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PROPOSED TOPIC FOR A Ph.D. THESIS IN CHEMICAL ENGINEERING

"RHEOLOGY OF THORIA SOLS AND GELS"

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ABSTRACT

It is proposed to measure the rheological properties of thoria sols and gels in several types of viscometers, specifically including capillary and cone-plate types, and to relate these properties to sol-gel process control variables and to final oxide properties. It is also proposed to apply the data to testing existing electroviscosity theories and linear viscoelastic flow theories. It is hoped that it will be possible to make quantitative, predictive extensions of these theories into regions where their present applicability is now questioned or is unexplored, and to define regions of gel behavior suitable for extrusion and casting of nuclear fuel elements with colloidal thoria.

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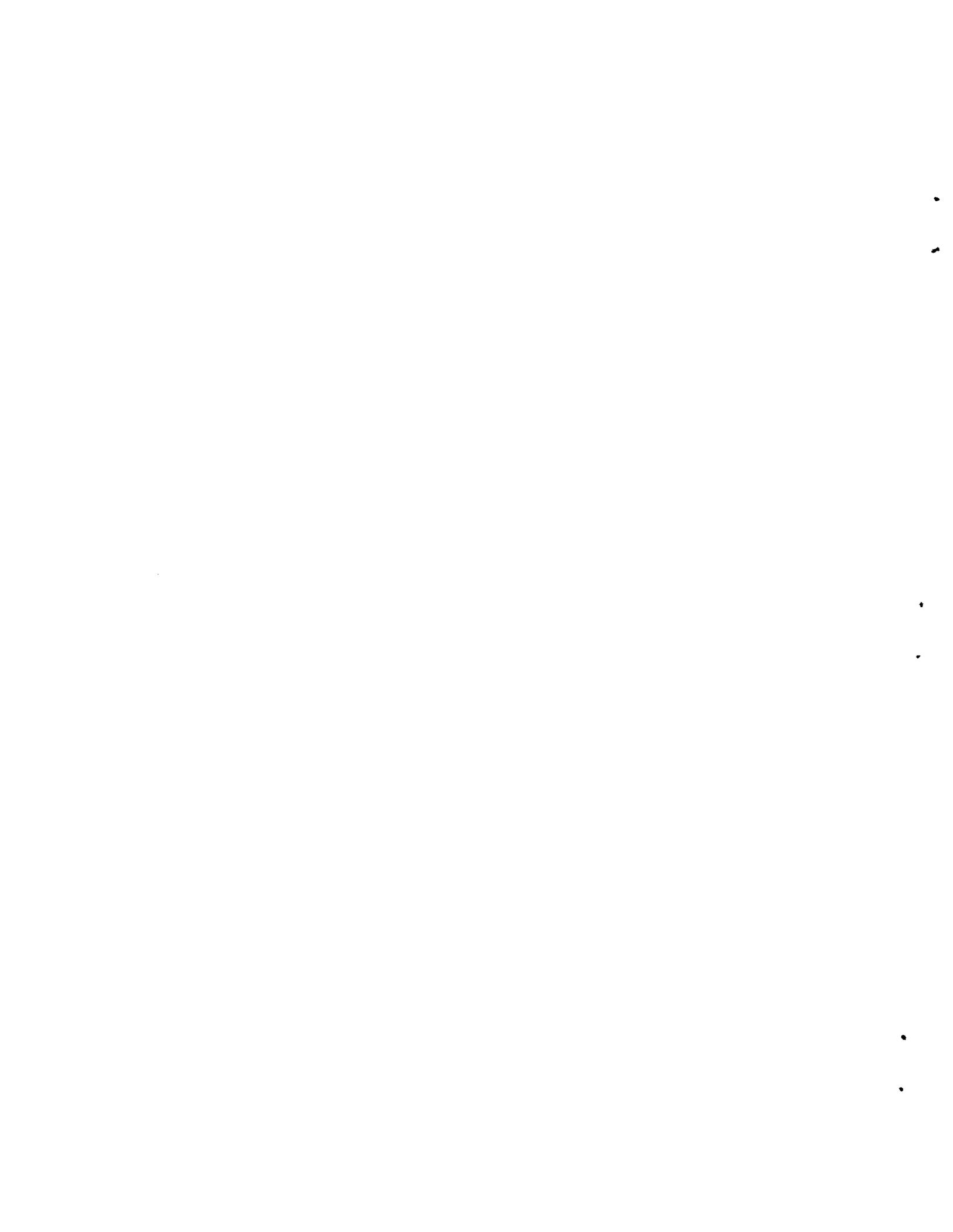
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I. Introduction

The proposed thesis topic, "Rheology of Thoria Sols and Gels," has two aspects: one is the mathematical description of flow properties as they relate to extrusion and forming processes, and the other is the use of rheological properties to describe the colloidal-molecular state of the sols and gels. Normally, concentration on a single aspect of the system would be appropriate for a thesis topic but in the present case the topic is broadened in order to qualify for financial support as a part of the sol-gel process development under the ORNL Fuel Cycle Program and at the same time to relate to the systematic studies of flow phenomena being carried out in the University of Tennessee Department of Chemical Engineering.

In outline, the sol-gel process (1,2) utilizes thoria from a variety of sources, usually steam-denitrated thorium nitrate or calcined thorium oxalate, to make a nitrate-stabilized sol which is dried and calcined finally at 1200°C to form strong, dense, millimeter-to-centimeter size fragments of thoria. Uranium up to 10% may be added to the sol as trioxide, nitrate, or ammonium diuranate. These fragments are then sized and packed by vibration into nuclear reactor blanket and fuel rods.

The allocation of project funds to the proposed thesis work is justified on the basis that the control of final product quality and an understanding of the process can be gained from a thorough physical chemistry study of the sol and gel states that occur. The recent development of the sol-gel process has been highly empirical. Quantitative knowledge of the relationships of the colloidal properties of the thoria sols and gels to chemical composition and colloid particle size is lacking, and

the effect of these parameters on final calcined oxide properties is not well-defined.

The variety of non-Newtonian flow properties that the thoria-water-nitrate system has exhibited in the course of the development of the sol-gel process suggests that extrusion and other forming methods might extend its usefulness to making reactor fuels with complex shapes. The behavior of thoria sol-gel has been observed qualitatively to range through plastic, dilatant, thixotropic, rheopectic, and viscoelastic. This versatility in a single chemical system makes it an attractive tool for experimentally exploring predictions of theoretical rheology. It has been suggested that the remaining major progress in the study of viscoelasticity will originate in experimental studies (3). Thus, not only would the rheology of the colloidal thoria system be a valuable analytical tool for describing the sols and gels in fundamental molecular terms, the macro-rheology itself would be important in the engineering development of extrusion or other forming process and for the study of theoretical flow models.

II. Previous Rheological Studies of Thoria Sols and Gels

The earliest quantitative viscometry of colloidal thoria suspensions found thus far was by Desai (4) in 1922, although thoria sols were prepared as early as 1874 (5). Further viscometric studies by Dhar and co-workers (6,7) and by Desai (8) were made, but all work was confined to chemically precipitated thoria, and with the exception of Dhar and Mitra (7) was confined to a few grams per liter thoria concentration. In 1953 Dobry (9,10) used precipitated dialyzed thoria sols to explore electroviscous effects at concentrations up to 2 wt % thoria and encountered

complex behavior due to unwinding of linear polymer species. Sturch (11) made a study of 2 M thoria sols derived from 800°C calcined thorium oxalate. He found extreme thixotropy and rheopexy combined with pseudoplasticity. In one instance of rheopexy the exponential time constant was about 30 min and the apparent viscosity increased from 125 centipoise (cp) initially to a steady-state value of 460 cp. Time-dependent phenomena of such exaggerated extent and duration becomes of practical design interest, unlike the usual cases in which design may be set by initial or by steady-state properties only. Even with the cases of more rapidly equilibrating time-dependent flows there are instances where design requires knowledge of relaxation times, such as in short-tube heat exchangers (12).

The major limitations of previous published viscometric studies of thoria sols is their restriction to chemically precipitated or dialyzed hydrous, poorly crystallized thoria at low concentrations. The two main exceptions are the work of Sturch (11) and of Dhar and Mitra (7). Both measured viscosities of 2 to 3 molar thoria sols stabilized by nitrate, and Sturch used a well-crystallized (222 Å diameter by x-ray line broadening) thoria.

All reported work was done with viscometers of low shear rate and nonconstant shear rate through the body of the fluid. A further limitation of the pre-1950 work is the lack of sufficient auxiliary characterization of the sols being examined viscometrically to permit confirmation of the conclusions based on viscometry. It has only been within the last decade that such important tools as anisotropic light-scattering and quantitatively accurate theories for electrophoretic effects have been developed. Until the work of Booth (13), the theory relating

electrophoretic measurements to viscosity was clearly inadequate for quantitative correlation. Even now the theory is limited to first order effects (sufficient dilution so that the only significant interaction is between the colloid particle and its local rate of shear).

Chemical analyses for impurities are lacking, and preparative procedures are sometimes ambiguous. Even subsequent to 1940 much of the available thorium contained a percent or so of cerium, and prior to that time it was exceptional for a thorium-bearing compound not to contain it. Only Sturch is known to have used a well-analyzed, cerium-free thoria source, although it is reasonable that Dobry may have had reactor-grade thoria available.

