ELECTROSTATIC CHARGE GENERATION
IN
HYDROCARBON LIQUIDS

by

PETER MICHAEL HIRSCH

B.S. Cornell University
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SUBMITTED IN PARTIAL FULFILLMENT
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Submitted to the Department of Chemical Engineering in August, 1979 in partial fulfillment of the requirements for the Degree of Master of Science

ABSTRACT

A concentric cylinder flow device was developed to study the electrostatic charging phenomenon observed with hydrocarbon liquids. The charging potential was measured as a function of the speed of rotation of the inner cylinder, the width of the annulus, and the electrical conductivity of the hydrocarbon. The conductivity was varied by doping with calcium dodecyl sulfosuccinate, a constituent of Shell Anti-Static Additive. The charging potential was found to depend on the product of the rotation speed and gap width, divided by the square root of the conductivity. These observations were compatible with dimensional arguments derived for the system, when combined with theoretical considerations of the electric double layer structure. The experimental method also enabled an order of magnitude approximation of the surface charge density of the double layer to be calculated. The liquid capacitance method, utilized for measurements of conductivity, was found to be complicated by polarization effects.

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I. Summary

The generation of electrostatic charge as a result of the flow of low conductivity liquids during transport operations, has long posed a hazard to industrial and commercial enterprises. The electrification phenomenon observed with flow through pipelines has been extensively studied both experimentally and theoretically by numerous investigators over the past 65 years. Unfortunately no completely satisfactory model has been developed to explain the charging process. The presently accepted formulations are not convincing in their interpretation of the charge flux at the solid-liquid interface. The postulated existence of an electrochemical oxidation-reduction reaction at the pipe wall seems to be an unreasonable assumption given what little is known about the reacting species.

Based on the hope of gaining further insight into the mechanism of the charging process, a novel method was developed to study the electrification of hydrocarbon liquids. The apparatus was similar to one used for studying electrochemical systems and resembled a coaxial cylinder viscometer in design. The electrically grounded, inner metal cylinder (bob) was rotated within an electrically insulated metal cup. The hydrocarbon liquid was contained in the annulus. The induced charge was measured as the electric potential difference across a capacitor attached to the cup wall.

The charging potential was measured as a function of the bob speed, the width of the annulus (gap width), and the electrical conductivity of the hydrocarbon liquid. Potentials in the range of ~0.1 to 100
volts were obtained. As one of the experiments, the conductivity of toluene was varied by doping with calcium dodecyl sulfosuccinate, a constituent of Shell Anti-Static Additive. The liquid capacitance method was utilized for measurements of conductivity. Although the measured conductivities agreed well with those reported in the literature, this method was found to be complicated by polarization effects.

The charging potential was found to depend on the product of the bob speed and gap width, divided by the square root of the conductivity. These observations were compatible with dimensional arguments derived for the system when combined with theoretical considerations of the electric double layer structure.

There has been no technique reported in the literature for independently measuring the surface charge density of the electric double layer in hydrocarbon solutions. The flow apparatus, however, enabled an order of magnitude estimate to be calculated from the "double-layer potential" observed at steady-state with the quiescent system. The identity of the charge carriers (i.e. electrons, ions, or both) and the mechanism by which they are generated and transported through the hydrocarbon solution have not been elucidated by this experimental work.
II. Electrification in Pipe Flow

A. Introduction

The possibility of generating substantial static charges in liquids of low electrical conductivity in well-grounded equipment, especially as a consequence of the flow of hydrocarbons through pipes, has long been a problem in the petroleum industry. For example, in early 1954 a large tank in Shell's refinery at Pernis in the Netherlands exploded 40 minutes after the start of a blending operation in which a top-naptha mixture was being pumped into straight run naptha. On the following day a second attempt was made to blend these materials and again an explosion occurred 40 minutes after the start of the pumping (Klinkenberg and van der Minne, 1958). Since then many more explosions similar to the above have occurred. During the last month of 1969, there were three separate incidents in which explosions occurred during the cleaning of supertankers, each of which had just discharged its crude oil cargo. All were extremely damaged and one sank (The Motor Ship, 1976). The disastrous explosions in "Mactra", "Marpessa", and "Kong Maakin VII" focussed the maritime world's attention on the dangers of washing cargo tanks during ballast voyages and prompted extensive studies into the possible causes of such grave accidents. But tanker explosions continue--the explosions on the "Kriti Sun" in Singapore in 1975 and the loss of the "Berge Istra" in 1976 have continued to focus attention on this vital problem (The Motor Ship, 1976).

Three criteria enter into the analysis of electrostatic hazards for any fluid. One involves the ability of the fluid to generate and retain a charge; the second involves the degree of charge build up necessary to
produce a spark of sufficient energy for ignition; while the last involves the flammability (or detonability) of the fuel-oxidant mixtures ignited by the spark. An electric discharge is characterized by the movement of ions and electrons between two regions differing in electric potential. The electrons and ions being accelerated in this electrostatic field transfer energy to other molecules upon their collision. As a result of this dissipation of energy, other active molecular fragments are created and the temperature increases. If sufficient energy is released in this process, ignition of a flammable mixture will result (Klinkenberg and van der Minne, 1958).

Static or friction electricity is produced whenever there is relative motion between two dissimilar phases or materials. If one or both of these phases is a good insulator, the separated charges may produce a high electric field strength. Electrostatic phenomena have been observed to occur for gas-liquid, liquid-liquid, and solid-liquid systems. The study of the various electrical phenomena which occur when a fluid flows past a solid surface forms the subject of electrokinetics. The electrokinetic phenomena for the pipeline flow of a liquid with a relatively high conductivity are comparatively well understood. In the last 20 years, progress has been made in the understanding of the electrokinetic phenomena for a low conductivity liquid in pipeline flow.

Experiments with petroleum products have shown that upon removal of all impurities (i.e. no molecules are present besides those of the hydrocarbon itself), electrification phenomena do not exist. This can be explained by the fact that certain trace impurities present in the hydrocarbon are the cause of the electrostatic effect. These materials may be
oxidation products, asphaltenes, metal salts of naphthenic and sulfonic acids, and other products resulting from certain treating operations. These compounds may either occur naturally or be formed during the manufacturing process.

Not only the charging effect, but also the electrical conductivity of a hydrocarbon is due to the presence of polar impurities. Although all hydrocarbons have a "natural conductivity" attributable to electron transfer processes, this conductivity is unimportant when superimposed upon that related to the presence of ionic impurities.

The actual mechanism of the charging phenomena is still unclear, but the unequal adsorption mechanism of dissociable impurities appears to have been generally accepted. According to this mechanism, at the interface between a liquid and any other material, whether it be solid (e.g., a liquid in a container), liquid (e.g., two immiscible liquids in contact) or gaseous (e.g., the air space above a liquid), there is a tendency for positive or negative ions, which normally exist together in a state of equilibrium, to separate. The ions of one polarity collect at the interface, the ions of the opposite polarity remain in the liquid. Thus, if a liquid is contained in a pipe, and if the positive ions are adsorbed in preference to the negative ions, the pipe wall will obtain a positive charge. Negative ions in the liquid will then try to neutralize the positive charge and therefore keep as close as possible to the wall. Consequently, there is a fixed layer of positive charges on the wall and a mobile, diffuse layer of negative charges in the liquid a finite distance from the wall. These two layers are known as the electrical double layer, and its behavior is controlled by a competition between electrical
forces and diffusive forces. Now, if the liquid is in motion, the negatively charged particles in the liquid will be entrained while the oppositely charged particles are left behind at the wall. If the pipe is grounded, this latter charge flows to earth; if insulated electrically, a charge will continue to build up until the back emf is sufficient to reduce the rate of charge generation to zero. The liquid flowing through the pipe carries a net negative charge and can be regarded as an electric current (see Figure 1).

The degree of charge that can be built up in a liquid can be related to its conductivity. If the liquid has a relatively high conductivity (> $10^{-10}$ ohm$^{-1}$ cm$^{-1}$), ionization of the liquid is sufficient so that any charges formed are rapidly dissipated and do not build up to hazardous levels. At very low conductivities (< $10^{-15}$ ohm$^{-1}$ cm$^{-1}$), higher velocities and longer residence times are usually required to bring about a static charge build up. However, any charge build up which does occur requires a long relaxation time for dissipation. Generally, the greatest hazards exist with liquids having intermediate values of conductivity since ionization would be sufficient to give significant charges at moderate flow conditions while the time required to dissipate the charges would still be long. It should be emphasized, however, that although electrical conductivity controls the rate at which charges are dissipated, it is not the sole determinant of the degree of hazard from static electricity. For given flow conditions, the presence of small amounts of particulate contaminants in a liquid can decrease the generation of charges without affecting the conductivity of the liquid.
Figure 1. Schematic representation of the charge generation process for the flow of hydrocarbons through pipe lines.
B. Literature Review

1. General Background. The electrokinetic phenomenon for the pipeline flow of a liquid appears to have been first recognized by Dolezalek (1913). He passed high resistivity liquids, such as benzene and ether through pipes under pressure and measured the charge separations. He detected these as an electrical potential on an insulated tank into which the liquids emptied. The voltages were found to be roughly proportional to flow rate. He measured up to 4000 volts with metal pipes, but only on the order of 100 volts with glass and porcelain tubes.

Russig (1913) found that minute quantities of impurities contained in the low conductivity liquid change the electrification by several thousand volts. He postulated the existence of an optimum impurity content for maximum electrification with zero electrification for pure liquids.

Pearson (1940) reported the striking effect of contaminants such as water, tetraethyllead, and iron oxide on the electrification of saturated hydrocarbons. In the case of turbulent flow through a pipeline, Pearson postulated a separation of charges between the liquid and the wall upon collision of impurities with the pipe wall.

Nitka (1941) conducted experiments to determine the effect of pipe material, diameter, and length of the electrification of hydrocarbons in pipe flow. His results indicated that the pipe material makes little difference, but small differences in smoothness have an appreciable effect on charge generation. He found that short pipes give high charge generation which is only slowly increased by length, and that the charge is
approximately inversely proportional to viscosity and decreases with increasing pipe diameter.

Mackeown and Wouk (1942) measured the magnitude of the charges produced when gasoline is pumped into a tank truck from a filling rack, when a tank truck unloads at a service station, and when an automobile receives gasoline at a service station. The current measurements showed that only in the case of filling a tank truck, when the tank truck is insulated from ground, is a sufficiently high charge generated to produce an electric spark. In all cases a direct proportionality between filling rate and charge generation was found to exist.

The electrification of electrolytes by flow in pipes can be explained in terms of an electrical double layer. Cooper (1953) suggested that some sort of electrical double layer similar to that described by Helmholtz (1879) was also produced in commercial grades of organic liquids, such as petroleum, by impurities. Cooper formulated a theoretical expression for the charging current in terms of the electrokinetic potential and the Reynolds number. He also notes that electrification will not be observed unless the resistivity of the liquid exceeds $10^{11}$ ohm-cm.

Ernsberger (1956) discarded the concept of an ionic double layer in favor of the assumption that a layer of chemically-adsorbed, electrically neutral molecules exist at the interface between the liquid and solid. Dynamic equilibrium between adsorption and desorption was assumed to exist. Charge separation occurs due to a certain proportion of "anomalous" desorptions in the sense that an adsorbed electron-donor (basic) molecule may occasionally desorb with a deficiency of electrons, or an adsorbed electron acceptor (acid) molecule may desorb with one or more
extra electrons. Such electron transfer need only occur once in about $10^{12}$ desorptions to account for typical current densities observed, which are on order of $10^{-11}$ amp/cm$^2$. This mechanism proposed by Ernsberger has not become generally accepted.

Keller and Hoelscher (1957) studied the mechanism of charge separation and the parameters governing electrification in liquids flowing through tubes, where both liquid and tube are relatively poor conductors. Charges on both the tubing and effluent liquid were measured and found to be equivalent. Electrification was found to be a linear function of flow rate and independent of tubing length for long tubes. Cooper's equation for electrification current was found to satisfactorily explain these results, providing the electrokinetic potential is assumed to be a linear function of Reynold's number.

Hampel and Luther (1957) attempted to characterize the charging phenomenon for controlled concentrations of different additives (e.g. alcohols, peroxides, fatty acids, amines) in purified n-heptane. Because of the large scatter as well as lack of sufficient data, they were unable to assess the effect of different polar additives on the observed charging currents. Their results did indicate that the electrostatic charging of technical hydrocarbon fractions was mainly caused by the oxidation products.

Rutgers, deSmet, and deMyer (1957) studied the effect of turbulence upon electrokinetic phenomena with various solutions of Zn-di-isopropyl salicylate in benzene in glass capillaries of various widths. From their experimental results it was possible to calculate the thickness of the diffuse part of the electrical double layer. It was found that the effect
of turbulence on the charging current is directly proportional to the radius of the capillary and inversely proportional to the thickness of the diffuse layer. Thus as the concentration of electrolyte increases, so does the enhanced effect of turbulence.

Boumans (1957) extended Cooper's theory to low conductivity using the mean charge density instead of the streaming current as a characteristic quantity describing the amount of charge transported by the flow. The mean charge density was shown to be only slightly dependent on the shape of the charge distribution in the turbulent core of the flow. In tubes of finite length the mean charge density was found to be influenced by charge relaxation, a possible saturation of wall current, and by the fact that the velocity profile close behind the tube entrance differs from that farther in the tube.

Klinkenberg and van der Minne (1958) provide an extensive review of the problems electrostatics have posed to the petroleum industry. The types of operations in which explosions and fires attributed to static charge generation are summarized and practical means for reducing the hazard of static electricity are outlined. Physical concepts pertaining to electrostatics are reviewed as are mechanistic and theoretical developments proposed to describe the electrification of hydrocarbons in pipe flow.

In a review article, Eichel (1967) summarizes the basic definitions, relationships, principles and quantitative aspects of electrostatics to allow engineers to calculate the magnitude of the charging currents for the flow of hydrocarbons through tubes. The equations used have been derived from the classical theory (Helmholtz, 1879).
Klinkenberg and Poulston (1958) have shown as a result of large scale tests in the refinery, that the dangerous accumulation of electrostatic charges could be prevented by increasing the electrical conductivity of the product. An antistatic additive (Shell, 1969) was developed expressly for the purpose of increasing conductivity in fuels to reduce electrostatic hazards. This antistatic additive is a mixture of equal parts by weight of chromium dialkylsalicylate, calcium dodecyl sulfosuccinate, and a copolymer of lauryl methacrylate and methylvinylpyridine, all as a 50% solution in a hydrocarbon solvent. The copolymer functions as a stabilizer which renders the salts immune from the destabilizing effect of contact with water, alkalis, or tetraethyl lead. The chromium salt is the most active in imparting increased conductivity to the hydrocarbon; however, a one-to-one mixture of the chromium and calcium salts imparts a conductivity which is far greater than the sum of the conductivities produced by each of the substances alone. Only parts per million (1 ppm = 1 mg/liter) concentration of the antistatic additive is required to increase the electrical conductivity of a petroleum product to a safe level, while not producing any discernible undesirable side effects. It was determined that a conductivity of at least $5 \times 10^{-13}$ ohm$^{-1}$ cm$^{-1}$ is sufficient for most refinery operations, but under extreme conditions (for instance when fueling jet aircraft), a conductivity of $5 \times 10^{-12}$ ohm$^{-1}$ cm$^{-1}$ is required.

