Simple Dielectric Liquids

Mobility, Conduction, and Breakdown

T.J. Gallagher

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BY

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Preface

This book is an attempt to assess recent work on some of the important electrical properties of dielectric liquids. Another purpose is to try to reconcile many of the earlier conflicting results, especially those of breakdown measurements. This subject is now in a period of rapid growth, having been largely neglected in former years in favour of the more fashionable, and tractable, study of materials in the gaseous and solid states. Despite this neglect, there have been four international conferences on this topic in the past fifteen years, which have resulted in a vast amount of published work. There is now a need for a connected and critical account of the progress that has been made.

It is intended to cover only the research specifically concerned with simple dielectric liquids. An extensive account of work on complex liquids, such as mineral oils, by Zaky and Hawley was published recently. The emphasis throughout is on experimental results. Theoretical analyses are presented briefly but, where necessary, application of the various theories to results is discussed critically. This book contains a substantial amount of material which has not been collated previously. In particular, much of Chapter 1 is devoted to the mobility of fast charge carriers and to electrohydrodynamic (EHD) phenomena in liquids; recent models of conduction and breakdown can be found in Chapters 2 and 3, respectively; Chapter 3 also contains a discussion of the statistical interpretation of breakdown measurements with pulse voltages.

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Mobility

1.1. Introduction

During the period of research which mainly concerns us in this book, namely the past 25 years, much of the early work emphasized the insulating, rather than the conducting, properties of dielectric liquids. Extensive measurements of the electric strengths of liquids were carried out but the results reported were often of a conflicting nature and a clear picture of the mechanisms of breakdown did not emerge from this work (Chapter 3). A vital clue, which could help to solve the secrets of breakdown, is hidden by the difficulty of identifying the main charge carriers involved in pre-breakdown conduction processes. Information about these carriers can be acquired through a measure of their mobilities. Consequently, in the last decade, considerable effort has been devoted to this type of measurement.

Interest in ion or electron charge carrier mobilities is not the sole preserve of those who have specialized in conduction and breakdown experiments in dielectric liquids. A knowledge of mobility is important for radiation chemists who wish to predict the kinetics of ion recombination and diffusion in liquids subjected to high-energy radiation. Nuclear physicists use dielectric liquids as the working media in particle counters and spark-chambers, and the operating speed of these devices is determined by the drift velocities of charges produced in the liquid. Furthermore, a proper interpretation of charge motion in fluids in terms of fundamental electron-atom, or ion-atom interactions can provide valuable information on the nature of the liquid state. Although our understanding of the mechanisms of conduction in insulating liquids still lags behind our comprehensive knowledge of the corresponding processes in the gaseous or solid phases nevertheless, in recent years, there has been substantial progress in the development of realistic theories to describe the charge transport properties of simple dielectric liquids. Mobility measurements have contributed significantly to this progress.

1.2. Methods of excitation and measurement

The 'natural' conductivity of dielectric liquids is generally very small and irregular. Therefore, to make the measurement of charge mobility easier it is

