Rheoelectric Effect in a Polar Liquid Interphase Layer

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The mechanical state of a polar liquid in an electric field is considered. Orientation of molecules by the field and dipole–dipole interactions contribute a retardation shear stress term to the equation governing the flow of the liquid. Expressions are deduced for the retardation stress term, the shear modulus, and the effective viscosity, which are field and deformation rate dependent. The relevant parameters in these equations are evaluated from the experimental data on chloroform of Andrade and Dodd (*Proc. Roy. Soc.* (*London*) **A187**, 296 (1946); **A204**, 449 (1951)). Comparison of experiment with theory shows them to be consistent. The expressions are then extended to the case of a low molecular weight polar liquid in an interphase layer or a dilute electrolyte solution in contact with a solid phase. Since complete rheological experimental data on water are unavailable, extrapolating chloroform parameters to water produces a tentative prediction that the relative viscosity saturates at about 2 kV/cm for deformation rates on the order of 10^3 sec^{-1}.

INTRODUCTION

The question regarding the mechanical state of surface liquid layers and the character of surface viscosity and elasticity has been of interest since the times of Plateau and Marangoni (1), over a hundred years ago. Nevertheless, until now there has been no generally accepted description of the surface layers and the existing views are often contradictory (2, 3). The present authors believe that the cause of these difficulties is that there is no general theory for the case of contact of a liquid with another phase. Since surface rheology may be caused by a number of factors, all of which may lead to mechanical anomalies, it is unlikely that one could formulate a theory which includes all of them.

This work concerns itself with the particular but important case of surface rheology of a low molecular weight liquid. Namely, the mechanical state of the surface and interphase layers of a polar liquid or a dilute electrolyte solution in contact with the solid phase. Specifically, the electroviscous effect in a polar liquid close to the phase boundary and within the diffuse electric double layer will be examined. The results also apply to the case of overlapping electric double layers within interphase layers or in thin capillaries. The authors are aware of only one original work in this area, that of Lyklema and Overbeek (4), which has been reviewed by Haydon (5).

Experimental proof for the existence of an increase in viscosity exists in the works of

Andrade and Dodd (6, 7). These authors studied the change in viscosity of flowing polar liquids in the presence of an external electric field which is perpendicular to the direction of motion. In their work, Lyklema and Overbeek assumed that a liquid within the diffuse electric double layer is subjected to the self-consistent field of the double-layer ions, this field being considered as external with reference to the molecules of the liquid. Following Andrade and Dodd, Lyklema and Overbeek found that the increase in viscosity is due to the change in the activation energy of the molecular dipoles within the electric field. They give an expression for the viscosity, which is

$$\eta(x) = \eta_0(1 + f(d\psi/dx)^2) \qquad [1]$$

where $\eta(x)$ is the viscosity within the double layer a distance x from the solid–liquid interface; η_0 is the bulk viscosity; $\psi(x)$ is the potential distribution within the electric double layer; $-d\psi/dx$ is the electric field, and f is the electroviscosity constant of Lyklema and Overbeek which they calculate to be: $f = 10.2\cdot10^{-12}$ V^{-2} cm^2. This is an order of magnitude higher than that found by Andrade and Dodd. Equation [1] shows that there exists a physical basis for the increase in viscosity and reflects the effect of an electric field on a polar liquid. In this sense, the work of Lyklema and Overbeek is fundamental in the field of surface rheology. However, it is not possible to say that Eq. [1] represents the effect fully, as it does not include dipole–dipole interactions between the oriented dipoles of the polar liquid. As will be shown below, when this interaction is included one finds that a liquid in an electric field acquires non-Newtonian rheological properties and the experimental curves of Andrade and Dodd may be fully characterized.

2. RHEOLOGICAL MODEL OF A POLAR LIQUID IN AN EXTERNAL ELECTRIC FIELD

Consider a polar liquid placed in an arbitrary electric field of intensity E. It is correct to neglect conduction effects when the liquid has a low impurity content as well as when the liquid is in the electric field produced by the ions of the electric double layer. The field orients the dipoles of the liquid and the interaction between the oriented dipoles produces an additional retardation force when the liquid is sheared at a rate $\dot{\gamma}$. It should be noted that Frenkel (8) had earlier indicated that there should be a connection between the rheological state of a polar liquid and visco-elastic phenomena which are related to structural changes. He noted that structuring may be due to molecular orientation as a consequence of which the relaxation times for the structural changes are much longer than for the individual molecule.