Townsend (1960) and Arthur D. Little, Inc. (1961) have studied the electrification of liquid methane and liquid hydrogen respectively in transfer equipment. Both studies revealed that significant electrostatic charges are generated to warrant observance of all safety precautions as
in handling other low conductivity hydrocarbons. Measurements of the electrical conductivity of cryogenic liquids are reported by Willis (1966) and White (1975). The range of conductivities reported \((10^{-17}-10^{-20} \text{ ohm}^{-1} \text{ cm}^{-1})\) are significantly lower than those found with liquid hydrocarbons. Thus any electrostatic charges generated in cryogenic liquids would have extremely long relaxation times.

Gavis and Koszman (1961) developed a theory for the electric charge generation in low-conductivity liquids in turbulent flow through pipes, based upon the equations of transport of ionic charge by diffusion, convection, and electric migration. The equations were solved for the special case of uniform velocity profile. They were shown to be the same as the previously reported experimental observations. The theory was extended (Gavis and Koszman, 1962a) into a form which could easily be tested experimentally, by use of correlations of turbulent mass transfer. The charging current was shown to be a universal function of a dimensionless group which was related to the ratio of the laminar sublayer thickness to the diffuse double layer thickness in the liquid. Their theory predicted the functional dependence of the charging current in the parameters of the generating system for all conductivity ranges and successfully predicted the magnitude of the current for low conductivity hydrocarbons. Extensive experimental work (Gavis and Koszman, 1962b) showed that the dependencies upon liquid conductivity, flow velocity, tube length and tube diameter were closely predicted by their theory. Although the current was found to be independent of tube material, it was found to be larger in rough tubes than in smooth tubes, and correlated qualitatively with the friction factor. Gibbings and Hignett (1968) reported that
during the flow of kerosene in stainless steel capillary tubes, electrification increased markedly on transition from laminar to turbulent flow; and that this increase was associated with a similar but smaller increase in skin friction. This finding is in agreement with the Gavis and Koszman conclusion that the charging current is effected considerably more by roughness than is the friction factor. Gibbings and Hignett suggest that the velocity gradient at the pipe wall may be a more significant parameter than mean flow velocity in determining the generation of charge.

Gavis and Koszman's (1962a) theory adequately explains most of the observed results but appears to break down when high-conductivity liquids ($\kappa \geq 10^{-12}$ ohm$^{-1}$ cm$^{-1}$) flow at relatively low velocities ($v < 5$ m/sec). It has also been observed by Gibson and Lloyde (1970), who studied the electrification of toluene in large diameter metal pipes, that at the highest liquid conductivities investigated ($10^{-11} - 10^{-10}$ ohm$^{-1}$ cm$^{-1}$), the current is proportional to $v^n$, where $n$ can be as high as 6.63, but decreases to about 2 at high flow velocities. This behavior is again not predicted by the Gavis and Koszman theory. Taylor (1974) has shown experimentally that a process of charge relaxation can occur at the pipe outlet and markedly reduce the streaming current predicted by the Gavis and Koszman theory when the product of the flow velocity and relaxation time of the liquid is comparable to or less than the distance from the pipe outlet to the collecting vessel. Taylor developed a theory to account for the loss of charge from the liquid stream, which can be used to extend the applicability of the Gavis and Koszman theory to higher conductivities and lower velocities.

Goodfellow and Graydon (1968 a,b) recognized that the theory of
Gavis and Koszman (1962a) did not place emphasis on the chemical nature of the fluid system. Hampel and Luther (1957) were the only investigators to date who had attempted to characterize the charging phenomenon for controlled concentrations of different additives. Goodfellow and Graydon measured the electrostatic charging currents as a function of different polar additives, tube diameter, electrical conductivity, and flow velocity. In general it was found that the flow of non-polar solvents of low conductivity containing alcohols, acids, nitrobenzene, and ASA-3 produced positive tube currents. The flow of non-polar solvents of low conductivity containing ketones, esters, and amines produced negative tube currents. The sign of the measured current could not be predicted theoretically; however, the current magnitudes showed very good agreement with those predicted by Koszman and Gavis.

Gibson and Lloyd (1970) concur with the above results as they have used the Koszman and Gavis form of presentation to indicate the effect of four chemically dissimilar additives on the electrification of toluene. Their investigations supported the view that the effect of a contaminant on the order of magnitude of the streaming current can be determined from a knowledge of the electrical conductivity of the mixture. The chemical composition of the impurity is relatively unimportant.

Bustin, Koszman, and Tobye (1964) have examined the rate of discharge of electrically charged hydrocarbon fuels. For fuels with an electrical conductivity greater than $10^{-14}$ ohm$^{-1}$ cm$^{-1}$, experimental results have verified that the charge decays exponentially with time and thus the Ohmic theory (constant conductivity) is valid. For fuels of very low conductivity (less than $10^{-14}$ ohm$^{-1}$ cm$^{-1}$), the experimental data exhibit
a faster than expected charge relaxation representable by a hyperbolic
time-decay. A theoretical charge relaxation rate was developed and shown
to be dependent on charge density and mobility rather than resistivity.
This result is obtained because it is incorrect to assume for a very low
conductivity fuel that the total number of charge carriers remains con-
stant upon charging of the fuel. Vellenga and Klinkenberg (1965) continued
the work of Bustin, et al. and showed that the hyperbolic theory was a
special case of their more general treatment. Also, it was shown that by
taking association and dissociation effects into account, it is possible
to describe certain types of relaxation curves which cannot be described
by either the hyperbolic theory or the Ohmic theory. From the equations
for the transport of charge in low dielectric constant fluids, Eichel
(1967) and Gavis (1967c) have derived expressions for the rate of relaxa-
tion of electrically charged hydrocarbon liquids which are in good agree-
ment with the above results.

In connection with the above findings, Klinkenberg (1967) has found
while measuring electrical conductivity by the direct current method that
a kind of polarization is observed in solutions of very low ionic con-
tent. This polarization resulted in the depletion of ions. It was shown
that by performing the measurements before a certain time has elapsed, or
by extrapolating to zero time, that the polarization effect would not
affect the results.

Since filters possess a tremendous amount of surface area upon which
the charge separation process can occur, they constitute a major source
of electrostatic charge generation in fuel handling systems. The pass-
age of hydrocarbon liquids through filters can result in charge densities
which are orders of magnitude larger than those arising during flow in tubes at similar volumetric flow rates. Leonard and Carhart (1970) found that the quantity of electrostatic charge generated when hydrocarbon fuels are passed through filters was dependent upon the conductivity and flow velocity of the liquid. As the conductivity of the liquid was increased, the charging current increased, passed through a maximum and then decreased. The sign of the charge on the fuel was found to be dependent upon the nature of the surface of the filter material. Gavis and Wagner (1968) proposed a scheme for predicting charging currents in terms of filter and fluid properties. They studied the case where the charge relaxation distance was large compared with the filter thickness. The charging current was found to depend upon the liquid relaxation time, its superficial flow velocity, and upon the nominal pore diameter and porosity of the filter. They proposed a formula for correlating their data for the streaming current and claimed that their dimensionless scaling law should be generally applicable. Huber and Sonin (1975) claimed that Gavis and Wagner's dimensionless analysis was not general as it implied that the charging current was independent of any physiochemical property of the filter or solid/fluid interface. This result conflicted with the view of the charging process as an electrokinetic one. Huber and Sonin proposed a relatively simple electrokinetic model for the charging mechanism in filtration, one which resembles those used for flows of aqueous saline solutions through charged membranes. An implicit analytic solution for the streaming current and potential as a function of filter and fluid properties and flow conditions was derived and it was shown that the model agreed with a series of experiments. However, the
particular solution was applicable only under conditions of relatively low flow speed and/or for high fluid conductivity, and many (if not most) filtration conditions of interest fall outside its range of validity. Later on, Huber and Sonin (1977a,b) generalized their theory to include high flow speed and low fluid conductivity. Their experimental results were in good agreement with their theory. Also, individual values for the mobilities of the positive and negative ions were obtained as a result of their analyses.

2. Theoretical Background. The first attempts to qualitatively explain the electric charge generation phenomena used the concepts of classical electrokinetic theory developed by Helmholtz, Smoluchowski, and Hui (1879). The convection current was given by

\[ i = 8\pi \varepsilon \varepsilon_0 \bar{v} \zeta \]  

(1)

where \( \bar{v} \) is the average linear velocity in laminar flow and \( \zeta \) is the electrokinetic (zeta) potential which is part of the interface potential and is determined as the difference in potential between the boundary of the sliding liquid and the solution.

The function \( i(\zeta) \) for fully developed turbulent flow was derived by Cooper (1953) in the form

\[ i = -\frac{C_f}{2} N_{Re} \bar{v} \pi \varepsilon \varepsilon_0 \zeta \]  

(2)

This equation was derived for the condition that the thickness of the diffuse part of the electrical double layer (\( \delta \)) is much less than the
thickness of the laminar sublayer ($\delta_{\text{s}}$), i.e. convective charge transfer occurs in the laminar zone. His theory is therefore strictly applicable to high conductivity liquids and not to most hydrocarbon solutions. This was recognized by Rutgers, et al. (1957) who studied the problem for the turbulent flow of low conductivity liquids. An expression was derived

$$i = \frac{\pi \varepsilon \varepsilon_0}{\delta} d \bar{V}$$

(3)

for the other extreme case where $\delta \ll \delta_{\text{s}}$ assuming that the charge in the turbulent zone is uniformly distributed.

Bustin, et al. (1957) added a pipe wall friction effect ($c_1 \bar{V}^{0.75}$) to the convection term, $\bar{V} \, dz/dz$, where $q$ is the charge density and $z$ is the axial coordinate of the pipe. The following result was obtained where $c_1$ is a proportionality factor that depends on the liquid, pipe material, and pipe diameter.

$$i = \frac{\pi d^2}{4} c_1 \tau \bar{V}^{1.75} (1 - e^{-L/\bar{V} \tau})$$

(4)

For the turbulent flow of low conductivity liquids through tubes, the diffuse layer extends out into the turbulent core. This condition makes the above approach unsatisfactory.

Shön, as reported by Hampel and Luther (1957), described the electrification phenomena by assuming a constant current density of ions ($j_A$) generated at the tube wall. As the space charge in the liquid increases, a radial conduction current develops which ultimately balances this charging current and leads to Equation (5).
Klinkenberg (1959) has assumed $j_A$ to be a diffusion controlled flux at the wall since all separation of charges must be due to unequal diffusion of ions. Convection does not separate charges and conduction can only reduce space charges according to the concept of relaxation. He solved the charge transport equation to obtain the following result:

$$i = \pi d j_A \tau \bar{v} (1 - e^{-L/\bar{v}\tau})$$  \hfill (5)

Koszman and Gavis (1962a) modified Klinkenberg's equation by solving for an average charge density and estimating the thickness of the diffusion-layer using Deissler's correlation (1955). The diffusion-layer thickness ($\delta_D$) represents an effective film thickness through which diffusion is governed by the laws of mass transfer. Thus within this layer, diffusion of ions to the wall is unaffected by the excess of charge in the liquid.

$$i = 0.314 \varepsilon \varepsilon_0 \frac{RT}{F} N^{7/8} \frac{L}{Re} \bar{v} (1 - e^{-L/\bar{v}\tau})$$  \hfill (6)

Koszman and Gavis' equation predicts the magnitude of the charging current as long as the electrical double layer thickness ($\delta$) is greater than the diffusion layer thickness ($\delta_D$). Using values for n-heptane at room temperature ($N_{Sc} \approx 500$) and assuming $C_s = 0$, Equations (6) and (7) agree to within ±5%. For $(L/\bar{v}\tau) \leq 0.1$ (i.e. low conductivity), the term
[1 - exp (-L/\bar{v} \tau)] \approx L/\bar{v} \tau \text{ and Equation (7) simplifies to Equation (8).}

\[ i = 0.07 \left( \frac{RT}{\nu} \right) N_{Re}^{7/8} N_{Sc}^{1/4} (1 - C_s/C_o) L \kappa \] (8)

In the derivation of Equation (9), Klinkenberg (1964) has considered only steady-state convective transport on the basis that the factor [1 - exp (-L/\bar{v} \tau)], being well known, could be added later.

\[ i = 0.07 \varepsilon \varepsilon_0 \left( \frac{RT}{\nu} \right) N_{Re}^{7/8} N_{Sc}^{1/4} \bar{v} (1 - C_s/C_o) \] (9)

Using the experimental results of Koszman and Gavis (1962b), Klinkenberg has shown that \( \delta/\delta_D = 1.3 \) is the minimum value of the ratio for which Equations (6), (7), and (8) can predict charging current magnitudes.

None of the above theories predict the observed maximum in the charging current magnitudes as the conductivity is increased. For this intermediate conductivity region, Koszman and Gavis (1962b) have derived Equation (10).

\[ i = \frac{2.78 \times 10^{-3} \nu D^{1/2}}{d^2} (\varepsilon \varepsilon_0)^{3/2} \left( \frac{RT}{\nu} \right) N_{Sc}^{1/4} N_{Re}^{21/8} (1 - C_s/C_o) (1/\kappa)^{1/2} \] (10)

This equation, which represents only an approximate description of reality, predicts that the current decreases as \( 1/\kappa \).

Goodfellow (1968:Thesis) studied the electrostatic charging currents for the flow of different liquids through small diameter stainless steel
tubes. He found that for low conductivity liquids \((\delta > 1.3 \delta_D)\), the measured charging currents increase as the conductivity increases. Charging current magnitudes exhibited no definite dependence on current polarity. In the intermediate conductivity region \((\delta = 1.3 \delta_D)\), the current magnitudes decreased with increased conductivity as predicted by Koszman and Gavis (1962a,b) theory.

A refinement in the work of Koszman and Gavis (1962a) is inherent in a non-linear partial differential equation for transport of electric charge developed by Gavis (1967a,b) for the flow of low conductivity liquids.

The above developments (Klinkenberg, 1959, 1964; Gavis and Koszman, 1962a, 1967a,b) are characterized by the absence of any characteristics of electrosurface properties of interphase boundaries (unit surface charge, zeta-potential, unit adsorption). This is manifested as indicated by Goodfellow and Graydon (1968a,b), by the fact that these expressions cannot predict the generated charge polarity which is determined by the concentration and physiochemical nature of polar impurities in the non-polar liquid and by the tube wall material. Experimental verification of these expressions showed that they are valid only in the range of relatively low conductivity \((\kappa < 10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1})\). At higher conductivities, the expressions derived by Koszman and Gavis (1962a) give a value of \(i\) which is significantly greater than that experimentally determined.