necessary to enhance the normal charge density in a controlled manner, usually by some form of transient external excitation. The most common methods used are indicated in Fig. 1.1. In method (a) an α-particle source, chemically deposited on one electrode, generates dense columns of positive ions and electrons along each α-track. The range of the particle in liquids is $\sim 50\ \mu m$ (Aniansson 1955, 1961) so that the excess charges are created very close to the emitting electrode. With particle energies in the region of 5 MeV (^{210}Po) about 10^5 ion pairs are generated per emission. However, because of recombination between the ion pairs, the number of electrons or positive ions escaping from each column is dependent on the applied electric field, a factor which can restrict mobility measurements to fields above 10^6 V m^{-1}, unless special techniques are used. An X-ray beam can be used to create positive and negative charges. This method has the advantage that the beam may be collimated and its energy varied to control the excess carrier densities and their place of generation. The bulk of the liquid may be irradiated or a very narrow section of it adjacent to one electrode, as shown in Fig. 1.1 (b). Electrons only can be injected into the liquid by ultraviolet (u.v.) illumination of a suitably chosen electrode, as in Fig. 1.1 (c), but care is needed to avoid charge generation in the body of the liquid itself. This problem is overcome by back-irradiation through a thin metal film evaporated onto a quartz window. However, in the latter case it is more advantageous to use electrons instead of u.v., as shown in Fig. 1.1 (d), since a thin metal layer may absorb almost all the light yet be practically transparent to an electron beam of several keV energy (Spear 1969). Furthermore, the density of electrons and their implantation depth in the liquid is easily controlled. Another method is to use a tunnel emitter of the metal–oxide–metal configuration, as in Fig. 1.1 (e). Under the bias conditions shown, 'hot' electrons, with temperatures equivalent to 15 000K, can penetrate the thin film of Al_2O_3 into the Au electrode with extra kinetic energy, from which some of them are ejected into the liquid. Currents of, at least, 100pA can be emitted in a simple and controlled fashion and this technique promises to be very useful in examining the transport properties of charge carriers in liquids. Detailed instructions for the fabrication of these devices are available in the articles by Mentalecheta, Delacote, and Schott (1966), Savoye and Anderson (1967), and Onn, Smetjek, and Silver (1974). Finally, when a fine metal-point or edge electrode is raised to a sufficiently high negative or positive potential to produce a field near its tip of about 10^9 V m^{-1}, electrons or positive ions, respectively, can be created in the vicinity of the point (Fig. 1.1.f). Cold field extraction of electrons from metals in liquids has been studied in some detail in recent years, and indeed field emission from the cathode has long been considered as one of the primary causes of breakdown in liquids (Chapter 3). On the other hand, field ionization of liquid atoms or molecules to create positive ions has received little attention. However, its occurrence, as shown by the experiments of Halpern and Gomer (1965; 1969 *a, b*) and Schnabel and Schmidt (1973), does indicate that if the
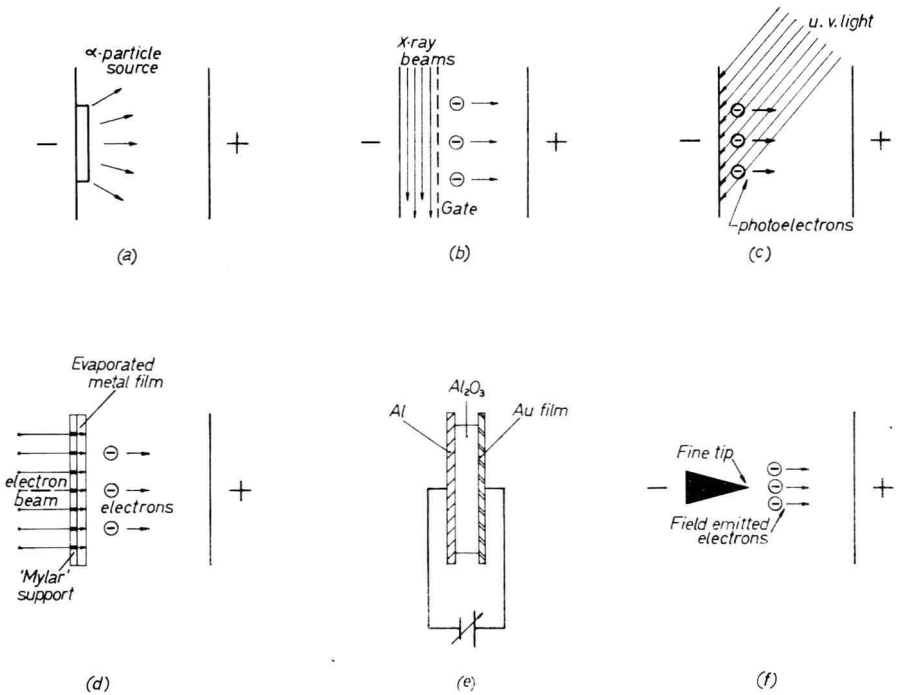
FIG. 1.1. Methods to enhance normal charge density in liquids: (a) α-particle emitter; (b) X-ray irradiation of a thin layer; (c) u.v. illumination of a photo-cathode, (d) electron beam; (e) tunnel emitter; and (f) field emission, or field ionization, from a fine metal point.

field at the positive electrode is large enough positive ions can be generated there. Field ionization, therefore, may also be an important factor in the mechanism of breakdown (section 3.5).

