

A STUDY OF HYDRODYNAMIC INTERACTIONS
OF MACROMOLECULES IN SOLUTION
BY MEANS OF PRECISION VISCOMETRY

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ABSTRACT

A precision capillary viscometer with a photoelectric timer has been designed and built for these investigations. On the assumption that the relative viscosity can be expanded in a power series in concentration, the intrinsic viscosity and the coefficient of the second order term have been measured for suspensions of spherical and rigid rod-like macromolecules. The viscosity of a known heterogeneous suspension of rods and spheres has been determined and has been interpreted in terms of interaction coefficients.

The Einstein theory of viscosity of dilute suspensions of spheres has been modified to form, together with the approaches of Burgers and Jeffery, a logically consistent theory for the intrinsic viscosity of spherical molecules in particular, and ellipsoid particles in general.

The second order theory in volume fraction for the viscosity of suspensions was reviewed. Previous work in this field was found to be in error. It was shown that, when properly interpreted, the linear solution of Burgers to the problem of the viscosity of dilute suspensions of spheres fully explains the variation of the relative viscosity with concentration. The linear theory of Burgers did not adequately explain the variation of the relative viscosity of rod-like molecules with concentration. This was attributed to mutual orientation effects. The study of the system consisting of rods and spheres also indicated that orientation effects might be important.

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INTRODUCTION

The continued isolation or creation of substances of very large molecular weight by industry and by the biological sciences has contributed to the increased interest shown in the rheology of dilute suspensions. Although it is possible to disperse large molecules or macromolecules as aerosols, the most frequent method of dispersion is to dissolve them. In biological systems the dissolved state is the naturally occurring one for the macromolecule.

In the dissolved state it is possible to determine the osmotic pressure, the sedimentation and diffusion rates of the macromolecule, the streaming birefringence of the solution and the viscosity of the solution. Additional measurements could include light scattering, dielectric dispersion and relaxation, X-ray analysis and electrophoresis of the solution. With proper preparation the macromolecule may be examined under the electron microscope. These techniques allow one to determine such important properties as size, shape, molecular weight, electrical charge and magnetic characteristics--of the macromolecule.

Among the important rheological properties of colloidal solutions and of suspensions is the variation of the properties of the solution with the concentration of the macromolecule. The viscosity, sedimentation coefficient, diffusion rate and streaming birefringence are all functions of the concentration.

Within the linear region there are more or less satisfactory theories to explain these variations. In the region of particle interaction the agreement of experiment with theory is not so satisfactory. The sedimentation rate and diffusion rates may be interpreted on the basis of the existence of a local viscosity lying between that of the solvent and that of the solution. The effective or local viscosity seen by the particle is due to interactions either chemical, hydrodynamic or both. It was felt that studies of a heterogeneous system might be helpful in obtaining a better understanding of these interactions. It was therefore decided to investigate particle interactions in two homogeneous populations of particles and in the heterogeneous system composed of these two types of particles. The main concern of the investigation was directed towards the hydrodynamic interactions of certain macromolecules.

Since the diffusion constant is in general only a weakly varying function of concentration, the viscosity, sedimentation or ultracentrifuge and streaming birefringence techniques of measurement were considered. Another portion of the laboratory has been and is conducting an active investigation of macromolecular solutions by means of streaming birefringence so attention was directed towards the ultracentrifuge and the measurement of viscosity.

Some preliminary investigations were conducted with the ultracentrifuge. The work led to the conviction that both

the experimental difficulties and the complexity of the flow field made the investigation of particle interactions extremely difficult. In addition there were some scheduling difficulties since the ultracentrifuge was not an integral part of the laboratory.

Viscosity measurements are a widely used method for characterizing macromolecules. Measurements in the non-linear range, i.e. with particle interactions, require a viscometer of a very high precision; a precision that is not found in the normal viscometer apparatus of a typical laboratory. It was felt that the construction of this viscometer aside from affording a wealth of experimental experience would add a valuable instrument to the laboratory. Such an instrument could be used in future investigations of anomalous viscosity effects, electroviscous effects and further investigations of hydrodynamic interactions.

The two most extensive methods used to measure viscosity of dilute aqueous solutions with viscosities in the neighborhood of one centipoise are the capillary viscometer and the couette viscometer. Although the couette viscometer permits the viscosity of a solution to be measured over a wide range of shears including very low shears, and is thus ideally suited to the investigation of the shear dependence of the viscosity of solutions, the apparatus in itself is inherently complicated and in general it does not have the reproducibility

and accuracy of a capillary viscometer. Most precision viscosity measurements have been made with capillary viscometers. A precision capillary viscometer was therefore designed for the investigation of particle interactions.

In the viscosity of macromolecules we must distinguish between two general categories: flexible and rigid molecules. The flexible molecule has no definite shape or configuration and may be visualized as a long chain. The chain may be loosely or tightly coiled depending upon the nature of the solvent. The analysis of the viscosity of solutions of flexible molecules is difficult and requires assumptions as to the statistical configuration of the chain.

The rigid molecules behave, as their name implies, as rigid bodies. The properties of such molecules can in a large measure be described by the choice of a suitable geometric model such as a sphere, ellipsoid, cylindrical rod, pearl string, etc....The appropriateness of a given model is determined to a large extent by agreement with experimental data. We shall confine our investigations to rigid molecules.

The definition of the viscosity of a suspension is based on an extension of that for a pure fluid. Thus for homogeneous incompressible liquids in the case that the terms of inertia are neglected one obtains the following equation for amount of energy dissipated per unit time

$$\frac{dw}{dt} = \frac{1}{2} \eta_0 \int_V \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right)^2 dv \quad i, k = 1, 2, 3$$

where η_0 is the viscosity of the liquid.

If the same equation were used for defining the viscosity of an heterogeneous medium it is clear that the instantaneous velocities would fluctuate with time. These velocity fluctuations are not, however, observable quantities in the standard viscosity apparatus so that η_0 defined as above is not an experimentally determinable quantity. The measurable experimental quantities are actually the mean values over time of the velocities of deformation. The above equation is valid then as a definition for the viscosity of a suspension if it is understood that we are referring to time-averaged quantities.

There are several terms used in referring to the viscosity of suspensions and fluids. The relative viscosity is

$$\eta_{rel} = \eta / \eta_0$$

where η_0 is the viscosity of the calibrating fluid or reference fluid and η is the viscosity of the suspension or other measured fluid.

The specific viscosity is

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_{rel} - 1$$

The reduced specific viscosity is the specific viscosity divided by concentration

i.e. η_{sp}/c

Finally a very important quantity in the viscosity of suspensions is the intrinsic viscosity which is the reduced

specific viscosity extrapolated to zero concentration and zero shear

$$[\eta]_0 = \left(\eta_{sp}/c \right)_{\substack{c \rightarrow 0 \\ q \rightarrow 0}}$$

q is the shear rate.

It is possible to define an intrinsic viscosity extrapolated to infinite shear. This will be denoted by

$$[\eta]_\infty = \left(\eta_{sp}/c \right)_{\substack{c \rightarrow 0 \\ q \rightarrow \infty}}$$

It is possible to expand the relative viscosity of a suspension at least in the dilute range, in a power series in the concentration. General experimental results and dimensional arguments indicate that this series is of the following form

$$\eta_{sp} = [\eta]_0 c + k [\eta]_0^2 c^2$$

It is the purpose of this investigation to determine the intrinsic viscosities of rigid rods and spheres. The value of k will be determined for rods and spheres separately and for a mixture of rods and spheres. The experimental results are then compared with those that might be expected from theory.

SECTION I

The purpose of this section is to review the development of the theory of the viscosity of dilute suspensions. Detailed investigation of physical assumptions and their mathematical expression will be found in the analysis section where applicable. The three theoretical approaches to the problem are represented by the hydrodynamic theory, the relaxation theory and the molecular theory of fluids. Several excellent reviews (1, 2, 3, 4) exist on the subject.

Hydrodynamic Theory

The hydrodynamic theory of viscosity of dilute solutions and suspensions originated with Albert Einstein (5). In this theory the molecular structures of the solvent and of the solute are completely ignored and the solvent is treated as a continuum. The presence of the macromolecule in the solvent perturbs the original flow field and this perturbation causes an increase in the energy dissipated and correspondingly an increase in the apparent viscosity. The solvent can, of course, be treated as a continuum only when the macromolecule dimensions are large with respect to the solvent molecules. To the first order in volume fraction good experimental agreement with theory is found for colloidal solutions and suspensions of rigid particles but not for pure solutions or mixtures of pure solutions. In the latter case the molecular structure of both the solvent and solute play

an important role. The viscosity in the case of pure fluids can depend on the surface activity of the solute, on the nature of the solute-solvent combination and on molecular associations within the liquid.

The development of the hydrodynamic theory of viscosity which is based on the Stokes approximation to the Navier-Stokes equations may be briefly summarized as follows:

1. Solution to the problem of the increase in viscosity due to a spherical macromolecule in an infinite flow field with different types of boundary conditions and including the case of rigid and non rigid particles.
2. Solution of the above problem with rigid ellipsoidal, dumbbell or pearl string macromolecules in the absence of Brownian motion.
3. Inclusion of the effect of Brownian motion in increasing the viscosity for non-spherical particles.
4. Solution to the problem of flexible molecules in an infinite medium.
5. Investigation of the effects of finite concentrations and the hydrodynamic interaction of the macromolecules.

Einstein solved the problem of a rigid sphere in an infinite medium. Since Einstein's procedure is fundamental to the entire hydrodynamic theory of viscosity it is discussed in some detail in the analysis section. Some of the assumptions of Einstein have in turn been relaxed by others.

G. I. Taylor (6) has treated the case of fluid spheres. Cerf (7) among others has studied the case of elastic particles. The wall effect has been investigated by Guth and Simha (8) and Vand (9). Simha (10) and Happel (11) replace Einstein's condition of the perturbation velocity vanishing at infinity with conditions on a large sphere concentric with the original sphere.

Jeffery (12) obtained the solution to the motion and viscosity increase of ellipsoidal particles in laminar flow in the absence of Brownian motion. The case of overwhelming Brownian motion has been treated by R. Simha (13) and by Kuhn and Kuhn (14).

The rather intricate calculations for ellipsoid particles have been avoided in several simple model investigations. Of these the rigid pearl necklace model of Kuhn and Kuhn (14) is perhaps the most illuminating. This model was instrumental in the development of the pearl necklace representation of flexible molecules.

Burgers (15) has developed an alternative procedure to that of Einstein for evaluating the effective viscosity of a suspension by utilizing the formulas originated by Oseen (16) for the effect of concentrated forces acting on a fluid. By this method he is able to derive Einstein's original result and also to treat the problem of the viscosity of cylindrical rods. Kirkwood and Riseman (17) have extended

this method to include rods and flexible centrosymmetric macromolecules. While Riseman and Ullman (18) in a further, but somewhat free extension, have used the method to calculate the concentration dependence of centrosymmetric macromolecules.

Guth-Simha-Gold (19) in a very involved calculation have obtained, after a fashion, the coefficient of the second order in sphere-sphere interactions. Simha (20) has similarly calculated the concentration dependence of dumbbells. The qualifying remarks used in the description of the theoretically calculated concentration dependence arise because of the existence of an improper indeterminate integral in all the above investigations. This is discussed more fully under analysis.

Vand (9) in an entirely different approach has attempted to calculate the contribution to the viscosity of collisions between spherical macromolecules.

The theoretical difficulties in the calculation of the concentration dependence of macromolecular solutions have led to several semiempirical methods. Thus De Bruyn (21), Brinkman (22), Saito (23), Robinson (24) and Vand (9) have all presented various phenomenological approaches.

The Relaxation Theory

The relaxation theory treats transport phenomena in condensed systems from the viewpoint of rate processes. The molecules in a condensed phase occupy positions of equilibrium and may be considered as vibrating about the minimum of a free energy well. The structure of all condensed systems may be thought as possessing a more or less regular lattice arrangement.

The effect of a stress on a body is to cause displacements from equilibrium along the various planes separating molecular layers. If the body is perfectly elastic then the stored potential energy is immediately and completely returned when the stress is released. The result is the return of the molecular patches to their original minimum positions in the energy wells. The elasticity modulus, shear modulus, bulk modulus, and hardness are all functions of the steepness of the energy wells.

If a relatively large stress acts constantly on a body, however, the molecular patches on the two sides of a shear plane jump with respect to each other over the energy barrier and take up new positions of equilibrium. In this way the stored potential energy is released as thermal energy. The statistical displacement of patches by jumping along shear planes continues as long as the stress acts, i.e. the substance flows in a direction such as to release the stress. This relative displacement to new positions along shear planes is called the relaxation theory of transport phenomena.

The fundamental equation for the shear rate in terms of molecular parameters was developed by Eyring (25). From this equation follows easily the relationship for the viscosity. The theory has been generalized to heterogeneous flow units by Taikyue Ree and Henry Eyring (26). The flow units can be either different molecules or different complexes of the same substances. The theory adequately explains both the variation of viscosity with pressure at constant temperature and the variation of the viscosity with temperature.

The Molecular Theory of Fluids

The most fundamental approach to the viscosity problem is through the method of the molecular theory of liquids. The theory is vastly more complicated than the corresponding theory for gases. It has only been recently that some concrete results have been obtained with the theory for monatomic liquids. This result is so complicated that its extension to more comprehensive systems has met with difficulty.

The molecular theory of liquids attempts to describe the properties of liquids in terms of the radial distribution function of nearest neighbors around a given reference molecule and in terms of the distribution of molecular velocities.

Since the molecules are very closely grouped to each other these distribution functions are primarily determined by intermolecular forces.

The central problem in the flow of liquids is to relate viscosity to the intermolecular potential. J. G. Kirkwood and collaborators are among the main contributors to the theory of liquids. Green (27) has summarized this development in his recent book.

The molecular theory of liquids is exceedingly complicated and does not offer too much hope at present for a solution to the problem of the viscosity of macromolecular solutions.

SECTION II

This section is divided into three parts:

(1) A brief development of the theory of capillary viscometry, the necessary corrections to the theory, and discussion of the possible sources of error in the measuring of viscosity by means of capillary tubes.

(2) A detailed outline of the experimental equipment that has been designed and assembled in order to measure the hydrodynamic interaction of macromolecules in an aqueous solution. The interactions are investigated by means of precision viscosity measurements. The experimental equipment consists of the viscometer, a precision timing device using photocells, and the temperature baths. In addition there is a description of the necessary auxiliary equipment. The materials tested in the experimental investigations are aqueous solutions of polystyrene latex (PSL) and tobacco mosaic virus (TMV).

(3) Details of the experimental procedure used in obtaining the data are explained. Accompanying this description of techniques is a discussion of the calibration of the viscometer and of the determination of surface tension correction.

Part I Theory and Error Discussion

Consider laminar flow in a circular pipe such that

$$u = v = 0 \qquad w = w(x,y)$$

where w is the flow along the pipe axis. From the Navier-Stokes equations

$$\frac{\partial p}{\partial x} = \frac{\partial p}{\partial y} = 0$$

The pressure is therefore constant across the pipe.

$$\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} = \frac{1}{\eta} \frac{dp}{dz}$$

The left hand side of the equation can be only a function of x, y , while the right hand side can only be a function of z . This can only be true if both sides of the equation are equal to a constant. We can therefore write the pressure gradient as

$$\frac{dp}{dz} = -\Delta p/l$$

where Δp is the pressure difference between the ends of the pipe and l is the length of the pipe. From symmetry it is evident that

$$w(x,y) = w(r)$$

We have, therefore, in polar coordinates

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dw}{dr} \right) = - \frac{\Delta p}{\eta l}$$

Upon integrating one has

$$w = \frac{-\Delta p}{4\eta l} r^2 + b \log r + c$$

The boundary conditions are

$$w = \text{finite} \quad r = 0$$

$$w = 0 \quad r = a$$

where a is the radius of the pipe. These conditions determine b and c

$$w = \frac{\Delta p}{4\eta l} (a^2 - r^2)$$

The velocity distribution is parabolic. The mass Q of fluid passing per second through the fluid is

$$Q = 2\pi\rho \int_0^a r w dr$$

and

$$Q = \frac{\pi \Delta p \rho}{8\eta l} a^4$$

This is Poiseuille's formula (29). For the viscosity one has

$$\eta = \frac{\pi}{8} \frac{\Delta p \rho a^4}{Q l}$$

Two corrections must be made to this formula. The kinetic energy correction and the Couette correction. Reference is made to Barr's treatise (30) for a derivation of the corrections. Briefly the kinetic energy correction relates

to the fact that the pressure forces also impart kinetic energy to the fluid in addition to working against the viscous forces. The true effective pressure is given by

$$\Delta p = h \rho g - \frac{\rho Q^2 m}{\pi^2 a^4}$$

where h is the head expressed in terms of the liquid of density ρ in the viscometer. The factor $m \approx 1$. The Couette correction accounts for the fact that the liquid entering the capillary is flowing in a converging stream. The effective length of the capillary is increased. Introducing these corrections into the theoretical equation one obtains

$$\eta = \frac{\pi a^4 h \rho g t}{8 V (1 + na)} - \frac{m \rho V}{8 \pi t (1 + na)}$$

Q has been replaced by V/t where V is the volume discharged in the time t . The factor n is slightly greater than 1. For a fixed geometry this equation becomes

$$\eta = \rho (A t + B/t)$$

In the measurement of relative viscosities the constants A and B can be determined by calibration with a liquid of known viscosity. In absolute viscosity measurements one calculates the viscosity from the actual geometric quantities in the theoretical equation. Needless to say absolute viscosity measurements are extremely difficult to make accurately as there exist many sources of error. Barr's treatise has an excellent discussion of the problems encountered in absolute viscosity measurements.

Almost all experimental investigations of macromolecular solutions involve the use of relative measurements. Relative viscosity measurements are easier because several sources of error are removed in the calibration.

Philippoff in "Viskosität der Kolloide" (31) gives an excellent discussion of the sources of error in relative measurements with capillary viscometers. There are two classes of errors: Those of systematic nature and those due to experimental conditions such as poor temperature control, inexact time measurement, dust particles in the solution, etc....

The systematic errors are

1. Inexact filling of the viscometer
2. The kinetic energy correction
3. Drainage errors
4. Effect of surface tension on the working head

The first error is concerned primarily with the widely used "Ostwald viscometer." The Ubbelohde viscometer eliminates this error by the introduction of a suspended level.

As indicated in the theoretical analysis the kinetic energy correction can be obtained by calibration.

The drainage error correction is particularly troublesome when viscosities over a fairly wide range are to be measured in the same viscometer. In a careful investigation Jones and Slauffer (32) showed that the amount of fluid remaining back on the walls of the viscometer bulbs obeys the following relationship

$$t \Delta V = \text{const } \nu$$

where ΔV is volume of liquid clinging to the wall
 t is flow through time
 ν is the kinematic viscosity

Disregarding the energy correction, the flow-through time, when the effective pressure is due to the weight of the fluid itself, is given by

$$t = A \nu$$

so the error ΔV is independent of the viscosity. Inclusion of the kinetic energy correction gives an error below the precision of our measurements for the viscosity measured in these experiments. This is mainly due to the fact that, for relative measurements, we are interested in the differences in the error between the fluid being tested and the calibrating fluid.

