THE DISRUPTION AND ELECTRIFICATION
OF LIQUID JETS

by

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ABSTRACT

The research described in this thesis investigates the charge separation which occurs when liquids are broken up by the action of mechanical forces.Itis shown that the problem of the charge separation is often the problem of the separation of charge in a single breaking jet. A series of experiments is described in which jets were produced under closely controlled conditions and by a variety of methods from volumes of liquids, usually aqueous solutions. The jets were produced by, the splashing of drops on a surface, the pulling of a capillary vertically from a horizontal liquid surface, and by the breaking of small isolated drops. The charges on the drops resulting from the breaking of these jets were measured as a function of the concentration of solutes in the liquids, and also as a function of certain geometrical factors. The results showed that great care must be taken to eliminate any charges which are separated by induction in the fields of contact potentials which are often present.

It is shown that the charge separation can be explained in terms of the shearing of the electrical double layer which is found on the surface of the liquids, either during the deformation of the liquid to form the jet, or during the breaking of the jet into drops.A theoretical expression for the charge separated by the later method is derived. This gives reasonable agreement with the experimental results

provided that allowance is made for inaccuracies introduced into the theory by certain simplifying assumptions. It is also shown that charge separation in aqueous jets islimited by conduction for jets of radius greater than about one micron.

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CHAPTER ONE

Introduction and Review of Previous Work

1.1. Introduction

The breaking up of liquids to form small droplets has long attracted the attention of scientists. This is doubtless due, in some part, to the beauty of the process, especially when seen in slow motion. One of the earliest documented observations is quoted by Worthington (1895) who tells of a schoolboy who noticed the peculiar behaviour of an inkdrop splashing on a surface. These observations were the inspiration of Worthington, whose experiments, together with the theories and experiments of Rayleigh, formed the basis of the study of the break-up of liquids. These early experiments often used new and ingenious photographic techniques to study the breaking liquid.

Early in these studies it was observed that electrification could be produced by breaking up water, for example, considerable sparks could be seen near some waterfalls, apparently produced as a result of electrification caused by the splashing of the water. This electrification has often been measured since these early days, but in most cases these measurements have been divorced from a study of the physical processes involved in the break up of the liquids.

The electrification produced by the disruption of drops was also thought by Simpson (1909) to be the cause of the electric charges in thunder clouds. Mason (1962) has shown however that this mechanism is not sufficiently effective to build up the observed charges during the life time of a typical storm. It has also been suggested that the breaking of drops could cause the positive pocket of charge observed under the main charged regions of many thunder clouds. This has also been doubted and it now seems probable that the charging is due to the production of small charged droplets by bursting bubbles in melting ice pellets (Drake, 1966). Blanchard (1963) has suggested that the breaking of bubbles at the sea surface is an important factor in carrying positive charge from the earth into the atmosphere. He estimated that even in the absence of electric fields a current of 150 amps could be carried into the atmosphere by this process.

The splashing of drops from the skin of an aircraft often results in considerable charging which can give rise to many problems. Fordham-Cooper (1953) has pointed out that the flow of liquids through pipes can cause considerable charge separation which has been responsible for a number of fires where inflamable, non-conducting, liquids are used.

The object of this thesis is to show how some of the electrification measurements can be explained and to estimate the importance of drop break up in atmospheric electrification. In order to do this, simple ideas about the flow of liquid in a breaking jet will be used, together with an elementary model of the surface structure of liquids.

This chapter is concerned with previous work on the breaking and electrification of liquid jets. The first section considers ways in which liquids can be broken up and shows how all of these methods are dependant on the breaking of a single jet. The mathematical theories of the breaking jet are then considered in detail. The next section considers the electrical measurements of various workers and how these led to theories for the surface structure of liquids. Another section details the various charging mechanisms which have been suggested and considers their relative importance. These are also considered in the light of recent electrical measurements. The final section shows how all these experiments depend for their interpretation on the idea of charge separation occuring as a jet breaks and how this thesis will try to clarify this process.

1.2. The Break Up of Liquids

1.2.1 Methods of breaking up liquids

A volume of liquid which is under the action of small surface tension forces can be broken up very easily by the application of very small mechanical forces. The main method of causing a large drop, or volume of liquid, to break up are:

(i) Large drops falling onto solid or liquid surfaces break up to form drops of 100 - 1000 microns radius, together with a number of sub-micron drops.

(ii) Liquids can be forced through a hole or tube. The resultant spray contains drops of radii comparable with that of the hole, as well as some smaller drops.

(iii) Large drops falling at their terminal velocity, or smaller drops in an air blast, break up to form a large number of very small droplets together with a few large drops.

(iv) The bubbling of gas through a liquid causes the formation of drops of a wide range of sizes, from sub-micron, to more than 100 microns radius. Tracings of photographs which have been obtained by various authors during the past 80 years are shown in fig 1.1.

Worthington (loc.cit) obtained photographs of the splashing of drops of water, milk, and mercury, on solid, or liquid-covered surfaces. The diagram shows a liquid drop splashing on a solid surface. It was observed that the drops deformed on impacting on the plate. They became dimpled at the centre to form a crown of liquid. The crown was unstable and, under the action of the force of impact, formed several arms of liquid. These arms broke up to form small droplets which were thrown upwards with considerable force.