The equation governing the flow of a liquid in an electric field may be written

$$\tau = \eta\dot{\gamma} + \theta(E, \dot{\gamma}) \qquad [2]$$

where τ is the shear stress; $\theta(E, \dot{\gamma})$ is the retardation shear stress which is a function of the electric field and deformation rate; and η is the Newtonian viscosity.

The retardation stress $\theta(E, \dot{\gamma})$ will now be deduced. In an electric field, polar molecules acquire a statistical orientational distribution about its direction, which permits one to consider it as a nematic liquid crystal. The usual picture of a nematic liquid is that of a fluid with a one particle orientational distribution function which is axially symmetric. Although several authors have considered this mesophase (9–11), the model assumed is that used in the statistical mechanical treatment of Maier and Saupe (12). The orientational interaction is taken to be of dipole–dipole type. The effective interaction between the molecules is obtained by averaging the energy of two molecules over all directions of the intermolecular vector. This is equivalent to assuming that each molecule is fixed in some average position on a lattice. The result from this treatment is that there exists a temperature below which the molecules tend to orient about some preferred direction. Alternatively, alignment may also be obtained in the presence of an electric field (13).

In the following, it will be assumed that alignment of the molecules in the liquid is produced by an external electric field or the equivalent electric field, considered to be external, which results from the interaction of two electric double layers of ions in the interface. Due to mutual interactions between the oriented molecules, the liquid crystal acquires a shear modulus G_0.

Figure 1 shows a system of neighboring layers of oriented dipoles. The magnitude of the dipoles, P_E, is the time averaged projection of the molecular dipole moment onto the field direction. The interaction energy, U_{ij}, between two statistically oriented dipoles, i and j, in neighboring layers, each having a projection P_E onto the straight line passing through the dipole centers and parallel to the field direction, is given by

$$U_{ij} = -2P_E^2/r_{ij}^3 \qquad [3]$$

where r_{ij} is the distance between the centers of the dipoles being considered. If due to shear there is a small angular displacement γ, the new distance between the dipoles becomes $r_{ij}(\gamma) = r_{ij}/\cos\gamma$ and the projection of the dipole onto this axis is $P_E(\gamma) = P_E \cos\gamma$. The interaction energy between two neighboring dipoles which have shifted through the angle γ may be written as

$$\begin{aligned} U_{ij}(\gamma) &= -2P_E^2(\gamma)/r_{ij}^3(\gamma) \\ &= -2P_E^2 \cos^5(\gamma)/r_{ij}^3. \qquad [4] \end{aligned}$$

When $\cos\gamma$ is developed in a power series in terms of γ and all terms of power greater than two are neglected, the energy may be rewritten

$$U_{ij}(\gamma) = -2P_E^2(1-\gamma^2/2)^5/r_{ij}^3. \qquad [5]$$

Further, applying the binomial expansion to the term in brackets and retaining terms of order two and less

$$U_{ij}(\gamma) = -2P_E^2(1-5\gamma^2/2)/r_{ij}^3. \qquad [6]$$

Since the molecules lie on a lattice, the change in energy between any two corresponding molecules in adjacent layers may be found by use of equations [3] and [6] when the layers undergo a displacement. Thus,

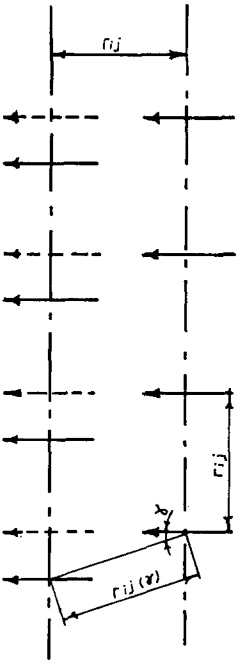

FIG. 1. Relative displacement through the angle γ of two representative neighboring layers.