The surface tension correction will be discussed later under experimental procedure.

There are three principal non-systematic sources of error in viscosity measurements.

These involve:

1. Measurement of flow-through times
2. Variations in orientation of the viscometer
3. Maintenance of constant temperature

Flow-through times are determined by measurement of the elapsed time for the passage of the meniscus of the liquid

between fiducial marks above and below the viscometer bulb. The standard method is to measure the elapsed time by means of a stop-watch. This introduces a subjective error according to Philippoff of from 20 to 30 milliseconds.

The effective pressure acting on the fluid depends on the mean head of the fluid. This head varies if the orientation of the viscometer is changed.

The viscosity of water near room temperature changes approximately 2% for each degree change in the temperature of the bath.

Thus, controlling the temperature accurately is a prime requisite for precision viscometry. For accurate viscosity measurements in present day chemistry and biological laboratories the temperature is usually controlled to $\pm .01^{\circ}\text{C}$. Frequently measurements are made with the temperature controlled to only $\pm .05^{\circ}\text{C}$.

It will become evident in the description of the experimental equipment how each of the difficulties listed above has been minimized.

Part II Experimental Equipment

Viscometer

A multigradient viscometer consisting of three bulbs with mean hydrodynamic heads of 5, 10, and 15 cm was built for the experimental investigations of the interactions of macromolecules. Reference is made to photographs one and

two, page 95. The viscometer has the high accuracy characteristic of standard capillary viscometers and at the same time allows in some measure the shear dependences of the test solutions to be extrapolated out. The viscometer was designed to give moderate mean shears of approximately 180, 120, 60 sec^{-1} for water at 28 °C. The efflux times for all three bulbs are approximately 200 seconds over the range of viscosities measured. The capillary is 170 cm long and has an inside diameter of 1.15 mm. The long length reduces the shear rate to the moderate values given above.

The capillary tube was formed into a helix with a 7.5 cm diameter so that it would fit in a reasonable size temperature bath. The helix construction also permits a long tube with a small head. The size of the inside diameter of the capillary was chosen to minimize the influence of monolayers that might adhere to the capillary walls. In order to minimize surface tension effects and to eliminate the working volume error characteristic of the Ostwald viscometer an Ubbelohde hanging level was incorporated in the viscometer.

The viscometer is inserted and cemented into two end plates made of plexiglass. The end plates are spaced by three stainless steel rods. The entire unit of end plates, rods and viscometer forms a rigid body which is permanently screwed onto the plexiglass lid of the temperature bath. The rigidity of the system eliminates errors due to changes in the orientation of the viscometer. A spirit level is permanently glued to the top end plate.

Photocells and Lighting Arrangement

The generally accepted method for determining the efflux time of a given capillary bulb is to time the transit of the meniscus between two lines above and below the bulb by means of a stop-watch. This introduces a subjective error on the part of the operator who must judge the moment the meniscus passes the fiducial mark. This subjective error has been eliminated by the introduction of a transistorized photocell system. Although Jones and Talley (33) have previously used a photocell arrangement it is believed that this is the first time that transistor photocells have been used in viscosity measurements. The use of transistors makes for a particularly simple and practical arrangement.

Permanently attached to the viscometer are two glass tubes (see photographs) on either side of the glass column containing the three viscometer bulbs. These tubes project through the top end plate and are so oriented that with a light source in one of the tubes and a photocell in the other the passage of the meniscus in the capillary interrupts the light falling on the photocell. Thus with a light source and photocell aligned on the upper fiducial mark and a similar unit aligned on the lower fiducial mark, the pulses generated by the passage of the meniscus can be used alternately to start and stop a timing device. A Beckman 7360 counter was used to record the transit times, although for less precise work a simple electric clock could be used.

The light sources consist of 6 Welsh Allyn No. 2 lamps. These lamps were chosen because of their small size and relatively high light intensity. They are about .7 inch long and have a diameter of .2 inches. The lamps were fitted into an aluminum bar which in turn was inserted into one of the glass tubes. The openings in the aluminum bar help channel the light in the direction of the opposing photocell. The lamps themselves have, in addition, a built-in focusing lens. It was found necessary to power the lamps from D. C. batteries. The aluminum bar was fitted to the glass tube by means of a rubber stopper. The stopper was in turn glued and taped to the glass tube. This made a rigid unit but at the same time it was relatively easy to remove the light sources when needed.

The 6 photocells are N-P-N grown junction germanium transistors type 800 made by the Texas Instrument Company. These transistors, which find application in computers, were chosen because of their small size and reduced power demand. The photocells are very sensitive to the relative position of the light on the photosensing bar. They are thus ideally suited to responding to the interruption of light due to the passage of the meniscus of the test fluid. The photocells are attached to a rigid aluminum strip which is inserted into the glass tube facing the light source. This strip is glued and taped to the glass tube in the same manner as the light sources.

All electrical wiring is brought into two Johnson plugs which are attached to the top end plate. The leads for the power of the lamps and for the amplifying circuits of the photocells are simply plugged into the appropriate Johnson plug. In this manner the photo sensing equipment and the viscometer form a single assembly which can be removed from the temperature bath as a unit if it is so desired. The arrangement further prevents the possibility of relative motion between the photocells and light sources and between the sensing equipment and the viscometer.

The detailed circuitry of the photocell-amplifier circuit is quite straightforward

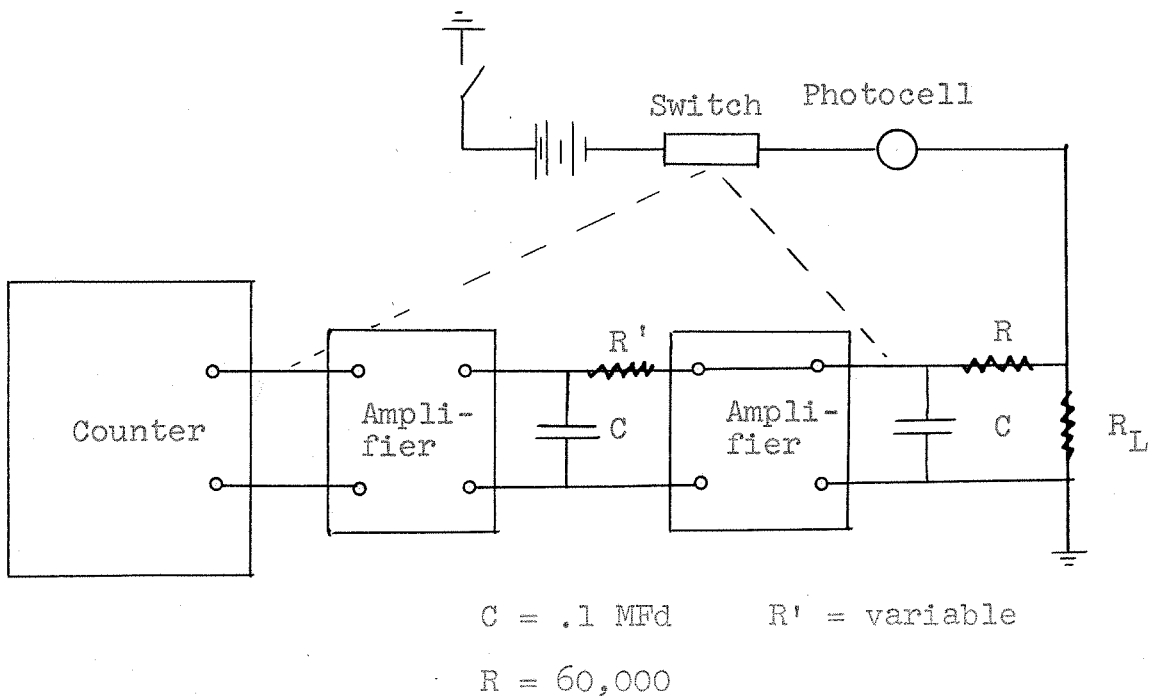


Figure 1

Each photocell was placed in a separate circuit. The switch indicated in the figure was ganged with the amplifiers and with the counter. On switching from one photocell to another the amplifiers were simultaneously switched into the circuit of the new photocell and the input to the counter was changed to the appropriate start or stop channel. Due to nonuniformity of the transistor photocells the load resistor varies somewhat for each photocell. In general it has a value of about 1 megohm. The transistor photocell is inherently a high noise device. The signal taken from the load resistor is passed through an RC network which, when combined with the input capacitance of the amplifier, removes the white noise. The DC component of the signal is also removed. Both amplifiers are commercial Hewlett - Packard 450 A. The first amplifier multiplies the signal by a factor of 100. The RC network between the amplifiers serves the purpose of decoupling them. Without this network there were objectionable oscillations. The second amplifier again multiplies the signal by a factor of 100. The resulting pulse has a rise time to one volt of the order of 1 millisecond. The final signal alternately starts and stops the Beckman counter. The counter is set so that negative excursions of more than .25 volts in the input signal will start or stop the counter. It was found necessary, in order to eliminate stray signals in the amplifier circuits, to make all connections by shielded cables. The two amplifiers

and the counter were operated from separate Sola constant voltage sources. Reference is made to photograph 3 page 96 . Connected to the viscometer is the complete sensing and recording equipment; including counter, amplifiers, central switch, cables and connectors.

Temperature Bath

Preliminary measurements showed that a more or less elaborate system would be necessary to control temperature to the desired accuracy of a few thousandths of a degree centigrade. The temperature bath (see photographs 4, 5, 6) consists of two concentric jars and the cover assembly formed by the lid, and a plexiglass box placed on top of the lid. Both the exterior and interior jars have their temperature regulated by control units. The lid of the jars also has its temperature regulated.

The exterior bath consists of a specially constructed plexiglass jar 17 inches in diameter, 17 inches high and 1/2 inch thick. Plexiglass was chosen because it is easily worked, transparent and a good insulator. The jar is filled with water and there is space for two inches of coolant around the sides of the interior jar and for 1/2 inch at the base of the jar. A copper cooling coil is placed between the two jars both on the sides and at the base. Through the copper coils is pumped water which is regulated to about .01 °C. A Precision Scientific Instrument Company Control was the

regulating unit. The thermoregulator in this unit is a mercury switch with an off-on action. The temperature of the circulating water was determined by a thermometer reading directly to $.05^{\circ}\text{C}$. The outside jar was maintained at a temperature of about 1°C below that of the interior jar. The jar rests on a balancing board which is used in properly orienting the viscometer.

The interior bath consists of a water filled glass jar 12 inches in diameter and 16 inches high. Into this jar is placed the viscometer, the stirring and heating column and the sensing element of the interior control. A Sargent Thermonitor model S W regulator was chosen as the control unit. This regulator has several advantages. The heating elements are centrally located in the stirring column. The sensing element is a thermistor which has a high response for small changes in temperature. The sensing element is located close to the stirring column to eliminate temperature cycling. Both the stirring column and the stirring motor are suspended by a special attachment from the ceiling. This eliminates excessive vibrations of the viscometer.

Electrically the control element consists of an AC energized Wheatstone bridge, one arm of which is the thermistor. A temperature change causes the thermistor to unbalance the bridge. The output of the bridge is fed through two stages of amplification and is then applied to the grid of a thyra-ton tube which acts as an electronic switch. The power

supplied to the heating elements is proportional to the unbalance of the bridge which in turn is proportional to the temperature change. This proportional control minimizes cycling. Under optimum conditions the manufacturer claims that the control is capable of maintaining the temperature to .002 C. The results of the experimental investigation would appear to support this claim. The control temperature was 28 °C.

Although it is a high response device, the thermistor suffers from a lack of long term stability. For this reason the temperature was determined from a precision thermometer reading directly to .01 °C. By means of a quality thermometer viewer the temperature was estimated to the nearest .001 °C.

The plexiglass lid is $1\frac{1}{2}$ inches thick and projects about $\frac{1}{2}$ inch over the side of the exterior jar. The lid is hollow and contains a layer of water one inch thick, except for the center portion, where space is left for the insertion of the stirrer and viscometer in the interior. There are several turns of copper cooling coil placed in the water and the lid's temperature is regulated by the same unit that controls the outside jar. The upper surface of the interior and exterior jars lies in a plane and the lid has two circular grooves into which the jars are fitted. The viscometer is screwed down to the center part of the lid where space is also supplied for the stirring column, thermistor and reading thermometer. (See photograph 5 page 97). Finally the

lid is attached by means of clamps to the outer plexiglass jar. This again prevents any change in the vertical orientation of the viscometer.

Enclosing the entire upper part of the lid is a plexiglass box which further serves to insulate the interior jar from the external environment. The control of the exterior jar and the control of the lid as well as the plexiglass box all help to insure that the interior jar sees an essentially uniform external temperature.

Auxiliary Equipment

The auxiliary equipment necessary to complete the accurate determination of the viscosity of macromolecules is associated primarily with the determination of the density of the solutions. An accurate analytical balance and appropriate pycnometers are needed. Since one of the substances used in the experiment is a virus it was necessary to control the Ph of the solutions. In order to fill the viscometer with dust free solutions a special pipette was also designed.

A semi-micro TCY Ainsworth analytical balance was used for all weighings. The designation semi-micro means that the scale is capable of weighing specimens to the nearest .01 mg. When weighing to this accuracy it is necessary to make a buoyancy correction for the specimen. For this reason, at each weighing the barometric pressure was determined and the relative humidity measured by a sling psychrometer. A

simple design was selected for the pycnometers so that they could be easily cleaned. The pycnometers used were essentially volumetric flasks with a thin etched line around the capillary neck. This line defines the volume of the pycnometer. The pycnometers were built to order by the Cal Tech Chemistry Glass Shop and have a volume of approximately 20 ml with a capillary of around 1 ml. Attached to the plexiglass end plate of the viscometer is a platform on which the pycnometer rests when in the temperature bath. (See photograph 8 for pycnometer and photograph 1 for the platform.)

A Beckman model G Ph meter was used for all Ph measurements. The Ph was determined to nearest .01 units. Photograph 8 shows the special pipettes used in filling the viscometer. The standard volumetric pipette was fitted with a detachable fritted disc. The liquid entering the pipette has any dust or extraneous particles filtered out by the porcelain filter. The filter is then removed and a known volume of fluid can be introduced into the viscometer.

Experimental Materials

The viscosities of two rigid macromolecules were investigated. The two test substances consisted of polystyrene latex and tobacco mosaic virus.

Polystyrene latex is an industrially produced polymer. It is particularly well suited as a test substance since it is an inert, rigid sphere whose diameter is closely controlled. The mean diameter of the PSL used is 880 ⁰Å with a

standard deviation of 80 \AA . The size distributions were obtained by electron microscope examination (34). The sample was supplied by Dow Chemical Company.

Tobacco mosaic virus has been extensively investigated so that its properties are well known. It has the shape of a rigid uniform rod of about 2880 \AA in length and 180 \AA in diameter. These dimensions have been obtained by electron microscope examination (35). One of the difficulties encountered in working with TMV is its tendency to dimerize. A very uniform population was furnished by Dr. Norman Simmons of UCLA. The uniformity of the population was indicated by a sedimentation experiment.

Experimental Procedure

The preparation of the solutions, measurements of the efflux times and determination of the density are included under experimental procedures. The method of calibration and the calibration results as well as the experimental determination of the surface tension correction are also discussed below.

Solutions

Some difficulties were encountered in the preparation of a solution of PSL which was compatible with the TMV. When a solution of the PSL as received from the Dow Company was mixed with the TMV a milky white precipitate separated from the solution. This difficulty was traced to the fact that the

emulsifying agent of the PSL was an ionic-sulfonate detergent. Unfortunately the sulfonate ion reacts with TMV in such a manner as to strip the protein from the molecule leaving the nucleic acid. The process is termed denaturization of the TMV. The milky white precipitate was the protein. Experimental work of Dr. Simmons (36) and others (37) has shown that nonionic detergents are compatible with TMV.

In addition to forming a part of the solvent, the emulsifying agent is adsorbed on the surface of the PSL. It was therefore necessary to replace the sulfonate by repeated washings in a preparatory centrifuge with a .02 % by volume nonionic detergent, Tergitol TMN (trimethyl nonyl ether of polyethylene glycol). With the new emulsifier the PSL proved compatible with the TMV.

The concentration of the PSL was determined by drying a portion of the original solution to constant weight in an oven. Further concentrations were determined by dilution of the base solution. The dilutions were made by weighing and also by dilution in the apparatus with pipettes.

Since TMV is a virus one must be careful in controlling its environment. TMV tends to denature if the Ph is below 7.0 and to aggregate or dimerize if the Ph goes above 7.5. For this reason the solvent of the TMV contains a buffering agent. The buffering agent acts in a direction to oppose changes in the Ph. The basic solution for the TMV was a .01 M phosphate buffer with .001 M versene at Ph 7.34. Higher ionic

strengths than those of the buffer described have a tendency to cause the TMV to aggregate. Another component of the buffered solution is .02% tergitol TMN. This insured that in the preparation of a mixture of PSL and TMV the concentration of the emulsifier was not changed. The solvent for the PSL was also the same buffered solution consisting of phosphate, versene and Tergitol TMN.

The addition of the nonionic detergent complicates matters somewhat as it reacts mildly with the phosphate buffer. It was found necessary first to make a phosphate buffer to Ph 7.00. Upon mixing with the tergitol the resulting solution had a Ph 7.34 and still displayed good buffering capacity. The original TMV concentration was determined by measuring the optical density of the solution at 265 m μ in a Beckman model DU spectrophotometer (38). Further concentrations were determined by dilution of the base solution as in the case of the PSL.

Efflux Times

The presence of dust or extraneous particles is always a troublesome problem in viscometry. At first all solutions were filtered through millipore filters directly into the viscometer in order to eliminate dust particles. It was found, however, that the filter also removed some of the TMV and PSL. At this point the pipettes with attached fritted discs were designed. With these pipettes it was possible to deliver a known amount of dust free solution to

the viscometer. After the insertion of the solution it was allowed to stand in the apparatus for approximately an hour to insure temperature equilibrium.

The system of valves and tubing shown in photograph 5 allowed one to pump the solution into the capillary bulbs. Filtered air was forced into the large receiving tube of the viscometer. This forced the solution up to the suspended level and into the air vent tube. The air vent was then closed and the solution forced through the capillary and up into the capillary bulbs. At the beginning of a run the pressure was released in the filling tube and all three tubes consisting of air vent, filling tube and capillary tube were interconnected by means of tygon tubing. The weight of the solution caused it to flow through the capillary. This method has the advantage that no outside air, which might have dust particles, is introduced into the viscometer during a run.

The solution was passed once through the three bulbs and the capillary without taking measurements. This was done because it is an experimental fact that in the first passage of the test fluid through a dry capillary the measured time is invariably higher than the following passages. In general two runs of the same solution were made for each bulb. The readings for each run often differed by as little as 1 millisecond. The maximum difference between the two readings was not in excess of around 20 milliseconds. The completion of the two runs usually took about an hour.

