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Polar Liquids: A Survey of Purification, Conduction Mechanisms, and Interfacial Effects

A. W. BRIGHT, B. MAKIN
Electrical Engineering Department, The University, Southampton, UK

Interest is reviving in the dielectric properties of liquids. The present paper is concerned with a specific group of polar liquids having electrical conductivities which lie in the intermediate range between those of insulating oils and those of liquids such as electrolytic solutions.

It has been found recently that ion exchange techniques provide a powerful means of purifying polar liquids. In this way, liquids have been deionised so effectively that their resistivities have been increased by three orders of magnitude as compared with previously published values.

Published work on this subject is summarised. Removal of trace impurities from liquids may help to clarify mechanisms of electrical conduction, charge injection, and charge exchange phenomena in polar liquids.

Preliminary results of investigations made by the authors are included in the article.

1. Introduction

Liquids are frequently classified in terms of their electrical conductivities into three groups. The first includes insulating liquids having conductivities of around 10^{-11} mho/m. Liquids in this group generally have a high electrical breakdown strength and can withstand fields of 10^6 to 10^8 V/m. A second group includes electrolytic solutions. In this group, the liquids are relatively good conductors, having conductivities from 10^{-2} to 1 mho/m or more. These are still a factor of 10^5 or more lower than the conductivities of the common metals. In the second group, the conductivity depends upon the strength of the ionic solutions and the degree of dissociation. Here, reference may be made to the early basic papers of Debye and Hückel [1] and Onsager [2], and also to standard works on electrochemistry, such as Potter [3]. There is a third group of polar liquids which, when relatively pure, have conductivities which lie in the region between those of the first two groups. In the third group, impurities have been removed by the best available techniques, and published figures of conductivity reflect the extent to which it is possible to reduce the impurity levels. H_2O is an important member of the third group.

In the present paper, we will be concerned with the third group only. Progress in purification of polar liquids has been extremely rapid since 1963, and much of the most interesting recent work has not yet been published. The present paper is not intended to present a complete survey of all work which has been carried out on deionisation of polar liquids, but a selection of what the authors feel to be the main recent contributions in this field.

2. Deionisation of Polar Liquids

It is never possible to remove all impurities from a liquid and usually the nature of the residual impurities is not known. For this reason, it is difficult to know whether the observed conductivity is due to ionic conduction by the impurities or whether the intrinsic conductivity of the liquid is being observed. In some cases impurities may be present in concentrations of 1 part in 10^6 or less.

These difficulties have led to the considerable differences in published data for resistivities, as shown for example in table I.

The possibility of producing high-resistivity liquids having a high dielectric constant was first postulated by Felici [4] in 1959.

TABLE I

Liquid	Resistivity ρ ($\Omega \times$ m)			Dielectric constant
	(at 18° C)	(at 25° C)	(at 25° C)	
Ethyl alcohol	3.0×10^3	7.4×10^6	4.4×10^8	25.8
Methyl alcohol	1.4×10^3	4.3×10^4	1.1×10^7	31.2
Data published	1938	1963	Felici (1963)	

The 1938 values were taken from a standard physics [5] textbook of that date. The 1963 figures indicate the improvement in purification methods up to that time. In general, vacuum distillation was employed. The figures in the third column, which were obtained by Felici, indicate the very considerable reductions in impurity levels, and hence in conductivity, which result from using ion exchange columns and molecular sieves. By using ion exchange techniques, it has been possible to approach the theoretical values of conductivity where these can be calculated, as for example in the case of H_2O. Ion exchange methods have previously mainly been used for the removal of ionic impurities from water, and the extension of these techniques to other polar liquids by Felici and his co-workers in Grenoble University has been of the greatest importance.

2.1. Ion Exchange Methods for Aqueous Solutions

Modern ion exchange resins are available in a wide range of formulations. There are many published papers on this topic and a number of books. Those by Kitchener [6], Kunin [7], Wilson [8], Nachod and Schubert [9] are a representative selection and there are many others. A great deal of valuable practical information on the performance and treatment of these materials is also available from the manufacturers of resins.

