

THE UNIVERSITY OF MANITOBA

HIGH-FIELD ELECTRIC CONDUCTION
AND ELECTROLUMINESCENCE
IN DIELECTRIC LIQUIDS

By

MOHAMED M. RASHWAN

A Thesis

submitted to the Faculty of Graduate Studies
in partial fulfillment of the requirements for the
Degree of Doctor of Philosophy

Department of Electrical Engineering

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ABSTRACT

The work presented in this thesis consists of two parts. The first part deals with high field electric conduction and the second part deals with electroluminescence in dielectric liquids. In the first part, a model based on the theory of filamentary single injection and field enhanced trapping mechanism is presented, and an expression for the high-field conduction current as a function of applied field and temperature has been derived. This model fits well the experimental results on both aliphatic and aromatic hydrocarbon liquids and explains the field dependence of the thermal activation energy for electric conduction in these liquids.

In the second part, experimental results for electroluminescence as a function of applied field, hydrostatic pressure and temperature in n-hexane, cyclohexane, chloroform, benzene, n-hexane mixed with ethyl alcohol, and carbon tetrachloride are presented. There are two contrary results in the pressure dependence. The electroluminescent intensity increases with increasing pressure for benzene, but decreases with increasing pressure for the other liquids under investigation, except carbon tetrachloride in which no light emission in the visible region has been detected at fields up to a value close to its breakdown strength. The electroluminescent intensity is temperature dependent. The light intensity is fluctuating with time even at a fixed voltage and at a fixed temperature. These electroluminescent phenomena are attributed to the impact excitation of molecules. Other effects such as electrohydrodynamic motion and

microcavity formation at higher fields which may play a role in these phenomena are also discussed.

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LIST OF MOST USED SYMBOLS

D	Diffusion coefficient of electrons
d	Gap length
E_{av}	Average electric field
E_{bd}	Breakdown strength
E_c	Electric field at the cathode
h	Planck's constant
I_T	Total conduction current
J	Current density
J_c	Current density at the cathode
J_{zo}	Current density at the center of the filament
k	Boltzmann's constant
L_v	Latent heat of vaporization
n	Concentration of electrons
q	Electronic charge
r_d	Radius of filament
T	Temperature
T_b	Boiling point of the liquid
T_o	Initial temperature of the liquid
V	Applied voltage
ϵ	Dielectric constant
μ	Mobility of electrons
λ	Average distance between traps
λ_1	Mean free path

CHAPTER 1

INTRODUCTION

Of the various properties of dielectric liquids, high-field conduction, prebreakdown phenomena and breakdown processes are of great interest and importance to electrical engineers because dielectric liquids are still one of the most important insulation media for high-voltage power apparatus. The study of these properties and the mechanisms responsible for them has been the subject of research for more than 50 years. Before 1955 most experiments were performed in transformer oil [Gemant 1950, Tropper 1961, and Kok 1961]. Later, investigators have thought that in order to explore the insight of these properties, pure liquids of simple chemical structure such as hydrocarbons, saturated and unsaturated, should be used. During the past 20 years several active groups such as Sharbaugh's group in the United States, Lewis's group and Kao's group in England, Felici's group in France, Adamczewski's group in Poland and Toriyama's group in Japan contributed greatly to the understanding of this field.

Recently, on the basis of experimental facts that electrical conduction at high fields is filamentary, which was observed by Kao and his group [Hwang and Kao 1974 and Saji and Kao 1976], Kao [1975, 1976] has formed a filamentary single injection theory for high field electric conduction and breakdown in dielectric liquids. His theory is, so far, the most successful one and it predicts well the field and temperature dependence of electric conduction current; and the temperature, pressure and

chemical structure dependence of breakdown strength in hydrocarbon liquids. His theory is based on the assumption that both the permittivity and the carrier mobility are constant for mathematical simplicity. However, Kao [1976] has pointed out that a more rigorous treatment should include the field dependence of permittivity, carrier mobility and possibly other parameters due to the effects of space charge, impurities, and electrohydrodynamic motion; and that to solve electric transport problems in dielectrics (either solids or liquids) it is more convenient to assume that the carrier concentration is controlled by the carrier injection mechanism and that the carrier mobility is controlled by the trapping and detrapping processes. The field dependent carrier mobilities in several hydrocarbon liquids (n-hexane, benzene and toluene) have been experimentally observed by Schmidt and Allen [1970], and Minday et al. [1971], and the effects of traps on carrier mobility and electric conduction have been reported by Secker and Belmont [1972] and Devins and Wei [1972]. On the basis of all these facts and concepts Kao's theory has been extended to include the field dependence of carrier mobility.

It is interesting to note that in the literature the high-field electric conduction data are very scarce. Since the publication of LaPage and DuBridge of their results on the field and temperature dependence of conduction current in toluene in 1940 and later the publication of Kao and Calderwood of their results in n-hexane and carbon tetrachloride in 1965, there is practically no other systematic data available in this field. For this reason we have measured systematically the conduction current as a function of applied field and temperature in

n-pentane, n-hexane, n-heptane (saturated hydrocarbon liquids), benzene and toluene (unsaturated hydrocarbon liquids), and also to correlate these results with our theory.

One of the interesting prebreakdown phenomena in dielectric liquids is electroluminescence. Darveniza and Tropper [1961] have observed the emission of light in transformer oil and reported that its intensity increases with increasing applied field. Since their publication in 1961, several investigators [Murooka et al. 1963 and Jones and Angeror 1966] have investigated further this phenomenon in transformer oil. However, Kao's group in England were the first to observe a similar phenomenon in pure n-hexane using an image intensifier [Smith, Kao, Calderwood and McGee 1966]. To explore this phenomenon further, a series of experiments using the same techniques adopted by Kao and his co-investigators have been performed on a number of dielectric liquids at various hydrostatic pressures and temperatures in order to study the relation of the threshold field for the onset of the light emission and the light intensity with some physical parameters of the liquids.

Before presenting our results and theory, it is desirable to review briefly the most important work relevant to this thesis in order to give a clear view of the present state of knowledge in this field. Thus, Chapter 2 will be devoted to the review. Chapter 3 will describe the experimental techniques involved in this investigation. The major work on high field electric conduction, both theoretical and experimental, is presented in Chapter 4, and that on electroluminescence in Chapter 5. The general conclusions arising from the present work are given in Chapter 6.

CHAPTER 2

REVIEW OF PREVIOUS WORK

In this chapter a brief review of the previous work on high-field conduction, prebreakdown, and breakdown phenomena in hydrocarbon liquids is presented. Although our interest is high-field phenomena in pure liquids, the presence of impurities which controls the electrical properties in liquids at low fields is also responsible for most phenomena observed at high fields. At fields lower than 10 kV cm^{-1} the conduction current rises linearly with the applied electric field and obeys Ohm's law as has been reported by Adamczewski [1969]. If the conduction is ionic and the carrier source is mainly due to thermal excitation and extraneous radiation, a sub-ohmic region would be expected to exist in which the conduction current tends towards saturation. However, such a saturation region is not precisely defined, and instead, the current is increasing slowly with the field indicating a new mechanism, possibly carrier injection from electrodes starts to become important beyond the ohmic region [Green 1955]. The following review is concentrated mainly on this non-linear region.

2.1 HIGH FIELD CONDUCTION

When applied electric fields are higher than approximately 80 kV cm^{-1} the current tends to rise non-linearly with the increase of the field, and at sufficiently high fields breakdown occurs. Typical current-field characteristics are shown in Fig. 2.1. Many investigators in this field [House 1957, Lewis 1960, Watson and Sharbaugh 1960, Kao and Calderwood 1965, and Kao 1976] have investigated the effects of applied

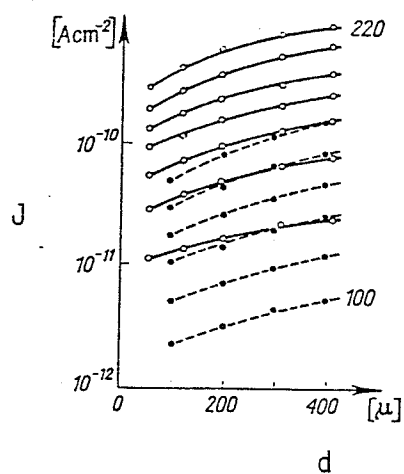


Fig. 2.1 Current density $J(\text{A cm}^{-2})$ as a function of electrode separation (μm) at various applied fields (from 100 to 220 kV cm^{-1}) for n-hexane. \circ - phosphore bronze parallel plane electrodes; \bullet - stainless steel parallel plane electrodes [after Goodwin and MacFadyen 1953].

electric field and temperature on the conduction current. They have attributed the marked increase in the conduction current with increasing applied field to the electron emission from the cathode either due to Schottky thermionic emission following the equation

$$J = a_s T^2 \exp\left\{-\frac{q(\phi - \sqrt{\frac{qE}{\epsilon}})}{kT}\right\} \quad (2.1)$$

or due to Fowler-Nordheim field emission following the equation

$$J = a E^2 \exp\left(-\frac{b}{E}\right) \quad (2.2)$$

where a_s , a and b denote constants characteristic for a given metal and surface condition and $q\phi$ is the work-function of the metal.

In general, most investigators have considered the straight line of the plot of $\ln J$ versus \sqrt{E} as the indication of the Schottky emission mechanism, and the straight line of the plot of $\ln(J/E^2)$ versus $1/E$ as the indication of the Fowler-Nordheim field emission. However, Watson and Sharbaugh [1960] have reported that their experimental results can fit well both Schottky emission equation [Eq. (2.1)] and Fowler-Nordheim cold emission equation [Eq. (2.2)].

Recently Kao [1976] has pointed out that these two equations were originally derived for electron emission from a clean metal to vacuum based on a uniform field, and it could lead to an incorrect conclusion if these two equations were used directly without being modified to correlate with the experimental current voltage characteristics of the liquid. In liquids the effects of space charge and electrode surface

conditions cannot be ignored [Kao 1976], since these modify the field distribution in the liquid gap and hence, affect the efficiency of electron emission.

The investigation of high field conduction in hydrocarbon liquids may be divided into the following areas:

- (i) the effects of solid and gaseous impurities,
- (ii) the effects of electrode materials,
- (iii) the processes occurring in the bulk of the liquid, including the effects of molecular structure, temperature and hydrostatic pressure.

In the field of electric conduction in dielectric liquids at high applied fields, the investigators are always faced by the difficulty of obtaining reproducible results. The divergence of the experimental results reported by some investigators [Green 1955, House 1957, Chong and Inuishi 1960 and Zaky et al. 1963] may be due to different methods adopted by them for treating their liquid samples and electrodes. However, Kao and Calderwood [1965] have adopted a conditioning technique which has enabled them to obtain reproducible results. With this technique the liquid sample is stressed electrically for 40 minutes at each of four or five different increasing fields. After such a step by step conditioning process with fields up to 80% of the electric breakdown strength of the sample, the conduction current is then measured 15 minutes after attaining its steady state value. Using this technique they have found that the conduction current measured is negligibly different from that measured several hours later.

2.1.1 The Effects of Impurities

a) Solid impurities

Solid impurities are unavoidably present in dielectric liquids because of many possible sources for the solid impurities to get into the liquid sample such as the release of impurity particles from the walls of the test cells and the surfaces of electrodes. In 1963 Lewis and Sletten have reported that particles of the order of $1\text{ }\mu\text{m}$ size could be observed in n-hexane during high field experiments with a microscope. Krasucki [1968] has studied the motion of spherical particles of radius R in a liquid subjected to an electric field, and the effect of such particles on electric conduction in liquids. Krasucki [1968] has assumed that (i) the particle is conducting, (ii) the particle is instantaneously charged to a value Q on contact with the anode, and (iii) later it is attracted to the cathode due to the electrostatic force QE , where it is instantaneously neutralized and acquires a charge $-Q$. The particle is then attracted back to the anode and this oscillatory motion between the electrodes continues. The expression for Q derived by Krasucki [1968] is given by

$$Q = \left(\frac{2}{3}\right) \pi^3 \epsilon R^2 E \quad (2.3)$$

and the expression for the average current due to the particle motion between the electrodes is given by

$$I = \frac{Q}{\tau} \quad (2.4)$$

where τ is the transit time required for the particle to travel across the gap. With the aid of Eq. (2.3) and Eq. (2.4), Krasucki [1968] has

calculated the dependence of current on the applied field, and reported that the calculated current-field characteristics for n-hexane is in good agreement with the experimental results of House [1957]. In 1972 Birlasekaran and Darveniza have used Krasucki's model to analyse the role of particles in prebreakdown processes and in particular, their contribution as charge carriers to conduction current. From the comparison of their calculated current-field characteristics in n-hexane with the experimental results of House [1957], Sletten and Lewis [1963], and Zaky et al. [1963], they have estimated the possible sizes of conducting particles in the n-hexane samples used in their experiments.

Rhodes and Brignell [1971, 1972] have examined the conduction process in n-hexane under natural contamination conditions. The small degree of contamination was achieved by using the same test cell for several months but with fresh samples of filtered n-hexane. Based on their experimental results, they have reported that contrary to the idea of conducting spherical particles, the particles observed are moderately insulating, their travel time across 100 μm gap is 10 μsec while their dwell time on either electrode is greater than 100 msec. The large dwell time has been attributed to the presence of an insulating layer on the surfaces of the electrodes that impedes the neutralization between the charged particles and the electrode.

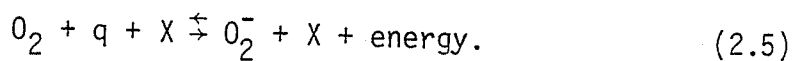
Pulse activity or (current fluctuation) during conduction current measurements has been observed by many investigators [Kao and Calderwood 1965, Megahed and Tropper 1971, and Rhodes and Brignell 1972]. Megahed and Tropper [1971] have attributed the large pulses in transformer oil to

particle movement, and the small pulses to ionization of microscopic gas bubbles by electrons injected from the cathode. However, Kao and Calderwood [1965] have reported that the conditioning process greatly reduced the current fluctuation, but fluctuation ten times the steady state current still occasionally occurred during measurement. They have attributed the current-fluctuations to the transient presence of tiny bubbles occasionally formed in the liquid gap and this bubble formation is greatly reduced under applied hydrostatic pressure.

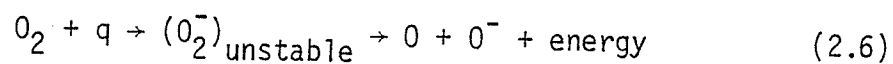
An appraisal of the above mentioned results suggests that the conduction processes are at least partly controlled by impurities.

b) Gaseous impurities

Gaseous impurities constitute another experimental variable in high-field conduction measurements in dielectric liquids. Sletten [1959] has reported that the addition of small quantities of dissolved oxygen to degassed n-hexane has the effect of stabilizing the current fluctuations, and with oxygen dissolved in n-hexane he could measure the conduction current up to the field close to the breakdown strength of the liquid. Two possible mechanisms have been suggested to explain this phenomenon. The first mechanism is that oxygen is an electronegative gas and tends to capture electrons emitted from the cathode to form negative ions of low mobility [Hurst and Borthers 1959]. The negative ion may be formed through a three body collision following the process



Any foreign atoms or molecules may act as the third body X. The second mechanism has been proposed by Schultz [1962] and is represented by



which involves the formation of a negative atom.

Based on the above experimental fact, it can be concluded that the presence of oxygen in hydrocarbon liquids leads to stabilizing the conduction current due to its scavanging effect. To our knowledge, very little work has been done to study the effect of any other dissolved gases on the conduction current in dielectric liquids.

2.1.2 The Effects of the Electrode Materials

The effects of electrode materials may be due to the electrode material itself or due to the electrode surface conditions, or both. Since high field conduction may involve carrier injection from the cathode, Green [1955] has reported that, using four cathode materials Fe, Ni, Au and Cu whose work function increases in the above order, the value of the conduction current at a fixed field does not increase as the work function increases, and the J-E characteristics are strongly dependent on electrode material and its surface conditions as shown in Fig. 2.2. Green has concluded that there is no simple relation for the dependence of electric conduction on the electrode work function and that the crucial factor is the condition of electrode surfaces rather than the metal itself. He has also suggested that positive ions generated in the liquid by external radiation or dissociation of impurity molecules, which are accumulated

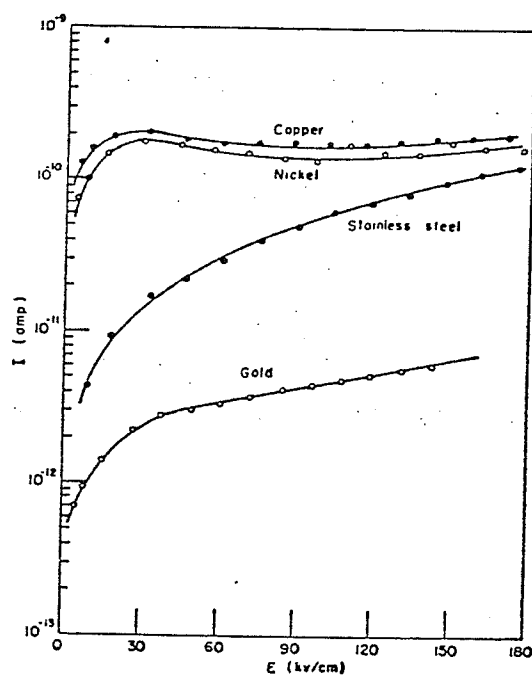


Fig. 2.2 Emission characteristics for cathodes of various materials with a fixed gap length [after Green 1955].

in front of the cathode, set up an intense local field across the surface layer. It is this field which induces the generation of electrons by field emission. Thus, for a given applied field, the local field established is determined by the balance in the supply of positive ions from the liquid and the neutralization of these ions by electrons emitted from the cathode. The efficiency of the neutralization process will then depend on the conductivity, homogeneity and thickness of the surface layer.

Zaky et al. [1963] have also studied the effects of electrode material and electrode oxidation on the conduction current in n-hexane. They have reported that when a copper electrode, previously oxidized, was used either as cathode or anode, there was no marked change in the conduction current between the two cases. However, using a stainless steel electrode, such an interchange of electrodes in the same liquid, produced a marked change in the shape of the current-field characteristic. In 1975 Gallagher has suggested that the findings of Zaky et al. [1963] are possibly due to an anode effect rather than a cathode effect. Swan and Lewis [1961] have proposed that for an anode effect to appear, two conditions must be met: (i) the liquid should contain certain amount of impurities which would trap electrons emitted from the cathode to form negative ions, and (ii) the anode should be covered with an insulating layer which can block the neutralization of these negative ions. A blocking anode can cause a build up of negative space charge which will limit the anode current. The result is that the field at the cathode will be depressed and that at the anode enhanced. Ultimately, the field in the anode region may become high enough to produce positive ions via electron

collision with liquid molecules. These positive ions when moving to the cathode will enhance the field there to increase the electron emission process. This type of feedback will have an influence on the field distribution and may lead to the rapid increase of current with applied field as has been observed by Zaky et al. [1963]. The two conditions proposed by Swan and Lewis [1961] may be present to a certain degree in most experimental conditions because no matter what degree of purity of the liquid is, it always contains certain amount of impurities. The second condition may always exist to a varying degree as the different methods of electrode preparation are adopted. The wax formation on the anode has been reported by MacFadyen [1955] and more recently by Aplin and Secker [1972]. Such a waxy insulating layer formed on the tip electrode appeared only when it was used as an anode in hydrocarbon liquids. They have attributed this wax formation to localized liquid ionization which is accompanied by liquid polymerization. Thus the current-field characteristics are also partly controlled by the combined action of the cathode and the anode and particularly the conditions of their surfaces.

2.1.3 The Processes Occurring in the Bulk of the Liquid

An interesting controversy has existed for many years on the question whether collision ionization occurs in liquid hydrocarbons [α -process] at high fields. House [1957] and earlier Goodwin and MacFadyen [1953] favor the existence of an α -process in liquid hydrocarbons. However, Green [1956] doubts the existence of an α -process in liquids. Green [1956] observed no catastrophic current increase up to

a field of 1.06 MV cm^{-1} and set an upper limit of α equal to 2 at fields above 0.8 MV cm^{-1} if it existed at all, while House [1957] believed that an α -process should occur at fields higher than 1.5 MV cm^{-1} . Both investigators used a sphere-plane electrode system. Watson and Sharbaugh [1959,1960], using flat electrodes and pulse voltages, have reported that there is no evidence of α -process in n-hexane for applied average fields up to 1.2 MV cm^{-1} and that such process may begin at fields higher than 1.3 MV cm^{-1} as shown in Fig. 2.3. In 1972 Devins and Wei have reported that the electron trapping distance in n-hexane is of the order of $1 \mu\text{m}$ which is less than 2% of the smallest gap length used by Watson and Sharbaugh [1960], thus many electrons emitted from the cathode may probably be captured by impurity molecules within a short distance from the cathode so that the number of electrons capable of causing ionizing collisions should be reduced considerably. Under these conditions an α -coefficient would be very small as has been reported by Watson and Sharbaugh [1960].

In 1975 and 1976 Kao has suggested that the conduction current at high fields is filamentary. Based on this assumption and supported by the observation of current filaments in chlorobenzene by Goodwin [1956], he has derived an expression for the conduction current which is given by

$$I = J_{z0} (2\pi d^2) \left[\frac{16}{3M} \frac{D}{\mu V} \right] \cdot \left\{ \ln \left[1 + \left(\frac{3M}{16} \frac{\mu V}{D} \right)^{\frac{1}{2}} \frac{r_d}{d} \right] + \left[1 + \left(\frac{3M}{16} \frac{\mu V}{D} \right)^{\frac{1}{2}} \frac{r_d}{d} \right]^{-1} - 1 \right\}, \quad (2.7)$$

where r_d is the radius of the filament; J_{z0} is the current density at the center of a cylindrical filament, which is given by

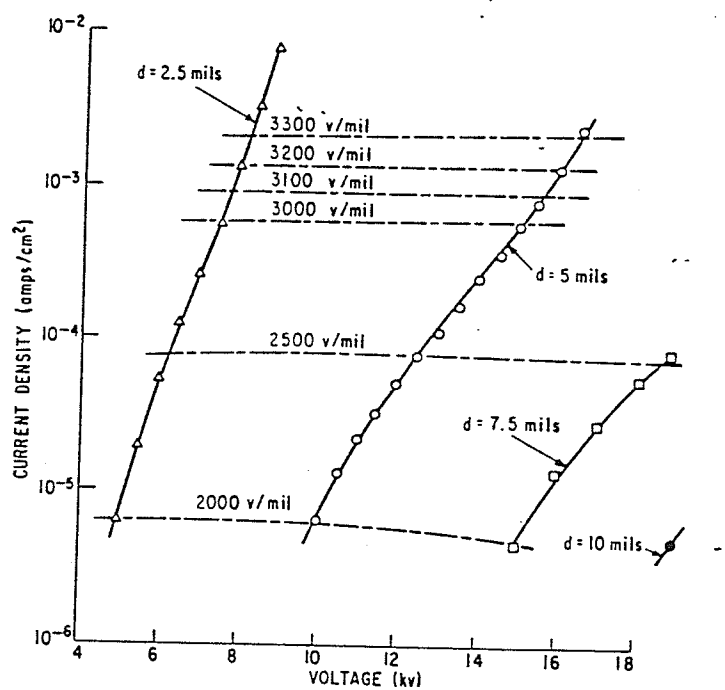


Fig. 2.3 The dependence of conduction current density upon voltage for various electrode separations in n-hexane [after Watson and Sharbaugh 1959].

$$J_{z0} = \frac{9}{8} \epsilon \mu \frac{V^2}{d^3} M, \quad (2.8)$$

in which

$$M = \frac{4Y^2 - 3}{6} + \left[\left(-\frac{4Y^2 - 3}{6} \right)^2 - \frac{16Y^3(Y - 1)}{27} \right]^{\frac{1}{2}}, \quad (2.9)$$

and

$$Y = \frac{E_c}{E_{av}}, \quad (2.10)$$

which is the ratio of the electric field at the cathode to the average applied field. He has also derived the equation for the current density as a function of r which is given by

$$J_z(r) = J_{z0} \left[1 + \left(\frac{3M}{16} \frac{\mu V}{D} \right)^{\frac{1}{2}} \frac{r}{d} \right]^{-2}. \quad (2.11)$$

Figure 2.4 shows the value of M as a function of Y based on Eq. (2.9) and $J_z(r)/J_{z0}$ as a function of r based on Eq. (2.11). It can be seen that $J_z(r)$ depends on the values of M and E_{av} , and that $J_z(r)$ decreases very rapidly with increasing r . To evaluate J_{z0} and hence I , the value of Y and then M has to be determined. Kao [1976], by equating J_{z0} and the current density at the cathode for the assumption that the electron injection following Eq. (2.2), has obtained the following expression for Y ,

$$Y = \frac{8}{27[Re^{-s} + \frac{2}{3}]^2 + 4} + \left\{ \left(\frac{8}{27[Re^{-s} + \frac{2}{3}]^2 + 4} \right)^2 + \frac{27Re^{-s}}{27[Re^{-5} + \frac{2}{3}]^2 + 4} \right\}^{\frac{1}{2}} \quad (2.12)$$

where

$$R = \frac{8ad}{9\epsilon\mu} \quad \text{and} \quad s = \frac{b}{YE_{av}}.$$

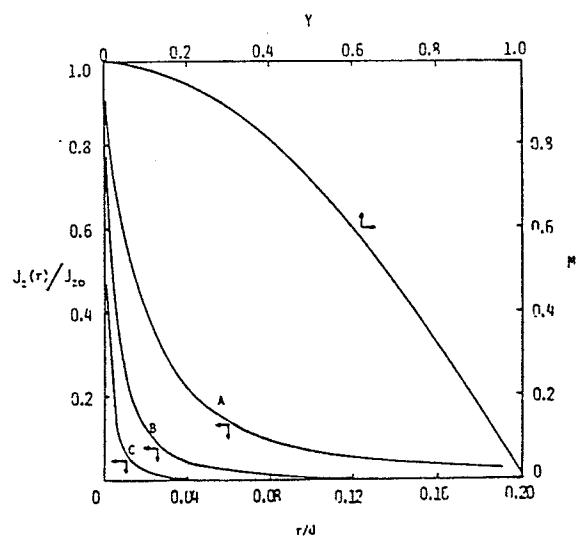


Fig. 2.4 M as a function of Y and $J_z(r)/J_{z0}$ as a function of r/d . A: $M = 16/300$, $d = 0.02$ cm, and $E_{ay} = 10^5$ V cm $^{-1}$; B: $M = 16/300$, $d = 0.02$ cm, and $E_{ay} = 10^6$ V cm $^{-1}$; or $M = 16/30$, $d = 0.02$ cm and $E_{av} = 10^5$ V cm $^{-1}$; C: $M = 16/30$, $d = 0.02$ cm and $E_{av} = 10^6$ V cm $^{-1}$ [after Kao 1976].

