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Basic Considerations in Flowing Electrorheological Fluids

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The physical and chemical properties of electrorheological (ER) fluids are reviewed, and an outline theory of their mode of action is proposed. Rheologically, the Bingham plastic model gives an acceptable representation of ER fluids flowing in a field and it has recently been shown that the plastic viscosity may be field-dependent in some circumstances, as well as the yield stress. The variation of the former with field is strongly influenced by the specific chemical nature of the ER fluid, while the field dependence of the latter has a similar form in all the ER fluids investigated. However, interpretation of observations is complicated by concentration of solid in the working gap and interplay between local electrical conductivity and shear rate.

KEY WORDS: Electrorheological fluids; ER fluids; suspensions; rheology.

1. INTRODUCTION

Electrorheological (ER) fluids are materials which show a significant increase in flow resistance when exposed to an electric field. All the ER fluids so far described are concentrated suspensions of finely divided solids dispersed in base liquids: they are usually formulated to have approximately Newtonian flow characteristics, like normal liquids, in the absence of a field. ER fluids can form a virtually ideal interface between mechanical devices and electronic controls and so have attracted considerable commercial interest. The science is no less fascinating. Although the first ER fluids were described as early as 1947, by Willis Winslow,(1) there is still no general agreement on the fundamental basis of the effect.

The first part of this paper sets out the general properties of ER fluids, relating these where appropriate to the theory proposed by the author and

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his colleagues. In the second part, these properties are related to the interpretation of rheological measurements, which are central to the study of ER fluids as a whole.

2. BASIC PROPERTIES

If two parallel plates are plunged into an ER fluid and a voltage sufficient to give about 2 kV/mm applied between them, the ER fluid between the plates can be withdrawn as a solid lump. This lump will remain as long as the voltage is maintained: it does not flow gradually, like a viscous liquid, although the pure base liquid will gradually drain down from the solid. If voltage is slowly reduced, apart from edge effects, the lump will stay on the electrodes until, below a certain field, it slides off: it does not pass through a "viscous" phase. In rheological terms, the field evokes a "yield stress" in the ER fluid, i.e., no flow takes place until this stress is exceeded at some point in the fluid. In contrast, in a "normal" Newtonian fluid, any stress, no matter how small, leads to flow.

The exact relationship between the yield stress of an ER fluid and the field is not generally agreed, and, indeed, it may be variable. A mechanism based on induced dipoles predicts that the yield stress should vary as the square of the applied field,(2) and some fluids appear to behave in this way, particularly the less active fluids at low field.(3) However, a linear relationship, with a "threshold" field, seems to provide the best description for virtually all the active ER fluids we have examined, and published data for many other ER fluids can be fitted to this model.(4) Often, experimental data are not sufficiently precise to allow an objective decision to be made between the two models. Data can obviously be fitted to a power law, but the power is found to vary quite widely between fluids. This would imply that there is a wide range of fundamental mechanisms, which seems rather unlikely in the light of other evidence. The linear model is adopted in the rest of this paper: the relationship between yield stress and field is approximated by a straight line with slope S/E and intercept, on the field axis, of E_0. Limits of error, where indicated, are 95% confidence limits calculated from the scatter of experimental results.

It is generally agreed that ER fluids respond to electric field, rather than current, but direct evidence for this is rather scanty. All ER fluids pass some current, and this may be large enough to become a serious limitation in some practical applications. ER fluids generally do not obey Ohm's law, but there is no general agreement on the form of the conduction. Under static conditions, a good representation of the current density j as a function of the field E is

$$j = PE + QE^2$$

where P and Q are constants of the fluid.(5) Of these, Q is particularly interesting, since it varies systematically with temperature according to the Boltzmann law, with an activation energy in the range 60–90 kJ/mole in all ER fluids that have so far been examined, regardless of their detailed chemistry.(6)