$$\Delta U_{ij}(\gamma) = U_{ij}(\gamma) - U_{ij} = 5P_E^2\gamma^2/r_{ij}^3. \qquad [7]$$

Given that the number of molecules per unit volume is $n = r_{ij}^{-3}$, the change in potential energy per unit volume is

$$\Delta U = U_{ij}(\gamma)n = 5P_E^2\gamma^2/r_{ij}^6 = 5P_E^2n^2\gamma^2. \qquad [8]$$

From classical theory of elasticity (14), the energy ΔU is also given by

$$\Delta U = G_0\gamma^2/2. \qquad [9]$$

From the last two expressions, the shear modulus in terms of the dipole moment and dipole density is given by

$$G_0 = 10P_E^2/r_{ij}^6 = 10P_E^2n^2. \qquad [10]$$

The equation of state of a polar dielectric from Kirkwood's theory (15) is

$$\frac{(\epsilon-1)(2\epsilon+1)}{9\epsilon} = \frac{4\pi n}{3}\left\{\alpha + \frac{gP_0^2}{3kT}\right\} \qquad [11]$$

and the time averaged projection of the dipole moment on the direction of a field is

$$P_E = (\alpha + gP_0^2/3kT)E \qquad [12]$$

where P_0 is the permanent dipole moment of a molecule of the liquid, α is the polarizability of a molecule, k is Boltzmann's constant, T is the absolute temperature, and g is a constant characteristic of a given liquid which describes the effects of a dipole assembly on a given dipole from it. Its value depends upon the spatial distribution of molecules.

The number of dipoles per unit volume may be obtained from Eq. [11]

$$n = \frac{3}{4\pi}\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon}\left[\alpha + \frac{gP_0^2}{3kT}\right]^{-1}. \qquad [13]$$

Using Eqs. [12] and [13] in Eq. [10], the shear modulus may be expressed as

$$G_0 = \frac{5}{8\pi^2}\frac{(\epsilon - 1)^2(2\epsilon + 1)^2}{9\epsilon^2}E^2. \qquad [14]$$

From crystal theory (16, 17) one obtains a relationship between the yield stress modulus θ_0 and shear stress modulus G_0

$$\theta_0 = G_0/L \qquad [15]$$

where L is a proportionality constant which varies between 10 for an ideal monocrystal to 10^4 when account is made for dislocations within a crystal. Further, it will be shown that using the model under discussion and experimental results from Ref. (6), L is found to lie between these limits.

It should be noted that Eq. [14] was deduced for a lattice of dipoles which has the average distance between dipoles as a lattice parameter. Unlike a solid crystal, in a liquid crystal one should rather look for dynamic elastic behavior of the type that may be represented by Maxwell's rheological model. In such a model, when the load is removed the elastic shear stress relaxes according to

$$\theta(t) = \theta_0 e^{-t/T^*} \qquad [16]$$

where t is current time. T^* is the relaxation time of elastic stresses which for the generalized Maxwell model is given by

$$T^* = \eta/G(T^*). \qquad [17]$$

Expression [17] is a functional equation. Thus, in order to determine T^*, the following physical assumptions are made. Since $G_0(E)$ is the largest value the shear modulus may take on in the presence of a field, then it will always be true that $G(T^*) < G_0(E)$, where the right-hand side of the inequality is given by Eq. [14]. $G_0(E)$ is independent of the deformation rate $\dot{\gamma}$ but the Maxwell relaxation time is not. Thus $G(T^*)$ may be expressed in the following form

$$G(T^*) = G(E, \dot{\gamma}) = G_0(E)G(\dot{\gamma}). \qquad [18]$$

The dimensionless coefficient $G(\dot{\gamma})$ relates the modulus of the ideal crystal model $G_0(E)$ to the modulus of a polar liquid $G(E, \dot{\gamma})$. It is natural to assume that $\lim_{\dot{\gamma}\to 0} G(E, \dot{\gamma}) \to$ minimum of G and $\lim_{\dot{\gamma}\to\infty} G(E, \dot{\gamma}) \to$ maximum of G. This assumption is sufficient to ensure that the shear modulus of a liquid with oriented dipoles will be larger with faster deformation rates. It is also reasonable to assume that for small rates of deformation $G(\dot{\gamma})$ will be a linear function of $\dot{\gamma}$. The simplest function fulfilling all these requirements is