The basic principle of operation of ion exchangers is relatively simple when they are used normally. They are also being used currently in electrodialysis cells under conditions where the mechanism is less well understood.

Ion exchangers operate by exchanging ions in solution for ions contained in the resin. One group of resins is used for removal of cations and another for removal of anions. Each of these two main groups has many subdivisions, but, in general, workers using these materials for deionisation of polar liquids use strongly acidic cation resins and strongly basic anion resins. Many different resin bases are available including phenolic, polystyrene, acrylic, and others. Polystyrene resins are most commonly used in the manufacture of ion exchange materials because they are extremely stable and their capacity does not depend on pH.

One example of the exchange process is given for the case of a weak NaCl aqueous solution, reacting with a strongly acidic cation resin having an active sulphonic acid group (SO_3H) which exists in the hydrogen form. The NaCl would dissociate and the Na^+ ion would react with the resin as follows:

$$R^- H^+ + Na^+ \text{ aq} = R^- Na^+ + H^+ \text{ aq}$$

This equation is deceptively simple and it represents an oversimplification of the complete ion exchange process. It is however a useful first approximation. It is customary to describe the linking of the sulphonic acid SO_3H to the resin structure by writing $R'.SO_3^-H^+$, where R' is an organic grouping characteristic of the resin. The H^+ ion is available for exchange. One may replace $R'.SO_3^-$ by R^- as a convenient shorthand. For a more detailed description of the ion exchange equilibria, reference may be made to specialist works such as Kitchener [6].

The Na^+ ion is retained by the resin and the H^+ ion released. The corresponding reaction for a strongly basic anion resin would be:

$$R^+ OH^- + Cl^- = R^+ Cl^- + OH^-$$

By using the two resins in a complete system under certain conditions, the H^+ and OH^- ions may recombine to produce water in an equilibrium reaction. The resins have different affinities for different ions. Also the rates at which ions react with the resins depend upon the nature of the ion. As an example the following list of ions is given in order of increasing affinity with sulphonic acid cation resins: Li^+, H^+, Na^+, K^+, NH_4^+, Cd^+, Mn^+, Mg^+, Zn^+, Cu^+, Ca^+, Al^+. It has been possible to separate ions of the same sign by pumping the mixture through the resin medium at carefully controlled rates. These materials provide an extremely powerful means for deionisation of liquids because the exchange mechanism is able to remove a very wide spectrum of ionic impurities. In addition, being porous, the ion exchangers also remove very fine non-ionic particles by physical trapping in their interstices.

The materials are available in the form of beads (with diameters in the range 10 to 100 μm or so) and membranes. Membranes are particularly useful as they can be used to form partitions in conductivity cells (see fig. 1). On application of a dc voltage between the two electrodes, cations and anions collect in the outer compartments and the centre compartment becomes denuded of ionic impurities. This method is used for purification of brackish water on an industrial scale.

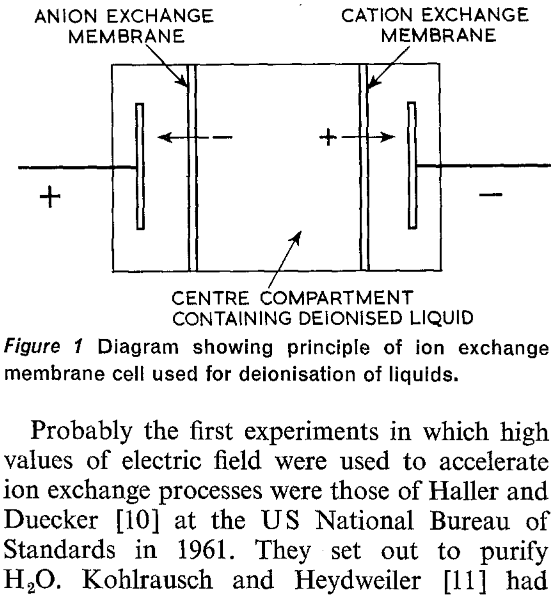

Figure 1 Diagram showing principle of ion exchange membrane cell used for deionisation of liquids.