In the published work found thus far, there is a general lack of non-Newtonian flow, high shear rate rheological information for thoria sols. The usefulness, and even the validity of the pre-1940 work is questionable because of the lack of adequate experimental definition and control. For example, Dhar and Mitra describe their starting hydrous thoria as being "freshly precipitated and thoroughly washed" without stating the precipitant or giving any quantitative indication of how thorough "thoroughly washed" really means. The analytical determination of the nitrate content is absent, and the complexing power of thoria for nitrate ion led to persistent analytical difficulties at ORNL until special care and effort was taken to desorb the nitrate.

Not until Dobry applied the modern tools of electron photomicrography and anisotropic light scattering in conjunction with viscometry was adequate evidence for the structure of hydrous thoria presented (14).

It is clear from the conflicting views of thoria sol structure that were deduced by the early investigators that auxiliary characterization methods, the more the better, must be brought to bear simultaneously in order to avoid ambiguity and fallacious interpretations. The pre-1950 studies are so clouded by ambiguities of preparative procedures, lack of chemical analyses for impurities, primitive development in the theory of their auxiliary characterization methods such as flocculation numbers (15), and lack of an adequate theory to connect quantitatively electrophoresis with electroviscosity that only qualitative trends can be extracted with confidence.

Of the more recent work, Dobry's was limited to highly hydrous, dilute thoria sols whose particle morphology is known to differ radically from the refired sol-gel process thorias. Although Sturch used a refired sol-gel process thoria which was well characterized chemically, he investigated only a narrow range of thoria and nitrate compositions on a single particle size sol with an empirical, unmodified 4 speed (all low shear) Brookfield viscometer. The complexity of flow behavior which was encountered limited Sturch to qualitative conclusions as to trends.

Intercomparison of the previously published work is difficult and generally sterile.

III. Data to be Derived from the Proposed Work

(a) Rheological Data

The main body of data will consist of a shear stress that develops at the boundaries of a body of the thoria-nitrate-water colloidal system as a function of an imposed rate of shear. The specified independent

conditions at each data point will be rate of shear, temperature, thoria content, nitrate content, sol age, and the apparent colloidal particle size as estimated by a combination of electron photomicrography, x-ray line broadening, BET surface area, and light-scattering of stagnant samples. For those samples exhibiting time-dependent flow phenomena it will be necessary to give a shear rate history at points in time in addition, and for those samples exhibiting viscoelasticity it will be necessary to take additional stress measurements orthogonal to the imposed shear.

(b) Auxiliary Data to Permit Interpretation of the Rheological Behavior in Structural Terms

The extent to which the following supplementary studies will be pursued cannot be clearly delineated at present. The need for them will depend upon the adequacy of the available theoretical bases for data interpretation and the complexity of the behavior encountered.

When the temperature, pressure, thoria, nitrate, and water content of the system are specified, the equilibrium state is completely determined. A colloid is inherently a nonequilibrium system and is not well characterized in terms of thermodynamic variables only, but it can be treated as a thermodynamic system if the particulate and solution phases do not significantly change in composition over some "reasonable" length of time. Qualitative observations suggest that thoria sols undergo mild aging effects over a period of several days and then are sufficiently stable to be treated as equilibrium systems on a time scale of weeks. In theory, using existing stability constants for the thorium⁺⁴-nitrate complexes (17) and the hydrolysis of the Th⁺⁴ ion one could calculate the concentration of each chemical species, but there exists considerable divergence

of opinion in the literature as to just what hydrolytic species exist for the Th^{+4} ion (18).

It is necessary to have more than the thermodynamic minimum number of chemical determinations in order to specify practically a state of the sol, and pH suggests itself. The pH of a sol is not a well defined quantity, however, because of the so-called suspension effect or Donnan potential. This effect can be roughly corrected (19) by calculation but with the present theory one must arbitrarily assume a liquid junction diffusion potential.

The slowly reversible equilibria between thoria surface hydroxyl (20), ionic nitrate and complexed nitrate make it desirable to obtain independently the pH and nitrate analysis on the equilibrium intermicellar fluid.

It is proposed to determine in addition the electrical conductivity of the sols and ultracentrifugate of the sols. The electrical conductivity measurements are used in conjunction with some measurements from which zeta potential may be calculated to estimate first order electroviscous effects using Booth's (13) improvements over the simpler theory of Smoluchowski (21,22). The improved theory had received some experimental confirmation (23), but its limitations are not clearly defined. The existence of a second electroviscous effect due to interaction of counterion atmospheres with one another has been described qualitatively (24) as have effects of particle assymetry (25) and solvent immobilization on the particles (26) but the applicability of these interpretations to alleged departures of experiment from Booth's theory has been challenged (27).

Electrokinetic data for thoria in the water-nitrate system has been collected at ORNL by Holmes and Secoy (28), by Sowden, et al. (29), and by Douglas and Burden (30). The latter two references cover ranges of nitrate content comparable to those in sol-gel process suspensions.

The application of these data to the proposed viscometric measurements is much less desirable than having electrokinetic measurements on the sols under study. Sowden's data showed $\pm 50\%$ variation in zeta potential at nominally the same experimental conditions but with thoria from different sources. Holmes (28) has suggested what seems to be a reasonably simple experimental technique for obtaining an electrokinetic measurement on thoria gels (see Appendix B) but the actual experimental attainment of meaningful electrokinetic measurements is notorious for generating unforeseen difficulties. It is presently planned to make some simple (hopefully) electrokinetic measurements and not to have to fall back on correlation with values of zeta potential reported in the literature.

Another major method for colloid characterization which has undergone great development within the last two decades is light-scattering. Since one of the least well-defined conditions of the sols in the "particle size" it is proposed to take simple light extinction data to measure particle size with presently available equipment at ORNL. Light scattering methods have now been refined to the point of giving particle shape information (31, 32) but unless it is clearly necessary to define particle shape in addition to electron photomicrographic evidence it is expected to confine light scattering measurements to simple extinction.

The so-called "anomalous" flocculation characteristic of thoria sols is said to be associated with plate-like particles (15) but the unshadowed electron photomicrographs now at hand for the thoria sol particles are inconclusive.

M. E. Wadsworth at the University of Utah has recently indicated a desire to initiate light-scattering experiments on thoria sols and gels (33) which may supplement the rheological studies proposed here.

It should be noted that light scattering is a "soft" measure of particle size, and will detect weak flocs that x-ray line broadening, or even BET surface area, will not find.

The list of possibly desirable property determinations can be extended almost indefinitely and includes small-angle x-ray scattering, osmotic pressure, freezing point depression, coagulation behavior, dielectric properties, etc. However, limitations on time and funds preclude much extension past chemical analyses, and simple light scattering and electrophoresis. Colloidal systems cannot be required a priori to behave with some predetermined degree of simplicity most convenient for an experimenter, so is not possible to exclude rigidly and totally the possibility of having to re-evaluate the need for various auxiliary studies.

IV. Scope of the Proposed Independent Variables

The principal experimental basis of the proposed work is the measurement of the rheological properties of the thoria-nitrate-water system over wide ranges of the following parameters:

(1) Thoria concentration from 0 to approximately 20 molar. The selection of the number and the spacing of the intermediate concentrations to be studied will depend on the rate of change of viscosity and the number

of regions of qualitatively differing flow regimes that are encountered. A reasonable expectation for wide-range scouting of effects would be a total of 10 different concentrations to define 3 time-independent flow regimes. For time dependent phenomena or detailed testing of theory, additional and close-spaced levels of concentration will be required.

(2) Nitrate to thoria mole ratios from 0 to about 0.5. It is expected that nearly all of the significant effects will be confined to ratios between 0.05 and 0.25. Again, the number and spacing of the data points will depend on the number of different regimes encountered. There can be four regimes, depending on the nitrate to thoria mole ratio. These are electrolyte deficiency flocculation, stable peptization, electrolyte-excess gelation, and electrolyte-excess flocculation. It is in the region of electrolyte-excess gelation that the exaggerated time-dependent flow properties are expected to occur.

(3) Thoria sol crystallite size from approximately 50 \AA to 700 \AA , as measured by x-ray line broadening, electron photomicrography, and confirmed by BET (Brunaur-Emmett-Teller) nitrogen adsorption surface area, and by light scattering. This important parameter is undesirably but unavoidably vague. When one speaks of "particle size" a particular measurement method for defining the size is automatically implied. Different size-measurement methods give different averages. Microscopic examination gives number averages. X-ray line broadening in an experimental test by the writer appeared to give a volume average although number average was expected. The BET method gives area averages, the colligative properties give number averages, and the light scattering

gives volume averages. The only way to have confidence in a particle size parameter is to bring at least two independent methods into substantial concordance. In the lower crystallite-size range, substantial concordance is generally achieved between the electron photomicrographs and x-ray crystallite size. The BET surface area is used as a measure of the dispersion of sizes about the average. The log-normal deviations (σ_g) which have been calculated are generally rather low, 1.1 to 1.2, indicating reasonable uniformity. The recalcination procedure which is required for obtaining the larger sizes also broadens the distribution and it is expected that size cuts from ultracentrifugation will be necessary to control the σ_g of the dispersion. The first three of the proposed particle size measurements are "hard" measures and will ignore or may disrupt weakly bound floc-type particles.