Upon finishing the first test the solution was diluted in the viscometer by the addition of a known amount of buffer. After waiting about an hour for equilibrium the test procedure was repeated. Usually a second dilution was then made and another test completed. Thus three different concentrations of the solution were tested with one filling. The viscosity was calculated in each case by use of the basic equation, previously developed and with the constants A and B determined by calibration.

At the completion of the tests the apparatus was cleaned. The position of the viscometer was not changed during cleaning. The original cleaning was done with concentrated sulphuric acid and chromate solution. After this the apparatus was washed with a detergent and rinsed with distilled water. All future cleanings of the apparatus were essentially rinsings with distilled water. This was possible since the buffer in itself contained a detergent. The PSL solution and mixture required a bit more complicated procedure. The viscometer was first rinsed with methyl ethyl ketone which is a solvent for PSL. This was followed by acetone and several rinsings with distilled water. The apparatus was then dried by passing warm filtered dry air through it.

During the entire period of the tests the outside control was on continuously. An automatic timer turned on the interior control about three hours before the beginning of the tests in the morning. Thus the temperature control of

the entire bath had been functioning about four hours before any tests were conducted.

Density Determination

The accurate determination of density, although a fairly standard technique, requires some attention to detail. The article by N. Bauer (39) contains an excellent discussion of density determinations and the factors affecting its accuracy. The density will be defined by

$$d^t = m/V_{ml} \quad (g/ml)$$

where m is grams of mass

and V_{ml} is the volume of milliliters.

The weight in grams is given by

$$W = m g$$

so that if both V_{ml} and m are measured in gram weights at the same location the value of the density remains the same. The standard method of determining the density is to find the weight of a known volume of liquid defined by the shape of a given pycnometer. The pycnometer is calibrated by determining the weight of pure water that it holds at a given temperature. From the known density of water it is possible to calculate the volume of the pycnometer. For any other liquid one simply determines the weight of the solution and then divides by the calibrated volume to obtain the density. The density was measured to 5th place accuracy.

The density of water at room temperature changes about 0.03% for each degree °C rise in temperature. Thus the control of the viscometer bath temperature to about .002 °C is more than adequate for the density determination.

All weighings were made to an accuracy of .01 mg using class S metric weights and the TCY analytical balance. A tare (dummy pycnometer) was used whose weight matched that of the pycnometer to within one gram. This eliminated the buoyancy correction for the weight of the pycnometer. Since the weight of a glass object can change by several milligrams due to the adsorption of moisture both tare and pycnometer were wiped with a moistened chamois to equalize the amount of water adsorbed. Both vessels were then allowed to stand in the balance case for 3/4 of an hour before weighing. When weighed empty the stoppers of both vessels were removed and the air inside flushed out with air from the balance room. The filled pycnometer was also flushed with balance room air shortly before weighing. To eliminate erratic weighings due to electrostatic charge effects a polonium staticmaster brush was used. After the empty weighing the pycnometer was filled by means of a hypodermic and placed in the temperature bath on the special platform provided for it. This platform insured that the pycnometer was always immersed to the same depth and could always be oriented in the same direction. After equilibrium was reached the level of the meniscus was adjusted to the etched line of the capillary neck.

This was done under magnification and always on the same part of the etched line. After this adjustment the pycnometer was removed and the previously described weighing procedure was followed. The buoyancy effect of the displaced air must be considered when accuracy to the fifth place is sought. In order to determine the density of the air the barometric pressure and the wet and dry bulb readings of a sling psychrometer were taken. The density of air may be obtained from tables (28) or calculated from a formula given by Bauer. It can be shown that the true weight difference between the filled pycnometer and tare is

$$W = W' + V_p D_{\text{air}} - \frac{W'}{8.5} D_{\text{air}}$$

where W is the true weight difference
 W' is the apparent weight difference
 V_p is the volume of pycnometer
 D_{air} density of air

This assumes that the density of the weights is approximately that of brass 8.5. Repeated measurements showed that accuracy to better than 1 in the fifth place was obtained. In the normal case when two dilutions were made in the viscometer, the densities of only the first and third tests were determined. The density of the second test was obtained by interpolation. The small changes in the densities of the solution made this procedure acceptable.

Calibration

The calibration of the viscometer was accomplished by measuring the viscosity of water at 5 temperatures. The range of temperatures was from about 24 °C to 28 °C. This represents a range of relative viscosities based on the viscosity of water at 28 °C from 1 to more than 1.09. The basic viscosity equation derived previously is

$$\eta = \rho (A t + B/t)$$

The viscosity and density of water is known. From the equation it is evident that if we plot

$$\eta/\rho t \text{ vs } 1/t^2$$

we will obtain a straight line whose intercept is the constant A and whose slope is the constant B that is

$$\eta/\rho t = A + B \left(\frac{1}{t^2}\right)$$

The data for this equation is included in table one page 92 . A least square line was fixed to the data. This gave the following calibration constants.

The viscometer bulbs are numbered consecutively from the top

	A	B
bulb # 1	0.00444308	0.5706
bulb # 2	0.00378363	0.3784
bulb # 3	0.00406509	1.0002

These constants were used to calculate all other viscosities from the measured efflux time and densities. Since we are interested only in the relative viscosities the calculated viscosity was divided by the viscosity of water at 28 °C. Thus with

$$\eta_{28} = 0.8359$$

$$\eta_{rel} = \rho / 0.8359^\circ [A t + B/t]$$

Surface Tension Correction

There are several thorough discussions (40, 41, 42) of the effect of surface tension on the measurement of viscosity. The discussion of G. Jones (43) in English gives some idea of assumptions and complicated calculations that are necessary to obtain this correction theoretically. By a fairly straightforward procedure due to Philippoff it is possible, however, to obtain the correction experimentally.

The increase in head due to surface tension in a viscometer bulb of diameter $2 r$ is given by

$$h = 2 \sigma / g r \rho$$

where σ is the surface tension in dyn/cm. and ρ is the density in g/cm^3 . This capillary rise means that the effective head operating on the liquid is decreased. The surface tension therefore increases the flow-through time over that which would occur if there were no surface tension. The theoretical flow-through time is then related to the experimental

flow-through time by the following equation

$$t_{\text{exp}} = t_{\text{th}} \cdot \frac{H_0}{\left(H_0 - \int_{h=H_a}^{h=H_e} \frac{\sigma}{r(t)} dt \right)}$$

where H_0 is the mean effective head and H_a and H_e refer to the head at the beginning and end of the flow respectively. The integral can be replaced by constant C depending on the geometry of the apparatus so that one obtains

$$t_{\text{exp}} \doteq t_{\text{th}} \left(1 + C \frac{\sigma}{\rho} \right)$$

This is a relationship between the actual experimentally measured time to that of the theoretical time without surface tension. We are measuring our viscosities relative to that of water at 28 °C. We therefore wish to measure changes of the surface tension from that of water and not from the physically unrealistic condition of no surface tension. This means that if

$$t_{\text{exp}}^{\text{Lm}} = t_{\text{th}}^{\text{Lm}} \left(1 + C \frac{\sigma_{\text{Lm}}}{\rho_{\text{Lm}}} \right)$$

refers to the experimental flow-through time for water we are interested in referring our measurements $t_{\text{exp}}^{\text{Lm}}$ and not to $t_{\text{th}}^{\text{Lm}}$. For any other solution we have

$$t_{\text{exp}}^{\text{L}} = t_{\text{th}}^{\text{L}} \left(1 + C \frac{L}{L} \right)$$

This may be written as

$$t_{\text{exp}}^{\text{L}} = t_{\text{th}}^{\text{L}} \left\{ \left(1 + C \frac{\sigma_{\text{Lm}}}{\rho_{\text{Lm}}} \right) - C \left(\frac{\sigma_{\text{Lm}}}{\rho_{\text{Lm}}} - \frac{\sigma_{\text{L}}}{\rho_{\text{L}}} \right) \right\}$$

dividing by $1 + C \frac{\sigma_{Lm}}{\rho_{Lm}}$, expanding and ignoring C^2 with respect to C one has

$$t_{exp}^L = t_{th}^L \left(1 + C \frac{\sigma_{Lm}}{\rho_{Lm}} \right) \left\{ 1 - C \left(\frac{\sigma_{Lm}}{\rho_{Lm}} - \frac{\sigma_L}{\rho_L} \right) \right\}$$

So far the development has been straight forward. We have ignored, however, the fact that the Ubbelohde viscometer has a suspended level. The effect of the surface tension in the suspended level is opposite to that in the upper bulb. The effect of the surface tension is to increase the mean head and therefore to decrease the flow-through time. It would be possible by a proper selection of the size of the upper and lower bulb to minimize the effect of the surface tension. This is in fact one of the advantages of the Ubbelohde suspended level. Essentially the previous theoretical development is unchanged except for a difference in sign. The net effect of the surface tension is the difference between the contributions of the upper and lower bulbs. If we ignore the kinetic energy correction it follows that the relative viscosity corrected for surface tension $(\eta_{rel})_{th}$ is related to the actually measured relative viscosity $(\eta_{rel})_{meas}$ by the equation

$$(\eta_{rel})_{meas} = (\eta_{rel})_{th} \left\{ 1 \pm C \left(\frac{\sigma_{Lm}}{\rho_{Lm}} - \frac{\sigma_L}{\rho_L} \right) \right\}$$

The previous development makes this equation plausible. It is possible to determine the correct sign and the value of

C experimentally. The relative viscosity of the detergent TMN was determined in a very dilute range (.03% to .07%). Over this range the relative viscosity was a linear function of the concentration and the surface tension remained constant. A least square line was fitted to the data. By extrapolation to zero concentration one obtains

$$1 \pm C \frac{\Delta \sigma}{\rho}$$

The extrapolation showed that the plus sign is correct. The apparatus constants for each of the three bulbs are

bulb	C%
1	0.00861
2	0.01476
3	0.01576

These values are about the same as other experimental values of surface tension constants listed in Philippoff

Jones and Talley	0.0102
Jones and Fornwalt	0.0005
Ubbelohde with suspended level	0.0058

Surface tension measurements were made with a DuNody Tensiometer.

The effect of the surface tension correction may be seen in the following table of the specific viscosity of the buffer solution.

Bulb	Uncorrected	Corrected
1	.01105	.00784
2	.01353	.00794
3	.01370	.00780

It should be noted, however, that the finally determined curves for the TMV and PSL and for the mixture are not materially changed by the surface tension correction. This is due to the fact that the surface tensions of all solutions except the highest measured concentration of PSL were the same. The viscosity of the TMV solution, for example, was obtained by subtracting the specific viscosity of the buffer from that of the buffer - TMV solution. Both the surface tension corrected specifics and the uncorrected specific viscosities gave to within 3 or 4 in the fifth place the same value for the specific viscosity of the TMV by itself.

EXPERIMENTAL RESULTS

The data from which all curves are plotted is included in tables 2 and 3 pages 93 and 94. The viscosity of tobacco mosaic virus was measured in a 0.01 M phosphate, 0.001 M Versene and 0.2% Tergitol TMN aqueous solution at 28 °C. The range of concentrations was from approximately 0.4 to 0.025 g TMV/100 g water.

Graph 8 is a standard plot of reduced specific viscosity versus concentration

$$\eta_{sp}/c \quad \text{vs} \quad c$$

The units of concentration are grams TMV per 100 grams water. The curves for all three bulbs are similar and show a definite shear dependence. Below a concentration of about 0.06 g TMV/100 g water there is a distinct break in the experimental curves. Graph two is a plot of the logarithm of the specific viscosity vs shear. The extrapolated zero shear values from graph two are plotted on graph 8. The assumption is made that the specific viscosity can be expanded in a power series in concentration. That is

$$\eta_{sp} = [\eta]_0 c + B c^2 + C c^3$$

the zero shear curve may then be represented by

$$\eta_{sp} = 0.3892 c + 0.0342 c^2$$

The points below 0.06 g TMV/100 g water are ignored in this calculation. These points are neglected in the calculation because, as explained later, it is believed that they are displaced due to other physical effects. The variations of the reduced specific viscosity (η_{sp}/c) in the lower concentration range were within experimental error so that the second order term could not be determined. The intrinsic viscosity of the TMV in this region was obtained by extrapolation from graph 8

$$[\eta]_0 = 0.372$$

The units of intrinsic viscosity are 100 g water per g TMV.

The viscosity of polystyrene latex spheres with a mean diameter of 880 Å was also measured in a 0.01 M phosphate, 0.001 Versene and 0.2% Tergitol TMN aqueous solution at 28 °C. The range of concentrations was from approximately 1.2 to 0.12 g PSL/100 g water. Graph 3 is a plot of reduced specific viscosity vs concentration

$$\eta_{sp}/c \text{ vs } c$$

These curves show a definite shear dependence and an anomalous viscosity effect at low concentrations. Graph 4 is a plot of $\log \eta_{sp}$ vs shear. Graph five is a plot of $\log \eta_{sp}$ against inverse shear.

Using the value of the specific viscosity extrapolated

to zero shear and to infinite shear, the curves of reduced specific viscosity vs shear are plotted on graph six. The zero shear curve still shows the anomalous viscosity behavior at low concentration. In the infinite shear curve the anomalous behavior has disappeared. Disregarding the anomalous viscosity behavior for the zero shear case one has, expanding in a power series in concentration

$$\eta_{sp} = 0.0281 C + 0.0071 C^2 \quad (\text{infinite shear})$$

$$\eta_{sp} = 0.0344 C + 0.0072 C^2 \quad (\text{zero shear})$$

The intrinsic viscosities are thus

$$[\eta]_0 = 0.0344$$

$$[\eta]_\infty = 0.0281$$

The viscosity of mixtures of polystyrene latex and tobacco mosaic virus was also measured in the previously described buffered solution at 28 °C. The range of concentrations for the PSL was from approximately 0.3 to 0.6 g PSL/100 g water and for the TMV from approximately 0.135 to 0.35 g TMV/100 g water. Several tests were made with the concentration of the PSL at a constant value while the TMV concentration was varied. Other tests also varied the concentration of the PSL. The assumption is made that the specific viscosity of the mixture is given by

$$\eta_{sp}^{\text{Mix}} = \eta_{sp}^{\text{PSL}} + \eta_{sp}^{\text{TMV}} + \Delta \eta_{sp}$$

where $\Delta \eta_{sp}$ is the increment in the specific viscosity due to interactions. From the specific viscosity of the mixture was

subtracted the specific viscosity of the TMV and the specific viscosity of the PSL leaving $\Delta \eta_{sp}$. If the assumption is made that the increase of viscosity due to mixing is bi-linear in both concentrations one obtains

$$\Delta \eta_{sp} = f(g) C_{TMV} C_{PSL}$$

The function $f(g)$ is a function of the geometric parameters of the two molecules. Graph 7 is a plot of

$$\Delta \eta_{sp} \text{ vs } C_{TMV} C_{PSL}$$

It is seen that

$$f(g) = 0.0145$$

is a constant over the range of concentrations considered.

The following summary table is given for the experimental data

	$[\eta]_0$	$[\eta]_\infty$	$B \times 10^4$
TMV	0.3892		342
	0.3722*		
PSL	0.0344	0.0281	7.2
Mixture			145

* Below a concentration of .06 g TMV per 100 g water

DISCUSSION OF RESULTS

The two significant features of the TMV data are the variation of the reduced specific viscosity with concentration and the abrupt change in the specific viscosity around 0.05 g TMV per 100 g water. Boedtke and Simmons (44) report that the reduced specific viscosity was independent of concentration over the concentration range from 0.6 to 0.12 g/100cc. Yang (45) reports a linear dependence of the reduced specific viscosity on the concentration over the concentration range .8 to .3 g/100cc. It is possible that the variations in the reduced specific viscosity were below the accuracy of measurement in the case of Boedtke and Simmons.

A better understanding of the variation of the constant B of the second order term may be had by considering the hypothesis of Huggins (46) that

$$B = k_1 [\eta]_0^2$$

The interaction coefficient k_1 defined by this relationship is a dimensionless number. In general one may assume that

$$\eta_{sp} = [\eta]_0 c + k_1 [\eta]_0^2 c^2 + k^2 [\eta]_0^3 c^3$$

Graph one is a plot of the reduced specific viscosity vs the specific viscosity neglecting the points below 0.06 g TMV per 100 g water.

$$\eta_{sp}/c \text{ vs } \eta_{sp}$$

Clearly on the power series hypothesis one has

$$\eta_{sp/c} = [\eta]_0 + k_1 [\eta]_0 \eta_{sp}$$

The intercepts on graph 1 are either the reduced specific viscosity extrapolated to zero concentration or, in the case where the shear dependence has been extrapolated out, the intrinsic viscosity. The slope of the curves is $k_1 [\eta]_0$ or $k_1 (\eta_{sp/c})_{c \rightarrow 0}$.

It is from graph one that the values for $[\eta]_0$ and k_1 are computed

$$k_1 = 0.226$$

Over the range of experimental shears the factor k_1 did not vary. The experimental curves for viscometer bulbs (1) (2) (3) can thus be represented in a power series in concentration by

$$\eta_{sp} = (\eta_{sp/c})_{c \rightarrow 0} c + k_1 (\eta_{sp/c})_{c \rightarrow 0}^2 c^2$$

where $(\eta_{sp/c})_{c \rightarrow 0}$ is taken from graph one and $k_1 = 0.226$.

Returning to a consideration of Yang's data for TMV we obtain a value for k_1 of about

$$k_1 = 0.38$$

as opposed to our value of

$$k_1 = 0.226$$

Yang does not interpret the variation of the reduced specific viscosity with concentration as hydrodynamic interactions. It would be expected that Yang's value would be higher since his measured concentrations are somewhat above those in our investigation. Model experiments (47) on rod-like objects have given a $k_1 = 6$. This high value may be attributed to the lack of Brownian motion. Although there is extensive data (48) on the k value for flexible molecules where the value of k_1 ranges from about 0.20 to 0.50 there does not appear to be too much data on rigid rods. It is possible that the value 0.226 determined in these experiments is the first accurate experimental determination of the k_1 coefficient for rigid rods.

The break in the experimental curves of TMV below 0.06 g per 100 g water for the reduced specific viscosity may be due to one of two possible effects. In this concentration range one might expect that such an effect could be due to adsorption of the TMV either on preparatory glassware or on the interior surfaces of the viscometer. The process of adsorption removes some TMV from the solution. The actual concentration of the TMV in the solution is reduced and the relative viscosity is lower than that expected for the original concentration. This process is only important in extremely dilute solutions. Another possible hypothesis is that a small fraction of the TMV is dimerized and that in the very dilute range these dimers disassociate causing

the viscosity to drop.

For reasonably monodispersed systems Boedtker and Simmons (44) report an intrinsic viscosity of 0.367 ± 0.006 (in units of 100 cc/g). Schachman and Kauzmann (49) report 0.32 and Watanube 0.365 (50). Other values for non-mono-dispersed solutions have varied from 0.25 to greater than 0.6. Both values of intrinsic viscosity reported in this investigation are in good agreement with previous results. In units of 100 cc/g per g the experimentally measured intrinsic viscosities are

$$[\eta]_0 = 0.390 \qquad [\eta]_0^* = 0.373$$

In particular the lower value of 0.373 is within the experimental error of the value reported by Boedtker and Simmons.

