ELECTROKINETICS

1. — Electroviscosity and the Flow of Reservoir Fluids

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ABSTRACT

Liquids flowing through narrow capillaries frequently exhibit a viscosity that is higher than normal; usually it is high for low-conductivity liquids but is low for very conductive liquids or concentrated solutions. This effect may have some influence on the flow of oil and water through petroleum reservoirs, although little note has yet been taken of the possibility.

The theory underlying this electroviscous effect is simply developed and some calculations as to its order of magnitude are presented. An equation is given for the electroviscous effect in two-phase flow through a "Yuster" model.

INTRODUCTION

Experimental observations of an increase in the viscosity of a liquid flowing through a narrow capillary have been reported by a number of workers (Reekie and Aird, 1945; Terzaghi, 1931; Macaulay, 1936; Henniker, 1952), and a recent worker has published a theoretical analysis of the origin of such increase in viscosity (Elton, 1948).

The electrical origin of the effect was early recognized. In fact, Smoluchowski (1916) had given an equation for the "electroviscous" effect in suspension flow; Bull (1932) gave a simple derivation of the effect for flow through capillaries; and White, Monaghan, and Urban (1935) discussed the effect of electrical charges on flow through cellophane membranes. More recently, Lorenz (1952), in a sophisticated approach to electrokinetic phenomena, dealt with electroviscosity of liquid flow through both capillaries and porous plugs.

The effect is apparent only for flow through very small capillaries when it is controlled by the charge at the solid-liquid interface (perhaps more correctly the zeta potential), the conductivity of the flowing liquid, and its dielectric constant. We shall see that high interfacial potential and low liquid conductivity are the factors that contribute most to high apparent viscosity.

If an aqueous solution is relatively concentrated its conductivity is high, and even though the solid surface has a high charge, the interfacial or zeta potential nevertheless will be low because the double layer (vide infra) is compressed and there will be no discernable electroviscous effect. If the aqueous solution is dilute, however, conductivity is much lower, zeta potentials generally are high, and a real electroviscous effect may exist. For example, Reekie and Aird (1945) report five to ten times the normal bulk viscosity for water flowing through diaphragms of rouge, French chalk, and carborundum.

In non-aqueous systems we can expect that the conductivity normally will be very low, but, on the other hand, the zeta potentials may also be low although

[1]
there is some evidence that this is not always true (van der Minne and Hermanie, 1953). If the zeta potentials have some reasonable value coupled with very low conductivity, the electroviscous effect may be large.

Of course the flow of reservoir fluids is not generally a matter of simple single-phase flow. But even if oil alone were flowing the effect would be complicated because the mineral surfaces are usually water wet and therefore, the oil would not be in direct contact with the solid surface.

An immobile water film may exist, thick enough and conductive enough to provide a path for the back flow of any current generated, without such current flow affecting the fluid flow of the hydrocarbon. Or it is possible for a water film to be much thicker and to be flowing along with the oil. In either case the problem is further complicated by the fact that there will be set up not only a solid-water potential but also an oil-water potential which must be taken into account in considering the final effect.

In the following discussion some attempt is made to investigate these possibilities and to indicate the order of magnitude of the effects themselves. As the concepts of ε, the streaming potential, and electro-osmosis may be somewhat unfamiliar, a small space is first devoted to a discussion of the origin of surface charge and potential and to simple derivations of the equations for streaming potential and electro-osmosis.

**BASIC PRINCIPLES**

**Surface Charge**

Mineral surfaces in contact with aqueous solutions are almost invariably charged. The most important charging mechanisms are dissociation of ionogenic groups and the preferential adsorption of one ion from the solution (Mukherjee, 1920). The electrical potential resulting from these charges is called the zeta potential.

Inasmuch as Coulomb attraction exists between the charged surface and any oppositely charged ions in the solution, it may seem surprising that the surface remains charged rather than being immediately neutralized by combination with oppositely charged ions from the solution. In order to understand this, it is necessary to consider the forces existing between simple dissolved ions.

Consider the case of two oppositely charged univalent ions, for example, \( \text{Na}^+ \) and \( \text{Cl}^- \) in aqueous solution. The attractive force between them is

\[
F = \frac{e^+ e^-}{D x^2}
\]

where

- \( e^+ \) = electronic charge \( (4.8 \times 10^{-10} \text{ e.s.u.}) \)
- \( D \) = dielectric constant \( (80 \text{ for water}) \)
- \( x \) = distance separating the centers of the ions

However, as is well known, such ions do not coalesce by the operation of such a force because although the Coulomb attraction between unlike ions tends to draw them together, thermal (Brownian) motions tend to distribute them throughout the solution.