(4) Temperature from $\sim 0^\circ\text{C}$ to $\sim 95^\circ$. It is not expected that very much study of temperature dependence of rheological properties will be required unless unforeseen phenomena is encountered. Insofar as thoria sols are concerned, it is an unexplored region of study, and it is hoped that any effects encountered are in degree and not in kind. In the event of insupportable complexities in temperature dependence, it may be necessary to restrict the scope of the thesis to a small temperature range near ambient. However, since the nature of the proposed thesis is to be a general exploration, consistency with this goal implies inclusion of temperature as a variable.

(5) Sol aging. In a strict thermodynamic sense, all colloidal states are quasistable nonequilibrium states, and no colloidal aging study is complete as long as a colloidal state exists. In the case of thoria sols

in the range of compositions proposed for this study, it has been found that a quasistable state is attained in time ranges from a few hours to a few days. It is proposed to study in detail only those samples which have attained this state, and to study sol aging mainly as an incidental to assuring that some state of quasistability has actually been reached. Sturch (11) found it necessary to protect thoria sol from atmospheric exposure, presumably from CO_2 , in order to control a slight but definite apparent aging effect. Gradual long term aging effects are often noted in inorganic colloids, but unless some unusual aging phenomena is encountered no detailed study of long-term aging is proposed.

(6) Rate of shear from less than 1 sec^{-1} to $\sim 1000 \text{ sec}^{-1}$. In previous work on the rheology of coarse thoria suspensions, as part of the Homogeneous Reactor Project, it was found that data at quite high rates of shear in laminar flow were required in order to define the flow parameters (34). Unless the flow gradients are sufficiently intense to disrupt entirely the long-range interparticle structure, one has not defined the entire range of the different behavior regimes. In the case of $\sim 1 \mu$ particle thoria slurries it was necessary to attain pseudo-shears of about 600 sec^{-1} in order to ensure that the slurries flow was governed by the basic particle and not a multiple unit or floc (35). For a design basis one might expect similar floc strengths in the thoria sols and that 1000 sec^{-1} should be in the region that "colloidal shear thinning" is complete. At present there appears to be no high shear rate data on colloidal thoria by which a more rational estimation of the maximum shear rate needed can be made.

V. Relation of the Proposed Measurements to the Sol-Gel Process

The properties of immediate interest to the applications of the sol-gel process which are under current development are:

- (1) Fragment size.
- (2) Fragment shape.
- (3) Fragment density.
- (4) Fragment strength and attrition resistance.

At present, these properties are controlled by rules-of-thumb which apply only to certain empirical "recipes."

The data to be taken for this thesis should be sufficiently extensive and precise either to put control of these variables on a rational, quantitative basis or else to prove thoroughly the infeasibility of doing so.

Except for fragment shape, reasonably well rationalized and quantitative measures of these four properties are in current use for evaluating the sol-gel process product. It is therefore proposed to employ the existent tests on oxides derived from the sols and gels prepared for the rheological work. These tests consist of:

- (1) Particle size distribution by sieving.
- (2) Particle density by toluene immersion.
- (3) Particle strength by tumbling and spouted-bed tests.
- (4) Particle shape by qualitative description and by ranking in comparison with an existing set of photographs of "standard" fragments.

The application of the proposed work to potential, as distinct from current, development in the sol-gel process is primarily the direct employment of the rheological data for extrusion or other forming processes. Considerable expense and effort could be bypassed if direct casting of

dense, massive bodies could be substituted for the grinding-sizing-packing operations now employed to fabricate the fuel elements from the oxide fragments.

Whether or not the thesis work can be extended to applying the rheological data to experimental extrusion into fuel element shapes such as cones, plates, cylinders, spheres, etc., depends on the complexity of the flows encountered and on the occurrence of calcined oxide properties (primarily uniform shrinkage) that promise practical fabrication of nuclear fuel elements.

Under these conditions there would be reasonable expectation that experimental extrusion development could be supported as part of the ORNL Fuel Cycle Program, and hence would be feasible as a part of the proposed thesis.

Since the feasibility of this extension of the thesis hinges on contingencies that, while reasonable, are not truly firm, no detailed proposal for experimental engineering non-Newtonian flow in extrusion applications will be made. However, numerical prediction of two dimensional non-Newtonian flows and pressure drops are proposed.

VI. Data Analysis

(a) Newtonian Flow Regimes and Electroviscous Theory

At the higher dilutions (below 2 wt % thoria) it is expected that Newtonian flow will occur. It is in this region of concentration that the data will be the most interpretable in molecular terms based on developed or developing theories. All the flow data in this regime will be expressed as simple viscosity, η , derived from capillary flow. The absence of non-Newtonian flow behavior will be demonstrated by varying the shear rate with a 4-speed Brookfield viscometer.

The most promising existent theoretical equation for which to attempt data fitting is that of Booth (13).

Booth's final correlation is:

$$\eta = \eta_0 \left(1 + \frac{5}{2} \phi \left[\frac{1}{\sigma \eta_0 a^2} \left(\frac{\zeta \epsilon}{2\pi} \right)^2 \pi (ka)^2 (1 + ka)^2 Z(ka) \right] \right)$$

where:

η_0 is the viscosity of the supporting medium in the absence of solids

σ is the specific electrical conductivity of the system*

ϕ is the volume fraction of solids in the system

a is the particle radius

ϵ is the dielectric constant of the support medium

ζ is the electrokinetic (zeta) potential of the particle with respect to the supporting medium

k is an "effective relative thickness" of the electrical double layer surrounding the particle

Z is a complicated function which is graphed by Booth (13) and reproduced by Rutgers and Nagels (24).

The numerical value for k is calculated from the Debye-Huckel reciprocal length:

$$k^2 = 4\pi e^2 \sum_{i=1}^M n_i z_i^2 / \epsilon kT$$

* See footnote 14a of reference (24). It is not clear whether or not the relevant conductivity is that of the whole system, the intermicellar fluid only, or some average of these. In past experimental practice (13) it has been assumed to refer to the whole system.

where:

e is the unit electronic charge

n_i is the number concentration of ions of type i in the supporting medium

z_i is the ionization number of ion of type i

M is the number of different ion species present

k is Boltzmann's constant

T is the absolute temperature

The expected region of validity for these theoretical relations is the same as that for the Einstein equation (36) for the effect on viscosity of uncharged spheres:

$$\eta = \eta_0 \left(1 + \frac{5}{2} \phi \right) \quad \text{Lim } \phi \longrightarrow 0$$

The principal limitations on the validity of the Einstein relation are that the flow must be creeping (inertia terms neglected), the volume fraction must not exceed 0.05, and the particles must be spherical. In addition, the particles must be large compared to the molecules of the supporting medium and small compared to the container.

Booth (13) adds restrictions on the electrical properties of the particles. The particles must be nonconducting with an immobile charged surface layer which is thin compared to the particle radius.

The possibility that other relations simpler than Booth's might become applicable has been suggested by the qualitative observation that thorium sols show markedly increased mobility as the nitrate concentration is decreased toward the lower flocculation limit. If the double layer withdraws substantially inside the plane of shear as nitrate depletion occurs, one may find the Einstein relation or some nonelectrical generalization of it becoming applicable.

One extension of Einstein's limiting case is that of Guth and Simha (37):

$$\eta = \eta_0 \left(1 + \frac{5}{2} \phi + \frac{109}{14} \phi^2 \right)$$

Roscoe (38) and Vand (39) developed the concept of temporary "clots" of particles being formed by collisions and arrived at an equation which has received some experimental verification (40):

$$\eta = \eta_0 (1 - 1.35 \phi)^{-2.5}, \quad 0.05 < \phi < 0.30$$

Second order electroviscous effects (particle-particle interactions) have been measured and described qualitatively (24) but no quantitative theory appears to exist.

A third electroviscous effect due to coiling and uncoiling of flexible linear polymers can, in theory at least, be calculated from the effect of polymer charge and electrolyte concentration on chain dimensions (41) and hence on viscosity (26). This flexible chain-type structure, which has been found (9) for hydrous thoria sols, is often associated with the viscoelasticity of such polymers as polymethyl methacrylate (42) if the shear gradients are sufficiently strong to affect particle morphology and orientation.