$$G(E, \dot{\gamma}) = G_0B_1(1 - B_2e^{-\beta\dot{\gamma}}) \qquad [19]$$

with $0 < B_1 \leqslant 1$; $0 \leqslant B_2 \leqslant 1$ and $\beta > 0$. For deformation rates such that $\beta\dot{\gamma} < 1$ the exponent may be expanded in a power series and keeping terms to first order only, Eq. [19] may be rewritten as

$$G(E, \dot{\gamma}) = (B_1 - B_1B_2 + \beta B_1B_2\dot{\gamma})G_0. \qquad [20]$$

Letting $K_1 = B_1(1 - B_2)$ and $K_2 = B_1B_2\beta$, Eq. [20] is now written as

$$G(T^*) = G(E, \dot{\gamma}) = G_0(K_1 + K_2\dot{\gamma}). \qquad [20a]$$

Placing this result in Eq. [17] leads to

$$T^* = \eta[G_0(K_1 + K_2\dot{\gamma})]^{-1} \qquad [21]$$

Using Eqs. [16] and [21] one obtains the expression for the relaxation of shear stresses conditioned by the shear modulus $G(E, \dot{\gamma})$

$$\theta(t) = \theta_0 \exp\left[\frac{-tG_0(K_1 + K_2\dot{\gamma})}{\eta}\right]. \quad [22]$$

The shear stress reaches maximum once while the layers are displaced by an amount equal to the lattice constant r_0 along the planes. To find the retardation shear stress $\theta(E, \dot{\gamma})$ in Eq. [2], $\theta(t)$ as given by Eq. [22] must be averaged over the time it takes to displace the layers a distance r_0. This time, the characteristic deformation time will be denoted by T_d and is given by

$$T_d = r_0/\Delta V \quad [23]$$

where ΔV the rate at which the layers are displaced is given by

$$\Delta V = r_0 dV/dx = r_0\dot{\gamma} \quad [24]$$

and x as before is a coordinate perpendicular to the motion of the liquid; $\dot{\gamma} = dV/dx$ for one-dimensional flow (17).

From Eqs. [23] and [24]

$$T_d = \dot{\gamma}^{-1} \quad [25]$$

thus

$$\theta(E, \dot{\gamma}) = \langle\theta(t)\rangle_t = \frac{\eta\dot{\gamma}\theta_0}{G_0[K_1 + K_2\dot{\gamma}]} \times \left[1 - \exp\left(-\frac{(K_1 + K_2\dot{\gamma})G_0}{\eta\dot{\gamma}}\right)\right] \quad [26]$$

where the subscript t denotes that the averaging is performed over values of this variable $(0 \leqslant t \leqslant T_d)$.

Using Eq. [15] and placing Eq. [26] in Eq. [2] gives the following equation of the rheological state

$$\tau = \dot{\gamma}\left\{\eta + \frac{1}{(K_1 + K_2\dot{\gamma})L}\eta \times \left[1 - \exp\left(-\frac{(K_1 + K_2\dot{\gamma})G_0}{\eta\dot{\gamma}}\right)\right]\right\}. \quad [27]$$

The term in brackets is the effective viscosity

$$\eta_{\mathrm{eff}} = \eta\left[1 + \frac{1}{(K_1 + K_2\dot{\gamma})L} \times \left\{1 - \exp\left(-\frac{(K_1 + K_2\dot{\gamma})G_0}{\eta\dot{\gamma}}\right)\right\}\right]. \quad [28]$$

