the free energy becomes position dependent. In order to compensate for the spatial variation in free energy levels, concentration gradients are set up. The net effect is that the macromolecules migrate towards the region of low strain rate. These arguments have been criticised by some, since the method followed for the calculation of concentration profile apparently implies the application of equilibrium thermodynamics to an essentially non-equilibrium situation.

Tirrell and Malone [5] used a bead spring model to analyse the radial migration of macromolecules in a Poiseuille flow through cylindrical tubes. In a subsequent publication, Aubert and Tirrell [6, 7] have termed the thermodynamic argument for molecular migration as "ad-hoc" and concluded that entropy gradients do not lead to macromolecular migration. They show that such molecules migrate relative to the

undisturbed centre of mass solvent velocity. The only basis for their argument was their inability to reach an agreement with the thermodynamic analysis via micromechanic treatment of polymer solutions.

Shafer et al. [8] showed that the observed migration of DNA molecules in circular Couette flow results directly from the curved nature of flow. Aubert et al. [7] found that there was some form of migration in all flows, be they curved or uncurved. In parallel flows it was surmised that there was no migration perpendicular to the direction of flow. This means the polymer molecule will just lag or precede the flow along a single streamline. Further it was found that cross streamline migration takes place in curvilinear (for example, circular Couette) flow, when the curved flow was approximated as quadratic flow.

Sekhon et al. [9] showed the significance of hydrodynamic interaction on migration and how it fundamentally alters its characteristics. Indeed they showed that with the addition of hydrodynamic interaction terms, cross-streamline migration was possible, even in parallel flows.

Significant contributions to our theoretical understanding of the migration phenomena have been made by Brunn and coworkers [10 – 15]. A mechanistic analysis of slip has been proposed by Brunn [10] for the flow of dilute polymer solutions idealized as Hookean dumbbells. Brunn postulated that there is a hard core repulsion between the polymer molecule and the solid wall. It leads to the formation of a low viscosity layer near the wall. It is believed that any repulsion forces would give a deflection distance of the order of one molecular diameter. However, the slip layer thickness is at least an order of magnitude larger than the molecular diameter of the polymer. Therefore, it seems unlikely that Brunn's explanation can account for the large slip effects observed in the flow of polymer solutions. Brunn and Chi [11] used a bead spring model and by exploring the kinetic theory consequence of the hydrodynamic force it was shown that non-uniform concentration profiles are to be expected in non-homogeneous flows. Brunn [12] also calculated the cross migration velocity of linear polymers in non-homogeneous flow fields. The approximation used is valid only for the free draining limit and in the final form of the equation the cross migration velocity does not display molecular weight dependence. In his further work, Brunn [13] deduced that in the case of shear flows, the thickness of wall layers was independent of the strength of the flow field. Also Brunn's work [14] on diffusion in concentrated polymer solutions indicates that for the tube flow the degree of non-uniformity in concentration

will be generally small and the time scales required to reach these will be very large. In recent papers Brunn and Grisafi [15] have studied wall effects in simple shear flow of dilute polymer solutions, elucidating results for very narrow and very wide channels. On the basis of Hookean dumbbell macromolecular model, they have pointed out that the concept of a slip velocity or that of a pure solvent layer close to the wall, though extremely useful for the shear stress, may not be as useful in flows, where shear and normal stress effects are coupled.

In recent years more exact calculations have appeared. For instance, Petruccione and Biller [16] modelled a dilute polymer solution by linear and non-linear dumbbells suspended in Newtonian solvent. The Langevin equations governing the motion of the dumbbells in the tube were solved with the help of Brownian dynamics simulation. The model showed typical features such as the slip effect, the flow enhancement, and the reduction in viscosity with decreasing tube radius.

1.2 Experimental evidence on migration of macromolecules

Inspite of the extensive theoretical work on migration of macromolecules, it appears that there is no clear-cut and direct evidence of such depletion layers in highly stressed regions under flow conditions of interest. The set of papers by Ausserre et al. [17 – 18] provide some data under quiescent conditions obtained by using evanescent wave-induced fluorescence technique. They studied the interfacial layer between the polymer solution and a solid barrier for a semi-flexible polymer such as xanthan and demonstrated the presence of submicron depletion layer.

The bulk of the other experimental evidence in the literature pertains to the detection of changes in some macroscopic phenomena related to pressure drop [4], reduced film thickness [19], altered residence time distribution [20], enhanced mass transfer [21], etc., and these have been invariably linked through appropriate models to the depletion layers created by migration of macromolecules. Recently, Mueller-Mohnseen et al. [23] tried to make a direct determination of apparent slip for the flow of a polyacrylamide solution and obtained velocity profiles within a distance of 0.15 microns from the wall by using laser micro anemometer technique. They showed by an indirect calculation that in the slip layers the viscosity of the fluid is likely to be several times smaller than the viscosity of the bulk polyacrylamide solution measured by a conventional viscometer. The above observations clearly in-

dicated that although a variety of authors have predicted the presence of substantial depleted layers in highly stressed regions, there is no *direct* experimental evidence for the presence of such layers of low polymer concentration. The only direct evidence could be through the measurements of actual concentration profiles; it was this gap that prompted this investigation.