(b) Viscoelastic Flow and Linear Viscoelastic Theory

The mathematical description of general viscoelastic flow generates extremely complex models. For example, in the spring-and-dashpot representation of general cases it can become necessary to assume plastic instead of Newtonian dashpot fluids and non-Hookean springs (43). Even with severe simplification and linearization it is considered desirable to retain 5 experimental constants in describing viscoelastic rheology. Oldroyd's (44) recommended equations for simple shear (in rectangular coordinates) are:

$$\tau_{xx} = [(2\mu_1 - \nu_1)(F) - (2\mu_2 - \nu_2)\eta_0] \left(\frac{dU_x}{dy}\right)^2 - p$$

$$\tau_{xy} = \tau_{yx}$$

$$\tau_{yy} = \tau_{zz} = -[\nu_1(F) - \nu_2 \eta_0] \left(\frac{dU_x}{dy}\right)^2 - p$$

$$\tau_{xz} = \tau_{zx} = \tau_{yz} = \tau_{zy} = 0$$

where:

τ is stress

F is an "apparent viscosity" defined as $\tau_{xy}/\left(\frac{dU_x}{dy}\right)$, both of which are known quantities

p is an arbitrary hydrostatic pressure

η_0 is a reference viscosity term

$\mu_1, \mu_2, \nu_1, \nu_2$ are time parameters

U_x is linear fluid velocity in the x direction, which is the only fluid motion

It is hoped that the experimentally determined viscoelasticity can be adequately correlated by the foregoing equations. If sharply nonlinear effects are found it will be necessary to go back to Rivlin's more general forms and find some adequate specialization of them. Rivlin's (45) equations for a more general viscoelastic fluid in simple shear are:

$$\tau_{xx} = -p + \alpha_1 \left(\frac{dU_x}{dy}\right)^2$$

$$\tau_{xy} = \left(\frac{dU_x}{dy}\right) \left[\alpha_1 + 2\alpha_5 \left(\frac{dU_x}{dy}\right)^2 + 4\alpha_7 \left(\frac{dU_x}{dy}\right)^4 \right]$$

$$\tau_{yy} = -p + \left(\frac{dU_x}{dy}\right)^2 \left[(2\alpha_2 + \alpha_3) + 4(\alpha_4 + \alpha_6) \left(\frac{dU_x}{dy}\right)^2 + 8\alpha_8 \left(\frac{dU_x}{dy}\right)^4 \right]$$

$$\tau_{zz} = -p$$

$$\tau_{xy} = \tau_{yx}$$

$$\tau_{xz} = \tau_{zx} = \tau_{zy} = \tau_{yz} = 0$$

where the α are polynomials in the 2nd, 4th, and 6th powers of $(\frac{dU_x}{dy})$

An alternative, if the nonlinearity is not extreme, is to define a set of regions in which separate linear approximations are valid.

Formally, the constants in Oldroyd's equations are determined by 5 data points which can be all different values of shear rate, if values of τ_{xx} are available. A measure of static pressure normal to the plane of shear in a cone-plate viscometer is able to provide indirectly the needed value of τ_{xx} for use with Oldroyd's equations, in which $\tau_{\theta\theta}$ corresponds to τ_{xx} :

$$\tau_{\theta\theta} = \frac{d(p_r)}{d(\ln r/R)} + 2\tau_{rr} - \tau_{zz}$$

$$p_z \tau_{zz} = \tau_{rr} p_r$$

where:

p_z is pressure in the direction of the axis of rotation and is a function of r

r is variable radial distance along the cone

R is the cone outer radius

p_r is pressure in the radial direction

The second equation has experimental support but is not of necessity valid in general (46).

A complete and direct definition of shear state would require still another stress measurement which, however, is difficult to attain experimentally. In fact, if the liquid under shear is very viscous, getting static equilibrium for the manometric measurement of p_z is difficult.

Roberts speaks of "new devices" (47) for p_r measurements that he used but he neither described nor referred to description of these devices. They somehow entail Newtonian fluids in the outer part of the shear gap to transmit a pressure reading.

Some other indirect alternatives for determining a normal stress parameter have been suggested, for example, Phillipoff and Gaskins (48) have suggested that the diameter of a jet emerging from a capillary could measure viscoelasticity. A drawback of this approach is that it is necessary to assume a model for the nonviscoelastic component of flow behavior.

Metzner (49) derived the formula for the capillary jet radius assuming a power law dependency for the nonviscoelastic flow aspect:

$$\left(\frac{\frac{(n+1)}{2n\tau_w} \frac{n}{(3n+1)K^{1/n}}}{\frac{n}{(n+1)K^{2/n}}} \right) A - \left(\frac{\frac{2\tau_w}{n}}{\frac{n}{(n+1)K^{2/n}}} \right) B = \rho V^2 \left[\left(\frac{3n+1}{2n+1} \right) - \left(\frac{R_{cap}}{R_j} \right)^2 \right]$$

where:

- τ_w = wall shear stress
- R_{cap} = capillary radius
- R_j = jet radius
- ρ = fluid density
- V = area average linear fluid velocity
- n = power law exponent
- K = power law coefficient

The constants A and B are to be determined, and contain the information on viscoelasticity from measured R_j . If the nonelastic flow component is chosen to be Newtonian (for sake of simplicity in illustration) the equation reduces to:

$$(\mu A-B) = \frac{\rho R^2 \text{cap}}{8} \left[\frac{4}{3} - \left(\frac{R \text{cap}}{R_j} \right)^2 \right]$$

where: μ is viscosity

Introducing the same Newtonian assumption into Oldroyd's recommended equations reduces them to:

$$\tau_{xx} = -p + 2\eta_0 (\mu_1 - \mu_2) \left(\frac{dU_x}{dy} \right)^2$$

$$\tau_{xy} = \eta \frac{dU_x}{dy}$$

$$\tau_{yy} = \tau_{zz} = -p$$

$$\tau_{yz} = \tau_{zy} = \tau_{xz} = \tau_{zx} = 0$$

and we may identify $(\mu A-B)$ with $2\eta_0 (\mu_1 - \mu_2)$.

Just as there was no clear-cut end to the possibly desirable methods of characterizing a colloidal state, there is likewise no end to the conceivable complexity of real flow behavior and ways to describe it. For example, slip flow may occur. It is somewhat arbitrary to propose that the data analysis be limited to a linearized model, but much extension past this point is likely to involve a host of secondary effect corrections which are at best imprecise. Highly refined equipment is needed to keep temperature corrections and inertial effects of rotation minimized and calculable with sufficient accuracy to permit quantitative description of curvature in the data. The availability of equipment of the necessary refinement, such as that described by McKennell (50) is not foreseeable.

(c) Plastic and Dilatant Flow

"A nearly endless variety of equations have been proposed for portrayal of purely viscous non-Newtonian flow behavior, particularly for pseudoplastic fluids" (51). The simplest way to resolve the problem

of choosing a model is to take the most general one and truncate it to a form whose complexity is not beyond what the accuracy of the data can meaningfully define.

If one starts with the assumption that the stress in a fluid is a function only of the rates of strain and physical constants of the fluid one arrives at the expression (52):

$$\tau_{xy} = \eta_0 \frac{dU_x}{dy} \left[1 + \sum_{n=1}^k a_n \left(\frac{dU_x}{dy} \right)^{2n} \right]$$

or its inverted form:

$$\frac{dU_x}{dy} = \frac{\tau_{xy}}{\eta_0} \left[1 + \sum_{q=1}^k b_q (\tau_{xy})^{2q} \right]$$

for one-dimensional flow.

The data fitting to determine the constants in these equations can be tedious but is reasonably straightforward, particularly with the cone-plate viscometer geometry. It is doubtful that more than three parameters will be appropriate due to limitations on the accuracy and reproducibility of the data points.

Once the data for these flow regimes are expressed in the form of the equations just given, it becomes possible to evaluate whatever models suggest themselves as being appropriate.

The Rabinowitsch relation (53):

$$\frac{dU_x}{dy} = \frac{\tau_{xy}}{\eta} \left[1 + b\tau_{xy}^2 \right]$$

is an obvious special empirical case of the preceding equation.

The "power-law:"

$$\tau_{xy} = K \left(\frac{dU_x}{dy} \right)^n$$

is theoretically incorrect but possesses the advantages of ease of handling mathematically and a reasonable range of approximate applicability. In practical engineering design such advantages are not negligible.

The Powell-Eyring model (54) comes as close as any and closer than most proposals to having a reasonable theoretical basis. Their proposed equation is:

$$\tau_{xy} = \eta_0 \frac{dU_x}{dy} + a \sinh^{-1} b \left(\frac{dU_x}{dy} \right)$$

where a and b are semitheoretical constants.

This is a three parameter equation, and apart from its theoretical basis, (which has been challenged (55,56)) it would be surprising not to get a better fit of data than with a two parameter expression like the "power-law."

In addition to the Powell-Eyring relation, derived from absolute reaction rate theory, non-Newtonian flow phenomena has been explained in qualitative or crudely quantitative theoretical terms based on particle geometries, Van der Waal's forces and hydrogen bonding of water (57,58). While these explanations are qualitatively illuminating and are valuable as compact expressions for masses of results, it is easy to overestimate the certainty of their ultimate correctness and their quantitatively predictive value. There are so many possible physical-chemical mechanisms that might underlie a given flow behavior that the real problem is to prove some quantitatively predictive theoretical extrapolation rather than hypothesize an ex post facto justification for what has been observed to occur. In the present thesis it is proposed to make some tentative semitheoretical correlations to see if any promising avenues for reasonably detailed and quantitative theoretical development occur. For example, one

marginally possible region for development is to try to adapt Roscoe's (38) and Vand's (39) theories of particle-particle flow interaction to predicting second-order electroviscous effects.

