

CONDUCTION PROCESSES IN DIELECTRIC LIQUIDS

A CONFERENCE on "Electronic Processes in Dielectric Liquids" was held under the auspices of the Electronics Group of the Institute of Physics and the Physical Society, at Durham, in April 1963. The purpose of the meeting was to discuss electrical conduction and allied phenomena in pure dielectric liquids. The conference lasted three days, and included 43 papers, many of them from abroad.

In the past, a great deal of work has been reported in the literature on conduction and breakdown in liquid dielectrics; a feature of much of this work is that for interpretation it has leaned heavily on the classical studies of Townsend on conduction and breakdown in gases (and, to a lesser extent, on conduction processes in solids) rather than on the study of liquids, *per se*. Perhaps because of this conceptual bias, there has been a tendency to think of conduction in liquid in terms of electronic processes, and at high fields, to talk of ionizing collision, and electron avalanches. Indeed, the title of this conference may be taken as evidence of a preconceived notion that free electrons ought to exist in insulating liquids, whereas the experimental evidence presented at the meeting proved, if anything, rather the contrary.

One important function of the conference was to bring together those concerned with the theory of liquids and with transport properties of liquefied gases, and those who have largely specialized in conduction and breakdown processes in dielectric liquids. The value of the conference from this point of view was enhanced by the invited lecture, given by Stuart A. Rice (University of Chicago), who presented a stimulating survey of the present state of the theory of liquids.

As already implied, one of the most important problems in the examination of conduction processes in liquids is the identification of the charge carrier in the conduction process; a number of papers presented at the conference were concerned with this problem. The methods used depend on the measurement of the mobility of the charge carrier, and all these techniques rely on the production of carriers in the liquid by means of external radiation, by α -particles or X-rays, by the photo-generation of carriers, or by electron injection. (It remains to be seen whether these induced carriers are of the same type as those present under conditions of natural conduction.)

For a number of years now, the workers at the University of Gdansk have been measuring charge carrier mobilities in liquids, using X-rays to create both positive and negative species. These experiments have covered a wide range of liquids, but particular attention has been directed to the hydrocarbons. A large number of measurements of this type were reported by Adamczewski on behalf of the Gdansk group, and in the first paper of this series, mobility measurements in saturated hydrocarbons were described. Positive and negative carrier mobilities have been measured in a number of liquids, including cyclohexane, and the observations extended over a range of temperatures. The mobilities are of the order of magnitude predicted by Stokes's law for molecular ions; moreover, the temperature variation of mobility of the negative carrier shows it to be inversely proportional to viscosity, in agreement with Walden's rule. Jachym, working in the same research group, has made carrier mobility measurements in high viscosity hydrocarbon and silicone liquids, again using the X-ray injection technique. Stokes's law was obeyed by the negative carrier; but the positive carrier mobility varied rather more strongly with temperature, suggesting that the positive species are somewhat unstable.

Two other types of measurement were reported from Gdansk on the X-ray induced charge carriers: Gazda and Adamczewski have measured ion recombination coefficients, and their dependence on liquid viscosity and temperature; for the normal alkanes the recombination coefficients are found to be related to the number of carbon atoms in the molecule, and the results have been interpreted on the basis of Frenkel's hole theory of liquids. Gazda has also measured ion diffusion coefficients in *n*-hexane, using an ionization chamber the geometry of which was chosen to give one-dimensional diffusion in the direction perpendicular to the electrodes; these measurements confirm the validity of the Einstein relationship, for charge carriers in hexane.

A number of workers have used photo-injection techniques to create negative charge carriers in liquids. It has previously been shown that the optical threshold for this process is about the same as for the photo-emission of electrons from metals into vacuum—though more recent observations suggest a major difference between these processes. Inuishi and Chong have used the photo-injection technique up to quite high fields, and they described their measurements of charge carrier mobility in pure hexane and in hexane doped with alcohol. There is a marked decrease of negative carrier mobility with doping, and on this basis it has been suggested that the charge carrier is a polaron; that is, an electron trapped in the polarization field of its surroundings. Ions produced by the injection of photo-electrons from a cathode into the liquid were also investigated by Terlecki. The measurements were made in hexane, octane and decane, up to quite high fields; no change of carrier mobility with field was observed, in agreement with Inuishi and Chong. There is evidence that the carrier mobility increases more rapidly with temperature than predicted by Stokes's law—suggesting that in this case the negative species are somewhat unstable. Watson and Clancy described an electron-injection technique for investigating conduction processes in low vapour pressure liquids, including a range of siloxane fluids. Measurements indicate that virtually all the injected electrons are trapped near the point of injection in the liquid, to form stable carriers of low mobility. Currents are space charge limited, and from these measurements values of charge carrier mobility can be inferred.