1.3 Anomalies in terminal velocities of falling spheres

While looking at the possible experimental systems for a qualitative detection of migration in systems where macromolecular solutions are subjected to non-homogeneous deformations, we came across the interesting anomalies that have appeared in the literature concerning the time dependent terminal velocities of bubbles and solid spheres [24 – 27]. Based on these papers, as well as basing on some of the work done in our laboratory, it appeared that there is now a conclusive evidence to show that the terminal velocities of bubbles and solid spheres do depend upon the time interval between the injection of the bubbles or solid spheres in viscoelastic solutions (aqueous solutions of polyacrylamide). Figure 1 shows some typical data reported in the literature on the motion of gas bubbles and solid spheres where such anomalies have been observed. It is seen readily that when the time interval between the successive injection of rising bubbles or dropping of spheres is large, constant terminal velocities are obtained, irrespective of the time interval. On the other hand, when this interval is rather small, then the terminal velocities do depend upon the time of injection. The reason for this particular phenomenon is not clear and so far only some conjectures have been made. One of the interesting conjecture was made by Cho et al. [26] in trying to explain the time dependence of terminal velocities of spheres in aqueous polyacrylamide solutions. According to them, when a sphere moves through a viscoelastic medium, it opens or breaks a high molecular weight polymer matrix locally. As the sphere moves through the centre line, the solvent immediately fills the space left by the sphere in the central region, thus producing a relatively high concentration of solvent locally and thereby reducing the polymer concentration in this region. According to Cho et al. [26] the spheres fall faster under such disturbed conditions than those in the undisturbed condition. The low concentration of polymer molecules at the tube centre is expected to create spatial concentration gradients, and if this happens, then the polymer molecules will diffuse towards the centre line.

What is essentially suggested by Cho et al. [26] is that there is a concentration gradient created across the tube in which a sphere is dropped. This gradient is particularly sharp at the centre line, where a region substantially depleted in polymer molecules should exist, whereas away from it a region rich in polymer molecules should exist. In view of the background we have provided on the phenomena of stress-induced migration in the foregoing, we wondered as to whether the passage of a sphere through the centre line of the tube creates a highly stressed region there and whether the macromolecules might migrate away from this highly stressed regions to those of low stress regions away from the centre line. At sufficiently long times, of course, the concentration change would even out due to molecular diffusion. Thus when the spheres are dropped in quick succession then the depletion layer may exist in the central region for a longer time since the migrated macromolecules will take a longer time to diffuse back towards the centre line. The reverse phenomena should occur when enough time interval would be provided between the dropping of successive spheres. This possibility suggested by the experiments of Cho et al. [26] has been the motivation behind the present work. We performed careful experiments to measure the concentration changes of the polymer in the centre region to substantiate the basic hypothesis postulated by Cho et al. [26].

2. Experimental

The apparatus used for carrying out the sphere-dropping experiment consisted of a cylindrical glass column (internal diameter 8.6 cm, height 37.5 cm). A special system was designed to drop the individual spheres at the centre of the column. Stainless steel spheres with four different diameters (range 0.2 – 0.476 cm) were chosen to conduct these experiments.

Aqueous solutions of polyacrylamide (Separan AP-30) were used as test fluids. Polymer concentration in the range of 4500 to 7500 wppm were used. Experiments were conducted by dropping 100 steel balls of the same size along the centre line of the column after definite time intervals. The time intervals between successive dropping of spheres were varied from 2 s to 30 s. The initial and final concentrations of polymer molecules along the centre line of the column were measured. The samples at half the height of the column were withdrawn using a hypodermic syringe. A special arrangement was made to keep the inserted needle exactly vertical along the centre line so as to ensure that the test fluid along the center line was removed. The polymer concentrations were measured by the method of analysis described later.

Actual velocity measurements on falling spheres were carried out in a cylindrical glass column (internal diameter 3.5 cm, height 45.0 cm). Two photosensors were fitted, one at 5 centimeters and other at 15 centimeters from the bottom. These were illuminated by bulbs fitted at the opposite sides of the column at the same height. As the sphere went down the centre line of the column, the beam of light illuminating these photosensors was cut off and the time required for the ball to pass between the two sensors was recorded automatically by means of a digital time recorder which had an accuracy of 1 ms. The velocity measurements on the falling sphere were first carried out by using two Newtonian fluid viz. glycerol and ASTM standard oil (viscosity standard S 2000). The stainless steel spheres (diameter 0.476 cm) were dropped in these solutions by varying the time interval between the dropping of successive spheres from 5 s to 30 s.

The measurements of the concentration of the polymer in aqueous solutions of Separan AP-30 were carried out by the method of analysis described by Scoggins et al. [28]. A buffer solution with pH of 3.5 was prepared by using 25 g sodium acetate trihydrate, 110 ml glacial acetic acid and 0.75 g hydrated aluminium sulfate. The pH was adjusted to 3.5 with glacial acetic acid and then diluted to 1000 ml with water. Starch-cadmium-iodide colour reagent was prepared as described by Lambert [29] except that we used Sisco Research Laboratories iodometry grade potato starch powder. Sodium formate (1% solution) and saturated bromine water were the other reagents used.