3. GENERAL COMPOSITION OF ER FLUIDS

Table I lists some of the materials which have been tested as the solid phase of ER fluids, roughly in descending order of activity. Alginic acid, and its synthetic analogues polyacrylic and polymethacrylic acid are roughly three times more active than the more commonly used materials corn starch and silica gel.(6,7) As discussed below, some of the salts of these acids share this activity. Simple conductors, such as carbon and powdered metals, do not give active ER fluids, although the organic semiconductors invented by Block *et al.*(8) are quite active. Table II lists some of the base liquids that have been used, again in roughly descending order of activity. In general, halogenated materials give more active ER fluids than the parent hydrocarbon or silicone; which specific halogen is used does not seem to be important.(9–11)

The fact that a wide range of suspensions show some ER effect argues against a chemically specific mechanism or surface phenomenon; the latter

Table I. Some Solids Used in ER Fluids[a]

Biopolymers	Synthetic polymers	Minerals, etc.
Alginic acid(7)	Polyacrylates,(5) polymethacrylates,(5) phenol-formaldehyde polymers(26) (acid and alkali metal salts)	
	Condensed conjugated aromatic ketones(8)	
Starch(1)	Polyvinyl alcohol(24)	Silica gel,(1) vermiculite,(25) zeolites(23)
Dextrans(24)		
Cellulose(24)		Barium titanate(1)
Methyl cellulose(24)	Nylon(24)	Powdered metals(24)
Sucrose(24)	Polyacrylonitrile(24)	Sulfur(24)
		Powdered carbon(24)

[a] These are listed roughly in descending order of activity, although this may be greatly influenced by physical form. Materials below the dashed line have been shown to be inactive. The list is by no means exhaustive.

Table II. Liquids Used in ER Fluids[a]

Group A—Good		
Fluorosilicone(10)	Ar-bromodiphenyl methane(9)	Clorophenyl chlorotolyl methane
Bromonaphthalene	Polychlorinated biphenyls	
Pentachlorophenyl/aliphatic ethers(11)		
Group B—Moderate		
Mineral oils	Silicones	Halo-benzenes[b]
Halotoluene[b]		
Group C—Poor		
Benzene	Toluene	Methyl naphthalene
Fluorobenzene	Fluorotoluene	
Perfluoro-polyethers		

[a] These are divided into three rough groups, in descending order of activity. The list is by no means exhaustive. From ref. 27 unless otherwise specified.

[b] Excluding the fluoro compounds, which resemble the parent hydrocarbons.

are notoriously sensitive to trace materials. On the other hand, the significant increase in ER activity brought about by the introduction of an ionic group, e.g., from polyglucose (starch) to polymannuronic acid (alginic acid),(7) shows that chemical aspects are involved.

4. MECHANISM AND DETAILED COMPOSITION

When a thin layer of dilute ER fluid is exposed to an electric field under a microscope, a quite characteristic series of changes occurs. Initially, each particle (diameter approx. 10 μm) adheres to its immediate neighbors —a particle with no immediate neighbors definitely migrates to nearby groups—forming a more or less random arrangement. Gentle agitation in the field detaches the more loosely attached particles, which reattach themselves in new, and usually more favorable positions, so the initial random structure changes to definite fibers, parallel to the field. If a slight pressure is applied transverse to the field, these chains behave as if they are under tension: they bow, and finally slip at the electrode surfaces which form the walls of the channel. Migration of the particles to one or other of the electrodes (electrophoresis) is seldom seen in ER fluids.

Microscopic observations can be directly related to macroscopic behavior. Gentle agitation of a stationary ER fluid in a field usually leads to an increase in yield stress; in conventional suspension rheology, this is known as "rheopexy." Electrophoresis, when it occurs, is associated with low ER activity, as expected: the layer of pure base liquid acts as a lubricant.

In an early experiment,(12) carbon particles were encapsulated in epoxy resin and observed under the microscope. The particles initially formed a structure, as usual, but immediately collapsed to *both* electrodes, leaving a clear space in the middle. It was realised(13) that this was the fundamental behavior of a suspension of conducting particles in the microscope experiment. The electrodes are thin compared with the gap between them, so the field will be very inhomogeneous, and the dipoles induced in the conducting particles will migrate to the regions of highest field gradient, near the electrodes (dielectrophoresis). It was therefore clear that, although interaction between induced dipoles was occurring in ER fluids—it is probably responsible for bringing the particles together—there was an additional interparticle force which was able to overcome dielectrophoresis.