The plot of Y as a function of R for various values of s is shown in Fig. 2.5. Using Eq. (2.7), Kao [1976] has calculated the current-field characteristics for n-hexane and reported that the calculated characteristics are in good agreement with the experimental results of Goodwin and MacFadyen [1953] as shown in Fig. 2.6. His theory also accommodates both experimental results obtained by Goodwin and MacFadyen [1953] and by Watson and Sharbaugh [1960] without involving the α -process. He has attributed the difference between the two sets of experimental results to the difference in the electrode surface condition and the difference in the role played by space charge under direct voltage and under pulse conditions. He has suggested that in a liquid not only ionic impurities but also neutral impurities will be drawn into the high-field region in the liquid gap from its surroundings by the electrophoretic and dielectrophoretic forces, and these impurities will form scavenging traps which indirectly reduce the average mobility of charge carriers. As time is required for these impurities to be drawn to the liquid gap, the impurity concentration in the liquid gap would be much smaller and the average mobility much larger under pulse conditions than under dc-voltage conditions. Kao has suggested that this may explain why at a given average field the conduction current is much higher under pulse than under dc-voltage conditions.

2.1.4 Dependence of Conduction Current on Temperature and Hydrostatic Pressure

LePage and DuBridge [1940] were the first to carry out a systematic investigation of the effect of temperature on the conduction current at various applied fields using nickel electrodes in toluene and their

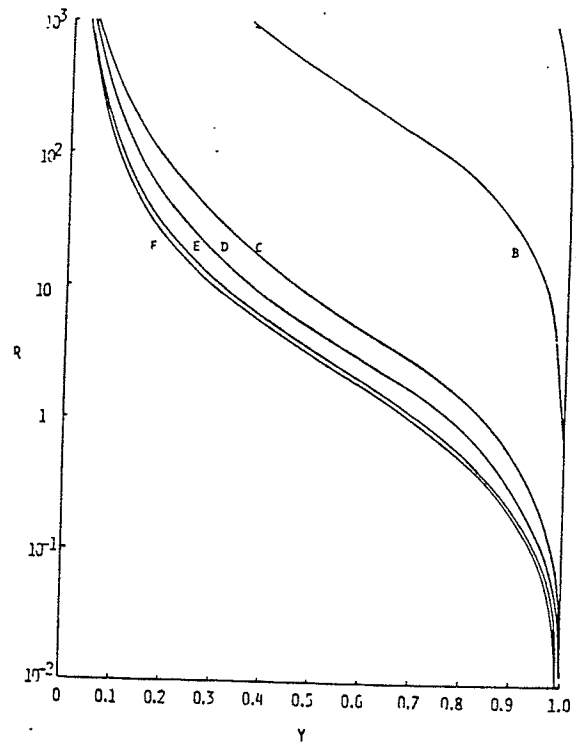


Fig. 2.5 Y as a function of R . A: $S = 10$; B: $S = 5$;
 C: $S = 1$; D: $S = 0.5$; E: $S = 0.1$; and
 F: $S = 0$. [after Kao 1976].

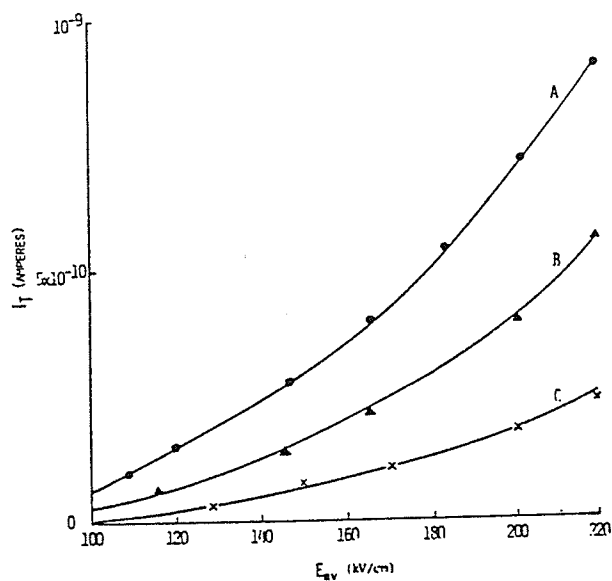


Fig. 2.6 Total current as a function of the average electric-field strength in n-hexane for three gap lengths. A: $d = 0.042$ cm, B: $d = 0.020$ cm, and C: $d = 0.0055$ cm; —: theoretical curves; ●▲x: experimental results with phosphor bronze electrodes [after Kao 1976].

experimental results are shown in Fig. 2.7. The most significant feature of their results is the field dependence of conduction current-temperature characteristics. They have reported that the conduction current over the temperature range used in their experiments (-15° to 70°C) follows Eq. (2.1) and suggested that the conduction current is mainly due to Schottky type thermionic emission.

Kao and Calderwood [1965] have studied the effect of temperature on the conduction current in n-hexane and carbon tetrachloride, their results are shown in Fig. 2.8. A comparison of their temperature dependence curves with those of relative fluidity in Fig. 2.8 indicates that there is a relation between conduction current and fluidity. They have attributed the increase of conduction current with temperature to the increase of ionic mobility but also to the increased number of ions created by temperature-enhanced dissociation of impurities and this may explain the difference between the slopes of the conduction current and the relative fluidity. From Fig. 2.8 it can be seen that when the temperature was lowered to its initial value the measured conduction current was always lower than that measured before the sample was heated. Kao and Calderwood [1965] have attributed this phenomenon to the change of the properties of the dielectric layers on the electrode surfaces due to the combined action of heating and electric field. They have also favoured a Schottky-type thermionic emission as the mechanism responsible for electric conduction at high fields.

As for the effect of hydrostatic pressure Kao and Calderwood [1965] have reported that the current fluctuations occurring at fields

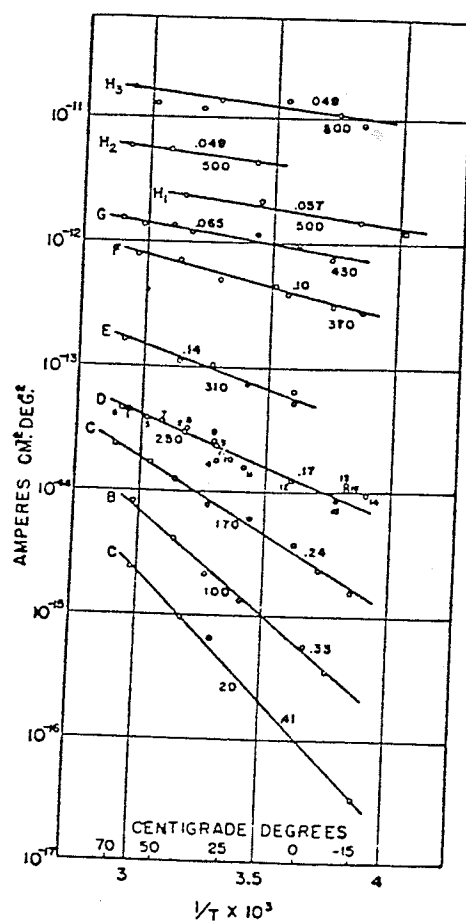


Fig. 2.7 Conduction current versus temperature at different applied electric fields in toluene [after LePage and DuBridge 1940].

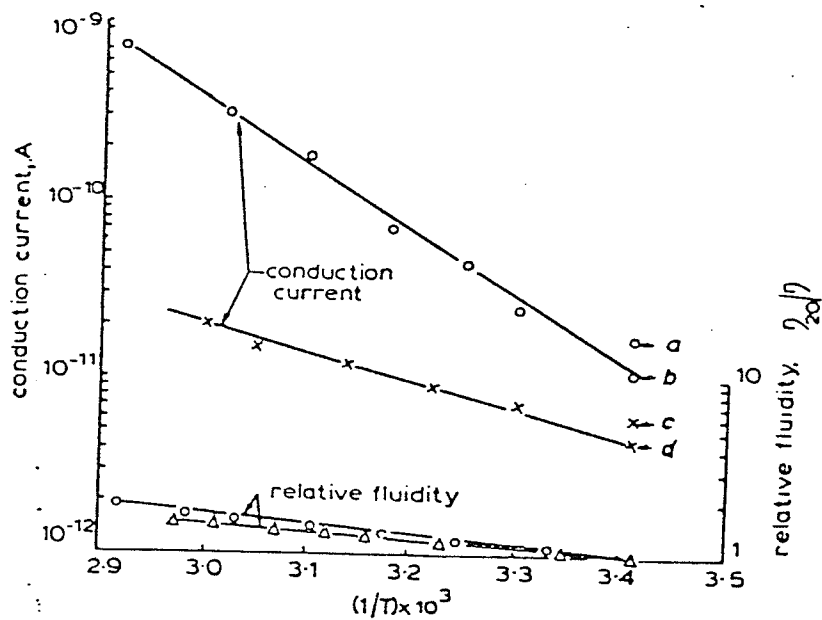


Fig. 2.8 Conduction current and relative fluidity as functions of temperature. o, carbon tetrachloride, 100 μm gap, 207 kV cm^{-1} ; $\times \Delta$, n-hexane, 120 μm gap, 240 kV cm^{-1} ; a, c before raising temperature; b, d after raising temperature [after Kao and Calderwood 1965].

above 300 kV cm^{-1} are greatly reduced under applied hydrostatic pressures, but the steady state current is stable and independent of pressure up to 11 atm. They have suggested that most liquids are practically incompressible at low pressures, and hence there should be no change in parameters like density and viscosity at such low pressures. However, Garben [1972] has reported that at different isothermals, the conduction current in dry benzene increased with applied pressure up to 5 k bar as shown in Fig. 2.9. Garben explained this phenomenon on the basis that charge carriers in dry liquid benzene are localized electrons and that the conduction process is by transition of these electrons between localized states.

2.1.5 Charge Carriers in Hydrocarbon Dielectric Liquids

LeBlanc [1959], Chong and Inuishi [1960] and Secker and Lewis [1965] have reported the values of the mobility of negative charge carriers in n-hexane ranging from $4.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ to $20 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$. They all have agreed that charge carriers are ionic in nature and are produced by attachment of electrons injected from the cathode surface to molecules of impurities or of the liquid itself or due to ionization of impurity molecules. Only recently it has been reported by Schmidt and Allen [1970] the presence of more mobile carriers in neopentane, 2,2-dimethylbutane, n-butane, n-pentane, n-hexane, cyclohexane and cyclopentane. Following this observation, Minday et al. [1972] have also observed excess electrons in 2-methylbutane, benzene, n-hexane and n-pentane. To observe electron behavior in dielectric liquids conventional purification techniques, such as distillation, electrolysis, vacuum pumping, are not adequate for this experiment. For this reason Minday et al. [1972] have

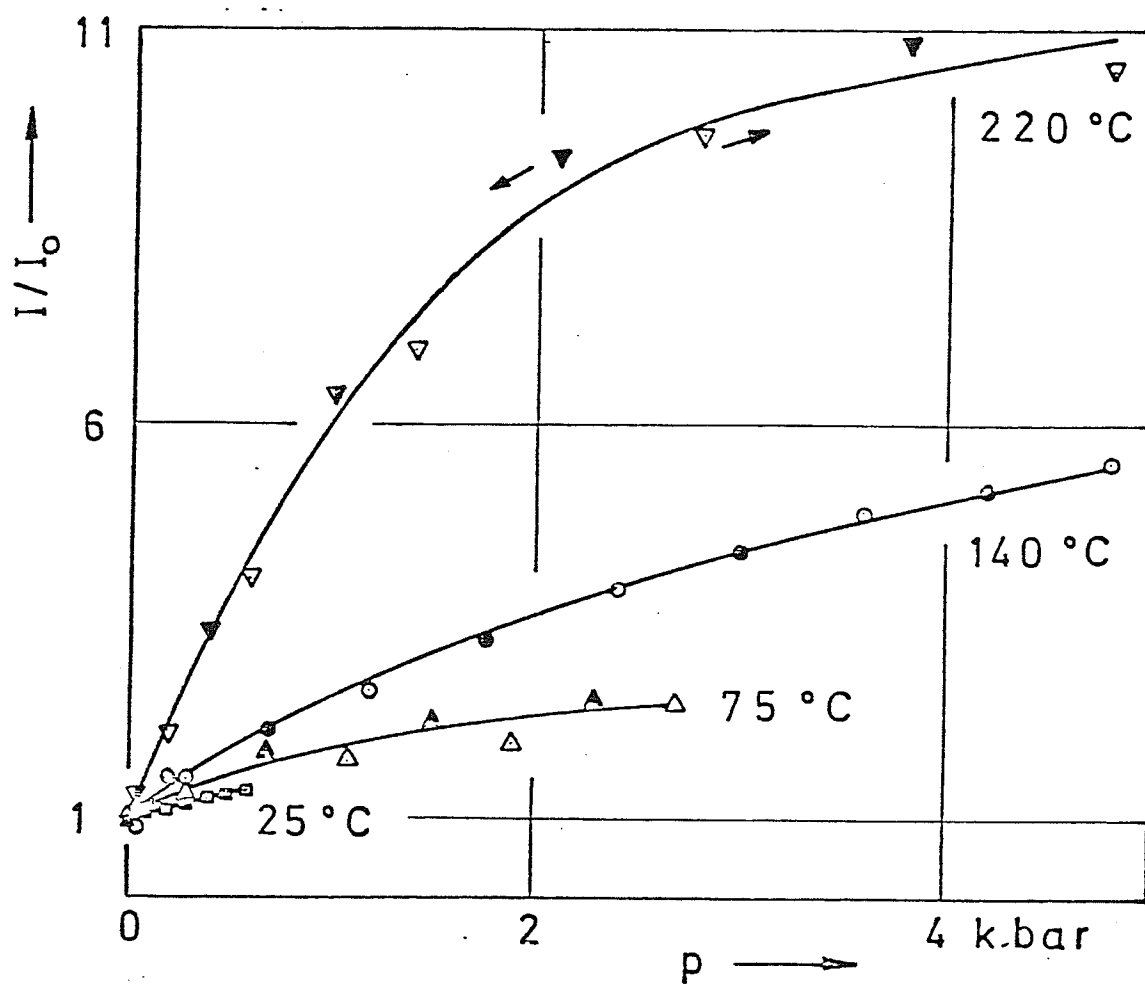


Fig. 2.9 Relative current as a function of pressure
[after Garben 1972].

adopted a technique elaborate enough to allow them to measure the mobility of the fast electrons. Their technique was as follows: the liquid sample was first transferred to a flask and was pumped to remove the air above and as much of the dissolved gases as possible. The sample flask was then sealed off under vacuum and attached through a glass breakoff seal to the vacuum system. Before the introduction of the liquid sample into the vacuum system, the vacuum system was baked for several days at 300°C to attain a pressure of the order of 10^{-9} torr. The liquid was then distilled between barium film getters followed by liquid nitrogen or ice-bath condensation. Figure 2.10 shows that the drift velocities of the negative charge carriers are much higher than those for negative ions in n-hexane, but less than that for a quasi free electron in liquified argon. Minday et al. [1972] have suggested two mechanisms of electron transport in hydrocarbon liquids. The first mechanism involves electron movement as a quasi free particle until it is trapped by a group of molecules in a configuration favourable for trapping. The electron then remains in the relatively immobile trap until thermally activated back to the conduction band. The activation energy of the mobility then arises from the thermal detrapping process. The second possible transport mechanism is that the electron tunnels from one trap site to the other. In this mechanism the electron remains trapped until a thermal fluctuation provides a neighbouring trap into which the electron may move to by tunnelling.

In 1974 Schmidt et al. have suggested that the mobility of electrons in dielectric liquids is independent of the field but only up to a critical field beyond which it becomes field dependent. Based on the

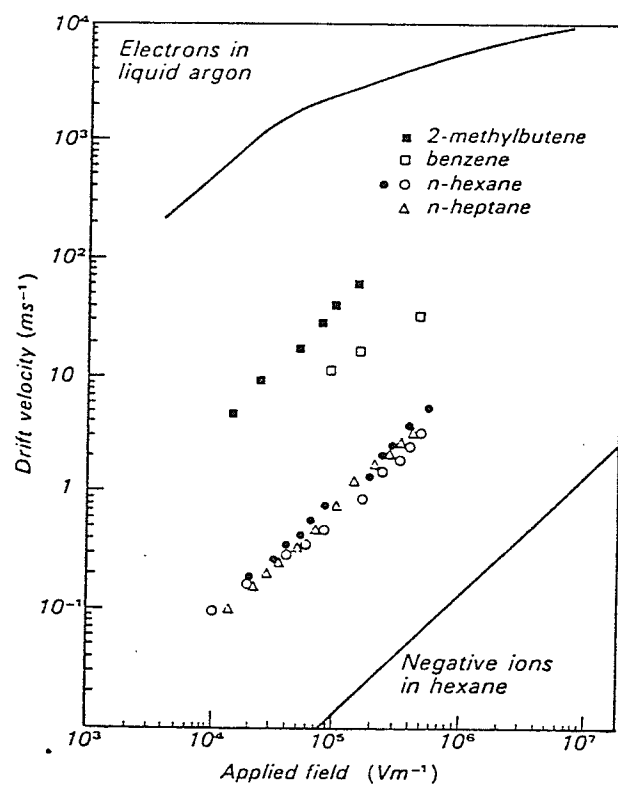


Fig. 2.10 Electron drift velocity versus applied field in several hydrocarbon liquids [after Minday et al. 1972].

thermally activated hopping model they have obtained an expression for the mobility of electrons in dielectric liquids. At high fields it is given by

$$\mu_h = \frac{2\lambda v}{E} \exp\left(-\frac{W}{kT}\right) \sinh\left(\frac{q\lambda E}{2kT}\right) \quad (2.14)$$

and at low fields it reduces to:

$$\mu_\ell = \frac{q\lambda^2 v}{kT} \exp\left(-\frac{W}{kT}\right) \quad (2.15)$$

where λ is the separation between traps, W is the average barrier height and v is the attempt to escape frequency. Equation (2.15) indicates that μ_ℓ is independent of the field at low fields. μ_ℓ has the usual exponential temperature dependence except that the pre-exponential factor is also dependent on T .

In aromatic hydrocarbons, Forester [1962] has attributed the increase in the conductivity of this group of liquids over normal saturated hydrocarbons due to the presence of π -electrons. Forester [1962] has suggested that the π -electrons are transported through the liquid via a hopping mechanism.

2.2 ELECTRIC BREAKDOWN

During the past fifty years many aspects of electric breakdown in dielectric liquids have been investigated. However, the results reported by many independent investigators show large variations and often appear to be in disagreement. As a result there is a diversity of opinion on the breakdown processes. Several theories have been put forward but each offers different mechanisms for breakdown [Lewis, 1959, Sharbaugh and Watson 1962, Kao

1965 and Adamczewski 1969]. Several experimental parameters have been found to influence breakdown measurements, such as measuring procedure, material preparation method and surface conditions of electrodes, gap length, temperature and hydrostatic pressure, etc. In the following we shall discuss these parameters are discussed separately. The breakdown strength is referred to the direct voltage breakdown strength unless otherwise stated [e.g., pulse breakdown strength].

2.2.1 Dependence of Breakdown Strength on Measuring Procedure

General experimental techniques used for breakdown measurements have been discussed in detail by Lewis [1959]. Two techniques have been adopted. The first one is the multi-shot technique. With this technique the breakdown strength is determined by applying a sequence of shots in the same sample of the liquid and same pair of electrodes until the shot giving a steady value is attained [Watson and Higham 1953, Maksiejewski and Tropper 1954, Brignell and House 1965]. In the sequence, the breakdown strength increases or decreases with the initial few shots, and then gradually reaches a steady level which can last for a certain number of shots but after this it deteriorates in a very erratic behaviour. This technique is some times referred to as the conditioning technique. After such a conditioning process the breakdown strength have been observed to increase in transformer oil [Watson and Higham 1953, Masiejewski and Tropper 1954]. But in pure hydrocarbon liquids, such as in n-hexane, reverse trend has been observed by Brignell and House [1965]. This conditioning effect has been attributed to the removal of adsorbed gases from the electrodes' surfaces [Maksiejewski and Tropper 1954], or to the

removal of microbubbles from the cathode surface [Hancox and Tropper 1957]. Lewis [1959], and Kao and Higham [1961] have proposed that during the conditioning process, each spark tends to remove an active site from the electrode surface. These sites could well be patches of low work function, with absorbed or adsorbed gas molecules or any surface irregularities. Although the discharge may remove some active areas, it also causes further damage on electrode surfaces and deterioration of the liquid. To avoid this, Watson and Higham [1953] and Saxe and Lewis [1955] have used a diverter circuit to divert the breakdown current from the liquid gap so as to limit the discharge in the liquid gap.

The alternate measuring procedure is to use for each breakdown measurement, fresh liquid samples and a new set of electrodes [Kao and Higham 1961]. It is obvious that the second method is more tedious to collect a large amount of results. However, this technique was very successful in obtaining consistent results [Kao and Higham 1961].