Probably the first experiments in which high values of electric field were used to accelerate ion exchange processes were those of Haller and Duecker [10] at the US National Bureau of Standards in 1961. They set out to purify H_2O. Kohlrausch and Heydweiler [11] had already produced pure water with a conductivity of 0.0429×10^{-4} mho/m at 18° C (as compared with the theoretical value of 0.0371×10^{-4} mho/m), but this was done by no less than thirty-six successive vacuum distillations. Haller and Duecker constructed an electrodialytic cell similar to that in fig. 1. An electric field of 1 kV/cm was maintained between the membranes, and the deionised water in the centre compartment was continuously circulated by a platinum impeller pump. Circulating electrolytic solutions of ammonium hydroxide and sulphuric acid were used to maintain low-resistance contact between the electrodes and the membranes in the cell.

By this means, it was possible to achieve a conductivity lower than that obtained by Kohlrausch and Heydweiler, corresponding to a residual ion content equal to an NaCl concentration of only 1 part in 10^9.

With such orders of purity, it is important to avoid contamination of the liquid by the containing vessel. In this case, the glassware was treated with steam which depleted the surface of the vessels of possible contaminating ions.

2.2. Ion Exchange Methods for Non-aqueous Solutions

Even in its most pure state, water cannot be regarded as a good insulator. Felici's team in Grenoble University started a research programme in 1960 with the object of producing low-conductivity high-permittivity liquids other than water. These were required as possible insulating media in electrostatic generators. Felici and Brière [12] investigated the use of so-called "mixed-bed" ion exchange technique. Here the liquid is passed through a glass column containing a mixture of anion and cation resin beads.

As has been described above, previous measurements on the conductivity of polar liquids such as the alcohols indicated that these liquids were highly sensitive to ionic pollution. One of the most serious contaminants is water and it is unfortunate that ion exchange resins are normally supplied in a water-saturated form. The early resins could be dried by heating up to around 40° C in vacuo, but tended to swell and crack when soaked once more in the liquid to be deionised. Resins are now commercially available which can be treated in this way without shattering. The method found most effective in Felici's early experiments was to use a dehydrant such as dioxane. In order to remove water from 1 lb (454 g) of resin, it was necessary to use some 2 gal (9 l) of dioxane per pound of resin. An apparatus was constructed in which the liquid to be purified was first passed through columns containing activated alumina and then through a mixed-bed column containing the previously treated beads. The activated alumina was necessary in order to remove water from the liquid to levels of around 10 ppm. Means for recycling the liquid through the ion exchange columns were provided and also for measuring the conductivity. It was found that, in the case of acetone, the conductivity changed by two orders of magnitude in 2 h. With nitrobenzene, a resistivity of 5×10^{10} ohm.m was obtained after more than 20 h. The previous highest value published was 9×10^{7} ohm.m.

For the alcohols, good agreement was obtained between the theoretical values of conductivity and the measured values (Bjerrum, Unmach, and Zechmeister [13]). The agreement was to within about 7% in the case of methyl alcohol which suggests that the liquid was almost completely deionised.

2.3. Electrodialysis

An important extension of the ion exchange column work was made in 1964 by Brière and Felici [14], when they published an account of their work on deionisation of polar liquids by electrodialysis. Here they employed a cell similar to that shown in fig. 1. Two ion exchange membranes divided the cell into three compartments. The membranes were made from polystyrene, the cation being a strongly acid sulphonic acid type and the other a strongly basic quarternary ammonia type. The membranes used were the commercial types AMF A60 and C60 for the anion and cation respectively.

When an electric field was established across the cell, ionic impurities were swept into the two outer compartments and low-conductivity deionised liquid was obtained in the centre compartment. An examination of the voltage distribution across the cell showed that over 99% of the potential difference was developed across the liquid in the centre compartment. It was possible to achieve fields of 10^{7} V/m between the two membranes.