There are actually three unusual features of the PSL data. The data shows shear dependence. The intrinsic viscosity $[\eta]_0$ is higher than the expected Einstein value of 0.025 and there is an anomalous viscosity effect at low concentrations. The data is subject to at least two interpretations. The viscosity of the nonionic detergent TMN shows a definite shear dependence when measured by itself. The buffered base solution which contains TMN does not show any shear dependence. In the presence of the PSL which is coated with TMN it is possible that the TMN molecule becomes extended. The effect of this extension would be that the

* Below 0.06 g 100 per 100 g water.

solution would show a shear dependence and the measured intrinsic viscosity of the PSL would be higher than that expected. Further since the amount of TMN in the solution is held constant, an anomalous viscosity effect would appear at the lower concentrations of PSL. If this hypothesis is correct one would further expect that on extrapolation to infinite shear the effect of the flexible TMN molecule would be minimized and one would have only the contribution of the PSL.

The extrapolation to infinite shear is consistent with the hypothesis. The anomalous viscosity effect is no longer evident and the intrinsic viscosity is within the range of that obtained by Maron et al (51, 52, 53). Maron (54) has shown that for latexes the true volume fraction v_t is related to the volume fraction v by the relation

$$v_t/v = 1 + 6\Delta/D_s$$

where Δ is the thickness of the adsorbed monolayer of emulsifier and D_s is the volume to surface average diameter of the dispersed particles as determined by soap titration. A typical thickness of the monolayer, which is related to the end to end distance of the emulsifier molecule, can range from 18 to 30 Å. Thus the correction in the case of 880 Å PSL can amount to values of

$$v_t/v = 1.12 \text{ to } 1.2$$

Converting the measured

$$[\eta]_{\infty} = 0.028^1$$

to units of volume fraction one has

$$[\eta]_{\infty} = 0.029^5$$

If we now apply the correction due to the monolayer of emulsifier one obtains values of

$$[\eta]_{\infty} = .024^8 \text{ to } .026^5$$

which is in excellent agreement with the Einstein value of .0250.

It is possible that an alternate hypothesis dealing, for example, with the nature of the emulsifier layer on the surface of the PSL may also explain the data. If the emulsifier were not completely effective long range ordering might occur or a tendency to form doublets would become evident. Extrapolation to infinite shear could in this case also produce the experimental curve obtained in this experiment. Further investigation with other emulsifiers and different size PSL particles is perhaps indicated. The technique of extrapolation to infinite shear would, however, appear to have considerable merit in the investigation of polydispersed systems containing spherical particles. It is quite possible that, as indicated in this investigation, the anomalous viscosity effects encountered by others (55, 56) may be due to changes in the emulsifier. The range of con-

centrations covered in the experiments is about a factor of ten smaller than previous investigations.

Since the coefficient of the second order term remains almost constant in the case of the extrapolation to zero shear and to infinite shear the value of the interaction coefficient varies from

$$k_1 = 0.61 \quad \text{zero shear}$$

to

$$k_1 = 0.90 \quad \text{infinite shear}$$

The value .9 is in excellent agreement with previously determined k_1 values for spheres (57). The value of .61 is smaller than the value $k_1 = .7$ determined by Eiler (58).

A comparison of the values of k_1 determined for PSL and for TMV shows that the TMV value is about 1/3 to 1/4 that of the PSL. This is contrary to what is generally expected. Philippoff (4) has said that one would expect the value of k_1 to increase with increasing nonsphericity. It is possible that some orientation phenomenon acts simultaneously to decrease the value of k_1 for rods.

The experimental results for the mixture of TMV and of PSL may be interpreted along the same lines as the homogeneous suspensions. The increment in the specific viscosity was given by

$$\eta_{sp} = 0.0145 C_{TMV} C_{PSL}$$

We therefore have

$$k_1 [\eta]_0^{\text{PSL}} [\eta]_0^{\text{TMV}} = 0.0145$$

and

$$k_1 = 1.04$$

It is believed that this is the first measurement of the interaction coefficient for a known polydispersed system. The interaction coefficient approaches that of spherical particles. We had previously postulated that the low value of k_1 for TMV might be due to an orientation effect of the particles. One would expect that this orientation effect would be disrupted by the presence of the spheres. This conjecture is supported by the experimental results.

Discussion of Errors

The sources of errors in viscosity measurements have been discussed previously in Section II pages 18-20. The efflux times in the neighborhood of 200 seconds show a standard deviation of

4 milliseconds

The density measurements were accurate to

$$1 \times 10^{-5}$$

The determination of the concentrations of the solution is perhaps the greatest source of error. In the case that dilutions were made by weighing an accuracy to

0.001 ml

was maintained. Dilution in the viscometer which was

accomplished by pipettes was estimated to be accurate to less than

0.004 ml

If all errors were attributed to the determination of the relative viscosity then the experimental data shows a standard deviation of approximately

0.00004

in the relative viscosity.

THEORY

We shall consider in detail the Einstein approach to the hydrodynamic theory of viscosity (of a dilute solution of spherical particles). It would be well to list again the physical assumptions:

1. The suspended particles have dimensions large with respect to the molecules of the solvent but small with respect to the characteristic length of the experimental apparatus.
2. The undisturbed flow of solvent is sufficiently slow so that inertial effects may be neglected. The flow is assumed incompressible.
3. The solvent adheres without slipping to the spheres.
4. The concentration of the suspended spheres is infinitely dilute. The action of suspended spheres is additive.

Since the first assumption permits one to treat the solvent as a continuum, the Navier-Stokes equations are basic to the entire theory. The condition that the particles be small with respect to the characteristic length of the apparatus is an experimental requirement that must be fulfilled in any verification of the theoretical results.

The neglect of inertial effects allows the use of the

Stokes approximation to the Navier-Stokes equations. The resulting linearity of the equations greatly facilitates the mathematical solution of the problem.

The adherence condition for viscous fluids has been extensively verified by experiment. It is reasonable to suppose that this condition would also be fulfilled by macromolecules. The last assumption eliminates consideration of particle interaction. Einstein assumed that the perturbation due to the presence of a sphere vanished at a great distance from it. Since the dilution is taken as effectively infinite, the distance between particles is infinite and there is no particle interaction. From the solution for a single sphere one then obtains the solution for a very dilute suspension by linear superposition.

We may now formulate the problem mathematically. The solution of the flow problem will consist of two parts.

1. The unperturbed flow
2. The perturbed flow due to the presence of the sphere.

The perturbed flow is the solution of the Stokes equations which vanishes at infinity and which, together with the unperturbed flow, satisfies the rigid adherence condition on the surface of the particle.

Let the total flow be

$$v_i = v_{oi} + v_{li} \quad i = 1, 2, 3$$

where

$$v_{oi} = \alpha_{ik} x_k$$

is the unperturbed flow and v_{1i} is the perturbed flow.

The linear tensor α_{ik} is assumed to be symmetric. There is therefore no relative motion of the perturbing sphere with respect to the fluid.

It is, of course, possible by a coordinate transformation to diagonalize α_{ik} so that we deal only with the principal dilatations. This will be done later in the analysis in order to conform exactly with Einstein's calculations.

The basic Stokes equations are

$$\eta_0 \nabla^2 v_i = \frac{\partial p}{\partial x_i} \quad i = 1, 2, 3$$

where

$$\nabla^2 v_i = \sum_k \frac{\partial^2 v_i}{\partial x_k^2}$$

and η_0 is the pure fluid viscosity.

The incompressibility condition is

$$\frac{\partial v_i}{\partial x_i} = 0$$

(Note the double index summation convention is used)

From this last condition it is clear that

$$\alpha_{ii} = 0$$

The boundary conditions are

$$v_{1i} \longrightarrow 0 \text{ as } r \longrightarrow \infty$$

where

$$r^2 = x_1^2 + x_2^2 + x_3^2$$

and $v = 0$ when $r = R$

where R is the radius of the sphere.

The initial pressure is constant and may be taken as zero.

The solution to the flow problem posed above is

$$v_{1i} = 5/2 \left(\frac{R^5}{r^4} - \frac{R^3}{r^2} \right) \alpha_{k1} n_i n_k n_1 - \frac{R^5}{r^4} \alpha_{ik} n_k$$

$$p = -5 \gamma_0 \frac{R^5}{r^3} \alpha_{ik} n_i n_k$$

where \bar{n} is a unit vector in the direction of the radius vector.

At large distances from the particle the perturbed flow is radial and proportional to the original flow field α_{ik} and the volume of the particle R^3 . The velocity field falls off with the square of the distance from the sphere.

Having determined the flow field we calculate the increase in energy dissipation due to the presence of the sphere. As will become evident in the analysis this energy dissipation may be related to an apparent increase in the viscosity of the suspension.

One may calculate the energy dissipated per unit time and per unit volume by calculating the rate of working of the pressure forces on the surface of a large sphere concentric with the particle. In the linear approximation the rate of working of the pressure forces must be the energy

dissipated since the change in kinetic energy which is of second order in the velocities is ignored.

$$\frac{dw}{dt} = \frac{1}{V} \iiint \sigma_{ik} v_i df_k$$

where the stress tensor

$$\sigma_{ik} = -p \delta_{ik} + \eta_0 \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right)$$

and

$$df_k = n_k df$$

At this point it would be well to note that had the standard definition for the dissipation of energy been used

$$\frac{dw}{dt} = 1/2 \eta_0 \iiint \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right)^2 dv$$

the cross product derivatives between the original flow v_{0i} and the perturbed flow v_{1i} would have been of $O(\frac{1}{r^3})$. The integral would have therefore been indeterminate upon attempting to integrate over all space. This type of integral is divergent in the sense that the result of the integration over all space although finite assumes different values depending upon the method of integration. The surface integral on the other hand has definite physical meaning and is determinate.

Upon diagonalizing the tensor α_{ik} the result of the integration is

$$\frac{dw}{dt} = 2 \beta_{ii}^2 \eta_o \left\{ 1 + \frac{1}{2} \frac{4\pi R^3}{3V} \right\}$$

where β_{ii} are the principal dilatations of the original flow. In the absence of the spheres the energy dissipated per unit time and volume of the pure solution is

$$\left(\frac{dw}{dt} \right)_{sol} = 2 \beta_{ii}^2 \eta_o$$

In the case of n spheres per unit volume one has

$$v_i = v_{oi} + \sum_j^n v_{ji}$$

and using the additivity assumption one has

$$\frac{dw}{dt} = 2 \beta_{ii}^2 \eta_o [1 + \phi/2]$$

where $\phi = \frac{4\pi nR^3}{3V}$ is the small volume fraction of the spheres. In analogy to the pure fluid dissipation of energy we define for the suspension

$$\left(\frac{dw}{dt} \right)_{susp} = 2 \eta^* \beta_{ii}^{*2}$$

where η^* is the apparent viscosity of the suspension and β_{ii}^* are the principal dilatations of the suspension. Thus we obtain

$$\eta^* \beta_{ii}^{*2} = \eta_o \beta_{ii}^2 [1 + \frac{1}{2} \phi]$$

In order to obtain the apparent viscosity η^* of the suspension we must calculate β_{ii}^* in terms of β_{ii} .

In the previous calculations we considered only a single sphere and simply added the effects of the other spheres. In order to evaluate the principal dilatation β_{ii}^* we must carefully define our coordinate system. First let $\beta_{ii}^* = \beta_i^*$. Let point x_j ($j = 1, 2, 3$) be a fixed point in the fluid. Then the flow at x_j due to a sphere at x_j^ν is obtained from our previous equations by substituting $(x_j - x_j^\nu)$ for x_i . Summing over all spheres ν and retaining only terms of order $O(\frac{1}{r^2})$ and $O(R^3)$ this flow written out in detail is

$$v_j = v_{oj} + v_j^\nu$$

$$v_j = \sum_{\nu} \left\{ \beta_j(x_j - x_j^\nu) - 5/2 \frac{R^3(x_j - x_j^\nu) \sum_{j=1}^3 \beta_j(x_j - x_j^\nu)^2}{[\sum_j (x_j - x_j^\nu)^2]^{5/2}} \right\}$$

Due to symmetry the principal dilatations β_j^* of the suspension are parallel to those β_j of the original flow.

By definition then

$$\beta_j^* = \left(\frac{\partial v_j}{\partial (x_j - x_j^\nu)} \right)_{x_j = x_j^\nu}$$

and

$$\beta_j^* = \beta_j + \sum_{\nu} \left(\frac{\partial v_j^\nu}{\partial (x_j - x_j^\nu)} \right)_{x_j = x_j^\nu}$$

$$\beta_j^* = \beta_j - \sum_{\nu} \left(\frac{\partial v_j^\nu}{\partial x_j^\nu} \right)_{x_j^\nu = 0}$$

Following Einstein we replace the summation of all particles by a volume integral over all coordinates of the particles times the number of particles. Thus

$$\beta_j^* = \beta_j - n \iiint_V \rho \frac{\partial v_j^\nu}{\partial x_j^\nu} \prod_{j=1}^3 dx_j^\nu$$

$n = \frac{N}{V}$ the number of particles per unit volume and

ρ is the distribution function of the particles

around the point x_j . The distribution function is normalized as

$$\frac{1}{V} \iiint_V \rho dx_1 dx_2 dx_3 = 1$$

The volume integral of $\frac{\partial v_j^\nu}{\partial x_j^\nu}$ is, as in the case of the energy calculation, of order $O(1/r^3)$. We cannot therefore integrate over all space. Einstein's procedure of averaging over a large sphere S of volume V is perhaps the only method of attack. It will ultimately be supposed that the sphere tends to infinity. Since nothing is known about the distribution function ρ it is assumed by Einstein to be uniform in the whole space.

Applying Gauss's theorem to the volume integral one obtains

$$\beta_j^* = \beta_j - n \iint \frac{v_j^\nu x_j^\nu}{r^\nu} df$$

$$(r^\nu)^2 = \sum_{i=1}^3 (x_j^\nu)^2$$

Einstein then integrated over the exterior surface of the sphere to obtain

$$\beta_j^* = \beta_j (1 - \emptyset)$$

This calculation is however incorrect since the domain of integration contains a singularity which was ignored in applying Gauss's theorem. We must therefore introduce a small sphere of radius ϵ about the origin and integrate over this interior surface and then allow $\epsilon \rightarrow 0$. It is immediately evident however that since $u \sim O(1/r^2)$ the integral is independent of r and that therefore the contribution of the outer sphere is the negative of the contribution of the interior sphere. The value of the integral is accordingly zero.

It has been suggested by Frish and Simha (3) that Einstein's result would be correct if we were to place a particle into the origin. The surface integral over the inner surface which in this case is the particle vanishes then because of the boundary conditions. This is also incorrect since the physical interpretation of the integral is an integration over all coordinates of the other spheres. On placing a particle at the origin no sphere can approach closer than $2R$ to the origin so that the integration must extend from $2R$ to the radius of the large enclosing sphere S . In this case the contribution of the inner sphere to the integral again cancels that of the outer.

Disregarding for the moment the fact that the principal dilatations obtained by Einstein are wrong we shall calculate the viscosity increase of the suspension.

$$\beta_{jj}^{*2} = \beta_{jj}^2 (1 - 2\phi) \quad (\text{summation convention})$$

$$\eta^* \beta_{jj}^2 (1 - 2\phi) = \eta_0 \beta_{jj}^2 [1 + \phi/2]$$

and

$$\eta^* = \eta_0 [1 + 2.5\phi]$$

As will be shown shortly in a rigorous development due to Burgers (15) this final result is correct. Even at this late date there appears to be some confusion in the literature as to the real nature of Einstein's result. Several investigators (59, 60) have tried to justify the Einstein obtained principal dilatations. This is perhaps motivated by a desire to extend the theory to second order in ϕ for in such an extension a similar integral occurs. It is believed that the source of the confusion lies in the fact that Einstein actually committed two errors which cancelled each other. If we again consider the energy calculation it is evident that Einstein in considering the energy dissipated in a large sphere S concentric with the original particle has essentially modified the condition satisfied at infinity by the perturbation velocity. It would appear reasonable that one should demand that the perturbation velocity vanishes on the surface of S . We can then interpret

the extension of S to infinity in the following interesting way. The growth of the surface of the sphere in the limiting process is always slower than the singularities which thus stay out of the region of integration.

We may satisfy the condition of the vanishing of the perturbation by superimposing a spherical harmonic such as to cancel the second term in

$$v_i = v_{oi} + v_{li}$$

on the surface of S. This is exactly the procedure followed by Jeffery (12) in his motion of an ellipsoid calculation. Jeffery does not make a comparison, however, with Einstein's calculations nor does he calculate the principal dilatations of the suspension but tacitly assumes them to be that of the original solution. Retaining terms to order $O(\frac{1}{r^2})$ one has with the summation convention

$$v_i = v_{oi} - 5/2 R^3 x_i \frac{\beta_j x_j^2}{r^5}$$

where

$$p = -5 \int_0 R^3 \frac{\beta_j x_j^2}{r^5}$$

When this is combined with the appropriate spherical harmonic one has

$$v_i = v_{oi} - 4 x_i \frac{p^5 - r^5}{p^5 r^5} (5/8 R^3 \beta_j x_j^2) + 5 \frac{p^2 - r^2}{p^5} \frac{\partial}{\partial x_i} (5/8 R^3 \beta_j x_j^2)$$

where P is the radius of the sphere S . This gives for the pressure on the surface of S

$$p = -25 \zeta_0^{5/4} R^3 \beta_j x_j^2 / P^5$$

If we now calculate the energy dissipated we obtain

$$\frac{dw}{dt} = 2 \zeta_0 \beta_{ii}^2 [1 + 2.5 \phi]$$

where ϕ is the volume fraction of a single particle or, upon use of the additivity assumption, of the whole suspension. Using now the fact that the dilatational components of the solution and of the suspension are the same to order $O(\phi)$ we obtain

$$\zeta^* = \zeta_0 (1 + 2.5 \phi)$$

The above interpretation is internally self consistent. The results of the calculations are in complete agreement with the rigorous approach of Burgers. They agree with the slightly different approach of Landau and Lifshitz (61) and they are in accord with Jeffery. The above interpretation removes some ambiguity that had existed in the Einstein procedure. We shall now turn to a detailed outline of the Burgers procedure of calculation of the viscosity increment due to a sphere in shear flow. In this analysis a comparison will be made with Einstein's approach.

J. M. Burgers (15) has developed an alternate approach to the calculation of the viscosity of a suspension of spheres. We shall outline the approach in detail and then compare it with that of Einstein.