The break up of liquid jets from a capillary has received the attention of many workers. Donnelly and

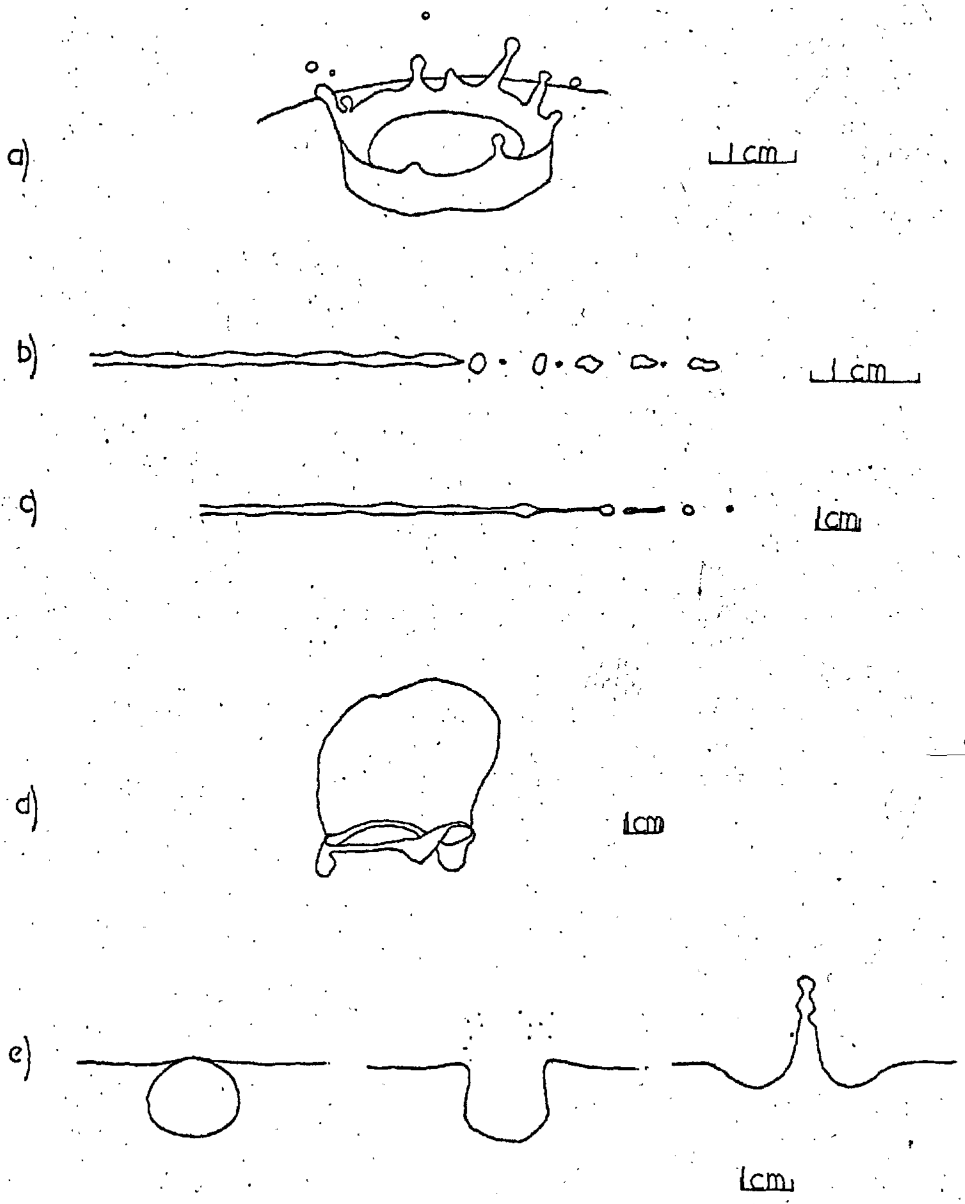


Fig 1·1 Methods of droplet formation

a) Drop splashing on a solid surface (Worthington, 1895)
b) Jet issuing from a capillary (Donnelly & Glaberson, 1966)
c) Viscous jet from a capillary (— " —)
d) Drop breaking at terminal velocity (Matthews & Mason, 1964)
e) Three stages in bubble bursting (Blanchard, 1963)

Glaberson (1966) have obtained photographs of the jet issuing from a vibrated capillary. The jet was seen to develop concavities which grew steadily until they broke up the jet into drops.

Matthews and Mason (1964) photographed drops breaking up while falling near their terminal velocities in air. Harper (1957) shows a photograph by Hochschwender (1919) of a smaller drop breaking under the action of a powerful air blast. In both cases the break up occurred in a similar way. A thin bag was blown out behind the drop, the main part of the liquid being contained in an annular ring at the front of the drop. The bag broke to form a number of small droplets. The ring was also unstable and broke into a small number of much larger drops. The bag drops were often of micron size or smaller but those from the ring were 100 - 1000 microns radius.