The mobility of a charge carrier is defined as its drift velocity per unit of electric stress. A direct estimate of mobility is determined by a time-of-flight method, which requires a measure of the time necessary for the charge to traverse a known distance in the liquid under the influence of a uniform electric field. Mobility values may also be inferred from a knowledge of the space-charge-limited currents for a given test-cell geometry. For detailed descriptions of the various experimental techniques of measurement the reader is referred to the extensive coverage given by Adamczewski (1969), and by Hummel and Schmidt (1971). A brief discussion of the basic principles is included here.

In its most simple form, the general arrangement for mobility measurements is illustrated by Fig. 1.2. Excess charge is created at the emitter electrode E by any of the methods outlined in Fig. 1.1. By applying the appropriate polarity of voltage V ions of one sign are swept to the collector electrode C. The motion of this ionic charge is manifest as a transient current in the external
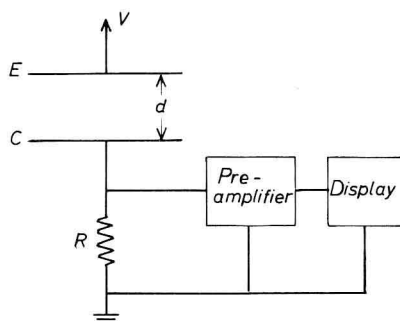
FIG. 1.2.   Simple diode arrangement for mobility measurement.

detection circuit, and its arrival at C is observed as a sudden change in the slope
of the signal across R. The transit time t for the carriers to drift a distance d
between E and C is measured from the oscillographic record of the signal across
R versus time, as shown in Fig. 1.3. The charge mobility μ is determined from
the relationship

$$\mu = \frac{d^2}{tV} , \qquad (1.1)$$
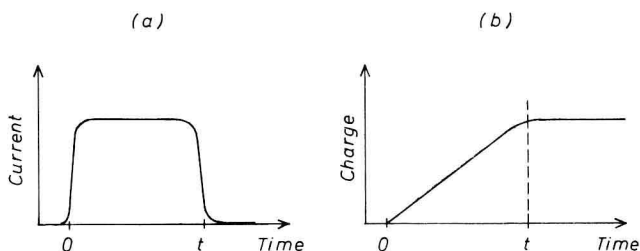
FIG. 1.3.   Ideal signal shapes when carriers are created close to the emitter electrode:
(a) current signal; (b) charge signal obtained from integration of the current
signal.

The use of eqn (1.1) implies that the internal field in the liquid is not signifi-
cantly perturbed by the drifting charge, and that it can be taken as the applied
field. Accordingly, to avoid space charge distortion of the field the number
density of the excess charge is limited to a small value (10^{11} to 10^{13} m^{-3}),
consistent with a measureable signal across R. In recent years the simple diode
arrangement of Fig. 1.2 has usually been converted to triode or tetrode-type
cells by the insertion of grid electrodes, suitably spaced between emitter and
collector. Meyer and Reif (1958) were the first investigators to use grids for