Let us compare the thermal energy of simple ions with the energy necessary to separate them. The radii of hydrated \( \text{Na}^+ \) and \( \text{Cl}^- \) ions are 2.5 and 2.0 Å,
So by equation (1)

$$F = \frac{(4.8 \times 10^{-10})^2}{80(4.5 \times 10^{-8})^2} = 1.4 \times 10^{-6} \text{ dyne}$$

To obtain a value for the work necessary to separate these ions we must integrate force times distance from \(x = r\) to \(x = \infty\), that is

$$\text{Work} = \int_{x = r}^{x = \infty} \frac{e^+e^-}{Dx^2} \, dx = \frac{e^+e^-}{Dr} = \frac{(4.8 \times 10^{-10})^2}{80(4.5 \times 10^{-8})} = 6.4 \times 10^{-14} \text{ erg}$$

The thermal energy of a molecule or ion is given by kinetic theory and is

$$\text{Kinetic energy} = \frac{3}{2} kT$$

where

- \(k\) = Boltzmann's constant \((1.37 \times 10^{-16} \text{ erg/molec./deg.})\)
- \(T\) = absolute temperature

Thus at 20°C

$$\text{Kinetic energy} = 6.10 \times 10^{-14} \text{ erg}$$

So we see that in water, the thermal energy of the separated ions and the energy necessary to separate them are very nearly the same. In solvents with dielectric constants smaller than it is in water, the force attracting the ions and the energy necessary to separate them will be much greater, and such ions are not dissociated in solution.

Similar considerations apply to the ions adsorbed on the mineral surfaces and the oppositely charged ions in the solution surrounding the surface.

**Electric Potential**

The work necessary to bring together from infinity two ions of opposite sign has the same magnitude as that necessary to separate them to infinity from their distance of closest approach. It is convenient to define the electric potential as the work required to bring unit charge from infinity to a charged point of like sign, or alternatively, as the work released when a unit charge of unlike sign is brought to this point from infinity.

The potential function is a property of the space surrounding electric charges, every point in space has a potential due to the presence of the ion, and if there are other ions in the space, the total potential at any point is given by the algebraic sum of the individual potentials at that point due to each ion. The work necessary to bring unit charge from infinity to a distance \(r\) from the center of an ion is equal to \(e/Dr\), and this is the potential at a distance \(r\).

**Zeta Potential and Double Layer Thickness**

The charged particle surface attracts water dipoles and is covered by a layer of strongly bound water molecules that become part of the kinetic unit. Trapped among the water molecules are commonly some positive charges that also become part of the kinetic unit and by their presence reduce the net charge on the particle (fig. 1).
When there is relative movement between the particle and the liquid, the plane of shear is at the outermost edge of the solvated layer, and so it is the net charge that is important in electrokinetic phenomena. The zeta potential then is determined by the work necessary to bring unit charge from infinity to the surface of shear.

Surrounding the particle, but relatively distant from it, is an atmosphere of ions in constant thermal movement. The number of positive ions (assuming the particle surface to be negative) in this atmosphere is greater than the number of negative ions, and there are enough positive ions, on a time average, to balance out the net negative charge on the particle. The ions of the ionic atmosphere form the "diffuse double layer." They are not immobilized by the Coulomb attraction of the particle but constantly move in and out between the double layer and the main body of the liquid. It is convenient to consider that the excess positive charges are on a concentric shell at a fixed distance from the particle, the shell is the electrical "center of gravity" of the ion cloud, and the distance from the surface of shear to the shell is the thickness of the double layer.

If a suspended charged particle is subjected to an electric field it moves to one or the other of the electrodes, at the same time the oppositely charged ionic atmosphere tends to move in the opposite direction and consequently to retard the motion of the particle. The distance from the surface of shear to the hypothetical concentric shell of oppositely charged ions is chosen so that if the ions were actually on this shell they would have the same retarding effect as the ion atmosphere. Thus, although we assume that the opposite charges are present only on the surface of the shell, nevertheless we can feel confident that their effect is the same as when they are scattered through the atmosphere.