When G_0 given by Eq. [14] is used in Eq. [28] the expression for the effective viscosity becomes

$$\eta_{\mathrm{eff}} = \eta\left[1 + \frac{1}{(K_1 + K_2\dot{\gamma})L} \times \left\{1 - \exp\left(-\frac{(K_1 + K_2\dot{\gamma})AE^2}{\eta\dot{\gamma}}\right)\right\}\right] \quad [29]$$

where

$$A = \frac{5}{8\pi^2}\,\frac{(\epsilon - 1)^2(2\epsilon + 1)^2}{9\epsilon^2}. \quad [29a]$$

Equation [29] may be further simplified if one notes that the Newtonian viscosity η is the increased viscosity η_0 of the liquid in accordance with Eq. [1],

$$\eta_{\mathrm{eff}} = \eta_0[1 + fE^2]\left\{1 + \frac{1}{(K_1 + K_2\dot{\gamma})L} \times \left[1 - \exp\left(-\frac{(K_1 + K_2\dot{\gamma})AE^2}{\eta_0(1 + fE^2)\dot{\gamma}}\right)\right]\right\}. \quad [30]$$

The first factor in brackets

$$J_1 = 1 + fE^2 \quad [30a]$$

is the same term as obtained by Andrade and Dodd and Lyklema and Overbeek for the increase in viscosity due to lowering of the molecular dipole energies in an electric field. The second term in brackets

$$J_2 = 1 + \frac{1}{(K_1 + K_2\dot{\gamma})L} \times \left[1 - \exp\left(-\frac{(K_1 + K_2\dot{\gamma})AE^2}{\eta_0(1 + fE^2)\dot{\gamma}}\right)\right] \quad [30b]$$

accounts for the effect of rheoelectric increase in viscosity of a polar liquid as a result of dipole–dipole interactions between oriented molecules.

3. RHEOLOGICAL INTERPRETATION OF THE EXPERIMENTS OF ANDRADE AND DODD

The results obtained permit the laying of a theoretical foundation for a reinterpretation of the classical experiments of Andrade and Dodd in the field of electroviscosity of polar liquids when they flow in a direction normal to the field. From Eq. [30] it is rather straightforward to obtain an expression for the relative change in viscosity

$$\frac{\Delta\eta}{\eta_0}=\frac{\eta_{\mathrm{eff}}-\eta_0}{\eta_0} =(1+fE^2)\left\{1+\frac{1}{(K_1+K_2\dot{\gamma})L}\times\left[1-\exp\left(-\frac{(K_1+K_2\dot{\gamma})AE^2}{\eta_0(1+fE^2)\dot{\gamma}}\right)\right]\right\}-1. \quad [31]$$

Experiments were done on selected organic polar liquids flowing through a planar capillary in fields whose maximum intensities were in the range 25–30 kV/cm. This gives the value of $fE^2 \approx 0.01$. Since the experimental values of $\Delta\eta/\eta_0$ are in the range of 0.1–1.0 an order of magnitude greater than the previous factor, Eq. [31] may be simplified as follows without introducing any serious errors.

$$\frac{\Delta\eta}{\eta_0}=\frac{1}{(K_1+K_2\dot{\gamma})L}\times\left\{1-\exp\left(-\frac{(K_1+K_2\dot{\gamma})AE^2}{\eta_0\dot{\gamma}}\right)\right\}. \quad [32]$$

When the field intensity is weak such that $(K_1+K_2\dot{\gamma})AE^2 \ll \eta_0\dot{\gamma}$ the exponential may be expanded and the expression for the relative viscosity has a parabolic dependence on the field for a given deformation rate

$$\Delta\eta/\eta_0 = AE^2/L\eta_0\dot{\gamma}. \quad [33]$$

When the field intensity is large, the relative viscosity approaches assymptotically the value of

$$\Delta\eta/\eta_0 = 1/(K_1+K_2\dot{\gamma})L. \quad [34]$$

The behavior at the limits described by the above two equations is typical of the experimental curves for $\Delta\eta/\eta_0 = \Delta\eta_1(E)$ obtained in Ref. (6) for a series of polar liquids in a constant electric field.

Andrade and Dodd studied chloroform in some detail. Experimental data were obtained at constant pressure and in the same range of electric field intensity for different capillary cross sections. This is equivalent to measuring at different deformation rates in order to obtain the rheological behavior [Ref. (6, Fig. 14)].