mobility experiments in insulating liquids. Two pairs were used as shown in Fig. 1.4 (a), and the technique of measurement was similar to that developed by Tyndall and Powell (1930) for ion studies in gases. Charge is generated by ^{210}Po α-particles at E, which is maintained at a high potential relative to earth. The grid pairs AB and DF act as electrical shutters, or gates, to allow the passage of carriers across the drift space BD. The gates are arranged to open or close with the frequency of an a.c. voltage applied to them. If this frequency is changed continuously the number of ions reaching C is a maximum when their transit time between the gates is equal to, or an integral multiple of, the period of the pulses. The variation in the collector current is shown in Fig. 1.4 (b), where the
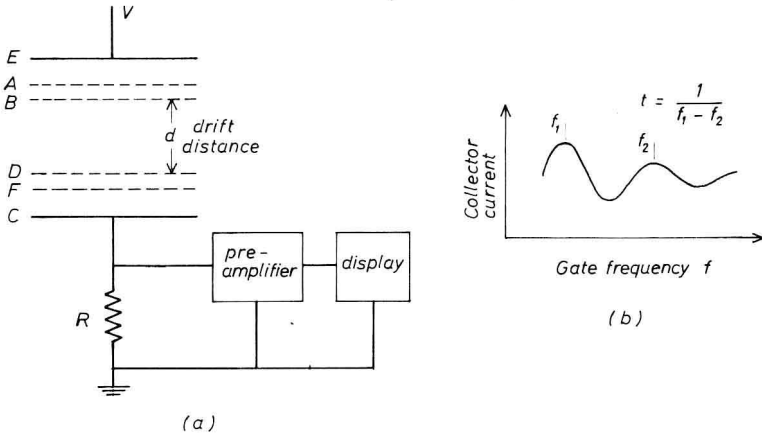

FIG. 1.4.   (a) Diagram of double gate arrangement for mobility measurement, and (b) collector current as a function of the frequency of the voltage on the gates (after Meyer and Reif 1958).

transit time t is given by the reciprocal of the difference in frequency corresponding to adjacent current maxima. The amplitude of the oscillations tends to fall as the frequency of the gate voltage is raised with the result that the sensitivity of the method is decreased as the drift field is increased and the transit time shortened. The method has only been used with fields up to 25 kVm^{-1} by Meyer and Reif (1958) working with liquid helium and by Schynders, Meyer, and Rice (1965, 1966) in liquid argon. Several variations on the circuit of Fig. 1.4 (a) have been developed (Cunsolo 1961, Bruschi, and Santini 1970) and cells containing one or two grids have gained widespread use in mobility studies. An upper limit to the applied field is now set by the mechanical stability of the finely-meshed grid or the risk of a discharge between the grid and the emitter. The use of gates permits extra control of the number of carriers extracted from the emitter region, provides better definition of the initial position of the injected charge, and improves the signal-to-noise ratio of the transient waveform.

1.3. Transport of slow charge carriers

The first extensive investigations of charge transport in liquids was made on organic fluids by Adamczewski (1937 a, b). In the interim, many papers have been published on this topic. Whilst there was a large disparity between the magnitudes obtained for mobility of either the positive or the negative carriers all investigators seemed to agree on one point—both species of ion behaved as slow-moving, singly-charged, carriers with molecular dimensions. Quite recently, there was a dramatic change in this situation. In 1969, both Minday, Schmidt, and Davis, and Schmidt and Allen, independently reported the detection, in n-hexane and tetramethylsilane, respectively, of quasifree electrons with mobilities four to five orders of magnitude greater than for negative ions. This discovery chronologically divides mobility measurements on organic liquids into 'slow' and 'fast' eras, and therefore, it is proposed to treat the motion of charge carriers under these separate headings. Measurements on cryogenic liquids will be treated in a similar fashion, although it is a long-established fact that the negative ion in liquid argon is a quasifree electron (Davidson and Larsh 1948).