2.2.2 Dependence of Breakdown Strength on Electrode Material

In the discussion of the effects of electrode material on the conduction current, their effects on the emission process of electrons from the cathode into the liquid had been mentioned. Naturally it would be also one of the important processes for breakdown. In n-hexane Salvage [1951] has reported some correlation between the breakdown strength and the work function for a range of metals Aluminum, Chromium, Silver, Nickel and Platinum. However, Maksiejewski and Tropper [1954] have found that the breakdown strength of n-hexane increases when the cathode metal is changed in the order Ag, Pt, Al, Cu, Fe, and Ni while the work function

of these metals increased in the order Al, Ag, Pt, Ni, Cu, and Fe. But they found that such a dependence disappeared when the electrodes and the liquid were degassed. Using pulse voltages Goodwin and MacFadyen [1953] have also reported a dependence of the pulse breakdown strength of n-hexane and methyl alcohol on electrode material using fresh electrodes for each measurement. While Zein El-Dine and Tropper [1956] have reported that under pulse conditions no dependence of the pulse breakdown strength of transformer oil on the cathode work function. These results indicate that there is no simple relationship between the breakdown strength and the cathode work function. Ward and Lewis [1963] have suggested that some of the discrepancies in the experimental results in this area could be due to wax layers formed on the electrodes which masks the true metal properties. Kao [1964] had observed the effects of a thin dielectric layer coating on the breakdown strength of carbon tetrachloride measured between point and plane electrodes. The breakdown strength of the liquid is higher when the plane electrode was covered with a thin glass layer (0.105 mm thick). Kao has attributed this phenomenon to the change in the electron emission characteristics of the cathode.

In order to investigate the true electrode effect on breakdown strength, attention has been drawn to liquids in which the by-products due to breakdown (such as carbon particles) in them can be reduced to a minimum. An obvious choice would be liquified gases. A great deal of results have been published on the breakdown strength of these liquids [Swan and Lewis 1961, Gallagher and Lewis 1964, Keenan 1972]. Swan [1961] has proposed a theory based on electron emission from the cathode

and collision ionization for the breakdown of liquified gases. The theory agreed well with the experimental results of Swan and Lewis [1960] in liquid argon. However, Swan [1961] did not suggest to apply directly this theory to the case of hydrocarbon liquids [e.g., n-hexane] due to the uncertainty of the presence of collision ionization in these liquids.

2.2.3 Dependence of Breakdown Strength on Gap Length and Electrode Geometry

The dependence of breakdown strength on gap length has been a subject of interest because the gap length dependence may indicate electron impact ionization in the liquid or other breakdown mechanisms. Lewis [1953] has reported that the breakdown strength of n-pentane, n-hexane, n-heptane, n-octane and n-decane is dependent on the gap length as shown in Fig. 2.11. However, Sharbaugh et al. [1955] have proposed that the gap length dependence of breakdown strength observed by Lewis [1953] using spherical electrodes may be an area effect rather than a gap length effect. Kao and Higham [1961] have observed that the breakdown voltage of n-hexane between sphere - sphere gaps ranging from 20 and 220 microns is a linear function of the gap length. They have attributed this effect to collision ionization process in the liquid. However, the process of collision ionization in liquid dielectrics has been the subject of dispute for many years now. It is believed that collision ionization may have to occur in order to produce an extremely high conducting path at fields close to breakdown strength.

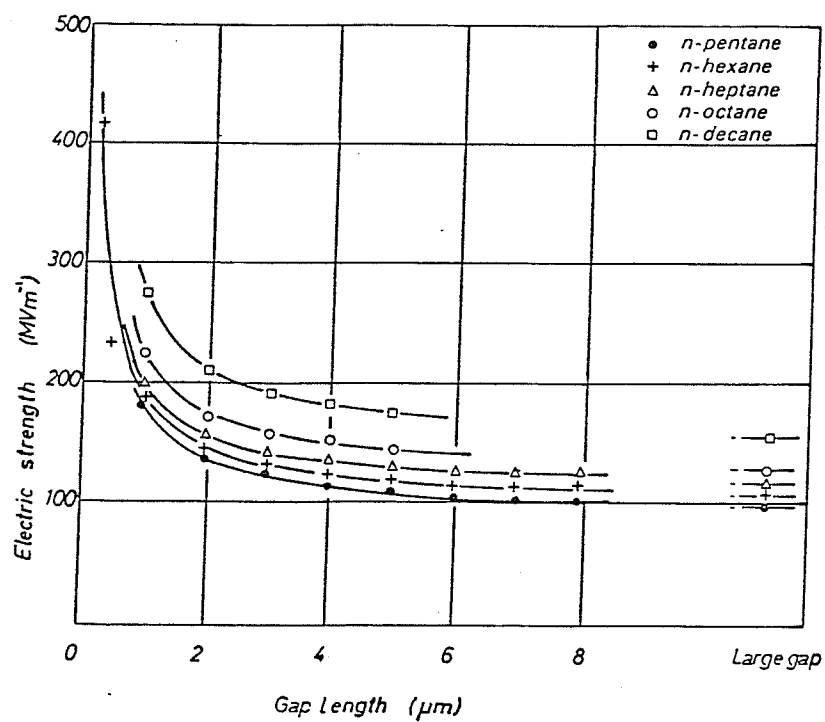


Fig. 2.11 Dependence of breakdown strength on gap length for paraffin hydrocarbon liquids [after Lewis 1953].

2.2.4 The Effects of Impurities on Breakdown Strength

a) Gaseous impurities

The breakdown strength is influenced by trace amounts of dissolved gases. Sletten and Lewis [1963] have reported that the breakdown strength of n-hexane increased from 0.8 MV cm^{-1} when degassed to 1.2 MV cm^{-1} when saturated with air, and that dissolved nitrogen had no effect on the breakdown strength. These experimental facts have led them to conclude that the increase in breakdown strength with dissolved air is due to the presence of oxygen. Hydrogen and carbon dioxide had no effect on the breakdown strength even when large amounts were dissolved, except that repeated breakdowns with the presence of CO_2 would cause the breakdown strength to rise. They have attributed the latter phenomenon to the release of oxygen. The minimum amount of dissolved oxygen to give an increase in the direct voltage breakdown strength is not known. Oxygen is not the only gas that can give such an effect on the breakdown strength. Nosseir and Hawley [1966] observed an increase in the breakdown strength of mineral oil when SF_6 was dissolved in it. Following their results obtained under direct voltage conditions, several investigators have reported that small traces of air or oxygen in benzene [Edwards 1951], transformer oil [Watson 1955], and n-hexane [Sletten and Lewis 1963] did not change the breakdown strength under pulse applied voltages of microseconds duration. Sletten and Lewis [1963] have suggested that the main role of oxygen is not the removal of electrons capable of causing breakdown, but rather the creation of a negative ion layer at the anode and around charged particles in the bulk of the liquid.

Therefore, under direct voltage condition electron trapping can produce appreciable number of negative ions, but under pulse voltages accumulation of similar numbers in the liquid or near the anode does not occur. They have also suggested that a higher stress is required for pulse breakdown and that the mean electron energy is greater than that under direct voltage condition. Thus, since attachment is a low energy process, its occurrence would be less probable under pulse condition. Ward and Lewis [1963] have shown that the pulse breakdown strength of n-hexane saturated with air increases from 1.5 MV cm^{-1} to over 2 MV cm^{-1} by using positive or negative prestressing with direct voltages. They have suggested that prestressing would set up charge layers on electrodes. It is possible that negative ion layers are formed when oxygen is present in the liquid. These layers would modify the emission and hence, change the pulse breakdown strength. It is obvious that the presence of gaseous impurities, such as oxygen, would produce discrepancies among the experimental results. It is important for comparison purposes to determine the gas content of the liquid being tested.

b) Solid impurities and additives

Direct evidence to the reduction of the breakdown strength of dielectric liquids due to the presence of solid particles has been reported by Kok [1961], and Crawly and Angerer [1966]. They found that the breakdown strength of mineral oils increased progressively as the filter pore size was decreased. Salvage [1951] has reported similar results earlier in n-hexane. Mirza et al. [1970] have reported that the

electrical conductivity of n-hexane and transformer oil decreases with decreasing pore size of filters used for filtering the liquid. They used millipore filters of sizes ranging between 100 μm to 10 nm for their experiments. Kok [1961] has suggested that impurity particles with permittivity greater than that of the liquid will be driven to the maximum stress region between the electrodes. These particles can align themselves with the applied field to form a conducting channel across the gap leading to breakdown. This theory may explain the breakdown of liquids containing large amounts of impurities but it is doubtful that it can explain the breakdown of pure liquids. The term 'pure liquids' may be a misleading term, since liquids classified as spectroscopic grade may still contain a mixture of isomers [Kahan and Morant 1965]. They have emphasized the importance of stating the grade of the liquid when reporting experimental results and suggested that if possible, chromatographic analysis should be used to check the purity.

Due to the importance of dielectric liquids in industrial applications, attention has been given to additives that may increase the breakdown strength. Angerer [1963] has carried out a detailed investigation about the effect of certain additives on the breakdown strength of transformer oil. The additives chosen were azobenzene, azoxybenzene, diphenyl, benzophenon, benzil, and anthracene in concentrations ranging between 2.3×10^{-6} to 4.59×10^{-3} mole/100 g of the basic liquid. He has reported that the breakdown strength of transformer oil increases in all these cases, and that a certain optimum concentration would produce the highest breakdown strength in each case. He has also suggested a model

to explain the effect of additives on the strength of transformer oil. His model consisted of three phases: (A) an initial phase during which the formation of microscopic cavities due to thermal fluctuations is enhanced by the presence of the electric field and mechanical effects caused by the field; (B) a second phase, during which the electrons moving through the liquid can give enough energy inside microcavities to bring about dissociation, accompanied by gas evolution, so that microbubbles can form, and this phase may be regarded as initiating or triggering the final breakdown; and (C) a gaseous breakdown which takes place when the rate of bubble formation exceeds the rate at which the evolved gas can be absorbed by the liquid. The presence of additives would affect the second phase of this model since these additives enter the primary bubble in the form of vapour and may exert a quenching effect on the electrons by reducing their acceleration inside the bubble and may thus slow down the dissociation process. This, in turn, will have a restraining effect on the growth of this bubble, which ultimately would tend to increase the breakdown strength.

A similar phenomenon has been observed in n-hexane by Kao and Higham [1961]. They have reported that the breakdown strength of n-hexane is significantly increased by the addition of a small percentage of certain other liquids, reaching a peak value with the addition of about 5% and falling from there as the percentage is increased. The addition of 5% of carbon tetrachloride gives an increase in breakdown strength of about 35% and the corresponding increases for chlorobenzene, chloroform and ethyl alcohol are 28%, 13% and 7%, respectively. They have

attributed this increase to the presence of oxygen or halogen groups in additives molecules which would tend to capture the electrons emitted from the cathode. Kao and Calderwood [1965] have reported that the conduction current in distilled and filtered n-hexane is appreciably increased by the addition of 7% by volume of untreated ethyl alcohol, also the breakdown strength is increased from 0.8 MV cm^{-1} to 0.9 MV cm^{-1} . They have attributed the cause of this increase in the conduction current to electrolytic dissociation of ethyl alcohol molecules. Ethyl alcohol molecules would be drawn into the intense-field region in the gap, owing to the difference in permittivity between the two liquids. The presence of these polar molecules may modify the electron-emission characteristics of the cathode, owing to an increase in the permittivity of the liquid; and it may also reduce the electron mobility and increase the probability for attachment and recombination with the result that the conduction current becomes predominantly ionic and the charges in the gap become more uniformly distributed. If bubble formation is caused by electrostatic repulsion of local space charges the uniform distribution of charges would hinder the occurrence of this process. This could explain the increase in the breakdown strength of n-hexane by the addition of ethyl alcohol.

2.2.5 Dependence of Breakdown Strength on Molecular Structure

Dependence of breakdown strength on molecular structure has been examined in highly purified n-paraffines by Crowe et al. [1954]. They have reported that the breakdown strength increases as the chain length increases. The density of the liquid alone is not a deciding

factor since measurements on a series of alkylbenzenes gave different breakdown strengths although for some cases their densities are approximately the same [Sharbaugh et al. 1956]. Lewis [1956] adopted the suggestion of Von Hippel [1937] which states that a vibration collision provides the most efficient mechanism of energy transfer. He has proposed that the energy balance equation at breakdown could be used to predict the breakdown strength

$$qE\lambda_m = Ch\nu \quad (2.16)$$

where λ_m is the mean free path corresponding to the maximum cross-section for this type of collision, $h\nu$ is the quantum of energy lost by an electron during a vibrational collision and C is a constant to take account of various experimental conditions. By assuming that the major energy loss occurs in exciting CH, CH₂ and CH₃ bond vibrations in normal paraffines and the same in alkylbenzenes, Lewis [1956] has obtained an expression for the breakdown strength which is given by

$$E_{bd} = KN[n_1Q_1 + n_2Q_2 + n_3Q_3] \quad (2.17)$$

where K is a constant combining C and $h\nu$ from Eq. (2.16), N is Avogadro's number and the suffixes refer to the CH, CH₂ and CH₃ groups, respectively. Lewis [1956] have reported that Eq. (2.17) fits well the experimental results obtained by Sharbaugh et al. [1956]. Adamczewski [1969] has proposed a similar model for hydrocarbon liquids, but based on the hypothesis that the C-C bond vibrations are the major barrier to electron acceleration. The breakdown strength derived by Adamczewski [1969] is

given by

$$E_{bd} = h\nu\lambda\ell(n - 1)N \quad (2.18)$$

where λ is the mean distance between molecular axes, ℓ is the C-C bond length projected on that axis, n is the number of carbon atoms. Adamczewski [1969] has calculated the breakdown strengths for both saturated and aromatic hydrocarbons based on Eq. (2.18). His calculated results are also in good agreement with the experimental results of Sharbaugh et al. [1956].

It is true that both of the aforementioned theories can explain and predict the breakdown strength of dielectric liquid hydrocarbons as a function of the molecular structure but both of them fail to explain the dependence of the breakdown strength on hydrostatic pressure within the range of pressure applied in experiments. Kao [1975, 1976] has proposed a filamentary single injection model. This model is based on the postulates that at the field near the breakdown strength there is only one filament in which the current density is much higher than that in other filaments or in other regions. Breakdown occurs when the current density reaches such a value that the Joule heating produced is sufficient to raise the temperature to the boiling point of the liquid. By using the following balance equation for breakdown under pulse conditions

$$C_{pg} \frac{dT}{dt} = J_{zo} E_{av} = \frac{9}{8} \epsilon\mu \frac{M}{d} E_{av}^3 \quad (2.19)$$

and by assuming that

$$\mu = \mu_0 \exp\left(-\frac{W}{kT}\right) \quad (2.20)$$

TABLE 2.1
BREAKDOWN STRENGTHS OF SATURATED HYDROCARBON LIQUIDS
(After Kao 1976)

Liquid	Breakdown Strength, MV cm ⁻¹	
	Experimental	Theoretical
n-Hexane	1.56	1.56
2-Methyl-pentane	1.49	1.47
2, 3-Dimethyl-butane	1.38	1.46
2, 2-Dimethyl-butane	1.33	1.35
n-Heptane	1.66	1.67
2, 4-Dimethyl-pentane	1.44	1.48
n-Octane	1.79	1.86
2, 2, 4-Tri-methyl pentane	1.40	1.47
n-Decane	1.92	1.91



TABLE 2.2
 BREAKDOWN STRENGTHS OF AROMATIC HYDROCARBON LIQUIDS
 (After Kao 1976)

Liquid	Breakdown Strength, MV cm ⁻¹	
	Experimental	Theoretical
Benzene	1.63	1.94
Methyl-benzene	1.99	2.15
Ethyl-benzene	2.26	2.27
n-Propyl-benzene	2.50	2.30
i-Propyl-benzene	2.38	2.20
n-Butyl-benzene	2.75	2.50
t-Butyl-benzene	2.22	2.35

he has obtained the expression for the breakdown strength as

$$E_{bd} = \left\{ \frac{8}{9} \frac{c_p g k d}{W \epsilon \mu_0 M \tau} \cdot [T_o^2 \exp(\frac{W}{k T_o}) - T_b^2 \exp(\frac{W}{k T_b})] \right\}^{1/3} \quad (2.21)$$

where c_p and g are, respectively, the specific heat and the density of the liquid; T_o and T_b are respectively, the initial and the boiling-point temperatures of the liquid within the filament; μ_0 and W are, respectively, the pre-exponential factor and activation energy for carrier mobility; and τ is the pulse duration. Equation (2.21) involves the physical parameters ϵ , c_p , g and T_b which depend on the chemical structure. He has computed the breakdown strengths based on Eq. (2.21) and the results agree well with those of Crowe et al. [1954] for saturated hydrocarbons as shown in Table 2.1, and of Sharbaugh et al. [1956] for aromatic hydrocarbons as shown in Table 2.2.

2.2.6 Dependence of Breakdown Strength on Temperature

Salvage [1951], Lewis [1953], Goodwin and MacFadyen [1953], Kao and Higham [1961] and Brignell and House [1965] have investigated the effect of temperature on the breakdown strength of hydrocarbon liquids. They have all agreed that the breakdown strength falls off rapidly at temperature near the boiling point of the liquid. Kao [1976] has used Eq. (2.21) to calculate the breakdown strength as a function of temperature for n-hexane. His calculated results fit well the experimental results of Kao and Higham [1961] as shown in Fig. 2.12.

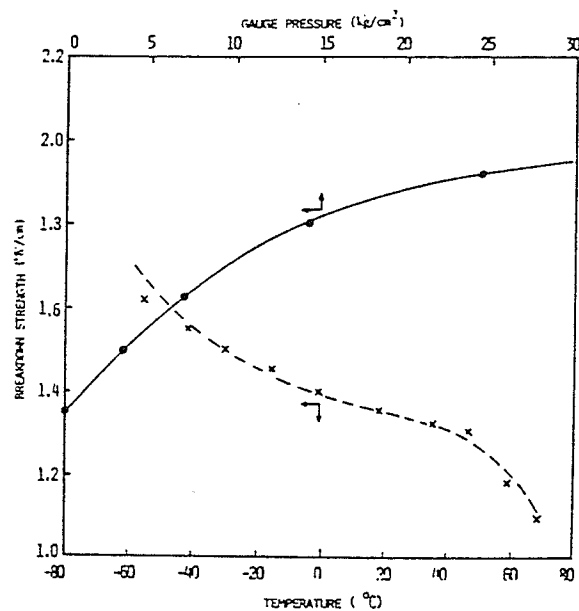


Fig. 2.12 Breakdown strength of n-hexane as a function of pressure and temperature for a pulse duration of 4.5 μ sec and gap length of 0.02 cm — and ----: theoretical curves, x: experimental results with stainless steel electrodes [after Kao 1976].

2.2.7 Dependence of Breakdown Strength on Hydrostatic Pressure

Kao and Higham [1961] have investigated the effect of hydrostatic pressure on the breakdown strength of various organic liquids, under well controlled conditions. Most of the measurements were obtained using stainless steel electrodes and using a single shot technique with each liquid sample and fresh pair of electrodes to avoid the usual conditioning effect. The range of pressures studied was from 0 gauge pressure (atmospheric pressure) to gauge pressure of 36.6 Kg.cm^{-2} under both direct and pulse voltages of duration $0.5 \text{ } \mu\text{sec}$ to 1 msec . Figure 2.13 shows some of their experimental results. It is interesting to note that for linearly rising fields having rates greater than $4 \text{ MV.cm}^{-1}.\text{sec}^{-1}$ the pressure dependence of breakdown strength of n-hexane and transformer oil disappear [Kao and McMath 1970] as shown in Fig. 2.14. Kao [1975, 1976] has explained this behaviour as due to the fact that under such conditions the breakdown is not associated with thermal instabilities in the liquid gap. Several theories have been proposed in attempt to explain the pressure dependence of breakdown strength. Kao has proposed first in 1965 that bubbles may be formed in the liquid by the following processes: (i) from the gas which accumulates in microscopic activities on the electrode surfaces, (ii) from the liquid itself by local evaporation on the surface of the electrodes, and (iii) due to electrostatic forces overcoming the surface tension. These bubbles then tend to elongate from their spherical shapes in the direction of the field with the volume remaining constant. The expression for the breakdown strength as given by [Kao 1960] is

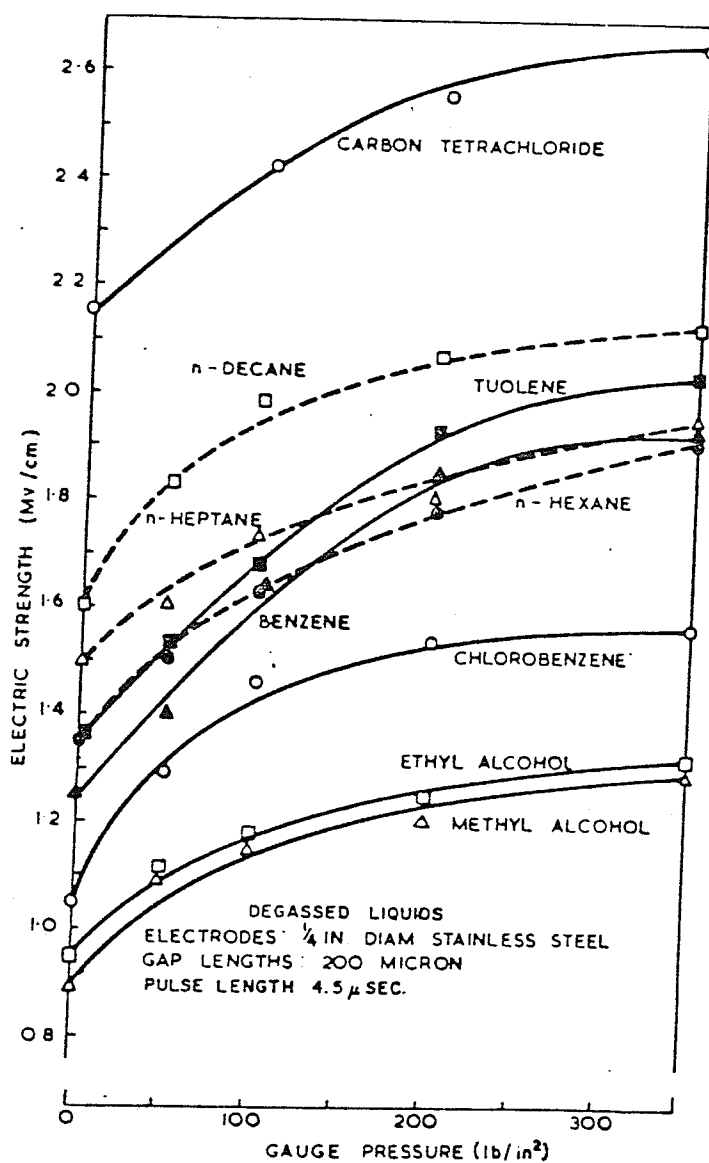


Fig. 2.13 The dependence of breakdown strength of some organic liquids upon applied hydrostatic pressure ($1 \text{ lb inch}^{-2} = 0.0933 \text{ kg cm}^{-2}$) [after Kao and Higham 1961].