In an ER fluid flowing in a field, the increased energy dissipation presumably results from the work done overcoming the interparticle forces when the particles are torn apart. However, it appears that only a contact force will have this effect. Considering one particle passing another, a long-range force would put as much energy into the system as the particles approached each other as would be lost as they separated. Pictorially, therefore, the field appears to make the particles "sticky." An argument based on the behavior of a pair of particles may not apply to a concentrated suspension, but, on the other hand, ER activity can be detected in suspensions containing as little as 5% by volume of solid.(14)

A possible clue to the nature of the interparticle force is provided by the work of Kruyt and van Selms.(15) These authors showed that suspensions of hydrophilic particles such as starch in hydrophobic liquids such as xylene become stiff gels when small amounts of water are stirred into them. The water forms "bridges" between neighboring particles, locking them together by the interfacial energy of the oil–water interface. The similarity between the suspensions used by Kruyt and van Selms and ER fluids is striking.

The apparent lack of a source of water in ER fluids is not a serious difficulty. Water adsorbs very strongly to almost any solid surface, and usually requires severe treatment, causing irreversible breakdown of most materials, to remove it. It is reasonable to assume that virtually all the solids used in ER fluids will have appreciable amounts of adsorbed water unless it is very rigorously excluded. The properties of this water will be quite different to those of "normal" water: being strongly bound to the substrate, it will not boil off at 100°C, nor freeze at zero. The molecular rotation may be inhibited, so the low-frequency dielectric constant may be low. However, just as a high electronic work function in metals does not imply a low conductivity, so strongly bound water could be free to move over or through the substrate.

If adsorbed water is involved in the ER process, it would be expected that varying the amount of adsorbed water would strongly influence the ER response. Figure 1 shows that this is indeed so: as adsorbed water is removed, E_0 rises and S/E increases to a maximum and then falls. This pattern is quite general; it has been seen in all ER fluids that have been examined, including some so-called "water-free" systems.$^{(16,17)}$

Further evidence that adsorbed water is involved in the ER response is provided by the influence of the submicroscopic structure of the solid. The solid used in most of our work is made by polymerizing lithium methacrylate, to which a small amount of methylene *bis*-acrylamide is added as a cross-linking agent, in 10% aqueous solution. A solid gel is formed, which is then broken up, washed, dried, and ground. The resulting solid is very porous: in air of 60% humidity, it will take up 20% by weight of water and remain apparently dry.$^{(18)}$ Pictorially, the solid particles resemble balls of cotton wool rather than lead shot. Changes which reduce this porosity also reduce the ER activity. This can be done by increasing the proportion of cross-linking agent$^{(19)}$ or by exhaustive drying, which

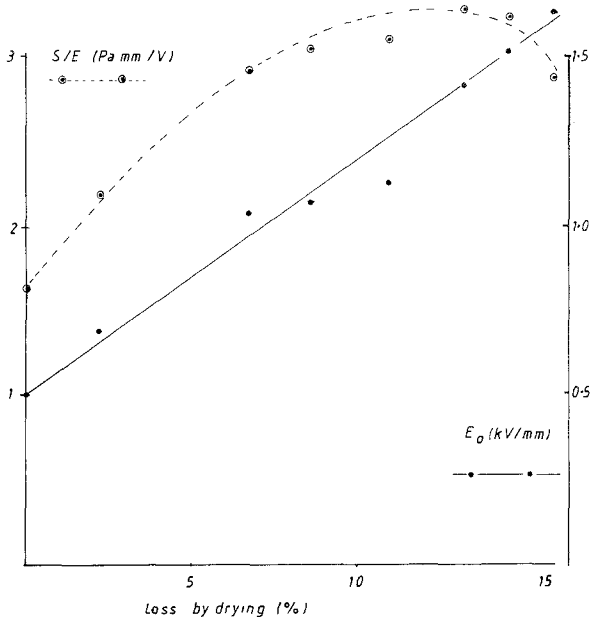

Fig. 1. Effect of adsorbed water. The weight loss of a batch of lithium polymethacrylate followed as it was progressively dried. Periodically, samples were removed, made up into ER fluids (30% v/v in bromodiphenyl methane) and tested under static conditions.