The electric field distribution in the liquid was investigated by using the Kerr effect. John Kerr discovered in 1875 that the optical properties of certain liquids were changed when an electric field was applied. The effect of the field was to rotate the plane of polarisation. In a so-called Kerr cell, two beams of polarised light having their planes of polarisation at right-angles traverse the cell, and a pair of electrodes are provided between which an electric field is established. Interference between the rays results, and the light emerging from the cell is a function of the applied field. Under certain circumstances, a very small percentage change in field can produce a considerable change in transmitted light, and the method is useful for investigating the uniformity or otherwise of electric fields. By using the Kerr effect, Felici and Brière deduced from the absence of fringes that the inter-membrane field was extremely uniform. Between metallic electrodes, this uniformity of field was not observed, and this indicates that the ion exchange membranes were acting as electrodes having the property of preventing accumulation of space charge on the surface, even with intense electric fields.

A more recent paper by Brière, Felici, and Filippini [15] describes a refinement of the membrane technique, in which the electrodes were placed in contact with the membranes. This was found to be preferable to using electrolytic solutions in the outer compartments as with Haller and Duecker, or even to having the arrangement of fig. 1. Various inter-membrane distances were used, from 1 to 10 mm, with dc fields from 10^{6} to 4×10^{7} V/m. The pretreatment of the membranes is not described. It was found that the charging current of the cell followed a law $I = I_l + A\,t^{-n}$, where A and n were independent of time and the variation of I_l was negligible in the time interval of the measurement (about 10^{2} sec). If the applied field was $< 3 \times 10^{6}$ V/m, the discharge current of the cell followed an exponential law, suggesting that the liquid possessed a true intrinsic resistivity.

The highest recorded values of resistivity for nitrobenzene were as shown below:

	(at 25° C)	
E (V/m)	3×10^{6}	3.9×10^{7}
ρ ($\Omega \times$ m)	3.10^{12}	10^{11}

Unlike the Maxwell-Wagner effect in insulators, the charge and discharge current variations did not both follow the exponential law. It was deduced that this was due to the irreversible effect of charge removal by the membranes. When charging, the ionic impurities contributed to the conduction current as they passed through the membranes. When discharging, the current was entirely due to displacement of charges remaining in the inter-membrane space.

Kerr-effect measurements confirmed the uniformity of the field to within 2%. For fields in excess of 1.7×10^{7} V/m, distortion of the membranes occurred.

An experiment was conducted by the authors to investigate if ion exchange resin beads packed in an electrodialysis cell might prove more effective than membranes – because of the increased surface area. A symmetrical cell was constructed with planar stainless-steel electrodes as shown in fig. 2. The ion exchange beads were contained in the space between the stainless-steel electrodes and two sintered-glass discs. In the first experiment, the cell was tested without any ion exchange material. Both of the glass sinters were carefully washed and vacuum dried to remove any impurity. Analar nitrobenzene was used which had an original resistivity of 8.1 × 10^5 ohm.m. After 50 min of continuous purification, the resistivity had risen to 3 × 10^6 ohm.m as shown in fig. 3. A similar experimental result had been determined by Essex and Secker [16] (1966) who had also used glass sinters but with a more elaborate electrode system.

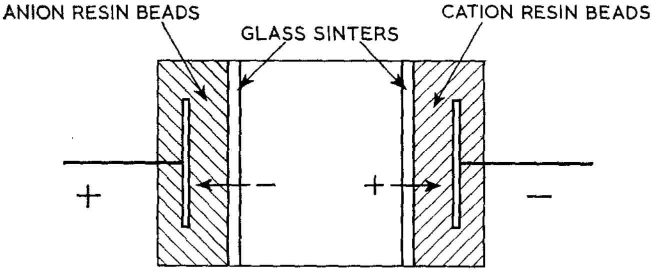

Figure 2 Diagram showing deionisation cell in which ionic impurities pass through glass sinters into end compartments packed with ion exchange beads.