With this model, a large, non-conducting particle, together with its double layer, constitutes a parallel plate condenser with its plates separated by a distance \( \lambda \), the "thickness" of the double layer. In the next two sections we shall examine (a) the effect on zeta of varying the distance of separation of two such plates (at a fixed surface charge density), and (b) the effect of concentration and type of electrolyte in solution, on the double layer thickness. The two taken together show the effect of concentration on zeta at constant surface charge density.

**Effect of Double Layer Thickness on the Zeta Potential**

Consider a particle of radius \( r \) and charge \( Q \) surrounded by a concentric shell of radius \( r + \lambda \) and charge \(-Q\) (fig. 2).

![Fig. 1. - A charged spherical particle and its bound water molecules.](image)
The potential at the surface of the sphere is \( \frac{Q}{Dr} \), this being the work necessary to bring unit charge of like sign from infinity to a distance \( r \) from the center of the sphere. The resultant potential of a condenser consisting of two such concentric spheres is the algebraic sum of the potentials due to the inner sphere at its surface and the outer sphere at the surface of the inner sphere.

The potential on the surface of the inner sphere in the absence of the outer sphere would be \( \frac{Q}{Dr} \); the potential due to the outer sphere at any point inside it is \(-\frac{Q}{D(r + \lambda)}\); therefore,

\[
\zeta = \frac{Q}{Dr} - \frac{Q}{D(r + \lambda)} = \frac{Q}{Dr} \cdot \frac{\lambda}{r + \lambda}
\]

and since \( \lambda << r \)

\[
\zeta = Q\frac{\lambda}{Dr^2}
\]

If the surface charge density is \( \sigma \), then \( Q = 4\pi r^2 \sigma \) and

\[
\zeta = 4\pi \sigma \lambda / D
\]  

(2)

Although the latter equation has been obtained by considering a spherical particle, it is generally applicable and the potential difference between two parallel plates of surface charge density \( \sigma \) when separated by a distance \( \lambda \) in a medium of dielectric constant \( D \) is also given by equation (2).

Effect of Concentration on Double Layer Thickness

As we have seen, the double layer is actually diffuse, and the ions forming it are not fixed at any one distance away from the particle surface, but form an atmosphere around it. There is competition between the thermal Brownian movements tending to distribute the ions evenly throughout the solution and the attractive forces of the charged surface drawing unlike ions to it. Like ions tend to be driven away from the surface by repulsive forces, and a large negatively charged particle will have more positive than negative ions near its surface; nevertheless, in an element of volume remote from the surface, the number of positive and negative ions will be equal.

If the resultant potential due to the charged surface and the ionic atmosphere is \( \psi \), energy equal to \( e\psi \) is released when a positive ion is brought up from the main body of the solution to a point of potential \( \psi \), and an amount of energy equal to \(-e\psi \) is required to bring a negative ion to the same point.

When equilibrium is established, by Boltzmann's principle the number of negative ions \( (n_-) \) per unit volume is

\[
n_- = ne^{-e\psi/kT}
\]

where \( n \) is the total number of ions per cc. in the bulk solution. Similarly the number of positive ions \( (n_+) \) is

\[
n_+ = ne^{+e\psi/kT}
\]
The charge density \( \rho \) in unit volume of potential \( \psi \), is

\[
\rho = (n_+ - n_-)e = (e^{-\psi/kT} - e + e\psi/kT) ne = -2ne\sinh e\psi/kT
\]

and if the potential is small so that \( e\psi/kT << 1 \), \( \sinh e\psi/kT \) can be replaced by \( e\psi/kT \), and so

\[
\rho = -2ne^2\psi/kT \quad (3)
\]

Poisson’s equation states that in every point of the space charge

\[
\nabla^2 \psi = -4\pi \rho/D \quad (4)
\]

\( (\nabla^2 = \text{Laplace operator} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} ) \)

Combining equations (3) and (4) we get

\[
\nabla^2 \psi = 8\pi ne^2/DkT \cdot \psi \quad (5)
\]

The expression \( \sqrt{\frac{DkT}{8\pi ne^2}} \) has the dimensions of a length and is set equal to \( 1/\kappa \) and can be shown (see appendix) to be equal to \( \lambda \).