removes the adsorbed water and encourages the formation of internal hydrogen bonds. Moderate amounts of water added to such dried material do not reverse the loss in ER activity: the ER fluid produced is unusually conductive, suggesting that the added water stays on the surface of the particles. However, if excess water is added, the rise in internal dielectric constant weakens the hydrogen bonds, so the solid reverts to its original condition, as shown by a complete restoration of ER activity when it is dried to its original water content.(20) This suggests that the porous structure, which favors water adsorption, also favors ER activity; it will also allow ions to move through the particles as well as over their surfaces.

When a field is applied to an ER fluid, it is generally agreed that mobile charges within the particles will move to generate induced dipoles. In the materials in Table I, "mobile charges" are more likely to represent ions than electrons. However, cations particularly, with their high charge density, are known to be strongly hydrated, so as these ions move through the particles, they will carry water molecules with them. This will concentrate the water at the positive end of the induced dipole, which will become "wet" and capable of forming "bridges," as in the experiment of Kruyt and van Selms.

If adsorbed water is moved by mobile cations, it would be expected that changing the cations within the particles would greatly influence the ER response. Figure 2(20) shows that this is indeed the case. A series of salts

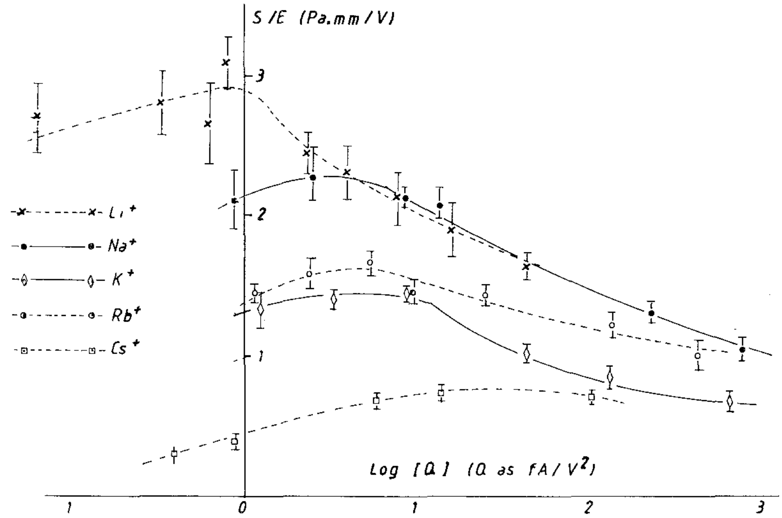

Fig. 2. Effect of counter ion. Monobasic salts of the alkali metals were condensed with formaldehyde. After initial drying and grinding, the resultant polymers were progressively dried. Periodically, samples were made up into ER fluids (30% v/v in bromodiphenyl methane) and tested. Log(Q), the ordinate in this graph, is linearly related to water content.

Table III. Properties of Alkali Metal Ions(28)

	Li	Na	K	Rb	Cs
Crystal radius (Å)	0.60	0.95	1.33	1.48	1.69
Hydrated radius (Å)	3.40	2.76	2.32	2.28	2.28
Hydration energy (kJ/mole)	123	97	77	70	63
Hydration number	25.3	16.6	10.5	—	9.9
Ionic mobility	33.5	43.5	64.6	67.5	68

of phenol-formaldehyde resins were made up: the counter-ions were lithium, sodium, potassium, rubidium, and cesium. All five samples were treated in the same way: each was finally made up into a series of ER fluids containing different amounts of adsorbed water—Q, the quadratic term in the conductivity law, was used to put all the samples on a common scale, since it has been shown(5) that $\log(Q)$ is linearly related to water content. Figure 2 shows the results obtained. In general, the larger the ion, the less active the ER fluid, except that potassium and rubidium are reversed. Table III shows the properties of the various ions, and it is quite clear that the "ranking" of the ions in the ER fluids corresponds most closely to the hydration energy—in other words, the more firmly a given ion holds water, the more effective the final ER fluid. This is exactly as the theory would predict. There is other evidence. The bond between polyvalent ions and the anionic matrix would be expected to have significant covalent character; these ions would therefore be fixed, and the corresponding salts would not form active ER fluids. This is observed in practice.(20) Finally, since anions are known to be much less strongly hydrated than cations, cationic polymers with mobile anions would be expected to be inactive. This is also observed.(21)