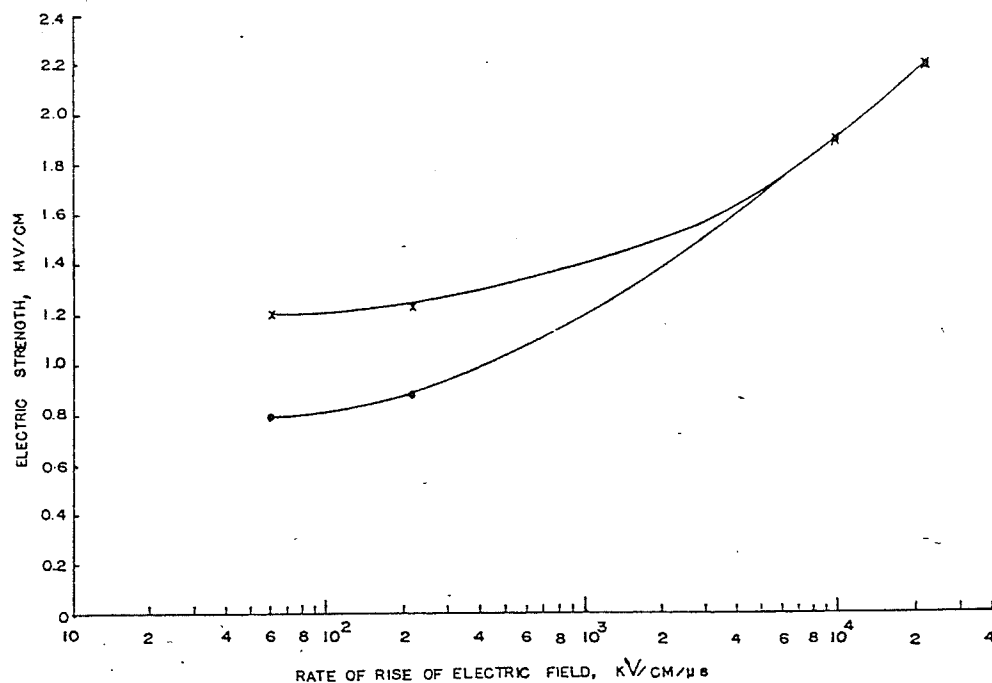


Fig. 2.14 Breakdown strength as a function of the rate of rise of electric field for n-hexane. o: gauge pressure 0 Kg cm⁻², x: gauge pressure 18.6 Kg cm⁻², Gap length: 0.091 cm, Electrodes: 2 cm diameter stainless steel spheres [after Kao and McMath 1970].

$$E_{bd} = \frac{1}{(\epsilon_1 - \epsilon_2)} \left[\frac{24\pi\sigma(2\epsilon_1 + \epsilon_2)}{r} \left[\frac{\pi}{4} \sqrt{\left(\frac{V_b}{2rE}\right) - 1} \right] \right]^{\frac{1}{2}} \quad (2.22)$$

where ϵ_1 and ϵ_2 are the dielectric constants of the liquid and the bubble respectively, σ is the surface tension, and r is the initial radii of the bubble. The theory explains qualitatively the dependence of breakdown strength on hydrostatic pressure. However, Eq. (2.22) does not give a quantitative picture of the breakdown strength.

Since the publication of the pressure dependence results by Kao and Higham [1961] many investigators have attempted to form a theory to explain this phenomenon. Sharbaugh and Watson [1962] have proposed a thermal mechanism in which bubbles of liquid vapour are formed by injection of large electron densities with high energies from asperities on the cathode. The breakdown criterion is based on the balance condition between the heat needed for vaporization and the energy input. The breakdown strength is given by

$$A E_{bd}^n \tau = c_p(T_b - T_0) + L_v \quad (2.23)$$

where n is a factor in the range of 1.5 to 2, τ is the duration of the application of voltage, c_p is the specific heat at constant pressure, T_b is the boiling temperature of the liquid, T_0 is the initial temperature of the liquid, and L_v is the latent heat for vaporization. Sharbaugh and Watson [1962] have attributed the pressure dependence of breakdown strength to the change in the boiling temperature of the liquid with applied pressure. Their computed results based on Eq. (2.23) for breakdown strength as a function of pressure are in good agreement with the experimental results of Kao and Higham [1961].

Another bubble theory for breakdown of dielectric liquids has been developed by Krasucki [1966]. However, his theory is similar to Kao's theory [1960] except that Krasucki takes into account the change in the volume of the bubble when it elongates along the field.

However, the bubble theory or cavitation theory can explain the dependence of breakdown strength on hydrostatic pressure but there is no direct evidence of the formation of bubbles in simple dielectric liquids of high purity. For this reason Kao [1975, 1976] has proposed another mechanism. His model has already been discussed in section 2.2.5. Equation (2.21) can explain the pressure dependence of breakdown strength through the pressure dependence of T_b as has been proposed by Sharbaugh and Watson [1962]. The computed results based on Eq. (2.21) by Kao [1976] are in good agreement with the experimental results of Kao and Higham [1961] as shown in Fig. 2.12.

2.2.8 Dependence of Breakdown Strength on Pulse Duration

Crowe [1956] has measured the pulse breakdown strengths of n-hexane, n-heptane, n-octane and n-decane as functions of pulse duration. Similar measurements have also been performed by Kao and Higham [1961] in n-hexane, n-heptane and n-decane with pulse duration up to 11 μsec . Both groups of investigators have agreed that beyond a certain duration the breakdown strength is virtually time-independent but it increases rapidly for times less than t_0 . Kao and Higham have also reported that the time to breakdown is nearly the same as the pulse durations if the durations are less than about 3.5 μsec , but it is variable and usually considerably less than the pulse duration if the durations are about 10 μsec or more. They have also

reported that for pulse duration less than 3.5 sec the breakdown strength is critically dependent on pulse duration. The critical time lag has been observed for gaps of about 200 μm and it is dependent on the gap length but is independent of pressure and temperature and chain length in saturated hydrocarbons. These observations are in agreement with Crowe [1956] but in disagreement with Goodwin and MacFadyen [1953]. Kao and Higham [1961] have attributed their results to the time required to accumulate a space charge in order to enhance the field to a value high enough to cause elongation of bubbles formed in the liquid and the discrepancy between their results and Goodwin and MacFadyen would be due to cathode surface conditions. However, the formation of bubbles in simple pure hydrocarbon liquids is doubtful though this may happen in liquids such as in transformer oil.

2.3 ELECTROLUMINESCENCE

Electroluminescence in transformer oil has been observed by Darveniza [1959], and Darveniza and Tropper [1961]. Electroluminescent intensity as a function of the applied electric field, dissolved air and nitrogen as well as the effect of applied pressure has been investigated. The electroluminescent intensity and associated conduction current both increase with the increase of the applied electric field as shown in Fig. 2.15. However, no dependence of electroluminescent intensity on the presence of either nitrogen or air into the liquid, and no pressure dependence for the pressure ranging from -350 mm Hg to 760 mm Hg has been detected. Darveniza and Tropper [1961] have also reported that no visible

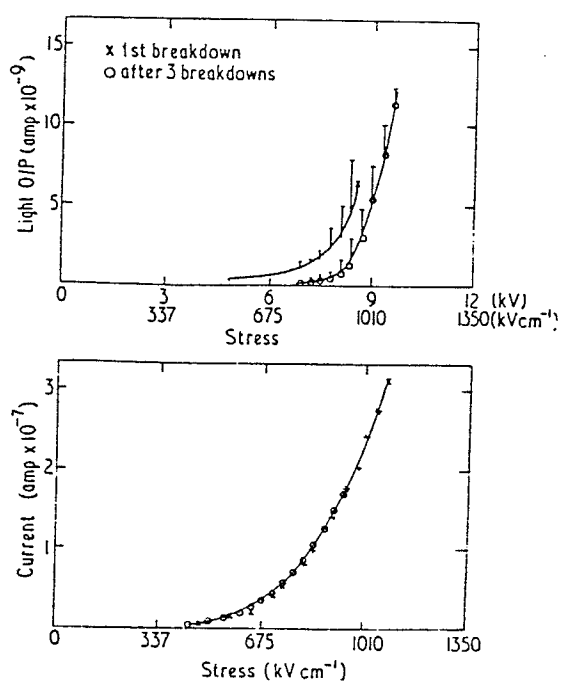


Fig. 2.15 Light-voltage (above) and current-voltage (below) characteristics in transformer oil [after Darveniza and Tropper 1961].

light was observed in purified n-hexane and only when the liquid was doped with $1 \text{ g } \ell^{-1}$ of scintillation grade anthracene visible light was observed in the doped liquid. They have attributed the phenomenon of electroluminescence to the excitation collision of electrons injected from the cathode with liquid and impurity molecules. The excited molecules release their energy absorbed during the collision from the electrons thus causing the light emission. Following the pattern of doping dielectric liquids to study the phenomenon of electroluminescence, Kalinowski and Dera [1964] have investigated the electroluminescent intensity in benzene when doped with the scintillator PoPoP (20 mg/litre), and Kalinowski [1967] has also derived an expression for the electroluminescent intensity as a function of the electric field, which is given by

$$\phi(E) = PE \exp \left(- \frac{G}{E} \right) \quad (2.24)$$

where P and G are constants depending on the electrode material and the condition of its surface, the mobility and the mean free path of electrons in the liquid, the excitation potential of molecules and the probabilities of non-elastic collision and light emission. Chadband and Wright [1965] have reported that there is a change in refractive index near the cathode n-hexane. This change of refractive index in the electrically stressed region has been observed earlier by Hakim and Higham [1961] in n-hexane using the same technique - Schlieren optical technique. Both groups of investigators used a high speed streak camera (100,000 rev/min) to investigate the growth of this prebreakdown phenomenon in n-hexane. Such a change in refractive index starts at the cathode after a short delay, crosses the electrode gap.

at an approximately constant speed, and when it has crossed almost four fifths of the gap, breakdown ensues. They have suggested that electrons emitted from the cathode may gain enough energy from the accelerating field to cause excitation of molecules, and after an electron has transferred its energy to a molecule, it may be either accelerated again to repeat the process or attach itself to a neutral molecule to form a negative ion. The light emission at fields below breakdown strength may be associated with the energy release from the excited molecules. However, Kao's group in England [Kao 1965, Smith et al. 1966A, 1966B] were the first to use an image intensifier system to investigate the electroluminescence phenomena in filtered n-hexane using different electrode configurations at room temperature and atmospheric pressure. They have reported that the electroluminescence always commences in the cathode region regardless of the geometry of the electrode system, and that using a positive point and a negative sphere, electroluminescence occurred first at the sphere, but following its travel to a certain distance in the liquid gap, light emission also started at the positive point electrode. They have explained this behaviour as due to the fact that some free electrons when reaching the intense field region near the positive point electrode may gain enough energy to cause ionization and then form a separate volume of plasma near the anode. In this case, breakdown occurs when the plasmas in the two regions extend until they bridge the gap.

Using an image converter camera system in conjunction with flash-illuminated Schlieren optics to obtain frame speeds of 1×10^7 frames/sec, McGrath and Nelson [1977] have investigated the prebreakdown events in

n-hexane. When a negative high-voltage pulse is applied to the point of a nonuniform field gap, a disturbance associated with discrete shock waves propagates outwards from the point. When the point is positive in polarity, the disturbance moves at supersonic velocity. In both cases the disturbance is identified as a region of closely packed microbubbles which ultimately fragments into isolated bubbles if breakdown does not intervene. Typical results are shown in Fig. 2.16, where photograph (a) was taken 5 μsec after the application of 25 kV negative pulse to the point electrode. This phenomenon may be similar to the disturbance due to refractive index changes. In photograph (b) the microscopic regions have been interpreted as small gaseous bubbles with diameters in the range of 2-60 μm . After longer delays Fig. 2.16c and Fig. 2.16d show that these bubbles continue to traverse the gap. They believe that microbubbles are responsible for the observed results. On the other hand, Birlasekaran and Darveniza [1976] believe that the observed luminescence in dielectric liquids is due to microdischarges caused by the field-induced motion of charged particles approaching the electrodes. Chiu [1976] has observed a luminescent zone in n-hexane with point-point electrode, and reported that the breakdown channel is initiated by this luminescent zone. This luminescent zone is of 40 to 150 μm in radius. The luminescent zone increases in size as the gap length is increased and is ten times smaller at the anode than that at the cathode. Chiu has explained this phenomenon in terms of the formation of ionic radicals, due to the electrolysis of n-hexane at low fields and chemical changes of the liquid at high fields. These ionic radicals may become attached

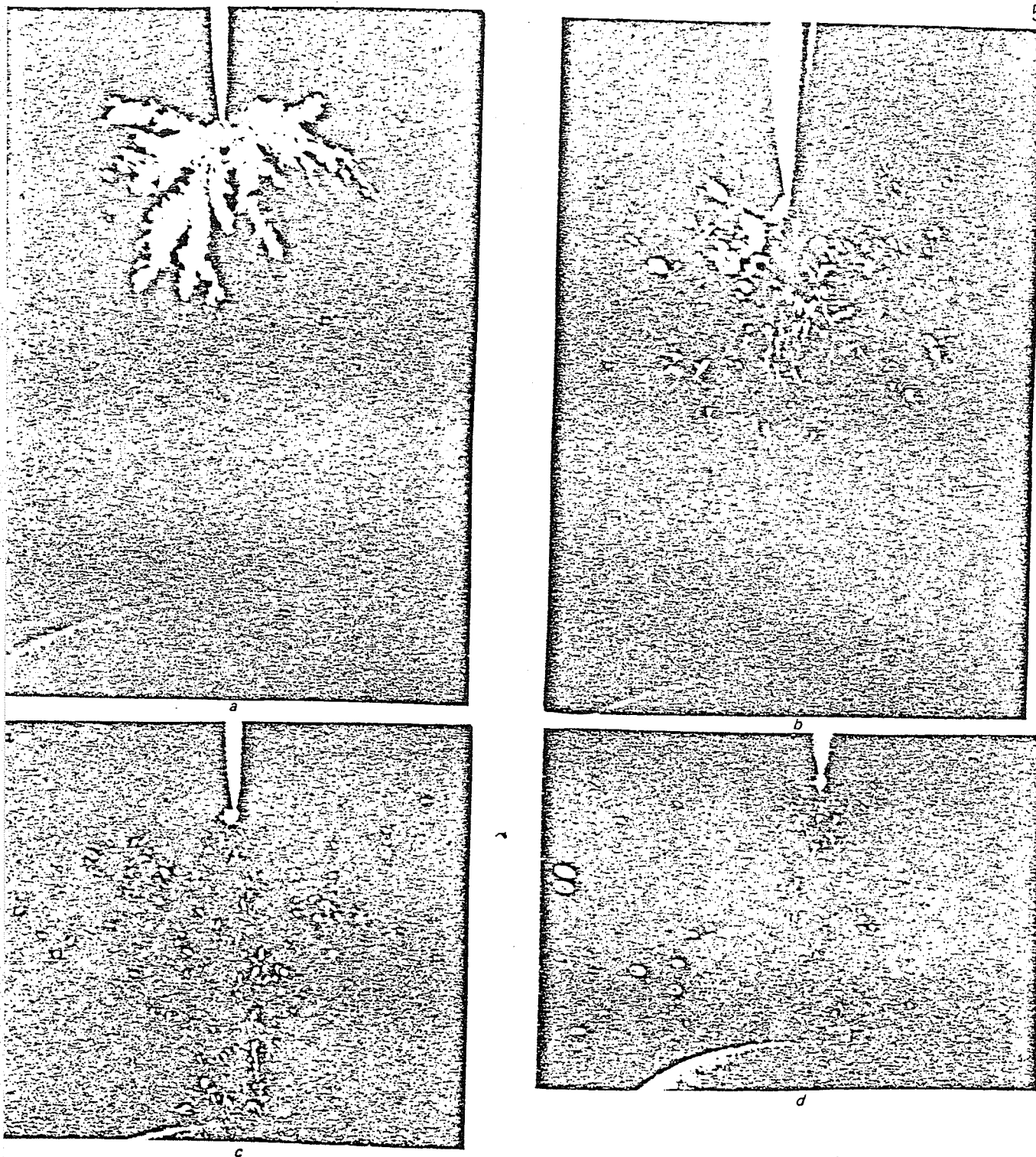


Fig. 2.16 The scattered-light emission photographs in n-hexane when a 0.2 cm liquid gap between a point and sphere electrodes is subjected to a negative pulse of 25 kV. a: Taken after 5 μ sec; b: after 300 μ sec; c: after 820 μ sec; d: after 4 msec [after McGrath and Nelson 1977].

to the electrode tip by dielectrophoretic forces and the transformed species have the property of absorbing electrons during their brief attachment life time at the cathode tip.

2.4 ELECTROHYDRODYNAMIC PHENOMENA

Felici [1971] has mentioned that although electrohydrodynamic phenomena in dielectric liquids has been known from Faraday's experiment, it has never been thought to be important in the conduction process in dielectric liquids. In 1956 Ostroumov was the first to photograph the motion of both benzene and transformer oil under the influence of applied electric field. He has observed that the direction of the motion and its intensity do not depend on the sign of the applied voltage. However, the intensity increases with the increase of the applied voltage. This may be due to the presence of ions in the liquid which developes an internal pressure in the liquid. This pressure is produced by the transfer of momentum of the ions to the liquid due to the friction between those ions and the liquid itself. The pressures created by this mechanism can be appreciable and can be several orders of magnitude higher than gas pressure on the liquid surface [Stuetzer 1959]. The increase in pressure has been reported by Hakim and Higham [1962] to be proportional to E^2 . However, Essex and Secker [1968] and, more recently, Kao [1976] believe that the turbulence occurring in the liquid or the motion of the liquid should affect, to a certain degree, the effective mobility of charge carriers.

CHAPTER 3

EXPERIMENTAL TECHNIQUES

Two groups of liquids have been chosen for the main work of our investigation: (A) Normal saturated hydrocarbons, these are of the type $C_n H_{2n+2}$ and they are in the form of long chains without branches and are generally referred to as "normal" hydrocarbons. In Table 3.1 are listed some of the physical properties of this group. (B) Unsaturated hydrocarbons, this group possesses fewer hydrogen atoms per molecule compared to saturated hydrocarbons with the same number of carbon atoms. One of the groups which belongs to unsaturated hydrocarbons, are aromatic liquids. In Table 3.2 are listed some of the physical properties for aromatic hydrocarbons.

For the conduction current measurements; n-pentane, n-hexane, and n-heptane of saturated hydrocarbons, and benzene and toluene of unsaturated hydrocarbons, both groups of spectroscopic grade, were used. For electroluminescence measurements other liquids such as cyclohexane and carbon tetrachloride of spectroscopic grade, and benzene and chloroform of technical grade were also used. The impurity contents of all spectroscopic grade liquids as received are given in Table 3.3.

3.1 PREPARATION OF THE LIQUID SAMPLES

For conduction current measurements the liquid sample was dehydrated by storing it for several days (at least 2 days) in contact with metallic sodium. The liquid was then filtered at least six times through a filtration system shown in Fig. 3.1, with the test cell as

TABLE 3.1
 PHYSICAL PROPERTIES OF NORMAL SATURATED HYDROCARBONS
 (After Kao 1965,1977)

Liquid	Molecular Weight	Density g cm ⁻³	Boiling point °C	Specific heat cal /g °C	Relative permittivity
n-pentane* C ₅ H ₁₂	72.14	0.627	36.3	0.527	2.1
n-hexane C ₆ H ₁₄	86.17	0.659	68.70	0.5440	1.890
n-heptane C ₇ H ₁₆	100.20	0.684	98.40	0.4900	1.920
n-octane C ₈ H ₁₈	114.22	0.703	125.50	0.5780	1.948
n-decane C ₁₀ H ₂₂	142.27	0.730	174.10	0.5280	1.991

*From Handbook of Chemistry and Physics, 57th edition, 1976-1977.

TABLE 3.2
 PHYSICAL PROPERTIES OF AROMATIC HYDROCARBONS
 (After Kao 1965,1976)






Liquid	Structure	Molecular Weight	Density g cm ⁻³	Boiling point °C	Specific heat cal/g °C	Relative permittivity
Benzene C ₆ H ₆		78.11	0.879	80.08	0.4060	2.284
Toluene C ₇ H ₈		92.13	0.866	110.60	0.4000	2.379
Ethyl-Benzene C ₆ H ₅ -C ₂ H ₅		106.16	0.867	136.15	0.4164	2.412
n-propyl-Benzene C ₆ H ₅ -nC ₃ H ₇		120.18	0.862	159.31	0.4240	2.373
n-Butyl-Benzene C ₆ H ₅ -nC ₄ H ₉		134.21	0.862	183.10	0.4340	2.359

TABLE 3.3
IMPURITY CONTENTS OF THE LIQUIDS USED

Liquid	Boiling Point °C	Impurity contents as given by manufacturer
n-hexane	68-70	Residue after evaporation 0.001% Acidity as CH ₃ COOH 0.002% Sulfur compounds 0.005%
n-pentane	36.074	Not available
n-heptane	98.428	Not available
benzene	80.1 ± 0.1	Residue after evaporation 0.001% Thiophene 1 ppm Sulfur compounds 0.005% Water 0.05% Heavy Metals as (pb) 0.1 ppm Iron (Fe) 0.1 ppm Copper (Cu) 0.1 ppm Nickel (Ni) 0.1 ppm
toluene	110.6 ± 0.1	Residue after evaporation 0.001% Sulfur compounds 0.003% Water 0.02% Heavy metals as (pb) 0.1 ppm Iron (Fe) 0.1 ppm Copper (Cu) 0.1 ppm Nickel 0.1 ppm
cyclohexane	80.7 ± 0.1	Residue after evaporation 0.002% Water 0.02%
carbon tetra-chloride	76.7 ± 0.1	Residue after evaporation 0.001% Sulfur compounds 5 ppm Chloride (Cl) 2 ppm Heavy metals (as pb) 0.1 ppm Water 0.02%

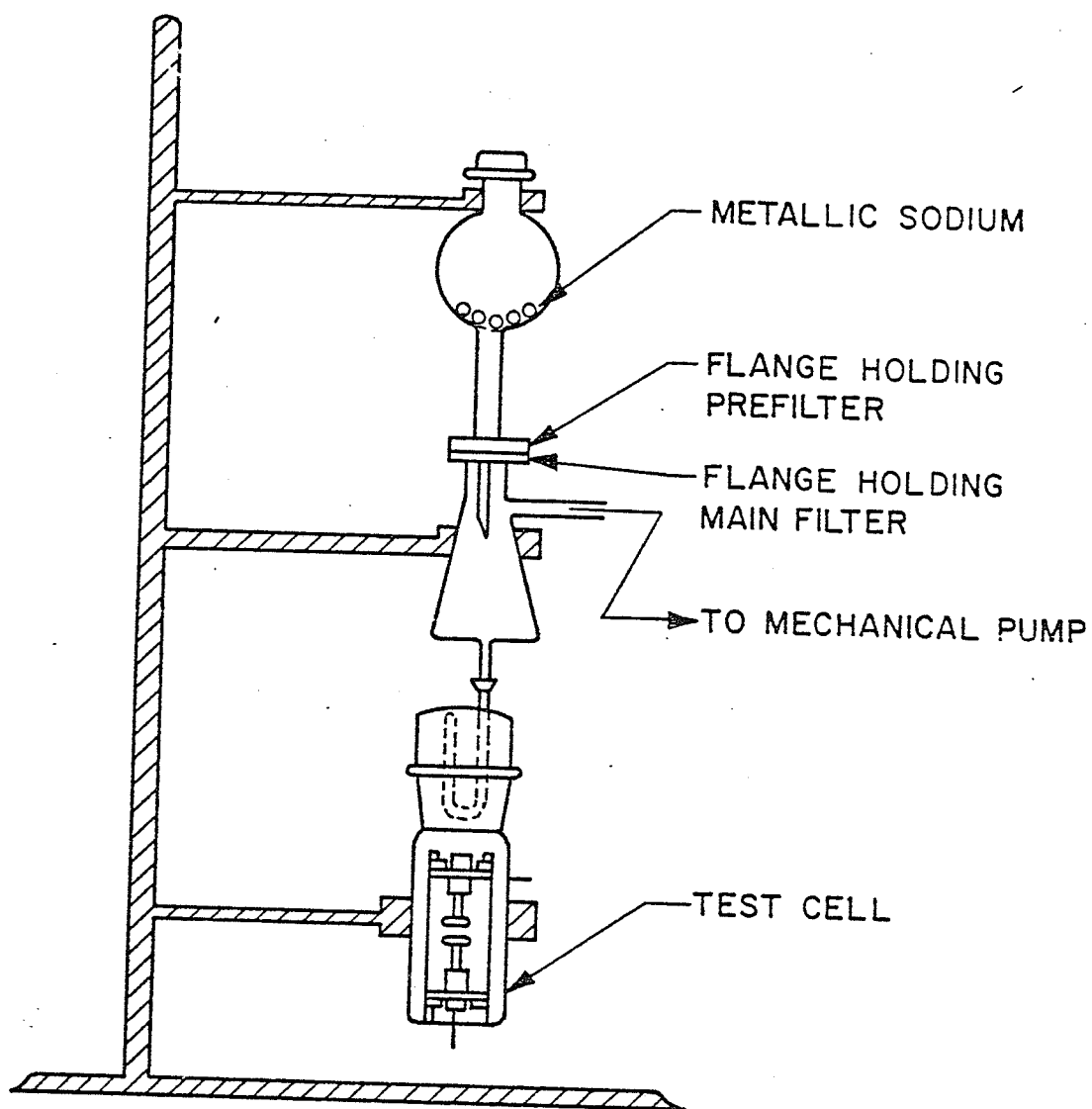


Fig. 3.1 The liquid filtration system

part of the system. Two filters in series were used and both were mounted in a pyrex filter holder. The filters and the filtration system were supplied by Millipore Limited, the pore size of the prefilter and the final filter being 500 nm and 25 nm, respectively. The filters were replaced with new ones after each filtration. The electrodes were mechanically polished, with soft mops and polishing compounds, until there were no pits or scratches visible under the microscope. Following the polishing, the electrodes were cleaned several times by petroleum ether and then by n-hexane. After this process they were further cleaned by immersing them in boiling n-hexane for 30 minutes. After the electrodes were assembled in the electrode system, the whole assembly was finally cleaned for one hour in clean boiling n-hexane. Boiling n-hexane was used as cleaning reagent for experiments with n-hexane. For experiments with other liquids, the particular liquid for experiments was used as a cleaning reagent. This was, in fact, the same technique used earlier by Kao and his co-workers [1961, 1965]. The liquid samples were not degassed because partial degassing had been noticed to cause current fluctuations and inconsistent results as had been reported by Kao et al. [1965]. Thus, the liquid samples were allowed to be saturated with dry air. The liquid samples saturated with gas usually gave consistent and reproducible results. The purification technique was simple, but solid particles of sizes larger than 25 nm in diameter as well as traces of water were carefully removed by slow filtration and strong flushing of the test cell and the electrode system.