(d) Time-Dependent Flow

Rheopexy (increasing apparent viscosity with time at constant shear) was discovered by Freundlich and Juliusberger (59) in 1935. Quantitative rheopectic data are sparse and crude, and a quantitative theory has not been found. A generally accepted qualitative explanation of rheopexy is that a contacting or aligning action between inherently attractive particles is induced by gentle shearing, which allows more rapid re-formation of structure than occurs if the colloid particles must restructure a gel unaided against the disruptive influence of brownian type motion (60). It is consistent with this picture that many rheopectic systems are also thixotropic with long resetting times if not undergoing shear (61).

Insofar as systematic, quantitative interpretation of rheopectic data is concerned neither Overbeek (60) nor Roscoe (61) in their reviews make even general suggestions. In a formal way, it seems to me it should be possible to express rheopexy by making the rate of re-entanglement constant a function of shear rate in the Hahn, et al (62) derivation of thixotropic flow equations from absolute reaction rate theory.

Hahn, et al, present their thixotropic flow equations in two forms: first as a description of the hysteresis loop on a stress-shear plot for constant rate of stress increase and decrease between zero and some maximum, and second as a stress relaxation at constant shear rate. The second form is the more adaptable to the viscometers proposed for use in this thesis, and is:

$$\ln \tau_{xy} - (\tau_{xy})_{eq} = p - at$$

where:

$(\tau_{xy})_{eq}$ is the long-time equilibrium shear stress at constant shear rate

t is time

p and a are semitheoretical constants

The terms $(\tau_{xy})_{eq}$, p , and a all have definitions in terms of rational parameters generated from the theory of absolute reaction rates, but the remoteness and the number (sixteen) of the theoretical parameters that were counted in tracing the chain of definition to its source makes "proof" of the theoretical validity of the preceding equation practically impossible. A more reasonable objective might be to compare the consistency of this equation with the data versus other proposed equations such as Weltmann's (63):

$$\tau_{xy} = \alpha - \beta \ln t$$

It is worth noting, however, that Metzner (49) singles out the Hahn-Rhee-Eyring development as being the only one that can be recommended.

(e) Concluding Remarks

The foregoing treatment of the various flow phenomena that are expected has been on the basis of no slip and that the systems are sufficiently fluid that flow equilibrium is established in no longer than a matter of hours at most, and in a few minutes in general. The transition, sol to soft gel to solid gel, is not clear-cut, however, so it is necessary to make an arbitrary cut-off in flow properties beyond which no data will be taken. It is proposed not to extend the thesis to creep and fracture flow.

The theory of creep and fracture has developed more nearly from ceramic and metallurgical solid-state theories (64) than from chemical engineering fluid flow, and is perhaps more fruitfully developed from a solid-state than from a fluid flow viewpoint.

VII. Viscometric Methods

There are three types of viscometers immediately available:

- (1) Ostwald-type capillary
- (2) Stormer concentric cylinder type
- (3) Brookfield rotating spindle type

The Ostwald viscometers yield precise viscosity determinations for Newtonian fluids, and it is proposed to initiate the experimental portion of this thesis by using these viscometers with sols sufficiently dilute to be Newtonian. This viscometer has, however, inherently low and variable shear, and it is unsuitable for defining non-Newtonian flow parameters.

The Brookfield and the Stormer viscometers, as they now exist, are empirical instruments which give data not quantitatively absolute or intercomparable with results obtained in dissimilar flow geometries unless the fluid properties are simple, such as Newtonian or possibly Bingham Plastic.

Narrow-gap cone-plate and concentric-cylinder geometries are needed for taking high shear rate data on non-Newtonian fluids because only in such geometries are the flow pattern sufficiently simplified and the temperature effects sufficiently controllable to permit quantitative interpretation beyond simple models (65).

Among commercially available viscometers known to the writer, the Rotovisco appears to possess a large price advantage and unusual versatility.

It is the only commercial viscometer with interchangeable cone-plate and Couette heads, and auxiliary equipment for measuring viscoelasticity is available. The total price for a well-equipped Rotovisco is about \$3700. A basic unit with 3 cone-plate heads only would cost about \$2000. By way of contrast, the Shirley-Ferranti cone-plate viscometer described by McKennell (50) was priced to the writer at \$8000 with no provision for Couette heads or viscoelastic measurements. Gaskins' cone-plate viscometer (66) in a photograph appears likely to have well exceeded even this amount.

In the writer's opinion, the Rotovisco should have long-continuing general usefulness for any fluid system that is not extremely rapid settling or under pressure. In particular, it would lend itself well to remote viscometry of minute (0.1 cc) samples of highly radioactive fluids. Further details of the Rotovisco viscometer are given in Appendix A.

If it is not possible to purchase a suitable viscometer, like the Rotovisco, it will be necessary to have fabricated at ORNL some narrow-gap cone-plate and Couette heads to replace the commercially supplied Stormer and Brookfield viscometer spindles and bobs.

The practical handling of capillary flow viscometers is described by Merrington (67). The main corrections are for kinetic energy effects and for extension of capillary flow into the reservoirs (Couette correction). The capillary viscometers to be used are commercial units designed to ASTM standards, thus the calibrating equation:

$$\eta = \rho \left(At - \frac{B}{t} \right)$$

where:

η is Newtonian viscosity

ρ is fluid density

t is time of discharge of the viscometer "head" reservoir

A and B are empirical constants

will be better than $\pm 1\%$ for t somewhat in excess of 200 seconds.

In order to preserve the accuracy of any viscometric measurement, temperature control must be exercised. The viscosity of some heavy oils can change 30% with a 1°C temperature change. However, it is not likely that the thoria sols and gels show such exaggerated temperature dependence. The existing temperature control bath is now controlled to $\pm 0.1^{\circ}\text{C}$, mainly because a thermometer graduated to this fineness was easily available. A thermometer graduated to $\pm 0.02^{\circ}\text{C}$ has been obtained. Control at the $\pm 0.02^{\circ}\text{C}$ level is needed only for low shear, high dilution, Newtonian flow sol viscometry. Temperature control, or calculable correction, within 1°C or thereabout is needed at all shears and flow regimes, to avoid being led into erroneously claiming the existence of time-dependent flow effects. Such misinterpretations and their avoidance have been discussed by Lower, et al. (68). In a typical "well designed" water-cooled Couette viscometer operated at about 450 sec^{-1} the real shear stress corrected for temperature was double the apparent shear stress (50). By way of comparison, the apparent shear stress was indistinguishable from the temperature corrected stress up to 2000 sec^{-1} in McKennell's apparatus.

Detailed design of modified heads for the Stormer and Brookfield instruments are given in Appendix A. The general design features of these heads would be:

(1) Fluid gaps to give from about 1 sec^{-1} to 1000 sec^{-1} with the Brookfield synchronous motor drives and from 100 sec^{-1} to $10,000 \text{ sec}^{-1}$ with the Stormer gravity weight drive.

(2) Water cooling sufficient to limit test-fluid temperature rise to within a range (several degrees Centigrade) that can be reasonably corrected by calculations.

(3) Geometrical accuracy of the fluid gaps to $\pm 2\%$.

(4) Radial pressure taps in the plate of the cone-plate heads for pressure measurement normal to the shear.

At present it is not thought that a high-pressure capillary viscometer will be required unless capillary jet diameter measurements are needed to supplement (or in lieu of) normal pressure measurements with the cone-plate viscometer. Relevant guidelines for design of such a viscometer are given by Merrill (19) and Sisko (70).



APPENDIX A

Details of Proposed Viscometers

The Rotovisco viscometer consists of a control box about 16 in. x 16 in. x 12 in. in size, a flexible cable drive which connects the control box to the measuring head, and a measuring head and stand which weighs about 3 pounds. The basic control box has 10 output rotation speeds from 3 to 486 rpm with a maximum torque of 500 gram-centimeters, and the cost for this unit with cable, stand, and cover is \$1,660.

The minimum accessories required to go with this basic unit are a cone-plate or Couette device and a temperature control assembly. Three cone-plates (full set) plus temperature control unit would cost \$225.30. The range of variables claimed for this assembly is:

Viscosity	-	40 to 1.8×10^6 cp
Rate of shear	-	60 to 10^4 sec ⁻¹
Maximum viscosity at maximum shear	-	600 cp at 10^4 sec ⁻¹

For comparatively little additional cost, the range and versatility of the instrument can be greatly extended:

(1) A 50-g-cm torque head can be added which permits measuring viscosities a factor of 10 lower. Cost: \$283

(2) A 1:100 gear reducer lowers all rotation speeds and hence rates of shear by 100. Cost: \$168.50

(3) A Couette head and temperature control unit permits measuring viscosities down to 1.4 cp. Cost: \$391.10

(4) A viscoelastic attachment with (3) permits measuring stress-relaxation in fluids. Cost: \$416.00

(5) A high viscosity Couette head permits measuring viscosity and viscoelasticity in fluids having viscosities up to 1.3×10^6 cp. Cost: \$181.90

(6) A $\pm 0.01^\circ\text{C}$, -60 to 150°C temperature control fluid supply designed for use with Rotovisco temperature control heads. Cost: \$315.00

Numerous alternate and additional auxiliary equipment are available, but the ones described above are the most applicable to the work proposed for this thesis. The cost for the set given above is \$3733.30.

A Rotovisco instrument was recently acquired by the Department of Chemical and Metallurgical Engineering, University of Tennessee, and it has been reported (71) that the device is reliable, accurate, convenient to operate, and in general performs according to the specifications given in the sales literature.