The mechanism proposed is an extension of the induced dipole theory: movement of ions, and consequent movement of water, is one way among many in which the induced dipoles may be set up. If other conduction mechanisms operate within the particles, the relative contribution of each may well depend on circumstances. This may well explain the range of yield stress/field relationships.

5. MEASUREMENTS ON FLOWING ER FLUIDS

Static or quasistatic measurements on ER fluids avoid many of the practical and theoretical difficulties associated with dynamic measurements. However, the latter are essential to evaluate ER fluids for the majority of applications. In planning such measurements and interpreting the results it is essential to bear in mind the fundamental aspects of ER fluids.

It has been pointed out that pure base liquid drips from a lump of ER fluid held between two electrodes, so the solids concentration in the lump increases. This process can be observed directly in ER fluid pumped between fixed plates of conducting glass, so constant solids concentration cannot be assumed with this geometry. Couette measurements are more reliable in this respect, but it is difficult to devise adequate temperature control. Also, rheopexy can give an ER fluid in a field "stick-slip" characteristics reminiscent of friction; this can excite resonance in the torque-measuring system of many conventional rheometers.(22)

The experimental data in a Couette measurement are the dimensions of the instrument, the rotational shearing speed, and the drag torque; the relationship between shear stress S and shear rate du/dx must be deduced from these. Figure 3 shows a section of the working gap of a Couette rheometer, bounded by the surfaces of the inner bob (R_i) and the outer cup (R_o). Let the depth of the cup be L, and suppose a torque T is being transmitted. It will be seen that the value of S at any radius x is given by

$$S_x = T/(2\pi x^2 L)$$

This pattern of shear stress will be independent of the test material. However, the behavior of the latter will define the value of du/dx

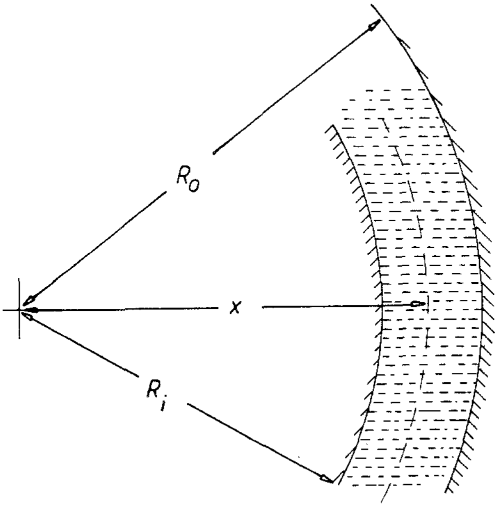

Fig. 3. Basis of Couette viscometry. R_i and R_o are the radii of the inner and outer elements: x is any annulus in the working gap between. If T is the transmitted torque and L the depth of the elements, then the shear stress S is given by $S_x = T/(2\pi x^2 L)$.

corresponding to S; the observed shearing speed will be given by the integral of du/dx between the two shearing surfaces.

Although numerical methods are available to derive flow equations from experimental data, it was felt that the simplest rheological model which included a yield stress would be the best. This is the Bingham plastic model, represented by the equation

$$du/dx = (S - Y)/\mu_{\mathrm{pl}}$$

where S is the shear stress, Y the yield stress, and μ_{pl} the "plastic viscosity." Figure 4 shows the effect of this model when applied to the Couette geometry. In the range of torques given by

$$Y/(2\pi R_o^2 L) < T < Y/(2\pi R_i^2 L)$$

the working gap will be divided into two regions, an outer region where S does not exceed Y, and therefore no shearing takes place, and an inner region where the fluid is shearing. This division will appear for all materials which show a yield stress, and must therefore be considered in all measurements on ER fluids, where the yield stress is a central feature of ER