3.2 CONDUCTION CURRENT MEASUREMENTS

The model SAME-KS 150-2 electrostatic generator was used as the direct voltage source, and the conduction current was measured with Keithley 601 electrometer. The glass test cell containing the liquid sample was placed in a thermostatically controlled bath containing transformer oil as heating medium. The test cell and the stopper provided with a U-tube were completely filled with the purified liquid sample. This liquid sample was then sealed with a drop of mercury put into the U-tube as shown in Fig. 3.2. Two parallel-plane stainless steel electrodes were used to avoid the possible effects of complicated field and space-charge distributions caused by other forms of electrode geometry. Each of the electrodes was shaped to give a Bruce type uniform field electrode with an overall diameter of 2 cm to avoid the edge effect. The error in parallelism is estimated to be less than 3%. Throughout the investigation the gap length was fixed at 0.2 cm. The electrodes were supported by a frame work of three rods and two circular discs, all of Lava stone. The arrangement for the conduction current measurements at various temperatures is shown in Fig. 3.2. To obtain reproducible results the liquid sample was electrically stressed for about 40 minutes at each of four different increasing fields. This time was usually long enough for the conduction current to reach a steady state value, but if not, sufficient time for this to occur was given before the field was raised. After such a step-by-step conditioning has been completed at room temperature the liquid sample was then heated. The liquid sample was maintained at the highest temperature of the temperature range used for this investigation for about two hours, and then the

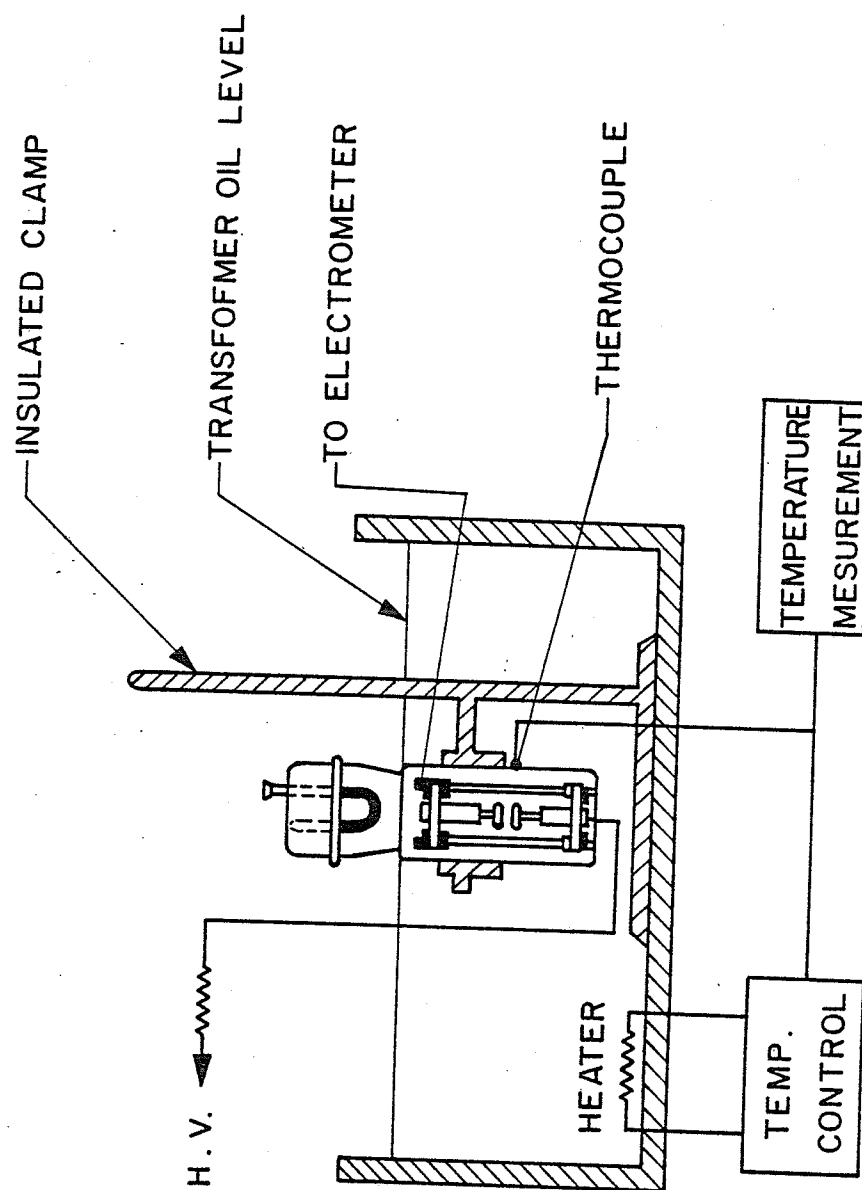


Fig. 3.2 Arrangement for measurement of temperature effect on conduction current

conduction current was measured as the temperature was decreased slowly to room temperature. This was also the same technique used earlier by Kao and Calderwood [1965].

3.3 ELECTROLUMINESCENCE MEASUREMENTS

For this investigation several liquids have been chosen in order to examine whether this phenomenon occurs in all dielectric liquids. The liquids used were n-hexane, cyclohexane, benzene and carbon tetrachloride of spectroscopic grade of purity, and also transformer oil, benzene and chloroform of technical grade. All liquids were used as supplied by the manufacturer without any further treatment. The glass test cell was equipped with a flat quartz window aligned with the electrode system and the liquid gap. The Westinghouse WL-32002 image intensifier system with its photocathode sensitive to visible and near infrared (photo response S-25), together with RCA 931A photomultiplier 9 stages (photo response S-4), Keithly 601 electrometer and Honeywell Elektronik 19 double pen recorder were used to record the electroluminescent intensity. Fig. 3.3 shows the arrangement for these measurements. For the effect of hydrostatic pressure measurements the test cell was placed in a pressure chamber similar in design to that used by Kao and his co-workers [1961, 1965]. The chamber consists of a perspex cylinder 12 inches in length, and 4 inches and 5 inches in inside and outside diameters, respectively. The two metal end plates are isolated from each other by six Permali rods of 3/4 inch in diameter. The chamber was filled with transformer oil up to the stopper of the test cell, but below the tip of the U-tube. The function of the

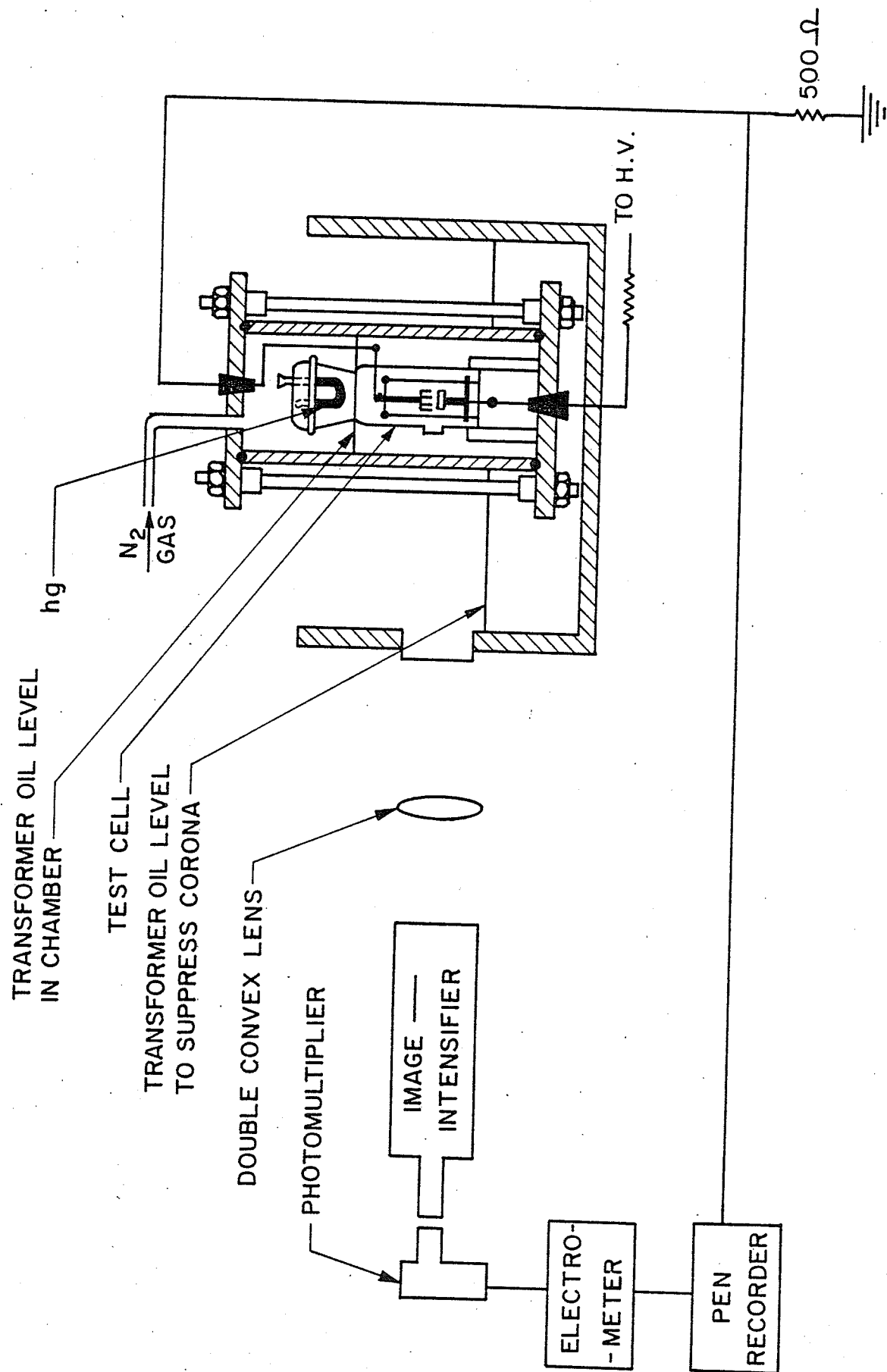


Fig. 3.3 Arrangement for electro-luminescence measurements

transformer oil is to act as a safety measure in case the pressure chamber bursts. Pure nitrogen gas was used as medium to transmit the pressure via the mercury seal to the liquid sample. The chamber was placed in a tank filled with transformer oil to a level below the test cell window, with the aim avoiding any corona discharge at the high voltage end of the chamber [bottom end]. The image intensifier system together with a double convex lens were mounted on a telescopic stand to facilitate fine adjustment of the position of the image intensifier to align with the liquid gap. The double convex lens could be accurately adjusted to give a better image. The photomultiplier was shielded and was fitted nicely to the eye piece of the image intensifier so that no external light could leak into the system. The output of the photomultiplier was measured with Keithly 601 electrometer and also with the pen recorder to record the details of the light signal variations. Another set of equipment was used simultaneously to measure the conduction current associated with the light signal. Apart from the electrometer and the double pen recorder the optical system was enclosed in a dark room. To align the liquid gap with the optical system, a small light bulb was placed inside the tank to illuminate the liquid gap so that the image intensifier can view the electrode system. By adjusting the horizontal distance between the lens and the liquid gap until a clear image of the electrodes was observed on the image intensifier screen, which was turned on at the ground level. The small light was then turned off and the setup is ready for electroluminescence experiments.

For this investigation the positive electrode was a stainless steel plane having the shape of a Bruce type uniform electrode and an overall

diameter of 2 cm. The negative electrode was a stainless steel sphere of diameter 0.3 cm if the electroluminescent intensity was sufficiently large, such as in some liquids of technical grade (e.g., benzene). For liquids, such as pure n-hexane, etc., the electroluminescent intensity was weak, then a cathode containing 4 steel points, each of which was of 0.008 cm in radius, aligned linearly with the separation of 0.4 cm between the nearest points, was used.

CHAPTER 4

HIGH FIELD ELECTRIC CONDUCTION

For a long time now there has been difficulty in accounting for the low negative carrier mobilities normally found in simple liquids such as n-hexane. The failure of mobility data to satisfy Walden's rule (which states that the product of mobility and viscosity is temperature invariant) indicates that carriers may not be pure ions in the host liquid. The recent finding of negative charge carriers of much higher mobility [Minday et al. 1971] has changed the concept about the role of impurities in controlling the electric conduction in dielectric liquids. However, the fast charge carriers observed are much faster than ions, but still several orders of magnitude slower than free electrons in liquified rare gases. Even though these fast charge carriers are electronic in nature their behaviour would be quite different from excess electrons in the rare liquified gases. In dielectric hydrocarbon liquids the presence of various impurities is inevitable. Such impurities may act as traps to trap charge carriers. In solids, charge carriers trapped in trapping sites are essentially stationary, whereas in liquids they can migrate in the field direction, but with a much lower mobility than that of free electrons. Thus the charge carriers in dielectric liquids may spend some time as free electrons and some time as trapped electrons during their migration under an applied field.

From the recent work of Kao [1976, unpublished] and the recent review [O'Dwyer 1973] on high-field electric conduction in dielectrics we believe that the conduction process at high fields involves field assisted

single injection and field enhanced detrapping. From the recent paper of Kao [1976] and the experimental evidence of filamentary conduction at higher fields in dielectric solids [Hwang and Kao 1974, Saji and Kao 1976, Nakashima and Kao 1977] and in dielectric liquids [Goodwin 1956], we also believe that the electric conduction is filamentary at high fields. In fact, the electric breakdown channel is always filamentary no matter whether it is in a liquid, a solid, or a gas; and a breakdown produces only a tiny spot of damage on each of the electrode surfaces.

Because of the trapping and the detrapping processes, the mean carrier mobility is expected to be field dependent, and this has been observed experimentally by Schmidt et al. [1974]. In this chapter the theoretical analysis will be presented first using similar methods and assumptions as was adopted by Kao [1976] except that the carrier mobility is not assumed to be constant but is controlled by the trapping and detrapping processes when a carrier moves from the cathode to the anode. This theory is then used to interpret the experimental results.

4.1 THEORY

Some important assumptions are made for the theoretical analysis and they are as follows:

- (a) At fields higher than the threshold field for the onset of electron injection from the cathode, the carriers are predominantly negative-charge carriers, free electrons and trapped electrons (trapped electrons may be considered as negative ions with a much lower mobility), and the flow

of such carriers constituting electric conduction is confined mainly in one or more filaments formed between two parallel plane electrodes (with the edge effect neglected). The total current can be expressed as

$$I_T = I_{\text{film 1}} + I_{\text{film 2}} + \dots = \sum_m I_m \approx HI \quad (4.1)$$

Equation (4.1) means that the total current can be represented by the current in one filament I multiplied by a parameter H which may be field-dependent. In this analysis we use cylindrical coordinates are used and only one filament formed with its center along the z -axis and confined in a domain of radius r_d is considered (the filament is generally not straight [Saji and Kao 1976]). The treatment is two dimensional with plane at $z = 0$ as the cathode and that at $z = d$ as the anode with the whole system symmetrical about the z -axis, the gap length being d .

- (b) In the filament, the longitudinal component of the diffusion current can be ignored because of the large longitudinal component of the electric field, and the radial component of the drift current can be ignored because of the small radial component of the electric field.
- (c) The concentration of thermally generated carriers in the bulk is negligibly small as compared with that of

injected carriers from the cathode and, therefore, can be ignored.

As has been mentioned earlier, the trapped electrons in the liquid are not stationary like those in solids, but move under an applied electric field and hence contribute to electric conduction. It is, therefore, more logical to postulate that the total concentration of free and trapped electrons n are due to electron injection from the cathode and that the electric conduction in one filament is mobility-controlled and governed by the current flow equation

$$\begin{aligned}\vec{J}(r) &= \vec{J}_z(r) + \vec{J}_r(r) \\ &= q\mu n E_z \vec{i}_z + (q\mu n E_r - qD \frac{dn}{dr}) \vec{i}_r\end{aligned}\quad (4.2)$$

the continuity equation

$$\frac{\partial n}{\partial t} = - \frac{1}{q} \vec{\nabla} \cdot \vec{J}(r) \quad (4.3)$$

and the Poisson equation

$$\vec{\nabla} \cdot \vec{E} = \vec{\nabla} \cdot (E_z \vec{i}_z + E_r \vec{i}_r) = \frac{qn}{\epsilon} \quad (4.4)$$

where E_z and E_r and \vec{i}_z and \vec{i}_r are, respectively, the fields and the unit vectors in the z and r direction and the other symbols have their usual meanings which have been defined in Chapter 2 [please see also the symbols list]. By assuming that electron motion occurs through thermally activated jumps from one trap to another with an average trap depth (or an average barrier height) W , separated by an average distance λ . The effective

carrier mobility given by Eq. (2.14) is now rewritten as follows

$$\mu = \frac{\lambda v}{E} \exp\left(-\frac{W}{kT}\right) \left[\exp\left(\frac{q\lambda E}{2kT}\right) + \exp\left(-\frac{q\lambda E}{2kT}\right) \right]. \quad (4.5)$$

At high fields the term $\exp(-q\lambda E/2kT)$ is small and can be neglected, hence the mobility μ_h at high fields may be written as

$$\mu_h = \frac{\lambda v}{E} \exp\left(-\frac{W}{kT}\right) \exp\left(\frac{q\lambda E}{2kT}\right). \quad (4.6)$$

In the steady state, $\partial n / \partial t = 0$. Thus Eq. (4.3) reduces to

$$\vec{\nabla} \cdot \vec{J}(r) = 0. \quad (4.7)$$

By substituting from Eq. (4.2) into (4.7), we obtain

$$\vec{\nabla} \cdot \left[q n E_z \vec{i}_z + (q\mu_n E_r - qD \frac{dn}{dr}) \vec{i}_r \right] = 0. \quad (4.8)$$

Equation (4.8) can be separated to

$$\frac{d(\mu_n E_z)}{dz} = 0 \quad (4.9)$$

and

$$\begin{aligned} \mu_n r \frac{dE_r}{dr} + \mu E_r \frac{dn}{dr} + n E_r r \frac{d}{dE_r} \frac{dE_r}{dr} + \mu n E_r \\ - D \frac{dn}{dr} - Dr \frac{d^2 n}{dr^2} = 0. \end{aligned} \quad (4.10)$$

Since E_r is very small based on assumption (b) but dE_r/dr is not and follows the Poisson equation, thus Eq. (4.10) becomes

$$\mu n r \frac{dE_r}{dr} + n E_r r \frac{d\mu}{dE_r} \frac{dE_r}{dr} = D \left[\frac{dn}{dr} + r \frac{d^2 n}{dr^2} \right]. \quad (4.11)$$

The Poisson equation in the radial direction is

$$\frac{1}{r} \left[r \frac{dE_r}{dr} + E_r \right] = \frac{qn}{\epsilon}. \quad (4.12)$$

Ignoring E_r term, Eq. (4.12) reduces to

$$\frac{dE_r}{dr} = \frac{qn}{\epsilon}. \quad (4.13)$$

From Eqs. (4.13) and (4.12), we have

$$\frac{q\mu n^2}{\epsilon} + \frac{qn^2}{\epsilon} E_r \frac{d\mu}{dE_r} + \mu E_r \frac{dn}{dr} = D \left[\frac{1}{r} \frac{dn}{dr} + \frac{d^2 n}{dr^2} \right]. \quad (4.14)$$

Physical reality requires n to be finite for all values of r , and this demands that dn/dr must approach zero when $r \rightarrow 0$. Thus Eq. (4.14) reduces to

$$\frac{q\mu n^2}{\epsilon} + \frac{qn^2}{\epsilon} E_r \frac{d\mu}{dE_r} = D \frac{d^2 n}{dr^2}. \quad (4.15)$$

Due to the fact that E_r is very small, then the effective mobility of charge carriers in the radial direction can be assumed to be independent of the applied electric field, and is μ_ℓ as given by Eq. (2.15). Thus Eq. (4.15) reduces to:

$$\frac{q\mu_\ell}{\epsilon} n^2 = D \frac{d^2 n}{dr^2}. \quad (4.16)$$

Using the boundary conditions: $n \rightarrow n_0$ (the carrier concentration at the center of the filament) when $r \rightarrow 0$ and $dn/dr \rightarrow 0$ and $n \rightarrow 0$ when $r \rightarrow \infty$, the solution of Eq. (4.16) yields [For details, please see Appendix A].

$$n = n_0 \left[1 + \left(\frac{q\mu_e n_0}{6\epsilon D} \right)^{\frac{1}{2}} r \right]^{-2}. \quad (4.17)$$

Equation (4.17) has been derived earlier by Kao [1975, 1976].