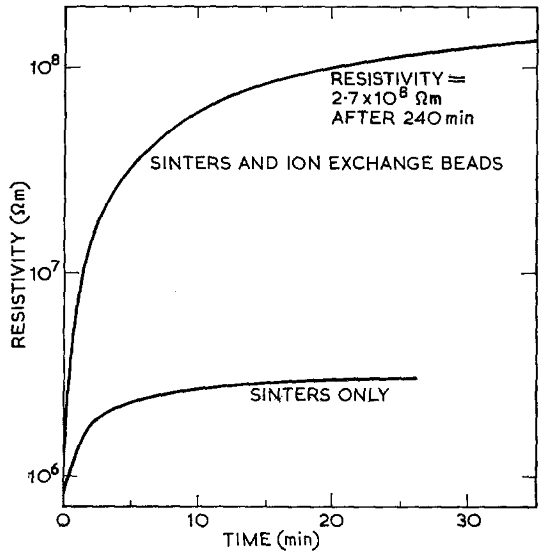

Figure 3 The dependence of resistivity of nitrobenzene on time, showing the effect of sinters only and sinters plus ion exchange beads.

The chambers between the electrodes and sinters were then filled with strong acidic cation resins and strong basic anion resins supplied by Permutit and Co Ltd. The rate of increase of purification is shown in fig. 3, producing an ultimate resistivity of 2.7 × 10^8 ohm.m with a field strength in the liquid of 4 × 10^5 V/m (or 4 kV/cm). Although this resistivity value is 10 000 times smaller than the best published figures of Felici, no special attention was given to the preparation of the nitrobenzene. It is the opinion of the authors that ion exchange resins should be capable of cleaning polar liquids to the same extent as membranes and might be less liable to damage in the event of electrical breakdown in the liquid. Further work along these lines is being pursued.

3. Electrical Conduction in Polar Liquids

Electrical conduction in polar liquids may be considered to involve two separate mechanisms. The first conduction mechanism is due to the presence of impurities in the liquid and the second is the intrinsic conduction process in the pure liquid itself. The purification techniques which have been described above have made it possible to study intrinsic conduction in polar liquids. Conductivity measurements in a number of deionised polar liquids have been described by Brière [17] in 1964. The conduction current for the liquid was measured as a function of applied dc field for uniform gaps between electrodes. It was found that, for applied fields of the order of a few kilovolts per centimetre, the current was proportional to field, and Ohms law was obeyed. As the field increased, the linear relation between current and field no longer applied.

At a critical value of applied field, the current increased as an exponential function of applied field. The critical value of field depended on the electrode material and on the electrode spacing. The rate of rise of current with increase of electric field was greater with small values of electrode spacing than with large values. The relation between current and field was not a simple one. It appeared that the conductivity was proportional to the function exp $E^{\frac{1}{2}}$, so that the current was proportional to E exp $E^{\frac{1}{2}}$. It was observed that, beyond the critical field, the material of the electrodes became important. For a given value of electric field, it was found that platinum electrodes gave the lowest current. Even with platinum electrodes, however, it was found that for fields exceeding a few kilovolts per centimetre Ohm's law was no longer valid.

Some experiments were made in which pulses of varying duration from 1 μsec to 1 msec were applied to the measuring cell. At low values of electric field, it was found that, once more, Ohm's law was obeyed, and similar results to those obtained with dc measurements suggested that polarisation effects were not important. With higher fields, however, the current was no longer independent of the duration of the pulse, and a complicated relationship between pulse current and pulse voltage was observed. This was attributed by Brière to charge accumulation at the surface of the electrodes. This hypothesis was supported by results obtained when the electrodes were rotated at high speeds or when the liquid was agitated.

Forster [18] investigated the voltage-current characteristics for benzene using gold electrodes. With dynamic conditions, the current was initially proportional to $V^{3/2}$. At a field strength of 2×10^6 V/m, the current remained constant, but on increasing the field the current rose. The regime of constant current was found to be more pronounced for small electrode separations. This performance has been attributed to a space-charge barrier at the anode. A similar mechanism was postulated by Rose [19].