Let the undisturbed flow field be

$$u_i = Dx_2 \delta_{li}$$

In the liquid we consider a small spherical particle of radius R which for convenience we place at the origin of our coordinates. The undisturbed flow induces a rotation of the sphere equal to $D/2$. The rotation alone does not fulfill the no-slip condition on the surface of the sphere. The velocities of a point on the surface are indeed given by

$$v_1 = \frac{1}{2} Dx_2 \quad v_2 = -\frac{1}{2} Dx_1 \quad v_3 = 0$$

We must introduce a perturbed flow u_i' such that on the surface of the sphere

$$u_i' = v_i - u_i$$

or

$$u_1' = -\frac{1}{2} Dx_2 \quad u_2' = -\frac{1}{2} Dx_1 \quad u_3' = 0$$

The perturbed flow u_i' vanishes at infinity. It is noted that the relationship between the coordinates and the velocities is given by a constant symmetric tensor. The solution to this problem has been given previously in the

explanation of Einstein's method. Specializing the tensor α_{k1} to the case of couette flow and letting

$$\begin{aligned} x_1 &= x & x_2 &= y & x_3 &= z & \text{one has} \\ u' &= -5/2 D \left(\frac{R^3 x^2 y}{r^5} \left(1 - \frac{R^2}{r^2} \right) - \frac{1}{2} \frac{R^5 y}{r^5} \right) \\ v' &= -5/2 D \left(\frac{R^3 xy^2}{r^5} \left(1 - \frac{R^2}{r^2} \right) - \frac{1}{2} \frac{R^5 x}{r^5} \right) \\ w' &= -5/2 D \left(\frac{R^3 xyz}{r^5} \left(1 - \frac{R^2}{r^2} \right) \right) \end{aligned}$$

We now consider the field of flow to be bounded by two planes with coordinates y_1 and y_2 . At these surfaces the normal component of the perturbed velocity must vanish. Burgers accomplishes this by adding a potential field β^* satisfying the equation $\nabla^2 \beta^* = 0$ in the interior of the field and satisfying the boundary conditions

$$\left(\frac{\partial \beta^*}{\partial y} \right)_{y_2} = 5/2 \frac{Dxy_2^2}{r^5} ; \quad \left(\frac{\partial \beta^*}{\partial y} \right)_{y_1} = 5/2 \frac{Dxy_1^2}{r^5}$$

As will become evident in the development of Burgers' method we do not need to calculate the field β^* .

With no particles in the fluid the velocities of the flow in the planes y_1 and y_2 are given by

$$u_1 = D y_1 \qquad u_2 = D y_2$$

The change in the x component of velocity due to the field β^* is given by

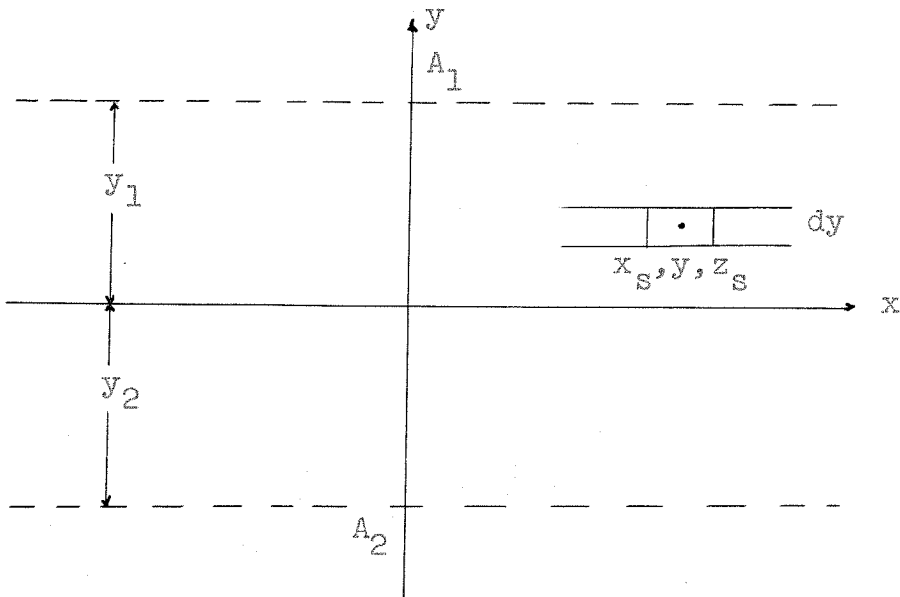
$$\frac{\partial \beta^*}{\partial x}$$

The total change in the horizontal component of velocity due to the potential flow vanishes

$$\iint_{-\infty}^{\infty} \frac{\partial \beta^*}{\partial x} dx dz = 0$$

in consequence of the circumstance that β^* itself vanishes at infinity.

In the suspension consider a layer parallel to the x z plane with coordinate y, $y_2 < y < y_1$ and thickness d y. Let x_s, y, z_s be the coordinates of the center of the sphere in this layer.



The additional flow due to the presence of the sphere has been calculated above. At the point A_1 ($x = 0, y_1, z = 0$) its x-component is, ignoring higher order terms

$$u'_s = - 5/2 D R^3 x_s^2 (y_1 - y) r_s^{-5}$$

where the subscript s indicates that we are measuring distances from the sphere.

The additional flow produced by $n dx_s dy dz_s$ particles contained in an element of volume around the point x_s, y, z_s has the x component $u'_s n dx_s dy dz_s$. This component produces a retardation of the flow and the total retardation due to all particles contained in a layer dy obtained by integration is

$$\delta_1 = - 5/2 D R^3 (y_1 - y) n dy \iint_{-\infty}^{\infty} x_s^2 y_s^{-5} dx_s dz_s$$

and since

$$\iint_{-\infty}^{\infty} x_s^2 r_s^{-5} dx_s dz_s = 2/3 \pi (y_1 - y)^{-1}$$
$$\delta_1 = - 5/3 \pi D R^3 n dy$$

It is important to note that this value is independent of y and of the position of the point A_1 in the plane $y = y_1$.

Similarly the additional flow at y_2 is

$$\delta_2 = + 5/3 \pi D R^3 n dy$$

The relative horizontal velocity $D(y_1 + y_2)$ of the two flow planes $y = y_1$ and $y = -y_2$ is now changed by the amount

$$\delta = \delta_1 - \delta_2 = - 10/3 \pi D R^3 n dy$$

Integrating the effects of all layers from $-y_2$ to y_1 one finds that the relative horizontal velocity of the two layers is given by

$$D(y_1 + y_2) [1 - 10/3 \pi R^3 n] = D(y_1 + y_2) [1 - 2.5 \phi]$$

If we now consider the change in the velocity gradient

$\frac{\partial u}{\partial y}$ at the point A_1 we find that the changes produced by the particles are partly negative and partly positive and its integration over all space is zero.

i.e.
$$\frac{\partial u^1}{\partial y} = - 5/2 (x_s^2 r_s^{-5} - 5 x_s^2 y_1^2 r^{-7})$$

and the integration over the $x z$ plane is

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\partial u^1}{\partial y} dx_s dz_s = 0$$

The contribution of the potential field β^* also vanishes on integration.

This result has a direct physical interpretation for the frictional force τ_{yx} per unit area of a plane parallel to the xz plane is given by

$$\tau_{yx} = \eta \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)$$

If we regard y_1 and y_2 as the walls of our viscometer we can see that the total value

$$\iint \tau_{yx} \, dx \, dz$$

of the frictional force transmitted across the plane $y = y_1$ does not change. The constancy of the shear stress on the wall allows us to calculate the effective viscosity.

Let $y_1 + y_2 = d$ and let U be the relative velocity of the two walls of the viscometer. With a pure solvent and running at a speed of U_0 the shear stress measured on the walls of the viscometer is

$$\tau_0 = \eta U_0/d = \eta D$$

with the introduction of the particles

$$U = d U_0 (1 - 2.5 \phi)$$

but from the definition of viscosity one has

$$\tau = \eta_{\text{eff}} U/d = \eta_{\text{eff}} \frac{U_0 (1 - 2.5 \phi)}{d}$$

since we have shown that $\tau = \tau_0$ we have

$$\eta U_0/d = \eta_{\text{eff}} \frac{U_0 (1 - 2.5 \phi)}{d}$$

$$\lambda = \lambda_{\text{eff}} (1 - 2.5 \phi)$$

and since ϕ is small

$$\lambda_{\text{eff}} = \lambda_0 (1 + 2.5 \phi)$$

which is the well known Einstein formula.

On comparing the modified Einstein procedure with that of Burgers one finds that, although the flow fields are slightly different, the mathematical steps are essentially the same. The perturbation field is first solved for all space. In theory one could then calculate the increase in energy dissipation over all space due to the perturbation field. The volume integral involved is, unfortunately, of $O(1/R^3)$ and therefore indeterminate upon integrating over all space. One is therefore forced to confine the integration to a finite region. Einstein does this by considering the rate of working of the pressure forces on a large sphere concentric with the original perturbing sphere. Burgers considers two parallel planes in the same calculation. Physically Burgers' geometry is more satisfying since it has an exact physical analogy in the couette viscometer. In the case of Einstein, the dimensions of the large sphere drop out of the calculations upon evaluation of the energy dissipation integral in terms of a surface integral. This unfortunately leads to a tendency to refer to the large sphere as effectively infinite. But it is exactly the fact

that the volume of integration is finite that makes the calculation possible. One must, therefore, introduce a compensatory flow which causes the perturbation flow to vanish on the boundary. In the corrected Einstein method this is done.

Burgers introduces a compensational field for the normal velocities at the surface of the two planes. Instead of introducing a compensational field for the horizontal velocity he, as has been shown, calculates the total change in the velocity over the plane. Since the total frictional force does not change he can then calculate the effective viscosity.

In the corrected Einstein method we consider a different integral of a derivative of the perturbed velocity, which is interpreted as the contribution to the principal dilatation of the suspension of the perturbed flow. This integral also vanishes. The vanishing of the contribution of the perturbed flow to the frictional force in Burgers' case and of the contribution of the perturbed flow to the principal dilatations in Einstein's case has a definite significance for any theory of viscosity to the second order in the volume fraction. It has, perhaps, been the desire to extend the theory to the second order which has motivated some of the previous rationalization of Einstein's original calculations.

Second Order Theory of Viscosity

In the second order theory of viscosity an attempt is made to relax Einstein's fourth assumption, which is that the solution is infinitely dilute and that the particles do not interact. This is accomplished by expanding the perturbation field of a given sphere in a Taylor's series in the neighborhood of a second sphere. The Stokes equations are then solved for the perturbation flow due to the second sphere in the modified flow field. The perturbation vanishes at infinity and, together with the original flow field plus terms from the Taylor expansion, fulfills the condition of no-slip on the surface of the sphere.

In the neighborhood of a given sphere we shall assume that the perturbation field due to a second sphere at a fixed location is expanded in terms of a Taylor series. From the original solution that we obtained for the perturbed flow of a spherical particle in a symmetrical flow field, we can obtain the derivatives of the velocities.

These are

$$\frac{\partial u_{11}}{\partial x_m} = \frac{5}{2} \frac{R^3}{r^3} \left\{ \left(5 - 7 \frac{R^2}{r^2} \right) n_1 n_m n_k n_l \alpha_{kl} \right. \\ \left. - \left(1 - \frac{R^2}{r^2} \right) \delta_{im} n_k n_l \alpha_{kl} - 2 \alpha_{ml} n_i n_l \right. \\ \left. + 2 \frac{R^2}{r^2} (n_i n_l \alpha_{ml} + n_l n_i \alpha_{lm}) \right\} - \frac{R^5}{r^5} \alpha_{im}$$

The contribution of the terms due to the Taylor's expansion is divided into symmetric and antisymmetric parts.

With

$$\alpha_{im}^i = \frac{1}{2} \left(\frac{\partial u_{li}}{\partial x_m} + \frac{\partial u_{lm}}{\partial x_i} \right) \quad \omega_{im}^i = \frac{1}{2} \left(\frac{\partial u_{li}}{\partial x_m} - \frac{\partial u_{lm}}{\partial x_i} \right)$$

the flow due to the second sphere in the neighborhood of the first is given by

$$u_{2i} = \alpha_{im}^i x_m + \omega_{im}^i x_m$$

The second part of this expression causes the sphere to perform a rigid rotation. We are interested only in the first term. It is seen that the original flow field

$$v_{oi} = \alpha_{ik} x_k$$

has been replaced by

$$v_{oi}^i = (\alpha_{ik} + \alpha_{ik}^i) x_k$$

The quantity $(\alpha_{ik} + \alpha_{ik}^i)$ is a symmetric constant tensor so that our original general solution to the perturbation problem does not change. We have therefore

$$v_{li}^i = \frac{5}{2} \left(\frac{R^5}{r^4} - \frac{R^3}{r^2} \right) (\alpha_{kl} + \alpha_{kl}^i) n_i n_k n_l$$

$$- \frac{R^5}{r^4} (\alpha_{ik} + \alpha_{ik}^i) n_k$$

$$p = -5 \eta_0 \frac{R^3}{r^5} (\alpha_{ik} + \alpha_{ik}^i) n_i n_k$$

The solution is perfectly general and may be specialized to the case of dilatational flow and couette flow. Some significant results may be obtained without specialization. If we obtain the energy dissipated by calculating the rate of working of the stresses on the surface of a large sphere we obtain products of the following form

$$R^3 (\alpha_{ik} \alpha_{kl} + \alpha_{ik} \alpha'_{kl} + \alpha'_{ik} \alpha'_{kl})$$

Only the term $R^3 \alpha_{ik} \alpha'_{kl}$ is of $O(R^6)$ i.e. $O(\phi^2)$. This is the term we are trying to calculate in the second order theory. It is however linear in α'_{kl} . We must average over all orientations of the second particle with respect to the first. Under the assumption that all orientations are equally likely the average value of α'_{kl} is zero

$$\bar{\alpha}'_{kl} = 0$$

This is clear mathematically since

$$\bar{\alpha}'_{kl} = \frac{1}{V} \iiint \alpha'_{kl} dV$$

The integration is to be performed over the volume bounded by an interior sphere of radius $2a$ and a large concentric sphere. Upon conversion of the volume integral to a surface integral it is seen that the term involving (R^3) of the integrand is of $O(\frac{1}{r^2})$. The value of the integrand is therefore independent of r and the contribution of the interior

spherical surface cancels that of the large spherical surface. This result is independent of the original flow field as long as the tensor α_{ik} describing that field is symmetric.

In an elaborate calculation Guth-Simha-Gold (19) have calculated the effect of interaction of spheres in dilational flow. In this calculation they follow the same procedure we have outlined above. They fail, however, to integrate over the surface of the inner sphere. The result of this incorrect analysis is a value of

$$14.1 \phi^2 = k_1 [\eta]_0^2 \phi^2$$

The value of k_1 with $[\eta]_0 = 2.5$ is 2.26. Chang and Schachman (62) claim to have verified this quasi-theoretical result by measurements on polystyrene latex. Most other measurements give an experimental value in the neighborhood of

$$7.0 \phi^2 = k_1 [\eta]_0^2 \phi^2$$

The corresponding k_1 is ~ 1 .

Riseman and Ullman (18) in a different approach based on the use of the Oseen tensor have developed theoretical interaction coefficients for dumbbells, rods and flexible centrosymmetric molecules. Their predicted k_1 values are

$$k_1 = 11/15 \text{ dumbbell}$$

$$k_1 = 11/15 \text{ rod}$$

$$k_1 = 3/5 \text{ flexible molecule.}$$

Their calculations ignore again the integration over the interior spherical surface in integrals similar to those in the Guth, Simha and Gold calculations. Upon proper evaluation the second order term vanishes.

For spherical molecules and rigid and flexible centrosymmetric molecules the second order term due to hydrodynamic interactions between the particles vanishes.

Specializing our general solution to the case of couette flow one finds that the change in velocity at a point on the plane surface is given by

$$\mathcal{J}_1 = - \frac{5}{3} \pi (\beta_{12} + \beta'_{12}) n dy$$

where $\beta_{12} = - \frac{1}{2} D$ and β'_{12} is

$$\beta'_{12} = \frac{1}{2} \left(\frac{\partial u_1'}{\partial x_2} + \frac{\partial u_2'}{\partial x_1} \right)$$

The result is linear in β'_{12} . We must average this quantity over the space defined by the two planes y_1 and y_2 . It is noted that this expression, except for a multiplicative constant, is identical to the expression for the additional shear stress on a plane y . On integrating over all spheres of the same layer and then over all the layers one finds that the resultant value vanishes. In the Burgers method one then finds that the second order term also vanishes.

Vand (9) has considered successive reflections from one sphere to another. Thus a given sphere is subject to a flow

field of the form

$$v_{oi} = (\alpha_{ik} + \alpha_{ik}' + \alpha_{ik}'' \dots) x_k$$

where the α_{ik}' is the first reflection that we have previously considered α_{ik}'' and others are succeeding reflections. By the method used in evaluating α_{ik}' he arrives at a value for α_{ik}'' which gives a second order term of

$$1.56 \phi^2$$

In dilute solutions a second order term of this magnitude is very difficult to detect.

It would be appropriate at this point to consider a fundamental difference between the Einstein and Burgers approach. As we have seen to the first order in ϕ both give the Einstein value of 2.5. Einstein's calculation leads to a linear relation in concentration for the relative viscosity. Burgers method leads, however, to a linear dependence of the relative fluidity (fluidity is defined as the reciprocal of the viscosity $1/\eta$). We have

$$\eta_{rel} = 1 + 2.5 \phi \quad (\text{Einstein})$$

and

$$\frac{1}{\eta_{rel}} = F_{rel} = 1 - 2.5 \phi \quad (\text{Burgers})$$

where F_{rel} is the relative fluidity. If we were to accept the second equation as being correct then a plot of

$$\frac{1 - F_{\text{rel}}}{\phi} \text{ vs } \phi$$

should result, in the case of no interaction in a horizontal straight line. As graph 9 shows this is indeed the case for the PSL data extrapolated to infinite shear. Interpreted in terms of relative viscosities this means that

$$\eta_{\text{rel}} = \frac{1}{1 - 2.5 \phi}$$

It is to be noted that the intercept of graph 9 gives essentially the same intrinsic viscosity as obtained in graph 6. That is

$$[\eta]_{\infty} = 0.0280$$

On the basis of the first order term there is thus no distinction either theoretically or experimentally between the Burgers result and the Einstein result. The theory of Burgers, which is linear in relative fluidity, adequately explains, in addition, the variation of the relative viscosity with concentration. There is no need to postulate particle interactions for low concentrations to explain the variation of the relative viscosity with concentration. We have shown, indeed, that there are no second order interactions at the concentrations studied, or at most they are of such small magnitude as to be practically undetectable even with the precision viscometer used in these experiments.

CORRELATION OF THEORY AND EXPERIMENT

The interpretation of Burgers' theory in terms of fluidity explains the PSL data quite satisfactorily. Other experimental results reported in the literature are also in excellent agreement with the fluidity interpretation. Vand reports for the viscosity of glass spheres suspended in a solution of $Zn I_2$ in water-glycerol mixture an empirical equation of the form

$$\eta_{rel} = 1 + 2.5 \phi + 7.17 \phi^2 + 16.2 \phi^3$$

which agrees quite well even to the third order with

$$\eta_{rel} = \frac{1}{1 - 2.5 \phi}$$

It should be noted that the present theory would give an interaction coefficient of 1. That is

$$k_1 = 1$$

The work of Eirich et al (63) is also in agreement. The work of Maron (64), Bachle (65) and others (66) also supports the fluidity interpretation of Burgers' theory. In general there is considerable experimental evidence to support the interpretation of Burgers' theory advanced here.