From these various methods of studying charge carrier mobilities in liquids, a more or less consistent picture emerges; the majority of measurements indicate a negative charge carrier which is presumably a negative molecular ion, though it is possible that in highly polar liquids the polaron model is applicable. In the case of the positive ions, the picture is perhaps not quite so clear; the fact that the mobility of the positive carrier varies more rapidly with temperature than the negative species suggests that the positive ion is not necessarily a stable entity. However, both carriers appear to vary somewhat in behaviour, depending on the experimental conditions.

In view of the increasing body of experimental evidence on the trapping of charges in liquids, there is a need for further theoretical investigations of the nature of the trapping sites; many of the materials chosen for investigation show no tendency to attach electrons and form stable negative ions in the vapour phase, yet they show every indication of trapping electrons in the liquid phase. An adequate understanding of this process is needed. McCubbin reported on some theoretical work on the nature of carrier traps in paraffins in which he suggested that the

density and energy distribution of traps are controlled by the degree of (or lack of) long-range order in the material.

Four papers were presented on electronic and ionic processes in liquefied rare gases. Charge carriers of either sign can be produced by using α -particles to ionize the liquid. With this technique, previous workers have measured very high mobilities ($10 \text{ cm}^2/\text{V sec}$ and greater) for the negative charge carrier in liquid argon, and it has generally been accepted that these carriers are free electrons. New measurements from Chicago, which were presented by Rice, give quite low negative charge carrier mobilities in liquid argon (of the order of $10^{-3} \text{ cm}^2/\text{V sec}$), suggesting that the negative carrier is an impurity ion, despite the fact that the liquid used is of high purity. Results presented on behalf of Swan, on the other hand, confirm the high carrier mobilities reported by Williams and others, and suggest that in pure liquid argon the charge carrier is a free electron, but that with oxygen present, negative ions are formed. The attachment coefficient reported for oxygen in liquid argon appears to be of similar magnitude to that observed in oxygen gas, for low-energy electrons. The discrepancy between these two reports suggests that both types of negative carriers are normally present in liquid argon, but that individual experiments may not be capable of resolving both.

The work at the University of Rome on charge carriers in normal and super-fluid helium was described by Careri. The positive charge carrier in normal helium is believed to be He_2^+ ; the negative carrier may be an electron with a high effective mass caused by electrostriction of its surroundings. In super-fluid helium the nature of the charge carriers is still the subject of controversy. Recent measurements, described by Careri, have revealed that the mobility decreases in a stepwise manner at integral multiples of a certain critical field, and in the case of the positive carrier this has been followed up to six steps in mobility.

Photoconductivity measurements of various organic solutions were described by Ruppel. Solutions of aromatic amines in hexane have a low conductivity in the dark, but ultra-violet irradiation produces short-lived positive ions which increase the conductivity of the solution. Radical ions have been detected by conduction measurements when the solution is excited by a flash of light. Morant described studies of ultra-violet photoconduction in hexane, and reported that illumination of the anode or of the bulk liquid can give currents of almost the same magnitude as illumination of the cathode, implying that the mechanism of charge generation differs from what has been supposed in the past; however, the current is still found to depend on the electrode work function, indicating that it is not simply photo dissociation of the hexane which is involved. Measurements by Terlecki and Gzowski on the photo injection of charge carriers into hexane and decane were described. The currents were proportional to light intensity, and although the measurements were extended up to fields of 200 kV/cm , the current showed no tendency to saturate. In gases the saturation current is a well-established phenomenon; the fact that this is not observed in liquids may be due to space charge effects.

Four papers were presented on the use of liquid-filled ionization chambers. Two of these were by the Polish group, and two were by Blanc *et al.*, all of whom have used ionization chambers filled with dielectric liquids for the detection of nuclear radiation. The best results for fast neutrons, in terms of sensitivity, were obtained using *n*-hexane. Because of the low carrier mobility, however, the response is slow and for the detection of individual particles the best results were obtained with liquid argon.