Five ml of buffer solution was taken in a 50 ml standard volumetric flask. To it 5 ml of aqueous sample solution containing about 50 to 150 μg polyacrylamide was added. The solution was allowed to react with bromine and excess was
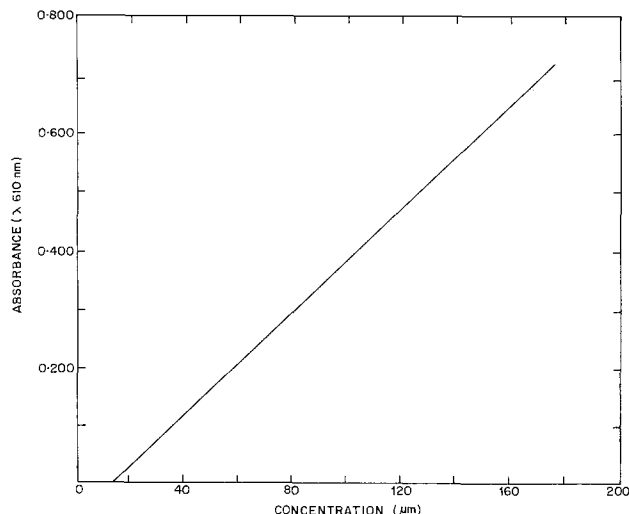

Fig. 2. Standard calibration curve of absorbance (wavelength = 610 nm) vs concentration of Separan AP-30 in aqueous solution forming starch-tri-iodide complex

neutralized by adding 5 ml of 1% sodium formate solution. After exactly 5 min, 5 ml of starch-cadmium iodide reagent was added and the solution was diluted to volume with water. After 15 min the absorbance was measured at 610 nm with water as a reference. From the standard calibration curve (see a typical curve in Fig. 2) the concentration of the
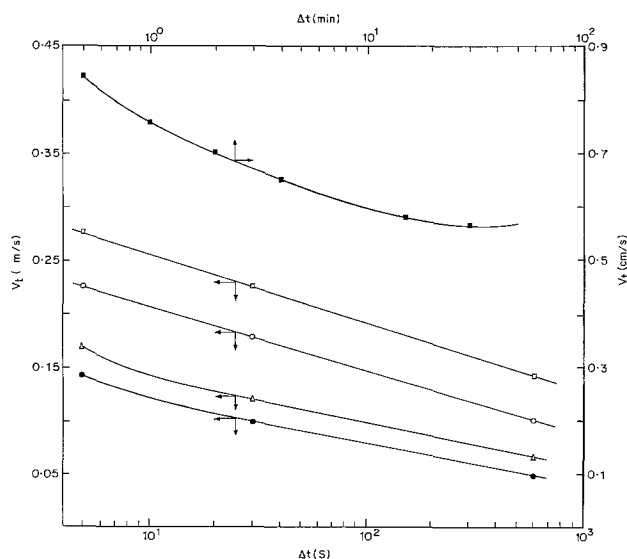

Fig. 1. Effect of injection period on the terminal velocity of bubbles and spheres in polyacrylamide solution observed in the literature. The bubble rise data with the following bubble volumes (m³) ● − 4.4×10⁻¹⁴, △ − 5.9×10⁻¹⁴, ○ − 13.6×10⁻¹⁴, □ − 21.0×10⁻¹⁴ are by Dekee et al. [25] and the sphere-dropping experiment data, ■ − 0.317 cm diameter stainless steel sphere is by Cho et al. [26]
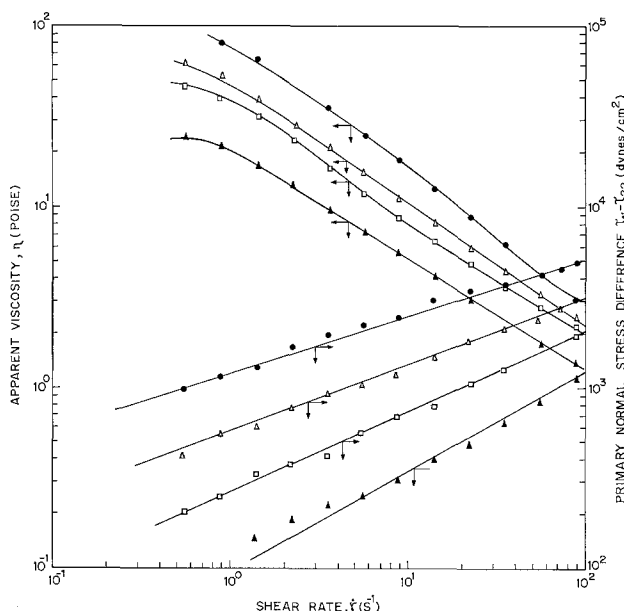