Gibbings and Hignett (1966, 1967, 1968) established some rules of electric charge generation based on dimensional analysis. The expression they derived for the streaming current
\[ i = \rho^{1/2} \left( \varepsilon \varepsilon_0 \right)^{1/2} d^{-1/2} \left( \frac{\varepsilon}{\kappa} \overline{v} \right)^{0.87 - 1.25 Re^{-0.12} \left( 1 - e^{(L - L_0)/\overline{v} \tau} \right)} \]  

(11)

includes length \( L_0 \), a correction term for the entry region (Gibbings and Hignett, 1965). Within this region, the flow is not yet fully developed and thus the boundary-layer velocity profile is changing. The rate of charging is correspondingly affected because at the entrance, the charge lies close to the wall. The above expression shows that \( i \) monotonically decreases with higher conductivity for a sufficiently long pipe \([L - L_0] >> \overline{v} \tau\].

Study of the function showed (Gavis and Koszman, 1962a; Goodfellow and Graydon, 1968a,b) that under constant flow conditions and pipe parameters, \( i \) increases, passes through a maximum, and then decreases with higher conductivity. Higher liquid flow velocities were found to displace this maximum toward higher conductivity.

Zhukov (1974) developed an expression for the charging current as a function of \( \zeta \)-potential valid over a wide range of liquid conductivity for the case of developed turbulent flow in a pipe. No assumptions were made concerning the relative magnitudes of the diffuse layer and laminar sublayer thicknesses. Therefore, the following general expression was obtained:

\[ i = \frac{\pi \varepsilon \varepsilon_0}{\delta} d \overline{v} \zeta \left( \frac{\delta_\zeta}{\delta} \right) + \frac{0.04 \text{ Re}^{3/4}}{d} \left[ \frac{\delta}{\left( \delta + \delta_\zeta \right) e^{-\delta_\zeta/\delta}} \right] \]  

(12)

When \( \delta_\zeta >> \delta \) (region of high conductivity), Equation (12) reduces to Cooper's (1953) Equation (2). When \( \delta_\zeta << \delta \) (region of very low conduct-
Equation (12) is predicted to within approximately 6% by Rutger's (1957) equation. The above expression indicates that the function of current flow versus electrical conductivity is extremal in character and that the maximum current occurs at a value of electrical conductivity at which the thickness of the diffuse layer is equal to the thickness of the laminar sublayer.
III. Electrical Conductivity of Low Dielectric Constant Liquids

A. Introduction

Electrical conductivity is the most significant solution parameter in determining whether a hydrocarbon liquid is prone to static charge generation. The electrical conductivity of hydrocarbons is associated with two mechanisms. The first, as discussed earlier, attributes the conductivity to the presence of low concentrations of ionic impurities remaining in the petroleum products after manufacturing operations (Klinkenberg and van der Minne, 1958). The second pertains to absolutely pure hydrocarbon liquids which contain no molecular compounds other than the hydrocarbon molecule itself. Such hydrocarbons exhibit an electrical conductivity known as the "natural conductivity" (Adamczewski, 1969). This property may be imparted by the presence of minute concentrations of ionized hydrocarbons produced by ordinary background radiation, or may be due to electron transfer mechanisms inherent to the hydrocarbon. The natural conductivity of aliphatic hydrocarbons is approximately three orders of magnitude lower than that of aromatic hydrocarbons, because the latter possess \( \pi \)-electrons which are capable of being excited to higher energy states and thus may transfer from one molecule to the next. Figure 2 illustrates the range of natural conductivities for various hydrocarbons as reported by numerous investigators.

The electrostatic charge generation phenomenon encountered in the flow of petroleum products through pipes may be attributed to the presence of foreign impurities because in the absence of such ionic constituents, the electrification phenomenon is not observed. Therefore, in further discussion of electrical conductivity, it will be assumed that the
Figure 2. Electric conductivity ($\kappa$) versus temperature ($T^{-1}$) for various hydrocarbon liquids. Regions A, B, C paraffinic hydrocarbons of technical purity or pure aromatic hydrocarbons. Regions E, F, some aromatic hydrocarbons, highly purified and dried. Regions H, I, paraffinic, highly purified, dried and degassed. Region J, some samples of standard paraffic hydrocarbons of highest purity under thick lead screen (influence of cosmic rays) (Adamczewski, 1969).
measured conductivity is attributable solely to the presence of solutes in solution with the hydrocarbon, capable of dissociation into ionic species. The hydrocarbon solution thus behaves as an extremely weak electrolyte.

Shell Oil Company (1969) reports that its refinery and petro-chemical raw materials, intermediates and finished products, contain ion concentrations of approximately $10^{-11}$ to $10^{-12}$ gram-ion/liter. Petroleum fractions such as gasoline, naptha, aviation turbine fuel, kerosine, and gas oil have electrical conductivities in the range of $10^{-15}$-$10^{-13}$ ohm$^{-1}$ cm$^{-1}$, all significantly greater than their natural conductivities.

It should be emphasized that there is no direct relationship between the concentration of solutes and the charging magnitude generated in a hydrocarbon liquid. These properties greatly depend on the chemical and physical nature of the impurity. For example, a particular impurity may increase the conductivity but leave the charging characteristics essentially unchanged. Therefore, the charging phenomena are not dependent on total solute concentration, but rather on the concentration of the dissociated ions and the physical properties of the ion itself; i.e. diffusivity, mobility, and adsorption characteristics.

B. Basic Concepts

The electric conductivity, $\kappa$, is the proportionality constant defined by Ohm's law

$$j = \kappa E$$  \hspace{1cm} (15)$$

where $\kappa =$ electric conductivity (ohm$^{-1}$ cm$^{-1}$)
\( \mathbf{j} \) = current density vector (A/cm\(^2\))

\( \mathbf{E} \) = electric field vector (V/cm)

\[ \mathbf{E} = -\nabla \cdot \phi \]

\( \phi \) = electric potential vector

The Poisson equation provides a relationship between the electric field strength and the free charge density

\[ \nabla \cdot (\varepsilon \varepsilon_0 \mathbf{E}) = q \quad (14) \]

where \( q \) = free charge density

\( \varepsilon_0 \) = absolute dielectric constant of vacuum

\[ \varepsilon_0 = 8.854 \times 10^{-14} \text{ A-sec/V-cm} \]

\( \varepsilon \) = the relative dielectric constant of the liquid

Upon substitution of Ohm's law into the Poisson equation, we obtain

\[ \nabla \cdot \left( \frac{\varepsilon \varepsilon_0}{\kappa} \mathbf{j} \right) = q \quad (15) \]

Conservation of charges gives the following expression:

\[ \nabla \cdot \mathbf{j} = -\frac{\partial q}{\partial t} \quad (16) \]

Equations (15) and (16) are combined assuming the ratio \( \varepsilon / \kappa \) is a constant.

\[ \frac{\varepsilon \varepsilon_0}{\kappa} \frac{\partial q}{\partial t} = -q \quad (17) \]
Upon integration we obtain

\[ q = q_0 e^{-t/\tau} \]  

(18)

where \( \tau = \varepsilon \varepsilon_0 / \kappa \)  

(19)

is the time constant of charge relaxation known as the relaxation time and \( q_0 \) is the initial free charge density of the liquid. The relaxation time depends only on the properties of the liquid. The time in which the charge density of the liquid is reduced by half is known as the half-value time, \( t_{1/2} \), and is given by the following expression:

\[ t_{1/2} = 0.693 \tau \]  

(20)

The relaxation time is an indicator of the order of magnitude of time necessary for a particular charge density to dissipate and is thus a very valuable parameter in determining the dangers of static-charge buildup in a liquid. Since the value of the dielectric constant for most hydrocarbons is approximately equal to 2, the magnitude of the relaxation time is inversely proportional to the electric conductivity of the hydrocarbon. It is for this reason that conductivity measurements are crucial in any study of static-charge generation in hydrocarbon liquids.

C. Methods of Measuring Electrical Conductivity, Polarization and Temperature Effects

The electrical conductivity is usually measured with a cell in which the liquid is contained between two electrodes. The geometry of
the cell may vary; however, two concentric metal cylinders are frequently utilized with the hydrocarbon liquid contained in the annulus. The inner and outer cylinders function as electrodes.

Two different methods have been utilized for determining the conductivity of low dielectric constant liquids, such as hydrocarbons. The first is known as the direct current method. In this procedure a constant dc potential difference is placed across the plates of the cell and the resulting current is measured. If the cell constant is known, Ohm's law (Equation 13) can be applied to calculate the conductivity of the liquid. The second technique is known as the liquid capacitance method. In this procedure the conductivity cell is initially charged to a known potential and the decay behavior is then measured in order to determine the relaxation time of the system. In this manner, the conductivity of the liquid may be obtained as described in Section III D.

Although the above mentioned principles are very simple in theory, certain complications arise due to the very low conductivity of the hydrocarbons studied. Not surprisingly, these complications stem from the formation of the very same electrical double layer as accounted for the electrification phenomenon in pipe flow. These effects have been more pronounced in the measurement of electrical conductivity by the direct current method than the liquid capacitance method, and thus all studies of the phenomenon apply to the former. The experimental observations to be accounted for are the following. First, the currents measured for a given applied potential usually decrease considerably with time. Secondly, the characteristics of the current-time behavior are dependent on the separation between the electrodes, the nature of the liquid, and the applied
potential difference.

The effects which have been found to cause departures from Ohm's law in the determination of conductivity may be subdivided into two categories. The first are time independent and arise from diffusion or kinetic limited rates of discharge at the electrodes. These are known as overpotential effects. The second are effects which cause the current in a conductivity cell, at constant potential difference, to decrease with time. These are termed polarization effects and may arise because of a slow change in charge density in the solution near the electrodes, because of ion depletion, or because of plating out of electrolyte on the electrode surface, gradually changing the properties of the electrode.

Overpotential effects are usually unimportant in low dielectric constant liquids because of the relatively low field strengths applied for the conductivity measurements. These effects, however, become pronounced with high conductivity liquids such as aqueous solutions in which measurement techniques usually employ ac because overpotential effects are thereby eliminated. Due to the fact that the relaxation time of a low conductivity liquid is large compared to the ac cycle time, the use of ac to eliminate "polarization" effects in conductivity measurements is not feasible. The capacitive current in such a measurement is so much greater than the resistive current that it prevents the latter from being measured accurately. Also, since these currents are out of phase, very expensive equipment is required to separate them. Experimentally, it becomes impossible to measure the resistive current in liquids with conductivities lower than order $10^{-10}$ ohm$^{-1}$ cm$^{-1}$ (Gavis, 1965). Therefore, dc methods must be used for conductivity measurements of hydrocarbon
liquids.

The factors previously attributed to the time dependent polarization effects found with hydrocarbon liquids are not all equally important. At current densities usually observed in direct current measurements, the total number of ions discharged would occupy only a minute fraction of the electrode surface if deposited, and thus could hardly be responsible for altering the electrode surface properties.

Ion depletion is caused by the process of passing an electric current through the hydrocarbon solution. The amount of ions removed, as can be derived from the current integrated over time, is small with respect to the total amount of solute in the solution. Thus, if the electrolyte is capable of fast redissociation, there will be no depletion, whereas, if the electrolyte cannot maintain ionic equilibrium, there can be depletion. This factor proves to be very important in relation to analyzing the data obtained from conductivity measurements by the direct current method. If depletion is assumed to occur, it is necessary to extrapolate the current-time plots to zero; but if assumed not to be important, the plots should be extrapolated to infinite time. Koszman (Koszman and Gavis, 1962b) and Klinkenberg (1967) advocate the former principle while Gavis (1964b) advocates the latter.

Gavis (1964b) attributed the polarization phenomenon entirely to the changing charge density in the diffuse double layer at the electrode surface, which results when the potential at the electrodes is altered by the applied potential. Gavis applied the linearized partial differential equation developed earlier (Gavis, 1964a) for the transport of electric charge in low dielectric constant fluids to the formation of a nonequili-
brium double layer when the potential of an electrode is raised to cause current flow. He found the derived current-applied potential-time expressions to consist of a transient polarization current which decays to a steady-state current. The decay rate of the transient was found to depend primarily upon the relaxation time of the solution. The theoretical expression predicted that the steady-state current obeyed Ohm's law only if the electrode spacing was much greater than the diffuse layer thickness.

Investigators continue to be in conflict concerning the origin of polarization effects in direct current measurements. No acceptable conclusion has yet been formulated. Studies, however, continue on the effect of ionic dissociation and recombination on the relaxation and transport of charge in low dielectric constant liquids (Gavis, 1969, 1975). As more is learned about the physical and chemical properties of the ionic impurities present in hydrocarbon liquids, a better understanding of the polarization phenomenon is inevitable.

As a result of the uncertainties posed by polarization effects in the direct current method of measuring conductivities, the liquid capacitance method has been selected over the former. Polarization effects similar to those discussed above, but of lesser magnitude, are also inherent in this form of measurement. The implications of such effects will be further qualified in Section III F.

Although the electrical conductivity of a liquid is essentially determined by the physical and chemical properties of dissolved impurities, an additional factor has been neglected which may actually play a significant role in conductivity measurements. This factor is the temperature of the liquid itself. In studies with benzene of various degrees of
purity. Forster (1962) has found the conductivity to follow a temperature dependence, normally associated with semi-conductors, namely

\[ \kappa = \kappa_0 e^{-E/kT} \]  

(21)

where \( \kappa_0 \) and \( E \) are material constants and \( k \) is the Boltzman constant. The value for \( \kappa_0 \) was found to increase with decreasing purity of benzene; however, the value of the activation energy, \( E \), was found to be independent of the level of impurities. Although impurities may cause an increase in the measured conductivity, it is evident that they do not cause a change in the actual conduction process in liquid benzene.

Forster's results indicate that for distilled, degassed, spectral grade benzene (\( \kappa_0 = 5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1} \), \( E = 0.42 \text{ eV} \)) a temperature increase of approximately 2°C doubles the value of the electrical conductivity. Therefore, the ambient temperature may have a profound effect on the measured conductivity and in order to obtain consistent results, the temperature of the liquid must be maintained at a constant value.

D. Experimental

1. Apparatus

A diagram of the conductivity measuring apparatus is shown in Figure 3. The conductivity cell consisted of two concentric cylinders. Both the outer cylindrical wall and the inner solid bar were made of 304 stainless steel. The actual dimensions of the cell are provided in Figure 4. The cell was electrically insulated with a teflon lid which held the inner cylinder in place. A small opening in the lid allowed access to a shielded cable which was soldered to the inner cylinder.
Figure 3. Diagram of the apparatus for measuring conductivity.
Figure 4. Diagram of conductivity cell.
This cylinder was electrically insulated with a teflon stand elevated one inch from ground with teflon supports. The conductivity cell was enclosed within a grounded Faraday cage during conductivity measurements.

Voltage measurements were obtained with a Keithley 610C electrometer and recorded with a Hewlett Packard 7004B X-Y recorder. In the voltmeter mode the electrometer had a range of 0.001 volt full scale to 100 volts full scale. The accuracy was \( \pm 1\% \) of full scale on all ranges and the input impedance was \( 10^{14} \) ohms shunted by 20 picofarads (pF). The input leads to the electrometer were teflon-insulated coaxial cable RG-142. External capacitors were of the silver-mica variety. Their capacitances were read on a Hewlett Packard capacitance bridge to an accuracy of \( \pm 1\% \). Electric potentials were applied with a 45 V Burgess dry cell battery.