1.3.1. Non-polar organic liquids

For a number of non-polar hydrocarbon liquids, Table 1.3.1 gives a summary of the negative (μ_-) and positive (μ_+) ion mobilities which were obtained using time-of-flight techniques and three different methods of excitation. The other methods of carrier generation (Fig. 1.1) have been confined mostly to measurements on cryogenic liquids. There is a significant dispersion in the values in Table 1.3.1, expecially for μ_- in n-hexane, which is the most widely investigated liquid. There are several reasons for the popularity of n-hexane as a medium for investigation. It is liquid at room temperature, has a low viscosity which allows easy filtration, and has a convenient boiling point (341 K) for distillation and purification purposes. In addition, n-hexane, C_6H_{14}, is part of the homologous series of straight chain hydrocarbons, symbolized by the chemical formula C_nH_{2n+2}, so that any dependence of μ on molecular structure is readily examined by a simple alteration of chain length. For the same reasons hexane is widely used for conduction and breakdown studies.

A first glance at Table 1.3.1 would suggest that the spread in values for μ_- and μ_+ is caused by the method of charge injection. This may partly be true since it has never been established that each form of excitation will produce an identical species of charge carrier. However, other factors such as sample preparation and induced motion in the liquid (sub-section 1.3.2) are mostly responsible for the scatter in results. We shall consider the results for μ_- first since, from a breakdown point-of-view, the behaviour of the negative carrier is of greater interest. Now, Minday et $al.$ (1969) could only observe fast carriers in n-hexane after removing oxygen and other electron-scavenging impurities by extremely rigorous purification of the liquid. Consequently, the persistent

Table 1.3.1.

Mobilities of slow charge carriers in hydrocarbon liquids

Liquid	Methods of excitation						
	X-rays			Photoemission		Field emission	
	μ_-	μ_+	ref.	μ_-	ref.	μ_-	ref.
	4.4	8.27	(1)	11	(10)	4 → 14	(15)
	13	4	(2)	10	(11)	1.5	(16)
	9.2	5.8	(3)	10	(12)	1.5	(17)
						6 → 8	
	13	6.8	(4)	10	(13)		
n-Hexane	9.1	8.5	(5)	7.5	(14)		
				1.5			
	20	10	(6)				
	2 → 2.5	2 → 2.5	(7)				
	10	5					
	6		(8)				
	2	2					
	10	-	(9)				
n-Heptane	6.6	4.2	(3)	11	(10)	2.4	(16)
n-Octane	5.2	2.9	(3)	7	(12)	3	(16)
n-Nonane	3.8	2	(3)	-		-	
n-Decane	2.7	1.5	(3)	3	(12)	2.1	(16)
Benzene				4.5	(11)		

Note: In Table 1.3.1 mobility values are given in $(m^2 V^{-1} s^{-1}) \times 10^8$. References are identified by: (1) Adamczewski (1937); (2) Gzowski and Terlecki (1959); (3) Gzowski (1962b); (4) Hummel, Allen, and Watson (1966); (5) Schmidt (1968); (6) Secker and Lewis (1965); (7) Gray and Lewis (1969); (8) Belmont and Secker (1972); (9) Schmidt and Allen (1970a); (10) LeBlanc (1959); (11) Chong and Inuishi (1960); (12) Terlecki (1962); (13) Minday *et al.* (1971); (14) Brignell and Buttle (1971); (15) Essex and Secker (1968); (16) Essex and Secker (1969); (17) Taylor and House (1972a).

appearance of slow negative carriers in pre-1969 studies must mean that excess electrons, injected into 'impure' organic liquids, are rapidly converted into negative ions. The constitution of these ions is still a matter of speculation. Four distinct transformations have been suggested, namely that the injected electron is (*i*) attached to a neutral molecule as a negative ion, (*ii*) held in a partly trapped state from which it occasionally escapes, (*iii*) self-trapped in a cage of polarized liquid molecules as a type of polaron (von Hippel 1946) or (*iv*) scavenged by an impurity.