The concentration n_0 at the center of the filament is related to the current density J_{z0} at $r = 0$ as follows

$$\begin{aligned} J_{z0} &= q\mu_h n_0 E_z \\ &= qn_0 \lambda v \exp\left[-\left(\frac{W}{kT} - \frac{q\lambda E_z}{2kT}\right)\right]. \end{aligned} \quad (4.18)$$

At the center of the filament and in the z direction Eq. (4.4) can be written

$$\frac{dE_z}{dz} = \frac{qn_0}{\epsilon}. \quad (4.19)$$

From Eqs. (4.18) and (4.19) we have

$$\frac{dE_z}{dz} = \frac{J_{z0}}{\epsilon\lambda v} \exp\left[\frac{W}{kT} - \frac{q\lambda E_z}{2kT}\right]$$

or:

$$J_{z0} dz = \epsilon\lambda v \exp\left(-\frac{W}{kT}\right) \exp\left(\frac{q\lambda E_z}{2kT}\right) dE_z. \quad (4.20)$$

Using the boundary conditions:

$$E \rightarrow E_c \quad \text{when } z \rightarrow 0$$

and:

$$V = \int_0^d Edz = E_{av}d$$

the solution of Eq. (4.20) yields [For details please see Appendix B].

$$J_{zo} = \frac{2kT\varepsilon v}{qd} \left\{ e \exp\left[-\frac{(W - q\lambda E_{av}/2)}{kT}\right] - \exp\left[-\frac{W - q\lambda Y E_{av}/2}{kT}\right] \right\} \quad (4.21)$$

where

$$Y = \frac{E_c}{E_{av}}.$$

The current density J_{zo} can be approximated as a function of the average value of the charge carrier concentration \bar{n}_0 , the average value of the carrier mobility $\bar{\mu}_h$ and the average value of the electric field E_{av} , and it may be written as

$$\begin{aligned} J_{zo} &= q\bar{\mu}_h\bar{n}_0 E_{av} \\ &= q\bar{n}_0\lambda v \exp\left[-\left(\frac{W}{kT} - \frac{q\lambda E_{av}}{2kT}\right)\right]. \end{aligned} \quad (4.23)$$

The combination of Eq. (4.21) and Eq. (4.23) gives

$$\bar{n}_0 = \frac{2\varepsilon kT}{q^2\lambda d} \left\{ e - \exp\left[-\frac{q\lambda E_{av}}{2kT} (1 - Y)\right] \right\}. \quad (4.24)$$

At high electric fields Y is smaller than but close to unity, hence Eq. (4.24) can be approximated as follows

$$\bar{n}_0 = \frac{2\varepsilon kTe}{q^2\lambda d} \left\{ 1 - \exp\left[-\left(1 + \frac{q\lambda E_{av}}{2kT} (1 - Y)\right)\right] \right\}. \quad (4.25)$$

By expanding the term $\exp[-(1 + q\lambda E_{av}/2kT (1 - Y))]$ and keeping in mind that $(1 - Y)$ is very small but is a positive quantity, then we can neglect terms involving $(1 - Y)$ with powers higher than unity. Thus Eq. (4.25) reduces to

$$\bar{n}_0 = \frac{4\epsilon k T e}{3q^2 \lambda d} \left[1 + \frac{q\lambda E_{av}}{4kT} (1 - Y) \right]. \quad (4.26)$$

Using \bar{n}_0 for n_0 in Eq. (4.17) and assuming that the low-field mobility μ_ℓ follows the Einstein relation $\mu_\ell/D = q/T$, the average negative charge carrier concentration along the z-direction as a function of r is given by

$$\bar{n} = \bar{n}_0 \left[1 + \left(\frac{q^2}{6\epsilon k T} \right)^{1/2} (\bar{n}_0)^{1/2} r \right]^{-2}. \quad (4.27)$$

substitution of the expression for \bar{n}_0 from Eq. (4.26) into Eq. (4.27) yields

$$\bar{n} = \bar{n}_0 \left\{ 1 + \left[\frac{2ed}{9\lambda} \left(1 + \frac{q\lambda E_{av}}{4kT} (1 - Y) \right) \right]^{1/2} \frac{r}{d} \right\}^{-2}. \quad (4.28)$$

Hence the current density $J_z(r)$ can be written as

$$\begin{aligned} J_z(r) &= q\bar{\mu}_h \bar{n} E_{av} \\ &= q\bar{\mu}_h E_{av} \bar{n}_0 \left\{ 1 + \left[\frac{2ed}{9\lambda} \left(1 + \frac{q\lambda E_{av}}{4kT} (1 - Y) \right) \right]^{1/2} \frac{r}{d} \right\}^{-2}. \end{aligned} \quad (4.29)$$

In Eq. (4.29) the term $q\bar{\mu}_h E_{av} \bar{n}_0$ is equal to J_{z0} , hence we can write

$$J_z(r) = J_{z0} \left\{ 1 + \left[\frac{2ed}{9\lambda} \left(1 + \frac{q\lambda E_{av}}{4kT} (1 - Y) \right) \right]^{1/2} \frac{r}{d} \right\}^{-2}. \quad (4.30)$$

Thus, the current confined in a filament of effective radius r_d is given by

$$\begin{aligned}
I &= \int_0^{r_d} J_z(r) 2\pi r dr \\
&= \int_0^{r_d} 2\pi J_{zo} \left\{ 1 + \left[\frac{2ed}{9\lambda} \left(1 + \frac{q\lambda E_{av}}{4kT} (1 - \gamma) \right)^{\frac{1}{2}} \frac{r}{d} \right]^{-2} \right\} r dr \\
&= J_{zo} (2\pi d^2) \left\{ \frac{2ed}{9\lambda} \left[1 + \frac{q\lambda E_{av}}{4kT} (1 - \gamma) \right]^{-1} \right. \\
&\quad \times \left[\ln \left[1 + \left(\frac{2ed}{9\lambda} \left[1 + \frac{q\lambda E_{av}}{4kT} (1 - \gamma) \right]^{\frac{1}{2}} \frac{r_d}{d} \right)^{-1} \right. \right. \\
&\quad \left. \left. + \left[1 + \left(\frac{2ed}{9\lambda} \left[1 + \frac{q\lambda E_{av}}{4kT} (1 - \gamma) \right]^{\frac{1}{2}} \frac{r_d}{d} \right)^{-1} \right]^{-1} \right] \right\}. \quad (4.31)
\end{aligned}$$

To evaluate J_{zo} and I , the value of γ must be first determined. The value of γ depends on the mechanism of single injection. In general, single injection in dielectrics is due either to Fowler-Nordheim or to Schottky emission. It is easy to find γ by making $J_{zo} = J_c$, where J_c is the current density at the cathode and depends on E_c (or $\gamma = E_c/E_{av}$) and the mechanism of single injection. In the present analysis electron injection has been assumed to be mainly due to Fowler-Nordheim emission [Gallagher 1975] from the cathode following the equation

$$\begin{aligned}
J_c &= aE_c^2 \exp\left(\frac{-b}{E_c}\right) \\
&= aE_{av}^2 \gamma^2 \exp\left(\frac{-b}{E_{av}\gamma}\right) \quad (4.32)
\end{aligned}$$

where a and b are constants depending on the interfacial condition between the cathode and the liquid. By equating J_{zo} and J_c and assuming that

$b/E_{av} Y < 1$ and $Y < 1$, then Y is given by the following equation

$$Y = \frac{b}{2E_{av}} + \left\{ \frac{b^2}{4E_{av}^2} + \frac{\epsilon k T e}{3 q d a E_{av}^2} \exp\left[-\frac{W - q \lambda E_{av}/2}{k T}\right] \right\}^{\frac{1}{2}}. \quad (4.33)$$

It should be noted that up to date there is no experimental evidence available about the mechanism of single injection to the liquid, and it is our belief that an experiment to determine this may not be easy to perform in liquids. However, the expression for Y for other injection mechanisms, such as due to Schottky emission, can be readily obtained using the above method.

For a fixed gap length and normal temperatures it can be assumed that the term

$$\left\{ \frac{2ed}{9\lambda} \left[1 + \frac{q\lambda E_{av}}{4kT} (1 - Y) \right] \right\}^{\frac{1}{2}} \frac{r_d}{d}$$

in Eq. (4.31) is very small, such that

$$G = \left\{ \frac{2ed}{9\lambda} \left[1 + \frac{q\lambda E_{av}}{4kT} (1 - Y) \right] \right\}^{\frac{1}{2}} \frac{r_d}{d} < 1. \quad (4.34)$$

Then, Eq. (4.31) can be written as

$$I = J_{zo} (2\pi d^2) \left\{ \frac{2ed}{9\lambda} \left[1 + \frac{q\lambda E_{av}}{4kT} (1 - Y) \right] \right\}^{-1} \\ \times \{ \ln(1 + G) + (1 + G)^{-1} - 1 \}.$$

By expansion of $\ln(1 + G)$ and $(1 + G)^{-1}$, the above equation reduces to

$$I = J_{zo} (2\pi d^2) \left\{ \frac{2ed}{9\lambda} \left[1 + \frac{q\lambda E_{av}}{4kT} (1 - Y) \right] \right\}^{-1} \\ \times \left\{ \frac{G^2}{2} + \frac{2G^3}{3} \right\}. \quad (4.35)$$

For simplicity, the term $2G^3/3$ is neglected. Then Eq. (4.35) reduces to:

$$I = J_{zo}(\pi r_d^2). \quad (4.36)$$

From Eq. (4.1) the total current is given by

$$\begin{aligned} I_T &= H J_{zo}(\pi r_d^2) \\ &= (H\pi r_d^2) \frac{2\varepsilon kT_v}{qd} \left\{ e \exp\left[-\frac{(W - q\lambda E_{av}/2)}{kT}\right] \right. \\ &\quad \left. - \exp\left[-\frac{(W - q\lambda Y E_{av}/2)}{kT}\right] \right\} \\ &= (2\pi r_d^2 H) \frac{\varepsilon kT_v e}{qd} \left\{ \exp\left[-\frac{W - \frac{q\lambda E_{av}}{2}}{kT}\right] \right\} \\ &\quad \times \left\{ 1 - \exp\left[-1 - \frac{q\lambda E_{av}}{2kT} (1 - Y)\right] \right\}. \end{aligned} \quad (4.37)$$

In Eq. (4.37) the first { } can be considered as the bulk-controlled factor and the second { } as the electrode controlled factor.

For single-type carrier conduction, Y is always less than unity [Kao 1976]. By assuming that the term in the second { } does not vary rapidly with E_{av} as the term in the first { }, then from Eq. (4.37) the total current can be written

$$\frac{I_T}{kT} \propto \exp\left[-\frac{W - q\lambda E_{av}/2}{kT}\right]. \quad (4.38)$$

4.2 EXPERIMENTAL RESULTS

For several fixed temperatures the conduction current in n-hexane has been measured as a function of average applied electric field for each fixed temperature the results are plotted in terms of $\log(I_T/kT)$ as a

function of E_{av} , and they are given in Fig. 4.1. A complete different series of measurements of conduction current in n-hexane as a function of temperature and by keeping the average applied electric field constant have also been performed. The results are plotted in terms of $\log(I_T/kT)$ as a function of $1/T$ for nine different fields are shown in Fig. 4.2.

For n-pentane, n-heptane, benzene and toluene the conduction current has been measured as a function of temperature at two fixed average applied electric fields, 30 kV cm^{-1} and 250 kV cm^{-1} . The results are also plotted in terms of $\log(I_T/kT)$ as function of $1/T$ which are shown in Fig. 4.3 for n-pentane and n-heptane and in Fig. 4.4 for benzene and toluene.

4.3 DISCUSSION OF EXPERIMENTAL RESULTS ON THE BASIS OF THE THEORETICAL MODEL

In Fig. 4.1 it can be seen that for fields higher than 250 kV cm^{-1} all six curves for six different temperatures are parallel to each other, which fit well the theoretically predicted relation (4.38). For fields between 100 kV.cm^{-1} and 250 kV.cm^{-1} the curves for low temperatures still follow closely Eq. (4.38) such as curves A and B, but at temperatures higher than 313°K , deviation from Eq. (4.38) begins. The higher the temperature, the higher is the field at which such deviation begins. This may imply that at high temperatures the term $q\lambda E_{av}/2KT$ becomes small and so the approximate expression for μ_h by neglecting the term $\exp(-q\lambda E_{av}/2KT)$ in Eq. (4.5) becomes inaccurate.

In Fig. 4.2 the deviation from Eq. (4.38) at high temperatures and at low fields shown in Fig. 4.1 is not seen. This may be due to the fact

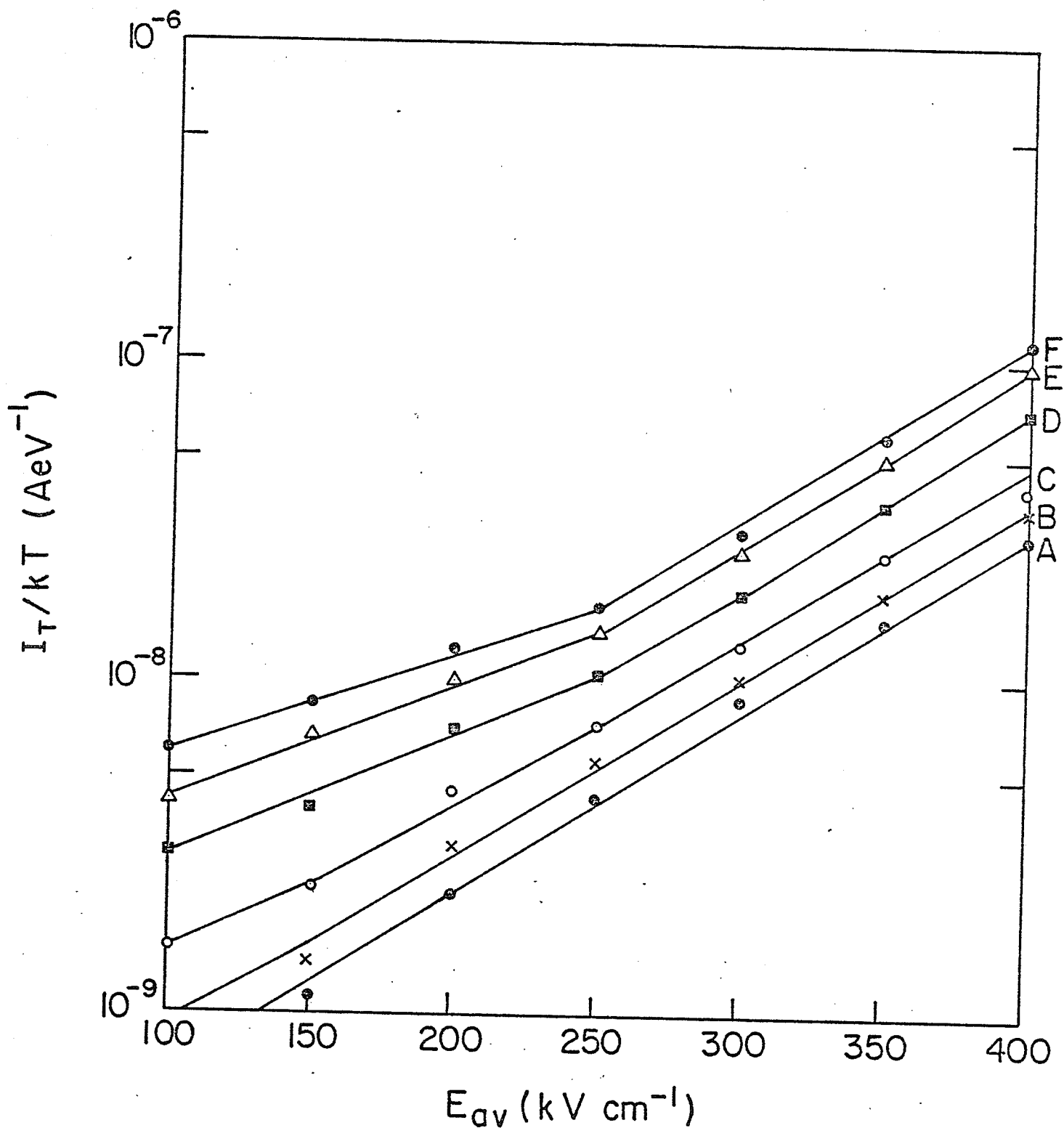


Fig. 4.1 I_T/kT as a function of E_{av} for n-hexane at T of
 (A) 2970K, (B) 3050K, (C) 3130K, (D) 3230K,
 (E) 3330K, and (F) 3380K

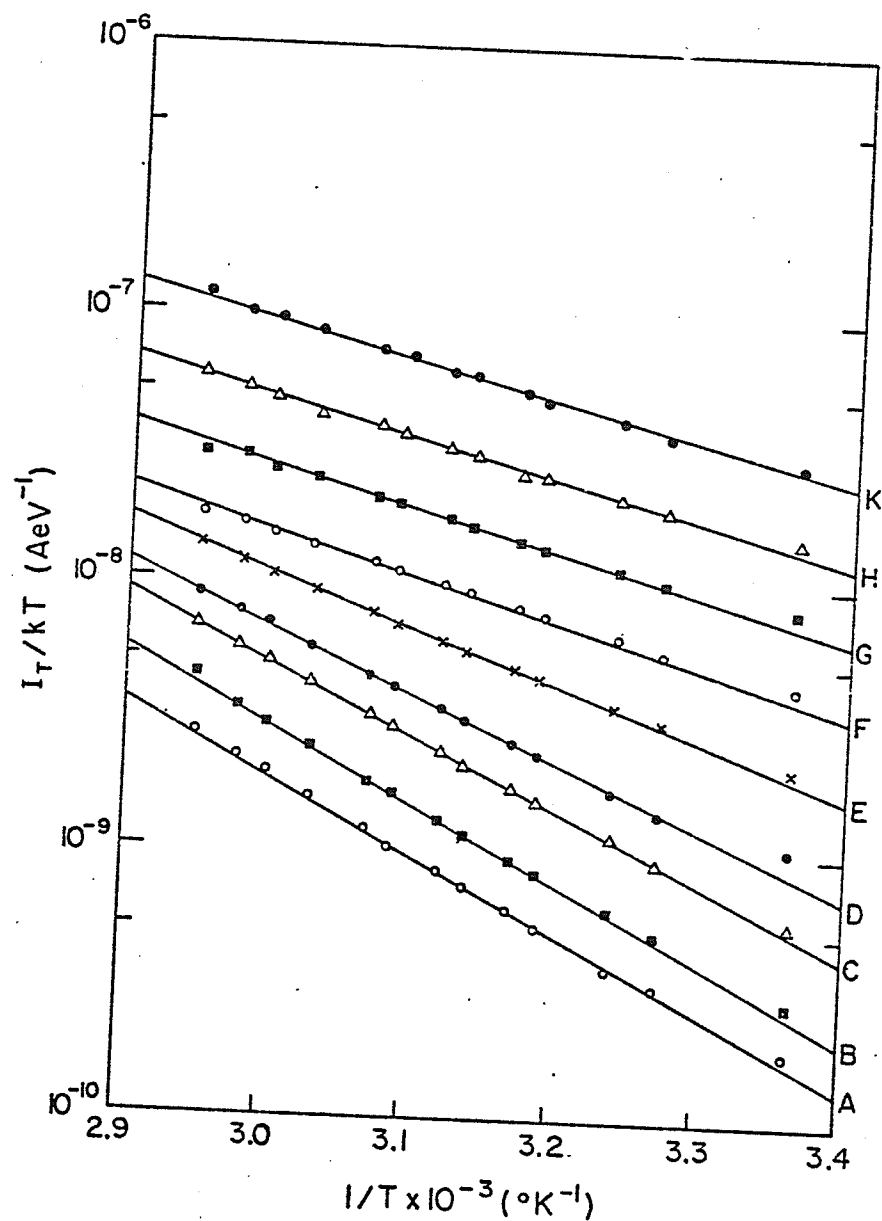


Fig. 4.2 I_T/kT as a function of $1/T$ for n-hexane at E_{av} of
 (A) 30 kV cm⁻¹, (B) 50 kV cm⁻¹, (C) 100 kV cm⁻¹,
 (D) 150 kV cm⁻¹, (E) 200 kV cm⁻¹, (F) 250 kV cm⁻¹,
 (G) 300 kV cm⁻¹, (H) 350 kV cm⁻¹, and (K) 400 kV cm⁻¹

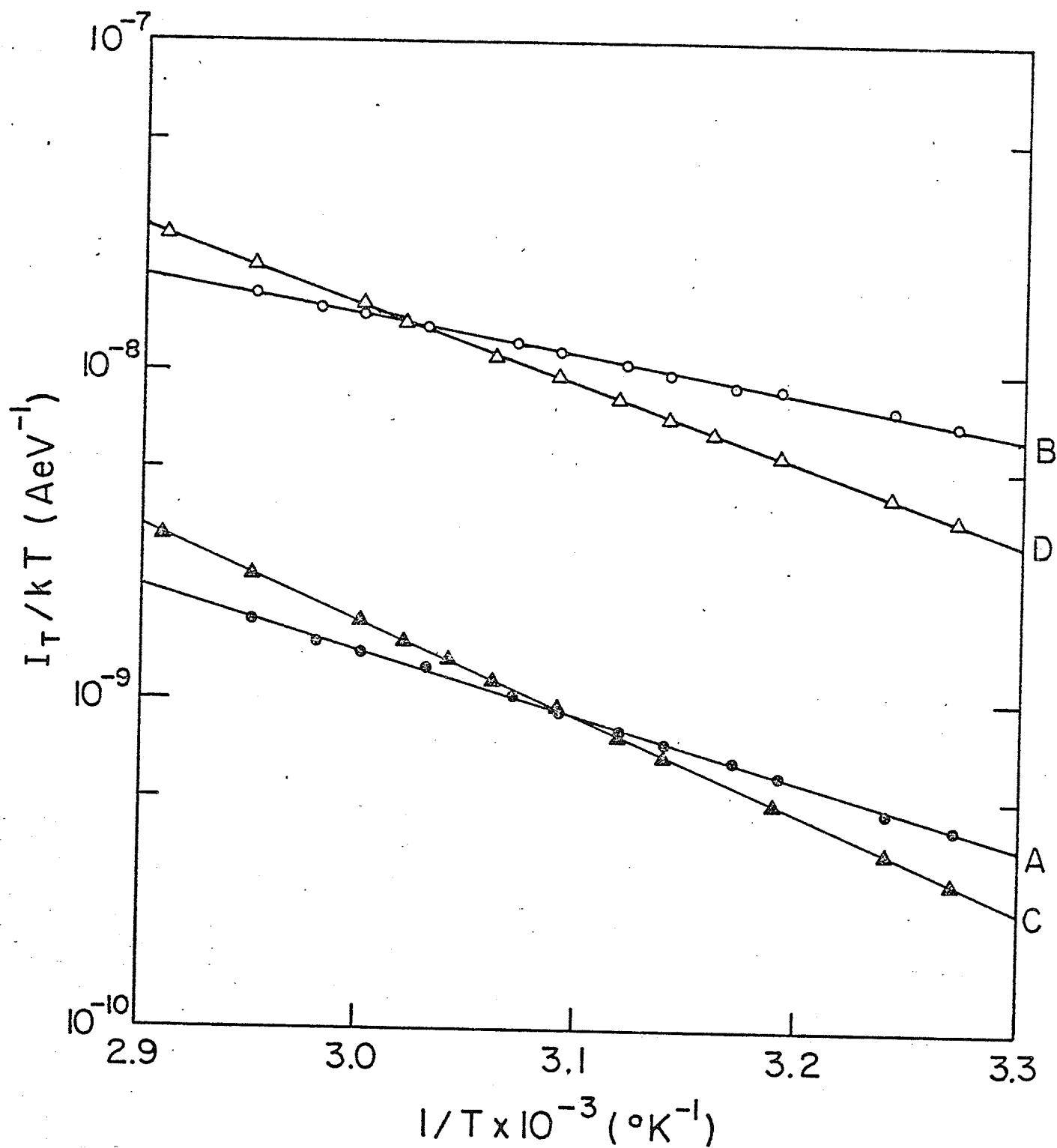


Fig. 4.3 I_T/kT as a function of $1/T$ for n-pentane at E_{av} of (A) 30 kV cm^{-1} and (B) 250 kV cm^{-1} and for n-heptane at E_{av} of (C) 30 kV cm^{-1} and (D) 250 kV cm^{-1}