Nowak has used an ionization chamber to investigate conduction processes in liquid benzene, and to determine the mobility of the charge carriers at different temperatures; preliminary measurements were also made of the recombination coefficients of the carriers. Benzene

seems to possess a relatively high natural conductivity, and it has been suggested that this is associated with the π electrons of the molecule. One might therefore expect to find some interesting features in its electrical behaviour. Forster has made d.c. conductivity measurements on the series of compounds, benzene, cyclohexadiene, cyclohexene and cyclohexane, and has noted a systematic decrease of conductivity along the series; a probe technique was used to determine the potential distribution in the conduction cell, and by this means it was possible to avoid errors which usually enter into d.c. conduction measurements as a result of electrode polarization phenomena. On the basis of their measurements, both Nowak and Forster suggested that the conduction mechanism in benzene involves an electron transfer process between molecules.

Conduction in purified polar liquids has been investigated by Felici and by Briere; in the past, highly polar liquids have been rather neglected in both research and engineering, and to a large extent this lack of interest may be ascribed to the sensitivity of these liquids to electrolytic impurities. The use of ion exchange materials and efficient dehydration techniques now makes it possible to purify these liquids to a considerable extent, and measurements were described on ethyl alcohol, for example, for which resistivities greater than 10^9 ohm cm have now been obtained; this probably represents the limit set by dissociation of the liquid itself. Coelho and Belloc described a novel type of technique to study impurity ions in liquids. They used two sets of coaxial electrodes, mounted in a flow system; the liquid (hexane) was subjected to a d.c. field between the upper electrodes and then passed on to the lower electrodes where an electrometer was used to analyse the residual charge in the liquid. Measurements of the net charge have shown that even at very low fields (100 V/cm) some impurity ions are removed. The passage of current through polar liquids is accompanied by an increase in apparent viscosity; Hart has shown that this visco-electric effect is not due to polarization boundary layers at the electrodes, but is probably due to momentum transfer from charge carriers; calculations indicate that the charge carriers are large, and may in fact be sub-microscopic dust particles.

The final day of the conference was devoted to high-field conduction, breakdown and applied phenomena in insulating liquids, and opened with a review paper by Macfadyen. Zaky, Tropper and House reported on their d.c. conduction measurements in hydrocarbon liquids, with fields up to 10^6 V/cm , and using various cathode surfaces. In order to obtain consistent measurements, it was necessary to condition the system by allowing current to flow for a considerable time—before conditioning, severe current fluctuations occurred. This erratic nature of d.c. conduction currents was also stressed by Morant and Kahan; they found that in highly purified hexane, at fields greater than 200 kV/cm , two distinct sets of currents vs. voltage characteristics could be obtained, and transitions between these values appeared to occur spontaneously. At the moment, no satisfactory explanation for this exists; but an adequate understanding of the part played by space charges may give the required answer.

There are a number of techniques for examining pre-breakdown phenomena in dielectric liquids: Murooka, Nagao and Toriyama have made high-speed camera studies using a bubble chamber as the test cell. By this means, pre-breakdown ionization and vaporization processes in the highly stressed liquids can be studied; interesting effects involving growth and movement of bubbles were shown. Toriyama, Sato and Mitsui presented a paper on the mechanism of breakdown of dielectrics, using Lichtenberg figures to investigate the distribution of ionization in the gap. It was concluded that discharges in the gas phase were often present, but that these may not be essential to breakdown.

One of the most interesting pre-breakdown phenomena in liquids is that of light emission at high fields. Gosling has examined the electro-luminescence of carefully purified fractions of mineral oils at high fields, and finds that both light output and conduction current vary in a manner similar to that found in solid phosphors. The position and brightness of the light emitted depends on the gas content of the oil, its chemical constitution, and the degree of electrode oxidation. Darveniza was among the first to observe light emission from liquids at high fields; recent work of his was reported, in which he investigated the phenomena in both liquids and in solid dielectrics doped with fluorescent solutes (these include anthracene and *p*-terphenyl).

The electric strength of liquids, measured with short rectangular pulses, can be changed appreciably by the application of a static stress to the system before the pulses are applied. Ward described measurements of this type in hexane; it was suggested that a static stress sets up charge layers on the electrodes and that these layers modify the emission from the cathode and hence change the pulse strength of the liquid. Gallagher has made breakdown measurements in liquid argon using direct and impulse voltages, applied to uniform and non-uniform gaps. The effect of gaseous impurities was investigated and small quantities of dissolved oxygen were found to increase the strength. It was noted that the breakdown strength depends also on the condition of both cathode and anode.