To use Eq. [32] for describing the behavior $\Delta\eta_1(E)$ for different deformation rates, the constants K_1, K_2, A, and L have to be determined. Taking the dielectric constant of chloroform as $\epsilon = 5$, then $A \approx 0.5$ as determined from Eq. [29a]. The other parameters are determined as follows.

As discussed above, one notes again that $\lim_{E\to\infty} \Delta\eta/\eta_0$ approaches an assymptotic value as determined by the deformation rate $\dot{\gamma}$ (see Eq. [34]). To ensure that this condition is true anywhere within the capillary, one makes the approximation that $\dot{\gamma}$ has everywhere the same value as in the vicinity of the surface. Under these conditions and denoting the limiting value of viscosity by $\eta(\infty)$, then from Eq. [30] it follows that

$$\eta(\infty) = \eta_0\{1+(K_1+K_2\dot{\gamma}_{\max})^{-1}L^{-1}\}.$$

From hydrodynamics the velocity profile within the capillary is

$$v(x) = Px(d-x)/2/\eta(\infty)D \quad [35]$$

where $0 \leqslant x \leqslant 2d$ is a coordinate measured from one of the edges, D is the length of the capillary, P is the pressure difference across the length, $2d$ is the thickness of the capillary.

From this

$$\dot{\gamma}_{\max}(d) = dv/dx|_{x=0} = Pd/D\eta(\infty). \quad [36]$$

Also, the pressure is related to the flux rate by $P = 3QD\eta(\infty)/2zd^3$, where z is the capillary width and thus

$$\dot{\gamma}_{\max}(d) = 3Q/2d^2z. \qquad [37]$$

Using the information from Ref. (6) that $d = 10^{-2}$ cm and $z = 1$ cm then Q = volume of liquid/time of flow = 0.125 cm^3/sec and from Eq. [37] $\dot{\gamma}_{\max}(0.01) = 2000$ sec^{-1}.

Since, from Eq. [36], $\dot{\gamma}_{\max}(d)$ is proportional to the thickness d, then $\dot{\gamma}_{\max}(0.011) = 2200$ sec^{-1} and $\dot{\gamma}_{\max}(0.014) = 2800$ sec^{-1}. Using these two values in Eq. [32] and the viscosity of chloroform $\eta_0 = 0.006$ poise, the solution of the resulting simultaneous equations gives $L = 300$, $K_1 = 1/900$, $K_2 = 1/180\,000$. Note that the calculated value of L lies within the range for crystals as discussed above. One can now use these parameters to obtain a plot of $\Delta\eta/\eta_0$ versus E for various deformation rates. Figure 2 shows these curves. As can be seen, they reproduce quite accurately the experimental results of Andrade and Dodd (6, Fig. 14). The character of the curves of Fig. 3 clearly shows that for small deformation rates there is no region where $\Delta\eta/\eta_0$ = constant, i.e., a region where the liquid retains a Newtonian character. This is in disagreement with the results obtained by Ostwald (18) for isotropic rheologic bodies but does agree with the results he obtains for liquid crystals (19, 20).

The result should be expected. In an electric field, the dipoles of a polar liquid tend to acquire a statistical orientation along the field and the liquid takes on the character of a liquid crystal which was the underlying model assumed.

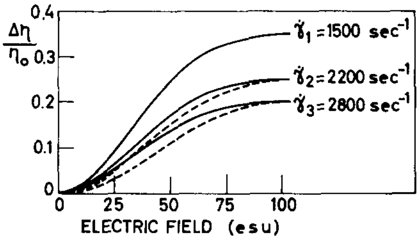

FIG. 2. Relative change in viscosity of chloroform as a function of electric field intensity for selected values of rate of deformation. Full line, predicted values from Eq. [31]; broken lines experimental date of Andrade and Dodd, Ref. (6).