For the general case of multivalent ions

\[
1/\kappa = \sqrt{\frac{1000D\text{RT}}{8e^2N^2\mu}}
\]

where

- \( e \) = electronic charge
- \( N \) = Avogadro’s number
- \( \mu \) = ionic strength = \( 1/2 \sum c_iz_i^2 \)
- \( D \) = dielectric constant
- \( c_1 \) = conc. of ion \( i \) (mols/litre)
- \( z_i \) = valence of ion \( i \)

At \( 25^\circ \text{C} \) in water

\[
\kappa = 0.327 \times 10^8 \sqrt{\mu}
\]

Figure 3 shows double-layer thickness plotted against normality for sodium chloride and calcium chloride solutions.
FLOW OF RESERVOIR FLUIDS

STREAMING POTENTIAL

When liquid is forced through a capillary tube, a potential difference (the streaming potential) may be produced between its ends.

Consider a tube of radius $a$ and length $l$ through which a liquid is caused to flow by a pressure difference $P$. The force causing the liquid to flow is $\pi a^2 P$ in the direction of flow. Let the velocity of the liquid at a distance $r$ from the axis be $v$; the velocity gradient will be $dv/dr$ so that the viscous force tending to retard the flow is $\eta \cdot dv/dr \cdot 2\pi a l$.

At equilibrium these two forces are equal so that

$$\pi a^2 P = -\eta \cdot dv/dr \cdot 2\pi a l$$

Assume that the capillary wall is charged and that this surface charge has associated with it a double layer of thickness $\lambda$, very small in comparison with the radius of the capillary. The velocity of liquid within the double layer varies linearly with the distance $x$ from the wall and is zero at $x = 0$; $dv/dx = -dv/dr$ can be replaced by $v/\lambda$, hence

$$\pi a^2 P = +\eta \cdot v/\lambda \cdot 2\pi a l \quad \text{or} \quad v = +\lambda P a/2 l \eta$$

Inasmuch as the surface charge density is $\sigma / \text{cm}^2$, the current of convection $I_o$ is

$$I_o = 2\pi a \cdot \sigma \cdot v = \pi a^2 P \lambda \sigma / \eta \lambda$$

This movement of charge is opposed by the streaming potential difference ($E$) between the ends of the capillary. The amount of charge carried back through the area $\pi a^2$ by the liquid of conductivity $K$ is

$$I_S = K \pi a^2 E/l$$

At equilibrium

$$I_o = I_S$$

and therefore

$$E/P = \lambda \sigma / K \eta$$

Inasmuch as

$$\sigma = D \zeta / 4 \pi \lambda$$

therefore

$$E = D \zeta P / 4 \pi K \eta$$

In practical units, with water of viscosity 0.01 poise,

$$E = \frac{\zeta D}{K} \frac{13.6 \times 981 \times 80 \times 300}{300 \times 9 \times 10^{11} \times 4 \times 3.14 \times 0.01} \quad \text{volts}$$

ELECTRO-OSMOSIS

Capillary

We have seen that fluid forced through a capillary tube gives rise to a streaming potential. Conversely, if a potential difference is applied across the tube it will give rise to an electro-osmotic flow of the fluid. A simple derivation of the velocity of electro-osmosis flow follows (Perrin, 1904; Butler, 1940).
Assume that the charge density of the double layer, which is free to move, is $\sigma$ and that it is distant $\lambda$ from the surface. If the applied potential difference has a strength $E$/unit length, an electrical force $E\sigma$ is imposed on the charge.

The frictional force retarding flow is $\eta v/\lambda$ and at equilibrium

$$E\sigma = \eta v/\lambda$$

and so

$$v = E\sigma\lambda/\eta$$

and if

$$\sigma = D\zeta/4\pi\lambda$$

therefore

$$v = ED\zeta/4\pi\eta$$

(7)

If the counter pressure ($P$) developed by the electro-osmotic displacement is measured, then this is determined for a single capillary of unit length by Poiseuille's law

$$\text{Vol} = \frac{\pi Pr^4}{8\eta} = \pi r^2 \times ED\zeta/4\pi\eta$$

or

$$P = 2DE\zeta/4\pi r^2$$

(7a)

Equation (7) can be expressed differently by the following substitutions

$$E = \frac{i}{\pi r^2K}, \quad V = \pi r^2v$$

Therefore

$$V = \pi r^2v = D\zeta/4\pi\eta \times i/K$$

(8)