2. Procedure

Before each measurement was taken, the conductivity cell was washed with an aqueous Alconox solution, rinsed thoroughly with distilled water, and then dried in an oven at 110°C. Finally, the cell was rinsed twice with ca 25 ml of the same liquid to be measured. For each measurement, the cell was filled with 900 ml of liquid and allowed to discharge to ground for approximately one hour. This was necessary because upon addition of the hydrocarbon liquid to the cell, sufficient electrostatic charge was generated to perturb the recorded decay behavior.

The cell was initially charged to approximately 45 volts with a dry cell battery. The voltage source was disconnected and the decay behavior was recorded with different values of applied capacitance, \( C_K \), in parallel with the conductivity cell. Two decay curves were analyzed for each
value of $C_K$ in order to obtain average values of the relaxation time. A minimum of two different values of applied capacitance are required to determine the liquid conductivity. The analysis of the data to calculate the conductivity is treated in the next section.

3. **Theory**

   Electrical conductivity is given by Equation (22):

   $$\kappa = \varepsilon \varepsilon_0 / \tau$$  \hspace{1cm} (22)

   where $\kappa$ = electrical conductivity of the liquid ($\Omega^{-1} \text{ cm}^{-1}$)

   $\tau$ = the relaxation time of the liquid (sec)

   $\varepsilon_0$ = the absolute dielectric constant of vacuum

   $= 8.854 \times 10^{-14}$ A-sec/V-cm

   $\varepsilon$ = the relative dielectric constant of the liquid

In order to calculate the conductivity of the liquid, it is necessary to determine the relaxation time of the liquid from the decay curves obtained with our experimental system.

The experimental apparatus (Figure 3) can be broken down into its individual electronic components as indicated in the following schematic. The electric potential is applied across the terminals of the capacitor $C_K$.
where $C_L =$ capacitance of the liquid in the conductivity cell (pF)
   $= \varepsilon C_c$
$C_c =$ the calculated capacity of the empty cell (10.5 pF)
$R_L =$ the resistance of the liquid in the conductivity cell (pF)
$C_K =$ the known value of applied capacitance (pF)
$C_W =$ the unknown capacitance of the wires and cables (pF)
$C_E =$ the internal capacitance of the electrometer ($\sim$ 20 pF)

The resistance of the wires and cables is assumed negligible as compared to the resistance of the hydrocarbon liquid. The capacitances denoted by $C_E$ and $C_W$ may be combined into a single capacitance $C_{EX}$ which represents the combined unknown capacitance external to the conductivity cell. The final system is illustrated below.

The total capacitance of the experimental system, $C_S$, may be written as

$$C_S = C_L + C_K + C_{EX} \quad (23)$$

The total resistance ($R_S$) of the experimental system is given by

$$R_S = R_L \quad (24)$$
The experimental system is representable by a simple RC-circuit as shown below.

\[ \begin{array}{c}
R_S \\
\hline \\
C_S
\end{array} \]

Consider this system to be charged to an electric potential \( V_0 \) at time, \( t = 0 \). The decay behavior is given by

\[ V = V_0 \exp(-t/\tau_S) \]  \hspace{1cm} (25)

where \( \tau_S \) represents the relaxation time of the system and for an RC-circuit is equal to

\[ \tau_S = R_S C_S \]  \hspace{1cm} (26)

Similarly the relaxation time, \( \tau \), of the liquid is equal to

\[ \tau = R_L C_L \]  \hspace{1cm} (27)

Upon substitution of Equation (27) into Equation (22), we obtain

\[ \kappa = \varepsilon_0 \varepsilon_R / R_L C_L \]  \hspace{1cm} (28)

We can solve for \( R_L \) from Equations (26) and (24) and substitute into
Equation (28)

\[ \kappa = \varepsilon \varepsilon_0 \frac{C_S}{\tau_S} C_L \]  

(29)

We can utilize Equation (25) to calculate \( \tau_S \) by analyzing the system decay behavior at two values of time, \( t_1 \) and \( t_2 \):

\[
\frac{V_1}{V_2} = \frac{\exp(-t_1/\tau_S)}{\exp(-t_2/\tau_S)}
\]

or

\[ \tau_S = \frac{\Delta t}{\ln(V_1/V_2)} \]  

(30)

where \( V_{1,2} = \) electric potential at \( t = t_{1,2} \) (volts)

\[ \Delta t = t_2 - t_1 \text{ (sec)} \]

Equations (30), (26), and (23) can be combined to yield the following expression:

\[ \frac{\Delta t}{\ln(V_1/V_2)} = R_S(C_L + C_{EX} + C_K) \]  

(31)

Consider a liquid whose decay behavior is determined for two different values of applied capacitance, \( C_K' \) and \( C_K'' \), and that measurements of \( \Delta t \) are made maintaining the ratio \( V_1/V_2 \) constant.

\[
\frac{\Delta t''}{\Delta t'} = \frac{C_L + C_{EX} + C_K''}{C_L + C_{EX} + C_K'}
\]  

(32)

Upon solving for \( C_{EX} \)
Equation (33) allows the external capacitance of the system to be independently calculated.

The total capacitance of the system can be calculated for a particular value of $C_K$ by combining Equations (23) and (33).

$$C_S = C_K + \frac{\Delta t' C_K'' - \Delta t'' C_K'}{\Delta t'' - \Delta t'}$$  \hspace{1cm} (34)$$

If $C_K = C_K'$

$$C_S = \frac{\Delta t'(C_K'' - C_K')}{\Delta t'' - \Delta t'}$$  \hspace{1cm} (35)$$

$$\tau_S = \Delta t' / \ln(V_1/V_2)$$  \hspace{1cm} (36)$$

Upon substitution of Equations (35) and (36) into Equation (29), recognizing that $C_L = \varepsilon C_C$, the following final result is obtained for the electrical conductivity of the liquid:

$$\kappa = \frac{\varepsilon_0(C_K'' - C_K')}{C_C} \frac{\ln(V_1/V_2)}{\Delta t'' - \Delta t'}$$  \hspace{1cm} (37)$$

Therefore, in order to calculate the electrical conductivity of a hydrocarbon liquid, two system decay curves are required. One curve for an applied capacitance $C_K'$ and the other for a different applied capacitance $C_K''$. It is necessary to obtain from each curve the values $\Delta t'$ and
\( \Delta t \) respectively, which represent the net times required for an incremental voltage drop from \( V_1 \) to \( V_2 \). Typical decay curves for a conductivity measurement are shown in Figure 5.

Equation (37) is a special form of the more general expression given below (applicable when \( V_1/V_2 \) is not constant).

\[
\kappa = \frac{\varepsilon_0 (C_K'' - C_K')}{C_c (\tau'' - \tau')} \tag{38}
\]

where \( \tau' = \Delta t'/\ln(V_1/V_2)' \) \tag{39}

and \( \tau'' = \Delta t''/\ln(V_1/V_2)'' \) \tag{40}

If the decay curves are replotted in the form \( \ln(V/V_0) \) vs \( t \), \( \tau \) may be obtained from the slope of the curve, which is equal to \(-1/\tau\). The conductivity is easily calculated from Equation (38).

E. Results

The hydrocarbons studied during the course of experimental work can be divided into two categories; aliphatic and aromatic. The chemical purity of these hydrocarbons generally fell under the classification of "reagent" grade, i.e. suitable for analytical use and more exacting syntheses. Occasionally, a hydrocarbon of greater purity was utilized. Such hydrocarbons were specially prepared reagents manufactured by MCB, an associate of E. Merck, Darmstadt, Germany. They were reagent grade hydrocarbons that were glass distilled to remove all inorganic and non-soluble organic impurities, and then passed through a one micron filter to remove particulate matter. It should be mentioned that for all
Figure 5. Sample conductivity calculation

\[ \kappa = \frac{\varepsilon_0 (C_K'' - C_K')}{C_C} \frac{\ln(V_1/V_2)}{\Delta t'' - \Delta t'} = \frac{(8.854 \times 10^{14} \text{ A-sec/V-cm})(465 \times 10^{-12} \text{ F}) \ln(40/10)}{(10.5 \times 10^{-12} \text{ F})(68.5 - 12.2 \text{ sec})} \]

\[ \kappa = 9.65 \times 10^{-14} \Omega^{-1} \text{ cm}^{-1} \]

- Graph 1: \( C_K' = 0 \text{ pF} \), \( \Delta t'_{40-10} = 12.2 \text{ sec} \)
- Graph 2: \( C_K'' = 465 \text{ pF} \), \( \Delta t''_{40-10} = 68.5 \text{ sec} \)
measurements it must be assumed that the hydrocarbon contains dissolved oxygen and water from contact with air, and this may significantly contribute to the reported conductivities.

Tables I and II summarize representative results obtained for aliphatic and aromatic hydrocarbons, respectively. The aliphatic hydrocarbons are listed in order of increasing chain length. Pentane is reported by Adamczewski (1969) to possess one of the lowest natural conductivities of the hydrocarbon family, i.e. approximately $10^{-19}$ ohm$^{-1}$ cm$^{-1}$. The conductivity reported for spectral grade pentane in Table I is three orders of magnitude larger than its natural conductivity. However, it is also an order of magnitude less than the other conductivities measured for the straight chain hydrocarbons. Heptane was consistently found to possess a conductivity of approximately $5 \times 10^{-15}$ ohm$^{-1}$ cm$^{-1}$, a value that was rather independent of reagent purity. The conductivity of n-octane was found also to be representative of those measured for aliphatic hydrocarbons. The conductivities of the aliphatic hydrocarbons studied, all fell essentially within the range $10^{-16}$ ohm$^{-1}$ cm$^{-1} < \kappa < 5 \times 10^{-15}$ ohm$^{-1}$ cm$^{-1}$.

It is interesting to note that those hydrocarbons denoted with an asterisk (i.e. glass distilled and filtered) all have conductivities of approximately $5 \times 10^{-15}$ ohm$^{-1}$ cm$^{-1}$ regardless of whether aliphatic or aromatic. This is not unusual, although the natural conductivities of benzene and toluene ($\sim 10^{-16}$ ohm$^{-1}$ cm$^{-1}$) are about an order of magnitude greater than that of heptane ($\sim 10^{-17}$ ohm$^{-1}$ cm$^{-1}$).

The measurements for toluene indicated that as the level of purity is increased, the conductivity correspondingly decreases. This is exactly what is to be expected. The xylenes were consistently found to exhibit
<table>
<thead>
<tr>
<th>Liquid</th>
<th>$C_K$ (pF)</th>
<th>$V_1$ (volts)</th>
<th>$V_2$ (volts)</th>
<th>$\Delta t$ (sec)</th>
<th>$\kappa (\Omega^{-1} \text{ cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>n-pentane (99+%)</strong></td>
<td>0</td>
<td>50.0</td>
<td>48.3</td>
<td>126.0</td>
<td>$2.84 \times 10^{-16}$</td>
</tr>
<tr>
<td></td>
<td>202</td>
<td>43.3</td>
<td>43.0</td>
<td>75.0</td>
<td></td>
</tr>
<tr>
<td>n-heptane (98%)</td>
<td>0</td>
<td>40.0</td>
<td>20.0</td>
<td>224.0</td>
<td>$1.89 \times 10^{-15}$</td>
</tr>
<tr>
<td></td>
<td>105</td>
<td></td>
<td></td>
<td>548.0</td>
<td></td>
</tr>
<tr>
<td>*n-heptane (99.6%)</td>
<td>0</td>
<td>46.6</td>
<td>43.3</td>
<td>20.0</td>
<td>$4.80 \times 10^{-15}$</td>
</tr>
<tr>
<td></td>
<td>202</td>
<td></td>
<td></td>
<td>46.3</td>
<td></td>
</tr>
<tr>
<td>n-octane (99+%)</td>
<td>0</td>
<td>40.0</td>
<td>35.0</td>
<td>68.8</td>
<td>$1.80 \times 10^{-15}$</td>
</tr>
<tr>
<td></td>
<td>202</td>
<td></td>
<td></td>
<td>195.0</td>
<td></td>
</tr>
</tbody>
</table>

*glass distilled, followed by filtration through a one micron filter

**Equation (38) is required to calculate the conductivity.
### TABLE II
Measured Conductivities of Aromatic Hydrocarbons

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$C_K$ (pF)</th>
<th>$V_1$ (volts)</th>
<th>$V_2$ (volts)</th>
<th>$\Delta t$ (sec)</th>
<th>$\kappa (\Omega^{-1} \text{cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0</td>
<td>40</td>
<td>30</td>
<td>100.0</td>
<td>4.45 x 10^{-15}</td>
</tr>
<tr>
<td>* (99+%)</td>
<td>202</td>
<td></td>
<td></td>
<td>210.0</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0</td>
<td>30</td>
<td>10</td>
<td>7.50</td>
<td>1.39 x 10^{-13}</td>
</tr>
<tr>
<td>(&quot;solvent&quot; grade)</td>
<td>105</td>
<td></td>
<td></td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0</td>
<td>40</td>
<td>35</td>
<td>17.8</td>
<td>1.06 x 10^{-14}</td>
</tr>
<tr>
<td>(&quot;reagent&quot; grade)</td>
<td>202</td>
<td></td>
<td></td>
<td>39.3</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0</td>
<td>40</td>
<td>30</td>
<td>98.0</td>
<td>3.52 x 10^{-15}</td>
</tr>
<tr>
<td>* (99.8%)</td>
<td>202</td>
<td></td>
<td></td>
<td>237.0</td>
<td></td>
</tr>
<tr>
<td>m-xylene</td>
<td>0</td>
<td>40</td>
<td>10</td>
<td>12.3</td>
<td>9.95 x 10^{-14}</td>
</tr>
<tr>
<td>(&quot;reagent&quot; grade)</td>
<td>464.5</td>
<td></td>
<td></td>
<td>69.4</td>
<td></td>
</tr>
<tr>
<td>o-xylene</td>
<td>0</td>
<td>40</td>
<td>30</td>
<td>1.2</td>
<td>2.97 x 10^{-13}</td>
</tr>
<tr>
<td>(99+%)</td>
<td>202</td>
<td></td>
<td></td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>1,2,4 trimethyl benzene</td>
<td>0</td>
<td>40</td>
<td>30</td>
<td>2.95</td>
<td>1.31 x 10^{-13}</td>
</tr>
<tr>
<td>(&quot;reagent&quot; grade)</td>
<td>202</td>
<td></td>
<td></td>
<td>6.70</td>
<td></td>
</tr>
</tbody>
</table>

*glass distilled, followed by filtration through a one micron filter
conductivities one to two orders of magnitude greater than those of toluene. 1,2,4 trimethyl benzene possessed a conductivity of similar magnitude to the xylenes. In general, it was found that the aromatic hydrocarbons had conductivities in the range of $5 \times 10^{-15} < \kappa < 1 \times 10^{-13}$ ohm$^{-1}$ cm$^{-1}$ which at the high end are approximately 20 times greater than those of the aliphatic hydrocarbons.
F. Discussion

The applicability of the liquid capacitance method for measuring conductivities has been demonstrated. Conductivities obtained agree well with those reported in the literature. It remains, however, to ascertain exactly how accurate these conductivity measurements are.