The bursting of a bubble at a liquid surface is a very complicated process but it has been successfully photographed. Blanchard (loc. cit) shows that the bubble rose and protruded through the surface covered only by a thin film of liquid. The cap drained from the centre and burst, the fragments being thrown a considerable height by the excess pressure in the bubble. A cavity was then left in the surface of the liquid. This was filled by liquid draining down the sides to form a jet which rose from the bottom of the cavity.

Instability in this jet caused it to break up to form one or more drops which were also thrown upwards.

Day (unpublished) has obtained photographs of drops splashing into a deep liquid. A jet was thrown upwards from the surface in the same way as the jet rose from the bubble cavity. This jet was also unstable and broke up into drops.

The break up of a thin film of liquid, such as that on a bubble cap, or the bag blown out behind a drop, was studied by Johonnot (1899) using interference methods. The film was observed to thin by draining towards the edges, and then it perforated to give a lace-like array of filaments. This lace-like structure has been photographed by Dombrowski and Fraser (1954). These filaments were observed to break up into a series of very small droplets. The films often reached a thickness of less than 10^{-5} cm, before breaking, although films stabilised by soap solutions could be thinned to about 10^{-6}cm or even thinner, before breaking. The droplets from a film could be thrown a considerable distance if the film contained gas under pressure. Blanchard suggests however that the bubble film perforates at only one point and then contracts to form a toroidal ring which subsequently breaks up.

It is seen that all the processes in which droplets are produced are the result, ultimately, of the breaking up of an unstable jet or filament of liquid. A concavity develops in the sides of the jet and grows until disruption occurs. We willconsider the breaking of a jet in more detail asthis will include the other methods of drop production.

1.2.2 The break up of a liquid jet

In attempting to explain the breaking up of a cylindrical column of liquid Plateau (1873) showed that when disturbances acted on the column, alternate swellings and contractions were produced by surface tension forces. If the wavelength of the disturbances exceeded the circumference of the column then the excess pressure under the contraction was greater than that under the swelling, which subsequently grew. Jets therefore with a length in excess of the circumference were unstable to random surface disturbances. This theory was further developed by Rayleigh (1879). He assumed that the amplitude α of the disturbance grew exponentially with time, that is $\alpha = \alpha_0 \exp qt$. Rayleigh showed that the amplification factor q depended on the wavelength λ of the disturbance. Ignoring the effects of viscosity he showed that for a liquid of surface tension γ

$$q = \left\{\frac{\gamma}{da^3}\right\}^{1/2} F(ka)$$

where a is the radius of the column
F(ka) is the function of $ka = 2\pi a/\lambda$
and d is the liquid density.

It was shown that the maximum value of q occured when $ka = 0.7$, when $F(ka) = 0.343$. This shows that a disturbance of wavelength equal to 4.5 times the column diameter would grow fastest. In the absence of any applied disturbance we would expect therefore a jet to break up with this wavelength, as this would be the fastest growing component of any random disturbances. Later Rayleigh (1892) extended the work to include viscous liquids and concluded that although viscosity would slow down the growth rate of the disturbance it would not affect the criterion for instability. It should be noted that although the theory assumes an increasing amplitude of the disturbance, the instability criterion is based on the assumption of an infinitely small disturbance. The theory was however used by Rayleigh to predict the drop sizes produced by jets from a pipe and these agreed very well with his experiments.

Castleman (1924) showed that Rayleigh's work was not applicable to moving jets of liquid such as those from a capillary. He also showed that the variation of F (ka) near the maximum was not very great so that the critical wavelength was not as sharply defined as Rayleigh had suggested. Later Castleman (1931) calculated the time taken for a jet to break up using Rayleigh's model. He let $\alpha \rightarrow a$, so that the disturbance broke up the jet. The calculated break up time for aqueous jets was then given by $t = 0.89\ a^{3/2} \log a / \alpha_0$, where α_0, the initial amplitude of the disturbance, can be taken as 10^{-5}cm for many jets.

Although Rayleigh's results were obtained for static jets they may be applied to moving jets if surface tension is the dominant force. Since, in this case, the break up time is independant of the jet velocity, the unbroken jet length should increase lineally with jet speed. Crane et al (1964) were able to produce very stable jets so that they could impress the break up frequency as desired. They measured the lengths of jets issuing from a pipe and found reasonable agreement with the theory, including the change in growth rate of the disturbance with the wavelength. At high accelerations of the jet however the theory broke down, as it did also at high ejection velocities.

At high ejection velocities the surface tension forces are less important and the action of the relative air motion dominates. The drag of the air on a plane water surface is small, Vines (1959) having shown as a result of his experiments that even at a relative speed of several meters per second the drag is under 1 dyne/cm^2. However if a perturbation of the surface occurs the air can act on this and this can lead to an increase in the growth rate of the disturbance. This type of air assisted break up has been treated by Weber (1931) who showed that the effects are small for relative velocities under 10 m/s. The jets produced at these speeds have decreased stability due to the wind action. This results in the drop sizes being decreased, the drop size decreasing with increasing velocity. At low speeds however the drop size should be independant of velocity. The critical wind velocity U_c was calculated by Ohnesarge (1936) who showed that for a jet of radius a of liquid with viscosity η

$$U_c^{4/3} = 1.6 \times 10^3 \left\{\frac{\eta}{da}\right\}^{1/3} \gamma^{1/2} .$$

This result was verified by the experiments of Merrington and Richardson (1947).