Porous Plug

Smoluchowski (1903) showed that equation (8) is applicable to flow through porous plugs. Then, if the measured cell constant of the plug is $C$ with a solution of conductivity $K$

$$i = KE/C$$

and so it follows that

$$V = D\zeta/4\pi\eta \times E/C$$

(9)

In order to express this in terms of an electro-osmotic pressure we must equate it to Darcy's equation rather than to Poiseuille's. Thus

$$V = Pr/A/\eta1 = D\zeta/4\pi\eta \times E/C$$

so that

$$P = D\zeta E/4\pi k \times L/AC$$

(9a)

where $k$ = permeability and $A$ = area of the plug.
ELECTROVISCOUS EFFECT

Capillary Flow

Consider, as before, a narrow tube with a relatively high surface charge through which a liquid is flowing. A pressure drop, \( P \), applied across the ends of the tube causes the fluid flow. The flow gives rise to a streaming potential, \( E \), as shown above, and the potential difference in turn gives rise to a back electro-osmotic pressure, \( P_1 \).

Because of the back pressure, the pressure actually causing flow, \( P_2 \), is less than the applied pressure, \( P \), by the back electro-endosmotic pressure \( P_1 \) (fig. 4), that is,

\[
P_2 = P - P_1
\]

To determine viscosity by the Poiseuille equation, the volume rate of flow through a tube is measured at some known pressure drop. For a narrow capillary this measurement gives a value for the viscosity which is greater than the true value because the magnitude of the pressure drop used in the equation is greater than that causing the flow. Thus

\[
\eta_a = \frac{P_2 r^2}{8l

\text{The true viscosity of the liquid is given by}
\[
\eta = \frac{P_2 r^2}{8l

\text{where} \; \eta_a = \text{apparent viscosity} \; \text{and} \; \eta = \text{true viscosity, because the pressure} \; P_2 \; \text{(less than} \; P) \; \text{is that which is actually instrumental in causing the fluid flow.}\n
\text{The streaming potential caused by the flowing liquid has a value of}
\[
E = \frac{P_2 D \xi}{4\pi \eta K}
\]

so that

\[
P_2 = \frac{4\pi \eta K E}{D \xi}
\]

This streaming potential causes an electro-osmotic back pressure of magnitude \( P_1 \) where

\[
P_1 = 2D \xi E/\pi a^2
\]

Thus, because

\[
P = P_1 + P_2
\]

\[
P = 4\pi \eta K E/\pi a^2 + 2D \xi E/\pi a^2
\]

From equations (10) and (11)

\[
\frac{\eta_a}{\eta} = \frac{P}{P_2}
\]

and so

\[
\frac{\eta_a}{\eta} = 1 + \frac{P_2}{P} \frac{\xi^2}{2\pi a^2 \eta K}
\]

Figure 5, which is a plot of \( \xi \) in millivolts against \((\eta_a - \eta)K\), shows how the zeta potential, conductivity, and tube radius affect apparent viscosity in aqueous solutions.
For example, with $\zeta = 50$ millivolts and $a = 0.8 \times 10^{-5}$, $(\eta_a - \eta)K = 0.156 \times 10^{-6}$. Therefore, if $K = 1 \times 10^{-6}$, $\eta_a - \eta = 0.156$ or $\eta_a = \eta + 0.156$. If $a = 0.2 \times 10^{-4}$, $(\eta_a - \eta)K = 0.025 \times 10^{-6}$, $\eta_a - \eta = 0.025$ or $\eta_a = \eta + 0.025$.

Flow Through Porous Plugs

We can apply similar reasoning to the flow of a liquid through a porous plug; the streaming potential has the same value as before and so also therefore has $P_2$. The electro-osmotic back pressure, $(P_1)$, is now given by equation (9a) and so

$$P = P_2 + P_1 = 4\pi \eta KE/D_\zeta^2 + D_\zeta E/4\pi k \times L/AC$$

As before

$$\eta_a/\eta = P/P_2$$

and so

$$\eta_a/\eta = 1 + D^2_\zeta^2/16\pi^2 k\eta K \times 1/F$$

(13)

where $F = AC/L$ = Formation factor, that is, the ratio of the resistivity of a rock saturated with electrolyte solution to the resistivity of the electrolyte solution.