Onsager [2] and Plumley [20] have proposed theories to explain the field dependence of the ionisation constant of weak electrolytes. With liquids having relatively low dielectric constants, such as n-hexane and n-heptane, both theories appeared to give results which are in agreement. The Plumley equation relating dissociation constant at zero field with dissociation constant at a particular value of applied field E is as follows:

$$K(E) = K(O) \exp\left(\frac{2e^{3/2} \left(\frac{E}{\epsilon_r}\right)^{\frac{1}{2}}}{kT} \right)$$

where $K(E)$, $K(O)$ are the dissociation constants at values of electric field of E, O, respectively, e is the electronic charge, k is Boltzmann's constant, T the absolute temperature, and ϵ_r the relative permittivity.

The Onsager equation has the form

$$K(E) = K(O)\ [1 + b + \frac{b^2}{3} + \ldots]$$

where $$b = \frac{e^3 E}{2\, \epsilon_r\, k^2\, T^2}$$

Brière found that, for water, excellent agreement was obtained with the Plumley equation. An additional complication arises however in that these experiments were made with trains of unidirectional pulses having durations varying from 0.5 to 10 μsec. It was possible to ascribe the current as being due either to field enhanced dissociation of the liquid, or to a combination of ionic dissociation and an electronic field emission process.

It is clear that electrode effects are important in determining the conductivity. In their paper dealing with deionisation of nitrobenzene (1965), Brière, Felici, and Filippini [15] described measurements in which a test cell consisted of platinum electrodes separated by distances of from 1 to 10 mm. These electrodes were covered by ion exchange membranes. The conductivity was calculated by assuming the membrane surfaces to be the effective electrodes of the test cell. With metallic electrodes, the inter-electrode distance is readily determined. With the electrodes covered by membranes, the effective inter-electrode distance was taken to be the inter-membrane distance. It was assumed that the conductivity of the membranes was high compared with that of the liquid. For a cell having two parallel membranes of area A separated by a distance d, the resistivity was taken to be $\rho = RA/d$, where R was the resistance measured between electrodes. No results were given for conductivity measurements with these deionised liquids using metallic electrodes, but it would clearly be of great interest to study electrode effects in the deionised liquids. The semi-permeable behaviour of a membrane places it in a different category from a metallic electrode, and the very high values of breakdown field which have been obtained in nitrobenzene between ion exchange membranes as electrodes are probably achieved because of the ability of the membranes to prevent charge accumulation and field distortion on their surface. The authors themselves found that in conductivity measurements the results depend to a large extent on the nature and pretreatment of the test electrodes. Reproducible results can be obtained, with electrodes of the same material, provided that the same pretreatment methods are employed, but it is not yet known exactly how the nature of the electrode material, metallic or ion exchange resin, affects the conductivity results.

The measurement of conductivity in deionised liquids does not present very great technical difficulties, but the interpretation of the results is often extremely difficult. At present, it would appear that conductivity measurements between platinum electrodes are those most likely to give consistent results. The method of pretreating ion exchange materials is somewhat indeterminate and results are likely to differ between different laboratories according to the precise way in which the ion exchange materials are prepared.

4. Interfacial Effects for Stationary and Moving Liquids

When any stationary conducting liquid is in close proximity to another phase, which can be either liquid or solid, a distribution of ionic charges will occur which differs from that in the bulk liquid. This phenomenon is important, particularly with liquids in contact with metals, for example at electrodes. Furthermore, the converse process, i.e. propagation of charge, will also be governed by these effects. This subject is closely related to the purification of polar liquids to the extent that the surface phenomena could well be the rate-limiting processes which determine the ultimate level of purification.