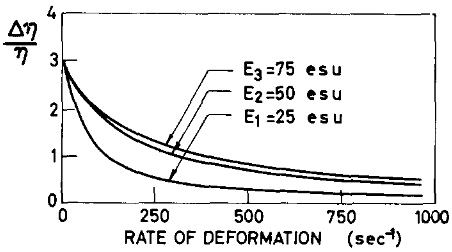

FIG. 3. Relative change in viscosity of chloroform as a function of rate of deformation for select values of electric field intensity.

From Eqs. [32] and [29a] it follows that $\Delta\eta/\eta_0 = \eta_1(E)$ saturates at smaller values of E when the dielectric constant of the liquid is larger. The experiments with acetonitrile confirm this. Thus, comparison with experimental results shows that the semiempirical expression assumed for $G(\dot{\gamma})$, Eq. [19] leads to Eq. [30], a functionally correct form for the effective viscosity.

4. EXTENSION OF RESULTS TO INTERPHASE LAYERS

Unfortunately there is a paucity of experimental data on polar liquids in electric fields or interphase layers which would enable one to determine their rheological properties using the theory presented above. As far as the authors are aware, the only detailed work is that of Andrade and Dodd, and even so the only liquid for which sufficient data was obtained to determine the parameters K_1, K_2, and L is chloroform. Taking the cue from the work of Lyklema and Overbeek where the viscoelectric constant f determined for several organic polar liquids was approximately the same and assumed to be valid for liquid water, the constants K_1, K_2, and L will also be assumed to be applicable for water. Thus, using $\epsilon = 81$, $\eta_0 = 0.01P$ in Eq. [32] one may determine $\Delta\eta/\eta_0 = \eta_1(E)$ and $\Delta\eta/\eta_0 = \eta_2(\dot{\gamma})$, which are displayed in Figs. 4 and 5, respectively. From Fig. 4 it may be readily seen that the relative change in viscosity begins to reach its saturation value at about

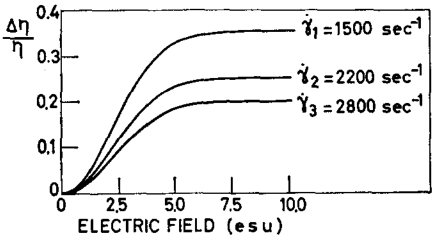

FIG. 4. Relative change in viscosity of water as a function of electric field intensity for selected values of rate of deformation.

$E = 2$ kV/cm, i.e., for field intensity an order of magnitude lower than for chloroform for the same rate of deformation. It should be understood that since there is a lack of detailed experimental data on water this result is tentative.

To consider the rheoelectric effect in an interphase layer or thin capillary where the electric double layers overlap, it is necessary to express E as the equivalent electric field of the diffuse layer of adsorbed ions. In the interphase layer of a plane capillary the potential of the field, from Ref. (21) is given by

$$\psi(x) = \psi_0 \frac{\cosh\left[\chi(x-d)\right]}{\cosh(\chi d)} \qquad [38]$$

where $\psi(x)$ is the potential at the position x measured from one of the capillary walls; $2d$ is the layer thickness; χ is the Debye–Hückel function and a constant for a given polar liquid or electrolyte solution; ψ_0 is the potential at the interface between the two phases. Equation [38] is valid for weak potentials only, i.e., when $\psi_0 \leqslant 25$ mV and it follows from it that

$$E^2 = \left(\frac{d\psi}{dx}\right)^2 = \chi^2\psi_0^2 \frac{\sinh^2 \chi(x-d)}{\cosh^2(\chi d)}. \qquad [39]$$

For the case of a cylindrical capillary of radius a the potential as determined by Elton (22) is

$$\psi(r) = \psi_0\left(\frac{r}{a}\right)^2\left(\frac{16\lambda^2 + r^2}{16\lambda^2 + a^2}\right) \qquad [40]$$

where $\psi(r)$ is the potential inside the capillary at the radius r, $\lambda = \chi^{-1}$ is the Debye radius. Equation [40] is likewise valid only for $\psi_0 \leqslant 25$ mV and when $a\chi \leqslant 1$. The square of the electric field is given by

$$E^2(r) = \left(\frac{d\psi}{dr}\right)^2 = \frac{16\psi_0^2 r^2}{a^4}\left(\frac{8\lambda^2 + r^2}{16\lambda^2 + a^2}\right)^2. \qquad [41]$$

Substitution of Eq. [39] or [41] in Eq. [30] will give the equation for the effective viscosity at a given point x or r of a plane or cylindrical capillary, respectively.