In the case of a porous plug it is perhaps more useful to consider the equation in terms of permeability reduction rather than of viscosity increase, if we put

$$k = \eta LV/P_2 A \quad \text{and} \quad k_a = \eta LV/PA$$

where $k$ and $k_a$ are true and apparent permeabilities, respectively. Then $k/k_a = P/P_2$ and

$$k/k_a = 1 + D^2_\zeta^2/16\pi^2 k\eta K \times 1/F$$

(14)
or the fractional decrease in permeability is given by

\[
\frac{k - k_a}{k} = \frac{D^2 \zeta^2}{16\pi^2 k\eta K F + D^2 \zeta^2}
\]

(15)

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<thead>
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<th>$D$</th>
<th>$k$</th>
<th>$F$</th>
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<td>2</td>
<td>$10^{-12}$</td>
<td>0.01</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Table 1 gives percentage reduction in permeability calculated by equation (15) for selected core permeabilities; the $k$ values are in darcies, $F$ is the formation factor, and each core is assumed to give a zeta potential of 100 mV in water and 5 mV in an oil of dielectric constant 2.

**EFFECT OF CONDUCTING FILM**

Mineral surfaces are more frequently water wet than oil wet, and so it is interesting to investigate the effect of a thin wetting film on electroviscosity. Reconsider the derivation of the electroviscosity equation; it is apparent that the magnitude of the streaming potential is dependent on the conductivity of the flowing liquid so that for the same zetas the streaming potential is low if conductance is high, and the streaming potential is high if the conductivity is low.

The streaming potential of a low-conductance liquid (for example, benzene) through a water-wet capillary is less than that expected in the absence of the water film because the streaming potential is determined by the apparent conductivity of the tube, that is, the conductivity due to the contribution of both liquids.

Consider such a tube of radius $R$ with a water film of thickness $\delta = R - r$.

Let

- $K_1 =$ conductivity of water
- $K_2 =$ conductivity of oil
- $K_3 =$ conductivity (apparent) of liquids in capillary

For a section of the tube of length $L$,

- Cell constant of water-filled part = $L/\pi(r^2 - r^2)$
- Cell constant of oil-filled part = $L/r^2$
- Cell constant of whole tube = $L/\pi R^2$

Then, if

Measured resistance of water section = $\rho_1$
Measured resistance of oil section = $\rho_2$
Measured resistance of whole tube = $\rho_3$
Fig. 6. — Effect of water saturation on apparent viscosity of oil flowing through a 1-micron capillary.

\[ \frac{1}{\rho_3} = \frac{1}{\rho_1} + \frac{1}{\rho_2} \]

and because

\[ \frac{1}{\rho_1} = \pi (R^2 - r^2) K_1 / L; \]
\[ \frac{1}{\rho_2} = \pi r^2 K_2 / L; \]
\[ \frac{1}{\rho_3} = \pi R^2 K_3 / L \]

therefore

\[ K_3 = \frac{r^2}{R^2} \cdot K_2 + \frac{(R^2 - r^2)}{R} \cdot K_1 \]

Now water saturation, \( S_w = \pi (R^2 - r^2) L / \pi R^2 L = (R^2 - r^2) / R^2 \)

and so

\[ K_3 = (1 - S_w) K_2 + S_w K_1 \]

In terms of thickness of the water layer

\[ K_3 = K_2 - 2\delta / R \cdot (K_2 - K_1) \]

and if \( K_2 \ll K_1 \)

\[ K_3 \approx \frac{2\delta}{R} K_1 \]

or

\[ K_3 \approx S_w K_1 \]

Figure 6 is a plot of \( \eta_a / \eta \) against \( S_w \) showing the rapid decrease of \( \eta_a \) as the wetting phase saturation increases. The tube considered has a radius of \( 0.5 \times 10^{-4} \) cm and exhibits a zeta potential of 30 mv when filled with a hydrocarbon of \( D = 2, K_2 = 10^{-12}, K_1 = 10^{-6} \).

**TWO-PHASE FLOW**

In considering flow of two phases through a capillary tube we will take the model used by Yuster (1951) of "a single capillary with the non-wetting phase flowing in a cylindrical portion of the capillary and concentric with it. The wetting phase will flow in the annulus between the capillary wall and the non-wetting phase."
Assuming that both the capillary surface and the oil surface are negatively charged, the charges at both surfaces are balanced by double layer charges carried in the solution in a Helmholtz double layer at a distance $\lambda$ from the surfaces. As the ionic concentration in the aqueous phase in contact with both solid and oil is identical, $\lambda$ is the same for both surfaces.