Some typical fluid gap dimensions for the cone-plate heads are diameters of 12, 20, and 28 millimeters with a cone angle of 20 sec. Couette heads available have sizes ranging from 42 millimeter diameter with 0.99 millimeter gap to 23.1 millimeter diameter with 1.45 millimeter gap.

The capillary viscometers are Ostwald-Fenske type ASTM Nos. 25, 50, 100, 200, 300, 400, and 600. Since these are highly standardized, common, commercial articles they will not be described in detail.

The two Brookfield torque heads on hand are:

Model LVF, 4 speed (6, 12, 30, 60 rpm) 673.7 dyne-centimeters maximum torque, $\pm 1\%$ error at full scale.

Model HAF, 4 speed (1, 2, 5, 10 rpm) 14,374 dyne-centimeters maximum torque, $\pm 1\%$ error at full scale.

If it is not possible to purchase the Rotovisco viscometer, it will be

necessary to purchase one additional torque head:

Model HBT, 8 speed (1/2, 1, 2-1/2, 5, 10, 20, 50, 100 rpm) 57,496 dyne-centimeters maximum torque, $\pm 1\%$ error at full scale.

The price of this torque head is about \$350.

The maximum apparent viscosities that can be measured with the HBT head range from 3000 cp at 900 sec^{-1} to 600,000 at 4.5 sec^{-1} . The cone-plate geometry for attaining these values are 4° half-angle divergence on the cone and 2 cm diameter. The fluid volume of the instrument would be 0.1 ml.

The minimum viscosity to give half-scale reading on the LVF head with the same cone-plate dimensions would be 1.8 cp at 90 sec^{-1} or 18 cp at 9 sec^{-1} . However, μ varies as the inverse cube of the radius and directly with cone angle so that increasing the cone diameter to 4 cm would drop the half-scale viscosity to about 1/4 cp at 90 sec^{-1} or 2-1/2 cp at 9 sec^{-1} . A simultaneous decrease of cone angle to 2° would drop the viscosities to 1/8 cp and 1-1/4 cp, respectively.

It would be proposed to make 3 cone-plate heads of stainless steel to the following specifications:

Cone radius	1 cm \pm 0.025 mm	2 cm \pm 0.037 mm	4 cm \pm 0.05 mm
Cone angle	$4^\circ \pm 1$ min, ave	$3^\circ \pm 45$ sec, ave	$2^\circ \pm 30$ sec, ave
Max surface irregularity	4 micron	3 micron	2 micron

The specifications called for here correspond to about $\pm 2\%$ accuracy with respect to constancy of shear in the gap.

The positioning procedure would be to screw out micrometers, supporting the plate evenly, until electrical contact is made, then to set the shoulder height between the cone and the plate with feeler gauges. Both

the feeler gauge and micrometer would need to be accurate to ± 0.001 in. The overall accuracy hoped for would be $\pm 5\%$ constancy of shear in the gap. Two thermocouples, near the center and near the edge of the plate, would be installed. Cooling water would be forced through holes in the plate.

The design equations for the cone-plate geometry are:

$$\text{Rate of shear} = \omega/\psi \text{ sec}^{-1}$$

$$\text{Shear stress} = 3 \tau/2\pi R^3 \text{ dynes/cm}^2$$

where:

ω is angular velocity, radians/sec

ψ is cone half angle, radians

R is cone radius, cm

τ is cone shaft torque, dyne-cm.

These equations are based on the assumption that inertial effects are small compared to viscous energy dissipation. The experimental conditions are made compatible with the assumptions by keeping the fluid gap narrow. The design specifications given here were patterned after the Ferranti-Shirley viscometer (50,56).

The Couette heads would be mounted in a yoke like the cone-plate head. The primary difference would be in the way that the cup would be centered around the bob.

The cup would be made 5 cm longer than the bob so that vertical positioning would have negligible effect on the gap between the bottom of the bob and the bottom of the cup. Horizontal positioning would be accomplished by inserting four equal shims between the bob and the cup at 90° intervals. The shims would extend the length of the cylindrical section so that gap uniformity from top to bottom would be attained. The

cup would then be glued to the plate with a solvent-sensitive cement such as Dupont Duco.

The Couette geometry is inherently more difficult to align than the cone-plate, so that the gap size must be relatively larger than with the cone-plate geometry. If the gap is made very large, however, the shear rate ceases to be nearly linear in r , and temperature corrections at high shear rate become difficult to make.

As a design criterion, it will be taken that the gap shall not exceed 5% of the radius, and that the maximum radius shall not exceed 4 cm. In order to evaluate slip, which is difficult to do on a cone-plate viscometer, it is desirable to have Couette heads of several radii. Mooney (72) suggests having 2 cups and 2 bobs so that three combinations exist:

<u>Cup Radius</u>	<u>Bob Radius</u>
R_1	R_2
R_2	R_3
R_1	R_3

If, T , the torque per unit length of cylinder is held constant, the equation:

$$\Omega_{12} + \Omega_{23} - \Omega_{13} = T\beta_2/\pi R_2^3$$

is valid (neglecting end correction).

where:

Ω is the angular velocity of the rotating cylinder

β_2 is the slip coefficient at R_2

If it is assumed β is a function of shear stress at the wall only, it is necessary to determine or assume a viscosity function. If the fluid is non-Newtonian and of unknown functional dependence, Mooney gives a

successive approximation formula based on a Taylor's series expansion of $1/\eta$ as a function of shear stress. His final equation becomes:

$$s\phi = \frac{\Omega}{\epsilon} - \frac{\epsilon s}{6 + 2\epsilon^2} \frac{d^2 U}{ds^2} + \frac{\epsilon^2 s^2}{9 + 12\epsilon^2 + 3\epsilon^4} \frac{d^3 U}{ds^3} + \dots$$

where:

s is average shear stress

ϕ is $1/\eta$, the "fluidity"

Ω is the angular velocity of the rotating cylinder associable with the viscous drag only

$$\epsilon = R_2^2 - R_1^2 / R_2^2 + R_1^2$$

$$U = \Omega/s$$

It can be seen that the evaluation of this expression becomes extremely tedious if the non-Newtonian character is sufficiently great as to require evaluation of the higher order terms.

In the present work, it is not expected that slip flow will occur except where the material is so nearly a set gel that the flow can be based on some simple mathematical model, perhaps Bingham Plastic or power law, and that it will not be necessary to make an empirical determination from the generalized relation of Mooney's.

As an insurance feature, however, it is worthwhile to design the viscometers on Money's basis to permit easiest evaluation of slip, should it occur unexpectedly under conditions of high fluidity. On this basis, 2 cups would be made having inside radii of 2 cm and $0.97 \times 2 \text{ cm} \pm 0.01 \text{ mm}$ and 2 bobs having outside radii of $0.97 \times 2 \text{ cm}$ and $(0.97)^2 \times 2 \text{ cm} \pm 0.01 \text{ mm}$. For these gaps, about 0.5 mm, the temperature correction at higher shear would be large, however, this is a limitation inherent in the problem of aligning and operating in a practical manner any Couette viscometer.

The cylinder length is set mainly by the consideration that the Couette heads would be used principally with the Stormer Drive on the more viscous samples. The Stormer Drive is rugged, and can support driving weights up to 1 kg or more. The lower limit of drive is simply that drag in the machine gears be a small fraction of the viscous drag. Since the static drag in the gears is about 2-1/3 grams it should be possible to make reasonably accurate determinations with 50 gram weight drives and a maximum weight drop rate of about 20 cm/sec. For the given geometry and 5 cm barrel length, this corresponds to a minimum viscosity of 14 centipoise. The maximum viscosity that one could get at 10^4 sec^{-1} shear rate with 1 kg drive is 280 cp and at 10^3 sec^{-1} shear rate is 2800 cp.



APPENDIX B

Discussion of Auxiliary Analytical Procedures

(1) For thoria concentration, a measured volume of sol, or weight of gel, shall be ignited in platinum to greater than 1000°C and the resulting thoria weighed to ± 0.2 milligram. Accuracy exceeding $\pm 0.01\%$ is easily attainable.

(2) For sol density, fast, approximate determinations of sol density shall be taken by immersion hydrometer. Accurate determinations shall be made by pycnometric weighing which is reproducible to about ± 0.03 wt %. Gel density will be estimated geometrically and by toluene immersion.

(3) For nitrate content, analysis is supplied as a routine service of the Analytical Chemistry Division at ORNL. Its reproducibility on duplicate samples is about $\pm 5\%$ at the 0.1 N/Th mole ratio level.

The procedure consists of sulfate displacement of the nitrate from the sol into solution, reduction to ammonia with da Varda's alloy, neutralization with sodium hydroxide, and then the standard Kjeldahl distillation-titration.

(4) For surface area, the BET nitrogen adsorption surface area is available as an analytical service at ORNL. The accuracy of the analysis is strongly dependent on the surface area of the sample under test in the range of 5 to 80 m²/gram, which is the probable range of application. The analyzed values are expected to have three significant figures with respect to reproducibility. Micro-surface area measurements are inherently nominal rather than physically absolute.