Because fast carriers are observed (*iii*) can be eliminated immediately. Model (*i*) is determined by the electron affinity of the neutral molecule and to the author's knowledge electron attachment, to form stable negative ions, has never been observed in non-polar hydrocarbons in the gas phase. It is most improbable, therefore, that electron attachment will occur to the molecules of any liquid listed in Table 1.3.1. LeBlanc (1959) has postulated model (*ii*) to explain the temperature dependence of mobility which he found for photoinjected electrons in n-hexane. As shown in Fig. 1.5, μ_- can be expressed by an Arrhenius-type relationship

$$\mu_- = \mu_0 \exp\left(-W/kT\right) \tag{1.2}$$

where $\mu_0 = 3 \times 10^{-5}$ m^{2}V^{-1} s^{-1}, and the activation energy $W = 0.14 \pm 0.02$ eV. LeBlanc also noted that the product of mobility and liquid viscosity η changed with temperature (Fig. 1.5), indicating a violation of Walden's (1906) rule, which stated that the product of $\mu\eta$ should be a constant, independent of the nature of the solvent, and its temperature (Walden and Ulich 1923). The anomalous behaviour with respect to Walden's rule and the low mobility were taken as proof that the carrier was neither a free electron nor a negative ion, whereas the small value for W was interpreted as the average activation energy of an electron in a shallow trap, having dimensions on a molecular scale.

Chong and Inuishi (1960), also using a photoemission technique, confirmed that $\mu_-\eta$ changed with temperature, and they obtained a value of 0.16 eV for W, in close agreement with LeBlanc. On the other hand, Gzowski (1962 *a*, *b*), using X-rays, verified Walden's rule for the negative ion in the series of n-paraffins hexane to decane. The positive species obeyed the relationship $\mu_+\eta^{\frac{3}{2}} = $ constant, in agreement with the earlier work of Adamczewski (1937 *a*, *b*). Similar findings were obtained for cyclohexane by Jachym (1963). The fact that results agree, or disagree, with Walden's rule appears to be over-emphasized in the literature. The rule cannot be considered quantitatively reliable for liquids with low relative permittivities (Robinson and Stokes 1965). Moreover, the rule is derivable from a form of Stokes's (1845) law:

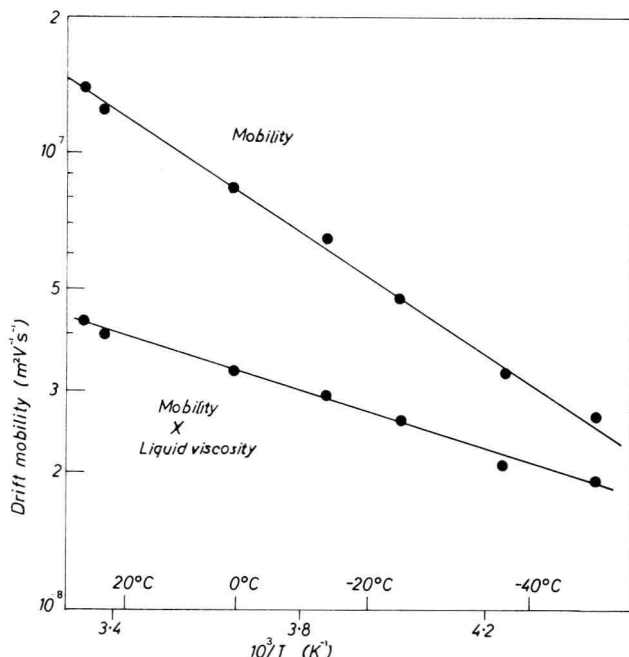$$\nu = \frac{F}{6\pi\eta R} \tag{1.3}$$

FIG. 1.5.   The temperature dependence of the slow negative carrier mobility in n-hexane, and of the product of mobility times liquid viscosity (after LeBlanc 1959).

which relates the velocity of an uncharged spherical particle of radius R to the driving force F and the viscosity of the fluid through which it moves. Because of polarization forces the viscous drag on an ion may be very different from the frictional resistance experienced by an uncharged particle and whilst a Stokes–Walden relationship may give some idea of the size of ions it yields little information about their structures or their interaction with the host liquid.