In the case of high surface potentials, large concentration of ions in the electrolyte or large rates of deformation, the factor given by Eq. [30a] may be the same order of magnitude or larger than that given by Eq. [30b]. It should especially be noted that Eq. [30a] does not depend upon the rate of deformation. Its contribution to the resultant effective viscosity is more significant when the rate of deformation increases, all else being held constant. Thus, in the general case of effective viscosity in thin capillaries one cannot admit the simplification made to obtain Eq. [32] from Eq. [30] and [31].

5. CONCLUSIONS

Comparison above of the present theoretical model with the experiments of Andrade and Dodd shows that the rheological behavior of a polar liquid in an electric field is consistent. It is impossible to explain the saturation in the electroviscosity curve as being due to the electrode wall polarization since Ohm's law was strictly valid for all potentials across them.

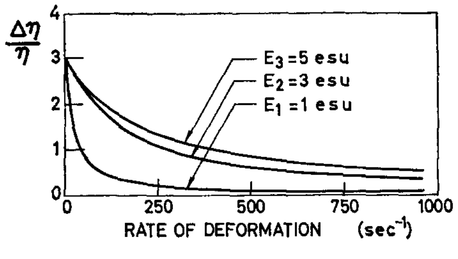

FIG. 5. Relative change in viscosity of water as a function of rate of deformation for selected values of electric field intensity.

Also, the resultant applied field is too weak to orient the molecules fully (4, 23).

Several experimental works confirm the presence of an effect in water flowing in thin capillaries. Henniker (24) studied the retardation of liquid water flowing in capillaries of $0.5 \cdot 10^{-5}$ cm radius and found a strong dependence of the time of flow on the ionic concentration, i.e., on the spatial extent of the ionic atmosphere. He shows that the observed retardation cannot be explained on the basis of the streaming potential deduced by Elton (22) for overlapping ionic atmospheres. Maximal retardation was observed with distilled water, that is when the overlapping double layers occupy most of the capillary space ($\chi \approx 10^5$). The effect almost vanishes with high ionic concentrations of electrolyte, i.e., when the double layers occupy least volume in the capillary. Accordingly, in this case the theory predicts that η_{eff} is almost equal to η_0, the bulk viscosity in most of the capillary, as a consequence of which the observed Poiseuille viscosity is unchanged. The experiments of Henniker were repeated in more detail by Grigorov and Fredericksberg (25). They find the maximum effective Poiseuille viscosity to be about 1.6 times as large as the bulk viscosity when distilled water flows in a capillary of $0.25 \cdot 10^{-5}$ cm. The effect diminishes with increasing capillary radii and practically disappears when the radius reaches $2 \cdot 10^{-5}$ cm. The effect also disappears when the ionic concentration is 0.1 g equiv/l even in capillaries of $0.25 \cdot 10^{-5}$ cm radius. Peschel and Adlfinger (26) in their careful and elaborate experiments find the same order of magnitude as above. Their results also indicate a dependence on shearing rate as described qualitatively by the equations above.

From the preceding analysis of electroviscosity and the work of references (24–26) the cause of the results obtained by Bastow and Bowden (27) becomes clear. These authors attempted to determine anomalies in the viscosity of water flowing in a clearance greater than 10^{-4} cm. For such dimensions the thickness of the electric double layer occupies an insignificant fraction of the volume as a result of which there is no additional resistance to flow.

In order to numerically compare the results of experiment with the present theoretical model, it is necessary to solve a rheological flow problem in which the viscosity is a function of position within the capillary and is given by Eqs. [30] and [39] for a planar capillary or Eqs. [30] and [41] for a cylindrical capillary. The approximation made in Section 3, that the viscosity inside the capillary is approximately constant and the same as the value at the wall is not valid anymore as the field E changes across the cross section of the capillary. The solution of this latter case will be presented in a future publication.

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