The available experimental evidence is not sufficient to prove the validity of a second order term as small as the value of $1.56 \phi^2$ advanced by Vand.

The simple linear theory is not adequate to explain the variation of the TMV viscosity with concentration. The Burgers theory would lead, when considered in terms of relative viscosity, to a second order term of about $1500 \phi^2$ as opposed to the measured $350 \phi^2$. It is felt that interactions between rod-like molecules would tend to orient them so as to reduce the viscosity. Orientation effects could not affect the viscosity of spherical particles so that a linear theory is adequate for spherical suspensions. In order to verify the hypothesis that the orientation of the molecules is the contributing cause in the reduction of the viscosity, it would be necessary to turn to some other form of measurement than viscosity. Streaming birefringence would be an excellent method of investigating the orientation hypothesis in any continuing program based on these investigations.

The increment in specific viscosity in the mixture of rods (TMV) and spheres (PSL) solution may, in the light of the above, be interpreted as a disruption to some extent of the orientations of the rods by the spheres. In this case the increment in specific viscosity due to mixing could be interpreted as an increase in the interaction coefficient k_1 of the TMV. This interpretation means that the value of $k_1 = 0.226$ would more than double in the presence of the spheres. An investigation of the disruption of the orientation of rods due to the presence of spheres by flow birefring-

ence might prove quite fruitful. In particular if this investigation were conducted on solutions of a spherical virus and TMV some of the difficulties encountered with the surface chemistry of PSL would be eliminated.

SUMMARY AND CONCLUSIONS

A precision capillary viscometer with a photoelectric timer has been designed and built for these investigations. The viscometer is capable of measuring relative viscosities of dilute macromolecular solutions with a standard deviation of 0.00004.

The assumption has been made that the specific viscosity can be expanded in a power series in concentration. That is

$$\eta_{sp} = [\eta]_0 c + B c^2$$

The intrinsic viscosity $[\eta]_0$ and the coefficient B have been determined for a suspension of spherical macromolecules (polystyrene latex) and for a suspension of rigid rod-like macromolecules (tobacco mosaic virus). It is believed that this investigation is the first accurate determination of the coefficient of the second order term for rigid rods. The viscosity of a known heterogeneous suspension of rods (TMV) and spheres (PSL) has been determined and been interpreted in terms of interaction coefficients. This is most likely the first viscosity investigation of the interaction of a macromolecular solution consisting of spheres and rods. The assumption was made that the increase in viscosity due to mixing was bilinear in both concentrations.

The following summary table is given for the experimental data

	$[\eta]_0$	$[\eta]_\infty$	$B \times 10^4$
TMV	0.3892		342
	0.3722*		
PSL	0.0344	0.0281	7.2
Mixture			145

The intrinsic viscosity (extrapolated to infinite shear) $[\eta]_\infty$ was considered to be more significant than $[\eta]_0$ in any explanation of the PSL data. It was felt that surface chemistry effects or changes in the shape of the emulsifier invalidated the significance of $[\eta]_0$ for the PSL. Two values of the intrinsic viscosity were obtained in the TMV data. The lower value was attributed to adsorption effects or to the breaking up of dimers.

The coefficient B was further interpreted in terms of a hypothesis due to Huggins as

$$B = k_1 [\eta]_0^2$$

where k_1 is a dimensionless constant. The value obtained for k_1 are

	PSL	TMV	Mixture
k_1	0.90 (infinite shear)	0.226	1.04
	0.61 (zero shear)		

*Below a concentration of .06 g TMV per 100 g water.

A comparison with other experimental data when it existed showed good agreement. The low value of k_1 for TMV was attributed to mutual orientation effects. The value 1.04 for the mixture could indicate a disturbance of the orientation of the rods by the spheres. It was pointed out that if the increment in viscosity due to mixing were attributed solely to a change in k_1 for the TMV the value 0.226 would be more than doubled in the presence of the spheres.

The Einstein theory of viscosity of dilute suspensions has been modified to form, together with the approaches of Burgers and Jeffery, a logically consistent theory for the intrinsic viscosity of spherical molecules in particular, and ellipsoidal particles in general. The modification was necessary in order to remove what had been termed an improper indeterminate integral in the Einstein procedure.

The second order theory in ϕ of the viscosity of suspensions was reviewed. Previous work in this field was shown to be in error. The conclusion was reached that for concentrations up to 1-2%, hydrodynamic interactions for spherical particles do not exist or if they do exist that their existence cannot be demonstrated by experimental measurements on dilute solutions. It was demonstrated that no second order interactions are found in theory and that they are not necessary to explain the experimental data of dilute suspensions of spheres.

It was shown that, when properly interpreted, the linear solution of Burgers to the problem of the viscosity of spherical suspensions fully explains the variation of the relative viscosity with concentration.

The linear theory of Burgers did not adequately explain the variation of the relative viscosity of rod-like molecules (TMV) with concentration. This was attributed to mutual orientation effects which would tend to decrease the viscosity of orientable macromolecules. The study of the polydispersed system consisting of rods and spheres also indicated that orientation effects might be important. The suggestion was made that future investigations of rod-sphere suspensions be made by means of streaming birefringence in order to validate the orientation hypothesis.

Table 1

CALIBRATION AND SURFACE TENSION
CORRECTION DATA

Run	Bulb	Time	ρ	η_{rel}	conc. %	
N ₁	1	191.852	.99630	1.01231	.064 ⁹	Surface Tension Correction $\Delta\sigma = 40.0$ $\sigma_{H_2O} = 71.5$ $\sigma_{TMN} = 31.5$
	2	225.875		1.01650		
	3	211.614		1.01954		
N ₂	1	191.318	.99628	1.00945	.043 ²	
	2	225.165		1.01327		
	3	210.758		1.01535		
N ₃	1	191.020	.99627	1.00786	.032 ⁴	
	2	224.727		1.01124		
	3	210.285		1.01304		
N ₄	1	191.997	.99630	1.01309	.069 ⁷	
	2	226.026		1.01718		
	3	-		-		
N ₅	1	191.434	.99628	1.01007	.049 ⁷	
	2	225.336		1.01405		
	3	210.884		1.01595		
N ₆	1	191.216	.99628	1.00891	.038 ⁷	
	2	224.862		1.01190		
	3	210.453		1.01386		

Temperature	Bulb	Efflux Time
28.000	1	189.521
	2	222.212
	3	207.584
27.250	1	192.591
	2	225.824
	3	210.953
26.660	1	195.060
	2	228.708
	3	213.612
24.980	1	202.469
	2	237.428
	3	221.725
24.018	1	206.844
	2	242.589
	3	226.478

Calibration
Water

Table 2

EXPERIMENTAL DATA TOBACCO MOSIAC VIRUS

Run	Bulb	Time	ρ	k	λ_{rel}	conc.
T ₁	1	217.316	.99884	.99682	1.14683	.372 ⁸
	2	256.166		.99453	1.14993	
	3	239.950		.99418	1.15367	
T ₂	1	209.563	.99856	.99682	1.10537	.266 ⁴
	2	246.830		.99453	1.10759	
	3	231.018		.99418	1.11004	
T ₃	1	201.863	.99826	.99682	1.06412	.155 ²
	2	237.557		.99453	1.06551	
	3	222.325		.99418	1.06756	
T ₄	1	198.468	.99813	.99682	1.04605	.105 ⁶
	2	233.466		.99453	1.04696	
	3	218.300		.99418	1.04790	
T ₅	1	196.419	.99804	.99682	1.03509	.075 ⁶
	2	230.994		.99453	1.03575	
	3	215.938		.99418	1.03636	
T ₆	1	194.892	.99800	.99682	1.02694	.052 ⁷
	2	229.018		.99453	1.02681	
	3	214.011		.99418	1.02696	
T ₇	1	193.778	.99796	.99682	1.02099	.037 ⁷
	2	227.808		.99453	1.02134	
	3	212.884		.99418	1.02145	
T ₈	1	193.138	.99793	.99682	1.01756	.027 ⁶
	2	227.038		.99453	1.01782	
	3	212.145		.99418	1.01784	
T ₉	1	194.413	.99798	.99682	1.02438	.047 ⁴
	2	228.583		.99453	1.02483	
	3	213.633		.99418	1.02511	
Buffer	1	191.324	.99782	.99682	1.00784	
	2	224.874		.99453	1.00794	
	3	210.096		.99418	1.00780	

ρ = density

k = surface tension correction

Table 3

EXPERIMENTAL DATA POLYSTYRENE LATEX AND MIXTURE

Run	Bulb	Time	ρ	k	λ_{rel}	conc.
P ₁	1	194.465	.99815	.99682	1.02483	.568 ⁵
	2	228.717		.99453	1.02561	
	3	213.926		.99418	1.02670	
P ₂	1	192.329	.99793	.99682	1.01327	.178 ⁹
	2	226.113		.99453	1.01366	
	3	211.400		.99418	1.01422	
P ₃	1	192.048	.99790	.99682	1.01175	.127 ⁹
	2	225.774		.99453	1.01211	
	3	211.068		.99418	1.01257	
P ₄	1	197.664	.99840	.99762	1.04290	1.158 ⁹
	2	232.534		.99592	1.04451	
	3	217.666		.99565	1.04665	

						Conc.	
						PSL	TMV
M ₁	1	210.078	.99874	.99682	1.10831	.596 ⁴	.221 ⁹
	2	247.552		.99453	1.11104		
	3	231.956		.99418	1.11479		
M ₂	1	205.533	.99857	.99682	1.08400	.596 ⁴	.158 ⁶
	2	242.053		.99453	1.08609		
	3	226.713		.99418	1.08917		
M ₃	1	203.875	.99851	.99682	1.07515	.596 ⁴	.135 ²
	2	240.061		.99453	1.07706		
	3	225.325		.99418	1.08238		
M ₄	1	219.492	.99905	.99682	1.15861	.535 ⁴	.355 ⁶
	2	258.861		.99453	1.16231		
	3	242.781		.99418	1.16765		
M ₅	1	211.090	.99870	.99682	1.11363	.382 ²	.253 ⁸
	2	248.723		.99453	1.11626		
	3	233.086		.99418	1.12023		
M ₆	1	208.200	.99861	.99682	1.09820	.296 ⁹	.220 ⁷
	2	245.256		.99453	1.10055		
	3	229.773		.99418	1.10406		