Fig. 3. Apparent viscosity-shear rate and primary normal stress difference-shear rate behavior for aqueous Separan AP-30 solution (cone-and-plate data) with concentrations (wppm) ▲ 4600, □ 6600, △ 7800, ● 10000
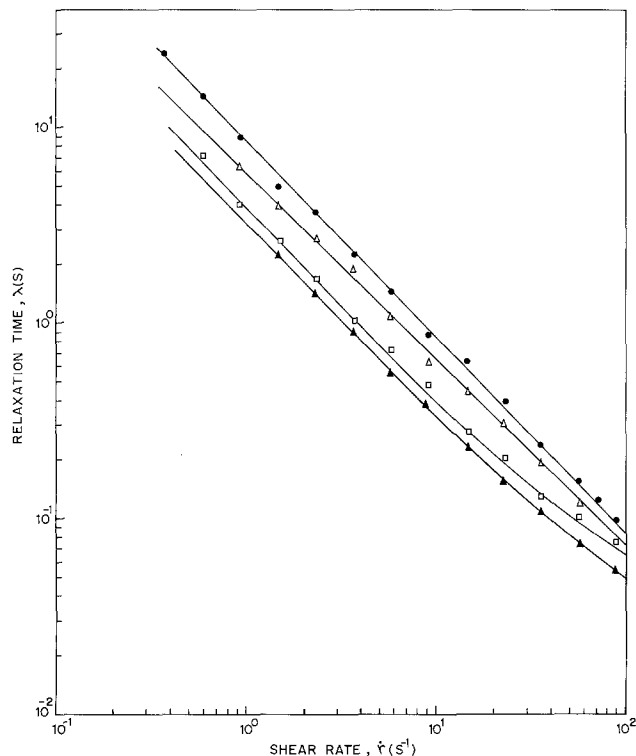
Fig. 4. Relaxation time vs shear rate for aqueous Separan AP-30 solutions (cone-and-plate data) with concentrations (wppm) ▲ 4600, □ 6600, △7800, ● 10000

solution was determined. Absorbance measurements were carried out using a Shimadzu uv 240 spectrophotometer. The technique of analysis was quite accurate and was seen to give results that were accurate to within ±20 ppm of polyacrylamide.
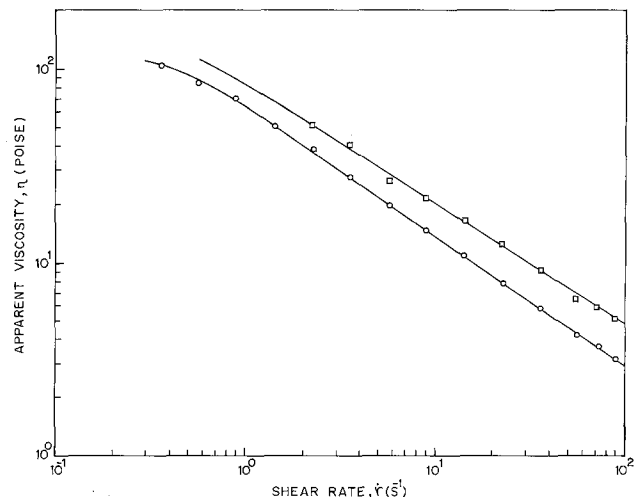

Fig. 5. Apparent viscosity vs shear rate for 7500 wppm Separan AP-30 solution in □ Ethylene glycol, ○ Formamide (cone-and-plate data)
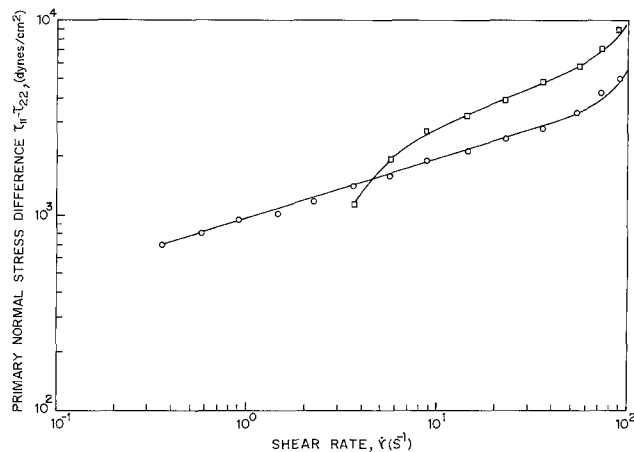

Fig. 6. Primary normal stress difference vs shear rate for 7500 wppm Separan AP-30 solutions in □ Ethylene glycol, ○ Formamide (cone-and-plate data)