From studies of the direct current method, it was found that the measured conductivity was very dependent on the time over which the measurement was performed. A conflict resulted over the question of ion depletion, whose importance lies in relation to interpreting the experimental data. It is important to know how applicable the measured conductivities are to correlations of experimental data. Assuming that measurements alter the "actual" conductivity in a uniform manner, correlations indeed are possible as have been demonstrated in the literature. However, it is likely that the measurement produces effects differing in degree for each liquid, depending upon its inherent properties. Since the measured conductivity of liquid hydrocarbons is due mainly to impurities which are ionic in nature, it is not surprising that application of an electric potential affects the concentration of these ions and perhaps their chemistry. All transformations occur at the electrode surface; i.e. within the electrical double layer. The applied potential may alter the characteristics of the double layer in such a manner that the measured current and potential characteristics are correspondingly affected. The potential profile obtained in a conductivity cell during a direct current measurement of pure liquid benzene (Forster, 1962), exhibits non-Ohmic behavior near the electrode surfaces. This indicates that the double layer may play a role in affecting the charge distribution in the cell.
Solute molecules in solution with the hydrocarbon are at equilibrium with dissociated ionic species. The concentration of these ions is extremely low as they are not stabilized in a highly non-polar medium. The application of an electric potential could significantly alter the dissociation equilibrium at the electrode surface. A new equilibrium may be established, different from that before application of the potential. The electrical characteristics would, therefore, not be indicative of the original solution state.

Application of an electric potential across the cell electrodes, although for only an instant as in the liquid capacitance method, should produce the same effect found with the direct current measurement, namely, a non-equilibrium electric double layer at the cell wall. The charge, however, is allowed to dissipate through a natural decay process, rather than a forced charge-transfer process as in the direct current method. Therefore, the final state of equilibrium should more closely approach that of the initial, and furthermore, ion depletion should be much less important. Also, the time necessary to re-establish equilibrium should be of shorter duration.

There is also an additional factor not previously mentioned, the possible occurrence of an electrochemical reaction at the electrode surface. Although such a phenomenon is unlikely, it must not be ruled out. The identities of the solute molecules has not yet been elucidated. Therefore, no plausible reaction mechanism can be postulated.

A significant difference between the liquid capacitance and direct current methods are the quantities actually ascertained in the measurement. Since a steady-state dc potential is applied in the direct current
method, it is not possible to measure any "ideal" capacitive elements (i.e. the voltage across the capacitor is proportional only to charge) because for such an element, \( i = C \frac{dV}{dt} \), and the capacitor thus behaves as an open circuit. With respect to the liquid capacitance method, however, \( \frac{dV}{dt} \neq 0 \) and therefore the response of the capacitive and resistive elements are both important.

Although polarization effects have not been previously reported with respect to the liquid capacitance method, there is good reason to believe such effects are actually present. The physical structure of an electric double layer resembles that of a parallel plate capacitor, and therefore has an associated capacitance known as the double layer capacity. The mathematical treatment of this concept is given in Appendix A. Careful examination of the data contained in Tables I and II reveal that the calculated external capacitance of the system \( C_{EX} \) for measurements in which the experimental set up was unaltered (the input cable to the electrometer was replaced during the course of experimental work), varies from one hydrocarbon liquid to the next (see Table III). The variation is too large to be solely attributed to experimental error. In formulating the equations for calculating the conductivity from the system decay behavior, it was assumed that the capacitance of the hydrocarbon liquid was identically equal to the quantity \( \varepsilon C_C \) where \( \varepsilon \) is the relative dielectric constant of the hydrocarbon and \( C_C \) the calculated capacitance of the empty cell. However, if an applied potential induces the formation of a significant capacitance, due to a double layer at the electrode surfaces, then the assumption that the capacitance of the hydrocarbon liquid is constant is invalid. Therefore, the calculated values obtained for
TABLE III
External Capacitance Calculated from the System Decay Data

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\varepsilon$</th>
<th>$\kappa(\Omega^{-1} \text{cm}^{-1})$</th>
<th>$C_{EX} \text{ (pF)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane (99%)</td>
<td>1.84</td>
<td>$2.84 \times 10^{-16}$</td>
<td>101.</td>
</tr>
<tr>
<td>n-heptane (99.6%)</td>
<td>1.92</td>
<td>$4.80 \times 10^{-15}$</td>
<td>133.</td>
</tr>
<tr>
<td>n-octane (99+%)</td>
<td>1.94</td>
<td>$1.80 \times 10^{-15}$</td>
<td>90.8</td>
</tr>
<tr>
<td>benzene (99+%)</td>
<td>2.28</td>
<td>$4.45 \times 10^{-15}$</td>
<td>160.</td>
</tr>
<tr>
<td>toluene (&quot;reagent&quot;)</td>
<td>2.38</td>
<td>$1.06 \times 10^{-14}$</td>
<td>142.</td>
</tr>
<tr>
<td>toluene (99.8%)</td>
<td>2.38</td>
<td>$3.52 \times 10^{-15}$</td>
<td>117.</td>
</tr>
<tr>
<td>o-xylene (99+%)</td>
<td>2.57</td>
<td>$2.97 \times 10^{-13}$</td>
<td>120.</td>
</tr>
<tr>
<td>1,2,4 trimethyl benzene (&quot;reagent&quot;)</td>
<td>2.37</td>
<td>$1.31 \times 10^{-13}$</td>
<td>134.</td>
</tr>
</tbody>
</table>
$C_{EX}$ given by Equation (33) would depend on the liquid studied.

The electric double layer may be modeled as a capacitance in parallel with a resistance. The experimental system may be represented by the schematic shown below.

where $C_{DL}$, $C_{DL}'$ = the double layer capacities at the respective electrodes (pF).

$R_{DL}$, $R_{DL}'$ = the double layer resistances at the respective electrodes ($\Omega$).

$C_B$ = the capacitance of the bulk liquid outside the double layers (pF).

$R_B$ = the resistance of the bulk liquid outside the double layers (pF).

$C_{EX}$ = the external capacitance of the electrometer and cables (pF).

$C_K$ = the applied capacitance (pF)

An analysis of this system is extremely difficult, because the values of the double layer capacities and resistances are unknown. Therefore, the initial values of the electric potential across the double layers cannot be determined.
In conclusion, measurements of conductivity by the liquid capacitance method are complicated by the presence of an electric double layer at the electrode surfaces. This phenomenon affects the measurements by inducing an additional unknown capacitance into the system.
IV. Electrostatic Charge Generation by Hydrocarbon Liquids in a Concentric Cylinder Flow Device

A. Introduction

Experimental investigations of the charging phenomenon in the flow of hydrocarbons through pipe lines have generated a great deal of practical information which has enabled industry to maintain electrostatic hazards at a minimum. Previous programs designed to study the charging current in pipeline flow have utilized apparatus consisting of three major components: a pressurized metal reservoir from which the hydrocarbon liquid was supplied at a controlled flow rate, a tube in which the flowing liquid generated charge, and a receiving tank for collecting the effluent liquid. The charging current was determined either by measuring the rate at which charge was carried by the effluent liquid to the receiving tank or by measuring the current conducted from the wall of the pipe to ground. Currents detected by either method have been shown to be equal in magnitude and opposite in sign (Keller and Hoelscher, 1957). The magnitude of the measured current was of the order $10^{-10} - 10^{-12}$ amps and therefore accuracy was seriously limited by the presence of leakage currents in the experimental equipment. Furthermore, it was very difficult to design an apparatus in which all of the charge was generated only in the test section being studied.

Previous theoretical models that have been formulated to explain the observed charging behavior in pipeline flow suffer from a serious conceptual inadequacy. There has been no mechanistic evidence provided to account for the charge flux observed at the liquid-solid interface. Koszman and Gavis (1962a) attributed its origin to the presence of a
possible oxidation-reduction process at the wall surface; however, no evidence has yet been presented to verify such a reaction.

The pipeline flow method of measuring charging currents does not afford any means of obtaining insight into the actual physical mechanism of the charging phenomenon, especially the process occurring at the liquid-solid interface. Therefore, a novel experimental approach has been developed to study electrostatic charge generation in hydrocarbon liquids.

The apparatus is similar to one employed to study electrochemical systems (Newman, 1973). The design resembles that of a coaxial cylinder viscometer. An electrically grounded, cylindrical metal surface (bob) is caused to rotate within a reservoir of liquid and the charge generated from the electrically insulated, stationary outer wall (cup) is collected onto a capacitor. The amount of charge is proportional to the electric potential measured across the capacitor. The steady- and unsteady-state charging process may be followed by recording the potential as a function of time. The measured potential represents the potential difference between the cup wall and ground which is also equal to the potential difference across the liquid contained in the annulus. Since the resistivity of hydrocarbon liquids is very large (10^{13} - 10^{16} \text{ ohm-cm}), currents as small as those generated in pipe flow experiments allow accurate measurement of the charging potential.

B. Experimental

1. Apparatus

A schematic of the charge generating apparatus is shown in Figure 6. A scale diagram of the bob-drive assembly is illustrated in Figure 7.
Figure 6. Schematic of the charge generating apparatus
Figure 7. Concentric cylinder flow apparatus.
The cup was a 1200 ml Vollrath stainless steel beaker whose rim was removed. This beaker was fitted with a 1/4" thick circular, teflon cover that possessed a 3/4" center hole to allow the 1/2" diameter bob shaft to enter. The cover served to electrically insulate the top of the cup and prevent evaporation of hydrocarbon liquid. The cup was also fitted with two concentric teflon rings which served to insulate this beaker from the two vari-grip clamps employed to mount the cup assembly to the ring stand. The entire assembly rested on a 1/8" thick teflon stand elevated 1" from ground with teflon supports. Therefore, the assembly was electrically floating. A length of teflon insulated cable was soldered to the outside center of the cup to allow for electrical measurements.

A Minarik control system was chosen to vary the bob speed. This unit consisted of a 1/5 h.p. Electro-Craft gearless motor generator adjustable from 0 to 110% rated torque, a Minarik TR9020 speed control capable of any input speed from 5 to 3000 rpm with an accuracy of 1%, and a Minarik TSIM4 torque and speed indicating meter, the accuracy of which is approximately 2% of the indicated speed.

The motor was vertically mounted on a stainless steel plate that was in turn mounted to an adjustable bench stand. The motor rotated the 1/2" stainless steel bob-shaft via a timing belt drive assembly, as shown. The shaft was securely mounted with two cast iron pillow block bearings. The bob cover was secured to the end of the shaft with two hex nuts and lock washers. The bobs were Vollrath stainless steel beakers (125 ml, 250 ml, and 600 ml) whose rims were removed. Each cover had a machined groove which allowed the respective bob to snap into place. In
this fashion it was possible to vary the bob size with little difficulty. If an aluminum cover was chosen, the bob was grounded through the entire metal assembly. If a teflon cover was chosen, it was possible to electrically insulate the bob from ground.

The drive assembly allowed for the optional use of a slip ring which could be mounted to the top end of the shaft, as shown in Figure 7. The slip ring was of the wetted mercury variety and was manufactured by Meridian Laboratories. This rotating electrical contact passes current from $10^{-6}$ to 5 amps, has a contact resistance of 0.001 ohms, and a rotational resistance deviation of 0.0005 ohms. The stainless steel shaft was hollow, thus allowing for a length of teflon-insulated coaxial cable to pass through it. The center conductor of one end of the cable was soldered to the inside surface of the bob and the other end connected to the stator of the slip ring. When a teflon cover was utilized, the bob, cable, and slip ring were electrically floating. Grounding the slip ring in this configuration was identical to grounding the bob through the drive assembly with a metal cover.

The desired orientation of the bob within the cup was obtained by adjusting the position of the entire drive assembly along the vertical of the bench stand. The entire charging apparatus was mounted on a 16 inch square, 1/2 inch thick aluminum base and enclosed within a grounded Faraday cage to prevent current loss and interference.

An individual silver-mica capacitor of known capacitance ($\pm 1\%$) was connected to the cup via the center conductor of the teflon insulated cable. The outer conductor of this cable served as a shield to the inner conductor. The capacitor rested upon a piece of teflon and was
isolated from all conducting surfaces within the Faraday cage. The induced electric potential across the capacitor was measured with a Keithley 610-C electrometer. In the voltmeter mode, this electrometer measures voltages from 0.1 to 100 volt full scale with an accuracy of ±1% for all scales. The input impedance is $10^{14}$ ohms shunted by 20 pF. This large impedance was necessary to prevent current loss to the electrometer. The input cables were teflon-insulated RG-142 B/U. The output from the electrometer was recorded on a Hewlett-Packard 7004B X-Y recorder. This recorder is accurate to 0.1% on all scales.

2. Procedure

Prior to each run, a bob size (Table IV) and an operation mode were chosen. There were three possible operating modes. First, the bob could be grounded through the drive assembly, and the potential measured from cup to ground. Secondly, the bob could be grounded from the slip ring through the electrometer chassis. Again the cup potential is measured relative to ground. Lastly, the cup could be grounded and the potential of the bob measured relative to ground. The first two configurations are electrically identical.

Once the desired operating mode was arranged, the bob was positioned centrally within the cup. The liquid hydrocarbon was added to the annulus and filled to 1/2" from the bottom of the bob cover. This prevented spraying and/or splashing when high speeds were reached. The teflon cover was then positioned over the cup, and the entire bob assembly aligned concentrically within the cup.

A capacitance was chosen and connected in parallel to the input leads of the electrometer. The appropriate scale settings were chosen
### TABLE IV

**Cup and Bob Dimensions**

<table>
<thead>
<tr>
<th>Beaker Size (ml)</th>
<th>Description</th>
<th>Diameter (mm)</th>
<th>( R_i/R_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>Cup</td>
<td>101.0</td>
<td>--</td>
</tr>
<tr>
<td>125</td>
<td>Small bob</td>
<td>51.5</td>
<td>0.51</td>
</tr>
<tr>
<td>250</td>
<td>Medium bob</td>
<td>65.3</td>
<td>0.647</td>
</tr>
<tr>
<td>600</td>
<td>Large bob</td>
<td>85.1</td>
<td>0.843</td>
</tr>
</tbody>
</table>
for the electrometer and X-Y recorder to yield a full scale reading of potential versus time for each particular bob speed. Before each trial the capacitor was grounded while the bob and fluid attained steady-state flow conditions. The ground was then removed and the X-Y recorder activated simultaneously. Charging was allowed to continue until a steady-state potential was reached. At this time the motor was inactivated and the decay behavior of the system recorded. The conductivity of each batch of hydrocarbon liquid was measured prior to each trial as described in Section IIIC.