(5) X-ray crystallite line-broadening particle diameter is an analytical service at ORNL. In the range of interest for the proposed thesis,

50 to 700 Å, the empirically determined reproducibility is $\pm 10\%$. It is usual for the nominal x-ray crystallite size to predict more area than the BET analysis finds. This discrepancy is interpretable as a geometric deviation of 1.1 to 1.3 about the mean assuming long-normal distribution of sizes.

(6) For measuring the pH of sols and ultracentrifugates, a Beckman glass electrode-calomel electrode meter is available directly to the writer, and a 30,000 gravity (nominal) ultracentrifuge can be made available by Dr. J. S. Johnson of the ORNL Chemistry Division. This centrifuge is suitable for separations only, not for in-operation measurements on the sample.

(7) Electrical conductivities measured at 1200 cps, 60 cps, and with D.C. are available from the ORNL Analytical Chemistry Division. It is thought that a suitable range of all conductivity cell sizes are available to give conductivity to three significant figures on systems of interest in this thesis.

(8) The "light scattering" apparatus available in the Analytical Chemistry Division is a spectrophotometer for measuring extinction. For Rayleigh scattering the formula (73):

$$\frac{I}{I_0} = \exp \left(- \frac{128\pi^5 a^6}{3\lambda^4} \left\{ \frac{m^2 + 1}{m^2 + 2} \right\}^2 \right) n l$$

applies where:

I = the unscattered radiation intensity

I_0 = the incident radiation intensity

a = the particle radius

λ = the wave length of the radiation, monochromatic

m = the relative refractive index, particle-to-medium, which 1.58 for thoria in water

n = the number density of particles in suspension

l = the path length through the scattering medium

A rule-of-thumb for the maximum particle size to which Rayleigh scattering applies is 1/10 of the wave length of the incident radiation. Van De Hulst (74) defines the regions of applicability of various radiation scattering regimes for both size and refractive index. For thoria in red ($\lambda = 0.7$ micron) light the limit is $500 \overset{\circ}{\text{A}}$ for Rayleigh scattering.

Scattering by larger particles becomes exceedingly complex. Measurement of scattered radiation intensity and polarization as a function of angle can become necessary, and the calculations for data interpretation become very complicated and tedious.

A light scattering apparatus for measuring scattered radiation intensity as a function of angle is available in the laboratory of Dr. J. S. Johnson at ORNL, should such measurements be required. It is expected, however, that Rayleigh scattering will occur for all sizes of interest for the proposed work, and that electron photomicrography will define particle size in any unusual cases.

(9) Electrokinetic measurements will be made in order to evaluate present electroviscous theory. Data from which a zeta potential may be calculated are needed. Dr. H. F. Holmes of ORNL has suggested (28) that a technique with promise of experimental simplicity would be to measure the potential developed across a gel cake or of a sol confined between millipore filter membranes as a function of pressure drop and fluid flow rate of its equilibrium ultracentrifugate. Potentials in the millivolt

range are expectable for pressure drops in the range of an atmosphere or so. The experimental complication that is anticipated is the need to have a simultaneous electrical conductivity through the medium in order to correct for gel compression or sol concentration at the bottom of the confining chamber under the influence of the flow or the pressure. Dr. Holmes has offered to evaluate the electrokinetic data, since he has a direct and continuing interest in this general area of study.

The basic equation is (75):

$$E/P = \epsilon \zeta / 4\pi \eta \sigma k$$

where:

E is the streaming potential

P is the driving pressure for flow

η is the viscosity of the medium

σ is the electrical conductivity of the medium (76)

ϵ is the dielectric constant of the medium

k is a geometrical cell constant

The desirability of measuring rather than calculating the conductance is also enhanced by the need to evaluate surface conductance of the thoria in addition to the electrolytic conductance of the fluid medium. More generally, σ is replaced by (77):

$$\left\{ 1 + \frac{x}{a\sigma} \right\}$$

where:

x is an effective surface conductance

a is particle radius

APPENDIX C

Sol and Gel Preparation Procedures

(a) Hydrous Thoria Precursor Preparation

To 4 liters of 0.5 M thorium nitrate solution at 70-80°C sufficient 6 M aqueous ammonia is added at a rate of 4 moles NH_3 /hr with stirring to give a pH of 6 to 7. The resulting precipitate is washed twice with 1 liter of 0.05 M aqueous ammonia, followed for four 1 liter washes with distilled water. The wet cake is dried under vacuum in a dessicator containing silica gel at room temperature. The hydrous thoria cake is stored under nitrogen or argon, and analyzed for:

NO_3 not to exceed 500 ppm

CO_3 not to exceed 100 ppm

SiO_2 not to exceed 20 ppm*

(b) Oxalate Thoria Precursor Preparation

To 2 liters 1.0 M thorium nitrate solution at room temperature a total of 2.2 moles of 1.0 M oxalic acid solution is added with stirring at a rate of 8 moles oxalic acid/hr. The resulting precipitate is washed with 1 liter of 0.05 M oxalic acid, followed by 2 liters of distilled water. The cake is dried at 110°C in air, and then calcined in air at 350°C until samples show constant loss-on-ignition. The cake is stored under laboratory air and analyzed for:

NO_3 not to exceed 500 ppm

SiO_2 not to exceed 20 ppm*

*This analysis is rather difficult, and occasional false high values are seen.

(c) Hydrothermal Denitration Thoria Precursor Preparation

One kg of hydrated thorium nitrate is placed in the laboratory rotary calciner and heated under a sufficient flow of steam so that all nitrate is carried away as nitric acid vapor rather than brown oxides of nitrogen. The temperature is raised to 450°C maximum and held at this temperature for 1 hr. The thoria is stored under nitrogen or argon, and analyzed for:

Fe not to exceed 50 ppm

NO₃ not to exceed 1 wt %

CO₃ not to exceed 100 ppm

Na, no specification

(d) Dry Denitration Thoria Precursor Preparation

One kg of hydrated thorium nitrate is placed in a muffle furnace and the temperature is raised slowly to 450°C maximum, holding it at this temperature for 1 hr. The thoria is stored under nitrogen or argon, and analyzed for:

NO₃ not to exceed 1 wt %

Na, no specification

The different types of precursor tend to give sols and gels of different average behavior. The hydrous thoria produces filamentary systems with elasticity and which fragment markedly on drying. The calcined oxalate thorias product systems of low elasticity and uniform particle size having compact shape. The hydrothermal precursor produces materials of small but compact particles, whereas the dry denitration precursor produces a relatively higher population of multiple-crystallite particles of large size.

The sol-making procedures for the various thoria precursors will vary in detail, but consists essentially of stirring the precursor with dilute nitric acid and removal of any undispersible sediment. Occasionally it is necessary to eliminate carbonate or disperse a refractory sample by adding excess nitric acid and the decanting or evaporating off the excess.

The proposed materials which may contact the sols under preparation and testing are Pyrex, Kimball Hard Glass, vitreous silica, stainless steel, and polyethylene. All glassware will be washed in KOH, boiled in distilled water, washed with HNO_3 , and rinsed before initial use. Sowden (29) has reported interference with electrophoretic measurements by silica leaching from his apparatus, but that atmospheric exposure of samples was not significant. Sturch (11) reported easily detectable and consistent changes in sol viscosity from atmospheric exposure.

APPENDIX D

Analysis of the Source Thorium

The source thoria for all experimental work will be derived from Lindsay Chemical Company (West Chicago, Illinois) reactor grade Lot 101 hydrated thorium nitrate. The degree of hydration, and to less extent the nitrate content, are sensitive to the conditions of storage of the compound. The significance of these changes has never been found to be other than purely stoichiometric, however.

When multiple values of an analysis are given the most likely value is given first. The only contaminant under question is Ce, for which no analysis is given. This omission is almost certainly inadvertent, and the level of the Ce should not exceed several ppm. The Ce analysis will be made.

Basis: 45.69 wt % ThO₂

<u>Contaminant</u>	<u>Contamination Level, ppm of the original sample wt</u>
Al	<10
B	2
Be	<1
Bi	<2
Ca	<200
Cd	<0.2
Cl	3 - <10 - 10
Co	<1
Cr	<5 - 6 - <10
Cu	1
Dy	2.0

<u>Contaminant</u>	<u>Contamination Level, ppm of the original sample wt</u>
Er	0.6
Eu	<0.1
F	<10
Fe	10 - 5 - 20
Gd	2.0
Ho	0.3
Lu	<0.2
Mg	20
Mn	<1
Mo	<1
Na	>100
Nd	4
Ni	4 - <10
P	<40
Pb	<1 - <10
PO ₄	50 - 25 - 15
Pr	1.5
Si	<10 - 13 - 15
Sm	1.3
Sn	<1
SO ₄	27 - 51 - 59 - 88 - 110 - 26 - <10
Tb	0.4
U	15
V	<10
Y	17
Yb	0.2

The high sodium does not appear to be particularly significant. Precipitation by either oxalate or ammonia reduces the alkali metals content to low levels. A thoria prepared by 650°C calcination of oxalate precipitated from Lot 101 nitrate solution had the following analysis:

Basis: 99+% ThO₂

<u>Contaminant</u>	<u>Contamination Level, ppm</u>
CO ₃ ⁼	3100
K	<10
Li	<10
Na	<10
Zn	<20

The high carbonate results from the fact that it is one of the thermal decomposition products of oxalate. Carbonate is reduced to acceptably low (100 ppm) levels by adding excess nitric acid followed by decantation or by ammonia washing.