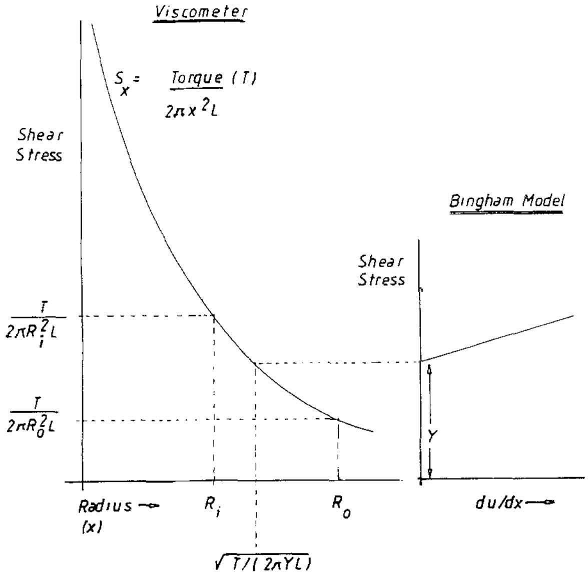

Fig. 4. Bingham plastic in Couette viscometer. For a range of values of the yield stress Y of the sample and observed torque T, the working gap of the viscometer is divided into two parts. Shearing only occurs in the inner of these two annuli.

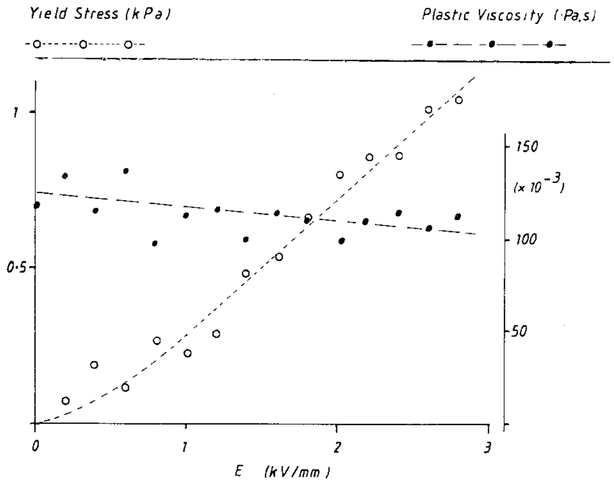

Fig. 5. Dependence of Bingham parameters on field. The sample was 30% (v/v) condensed aromatic ketone[8] suspended in chlorophenyl chlorotoly methane.

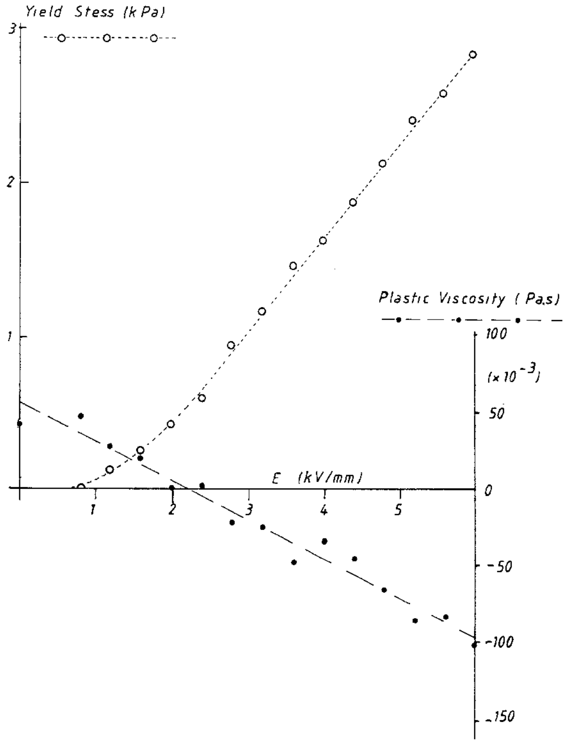

Fig. 6. Dependence of Bingham parameters on field. The sample was 30% (v/v) lithium polymethacrylate suspended in fluorosilicone oil.

fluids. Analyses which do not take this into account, and treat the data by some modification of normal Newtonian viscosity, are physically unrealistic, and likely to be seriously misleading.