C. Results

Prior to quantitative experimental work, preliminary runs were performed in order to ascertain the viability of this method for studying electrostatic charge generation in hydrocarbon liquids. Since heptane and toluene have been the most frequently studied hydrocarbons in the literature, they were likewise chosen for our experimental work. It was found that heptane did not exhibit any charging behavior in our apparatus. Toluene, however, readily generated charging potentials of the order of 100 volts. Additional runs utilizing pentane and hexane were consistent with the heptane behavior, whereas aromatics such as benzene and xylenes showed similar results as those found with toluene. The implication of these observations is discussed in Section IV-F. All of the remaining studies were performed with aromatic hydrocarbon liquids.

The charging and decay curves for a typical run are shown in Figure 8. The charging behavior of the system can be described by the equation
Figure 8. Typical charging and decay curves obtained with the concentric cylinder flow apparatus.

Reagent Toluene

- $\frac{R_i}{R_o} = 0.510$
- Bob Speed = 400 rpm
- $C_K = 464.5$ pF
- $V_F = 19.5$ volts
\[ \frac{V}{V_f} = 1 - e^{-t/\tau_s} \]  
\[ \text{(41)} \]

where \( V_f \) is the voltage across the capacitor at infinite time (the steady-state electrostatic charging potential) and \( \tau_s \) is the relaxation time of the system. The relaxation time of the liquid as given by Equation (19)

\[ \tau = \varepsilon \varepsilon_0 / \kappa \]  
\[ \text{(19)} \]

is inversely proportional to the conductivity for each particular hydrocarbon. The decay behavior of the system is similarly given by:

\[ V = V_f e^{-t/\tau_s} \]  
\[ \text{(42)} \]

The experimental charging and decay curves were symmetrical as predicted by Equations (41) and (42); however, \( V(t = 0) \) was not identically equal to zero. A small potential on the order of +0.1 volts was observed with the quiescent liquid. This zero speed potential \( V(0) \), induced an asymmetry in the charging and decay curves, particularly with runs for which \( V_f \) was relatively small.

At constant speed it was found that the measured steady-state charging potential was independent of the capacitance across which the potential was measured. A typical set of results are shown in Table V.

It was also found that charging occurred only when the bob was electrically grounded. If the bob was electrically insulated by
TABLE V
The Effect of the Applied Capacitance on the Steady-State Charging Potential

liquid = reagent grade toluene

\[ \frac{R_i}{R_o} = 0.647 \]

bob speed = 400 rpm

\[ \kappa = 4.51 \times 10^{-14} \Omega^{-1} \text{ cm}^{-1} \]

<table>
<thead>
<tr>
<th>( C_K ) (pF)</th>
<th>( V_f ) (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>202.</td>
<td>29.0</td>
</tr>
<tr>
<td>464.5</td>
<td>26.7</td>
</tr>
<tr>
<td>1007.5</td>
<td>28.2</td>
</tr>
<tr>
<td>3000.0</td>
<td>28.2</td>
</tr>
</tbody>
</table>
utilization of a teflon cover, the charging potential remained constant at the observed value of V(O). This observation, together with the observed independence of the charging potential on the applied capacitance, indicates that two opposing mechanisms of charge transport are operating; convection and conduction. When the charge generation in the liquid is of equal magnitude to the charge dissipation caused by back conduction through the resulting potential, then no net current flows through the liquid and a steady-state charging potential is observed. The details of the mechanism by which charge generation occurs is not elucidated by these observations; however, it is necessary to conclude that the grounded bob acts as an electron source or sink for the charging mechanism.

The dependence of the steady-state charging potential on bob speed was measured with both reagent grade toluene and m-xylene, for three different size bobs, i.e. R_i/R_o equal of 0.510, 0.647, and 0.843. The results obtained for toluene are shown in Figures 9, 10, and 11. The charging potential was found to depend linearly on the bob speed for each value of R_i/R_o. The results obtained for m-xylene are shown in Figures 12, 13, and 14. The charging potential was again found to depend linearly on the bob speed. The slope of the best line passing through the experimental points of a plot of V_f versus bob speed represents the sensitivity of V_f to flow velocity. We will define:

\[ \gamma \equiv \text{charging sensitivity (volt/rpm)} \]

The calculated values of \( \gamma \) for both toluene and m-xylene are shown in
Figure 9 Graph of Steady-State Charging Potential vs Bob Speed for Reagent Grade Toluene

\[ k = 5.18 \times 10^{-14} \text{ cm}^{-1} \]
\[ C = 1007.5 \text{ pF} \]
\[ Ri/Ro = 0.51 \]
Figure 10 Graph of Steady State Charging Potential vs Bob Speed for Reagent Grade Toluene.

\[ K = 3.75 \times 10^{-14} \text{ cm}^{-1} \]
\[ C = 200 \text{ pF} \]
\[ R_i / R_o = 0.647 \]
Figure 11 Graph of Steady-State Charging Potential vs Bob Speed for Reagent Grade Toluene
Figure 12 Graph of Steady-State Charging Potential vs Bob Speed for Reagent Grade m-Xylene

\[ K = 1.8 \times 10^{-13} \text{ cm}^{-1} \]
\[ C = 464.5 \text{ pF} \]
\[ \frac{R_i}{R_o} = 0.51 \]
Figure 13 Graph of Steady-State Charging Potential for Reagent Grade m-Xylene

\[ K = 3.55 \times 10^{-13} \text{ cm}^{-1} \]

\[ C = 200 \text{ pF} \]

\[ \frac{R_i}{R_o} = 0.647 \]
Figure 14 Graph of Steady-State Charging Potential vs Bob Speed for Reagent Grade m-Xylene
Table VI.

These results, in concert with some elementary dimensional analysis, suggest a relation of the form:

\[
\frac{\gamma}{(1 - \frac{R_i}{R_o})} \frac{\kappa}{\sigma} = f\left(\frac{\omega R_o^2}{\nu}\right)
\]  

(43)

where

- \( V_f \) = steady-state charging potential (volts)
- \( \omega \) = angular velocity (sec\(^{-1}\))
- \( R_i, R_o \) = inner and outer radius (cm)
- \( \kappa \) = electrical conductivity (\( \Omega^{-1}\) cm\(^{-1}\))
- \( \sigma \) = surface charge density (C/cm\(^2\))
- \( \nu \) = kinematic viscosity (cm\(^2\)/sec)
- \( \omega R_o^2/\nu \) = Reynolds number (dimensionless)

Furthermore, since it appears that the Reynolds number dependency is small, we can write:

\[
\frac{\gamma}{(1 - \frac{R_i}{R_o})} \frac{\kappa}{\sigma} \approx \text{constant}
\]  

(44)

The surface charge density, \( \sigma \), is the net charge of the fixed layer of adsorbed, ionic impurities within the electric double layer at the solid-liquid interface. A theoretical expression for \( \sigma \) is given by Equation (83) in Appendix A. If it is assumed that the zeta-potential is constant over the range of conductivities studied, then the surface charge density is proportional to \( \kappa^{1/2} \) and the quantity \( \gamma \kappa^{1/2} / (1 - R_i/R_o) \) should be constant. A test of this hypothesis is shown in Table VI.
### TABLE VI

The Dependence of the Charging Sensitivity On Gap Width and Conductivity

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$R_i/R_o$</th>
<th>$\gamma$ (volts/rpm)</th>
<th>$\kappa (\Omega^{-1} \text{cm}^{-1})$</th>
<th>$10^8 \times \sqrt{\kappa(1-R_i/R_o)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>0.510</td>
<td>0.112</td>
<td>$5.18 \times 10^{-14}$</td>
<td>5.21</td>
</tr>
<tr>
<td></td>
<td>0.647</td>
<td>0.0521</td>
<td>$3.75 \times 10^{-14}$</td>
<td>2.87</td>
</tr>
<tr>
<td></td>
<td>0.843</td>
<td>0.0284</td>
<td>$4.51 \times 10^{-14}$</td>
<td>3.84</td>
</tr>
<tr>
<td>m-xylene</td>
<td>0.510</td>
<td>0.0291</td>
<td>$1.80 \times 10^{-13}$</td>
<td>2.52</td>
</tr>
<tr>
<td></td>
<td>0.647</td>
<td>0.0362</td>
<td>$3.55 \times 10^{-13}$</td>
<td>6.13</td>
</tr>
<tr>
<td></td>
<td>0.843</td>
<td>0.00876</td>
<td>$1.80 \times 10^{-13}$</td>
<td>2.37</td>
</tr>
</tbody>
</table>
The constancy is remarkably good considering the uncertainties inherent in the measured quantities.

Although the results are compatible with Equation (44), the actual dependence of $\sigma$ on conductivity should be determined experimentally.

The surface charge density may be obtained independently through measurements of the double layer capacity (Appendix A). The techniques which have been utilized to measure this capacity in electrolytic solutions (minimum concentrations studied are of the order $10^{-7}$ N), rely on electronic circuits which in essence model the double layer as a capacitance in parallel with a resistance (Appendix B). As in conductivity measurements of hydrocarbon liquids, it is not feasible to employ ac measurements for the determination of the double layer capacity, since the relaxation time of the liquid is greater than the cycle time of the ac current (Section IIIC). Therefore, it is necessary that dc be used for measurements of the double layer capacity in hydrocarbon liquids. Unfortunately there have been no attempts reported in the literature of measuring the double layer capacity in hydrocarbon solutions. Furthermore, polarization effects would undoubtedly complicate any means of dc measurement.

The effect of conductivity on the charging phenomenon was studied by varying the concentration of calcium dodecyl sulfo succinate (CDS) in LiChrosolv toluene (MCB Manufacturing Chemists, Inc.). CDS, the less active salt found in Shell ASA-3, was donated in pure form as a solution in xylenes by Shell Chemical United Kingdom Limited. Since ASA-3 undoubtedly possesses complex mixture properties, it was logical to isolate the effect of only one of its constituents. The specific lot
The exact concentration of CDS in xylene was not reported by Shell and therefore all of the dilutions are given in ppm (volume %) of the original solution. Prior to each run, the conductivity was measured as described in Section IIID. The steady-state charging potential was measured as a function of bob speed for CDS concentrations ranging between 0 and 1 ppm (see Figures 15 through 23). The ratio $R/R_0$ was equal to 0.647 for all runs. A least squares analysis was carried out with the linear portion of each curve in order to determine the charging sensitivity, $\gamma$ (see Table VII).

The effect of CDS concentration on measured conductivity is shown in Figure 24. For conductivities greater than approximately $4 \times 10^{-14}$ ohm$^{-1}$ cm$^{-1}$, the dependence on concentration was found to be a linear one. A semi-log plot (Figure 25) of these results allowed further conclusions to be drawn. For very low concentrations of CDS, the conductivity decreased to a minimum; approximately one third the value obtained for pure toluene. As the concentration of CDS was further increased, the conductivity rose to its initial value and continued to increase linearly with CDS concentration.

The conductivity of the 0.07 ppm solution was found to be unchanged from the value obtained for pure toluene. The charging potential, however, reversed polarity from positive to negative. The polarity
Figure 15 Graph of Steady-State Charging Potential vs Bob Speed for Pure Lichrosolve Grade Toluene

\[ Ri / Ro = 0.647 \]
\[ K = 3.95 \times 10^{14} \text{n}^{-1} \text{cm}^{-1} \]
\[ \gamma = +0.0249 \text{ volt/rpm} \]
Figure 16 Graph of Steady-State Charging Potential vs Bob Speed for a 0.07 ppm (Vol %) Solution of CDS in Toluene

\[ -V_f (\text{Volts}) \]

-85-

\[ \frac{R_i}{R_o} = 0.647 \]

\[ K = 4.05 \times 10^{-14} \]

\[ \gamma = -0.010 \text{ volt/ rpm} \]
Figure 17 Graph of Steady-State Charging Potential vs Bob Speed for a 0.14 ppm (Vol %) Solution of CDS in Toluene

$\frac{R_i}{R_o} = 0.647$

$K = 1.44 \times 10^{-14} \text{ cm}^{-1}$

$\gamma = -0.0441 \text{ volt/rpm}$
Figure 18 Graph of Steady-State Charging Potential vs Bob Speed for a 0.18 ppm (Vol %) Solution of CDS in Toluene.

\[
\text{SPEED (rpm)}
\]

\[
-\frac{V_f}{\text{Volts}}
\]

\[
\frac{R_i}{R_o} = 0.647
\]

\[
K = 1.45 \times 10^{-14} \text{ cm}^{-1}
\]

\[
\gamma = -0.0299 \text{ volt / rpm}
\]
Figure 19 Graph of Steady-State Charging Potential vs Bob Speed for a 0.21 ppm (Vol %) Solution of CDS in Toluene

\[ \frac{R_i}{R_o} = 0.647 \]

\[ k = 1.21 \times 10^{14} \text{ cm}^{-1} \text{n}^{-1} \]

\[ \gamma = -0.0267 \text{ volt/rpm} \]
$\frac{R_i}{R_o} = 0.647$

$K = 2.24 \times 10^{-14} \text{cm}^{-1}$

$\gamma = -0.0210$

Figure 20 Graph of Steady-State Charging Potential vs Bob Speed for a 0.32 ppm (Vol %) Solution of CDS in Toluene
Figure 21 Graph of Steady-State Charging Potential vs Bob Speed for a 0.42 ppm (Vol %) Solution of CDS in Toluene

\[ Ri / Ro = 0.647 \]
\[ K = 1.32 \times 10^{-13} \text{ cm}^{-1} \]
\[ \gamma = -0.0376 \text{ volt / rpm} \]
Figure 22 Graph of Steady State Charging Potential vs Bob Speed for a 0.70 ppm (Vol%) Solution of CDS in Toluene
Figure 23 Graph of Steady State Charging Potential vs Bob Speed for a 1.0 ppm (Vol %) Solution of CDS in Toluene
TABLE VII

The Effect of Calcium Dodecyl Sulfosuccinate On the Charging Sensitivity

\[ C_K = 202 \text{ pF, } R_i/R_0 = 0.647 \]

<table>
<thead>
<tr>
<th>ppm (vol.%) CDS in Toluene</th>
<th>( \kappa \left( \Omega^{-1} \text{ cm}^{-1} \right) )</th>
<th>( \gamma ) (volt/rpm)</th>
<th>( 10^8 \times \gamma^{1/2} \left( 1-R_i/R_0 \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 3.95 \times 10^{-14} )</td>
<td>+0.0249</td>
<td>1.40</td>
</tr>
<tr>
<td>0.07</td>
<td>( 4.05 \times 10^{-14} )</td>
<td>-0.0101</td>
<td>0.576</td>
</tr>
<tr>
<td>0.14</td>
<td>( 1.44 \times 10^{-14} )</td>
<td>-0.0441</td>
<td>1.50</td>
</tr>
<tr>
<td>0.18</td>
<td>( 1.45 \times 10^{-14} )</td>
<td>-0.0299</td>
<td>1.01</td>
</tr>
<tr>
<td>0.21</td>
<td>( 1.21 \times 10^{-14} )</td>
<td>-0.0267</td>
<td>0.832</td>
</tr>
<tr>
<td>0.32</td>
<td>( 2.24 \times 10^{-14} )</td>
<td>-0.0210</td>
<td>0.890</td>
</tr>
<tr>
<td>0.42</td>
<td>( 1.32 \times 10^{-13} )</td>
<td>-0.0376</td>
<td>3.87</td>
</tr>
<tr>
<td>0.70</td>
<td>( 4.72 \times 10^{-13} )</td>
<td>+0.0131</td>
<td>2.55</td>
</tr>
<tr>
<td>1.0</td>
<td>( 8.52 \times 10^{-13} )</td>
<td>+0.0176</td>
<td>4.66</td>
</tr>
</tbody>
</table>
Figure 24 Graph of Conductivity vs ppm (Vol %) Calcium Dodecylsulfosuccinate in Lichrosolv Grade Toluene
Figure 25 Graph of Log Conductivity vs ppm (Vol %) Calcium Dodecylsulfosuccinate in Lichrosolve Grade Toluene
remained negative until a conductivity of approximately $5 \times 10^{-13}$ ohm$^{-1}$ cm$^{-1}$ was reached and then reverted back to its original value. The quantity $|\gamma| \cdot \kappa^{\frac{1}{2}}/(1 - R_i/R_o)$ was calculated as suggested by Equations (44) and (83), and found to be approximately constant for conductivities less than $4 \times 10^{-14}$ $\Omega^{-1}$ cm$^{-1}$. For greater conductivities, the value of $|\gamma| \cdot \kappa^{\frac{1}{2}}/(1 - R_i/R_o)$ increased about four fold in magnitude as the charging potential reversed polarity (see Table VII). This observed change in magnitude falls in the steep transition region of Figure 25. It would seem reasonable to postulate that a change in the mechanism has occurred in this region. The transition may be attributed to a change from one "active" species to another as is suggested by the observed reversal of polarity. It is unknown if these results may be generalized to all liquids or whether the observed transition is simply due to a competition between two different ionic species, perhaps opposite in polarity. It is interesting to note, however, that beyond this transition region, the values of the quantity $|\gamma| \cdot \kappa^{\frac{1}{2}}/(1 - R_i/R_o)$ are of similar magnitude to those reported in Table VI.