APPENDIX E

Error Analysis and Validity of Assumptions

The main assumptions and expected errors are usually stated with the relevant measurements in the main body of the report. In a few particular instances it is practically impossible to estimate quantitatively the error without experimental measurements such as for the estimation of the zeta potential, which requires surface conductance measurements.

Much of the error analyses will have to be statistical in nature and performed on the numerical data as it is taken. This is particularly true of those analyses supplied as analytical services. Attempts to estimate a rationally expectable error from certain simple analyses supplied as a service, such as pycnometric density of solids, has in the past resulted in being misled. It is expected that the main statistical assumption will be that net errors are due to numerous small, random, independent effects. In this case errors are Gaussian in distribution and Student's t test is applicable. Some simple statistics for small numbers of observations have been described (78) and are expected to suffice for the proposed measurements.

When plotting data as a function of some parameter, such as apparent viscosity versus thoria concentration, curve-fitting by least-squares linear regression is proposed. This procedure is outlined in numerous texts, of which only one will be cited (79). It should be noted that the actual validity of such a least-squares fit depends on assumptions which are seldom all realized in practice:

- (1) All errors are normally distributed.
- (2) The dispersion of the errors is not a function of the parameter being varied.

(3) The dependent variable is linear with respect to the independent variable.

None of the three assumptions is likely to be strictly true for viscometric measurements, and the third assumption is likely to be grossly violated. However, if the discovery of an alternative which is superior to least-squares fitting is attempted, one reaches the conclusion that there is none, at least none worth the effort unless a very large body of data in the same set exists. For less than ten observations statistical correlations tend to merge indistinguishably, and it is not likely that enough more than ten data points will be taken in any given data set to justify complication beyond least-squares linear (or linearized) regression.

The main area of rationalizable error analysis is in the geometrical and flow approximations in the viscometers. For the cone plate viscometer one must justify the following assumptions:

(1) That the fluid flow in each infinitesimal fluid ring of the thickness dr approximates flow between parallel walls. This approximation is equivalent to assuming $\cos \theta = 1$ where θ is the cone half-angle. At a maximum cone angle of 4° we have $\cos 4^\circ = 0.99756$. The percentage departure from the mean of 0.99756 and 1.00000 is only $\pm 0.12\%$ which is negligible.

(2) That surface and surface tension effects are negligible compared to viscous effects. The way to evaluate the existence of these sorts of effects is experimentally by measuring torque as a function of radius of the test fluid body. If the dependence of torque is other than linear in r^3 , surface effects exist. Although no such effects are expected,

significantly large surface viscosity departures from bulk viscosity have been observed in colloidal systems (80) and should be experimentally evaluated.

(3) That inertial forces in the fluid are negligible compared to viscous forces. So long as the flow is steady and laminar, inertial forces are self-cancelled in the main direction of flow. The cone-plate geometry, however, will cause an uncanceled radial circulation to be set up, outward along the rotating cone surface and inward along the stationary plate.

The total fluid centrifugal force will be:

$$F_{\text{centrifugal}} = \int_0^{R_{\text{max}}} \int_0^{\theta_{\text{max}}} (2\pi r \, dr)(r d\theta)(\rho) (\omega^2 r) \left(\frac{\theta}{\theta_{\text{max}}}\right)$$

$$F_{\text{centrifugal}} = \frac{2\pi\rho\omega^2}{\theta_{\text{max}}} \int_0^{R_{\text{max}}} r^3 \, dr \int_0^{\theta_{\text{max}}} \theta \, d\theta$$

$$F_{\text{viscous}} = \int_0^{R_{\text{max}}} (2\pi r \, dr) \mu \left(\frac{\omega}{\theta_{\text{max}}}\right)$$

where:

- θ_{max} is the cone half angle
- ω is the angular velocity of the cone
- μ is viscosity
- ρ is fluid density
- r, θ are polar coordinates
- R_{max} is the cone radius

For any given values of the parameters we ask that:

$$F_{\text{viscous}}/F_{\text{centrifugal}}$$

be large. With respect to turbulent transition, if one takes as a rough criterion that

$$\frac{V_{\max} \rho h}{\mu} \geq 2100$$

implies turbulence,

where:

V_{\max} = the fluid velocity against the cone at the perimeter

ρ = fluid density

h = the fluid gap at the perimeter

μ = viscosity

One can estimate that for 600 rpm, $\theta = 2^\circ$, $R = 4$ cm, $\rho = 2$ g/cc that turbulence is expected for viscosities less than 2 cp.

(4) That equipment drag be negligible compared to viscous drag. This effect is simply subtracted out by calibration of the equipment with a fluid of known viscosity.

The evaluation of the errors and assumptions in the Couette viscometer have surprisingly little in common with the cone-plate viscometer.

With respect to constant rate of shear in the gap we have:

$$\text{rate of shear} = \frac{2\omega}{r^2} \left(\frac{R_i^2}{R_o^2} - \frac{R_o^2}{R_i^2} \right)$$

If this expression is evaluated for $R_o = 0.95 \times 2$ cm and $R_i = (0.95)^2 \times 2$ we get:

$$\text{rate of shear at } R_o = 10.28 \times 2\omega$$

$$\text{rate of shear at } R_i = 9.77 \times 2\omega$$

per cent variation from the average $\pm 2.55\%$

Inertial effects are harder to evaluate because the onset of turbulence in Couette flow appears to depend on surface finish and geometrical accuracy of the apparatus. Taylor (81) deduced a rational formula for the critical velocity between concentric cylinders, quoted by Merrington (82), but it will probably be necessary to determine the critical point empirically for the particular apparatus.

Evaluation of anomalous surface effects is best done in the cone-plate viscometer, although the Couette head could be operated with a submerged bob.

Equipment drag is, again, to be empirically evaluated.

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"The discussion is reported here as it took place, but it will be found that it does not relate to the published text---. The paper was written nine months before the Congress, and during the Congress the author felt obliged---to modify her account---. Publication difficulties made it impossible to incorporate these modifications and explanations in the printed paper."
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NOMENCLATURE

Most of the nomenclature is defined at its point of use in the body of the report, and ordinarily it is the same as that of the original literature cited. This procedure has led to multiple meanings for some of the common symbols, but it is usually obvious from context which meaning is applicable.

A	empirical constant
A°	Angstrom units
B	empirical constant
F	apparent viscosity
F	force (p. 51 only)
I	light intensity
I_0	reference light intensity
K	power law coefficient
M	total number of ionic species
P	pressure
R, R_0 , R_{max}	fixed outer radii
R_{cap}	capillary tube radius
R_i	fixed inner radius
R_j	jet radius
T	absolute temperature
T	torque per unit length of cylinder (p. 36 only)
U	ratio of angular velocity to shear stress (p. 37 only)
U_x	point linear fluid velocity in the x direction
V	area average linear fluid velocity
V_{max}	maximum point linear fluid velocity
Z	function symbol

a	particle radius
a	semitheoretical constant (pp. 25 and 27 only)
a_n	empirical constant
b	semitheoretical constant (p. 25 only)
b, b_q	empirical constants (p. 24 only)
c_p	centipoise
d	differential operator
e	electron charge
h	fluid gap at the perimeter of a cone-plate viscometer
i	index of summation
i	inner (used only for R_i)
k	Debye-Huckel reciprocal length
k	Boltzmann's constant (only in kT)
k	limit of summation (p. 24 only)
k	geometrical cell constant (p. 42 only)
l	light path length
m	relative refractive index
n	power law exponent
n	index of summation (p. 24 only)
n	number density of particles in suspension (p. 41 only)
n_i	number concentration of the <u>i</u> th type ion (p. 17 only)
p	pressure
p	semitheoretical constant (p. 27 only)
p.,pp.	page(s)
ppm	parts per million by weight
p_r	pressure in the r direction

p_z	pressure in the z direction
q	index of summation
r	variable radius
s	average shear stress
t	time
x	surface conductance of a solid
z_i	ionization number of the <u>i</u> th type ion
α	empirical constant
$\alpha_{1,--8}$	even power polynominal functions of (dU_x/dy)
β	empirical constant
ϵ	dielectric constant
ζ	electrokinetic (zeta) potential
η	viscosity
η_0	reference viscosity
θ_{max}	cone half angle
λ	light wavelength
μ	viscosity
μ_1, μ_2	viscoelasticity time parameters
ν_1, ν_2	viscoelasticity time parameters
π	3.14159---
ρ	density
σ	specific conductance
σ_g	log-normal geometric standard deviation
τ	torque (p. 35 only)
τ_{xy}	stress acting in a plane normal to the x axis and directed along the y axis (x and y may be replaced by any coordinate direction symbols)

τ_w	wall shear stress
$(\tau_{xy})_{eq}$	thixotropic equilibrium shear stress
ϕ	solids volume fraction
ϕ	fluidity = $1/\eta$ (p. 37 only)
ψ	cone half angle
ω	angular velocity
Ω	angular velocity
x, y, z	Cartesian coordinate systems
r, θ, z	Cylindrical coordinate systems

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