LeBlanc's (1959) description (structure (*ii*) above) of the conduction state of a slow negative carrier in n-hexane is not supported by measurements of μ_- at high electric fields. Chong and Inuishi (1960) found that μ_- was independent of stress up to 5×10^7 V m^{-1}, the highest field at which direct mobilities have been recorded. Terlecki (1962) confirmed these findings in n-hexane, n-octane, and n-decane, as shown in Fig. 1.6. If the trapping model were valid then μ_- should increase rapidly at high fields because of a field-assisted reduction in the activation energy. This type of Poole–Frenkel effect is not observed (cf. Simmons 1967 for a treatment of this effect in solids). Consequently, model (*ii*) is rejected in favour of the remaining structure (*iv*), which involves the capture of electrons by impurity molecules. Further support for (*iv*) is provided by the observations of Schmidt and Allen (1970 *a*) who have shown that quasifree electrons are trapped to form conventional slow-moving carriers after the addition of impurities to ultra-pure liquids. Thus, some of the scatter of values in
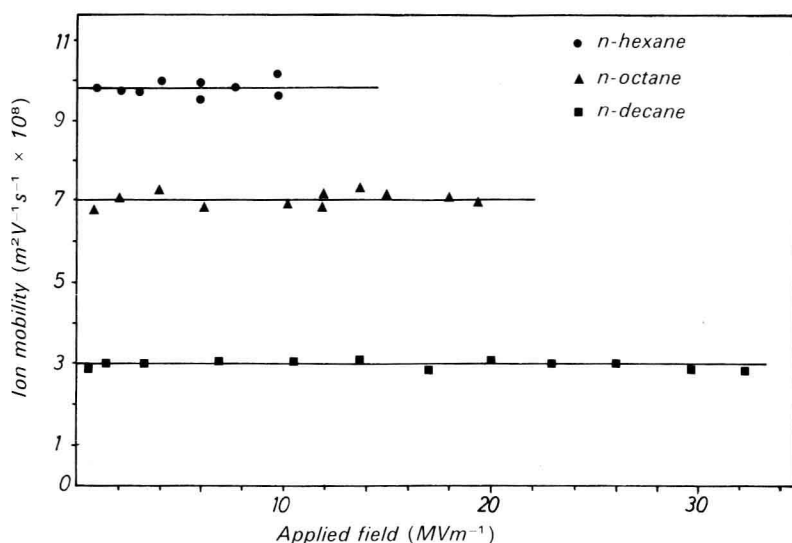
FIG. 1.6.   Mobility of slow negative carriers at high applied fields in three n-alkanes
(after Terlecki 1962).

Table 1.3.1 is easily reconciled with a variation in the amount and character of impurity in the liquids used by different investigators.

The principal impurity is probably dissolved oxygen. There is abundant evidence in the literature to show that in the gaseous phase oxygen can capture electrons to form negative ions of low mobility. Electron capture may occur by either of two mechanisms. Firstly, dissociative attachment to oxygen molecules is important at electron energies of several eV (Craggs, Thorburn, and Tozer 1957; Schulz 1962). This process can be expressed in reaction form by

$$O_2 + e^- \rightarrow (O_2^-)_{unstable} \rightarrow O + O^- + energy \qquad (1.4)$$
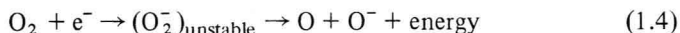
Secondly, the molecular ion may lose its excess energy in a three-body collision to form a stable negative ion (Hurst and Bortner 1959). This is represented by

$$O_2 + e^- + X \rightleftarrows O_2^- + X + energy \qquad (1.5)$$
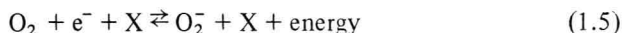
and occurs at electron energies < 1eV. Foreign atoms and molecules may act as the third body X in stabilizing the attachment reaction in eqn (1.5), and because of the close packing of atoms or molecules in a liquid, three-body collisions should be very efficient. Swan (1963) has shown that the cross-section for electron attachment to oxygen in solution in liquid argon is appreciably greater