D. Theoretical Considerations

Any development of a theoretical model for explaining the charging phenomenon observed with the concentric cylinder apparatus required a knowledge of the following characteristic quantities. First, it is important to recognize whether fluid flow is in the laminar or turbulent regime, as turbulence enhances mass transfer rates substantially. Secondly, it is essential to have a feeling for the relative order of magnitude of the viscous sublayer thickness and the diffuse layer thickness. For the case when $\delta/\delta_z$, the free charge density in the
double layer is not influenced by turbulent flow; however, for the case \( \delta > \delta_k \) the free charge is distributed into the turbulent region. The former condition usually applies to relatively high conductivities, whereas the latter applies to relatively low conductivities. Thirdly, the total ion concentration in the bulk solution can be obtained from a knowledge of the conductivity. Lastly, the surface charge density can be estimated by postulating the double layer potential, integrating the free charge density over the diffuse layer, and applying charge neutrality conditions. Together with a knowledge of the diffuse layer thickness, the free charge density can be estimated and compared with the bulk ion concentration.

The fluid flow between two cylinders, of which the inner one is rotating, is characterized by three flow regimes. At very low rotation speeds, laminar flow with concentric streamlines is observed. This simple flow pattern becomes unstable at higher rotation speeds resulting in the superposition of cellular motion (Taylor vortices) upon the flow around the inner cylinder. At still higher rotation speeds, the flow becomes turbulent and is characterized by rapid and random fluctuations of velocity, including a fluctuating component in the direction from one cylinder to the other. Therefore, in the consideration of ion transport across the annulus, the rate of mass transfer can be enhanced considerably by turbulent flow conditions.

The flow between rotating cylinders is characterized by two dimensionless quantities: the ratio of the gap width \( (R_o - R_i) \) to the inner radius \( R_i \); and the Reynolds number which is given by
where \( \omega \) = speed of rotation (radian/sec)
\( \nu \) = kinematic viscosity of the liquid (cm\(^2\)/sec)

For small values of \((R_o - R_i)/R_i\), simple laminar flow is stable for a Taylor number

\[
N_{Re} = \frac{(R_o - R_i) \omega R_i}{\nu} \tag{45}
\]

less than 1700. By means of empirical correlations (Taylor, 1936), it is possible to calculate the rotation speed at which the transition into fully developed turbulent flow occurs. Although the correlations pertain to infinite coaxial cylinders, they allow us to obtain an estimate for our system. We will consider the smallest gap widths studied \((R_i/R_o = 0.843)\) as the transition into turbulent flow occurs at lower rotation speeds for larger gap widths. With \((R_o - R_i)/R_i = 0.187\), turbulent flow prevails for Reynolds numbers greater than 3960 or Taylor numbers greater than \(3 \times 10^6\). The physical properties of toluene at room temperature are given in Table VIII. The speed at which the flow is turbulent is calculated with Equation (46) as approximately equal to 75 rpm. The results obtained for the charging potentials versus bob speed exhibit insignificant potentials at bob speeds less than 50 rpm (Figures 9-23). Furthermore, the linear dependence of charging potential on bob speed is usually not observed at such low speeds. These
TABLE VIII
Physical Properties of Toluene at 20°C

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon )</td>
<td>2.38</td>
</tr>
<tr>
<td>( \rho )</td>
<td>0.8669 g/cm(^3)</td>
</tr>
<tr>
<td>( \mu )</td>
<td>(5.9 \times 10^{-3}) g/cm-sec</td>
</tr>
<tr>
<td>( \nu )</td>
<td>(6.81 \times 10^{-3}) cm(^2)/sec</td>
</tr>
</tbody>
</table>
observations seem to indicate that the charging phenomenon is observed only when turbulent flow conditions prevail.

Even under conditions of turbulent flow, there is a small layer near the wall for which Newton's law of viscosity can be used to describe the flow conditions. This region, known as the viscous sublayer, is given by

\[ \delta_\ell = \frac{\alpha \nu}{u_\tau} \]  

(47)

where \( \delta_\ell \) = viscous sublayer thickness (cm)
\( \alpha \) = a constant (assume \( \alpha \approx 1 \))
\( u_\tau = \sqrt{\tau_w/\rho} \) (cm/sec)
\( \tau_w \) = wall shear stress (g/cm-sec\(^2\))
\( \rho \) = liquid density (g/cm\(^3\))

The viscous sublayer thickness for turbulent flow between two cylinders can be estimated from experimental correlations obtained for infinite coaxial cylinders (Dorfman, 1963). For a representative bob speed of 300 rpm and \( R_i/R_o = 0.843 \), we find for toluene (Table VIII):

\[ \tau_w \approx 15.3 \text{ g/cm-sec}^2 \]  

(48)

\[ \delta_\ell \approx 1.6 \times 10^{-3} \text{ cm} \]  

(49)

The Debye length is an approximate measure of the thickness of the electric double layer (see Appendix A). The Debye length for a
univalent electrolyte is given by

\[ \delta = \left( \frac{\varepsilon \varepsilon_0 D}{\kappa} \right)^{1/2} \]  

(50)

where  
\( \delta = \) double layer thickness (cm)  
\( \varepsilon_0 = \) absolute dielectric constant of vacuum  
\( = 8.854 \times 10^{-14} \text{ A-sec/V-cm} \)  
\( \varepsilon = \) relative dielectric constant of the hydrocarbon liquid  
\( D = \) diffusivity of the ions (cm\(^2\)/sec)  
\( \kappa = \) electrical conductivity (\(\Omega^{-1}\) cm\(^{-1}\))

If we assume a value of \(1 \times 10^{-5} \text{ cm}^2/\text{sec}\) for the ion diffusivity, the following expression is obtained for the double layer thickness

\[ \delta = 9.41 \times 10^{-10} (\varepsilon/\kappa)^{1/2} \]  

(51)

Thus for toluene \((\varepsilon = 2.38)\) at 300 rpm, we find:

\[ \delta/\delta_\ell > 1 \text{ for } \kappa < 8 \times 10^{-13} \Omega^{-1} \text{ cm}^{-1} \]  

(52)

\[ \delta/\delta_\ell < 1 \text{ for } \kappa > 8 \times 10^{-13} \Omega^{-1} \text{ cm}^{-1} \]  

(53)

For the range of conductivities studied with the concentric cylinder flow apparatus, we find Equation (52) to apply. Since \(\delta_\ell\) decreases at higher rotation speeds, it can be concluded that the double layer thickness is greater than the viscous sublayer thickness over most of the
experimental conditions studied.

An estimate of the bulk ion concentration can be obtained from Equation (54) where the ions are assumed to come from the equilibrium dissociation of dissolved solute impurities present in the hydrocarbon liquid.

\[ C_o = \frac{RT \kappa}{2Dz^2 F^2} \]  

(54)

where \( C_o \) = bulk ion concentration (moles/cm\(^3\))

\( z \) = charge number of the ions

\( F \) = Faraday's constant (96,500 C/mole)

\( R \) = gas constant (8.31 V-C/mole-°K)

\( T \) = absolute temperation (°K)

A reasonable estimate of the ion diffusivity is \( 10^{-5} \) cm\(^2\)/sec. A value of \( \pm 1 \) for the charge number is assumed because it is unlikely that multi-charged ions could exist in a hydrocarbon liquid. The ion concentration in terms of conductivity is given by:

\[ C_o = 1.33 \times 10^{-2} \kappa \]  

(55)

If we choose a representative conductivity for toluene equal to \( 5 \times 10^{-14} \) ohm\(^{-1}\) cm\(^{-1}\), the bulk ion concentration assumes the following value:

\[ C_o \approx 6.7 \times 10^{-15} \text{ moles/cm}^3 \]  

(56)
The ion concentration is extremely low as expected.

Consider the electric double layer illustrated in Figure 27. The surface charge density of the fixed layer is related to the free charge density of the diffuse layer by

\[ \sigma = -\int_0^\infty q(x) \, dx \]  

(57)

where \( \sigma \) = surface charge density (C/cm\(^2\))

\( q(x) \) = free charge density (C/cm\(^3\))

\( x \) = distance from the solid surface (cm)

The Poisson equation provides a relationship between \( \phi(x) \) and \( q(x) \):

\[ q(x) = -\varepsilon \varepsilon_0 \frac{d^2 \phi(x)}{dx^2} \]  

(58)

where \( \phi(x) \) = electric potential in the double layer

Equations (57) and (58) are combined:

\[ \sigma = \varepsilon \varepsilon_0 \int_0^\infty \frac{d^2 \phi(x)}{dx^2} \, dx \]  

(59)

Applying the condition that \( d\phi(x)/dx \to 0 \) as \( x \to \infty \), the final result for the surface charge density is obtained:

\[ \sigma = -\varepsilon \varepsilon_0 \left( \frac{d\phi(x)}{dx} \right)_{x=0} \]  

(60)
Thus, \( \sigma \) can be obtained from the initial slope of the potential function.

A crude estimate of the surface charge density for our system may be obtained from the electric potential experimentally observed when the bob is stationary. Since the bob is grounded, the measured potential \( V(0) \) should correspond almost entirely to the potential difference, \( \Delta \phi \), across one double layer. If the double layer is modeled as a parallel plate capacitor where \( \delta \) is the distance separating the oppositely charged plates, then the surface charge density is simply given by:

\[
\sigma = \varepsilon \varepsilon_0 \frac{\Delta \phi}{\delta} \quad (61)
\]

Upon substitution of Equation (50) into Equation (61), we obtain:

\[
\sigma = \left( \frac{\varepsilon \varepsilon_0 \kappa}{D} \right)^{1/2} \Delta \phi \quad (62)
\]

An order of magnitude estimate of \( \sigma \) can be obtained by assuming \( V(0) \sim 0.10 \) volts (as suggested by experimental observation), \( D \sim 10^{-5} \) cm\(^2\)/sec, \( \kappa \sim 10^{-14} \) \( \Omega \)^\(-1\) cm\(^{-1}\), and \( \varepsilon \sim 2.0 \).

\[
\sigma \sim 10^{-12} \text{ C/cm}^2 \quad (63)
\]

An approximate expression for the free charge density, \( q \), in the diffuse layer can be derived by dividing Equation (50) into Equation (62).

\[
q = \frac{\kappa}{D} \Delta \phi \quad (64)
\]
Upon substitution of the numerical quantities given above, we obtain an order of magnitude estimate for the free charge density.

$$q \sim 10^{-10} \text{ C/cm}^2$$  \(65\)

The free charge density in the diffuse layer can be compared to the total charge concentration in the bulk solution by solving for the ratio $q/FC_o$, where $q$ is given by Equation (64) and $C_o$ by Equation (54).

$$q/FC_o = 2z^2F\Delta \phi/RT \sim 10$$  \(66\)

At room temperature the free charge density of the diffuse layer is found to be approximately an order of magnitude greater than the bulk solution charge density. This result is in agreement with the physical nature of the double layer structure.

E. Conclusion

The charging potential was found to obey a relationship of the form $V_f \propto \omega R_o (1 - R_i/R_o)/\kappa^{1/2}$. The conductivity dependence is in agreement with the theoretical expression for the surface charge density which predicts that $\sigma \propto \kappa^{1/2}$ at constant zeta-potential. The dependence of the charging potential on the rotation frequency can be attributed to the relative magnitude of the fluctuating velocity component normal to the metal surfaces, because the measured potential results from a net charge flux in the same direction. The linear dependence on gap width is not surprising since the resistance of the liquid is proportional to the gap width; therefore, if the current flux is independent of the bob
size, the charging potential is proportional to the resistance of the liquid, and thus the gap width.

An interesting result obtained with this flow device is that aliphatic hydrocarbons did not exhibit any charging behavior. This cannot be attributed to the inherently lower conductivities of these hydrocarbons, since the relative magnitude of the double layer and viscous sub-layer thickness does not change within the range of measured conductivities ($\kappa < 8 \times 10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$). The natural conductivity of benzene is due to an electron transfer mechanism (Forster, 1962), and therefore, it seems reasonable to assume that toluene and xylenes possess a similar mechanism. This electron transfer process is usually observed during measurements of conductivity with the direct current method. Since large potentials (of the order of 200 volts) are applied across the cell electrodes, it is likely that the applied potential activates the electron transfer mechanism. No such activation energy, however, is supplied by the concentric cylinder flow device. Unfortunately, the identity of the charge carriers (i.e. electrons, ions, or both) and the mechanism by which they are generated and transported through the hydrocarbon solution have not been elucidated by this experimental work.
V. Appendices

A. The Gouy-Chapman Theory of the Electric Double Layer

The earliest model of the double layer was given by Helmholtz (1879) who postulated a layer of ions at the solid surface and a rigidly held layer of oppositely charged ions in the solution (see Figure 26). The Helmholtz double layer is equivalent to a simple parallel plate capacitor. Gouy (1910) extended Helmholtz' concept of the double layer structure to the extent of assuming a diffuse rather than a compact layer, because a compact layer would be destroyed by the thermal motion of the ions (see Figure 27).