The rheological characterization of some of the fluids used in the falling sphere experiments was carried out by using a Weissenberg Rheogoniometer (Model R-19). It was difficult to generate reliable primary normal stress difference data in the lower range of concentrations and hence it has not been reported. The rheograms for the solutions are shown in Figs. 3 – 7. The data are reported in terms of apparent viscosity ($\eta = \tau_{12}/\dot{\gamma}$) and the primary normal
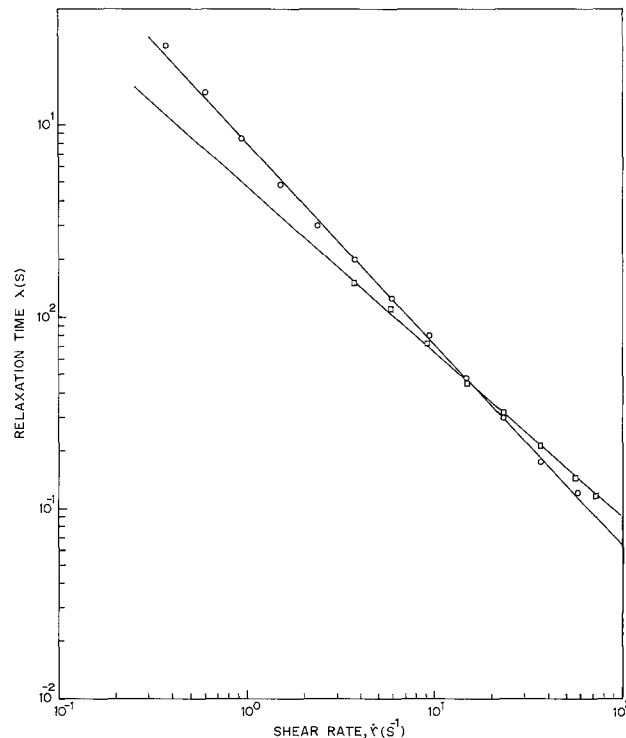

Fig. 7. Relaxation time vs shear rate for 7500 wppm Separan AP-30 solutions in □ Ethylene glycol, ○ Formamide
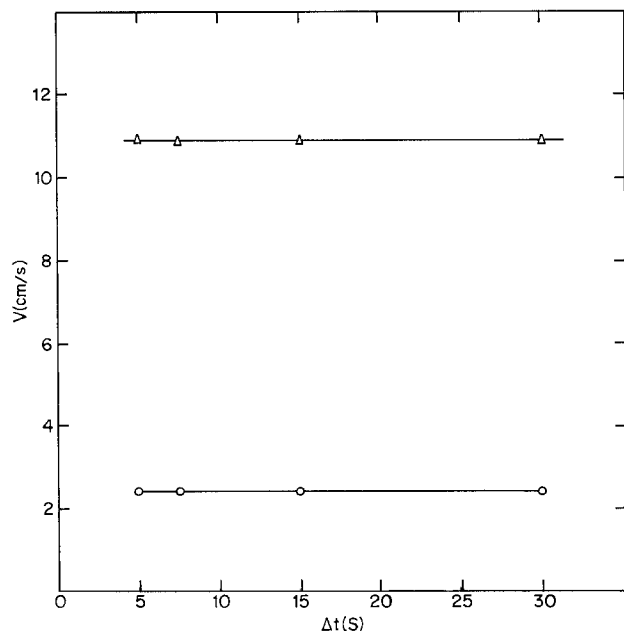
Fig. 8. Effect of time interval between dropping of successive spheres (diameter 0.476 cm) on their velocity in Newtonian fluids ○ — ASTM standard oil, △ — glycerol
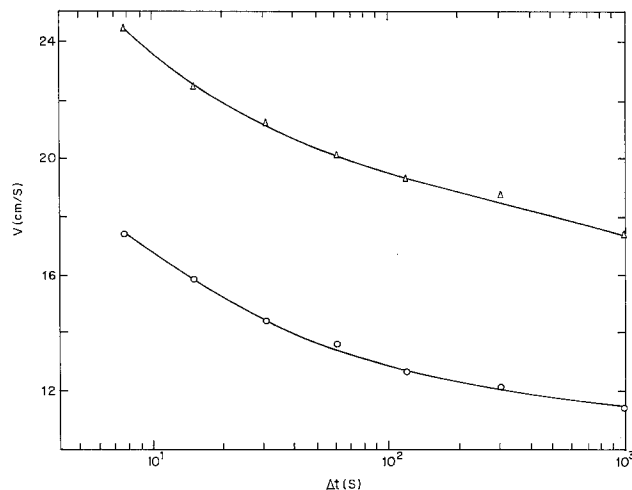

Fig. 9. Effect of time interval between successive dropping of spheres (diameter 0.476 cm) on their velocity in polyacrylamide (Separan AP-30) solution with concentration (wppm) ○ — 7850, △ — 6600

stress difference $(\tau_{11} - \tau_{22})$. The range of shear rates over which it was necessary to obtain data was approximately estimated as being of the order of the ratio of the settling velocity to the diameter of the sphere.