A thermal mechanism of liquid breakdown was described by Watson and Sharbaugh, based on their conduction current measurements under microsecond pulse conditions. It was suggested that local currents are large enough to be space charge limited, and the energy input needed to cause breakdown is that required to vaporize the liquid. Krasucki has shown that in viscous liquids the first stage of breakdown involves the formation of a region of low density, which has a lower breakdown strength than the surrounding medium. He suggested that this also occurs in non-viscous liquids, and a model was set up for the formation of the bubble involving the hydrodynamic equations of liquid motion adjacent to the cathode. It appears likely that under many conditions the breakdown of liquids involves a thermal process, and the formation of a vaporized region; it is therefore important to know the breakdown strength of liquid and vapour at high temperatures and pressures. Sharbaugh and Watson described measurements of the electric strength of hexane vapour and liquid. No discontinuity in strength was found in going through from vapour to liquid, in the critical region.

A number of conclusions regarding conduction processes in liquids can be drawn from the work presented at the conference. From measurements of charge carrier mobility, it is clear that, in insulating liquids in general, the conduction process is an ionic rather than an electronic process, and that except in the liquefied rare gases free

electrons do not normally exist in insulating liquids. An electron would be expected to have a mobility of $1 \text{ cm}^2/\text{V sec}$ or greater; for lower mobilities one can no longer talk of free electrons—though hybrid species may exist, such as thermally excited electrons, moving from trap to trap (the so-called 'hopping' electron). The low order of magnitude of carrier mobilities measured in organic liquids implies either an ionic carrier, or a hopping electron; moreover, the variation of the mobility with viscosity seems to follow a Stoke's law type of relationship (though the agreement is not perfect) so that an ionic species seems to be the most likely form of charge carrier. At very high fields the situation is less clear, and the fact that light emission has been observed from insulating liquids containing fluorescent additives, at fields approaching 10^6 V/cm , has been taken as evidence for the presence of energetic electrons in the liquid; other mechanisms of excitation are possible, however, so that even this evidence is not unequivocally in favour of a free electron.

There are a number of speculations as to the nature of the trapping site for electrons in liquids; hydrocarbons such as hexane, for example, do not trap electrons in the vapour phase, yet they seem to contain highly efficient electron traps in the liquid phase. It is possible that the traps are associated with the local degree of disorder of the liquid; the resulting traps must be deep ones, however, for a shallow square well (of the type required by the hopping electron model) does not predict the correct field dependence of mobility. The polaron model may be appropriate, particularly for highly polar materials. The mechanism whereby charge carriers are generated is beginning to look more complicated than had been suspected; until recently one had tended to assume that the charge transfer process, taking place at the interface between electrode and liquid, was similar to that between metal and vacuum, but recent results, implying photo-generation of carriers at both anode and cathode, must make us revise many of these views.

Turning finally to high-field conduction and electrical breakdown in liquids, the question of the relative importance of electronic processes in this region still remains; there is virtually no evidence for collision ionization in recently published work, though it was almost taken for granted a few years ago. Indeed, it is becoming increasingly evident that under the experimental conditions in use at present—even in the use of microsecond pulse techniques—electrical breakdown of liquids is probably not an electronic process in the generally accepted sense, but can often be explained in terms of thermal effects.

It has been impossible, in this report, to mention all 43 papers which were presented at this conference: for a complete list of these papers and authors, the reader is referred to a companion review by M. J. Morant, which is to appear in the *British Journal of Applied Physics*.

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INSTRUMENT DESIGN: MANUFACTURE AND USE

THE new headquarters of S.I.M.A., the Scientific Instrument Manufacturers' Association of Great Britain Ltd., at 20 Peel Street, London, W.8, were officially opened on January 14. The president, Mr. R. E. Burnett (Marconi Instruments Ltd.), in welcoming the guests referred to 1962 as a particularly busy year for the Association in which a number of significant developments in external relations occurred. The association was invited to co-operate with the National Economic Development Office in its initial examinations of certain sectors of industry, and a survey was made by the Association, based on available published statistics and certain

forecasts provided by the industry, of the growth potential of the instrument industry. The exercise disclosed the unsatisfactory nature of the official information, particularly in regard to the classification of products and to industrial employment.

Mr. Burnett emphasized the importance of closer collaboration with instrument manufacturers overseas and reported that during 1962 S.I.M.A. became associated with the Comité Européen de l'Optique et de la Précision de Mécanique. The Comité is an informal organization of parallel trade associations of the Common Market countries and is concerned with the exchange of information,