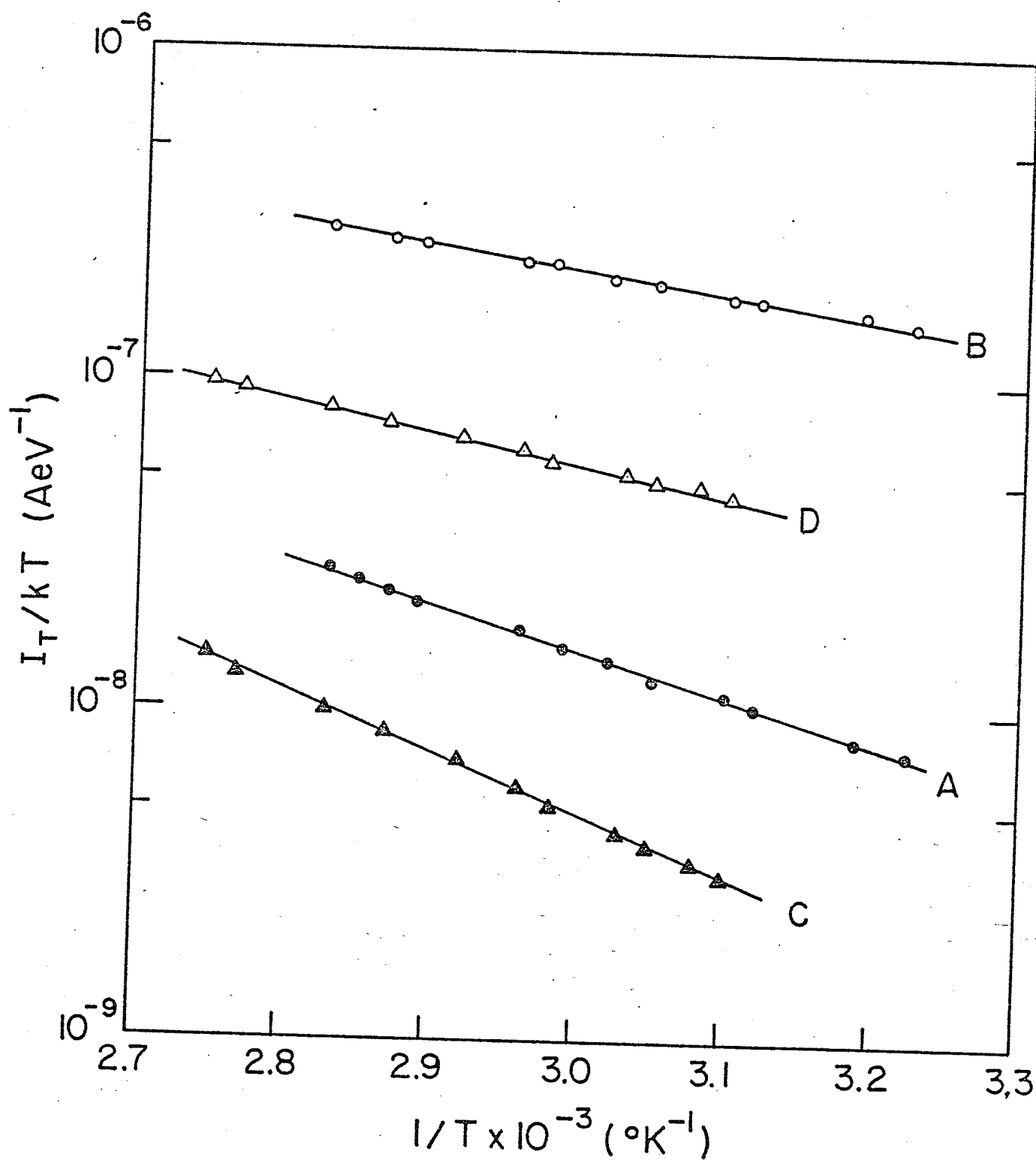


Fig. 4.4 I_T/kT as a function of $1/T$ for benzene at E_{av} of (A) 30 kV cm⁻¹ and (B) 250 kV cm⁻¹, and for toluene at E_{av} of (C) 30 V cm⁻¹ and (D) 250 kV cm⁻¹

that the gap length may have been slightly reduced at high temperatures and for such a small change in gap length, allowance has not been made for Fig. 4.2. Such change in gap length has been estimated to be less than 1% from 293°K to 338°K. By assuming that such a change is 1% from 293°K to 338°K, points on the curves for the values of $1/T$ smaller than 3.1×10^{-3} may be gradually brought down below the original points on the curves. However, this should not alter the general trend and slopes of these curves. On the basis of these curves the activation energies have been calculated and the results are given in Table 4.1. The activation energies for fields of 30 kV cm^{-1} and 50 kV cm^{-1} are equal, indicating that the activation energy and hence, the carrier mobility at low fields are practically independent of applied field. By taking the low-field activation energy of 0.57 eV as the average depth of the traps from the conduction band (the energy band in which the carriers act as free electrons and this term originated for crystalline materials has been generally used in the field of amorphous semiconductors), the average separation distance λ has been also calculated. Except for the values of λ at low fields which may be affected by neglecting of the term $\exp(-q\lambda E_{av}/2kT)$ in Eq. (4.5), the values of λ for fields higher than 200 kV cm^{-1} are consistent with the mean value of 161 \AA . The accuracy of all W and λ given in the tables depends on the accuracy of the current, voltage and temperature measurements, and the accuracy of drawing the straight lines. The overall possible error involved in the former is less than $\pm 3\%$ and that in the latter is less than $\pm 2\%$. Therefore, the accuracy of the computed W and λ should be within $\pm 5\%$. The variation of λ in Table 4.1 may be partly due to this accuracy limit.

TABLE 4.1
ACTIVATION ENERGIES OF ELECTRIC CONDUCTION IN n-HEXANE

E_{av} kV/cm	Activation Energy (eV) $\pm 5\%$	W (eV) $\pm 5\%$	$q\lambda E_{av}/2$ (eV)	λ $\left(\frac{\text{\AA}}{\text{O}}\right)$ $\pm 5\%$
30	0.57	0.57	-	-
50	0.57	0.57	-	-
100	0.53	0.57	0.037	74
150	0.48	0.57	0.081	108
200	0.41	0.57	0.158	158
250	0.43	0.57	0.226	180
300	0.31	0.57	0.260	173
350	0.30	0.57	0.269	153
400	0.28	0.57	0.286	143

TABLE 4.2
 ACTIVATION ENERGIES OF ELECTRIC CONDUCTION
 IN SATURATED HYDROCARBON LIQUIDS

Liquid	Activation Energy, (eV) $\pm 5\%$		W (eV) $\pm 5\%$	$q\lambda E_{av}/2$ (ev)	λ (\AA) $\pm 5\%$
	30 kV/cm	250 kV/cm			
n-pentane	0.39	0.25	0.39	0.143	114
n-hexane	0.57	0.34	0.57	0.226	180
n-heptane	0.58	0.46	0.58	0.111	89

TABLE 4.3
 ACTIVATION ENERGIES OF ELECTRIC CONDUCTION
 IN AROMATIC HYDROCARBON LIQUIDS

Liquid	Activation Energy, (eV) $\pm 5\%$		W (eV) $\pm 5\%$	$q\lambda E_{av}/2$ (eV)	λ (\AA) $\pm 5\%$
	30 kV/cm	250 kV/cm			
Benzene	0.27	0.15	0.27	0.120	100
Toluene	0.37	0.19	0.37	0.182	140

The good agreement between the experimental results and the simple relation (4.38) implies that the electric conduction is bulk-limited. This means that carriers injected from the cathode at high fields are ample to replace those flowing out of the liquid gap, or in other words, the conductance of the liquid gap is smaller than the conductance of the contact between the cathode and the liquid. The conduction current is therefore more sensitive to the change of the conductance of the liquid gap than to the change of the conductance of the contact caused by the increase of the applied field. The conductivity in the bulk must be associated with the mechanism of hindering the flow of carriers (or limiting the mobility of carriers). The theory based on a trapping model given in section 4.1 can well explain the field-dependent conductance and the field-dependent activation energy. Several investigators [Schmidt et al. 1974, Schmidt and Allen 1970, Minday et al. 1971 and 1972, Secker and Belmont 1972 and Devins and Wei 1972] have put forward a similar trapping model to explain their carrier mobility results. As has been mentioned in Chapter 3 the liquid samples used were not rigorously degassed, hence it is expected that the concentration of oxygen molecules in an air saturated liquid may be high enough to capture all injected electrons to form negative ions of low mobility. But the trapped electrons may not be permanently trapped during their transit to the anode and it is most likely that the effective mean mobility of carriers in the liquid gap follows the relation

$$\bar{\mu}_h = \frac{\mu_t t_t + \mu_f t_f}{t_t + t_f} \quad (4.39)$$

where μ_t and μ_f are, respectively, the mean mobilities of the trapped and free electrons, and t_t and t_f are, respectively, the total times for which the carrier moves as a trapped electron, (negative ion) and as free electron. The mobility of a free electron is determined by the scattering processes between the electron and the liquid molecules and impurities, while the mobility of a trapped electron depends mainly on the viscosity of the liquid. Since t_f is always much smaller than t_t and μ_f is always much larger than μ_t , it is obvious that if $t_f/t_t < \mu_t/\mu_f$ the electric conduction is ionic, and if $t_f/t_t > \mu_t/\mu_f$ the electric conduction is electronic but controlled by the ratio of t_f/t_t or, in other words, by the residence time of the electron in a trap. The mobility of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ for n-hexane measured by Minday et al. [1971] is not the free electron mobility but is the effective mean mobility controlled by traps. Up to date, there are no experimental data for μ_f available, but the effective mean mobility, however, should be equal to or higher than the ionic mobility depending on the ratio of t_f/t_t according to (4.39). As the residence time of an electron in a trap is proportional to $\exp(W/kT)$ [Davis et al. 1971 and 1972, Frommhold 1968], W is a measure of the energy required to release an electron from a trap. The value of W for n-hexane deduced from our results is 0.57 eV which is much larger than those for highly degassed and purified n-hexane reported by other investigators [Schmidt and Allen 1970 and Minday et al. 1971], and also larger than the activation energy for ionic mobility in n-hexane [LeBlanc, 1959]. The explanation for the difference in thermal activation energy W among these three cases is as follows:

- (i) In highly degassed and purified liquids a free electron could be trapped by a group of molecules to form a localized polaron [Minday et al. 1971]. W for this case represents the energy necessary to release such a trapped electron from a molecular trap before it can move as a free electron. Such a self-imposed trapping involves mainly the polarization energy between the free electron and its surrounding molecules. The value of W for n-hexane following this possible mechanism is 0.186 eV [Minday et al. 1971].
- (ii) In air-saturated but highly purified liquids such as those used for our experiments, a free electron could be first trapped by an oxygen molecule to form an O_2^- ion which is then surrounded by the molecules of the host liquid, which have been polarized by it to form a composite carrier during its migration through the liquid [Croitoru 1965, Degroot 1967 and Secker 1970]. W for this case represents the energy necessary to release such a trapped electron from such a composite carrier, and therefore the value of W should be larger than the corresponding value from case (i). It is possible that the energy required to detrap the electron from O_2^- alone is larger than that required to detrap it from a composite carrier because the surrounding polarized molecules tend to help pulling the attached electron out of the O_2^- ion. The value of 0.57 eV may be of the right order for W for n-hexane

following this possible mechanism. Furthermore, W should depend on the number of polarized molecules surrounding the negative ion. The larger the number of surrounding molecules, the smaller would be the value of W . Of course, the smaller the molecule size, the more would be the number of molecules being attracted to surround the ion. That the value of W decreases with decreasing molecule size as shown in Fig. 4.3 and Table 4.2 for saturated hydrocarbon liquids and in Fig. 4.4 and Table 4.3 for unsaturated hydrocarbon liquids supports this hypothesis. It should be noted that the agents to trap the free electrons are not necessarily oxygen molecules and could be other chemical impurities which have a high electron affinity and have not been removed from the liquid samples.

- (iii) In less purified liquids the electric conduction is mainly ionic. The activation energy for this case is a measure of the ease with which a stable negative composite carrier (a negative ion with its surrounding polarized molecules) can slide through the liquid and therefore should be closely related to the viscosity of the liquid. It can be expected the larger the size of the composite carrier, the higher would be the activation energy for a given liquid viscosity. This explains why the activation energy for ionic carrier mobility in *n*-hexane, which is about 0.14 eV [LeBlanc 1959], is higher

than the activation energy for viscosity in the same liquid, which is about 0.10 [Adamczewski 1969]. It should be noted, however, that the mechanism involved in the activation energy for ionic conduction is completely different from the mechanisms for W in case (i) and (ii).

If the above argument is reasonable, the average distance between adjacent trapping sites λ should reflect the concentration of traps. By a rough estimation, the concentration of traps is about $(1/\lambda)^3 \approx 2.4 \times 10^{17} \text{ cm}^{-3}$ corresponding to one trap in 10^4 - 10^5 host molecules. If the traps are dissolved oxygen molecules, the concentration of $2.4 \times 10^{17} \text{ cm}^{-3}$ of oxygen molecules in an air-saturated liquid is not unreasonable. However, our value of λ is much smaller than that reported by Devins and Wei [1972] based on their transient photocurrent analysis. This discrepancy cannot be explained because detailed information about the purity of their liquid samples and ours is not available. To determine the conduction current at a given field, both W and λ are important. In Fig. 4.3 the conduction current in n-pentane at a given field is larger than that in n-heptane at low temperatures, but this trend is reversed at high temperatures. This may be due to $W(\text{heptane}) > W(\text{pentane})$. The value of λ for n-heptane is smaller than that for n-pentane and n-hexane, and this may be due to different inherent impurities and different amounts of such impurities in different liquids. Kahan and Morant [1965] have reported that based on their gas chromatography analysis, n-hexane may contain up to 20% of hexane isomers and other impurities. Without identifying various impurities in these liquid samples it is impossible at this stage to give further comments about the values of λ .

So far, to our knowledge, the activation energies for high-field electric conduction as functions of applied field for saturated hydrocarbon liquids are not available in the literature, so no comparison can be made to our results. However, the activation energy for toluene at low fields (0.374 eV at $E_{av} = 30 \text{ kV cm}^{-1}$) is close to the value of 0.33 eV at $E_{av} = 10 \text{ kV cm}^{-1}$ for toluene reported by LePage and DuBridge [1940], but our value of activation energy for $E_{av} = 250 \text{ kV cm}^{-1}$ (0.193 eV) is much higher than theirs for the same field (0.049 eV). Again, this discrepancy can be attributed to different impurity contents in liquid samples. For both benzene and toluene the quantity $\log(I_T/kT)$ vs $1/kT$ plots follows the relation (4.38) and the activation energy decreases with increasing applied field, indicating that the same trapping model can also be used to explain high-field electric conduction phenomenon in unsaturated hydrocarbon liquids.

CHAPTER 5

ELECTROLUMINESCENCE

These are two prebreakdown phenomena which may be of great importance to the study of electric breakdown processes. One of these phenomena is the non linear current-voltage characteristics at high fields which has been discussed in some detail in Chapters 2 and 4. On the basis of this phenomenon Kao [1976] has formed a new theory for electric breakdown in dielectric liquids. The other phenomenon is the electroluminescence which occurs in most dielectric liquids at field close to their breakdown strength. Since electroluminescence always occurs in the cathode region Kao and his co-workers [1956, 1966A, 1966B] has concluded that the electron emission from the cathode is one of the processes causing the final electric breakdown in dielectric liquids. As Kao and Higham [1961] have made detailed measurements of variation of the breakdown strength with temperature and hydrostatic pressure, it is therefore, important to investigate the effects of temperature and hydrostatic pressure on the phenomenon of electroluminescence. This chapter reports some new results and our interpretation.

5.1 EXPERIMENTAL RESULTS

The electroluminescence has been observed in n-hexane, cyclohexane and benzene of spectroscopic grade and in benzene and chloroform of technical grade. The electroluminescence in all these liquids has been observed to appear always in the cathode region independent of electrode

geometry. With a sphere-plane electrode system (non-uniform field gap) the light occurs first near the sphere when it is used as a cathode. If the polarity is reversed, the light then appears first near the plane but at a much higher threshold voltage for its onset. After the onset of electroluminescence, its light intensity increases with increasing applied voltage. For a given gap length and at a given applied voltage, the point-plane electrode system gives a higher electroluminescent intensity than the sphere-plane electrode system, provided that the point and the sphere are used as the cathode. The spatial pattern and distribution of the electroluminescence vary with time, though they remain statistically in the forms reported earlier by Kao and his co-worker [Kao 1965, Smith et al. 1966].

When the electroluminescent intensity was recorded using the optical system described in Chapter 3, random light bursts have been observed at atmospheric pressure (zero gauge pressure) in n-hexane and cyclohexane of spectroscopic grade and in chloroform of technical grade, but there are practically no light bursts in benzene. The light bursts are always accompanied by current bursts as shown in Fig. 5.1. It should be noted that the amplitude and pulse width of the bursts are not constant, but vary to a great extent from time to time at a given applied voltage and the frequency of their occurrence is also at random.

All liquids under investigation exhibit electroluminescence, except carbon tetrachloride for which no electroluminescence has been detected at fields up to a value just prior to its breakdown strength.

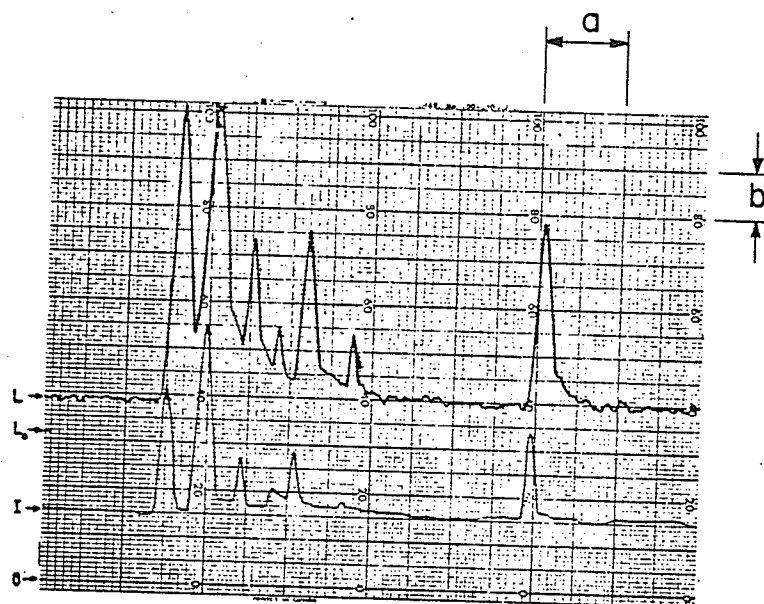


Fig. 5.1 Typical random bursts in n-hexane, upper trace: light bursts, lower trace: current bursts, scale 1 s/div. horizontal and 2×10^{-7} A/div. vertical (for current burst only), electrodes: 4 points-plane, gap length: 4mm, and applied voltage: 50 V.

a - horizontal div.
b - vertical div.

5.1.1 The effect of applied hydrostatic pressure

- (A) In the range of pressure applied in the present investigation [zero gauge pressure (atmospheric pressure) to gauge pressure of 14 kg cm^{-2}], the spatial pattern and distribution of the electroluminescence are not affected by pressure.
- (B) The applied hydrostatic pressure suppresses almost completely the random light and current bursts and reduces the electroluminescent intensity (marked L in Fig. 5.1) for n-hexane and cyclohexane of spectroscopic grade and for chloroform of technical grade. Typical results for n-hexane are shown in Fig. 5.2. It is interesting to note that for benzene the applied pressure enhances the electroluminescent intensity. Typical results in benzene are shown in Fig. 5.3. In Fig. 5.4, the relative intensity. (The ratio of $L-L_0$ at various gauge pressure to that at zero gauge pressure, L_0 being the background level of the image intensifier screen prior to the appearance of the light).
- (C) The pressure dependence is stronger for benzene of technical grade than for that of spectroscopic grade, indicating that the impurities play a very important role in this phenomenon.

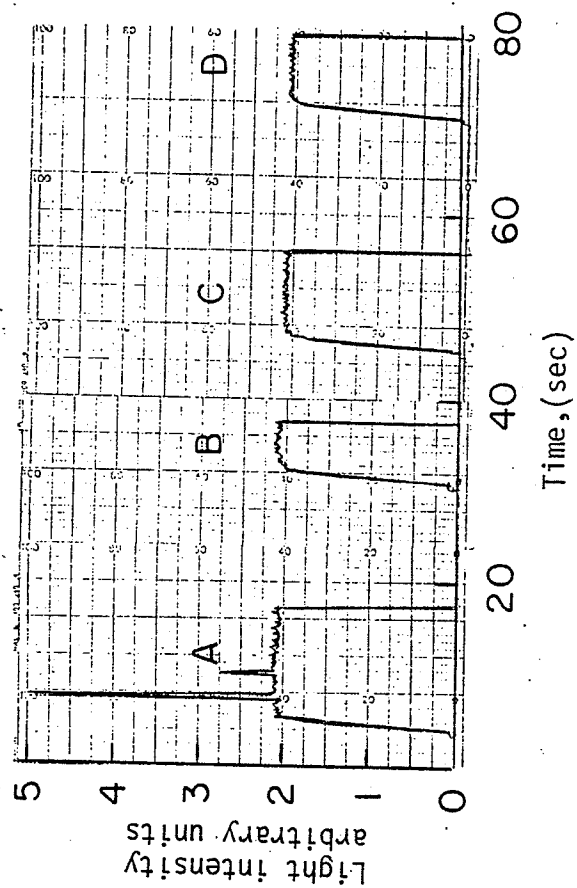


Fig. 5.2 The effect of hydrostatic pressure on electroluminescent intensity in n-hexane. (A) 0 gage pressure, (B) 3.5 kg cm⁻², (C) 7.0 kg cm⁻², and (D) 10.5 kg cm⁻², 4 points - plane electrodes, 2 mm gap, 22 kV.

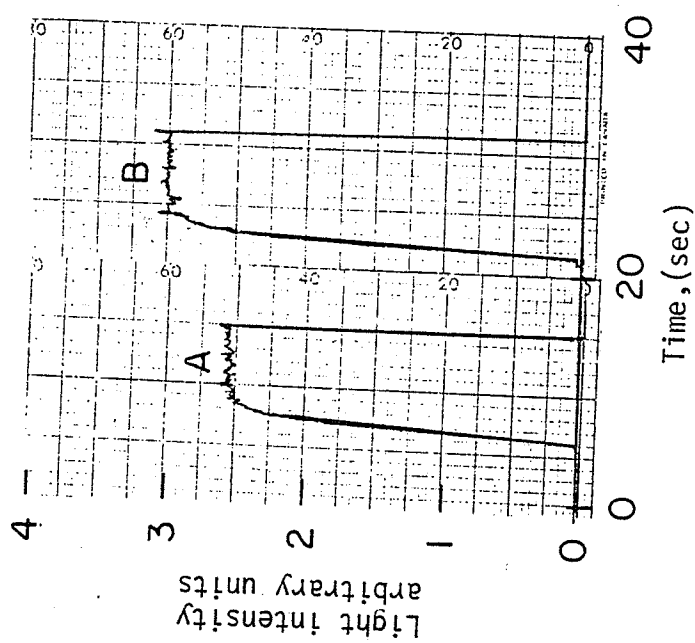


Fig. 5.3 The effect of hydrostatic pressure on electro-luminescent intensity in benzene. (A) 0 gage pressure, and (B) gage pressure 10.5 kg cm⁻² 4 points - plane electrodes, 4 mm gap, 25 kV.