The theory of a diffuse double layer with a statistical distribution of ions in the electric field was given independently by Gouy (1910) and Chapman (1913). The Gouy-Chapman theory bears close resemblance to the Debye-Hückel (1923) theory of strong electrolytes, which it preceded by a decade. Consider a one-dimensional and continuous system as shown in Figure 27, where $x$ is the distance measured from the solid surface. Two equations exist which relate the free charge density, $q$, and the electric potential $\phi(x)$. The first is the Boltzmann distribution given by:

$$ q = F \sum z_j C_j^0 \exp\left(-z_j \frac{F}{RT} \phi\right) \quad (67) $$

where $C_j^0$ = concentrations of ions $j$ in the bulk solution
$z_j$ = ionic valence of ions $j$
$\phi$ = the potential at $x$ with respect to the potential in the bulk
Figure 26. The Helmholtz model of the electric double layer.

Figure 27. The Gouy-Chapman model of the electric double layer.
of the solution, which is arbitrarily set equal to zero.

\[ F = \text{Faraday's constant (96,500 C/mole)} \]

\[ R = \text{gas constant (8.31 V-C/mole-°K)} \]

\[ T = \text{absolute temperature (°K)} \]

The second is the Poisson equation

\[ q = \frac{-\varepsilon}{\varepsilon_0} \nabla^2 \phi \quad (68) \]

which for our planar surface \( \frac{\partial^2 \phi}{\partial y^2} = \frac{\partial^2 \phi}{\partial z^2} = 0 \) is equal to:

\[ q = \frac{-\varepsilon}{\varepsilon_0} \frac{d^2 \phi}{dx^2} \quad (69) \]

The combination of Equations (67) and (69) yields the following differential equation for \( \phi \).

\[ \frac{d^2 \phi}{dx^2} = -\frac{1}{\varepsilon \varepsilon_0} F \sum z_j C_j^0 \exp(-\frac{z_j F}{RT}) \phi \quad (70) \]

The corresponding boundary conditions are given by:

1. \( \text{as } x \to \infty, \phi \to 0 \text{ and } d\phi/dx \to 0 \)
2. \( \text{at } x = 0, \phi = \zeta \)

where \( \zeta \) is known as the zeta potential. Equation (70) can be solved assuming that there exists a constant effective dielectric constant \( \varepsilon \). Although this assumption is invalid because of dielectric saturation in
the double layer, the consequences are not substantial.

For the case of a symmetrical binary electrolyte with $z_+ = -z_- = z$, Equation (70) becomes:

$$\frac{d^2\phi}{dx^2} = \frac{1}{\varepsilon \varepsilon_0} z F C_0 [\exp(-z F \phi/RT) - \exp(z F \phi/RT)]$$

(71)

or equivalently:

$$\frac{d^2\phi}{dx^2} = \frac{2z F C_0}{\varepsilon \varepsilon_0} \sinh(z F \phi/RT)$$

(72)

where $C_0$ is equal to the total ion concentration in the bulk solution.

Following the method of Verwey and Overbeek (1948), the following variable transformations are defined:

$$\theta = z F \phi/RT$$

(73)

$$\theta_0 = z F \xi/RT$$

(74)

$$\beta^2 = 1/\varepsilon^2 = \frac{2C_0 F^2 z^2}{\varepsilon \varepsilon_0 RT}$$

(75)

$$\xi = \beta x$$

(76)

Equation (72) thus becomes:

$$\frac{d^2\theta}{d\xi^2} = \sinh(\theta)$$

(77)

The transformed boundary conditions are given by:

(1) as $\xi \to \infty$, $\theta \to 0$ and $d\theta/d\xi \to 0$
Upon integrating Equation (77) once, we obtain

\[ \frac{d\theta}{d\xi} = -2 \sinh(\theta/2) + C_1 \] (78)

Application of boundary condition (1) yields \( C_1 = 0 \). Upon integrating again, we obtain:

\[ \ln \frac{\exp(\theta/2) - 1}{\exp(\theta/2) + 1} = -\xi + C_2 \] (79)

where \( C_2 \) is found from boundary condition (2).

\[ C_2 = \ln \frac{\exp(\theta_0/2) - 1}{\exp(\theta_0/2) + 1} \] (80)

Therefore, the final solution is given by:

\[ \exp(\theta/2) = \frac{\exp(\theta_0/2) + 1 + \{\exp(\theta_0/2) - 1\} \exp(-\xi)}{\exp(\theta_0/2) + 1 - \{\exp(\theta_0/2) - 1\} \exp(-\xi)} \] (81)

Although Equation (81) appears rather complex, it is found on plotting to give an approximately exponential decrease in \( \phi \) through the double layer as shown in Figure 28.

The charge on the solid surface per unit area, \( \sigma \), is related to \( \phi \) by Equation (60), which in terms of the transformed variables is equal to:

\[ \sigma = \frac{-\varepsilon \varepsilon_0}{z F} \frac{RT}{\beta} \left( \frac{d\theta}{d\xi} \right)_{\xi = 0} \] (82)
Figure 28. The potential distribution in the diffuse layer predicted by the Gouy-Chapman theory ($\zeta = +0.100$ volts, $z = 1$, and $T = 298^\circ$K).
Upon substitution of Equation (81) into Equation (82), we obtain

\[ \sigma = \frac{2e \varepsilon_0 RT \beta}{z F} \sinh(\theta_0/2) \]  

(83)

The differential capacity of the diffuse layer is thus given by

\[ C_d = \left( \frac{d\sigma}{d\zeta} \right)_{\mu,T,P} = \frac{e \varepsilon_0}{\delta} \cosh(\theta_0/2) \]  

(84)

where \( \mu \) is the chemical potential. Equation (84) indicates that the diffuse-layer capacity is proportional to the square root of the ionic strength, because of the composition dependence of the Debye length \( \delta \).

The diffuse-layer capacity of most smooth metal surfaces in aqueous systems has a value ranging from about 10 to 40 \( \mu F/cm^2 \) depending upon the potential \( \zeta \).

Measurements of the diffuse-layer capacity (Appendix B) are often used to obtain experimental data about double layers. From a knowledge of this capacity, Equations (83) and (84) can be applied to determine the surface charge density of the electrode surface.

B. Methods for the Measurement of the Differential Double Layer Capacity in Aqueous Electrolytic Solutions

Two distinct methods for the measurement of double layer capacity have been described in the literature, namely, the charging curve method and the impedance bridge method. Both of these methods are based on disturbing the steady-state condition of an electrochemical reaction in a cell and analyzing the relaxation behavior of the system in order to determine the double layer capacity.

The charging curve methods are based upon the charging of the double
layer by imposing either an applied potential or current, and therefore are termed potentiostatic and galvanostatic, respectively. In the potentiostatic method (Laitinen and Roe, 1960) a constant, current-independent potential is applied as a step function to a cell at equilibrium, and the decay behavior of the current is recorded oscillographically. In the absence of a charge transfer reaction, the equivalent circuit for a cell consisting of a small electrode and a much larger electrode is represented by the double layer capacity \( C_d \) of the small electrode, in series with the total resistance \( R_T \) composed of the electrolytic resistance and series circuit resistance. The charging current \( i_C \) is given by:

\[
i_C = \frac{V}{R_T} \exp(-t/R_T \cdot C_d)
\]  

(85)

where \( V \) is the magnitude of the voltage step. A plot of \( \ln(i_C) \) against time has an intercept of \( V/R_T \) and a slope of \(-1/R_T \cdot C_d\), from which the double layer capacity can be determined. The linearity of the plot constitutes a criterion for the validity of the equivalent circuit model.

In the galvanostatic method, the double layer is charged or polarized by applying a dc pulse of constant current \( I \) across the electrode being tested. The resulting change in potential \( \Delta V \) is observed as a function of time. The potential-time curve is called a charging or polarization curve. The initial slope of the curve is given by

\[
(dV/dt)_{t=0} = I \cdot C_d/A
\]

(86)

where \( A \) is equal to the apparent area of the electrode. The differential
double layer capacity is then calculated from Equation (86).

All methods of direct-current charging assume that any current supplied to the electrode is involved in charging the electrode double layer, i.e. an ideally polarizable interface is considered. Polarization current can be in the form of direct current or pulsed current. Brodd and Hackermann (1957) measured double layer capacities from potential time traces observed when a square wave signal was applied to the electrode. McMullen and Hackermann (1959) used an electric analog of the metal solution interface shown in Figure 29 to measure the double layer capacity. Ramaley and Enke (1965) charged the double layer by a controlled sinusoidal potential of constant amplitude. Schmid (1968) has designed a dc pulsed bridge which gave results of higher precision than a single pulsed charging method. The circuit diagram is shown schematically in Figure 30. The bridge consists of a dc pulse generator, a suitable electrochemical cell, a comparison arm made of a variable capacitor with a resistor box in parallel and in series, and an oscilloscope as a null detector. Measurement of the double layer capacity, parallel double layer resistance, and the electrolyte resistance could be achieved independently.

One of the principal limitations of the charging curve method is the very short time (on the order of one microsecond or less) and the small potential or pulse amplitudes (on the order of 5 mV) required for charging. The use of such short times and small potentials insure that the physical structure of the double layer will remain unaltered; however, limit the accuracy of the experimental technique.

The charging curve method is useful for measuring relatively large
Figure 29. An electric analog of the metal-solution interface for an aqueous electrolyte.

(McMullen and Hackerman, 1959).
Figure 30. A dc pulsed bridge for differential capacity measurements in aqueous systems. $A,A'$ are potential takeoff points. $R_e$ is the electrolyte resistance (Schmid, 1968).
capacities. When greater precision is required, an ac bridge method (Grahame, 1946) is suggested for measuring double layer capacities in aqueous systems. This impedance bridge contains the equivalent circuit of the electrode-electrolyte interface. For the most accurate measurements some form of Wagner earth arrangement is necessary (Armstrong, et al., 1968). Transformer ratio arm bridges (Nancollas and Vincent, 1961; Devanathan and Ramakrishnaiah, 1973) have also been used for measurements of the double layer capacity.

All the ac bridge methods suffer from the disadvantage that there is a frequency dependence of the measured value of the double layer capacity. With hydrocarbon liquids, ac methods are not feasible as previously discussed in Section IIIC. Further details pertaining to these methods may be obtained from the quoted references.
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Area (cm²)</td>
</tr>
<tr>
<td>C_c</td>
<td>Capacitance of the empty conductivity cell (pF)</td>
</tr>
<tr>
<td>C_DL</td>
<td>Capacitance of the electric double layer (pF)</td>
</tr>
<tr>
<td>C_d</td>
<td>Differential diffuse layer capacity (pF/cm²)</td>
</tr>
<tr>
<td>C_E</td>
<td>Internal capacitance of the electrometer (pF)</td>
</tr>
<tr>
<td>C_EX</td>
<td>Capacitance of the wires, cables, and electrometer (pF)</td>
</tr>
<tr>
<td>C_f</td>
<td>Friction factor (dimensionless)</td>
</tr>
<tr>
<td>C_j</td>
<td>Concentration of ions j in the bulk solution (moles/cm³)</td>
</tr>
<tr>
<td>C_K</td>
<td>Applied capacitance (pF)</td>
</tr>
<tr>
<td>C_L</td>
<td>Capacitance of the liquid in the conductivity cell (pF)</td>
</tr>
<tr>
<td>C_o</td>
<td>Total ion concentration in the bulk solution (moles/cm³)</td>
</tr>
<tr>
<td>C_s</td>
<td>Total capacitance of the system (pF)</td>
</tr>
<tr>
<td>C_S</td>
<td>Ion concentration at the pipe wall (moles/cm³)</td>
</tr>
<tr>
<td>C_w</td>
<td>Capacitance of wires and cables (pF)</td>
</tr>
<tr>
<td>d</td>
<td>Pipe diameter (cm)</td>
</tr>
<tr>
<td>D</td>
<td>Molecular diffusivity (cm²/sec)</td>
</tr>
<tr>
<td>E</td>
<td>Electric field strength (V/cm)</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant (96,500 C/mole)</td>
</tr>
<tr>
<td>i</td>
<td>Charging current (A)</td>
</tr>
<tr>
<td>I</td>
<td>Electric current (A)</td>
</tr>
<tr>
<td>j</td>
<td>Current density (A/cm²)</td>
</tr>
<tr>
<td>L</td>
<td>Pipe length (cm)</td>
</tr>
<tr>
<td>L_o</td>
<td>Pipe length entry correction (cm)</td>
</tr>
<tr>
<td>N_Re</td>
<td>Reynolds number (dimensionless)</td>
</tr>
<tr>
<td>N_Sc</td>
<td>Schmidt number, ν/D (dimensionless)</td>
</tr>
</tbody>
</table>
List of Symbols (Cont'd)

$N_{Ta}$ Taylor number, $\omega^2 R_i (R_o - R_i)^3/\nu^2$ (dimensionless)

$q$ Free charge density (C/cm$^3$)

$R$ Gas constant (8.31 V-C/mole °K)

$R_{DL}$ Double layer resistance ($\Omega$)

$R_L$ Resistance of the liquid in the conductivity cell ($\Omega$)

$R_S$ Total resistance of the system ($\Omega$)

$R_i$ Radius of the inner cylinder (cm)

$R_o$ Radius of the outer cylinder (cm)

$t$ Time (sec)

$T$ Absolute temperature (°K)

$u_\tau$ Reference velocity $(\tau_w/\rho)^{1/2}$ (cm/sec)

$\bar{v}$ Average flow velocity (cm/sec)

$V$ Applied potential (V)

$V_f$ Steady-state charging potential (V)

$V(0)$ Potential at $\omega = 0$ (V)

$x$ Distance from the solid surface (cm)

$z$ Charge number of the ions

$z_j$ Ionic valence of ions j

$\alpha$ Constant

$\beta$ Transformed variable, $\delta^{-1}$ (cm$^{-1}$)

$\gamma$ Charging sensitivity (V/rpm)

$\delta$ Diffuse layer thickness or Debye length, $(\tau D)^{1/2}$ (cm)

$\delta_D$ Diffusion layer thickness (cm)

$\delta_\lambda$ Viscous sublayer thickness (cm)
List of Symbols (Cont'd)

- **ε**: Relative dielectric constant (dimensionless)
- **ε₀**: Absolute dielectric constant of vacuum (8.854 x 10⁻¹⁴ A·sec/V·cm)
- **ζ**: Zeta-potential
- **θ**: Dimensionless potential, zFφ/RT
- **θ₀**: Dimensionless zeta-potential, zFζ/RT
- **κ**: Electrical conductivity (Ω⁻¹ cm⁻¹)
- **μ**: Viscosity (g/cm·sec)
- **ν**: Kinematic viscosity (cm²/sec)
- **ξ**: Dimensionless distance, βx
- **ρ**: Density (g/cm³)
- **σ**: Surface charge density (C/cm²)
- **τ**: Relaxation time, ε ε₀/κ (sec)
- **τ_S**: Relaxation time of the system (sec)
- **τ_W**: Wall shear stress (g/cm·sec²)
- **φ**: Electric potential (V)
- **ω**: Angular velocity (radians/sec)


Pearson, J.M., "Protection Against Static Electricity", Oil Gas J., 39, 140 (November, 1940).


Willis, W., "Electrical Conductivity of Some Cryogenic Fluids", Cryogenics, 6, 279 (1966).