By first deriving an equation for streaming potential, then for electro-osmosis, and combining them as was done above, (Street, to be published) it is possible to obtain expressions for the apparent viscosities in both the oil and the water phases. These expressions are

$$\frac{\eta_{aw}}{\eta_w} = 1 + \frac{D^2 (\zeta_1 + S_o \frac{1}{2} \zeta_2) \left\{ \zeta_1 - S_o \left[ 1 + \frac{R \eta_w}{4 \lambda \eta_o} S_o \frac{1}{2} \right] \right\}}{2 \pi^2 R^2 \eta_w K Z}$$

$$Z = (1 + S_o \frac{1}{2}) \left( 1 + S_o - \frac{S_w}{\ln S_o ^{\frac{1}{2}}} \right)$$

$$\frac{\eta_{ao}}{\eta_o} = 1 - \frac{D^2 \zeta_2 \left\{ \zeta_1 - S_o \left[ 1 + \frac{R \eta_w}{4 \lambda \eta_o} S_o \frac{1}{2} \right] \right\}}{8 \pi^2 R \lambda \eta_w K S_w}$$

where $\zeta_1$ and $\zeta_2$ are the zeta potentials at the mineral and oil surfaces, respectively; $K$ is the conductivity of the aqueous phase; $\eta$ is the viscosity of the aqueous phase; and $\eta_o$ that of the oil phase.

There are several points to be considered in the use of these expressions. First it is assumed that $\lambda$ is small in relation to $R-r$, that is, the two double layers in the water must not overlap. In fact, the double layers will affect each other even at quite large distances of separation. In the simple case of two equal potentials, $\psi_o$, separated by a distance $2h$, Elton and Hirschler (1949) show that

$$\psi_m = \frac{\psi_o}{\cosh h/\lambda}$$

where $\psi_m$ is the potential at a distance $h$ from either surface.

The oil phase will have a dielectric constant much less than the aqueous phase, most likely of the order of 2 rather than 80, and this affects the development of potential, the thickness of $\lambda$, and the concentration of dissolved substance in the oil phase (Verwey and Overbeek, 1948).

It is perhaps easier to see the effect on $\lambda$ using the approach of Klinkenberg and van der Minne (1958) who show that

$$\lambda = \sqrt{\Delta_m \frac{DE_o}{K}}$$

where $E_o$ = absolute dielectric constant of vacuum
$\Delta_m$ = coefficient of molecular diffusion

Since $\Delta_m$ is approximately the same value for both water and a hydrocarbon, then

$$\frac{\lambda_o}{\lambda_w} = \sqrt{\frac{2 \text{ Kw}}{80 \text{ Ko}}} \approx 1000 - 100,000$$
Thus the double layer thickness developed in the hydrocarbon phase is much greater than that developed in the aqueous phase. The electroviscous effect is apparent only when the capillary radius is small (1 x 10^{-4} cm or less) so normally the double layer thickness in the oil phase would be greater than its radius. Under these conditions we can assume a homogeneous distribution of charge throughout this phase and use Rutgers, de Smet, and de Moyer’s expression (1957) in calculating the contribution of this phase to the total streaming potential.

These considerations have been borne in mind in the development of equations (16) and (17), and these expressions should not be used when R-r approaches λ and certainly not if R-r < λ. In terms of water saturation we can say that the definite lower limit of applicability is

\[ S_w = 2λ/R \]

Because the movement of the two liquids through a capillary moves positive charges in the water phase and negative charges in the oil phase, the magnitude and sign of the streaming potential set up depends on the relative sizes of these charges, their sign, the viscosity ratios of the liquids, and their saturation in the tube, that is, on \( \zeta_1, \zeta_2, \eta, \eta_0 \), and \( S_w \). Since both positive and negative charges are transported it is possible for the streaming potential to be either positive or negative downstream, and the effect on liquid viscosity may be either to increase it or to decrease it.

It is perhaps appropriate to point out that \( \zeta_2 \) is the zeta potential measured in the water phase against the oil-water interface.

**DISCUSSION**

It has been shown in the foregoing that viscosity will be increased when an interfacial charge exists, but the increase will be unimportant unless the charge is high, the liquid conductivity low, and the flow channel narrow.

Although it could be expected that hydrocarbons would show a large effect because of their low conductivity, this need not necessarily follow because thin conducting films in narrow pores will increase the apparent conductivity so as to considerably reduce the back pressure.