ρ = density

k = surface tension correction

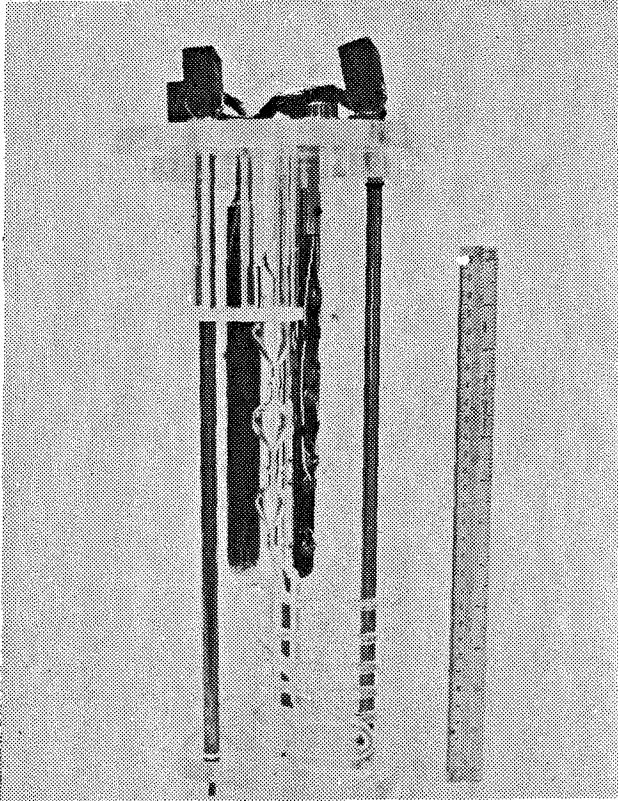


Photo 1
Side View of Viscometer

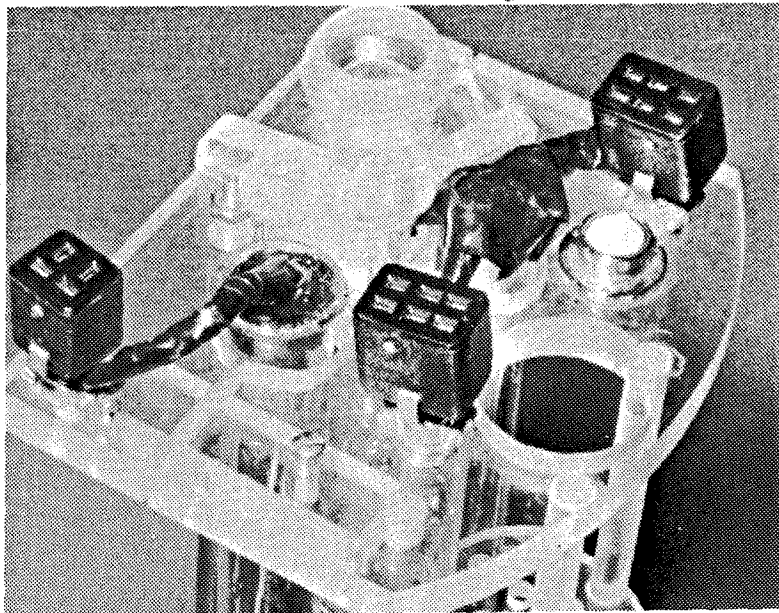


Photo 2
Top View of
Viscometer

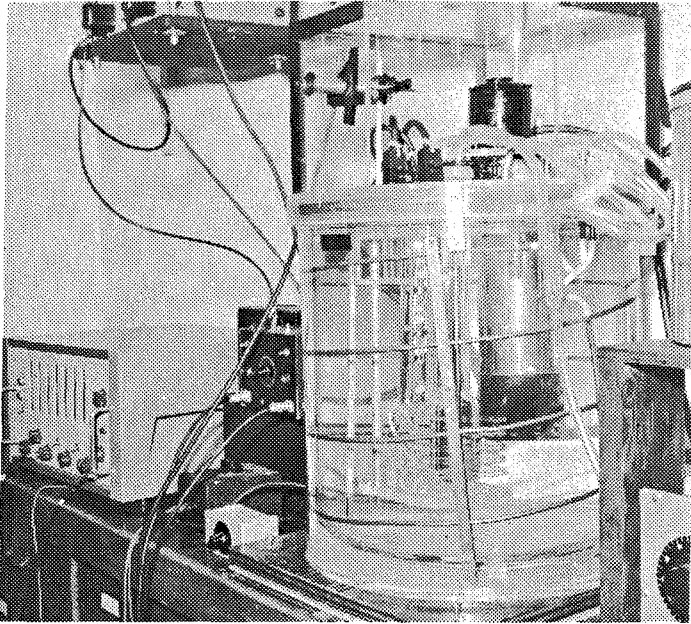


Photo 3
Viscometer Connected
to Sensing and Recording
Equipment

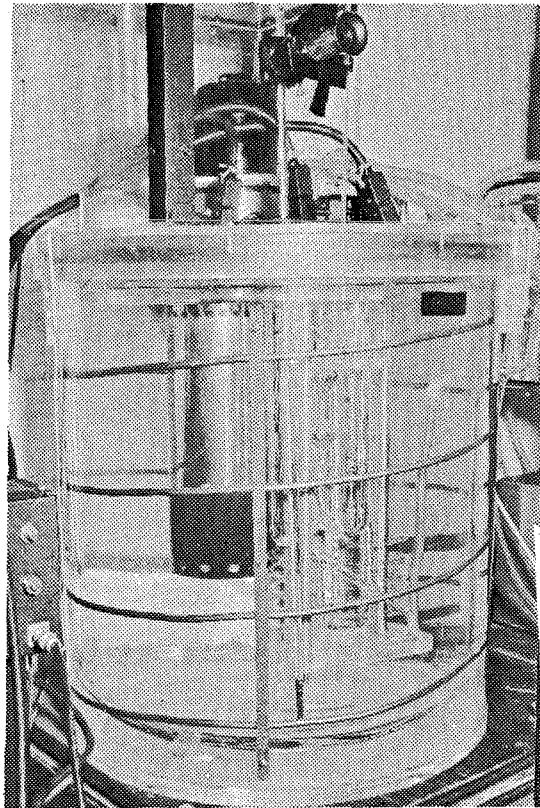


Photo 4
Temperature Bath and
Viscometer

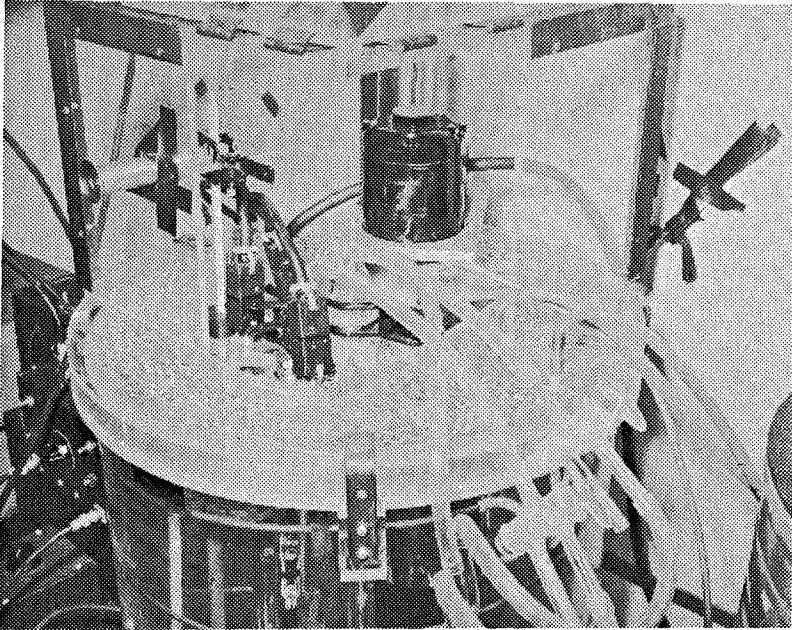


Photo 5
Top of Temperature
Bath

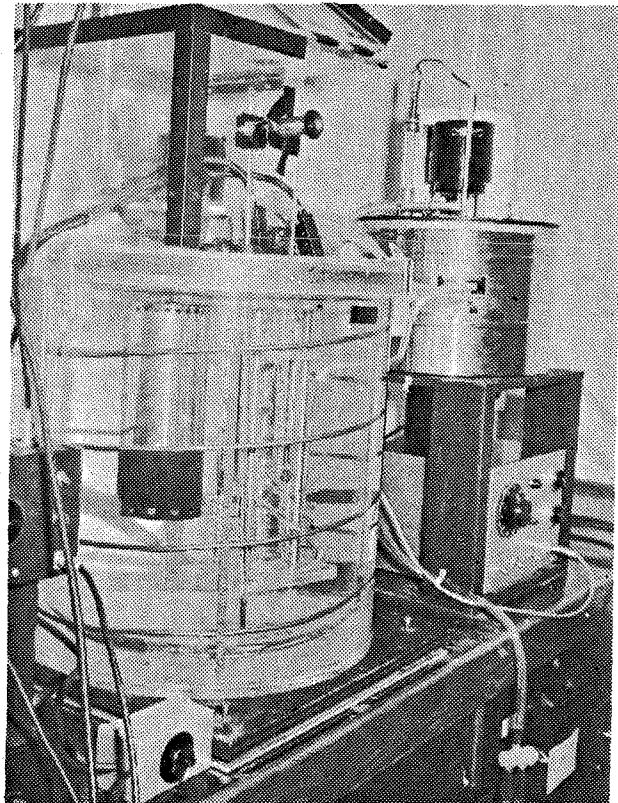


Photo 6
Bath and Temperature
Controls

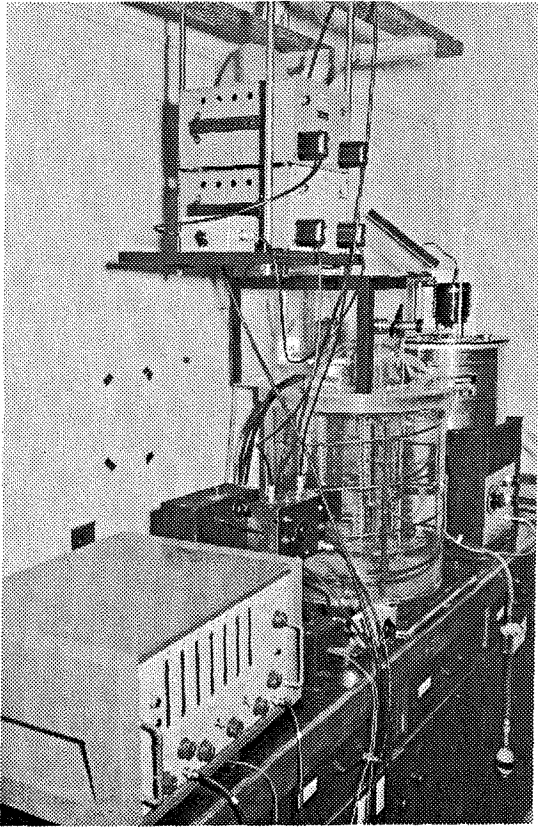


Photo 7
Overall View of Equipment

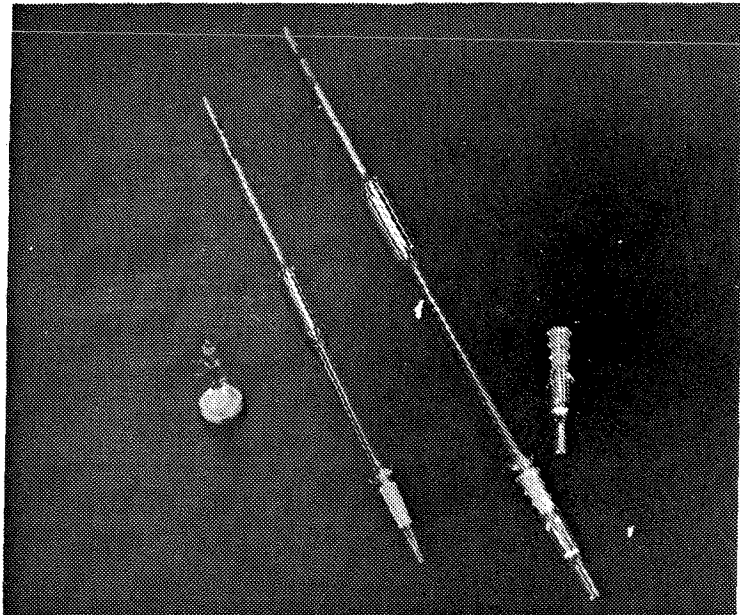
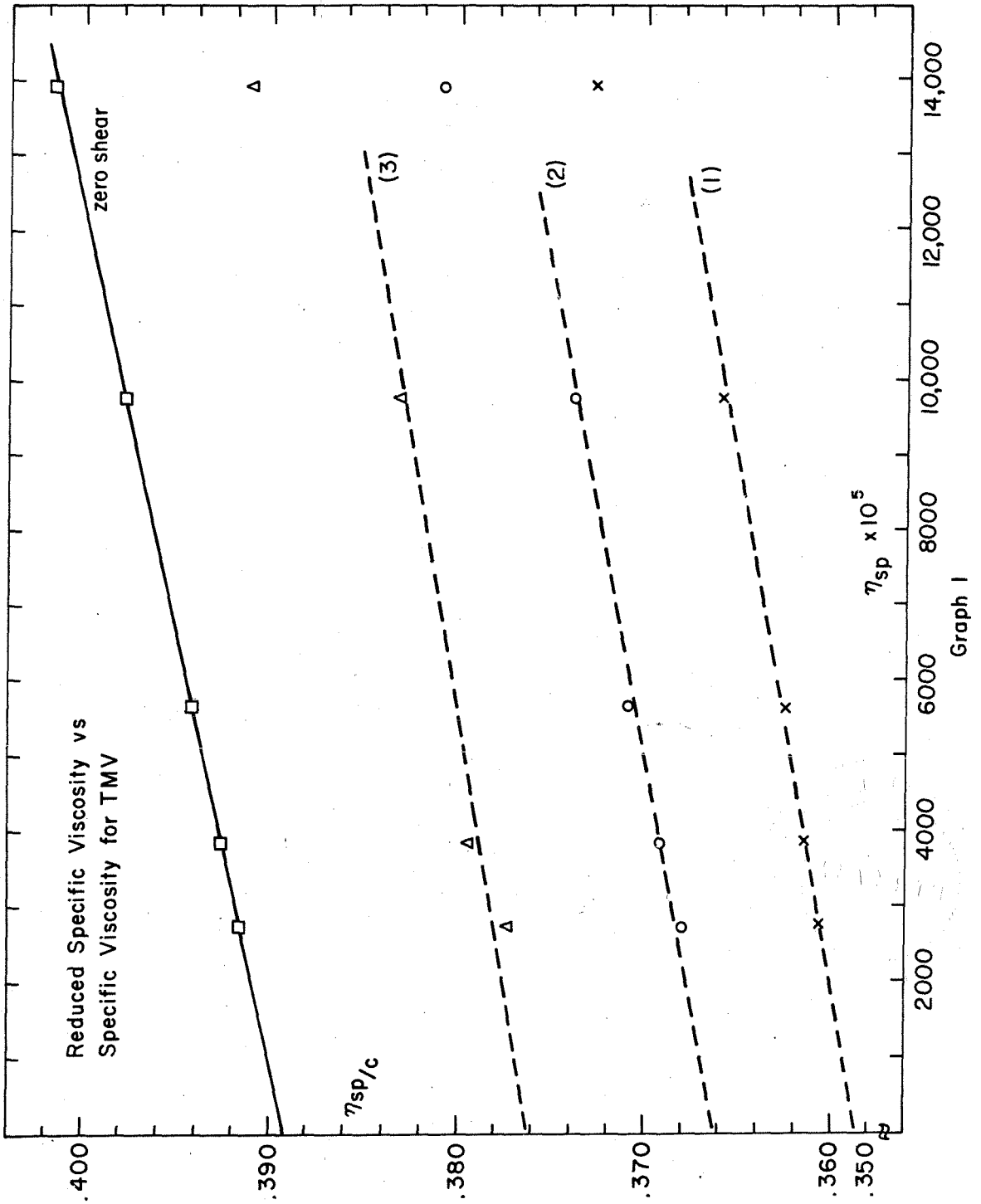
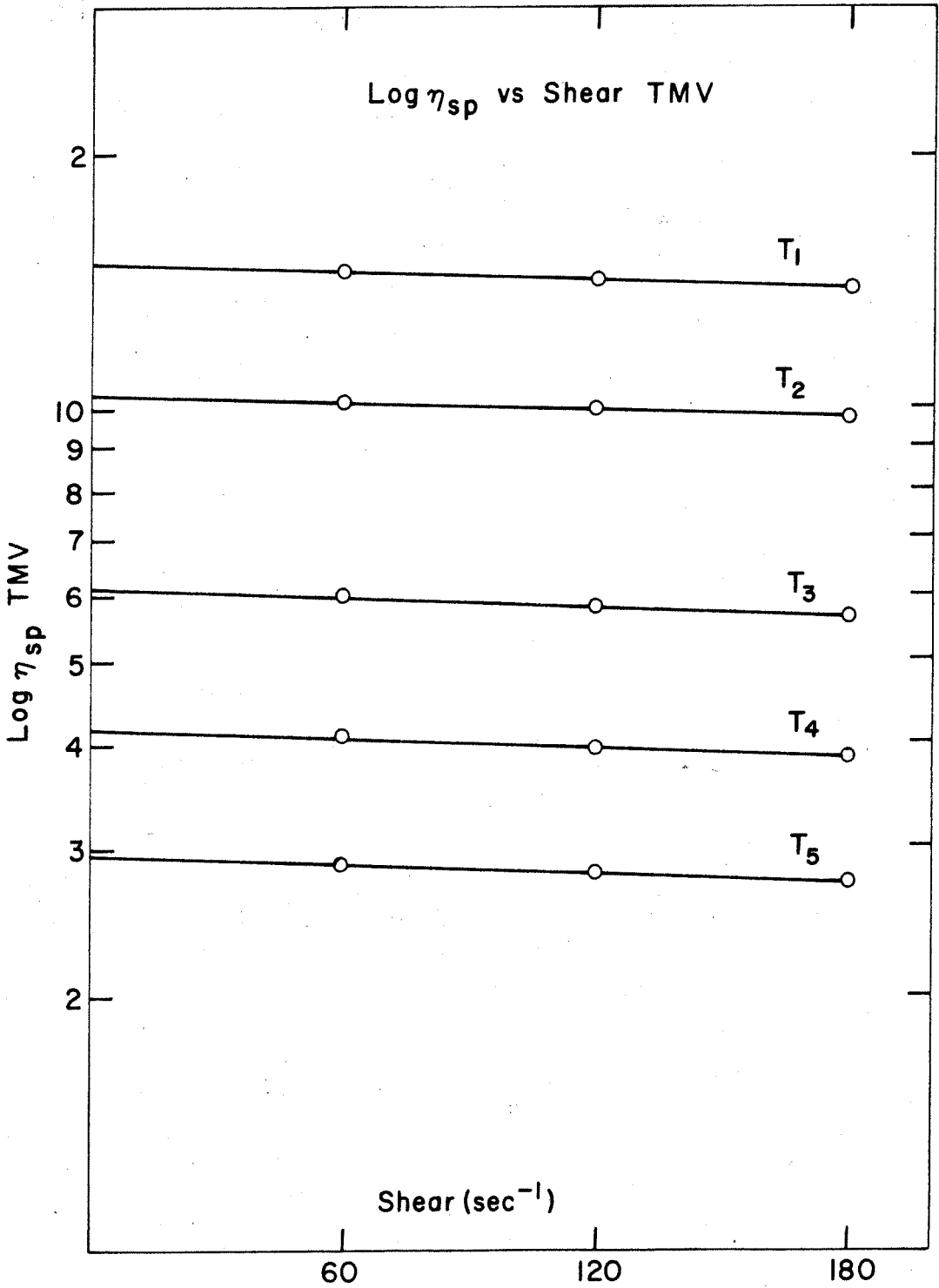
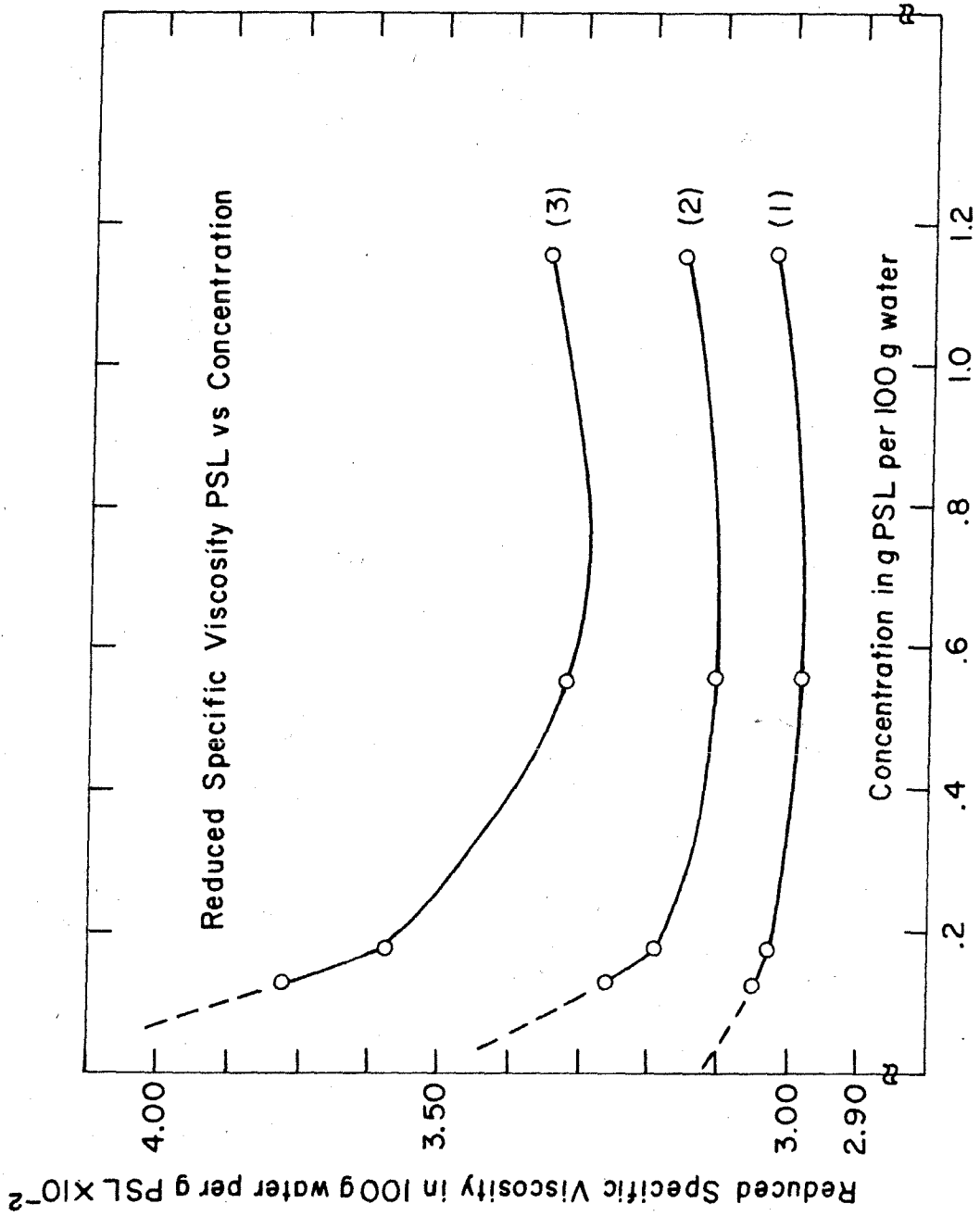