In order to judge the extent of viscoelastic relaxation of the fluid and its influence on the terminal settling velocities, it was necessary to quantify the rheological data in terms of an apparent relaxation time λ. This was defined as:

$$\lambda = \frac{\tau_{11} - \tau_{22}}{2\tau_{12}\dot{\gamma}} \ .$$

It is readily seen that the values of λ are in the range of 10^{-1} s to 20 s.
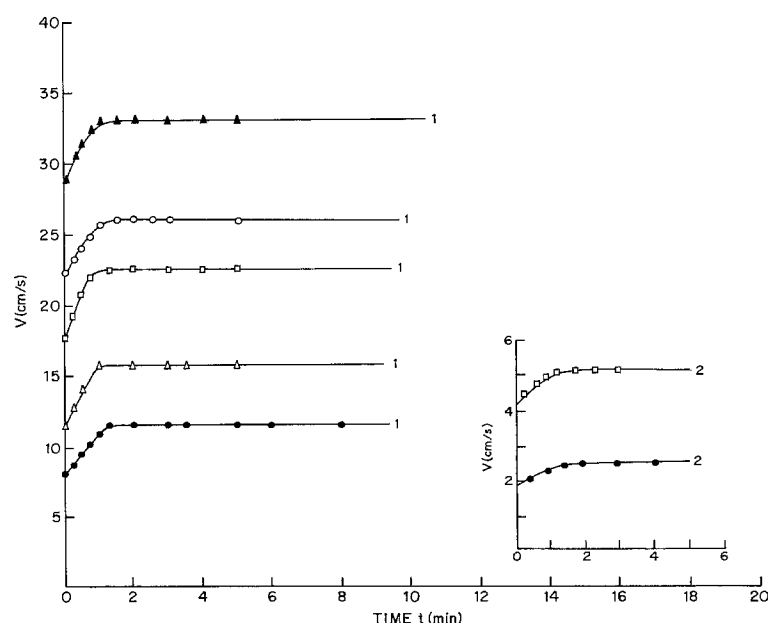

Fig. 10. At a fixed time interval ($\Delta t = 15$ s) increase in the velocity of spheres with time in falling sphere experiments in aqueous polyacrylamide (Separan AP-30) solution with concentrations (wppm) ▲ — 4600, ○ — 5500, □ — 6600, △ — 7800, ● — 10000. Plot No. 2 sphere diameter = 0.137 cm. Plot No. 1 sphere diameter = 0.467 cm

3. Results and discussion

3.1 Velocity data

Figure 8 shows data on velocities of the moving spheres in glycerol and ASTM standard oil as a function of the time interval between dropping of successive spheres. It was observed that the velocity of the sphere in the column was independent of the time interval between successive sphere dropping, as it should be. This standardization was necessary to make sure that there were no spurious effects in the experiments conducted by us.

Figure 9 illustrates our results of velocity of falling sphere (diam 0.476 cm) plotted against the time interval between dropping of successive spheres in aqueous solutions of Separan AP-30. There is an increase in the velocity as the time interval between successive dropping of spheres is decreased. Figure 10 shows our data of velocity of falling spheres vs time. These velocity measurements were being carried out in aqueous solutions of Separan AP-30 with different concentrations keeping the time interval between successive dropping of spheres constant ($\Delta t = 15$ s). The trends observed by us are quite consistent with those reported in the past in the literature [26].

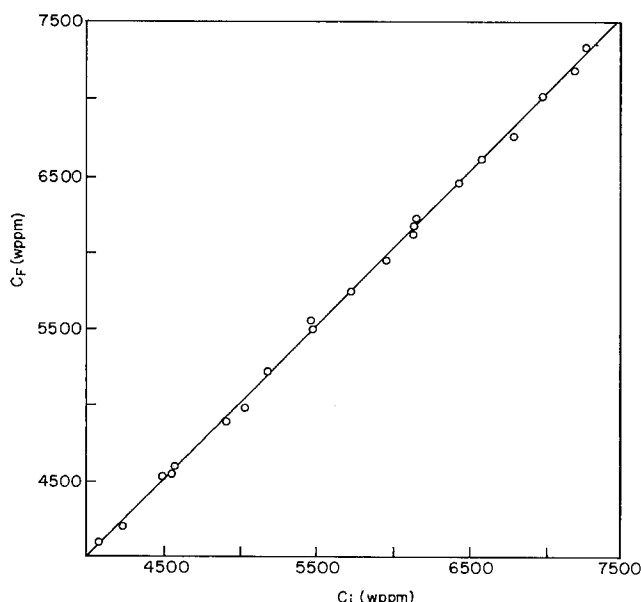It is important to note that not all our data are in the creeping flow regime. In fact the range of Reynolds numbers in which the data are reported varies from 0.05 to 15. However, we are not deeply concerned about the exact regime, since we were concerned more about creating a highly stressed region in the centre of the tube by letting the sphere pass at a rapid rate and then detecting as to whether the concentration changes occurred in the direction that was anticipated.

3.2 Concentration changes

The key results of this work are presented in Fig. 11. C_i represents the concentration of the polymer in the aqueous solution at the beginning of the sphere dropping experiment, whereas C_F represents the concentration when the ball-dropping experiment was completed. If migration of macromolecules from the centre line had occurred, then C_F would have been lower than C_i. What we actually find is that C_i is consistently equal to C_F throughout the range of variables covered experimentally in this work. No migration from the centre line as postulated by Cho et al. [26] or, as suspected on the basis of stress-induced migration postulates, has thus been observed by us.

What then is the reason for the time-dependent velocities in Figs. 1 and 9? Before we answer that question we must examine as to whether the experimental system used by us was an accurate and definitive one for the objectives set up by us.