The general subject of interfacial phenomena has been treated by many authors under the title of the electrical double layer. The original concept of Helmholtz [21] was to postulate a linear distribution of potential between the surface (which was assumed to contain a layer of similar charges, resulting from adsorbed ions) to a similar adjacent layer of oppositely charged ions. This basic model was modified by Gouy [22], Chapman [23], Stern [24], Overbeek [25], and Devanathan [26] into the modern concept of a triple layer. A comprehensive account of the development is described by Potter [3]. In the triple layer model, the distribution of charge is divided into three distinct zones. These are: (i) a layer of unsolvated adsorbed ions at the surface; (ii) a zone of solvated ions; and (iii) a diffuse layer from the double layer concept of Gouy.

The general principles of the double (or triple) layer have been verified for electrolytes and aqueous systems which readily dissociate. By using the triple layer model, the shape of a capacity-potential characteristic for a mercury/electrolyte interface can be explained. A detailed review of present double layer theories is given by Ross Macdonald and Barlow [27].

Electric charges are produced when a liquid moves over a surface or when a system of small particles settles in the liquid. The generation of electricity by this means has been known in both the petroleum and dry-cleaning industries for many years (Mackeown [28] and Hartshorn [29]). Further, in the transportation of hydrocarbon liquids, it is necessary to pump them through pipes and filters, and this process has been found to produce a sufficient accumulation of charge to initiate breakdown in the form of a spark or corona discharge. The accepted method of overcoming this effect is to increase the conductivity of the liquid by adding electrostatic inhibitors. For petroleum distillates, the Shell Group recommends a complex mixture of chromium and calcium salts (Klinkenberg and Van der Minne [30]). This mixture is added until the conductivity rises to the correct level. Experiments have shown that the resistivity should not be larger than 2×10^{10} ohm.m for refinery processes. In the aviation industry, jet fuels are pumped at flow velocities of 5 to 10 m/sec. At these velocities, it is recommended that the level of resistivity should not exceed 2×10^{9} ohm.m.

The accumulation of charges produced by pumping liquids is influenced by the hydrodynamic characteristics of the fluid flow. The current generated is known as the streaming current. Reviews of this subject have been made by Klinkenberg and Van der Minne [30] and Winter [31]. Using the concept of a double layer, the streaming current has been calculated by Cooper [32] and Klinkenberg [33]. In these theories, it was assumed that in the case of turbulent flow the double layer is small in comparison to the laminar sub-layer. For the case of a hydrocarbon with a resistivity of approximately 5×10^{11} ohm.m, the assumption is no longer valid. This has produced the suggestion that for liquids of high resistivity the charges are distributed by eddy diffusion, whereas for low-resistivity liquids the dominant process is molecular diffusion (Van Dyck [34]).

The convection of charge along a pipe has been examined theoretically by Kosman and Gavis [35]. From experiments with kerosene (resistivity 1.2×10^{11} ohm.m), Hignett and Gibbings [37] have obtained a modified expression for the current density incorporating an entry effect which takes into account the transition from the liquid container to the pipe. A complete interpretation of the charge transfer mechanisms is not available. A recent dimensional analysis of the electrostatic streaming current by Gibbings and Hignett [38] takes account of all of the important variables and fully discusses their physical significance.

With the advent of highly purified polar liquids with resistivities larger than 10^{11} to 10^{12} ohm.m, it is significant that the impurities are responsible for the greater part of the charge transfer. An interesting note on the importance of impurities was made by Ernsberger [36]. He reported that the rate of charge separation of aviation fuel when pumped through a pipe did not reach an asymptotic value as predicted by Cooper [32] but rose indefinitely. The observation was also made that, when trace impurities were removed from the liquid by first passing it through a bed of silica gel, the fuel became triboelectrically* inactive. Ernsberger found that, if the inactive fuel was doped with ethylene diomine (basic), positive electrification was produced. If the fuel was doped with oleic acid, negative charging resulted and finally doping with a neutral solution of n-dodecylalcohol produced no effect. One interpretation of these phenomena is that the charge transfer process is of an electronic nature rather than ionic and that the impurities were being retained on the walls of the pipe by a weak chemi-adsorptive force. The authors know of no other publication which has attempted to isolate the charge transfer mechanism in near-pure liquids of high resistivity.