Most of these experiments have not considered the behaviour of jets of viscous liquids. Tyler and Watkin (1932) measured the lengths of jets of various viscous liquids. Using the method of dimensions they obtained an expression for the amplification factor

$$q \propto \left\{\frac{\gamma}{da^3}\right\}^{1/2} \left\{\frac{\eta}{\gamma da}\right\}^n$$

where n is some constant.

This modified formula was found to give very good agreement with the results of their experiments. In particular the length L of a jet before it broke was shown to fit the formula.

$$\frac{L}{a} \propto V \left\{\frac{da}{\gamma}\right\}^{1/2} \left[1 + \frac{1}{4095}\left\{\frac{2\gamma da}{\eta^2}\right\}^{3/4} \right]$$

compared with Rayleigh's value of

$$\frac{L}{a} \propto V \left\{\frac{da}{\gamma}\right\}^{1/2}$$

where V is the jet velocity.

These observations however are contrary to many observations that the stable length increases with increasing viscosity.

These theories have considered liquid jets breaking in air. The break up may be considerably slowed by breaking the jet in a viscous medium. Tomotika (1935) showed that a static jet in a viscous medium would break at a rate dependant on the ratio of the densities and viscosities of the liquids. The motion of the medium would increase the jet stability (Tomotika, 1936). The resultant long thin thread of liquid would then break into fine drops as had been observed by Taylor (1934). These observations have recently been extended to very small jets by Rumscheidt and Mason (1962).

These theories, although giving quite good agreement with the experimental results for the break up times of liquid jets, have not considered the shape of the jet during break up. They have, like Rayleigh's theory, assumed an exponentially increasing amplitude of the disturbance which was believed to be sinusoidal in form. The diagram 1.1c shows that this sinusoidal assumption is far from true in the case of a jet of a viscous liquid. Goren (1964) considered a single wavelength of the disturbance and minimised the surface area, subject to the constraints of constant volume and an exponentially increasing amplitude. The theory predicted that the neck of liquid was not sinusoidal but consisted of a cylinder of liquid joining two almost spherical drops at either end. This was verified experimentally by Goren and is in agreement with the observed shapes of the neck photographed by other authors.

In summing up it is seen that there is adequate experimental and theoretical evidence that liquid jets in air will break up if their length exceeds their circumference.

Various theories predict slightly differing times for the break up especially if viscosity is introduced. For comparativly inviscid liquids, that is for those in which the surface tension forces exceed the forces exerted by viscosity for the velocities of the liquid in the jet, the jet break up times are in good agreement with Castleman's theories. At velocities above about 10 m/s the action of the air becomes important. The neck of liquid during the final stages of break up can be considered as a cylinder joining spherical drops. The agreement of the various theories with Rayleigh's work has led to the adoption of the expression 'Rayleigh instability' for this type of break up. The viscosity of aqueous solutions which will be mainly considered in this thesis, is sufficiently low for Rayleigh's theory to be a good approximation to the behaviour of breaking of aqueous jets.

1.3 Electrical Measurements

1.3.1 Early Work

Interest in the electrification occuring when volumes of water were broken up was initiated by the observations made by Elster and Geitel (1890) that in the regions near a waterfall the air became negatively charged and that the large drops formed by splashing were positively charged. Lenard (1892), in a series of controlled experiments, allowed water to splash onto a metal plate covered with a layer of water. He observed that there was no charge separation until the drops hit the surface. After the splash however, charge separation did occur, the sign of the charges being the same as those observed near the waterfall. The charge separation was greater for distilled water than for rain water, or water from a clear stream. Lenard attributed this charging to the breaking of the surface of the drop. He considered that the surface of the drop carried positive charge with a negative layer in the air near the drop. This negative layer was scraped off during splashing to give a negative charge to the air.

Thomson (1894) conducted a series of experiments similar to those of Lenard with drops splashing on liquid covered surfaces of different materials. The fragments were caught and the charges measured using an electrometer. The material of the plate had no effect provided that it was well covered with liquid. The electrification was found to depend on the gas surrounding the drop, and on the nature and concentration of any solutes dissolved in the drop. Several of Thomson's results are shown in fig 1.2, the unit of charge being the same for all the curves. Thomson believed that the electrification was in part due to the solvent and decreased as the solute concentration was increased. The other part was due to the solute, and increased with concentration. These two effects when summed would produce the observed separation which could vary with concentration in any of the ways shown in fig 1.2.