When both water and oil flow through a capillary the interaction of the various factors may cause the apparent viscosity of either phase to be less than the bulk viscosity instead of greater. Normally the high ionic concentration of an oil-field brine will reduce \( \lambda \) so as to give such low zeta potentials at both interfaces that the effect will be negligible. It is possible, however, that the effect could be significant in a fresh-water flood or, more important, that electrolytes could be added to the flood water to alter \( \zeta_1 \) and \( \zeta_2 \) so as to give maximum recovery.

In the laboratory, core experiments are frequently conducted with both fresh water and brine in order to determine their relative effects; any low permeability to fresh water is ascribed to the presence of swelling clays. While admitting that this is a potent factor in permeability reduction, it is also possible, especially in relative permeability experiments, that the electroviscous effect is also operating. The presence of clays will in itself tend to increase the zeta at the water-mineral interface (Street and Buchanan, 1956) and this may increase the viscosity even though the clays are of the non-swelling variety.

If the predictions can be borne out experimentally, then we would expect to find a dependence of relative permeability on ionic concentration in the aqueous phase during the flow of oil and water through low permeability cores.
At constant surface charge density, increase of ionic concentration decreases the zeta potential so that very little charge transport occurs in the water phase; however, the balancing negative charges in the oil phase will still be carried with the stream, and the tendency at higher concentrations should be for the oil phase viscosity to increase while that of the water phase stays relatively constant. However, if the ionic concentration or $S_w$ increases beyond a certain point, back flow of current through the solution annulus will cause the effect on the oil phase to become negligible also.

It is hoped to initiate laboratory tests in the near future with the object of correlating measured zeta potentials at oil-water and mineral-water surfaces with apparent viscosities of the flowing oil and water phases.

APPENDIX

The identity of $1/\kappa$ with the double layer thickness is by no means obvious and although an understanding of it is not essential to the solution of the problems involved here, nevertheless it would seem more complete to include it. The following is modeled closely on the treatment given by Abramson, Moyer, and Gorin (1942).

Let equation (5) be written as

$$\nabla^2 \psi = \kappa^2 \psi$$

Because for a flat surface, or one of large radius of curvature, the potential $\psi$ depends only on the distance $x$ from the surface, equation (5a) becomes

$$\frac{d^2 \psi}{dx^2} = \kappa^2 \psi$$

and a general solution of equation (5b) is

$$\psi = Ae^{-\kappa x} + Be^{+\kappa x}$$

and because $\psi = 0$ when $x \to \infty$ and $\psi = \zeta$ when $x = 0$, $B = 0$ and $A = \zeta$, so

$$\psi = \zeta e^{-\kappa x}$$

Because at any point the potential is the algebraic sum of that due to the charges on the particle surface and those in the double layer, and if $\psi^1$ is the potential due to the double layer charges, hence

$$\psi = \frac{Q}{Dr} + \psi^1$$

Then

$$\left( \frac{d \psi}{dx} \right)_{x=r} = - \frac{Q}{Dr^2} + \frac{d \psi^1}{dr}$$
and because anywhere inside the sphere and at its surface $\psi'$ is constant, thus

$$\frac{d\psi}{dr} = 0$$

and so

$$\left( \frac{d\psi}{dx} \right)_{x=r} = -\frac{Q}{Dr^2}$$

and because $Q = 4\pi r^2 \sigma$,

$$\left( \frac{d\psi}{dx} \right)_{x=r} = -4\pi \sigma/D$$

which for a particle of any shape has the general form

$$\left( \frac{d\psi}{dx} \right)_{x=0} = -4\pi \sigma/D$$

(5f)

Differentiation of equation (5d) gives

$$\frac{d^2\psi}{dx^2} = -\kappa \, \zeta e^{-\kappa x}$$

and substitution into equation (5f) at $x=0$ gives

$$\frac{d\psi}{dx} = -\kappa \, \zeta = -4\pi \sigma/D$$

therefore

$$\zeta = \frac{4\pi \sigma}{D\kappa}$$

(5g)

Comparison of equations (2) and (5g) shows that $\lambda = 1/\kappa$. It should also be noted that at any distance $x$ from the surface, the potential $\psi$ is given by

$$\psi = \frac{4\pi \sigma}{D\kappa} \, e^{-\kappa x}$$
FLOW OF RESERVOIR FLuids

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