5. Ion Injection

It is of interest to study the behaviour of ions which are injected into pure polar liquids. In some ways, the behaviour of ions is analogous to the behaviour of electrons in vacuum, because the deionised liquid behaves as an insulating medium. Until recently, it was not thought possible to produce ionisation in a polar liquid without causing considerable dissociation and disruptive breakdown. In 1962, Jorgenson and Will [39] described an experiment in which sharp electrodes were used to produce currents of the order of 55 mA in n-octane. In this case, ionisation occurred. Coe, Hughes, and Secker [40] have described injection of high currents into liquid hexane using field emission. In these experiments, the gap was approximately 1 mm and voltages of the order of 10 kV were used. Fields of about 8×10^7 V/cm were used and at this value it was certain that field emission was occurring. The liquid used was n-hexane and safety razor blades were used as electrodes. With a gap of 1 mm, it was found that currents of the order of 20 mA per blade could be achieved. It is interesting to note that the purity of this liquid was not particularly high and yet it was possible to obtain these appreciable currents without breakdown or excessive dissociation. As yet, no results seem to have been published for injection of charge into polar liquids having a high dielectric constant. Felici and Tobazéon [41] have carried out interesting experiments which suggest that high currents can be injected into polar liquids without dissociation provided that these liquids are pure. Currents of the order of 16 mA/cm of injecting electrode have been obtained for Pyralene which has a dielectric constant of 5.9. The fact that it is possible to obtain currents in liquids at high values of electric field which are analogous to corona currents in gas discharges is of great theoretical interest and also of great practical importance. After charge injection, Felici and Tobazéon were able to transport the charges mechanically by pumping the liquid at high speed away from the charge injection electrode.

The authors are currently engaged in a study of energy conversion using mechanical transport in polar liquids. If successful, the research programme will lead to the development of electrostatic machines which will have a power output per unit volume an order of magnitude or more greater than that of present electrostatic generators, in which compressed gas is used as the insulating medium.

6. Conclusions

Possibly the main conclusion to be drawn from the above discussion is that the properties of liquids depend to a very considerable extent upon the amount of impurities present. Many undesirable triboelectric effects in liquids appear to be due to trace elements in solution and are not observed in pure liquids. The resistivity of analar nitrobenzene can be increased by five orders of magnitude by using ion exchange purification techniques. Thus it is possible that polar liquids, previously considered to be poor conductors, may become useful as insulating media in engineering devices.

**Triboelectrification* is the name given to the process of electrification by rubbing, a mechanism which has been studied since the sixteenth century or even earlier.

Electrostatic generators, although currently available with power outputs as high as 10 kW, have power outputs per unit volume which are considerably less than those of electromagnetic machines. This is largely because electrostatic machines do not yet have insulating media at their disposal having a sufficiently high relative permittivity. All operate in either compressed gas or vacuum. The availability of the deionised liquids described above is likely to prove as important to the development of electrostatic generators as was high-permeability iron to the development of electromagnetic machines. At present, the most important aim of current research in the field is to develop simple and reliable purification systems which can provide adequate quantities of pure liquids. Nitrobenzene is a useful basic liquid to study as it has a relatively high dielectric constant, a high Kerr constant, and a relatively high breakdown field. Later, the investigations will be broadened in scope to include other liquids of higher relative permittivity. The new liquids may also prove to be of use to the cable and capacitor industries. Kerr cells for high-speed photography would also be improved by using these new liquids.

An appreciable amount of research is also being carried out on the dangerous aspects of electrostatic phenomena, for example in the petroleum industry. Current work on deionisation in liquids may well lead to the development of methods which eliminate the danger associated with the high-speed flow of many polar liquids.

To-date, the only liquids which have received special attention are water, methanol, ethanol, nitrobenzene, and aviation fuel. Further progress awaits a fuller understanding of the mechanism of the purification process and also the discovery of better diagnostic techniques for sampling and analysing trace impurities. When these are available, it is anticipated that a much wider range of liquids will come under investigation, for a variety of applications.

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