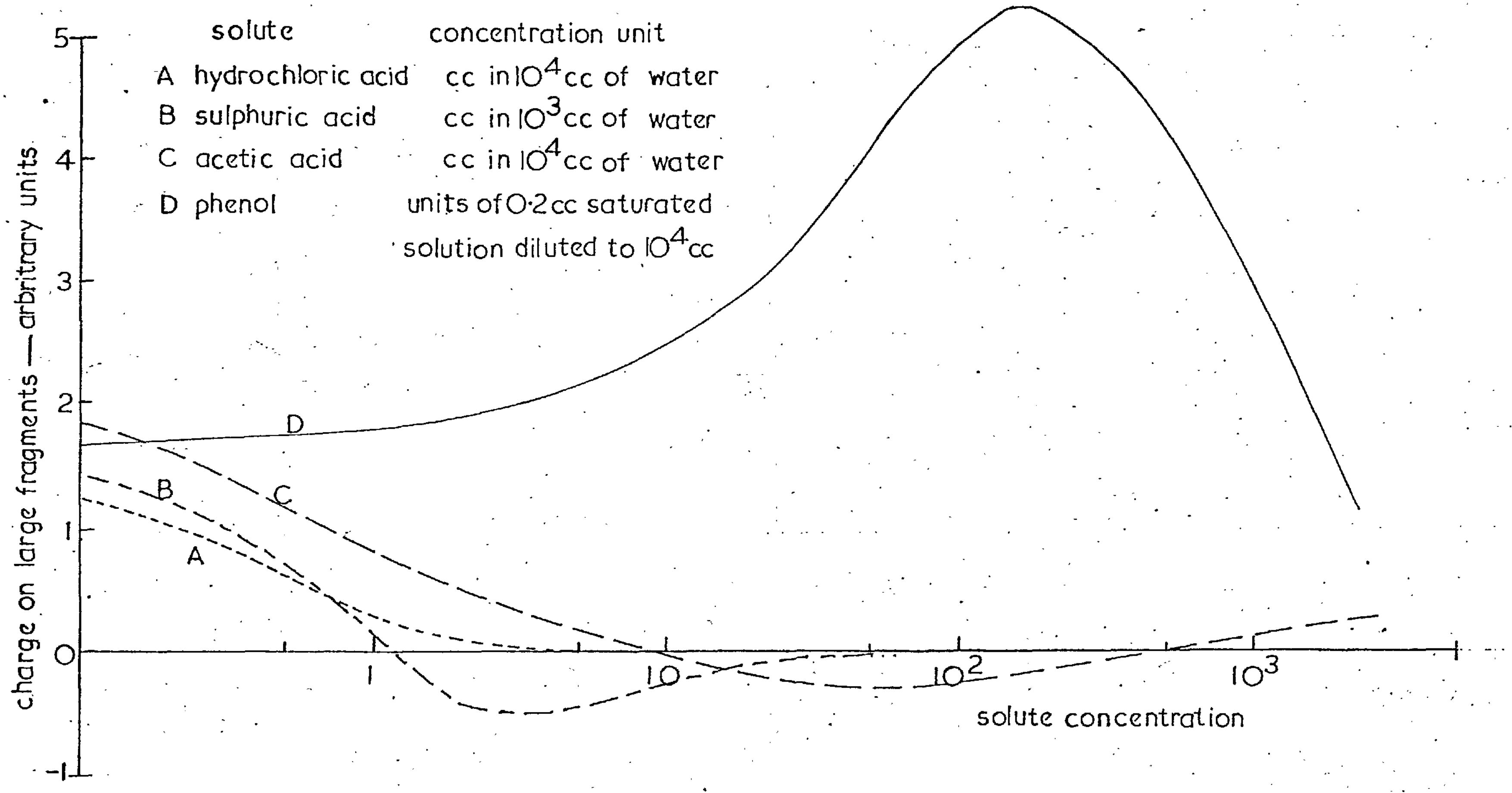


Fig 1·2 Charge separated by splashing (Thomson, 1894)

Lenard (1915) modified the theory slightly and suggested that both charged layers must be in the water. He also concluded, from the results of experiments carried out by himself and his co-workers that the negative surface layer was about 10^{-7}cm thick and the positive layer beneath this about 10^{-5} cm thick. He suggested that the splashing of the drops caused a separation of the two charged layers. There was no charge separation when a surface collapsed unless it broke into two or more parts. Lenard estimated that charges of about 6×10^{-3}esu were separated for each square centimeter of new drop surface created by the break up.

Coehn and Mozer (1914) had bubbled air through aqueous solutions of various concentrations. For pure water the spray produced contained only negativelycharged particles but increasing the solute concentration produced positive particles until at high concentrations, although charged particles of both signs were present, the net spray charge was almost zero. Lenard believed that the formation of positive particles showed that ions from the solute had been incorporated into the surface charged layers.

Experiments by Nolan and Enright (1922) showed that charges of about 2×10^{-3}esu/cm^2 could be separated by breaking up water drops in an air blast or by splashing. The charging was somewhat increased by purifying the water until the conductivity was reduced to about 2.4×10^{-6}ohm^{-1}cm^{-1}

These early experiments led to the idea that charged layers were present on the surfaces of some, if not all, liquids. This idea had also been suggested by workers who observed that bubbles in liquids would move through the liquid if an electric field was applied. The bubbles acted as if they had a charge.

1.3.2 Catophoresis and the idea of a double layer

Catophoresis is the name given to this motion of gas bubbles in liquids under the action of an electric field. The experiments are usually made by introducing a bubble into a tube full of liquid rotating about a horizontal axis. The electric field is applied parallel to this axis, the rotation of the tube minimising the gravitational effects on the bubble.