Firstly, was the concentration change expected on the basis of the change in velocity large enough to be detected, particularly in view of the fact that our technique of measurement of polymer concentration was accurate to within ± 20 ppm? We examined this carefully. We assumed that the major contribution to skin friction of the falling sphere occurred in the vicinity of the sphere, in fact, this forms the basis of the popularly used approximation technique for drag calculation used by Acharya et al. [30 – 32] and others [33]. We estimated with this approximation that the concentration changes in the centre region should have been of the order of 200 ppm to 1000 ppm, which is larger than the ± 20 ppm range of experimental accuracy used by us. This means that if at all there was migration, we would not have missed it.

The second question that assumes importance was whether, in the experimental system we used, there were any problems due to the recirculation patterns in the cylinder in which the sphere moved. Note that movement of 100 spheres in the downward direction would cause a downward flow and, hence, there would be a compensating upward flow. We did our experiments in a cylinder of 8.6 cm diameter and 37.5 cm height. The total volume of the system was

Fig. 11. Final vs initial polymer concentration (wppm) in aqueous solution of polyacrylamide (Separan AP-30) in falling-sphere experiment

thus of the order of 2000 cm³. If 100 spheres of say, 0.317 cm diameter were dropped, the total volume displacement due to sphere dropping would be only 1.67 cm³ during the time of experiment; this is barely 0.08% of the total volume. It is known that mixing times are typically three to five times the circulation times [34]. In other words, unless at least 6000 cm³ of solution had moved around during the time the sphere dropping experiment was conducted, no mixing would have occurred. This volume is very large in comparison to the 0.5 to 5 cm³ volume that was displaced in the range of experiments done by us. In other words, the possibility of our having obtained the same concentation, i.e., practically equal values of C_i and C_F due to gross circulation and the resultant mixing is ruled out.

If our experiments are reasonable, then in the light of the above comments we conclude that the dependence of terminal velocities on frequency of sphere dropping cannot be explained with the hypothesis proposed by Cho et al. [26].

3.3 Possibility of the influence of hydrogen bonded structures

Kulicke et al. [35–37] extensively studied the phenomena of time-dependent viscosity decrease observed in aqueous solutions of polyacrylamide and poly (acrylamide-co-sodium acrylate). They proposed a model and interpreted these phenomena as being due to the conformational transition within the single polymeric chains controlled via intramolecular hydrogen bonding (see Fig. 12) causing a viscosity decrease in polyacrylamide solutions. Hence, those additives which influence the hydrogen bonding, prevent these long-term conformational changes due to hydrogen bonding, and thereby, give stable solutions. Kulicke et al. [38] reported that solutions of polyacrylamide in formamide, ethylene glycol, and solution of poly (acrylamide-co-sodium acrylate) in 0.5 M NaCl show no time-dependent viscosity loss.

Kulicke et al. [38] investigated the possible existence of hydrogen bonds and their role in time-dependent viscosity loss in solution of polyacrylamide using IR spectroscopy. In the presence of additives such as formamide and ethylene glycol, polyacrylamide solutions show no time-dependent viscosity loss. These observations indirectly indicate that the hydrogen bonded structures, which are responsible for time-dependent loss in aqueous polyacrylamide solutions, are absent in the above-mentioned case. Indeed additives such as formamide are known to be used commonly for destroying hydrogen bonded
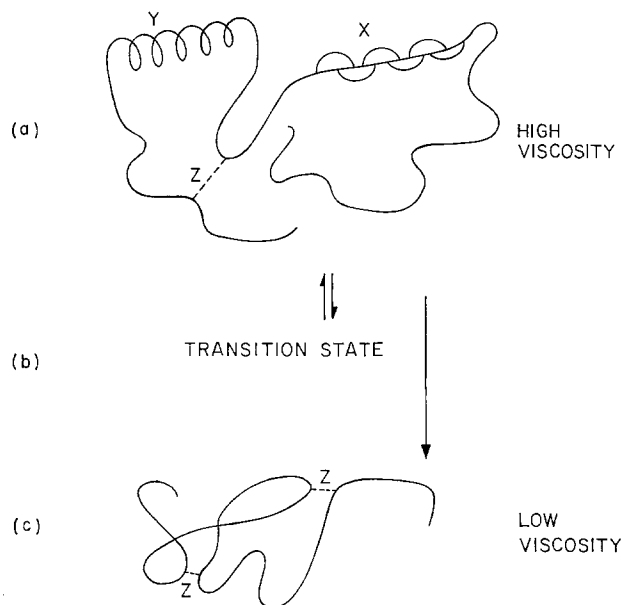

Fig. 12. Conformational transitions via intramolecular hydrogen bonding in polyacrylamide solution. Model given by Kulicke et al. [35]. X, Y, Z represent different structures due to hydrogen bonding

structures such as in the case of enzyme denaturation [39]. We wondered whether the "structured" polyacrylamide solutions stabilized by hydrogen bonds were temporarily disturbed when the spheres were dropped. If this was to be true then due to the reversibility of the phenomena, the solution could be slowly restored to its structured state after the sphere-dropping experiment was stopped. The easiest way to test this hypothesis would be to add formamide or ethylene glycol to polyacrylamide. The hydrogen bonds would be destroyed and no structure would exist due to the absence of intramolecular hydrogen bonding and then we should get time-interval-independent velocities in the falling ball experiments.