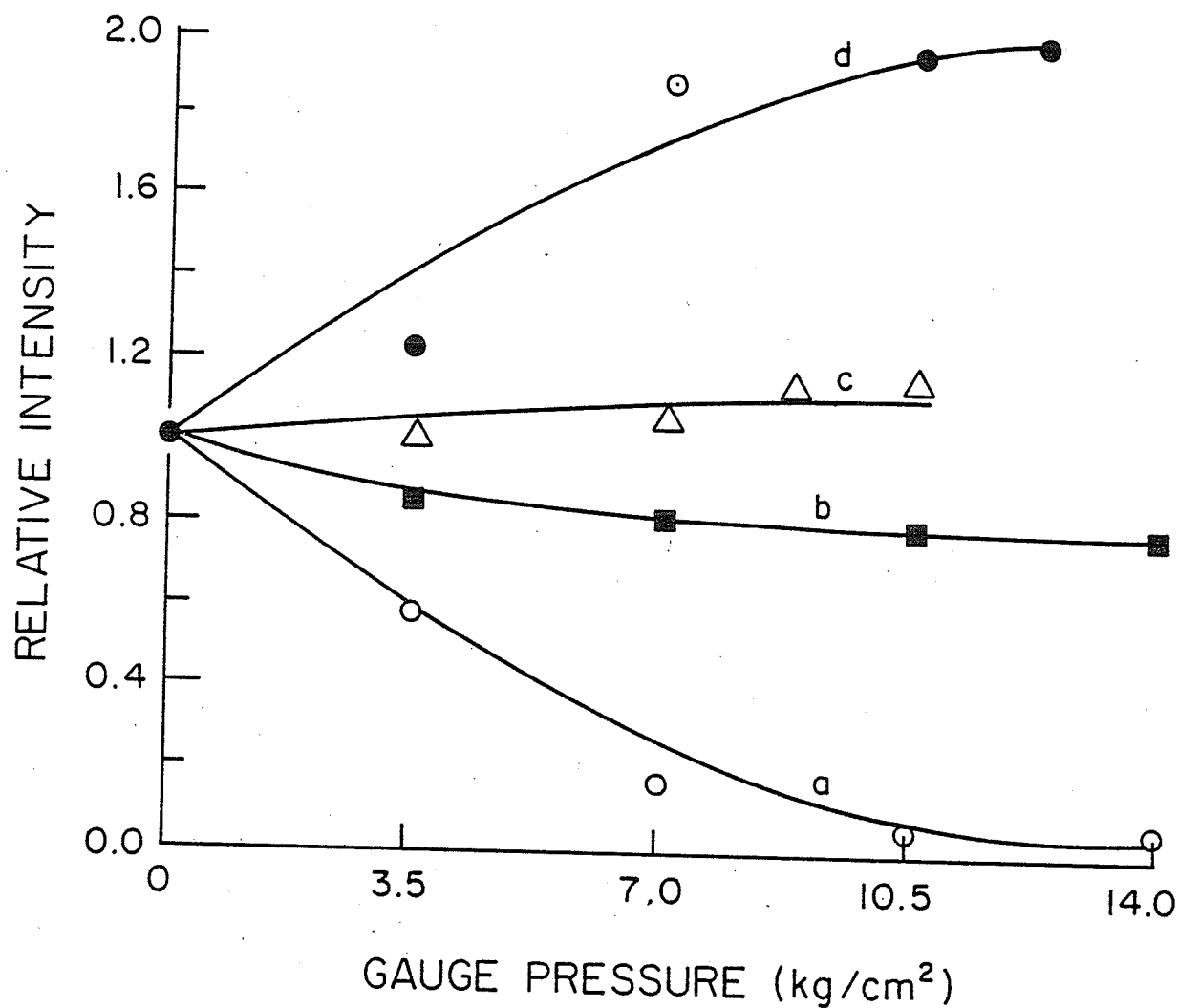


Fig. 5.4 Electroluminescent intensity as a function of applied hydrostatic pressure, (a) spectroscopic cyclohexane (4 mm gap, 40 kv); (b) spectroscopic n-hexane (2 mm gap, 25 kv); (c) spectroscopic benzene (4 mm gap 25 kv); and (d) technical benzene (4 mm gap, 25 kv)

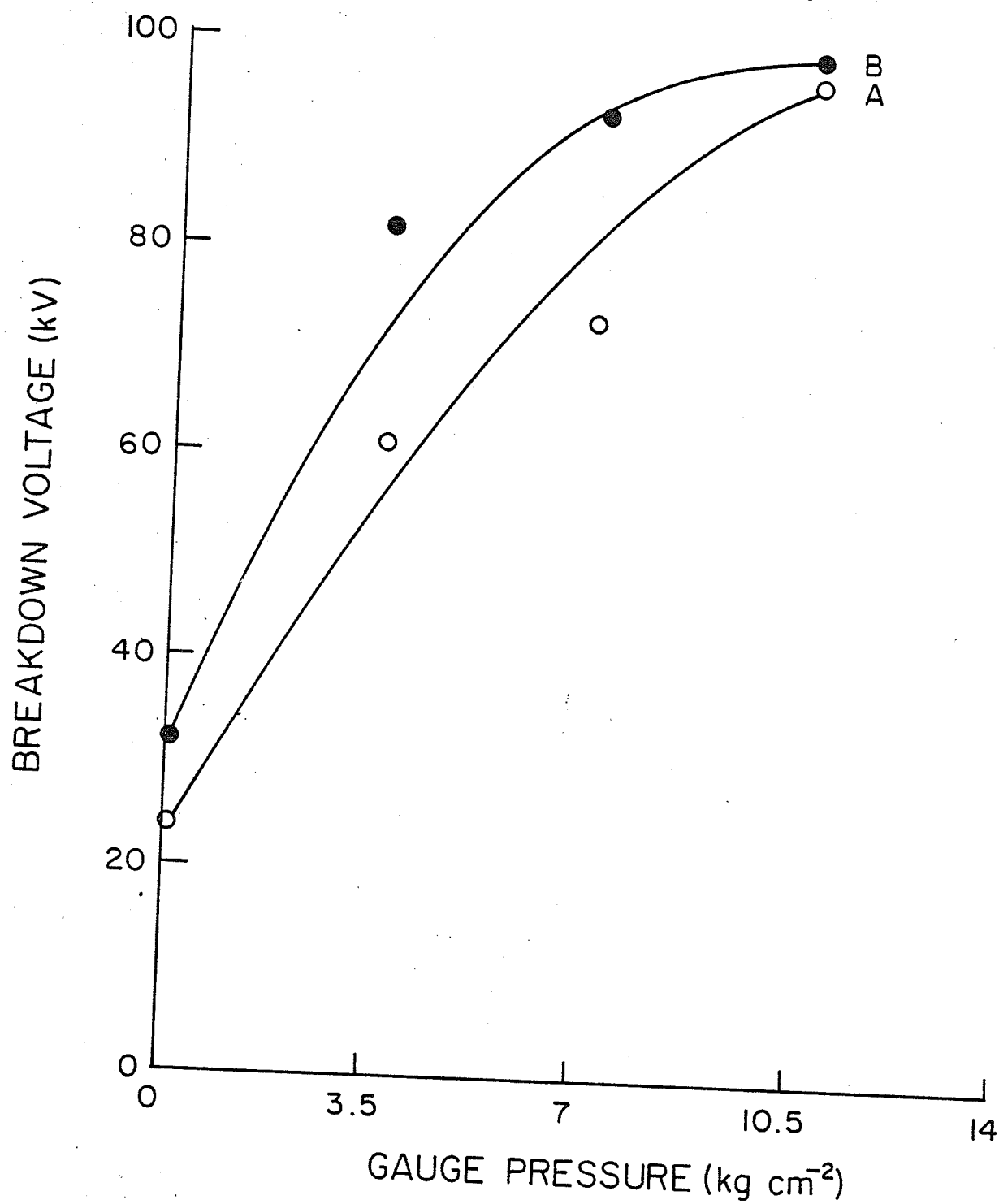


Fig. 5.5 Breakdown voltage as a function of hydrostatic pressure for (A) benzene (1 mm gap), and (B) cyclohexane (1 mm gap) with parallel stainless steel sphere - sphere electrodes of diameter 6.4 mm.

- (D) The steady-state conduction current at the nonburst level (marked I in Fig. 5.1) is not sensitive to pressure for the pressures under investigation.
- (E) The effect of pressures on the electroluminescent intensity in n-hexane and cyclohexane is contrary to that in benzene, but these liquids exhibit the same pressure dependence of the breakdown strength. The breakdown strengths of cyclohexane and benzene increase with the increase of applied pressure up to 14 kg cm^{-2} as shown in Fig. 5.5. The trend of these results is exactly the same as those reported earlier by Kao and Higham [1961]. The only difference is that our results were obtained under dc conditions and theirs under 4- μ sec pulse conditions.

5.1.2 The effect of temperature

The relative intensity as a function of temperature for n-hexane and cyclohexane of spectroscopic grade is shown in Fig. 5.6. It can be seen that the relative electroluminescent intensity decreases with temperature for both n-hexane and cyclohexane.

5.1.3 The effect of additives

The threshold voltage for the onset of electroluminescence decreased while the electroluminescent intensity and associated conduction current increased when a drop of ethyl alcohol (5% by volume) was added to n-hexane of spectroscopic grade. A similar effect has been reported earlier for the conduction current in n-hexane by Kao and Calderwood [1965].

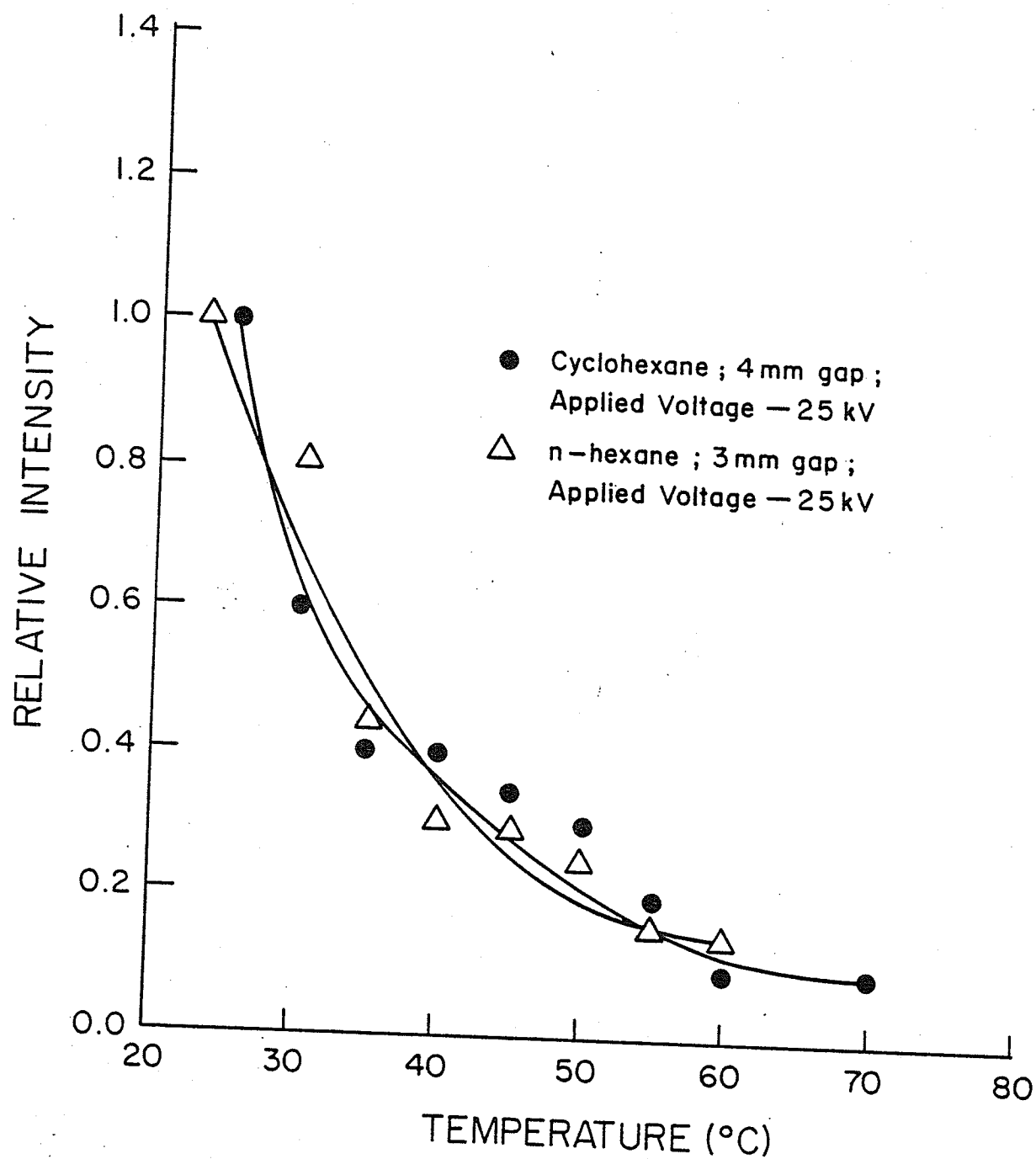
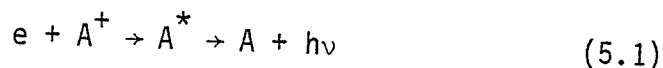


Fig. 5.6 The light intensity as a function of temperature for cyclohexane and n-hexane at a fixed applied voltage.

5.2 DISCUSSION OF EXPERIMENTAL RESULTS

That the electroluminescence always occurs in the cathode region indicates that it must be associated with the electron emission from the cathode. Electroluminescence is a phenomenon of radiative recombination. As the mean free path of an electron in dielectric liquids is of the order of 10^{-7} cm, it is hard to believe that an electron can gain a kinetic energy of the order 1-7 eV to excite an atom or a molecule without the secondary process involved, and of the order 10-20 eV to ionize an atom or a molecule even at a field of 10^6 V cm $^{-1}$. Since the electroluminescence which has been detected by our optical system is in the visible region, it involves an energy release of the order of 1.7 to 3.1 eV. Based on this information the following possible mechanisms are proposed.

- (1) Because of the ionization due to cosmic radiation and the thermal dissociation of molecules of impurities or of the liquid itself, there always exists positive space charge near the cathode, the electrons emitted from the cathode may then recombine with some positive ions to produce electroluminescence following the process:



where e denotes the electron, A^+ , A^* , and A denote the atom or molecule with one electron missing, in excited and in ground states, respectively; h is Planck's constant and ν is the frequency corresponding to emitted light spectrum.

- (2) Because of the presence of ions in the liquid there always exists an electrohydrodynamic turbulence in the liquid [Ostroumov 1956, Pickand 1963]. It is possible that this turbulence may create cavities near the cathode so that some electrons emitted from the cathode may be able to gain sufficient energy in the field to excite molecules of impurities or of the liquid itself. The critical field for this to occur is given by

$$E = h\nu/q\lambda_1 \quad (5.2)$$

where λ_1 is the mean free path of the electron, which is expected to be much larger in cavities than in the liquid.

It is likely that both mechanisms are important for n-hexane, cyclohexane, and chloroform. The suppression of light bursts and current bursts and the reduction of the electroluminescent intensity by the application of hydrostatic pressure indicate the formation of cavities or low-density zones possibly caused by electrohydrodynamic turbulence. The suppression of current bursts by hydrostatic pressure has been reported earlier by Kao and Calderwood [1965]. In Fig. 5.1 the bursts in light intensity and in current have almost the same shape and occur at about the same time. It should be noted that the visual difference in time between the two traces in Fig. 5.1 is due to slight misalignment of the initial

positions of the two pens of the recorder, and that our measuring arrangement is not sensitive enough to measure the time lag between the light bursts and the current bursts. However, it is likely that there are some large cavities transiently appearing near the cathode, and the current bursts are associated with the sudden acceleration of electrons by the field in the cavities and the light bursts are associated with the release of energy from molecules excited by those accelerated electrons.

- (3) The phenomenon that electroluminescent intensity in benzene increases with the increase of applied hydrostatic pressure may be associated with the presence of π -electrons in the benzene ring. Forester [1962] has reported that π -electrons are involved in the current transport mechanism either by a hopping or tunneling process in benzene. The application of hydrostatic pressure will enhance the efficiency of this process so as to make it easy for such electrons to gain enough energy in the field to cause excitation of molecules of impurities or of the liquid itself. The findings of Garber [1972] that the dc conductivity of benzene increases with increasing pressure is probably due to the enhancement of the charge transport mechanism. The observed increase in the pressure dependence of electroluminescent intensity in benzene of technical grade is larger than that in benzene of spectroscopic grade. This indicates that the presence

of some impurities in dielectric liquids may contribute to electroluminescence possibly due to the fact that lower energy is required to excite impurity molecules than to excite the molecule of the liquid itself. Earlier Darveniza and Tropper [1961], and Darveniza [1959] have reported that the fluorescent material added to transformer oil increases the light intensity. Recently, Birlasekaran and Darveniza [1976] have reported that electroluminescence in transformer oil is due to microdischarges appearing in the liquid when a conducting particle approaches the electrode. However, this hypothesis may explain this phenomenon in transformer oil in which the presence of such conducting particles is possible. But electroluminescence in pure dielectric liquids such as those used in the present investigation and also as has been observed earlier in pure n-hexane by Smith et al. [1966] may not be due to these microdischarges since the presence of such conducting particles is unlikely in these liquids.

For the temperature dependence of electroluminescent intensity, it is likely that the decrease of electroluminescent intensity with increasing temperature in n-hexane and cyclohexane, is due to the increase of the probability of collision between electrons and liquid molecules, or between the liquid molecules themselves. This would lead to reduction of the mean free path of the electron, which in turn would reduce the amount of energy that the electron could gain in the electric field.

If the molecules of the impurities or of the liquid itself have no excited states in the visible range, then no electroluminescence would be observed in this region. Carbon tetrachloride may be one of many liquids belonging to this category.

CHAPTER 6CONCLUSIONS

On the basis of the high field electric conduction investigation we can draw the following conclusions

- (i) The general expression for the filamentary single injection current-voltage characteristics taking into account the combined electrode and bulk effects has been derived on the basis of a simple trapping model, and this theoretical model fits well the experimental results on high-field electric conduction, and field dependent thermal activation energies in both saturated and unsaturated hydrocarbon liquids.
- (ii) This model predicts that the trap density in an air saturated hydrocarbon liquid is of the order of 10^{17} cm^{-3} which is not unreasonable.
- (iii) The presence of traps, particularly those formed by negative gas molecules tend to lower the average mobility of the charge carriers. This may be important to insulation engineers. It is possible that the doping of certain impurities may increase the discharge inception voltage and hence the breakdown strength of the insulation material.
- (iv) The idea of filamentary conduction is also of importance to insulation engineers. If the electrode surface is very nonuniform and the insulation is very inhomogeneous,

then the current passing through an insulation, for example, between the core and the sheath of a coaxial cable may be filamentary. The total current passing through the insulation material may be negligibly small, but this current may be concentrated in a few filamentary paths of extremely small cross-sections creating a very high current density in such filaments, which may lead to thermal instabilities and final breakdown of the insulation (or the cable). Therefore, to design a good insulation system it is important to choose a material of homogeneous structure and to make sure that the interface between the metal and the insulation is smooth so as to reduce the possibility of carrier injection at low applied fields to start the filament formation.

However, the trapping mechanisms involved are open to speculation. To gain a proper understanding of the fundamental mechanisms, work should be directed to examine the filamentary conduction and to study the pulse and dc conduction in ultra-pure hydrocarbons with precisely known impurity contents, and the effects of controlled doping impurities.

It should be noted that rigorous treatment of such high-field transport problems should include the field and temperature dependence of ϵ and other parameters due to the effects of space charge, impurities and electrohydrodynamic-motion. Obviously the solution taking into account all those effects will have to be numerical rather than analytical.

Regarding the electroluminescent phenomena in Chapter 5, we have proposed two possible mechanisms responsible for their occurrence and they are:

- (a) The electrons injected from the cathode may recombine radiatively with the positive charge existing near the cathode, which may be impurity ions or ions created by extraneous radiation.
- (b) The presence of ionic space charge in the liquid may create an electrohydrodynamic motion in the liquid. The turbulence produced by this motion may produce cavities near the cathode through which some electrons emitted from the cathode may be able to gain sufficient energy in the field to excite molecules of impurities or of the liquid itself. Such excited molecules may release radiative energy while returning back to their ground state. The spectrum of the radiation depends on the type of molecules excited.

It should also be noted that in the case of aromatic hydrocarbons π -electrons play a very important role in the electroluminescence processes.

APPENDIX A

DERIVATION OF EQUATION (4.17)

Equation (4.16) can be written as

$$\frac{d}{dr} \frac{dn}{dr} = \frac{q\mu_1}{\epsilon D} n^2. \quad (\text{A.1})$$

Multiplying the left hand side by dn/dn and let $dn/dr = P$, then Eq. (A.1) becomes

$$P \frac{dP}{dn} = \frac{q\mu_1}{\epsilon D} n^2. \quad (\text{A.2})$$

Integration of Eq. (A.2) gives

$$\frac{P^2}{2} = \frac{q\mu_1}{\epsilon D} \frac{n^3}{3} + A, \quad (\text{A.3})$$

where A is the integration constant. From the boundary conditions

$$\frac{dn}{dr} \rightarrow 0 \quad \text{when } n \rightarrow 0$$

Thus A must be zero. Therefore Eq. (A.3) becomes

$$\frac{dn}{dr} = \left(\frac{2}{3} \frac{q\mu_1}{\epsilon D} \right)^{1/2} n^{3/2}. \quad (\text{A.4})$$

Integration of Eq. (A.4) yields

$$-2n^{-1/2} = \left(\frac{2}{3} \frac{q\mu_1}{\epsilon D} \right)^{1/2} r \pm B. \quad (\text{A.5})$$

Using the boundary condition $n \rightarrow n_0$ when $r \rightarrow 0$, we obtain

$$B = \pm 2 n_0^{-1/2}. \quad (\text{A.6})$$

Substituting Eq. (A.6) into Eq. (A.5) and choosing + sign from the physical reality that n decreases with the increase of r , we have

$$n^{-\frac{1}{2}} = n_0^{-\frac{1}{2}} + \left(\frac{q\mu_1}{6\epsilon D} \right)^{\frac{1}{2}} r$$

or

$$n = n_0 \left[1 + \left(\frac{q\mu_1 n_0}{6\epsilon D} \right)^{\frac{1}{2}} r \right]^{-2}. \quad (\text{A.7})$$

APPENDIX B

DERIVATION OF EQUATION (4.21)

Letting

$$C = \epsilon \lambda v \exp\left(-\frac{W}{kT}\right), \quad (\text{B.1})$$

Eq. (4.20) can be written as

$$J_{zo} dz = C \exp\left(\frac{q\lambda E_z}{2kT}\right) dE_z. \quad (\text{B.2})$$

Integration of Eq. (B.2) yields

$$J_{zo} z + F = \frac{2kTC}{q\lambda} \exp\left(\frac{q\lambda E_z}{2kT}\right), \quad (\text{B.3})$$

where F is the integration constant and can be determined using the following boundary condition

$$E_z \rightarrow E_c \quad \text{when } z \rightarrow 0$$

Thus we have

$$F = \frac{2kTC}{q\lambda} \exp\left(\frac{q\lambda E_c}{2kT}\right). \quad (\text{B.4})$$

Equation (B.3) then can be written as

$$J_{zo} z = \frac{2kTC}{q\lambda} \left[\exp\left(\frac{q\lambda E_z}{2kT}\right) - \exp\left(\frac{q\lambda E_c}{2kT}\right) \right]. \quad (\text{B.5})$$

By rearranging the terms in Eq. (B.5), E_z can be written as

$$E_z = \frac{2kT}{q\lambda} \ln\left[\frac{q\lambda J_{zo}}{2kTC} z + \exp\left(\frac{q\lambda E_c}{2kT}\right)\right]. \quad (\text{B.6})$$

Using the boundary condition

$$V = \int_0^d E_z dz = E_{av} d, \quad (B.7)$$

and letting

$$M = \frac{q\lambda J_{zo}}{2kTc}, \quad (B.8)$$

and

$$h = \exp\left(\frac{q\lambda E_c}{2kT}\right), \quad (B.9)$$

we obtain

$$E_{av} d = \frac{2kT}{q\lambda} \int_0^d \ln(Mz + h) dz. \quad (B.10)$$

Integration of Eq. (B.10) yields

$$1 + \frac{q\lambda(E_{av} - E_c)}{2kT} = \left(1 + \frac{h}{Md}\right) \ln\left(1 + \frac{Md}{h}\right). \quad (B.11)$$

Expressing the term h/Md in terms of Eq. (B.8) and (B.9), we obtain

$$\frac{h}{Md} = \frac{2kT_{ev}}{qJ_{zo}d} \exp\left[-\left(\frac{W - q\lambda E_c/2}{kT}\right)\right].$$

This term is much smaller than unity so it can be neglected. Hence we can write Eq. (B.11) by approximation as

$$1 + \frac{q\lambda(E_{av} - E_c)}{2kT} \approx \ln\left(1 + \frac{Md}{h}\right), \quad (B.12)$$

and (B.12) as

$$e^{\frac{q\lambda(E_{av} - E_c)}{2kT}} - 1 = \frac{qJ_{zo}d}{2kT_{ev}} \exp\left[\frac{W - q\lambda E_c/2}{kT}\right]. \quad (B.13)$$

Then from Eq. (B.13) the current density J_{zo} can be written as

$$J_{zo} = \frac{kT\varepsilon v}{qd} \left\{ e \exp\left[-\frac{(W - q\lambda E_{av}/2)}{kT}\right] - \exp\left[-\frac{(W - q\lambda Y E_{av}/2)}{kT}\right] \right\}. \quad (B.14)$$

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