McTaggart (1922) showed that the direction of motion of air bubbles in thorium nitrate solutions reversed for concentrations greater than 6 x 10^{-6} normal. Alty (1924) measured the velocities of bubbles of various gases (helium, oxygen, acetylene, air and carbon dioxide) in water. A reversal in the motion of the bubble occurred for water of conductivity$>1.8 \times 10^{-6}$ ohm^{-1} cm^{-1}. The results were explained qualitatively in terms of a layer of charge on the surface of the liquid and the absorbtion of ions into this layer. The time taken for the ions to be absorbed gave the observed variation of bubble velocity with time. Alty (1926) derived a theory which fitted his results very well. He considered that the water molecules were polar and that on the surface the dipoles were partially oriented. Stray impurity ions in the water were then attracted to this oriented layer. The ions of one sign became tightly bound to the ends of the dipoles. Ions of opposite sign were attracted to this layer. The attraction was however opposed by random thermal motions in the liquid so that at any time there were fewer of these ions in the inner layer than in the outer layer. This left a mean charge on the layer surrounding the bubble. The application of the electric field caused the bubble, and the surrounding layers of charge, to move as though the charge was on the bubble. Alty suggested that for perfectly pure water the bubble velocity would be zero. The theory is open to two main objections. Firstly it predicted an ion concentration of about 10^{8} per cm^{3}. This is several orders of magnitude too small to account for the observed conductivity of the water of 10^{-6} ohm^{-1} cm^{-1}. Also, in the calculations no reference was made to any endosmotic correction, that is, a correction for the reverse motion of the liquid in the electric field.

Catophoresis experiments were also made by Bach and Gilman(1938). These authors applied a correction for endosmotic effects and found that there was a negative charge on all bubbles in inorganic liquids. There was no reversal of the charge at high concentrations, although apparent reversals were found if the correction was not applied. These authors came to the conclusion that there were charged layers on the surfaces of liquids. In the case of water the surface layer was believed to be negatively charged. They considered that since the liquid was neutral that the compensating positive charge must reside just below the surface layer.

It is seen that these catophoresis experiments suggested the same structure on the surface of water as was postulated by Lenard. These charged layers were combined to give what was known as a double layer of charge on the liquid surface.

1.3.3 The Electrical Double Layer

From these early experiments many elaborate theories of the surface structure of liquids have been evolved. It would however be out of place to consider these theories here, but sufficient to consider only the results. For the purposes of this thesis a simple idea of the surface structure will be sufficient, and the one summarised below has been extracted in part from Adamson (1960).

Asymmetrical molecules usually have a molecular dipole momement. In the bulk liquid this has no effect on the orientation of the molecules, but on the surface of the liquid the surface energy may be reduced if the molecules become oriented in one direction. The orientation is opposed by the thermal motion in the liquid so that for many liquids at room temperature there is only partial orientation of the surface layer. This orientation occurs very rapidly after the formation of a surface, a typical formation being of the order of the rotational period of molecules, about 10^{-10}sec. for water.

The presence of the oriented layer will set up a potential gradient in the liquid which will attract any ions present in the liquid. A layer of charge will become tightly bound to the inner ends of the dipoles, of opposite charge to the charge on this end of the dipoles. Since, however, the liquid as a whole is electrically neutral there will be a large number of ions of opposite sign present in the liquid. These will be attracted to form a diffuse layer of charge under the tightly bound, or compact, layer. The thicknesses of the components of the layer will depend on the temperature of the liquid as well as on the concentrations of ions present. The mathematics of the charge distributions will be given later in chapter 7 when they are considered in relation to the charge separation process. It will be sufficient here to quote the following results: The thickness of the diffuse layer is about $3 \times 10^{-8} c^{-\frac{1}{2}}$ cms. The variation of potential ψ with depth x below the surface is given by

$$\tanh\left\{\frac{ze\psi}{4kT}\right\} = \exp -K(x - x_0)$$

The charge below a plane at a depth x, per unit area, is

$$\sigma = \left\{\frac{2Dn_0kT}{\pi}\right\}^{1/2} \sinh\left\{\frac{ze\psi}{2kT}\right\}$$

where: (ze) is the charge on the ions of density n cm^{-3}
k is Boltzmanns constant, T the absolute temperature
D is the dielectric constant
c is the molar solution concentration

It is seen therefore that the charge distribution in the diffuse part of the double layer can be calculated. Translating the observations and theories of the early workers into the terms of the modern ideas of the double layer, it would seem that their experiments suggest that since the surface layer of charge was believed to be negative, then the diffuse layer would be positive. Lenard's estimate of about 10^{-6} cm for the depth of the negative layer was an overestimate since this layer would consist only of the oriented dipoles and the compact layer. This is believed to be a very tightly bound layer only about 10^{-7} cm thick. The diffuse layer would probably be about 10^{-5} cm thick for the solutions used by Lenard.

We see that the ideas of the early workers seem to agree quite well with modern ideas of the double layer. We shall now consider an experiment which gave a measure of the total potential difference at a water-air interface.

Chalmers and Pasquill (1937) were able to measure this total potential difference. Their measurements involved measuring a long chain of potentials including the required one. Using two different systems the potential was isolated. The water was found to be at a potential of -260 mv with respect to the air. This corresponds toabout 1 in 30 of the surface molecules being oriented with their positive ends inwards. Harper (loc.cit.) suggested from theoretical considerations that the potential should be +240 mv.