The two parameters of the Bingham plastic model, yield stress and plastic viscosity, can be calculated from the experimental data. Figures 5 and 6 show two such plots of these values as a function of the field. Figure 5 represents material made according to the patent of Block *et al.*(8) suspended in chlorinated phenyl tolyl methane; Fig. 6 was obtained from lithium polymethacrylate particles suspended in fluorosilicone. Corresponding values at each field strength were derived from least-squares fits on the original data which were averaged over six scans of the speed range. The values of yield stress could be checked against static measurements: an increasing torque is applied to the cup until shearing occurs. Agreement was good, provided rheopexy was avoided in the static tests. In Fig. 5, the plastic viscosity is approximately equal to the Newtonian no-field viscosity and essentially independent of the field. This behavior is normally assumed rather than observed. Figure 6 shows that this can be misleading: the plastic viscosity falls as the field increases, becoming negative at high fields. This is by no means an isolated instance of such behavior, but the conditions under which it occurs are not yet understood.

6. THE INTERACTION OF CURRENT AND SHEAR STRESS

As rheopexy develops in an ER fluid in a field, the current rises as more contacts are established between the conducting particles in the chains. Conversely, when the chains are broken by shearing the fluid, the current falls. This is commonly observed, but the implications have received very little attention.

Figure 7A represents the field across the working gap of a stationary Couette viscometer. The properties of the ER fluid are constant across the working gap, so the field is uniform. In Fig. 7B, the applied torque has increased slightly so shearing has started immediately adjacent to the inner surface. The current has dropped. However, the ER fluid in the outer layers is still stationary, so the fall in current must be due to an increase in resistance in the inner layers. Since the same current is flowing through both layers, the voltage gradient must be higher in the inner layer than in the outer. The overall voltage is unchanged, so the potential gradient in the inner layers must have increased relative to the static situation, and the gradient in the outer layers must have correspondingly decreased. Since the yield stress increases with the potential gradient, the ER fluid must become stronger in the inner layers and weaker in the outer layers on shearing.

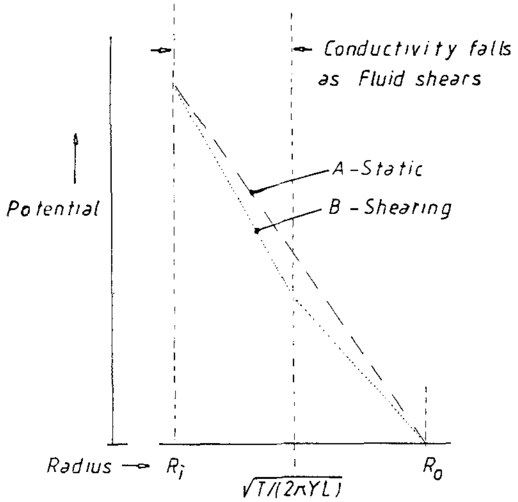

Fig. 7. Interaction of current with shear stress. Line A represents a static test: the ER fluid has uniform properties, leading to a uniform voltage gradient. Line B shows the effect of shearing, which occurs in the most highly stressed region, at the inner surface. The fall in current which is usually observed must therefore be due to a fall in the conductivity of these inner layers. This leads to a corresponding increase in voltage gradient in these layers and an equivalent fall in the outer layers.

Paradoxically, the ER fluid will get stronger where the shear stress is greatest.

This approach, which is based on the most basic observations and calculations, calls into question a basic (if unstated) assumption of conventional rheology, that the properties of the sample are everywhere the same. It is difficult to see how the techniques of conventional rheology can be applied without making this assumption. Resolution of this problem may well require both new techniques and methods of data reduction, but until this has been achieved, flow measurements must be regarded as semi-empirical at best. The apparent simplicity of ER fluids conceals many physicochemical subtleties which may not be completely understood for some time.

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