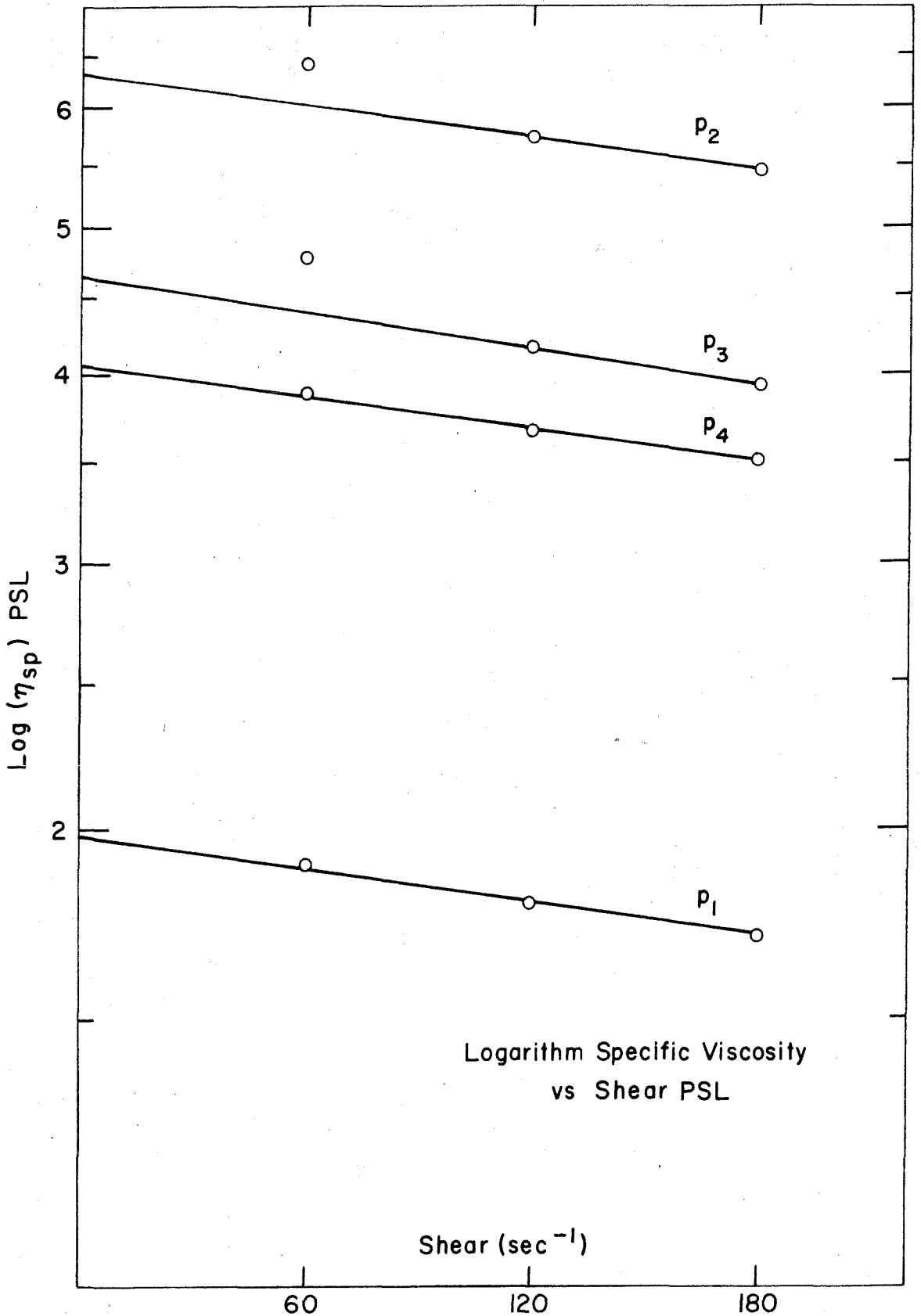
Photo 8
Pycnometer and
Pipettes



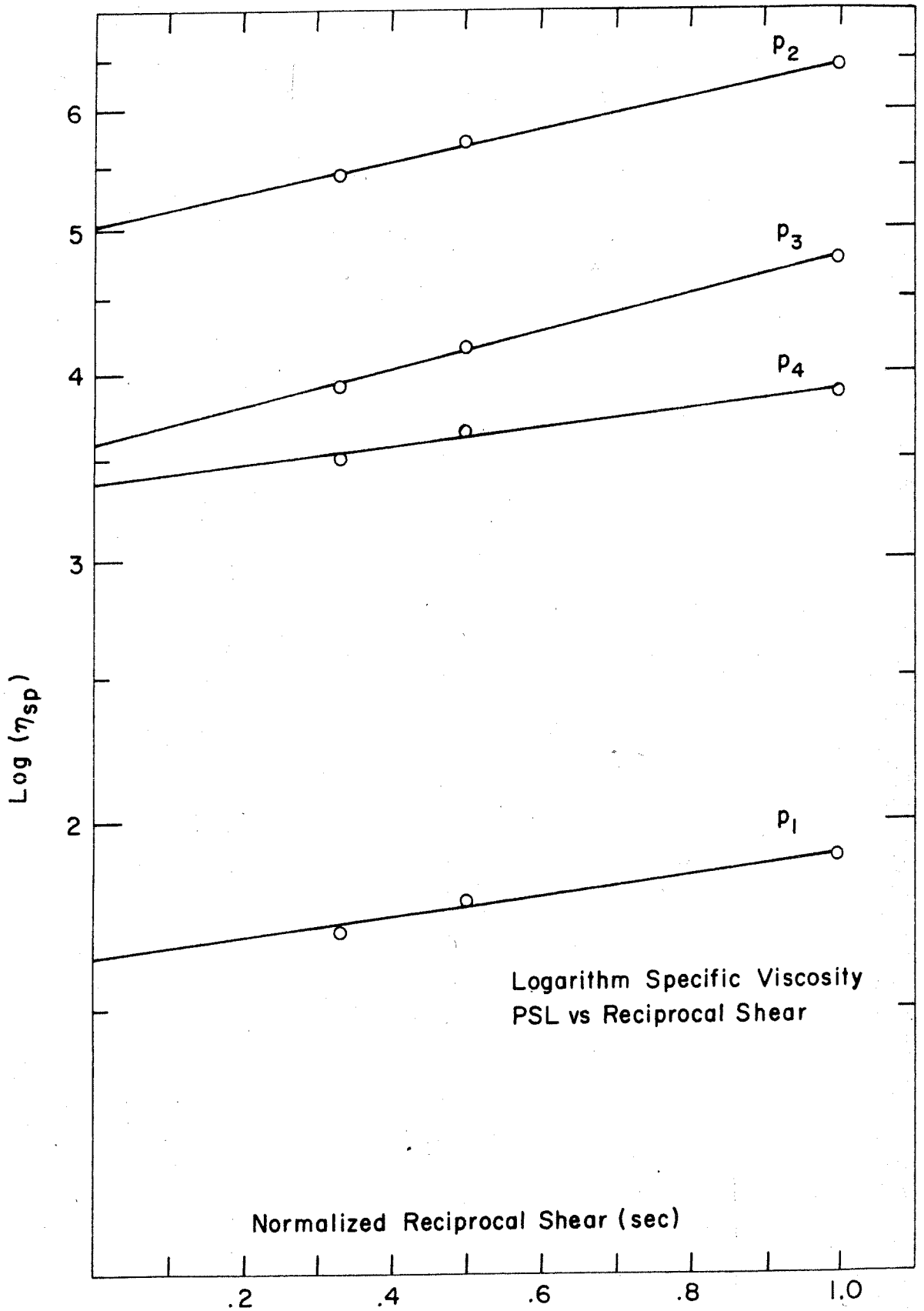


Graph 2





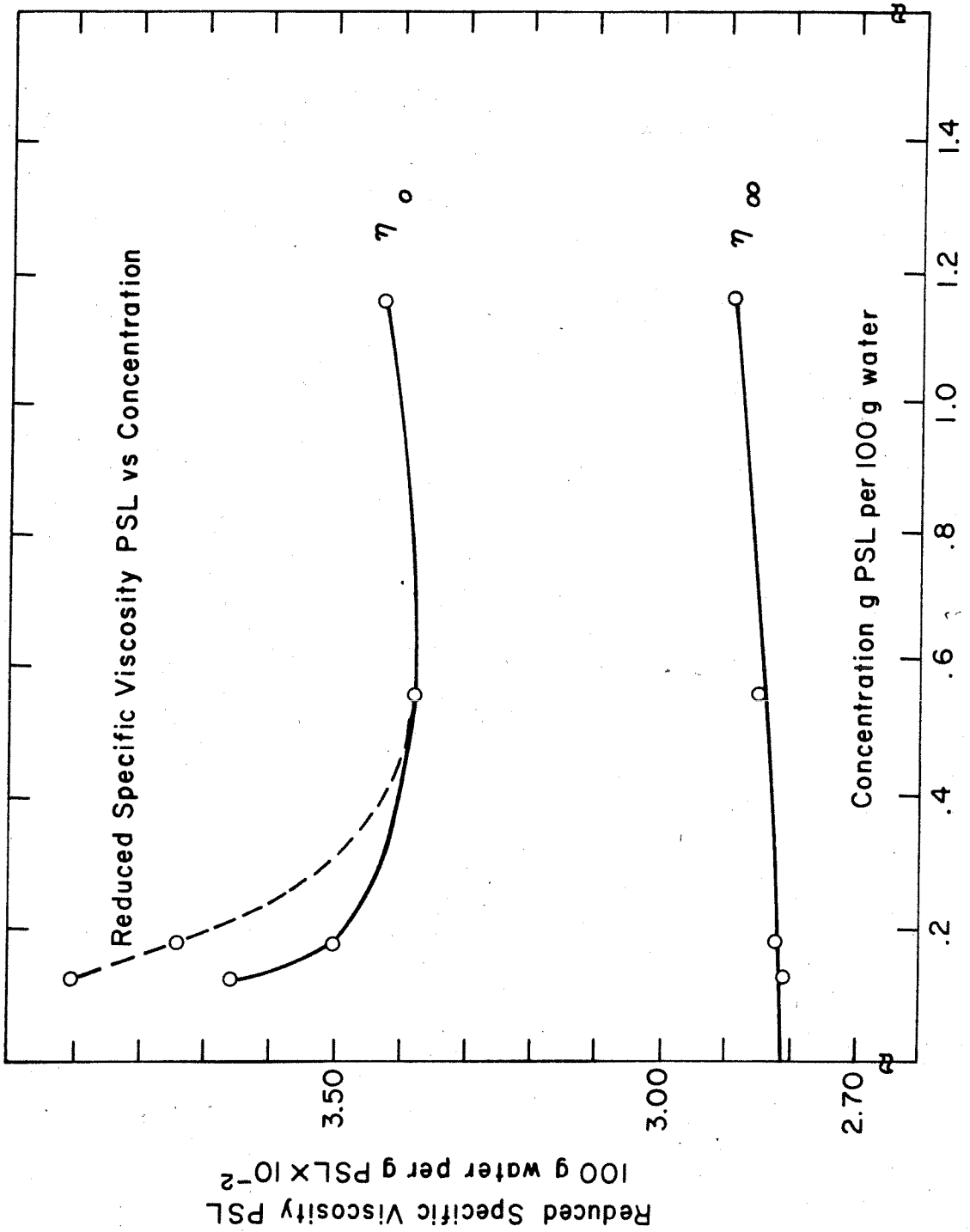
Graph 4



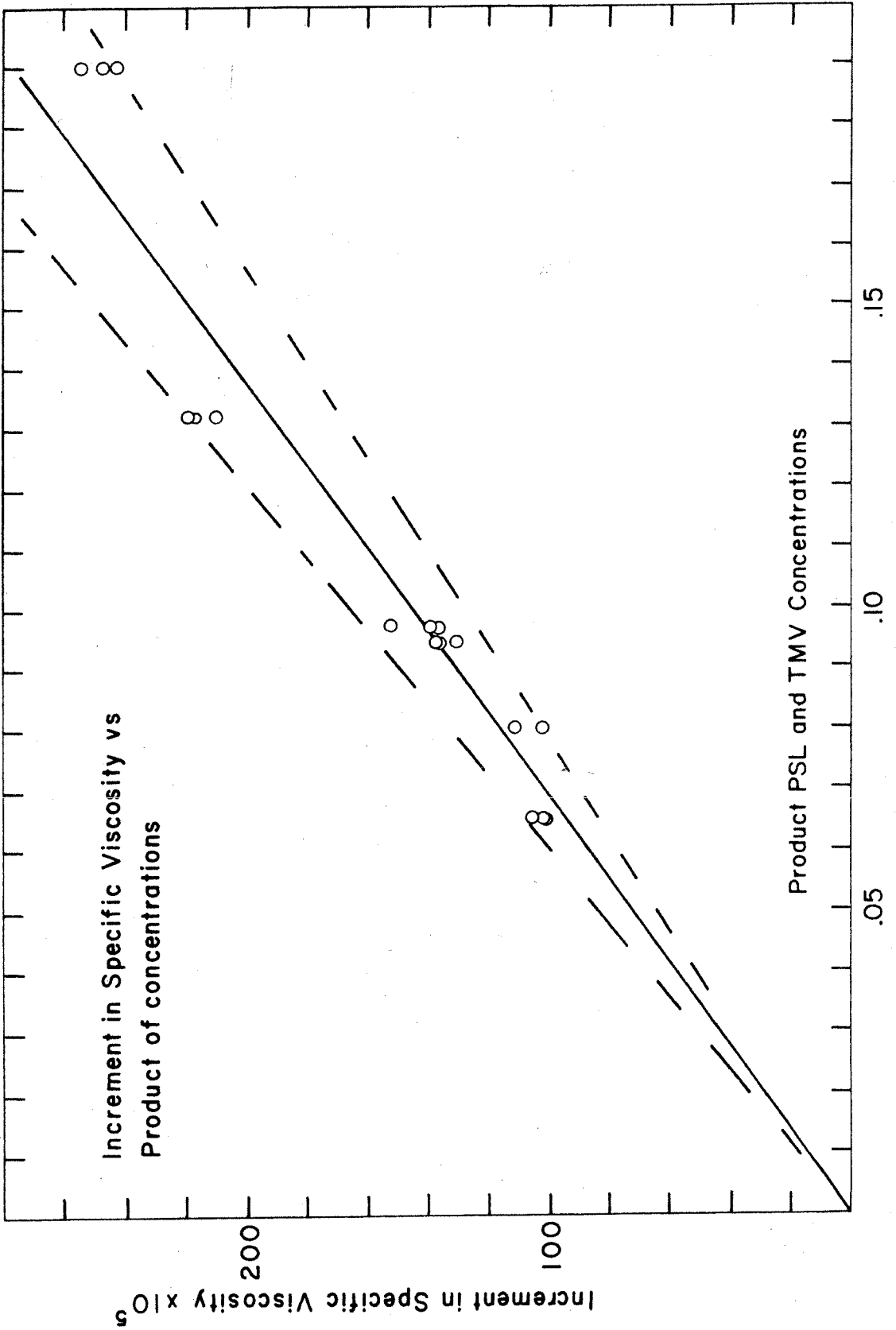
Logarithm Specific Viscosity
PSL vs Reciprocal Shear

Normalized Reciprocal Shear (sec)

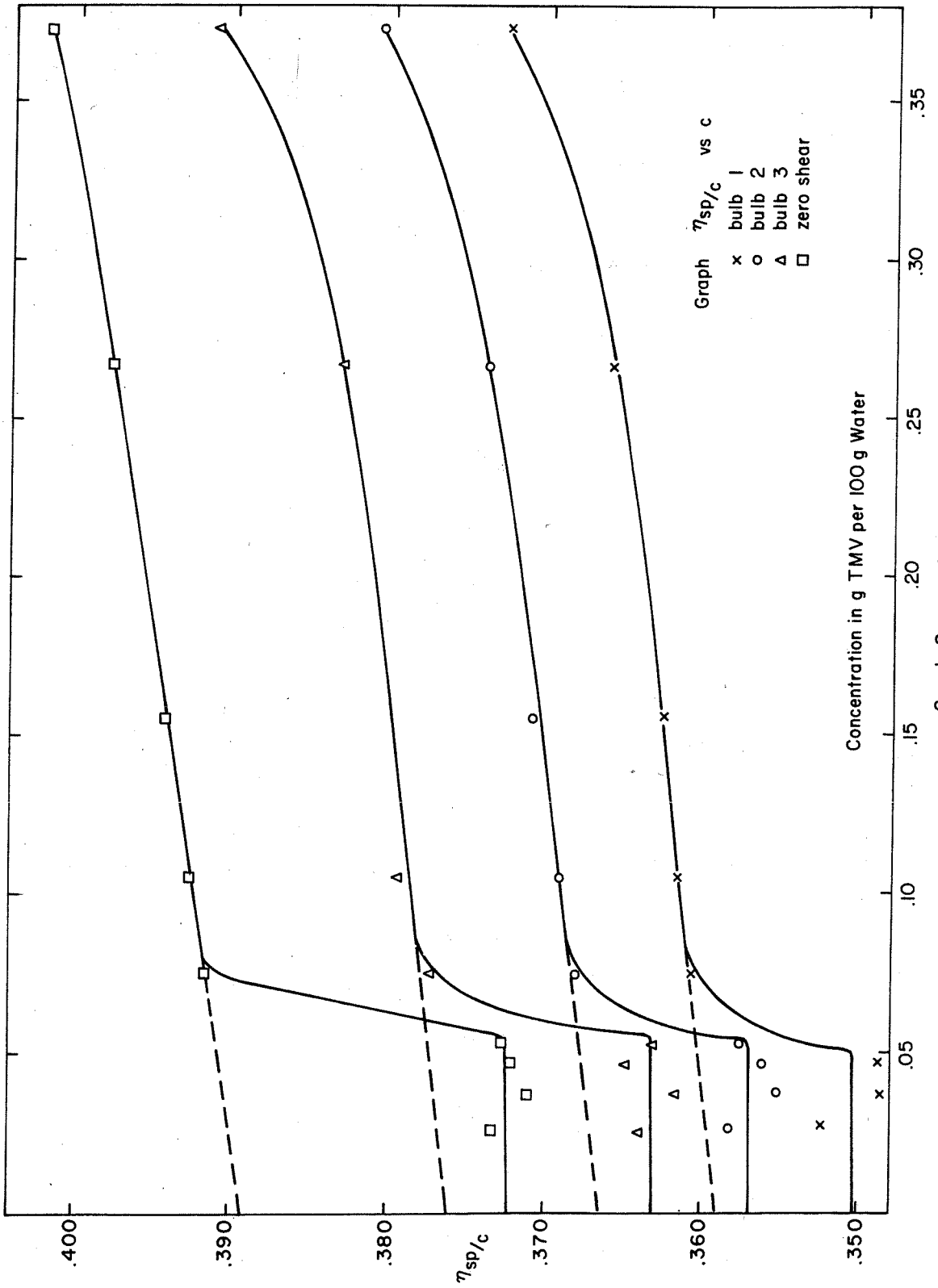
Graph 5



Graph 6



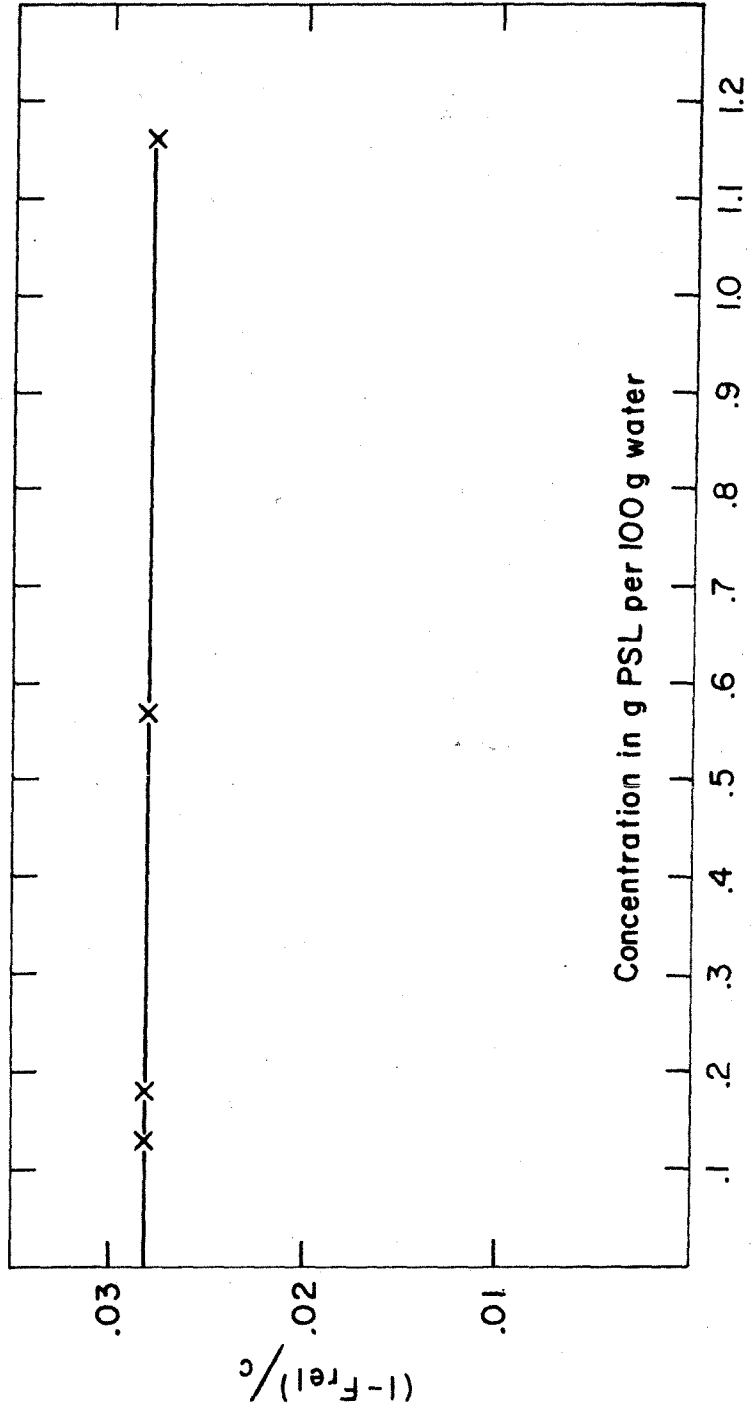
Graph 7



Graph 8

Graph of $\frac{1-F_{rel}}{c}$ vs c

where F_{rel} is the relative fluidity



Graph 9

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REFERENCES

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