Although his derivation of the magnitude of the potential seems reasonable it is difficult to follow his derivation of the sign of this potential.

We can sum up the structure of the double layer for dilute aqueous solutions, as derived from experiments and from the simple theory in terms of three parts.

(i) The outer layer of dipoles in which 1 in 30 is oriented, giving a potential across the surface of 260 mv.

(ii) A tightly bound layer of negative charge extending a few molecular diameters below the surface.

(iii) A diffuse layer of positive charge extending about 10^{-4}cm below the surface for pure water. This layer becomes thinner as ions are introduced into the solution.

Having considered the structure of the double layer and shown how it agrees with the structure postulated by Lenard, we can now consider the results of later experiments in the light of this, and other, charging mechanisms.

1.4 Charge Separation Mechanisms

1.4.1 Separation of the double layer

Many experiments have been performed in which the charge separation produced when drops break up has been measured. Many of these have been explained in terms of the original ideas of Lenard. They consider that charge is separated either by the formation of drops from different parts of the double layer, or that during the break up shearing of the double layer parallel to the surface occurs, thus separating charge.

Frumkin and Obrutschewa (1931) atomised a large number of organic and inorganic liquids by allowing them to fall onto a platinum plate. The charge given to the air was measured. Most of the liquids used had already been studied by Frumkin (1924a, 1924b, 1925) who measured their relative surface potentials. The charge separation occuring when these liquids were splashed was plotted against the surface potential. It is seen from fig 1.3 that there is a very good correlation between the two. The correlation is even more striking when it is realised that owing to the wide range of viscosity and surface tension in the liquids used the mode of break up of the drops probably varied a great deal.

These results however are a strong indication that charge is separated in some way dependant on the double layer. It does not rule out the possibility however of there being other charging mechanisms.

The charge separation accompanying spraying has been studied in detail by Chapman (1937). This work was later (1938a,b,) extended to include bubbling as well as spraying. Chapman analysed the charge on the air, or rather, on the small ions introduced into the air by the atomisation. The mobilities of the ions were determined by passing the air between charged plated and measuring the current due to ion movement. Typical results are shown in fig 1.4.

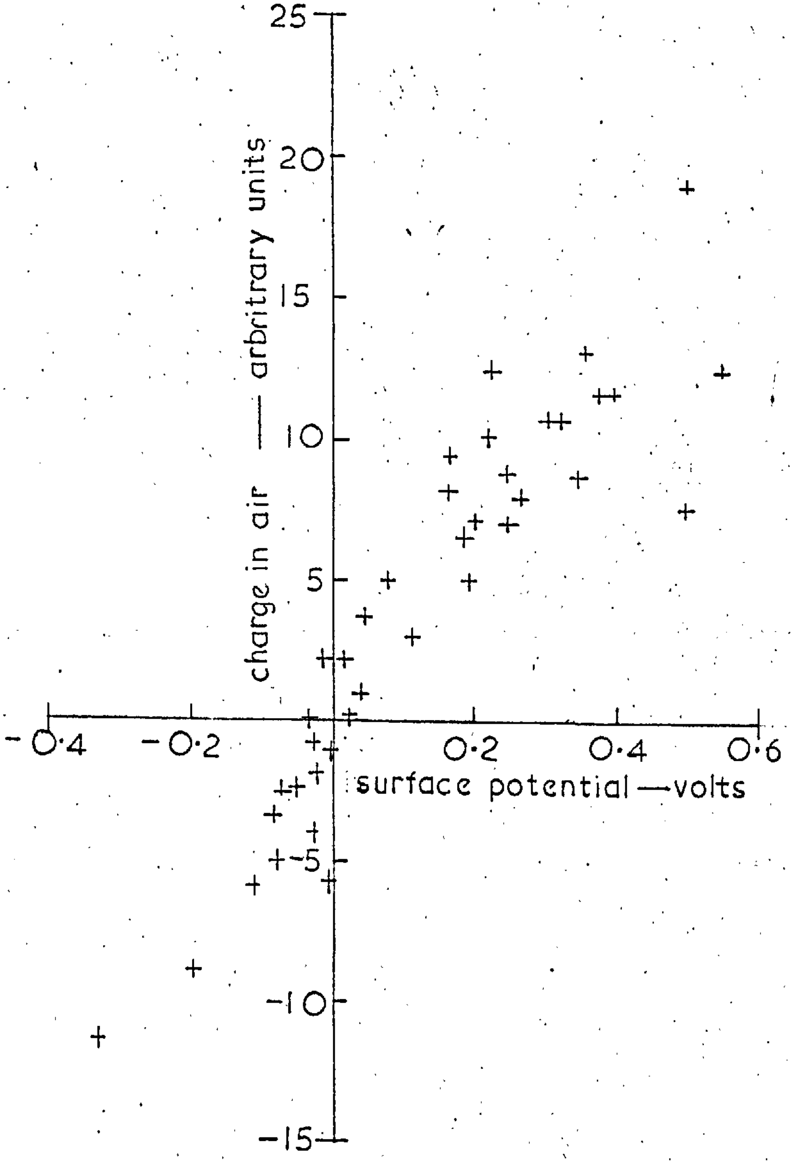


Fig 1·3 Charge separated by splashing many liquids
(Frumkin & Obrutschewa, 1931)