Figure 13 shows the plots of velocity of the falling sphere (diam 0.476 cm) against time interval between dropping of successive spheres in solutions of polyacrylamide in formamide and ethylene glycol. It is interesting to observe the velocity behaviour of moving spheres in these mediums. In the case of solutions of polyacrylamide in formamide and ethylene glycol the solution viscosity is more than that of aqueous solutions when compared at the same concentration and also the percentage change in the time-interval-dependent velocities of falling spheres observed is far more than that observed in the case of aqueous solutions. In fact, exactly the reverse phenomena should have taken place if the role of in-
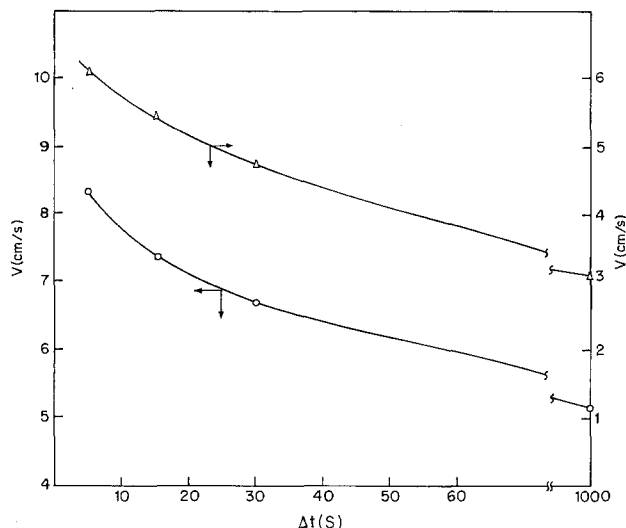
Fig. 13. Effect of time interval between successive dropping of spheres (diameter 0.476 cm) on their velocity in polyacrylamide (Separan AP-30) solution with concentration 7500 wppm using O − Formamide, △ − Ethylene glycol as solvents

tramolecular hydrogen bonding was as that postulated earlier. These experiments, therefore, clearly rule out the possibility of changes of structures on application of shear in such systems to be responsible for the change in velocities of falling spheres.

3.4 Restoration time

From Fig. 10 it is clearly seen that an increase in the velocity of a falling sphere is attained rapidly, i.e., an asymptotic value of maximum velocity at that particular time interval is reached within 1 − 2 min. Therefore, an attempt was made to measure the characteristic restoration time of the fluid. This characteristic restoration time is that time interval after which the ball dropped in the disturbed fluid moves with a velocity within 2% of the velocity of the first ball moving in the undisturbed fluid. We carried out experimental measurements for this purpose. An aqueous solution of Separan AP-30 with concentration of 7800 ppm shows this characteristic restoration time to be roughly of the order of 9 to 10 min. This time is very large in comparison to the relaxation time or time required for reorientation, which will be of the order of few seconds for such systems. As has been pointed out earlier, the range of fluid relaxation times was of the order to 10^{-1} s to 20 s for the solutions examined in this work.

4. Concluding remarks

Our observations indicate that the phenomena of time dependence of velocities of spheres cannot be explained on the basis of concentration changes occurring in viscoelastic fluids due to the moving sphere. Also, most probably it cannot be attributed to the changes in the structure formed due to intramolecular hydrogen bonding in polyacrylamide solution. As the relaxation times for these fluids are small compared to actual restoration times observed by us and others [26, 40], the time taken by the fluid for restoration cannot be explained on the basis of the time taken for reorientation of the molecular structures.

The problem investigated by us is probably of greater general interest. For instance, Dekee and Carreau [40] reported recently that a strong dependence of velocities of bubbles on injection period was most probably due to the strong orientation effects for highly developed molecular structures in polyelectrolyte solutions. In the last 3 years, there has been a sudden spurt of activity in related areas and a number of interesting findings on association in polymer solutions under flow conditions [41 − 48] have appeared. The time scales for creation and destruction of such subtle structures could well be substantially different than the ones that are probed by conventional rheological measurements and may well differ, depending on the characteristic time scale of the experiment and also the type of flow field. Polyacrylamide solutions have been used as model fluids over three decades now by many experimental rheologists and there is a continuing effort among the rheologists to test the validity of constitutive equations in different flows by experimenting with this model fluid. The exact details of the role of the molecular level phenomena implicit in the results presented in this work and others will have to be understood fully for this to be reasonably done.

These findings also raise a number of important, related and, we may say, disturbing issues. The first is that it is likely that polymer solutions are indeed "structured" and these "structures" might break down in the presence of a wall where the highest shear rate exists. The viscosity of such a layer is likely to be much less than that of the bulk fluid. It is important to note that viscosity reduction in the wall layer does not require a change in concentration of the polymer molecules. All this requires is a change of some "structure". If this happens within observed microscopic distances then pressure drop reduction or slip layers detected by velocity distribution measurements as done by Mueller-Mohnseen et al. [23] might occur.

This is, of course, a speculation which awaits further confirmation.

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