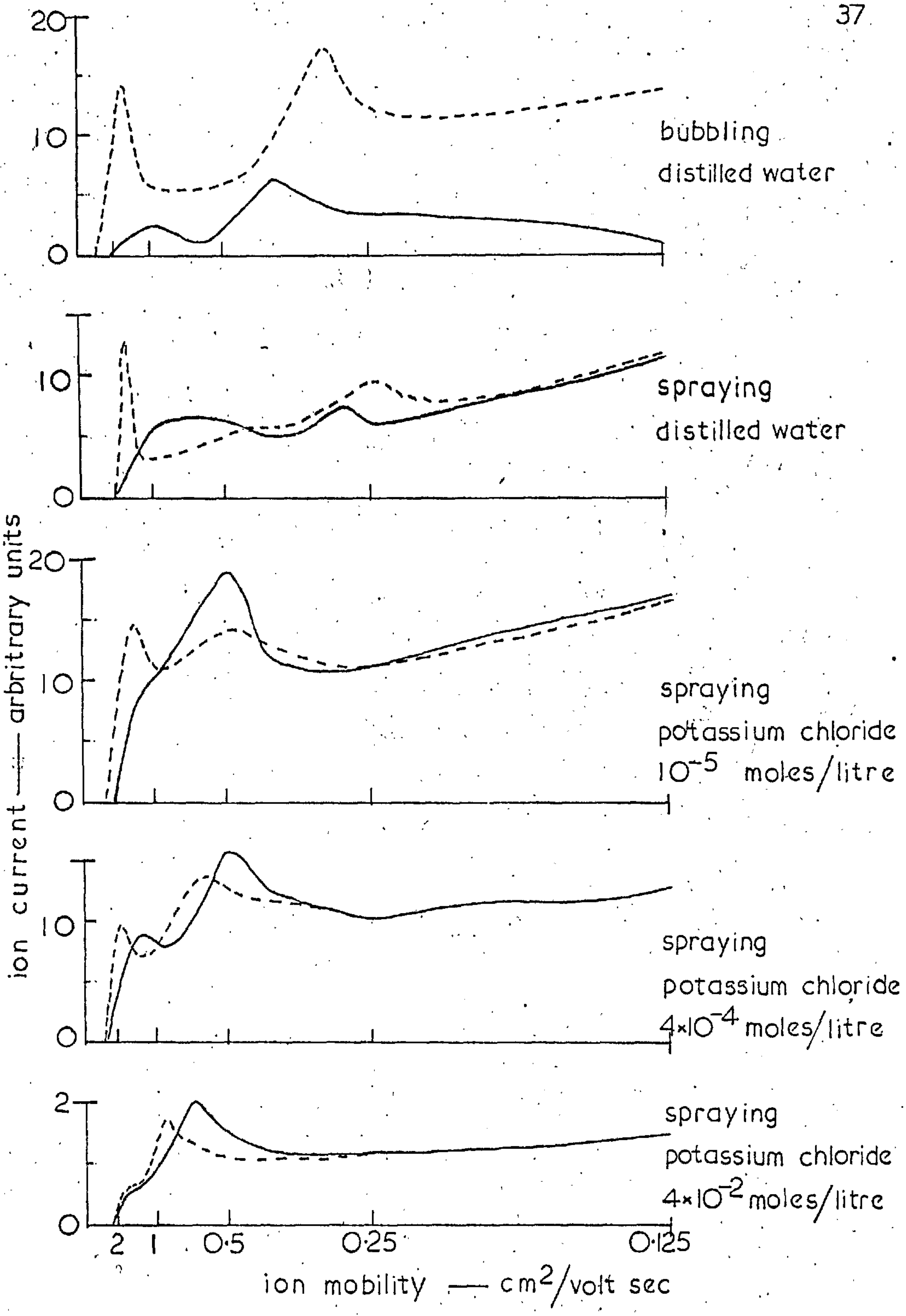


Fig 1·4 Mobility spectra of ions produced by bubbling and spraying (after Chapman)

—— positive ions ---- negative ions

It was found that the mobilities fell into distinct groups indicating that a series of different types of charged particles were produced. These were explained by considering that the ions were produced by the break up of thin liquid films. Johonnot (loc.cit.) had observed that as films thin they seem to do so in a series of steps of about 100 Å thick. Chapman suggests that the ions were produced from different parts of the film, each thickness zone producing a particular ion. The charging would then result from the fact that the thinnest parts of the film would not be thick enough to contain much of the diffuse layer and would therefore be negatively charged. Positive ions would come from the thicker parts of the layer into which the excess positive charge had been forced. Some of the charging was also though to be due to the incorporation of complex ions into the droplets which Bernal and Fowler (1933) believed were present in considerable numbers in water. Fig 1.5 shows the total charge separated in Chapman's experiments. It is seen that for most liquids the charge given to the air was negative, inaccordance with Lenard's observations.

The main disadvantage of Chapman's experiments was that only the charge on the ions in the air was measured. Banerji (1938) measured the charge in the air, on the bulk liquid, and on the large drops produced by atomisation. In his experiments aqueous solutions were broken up by

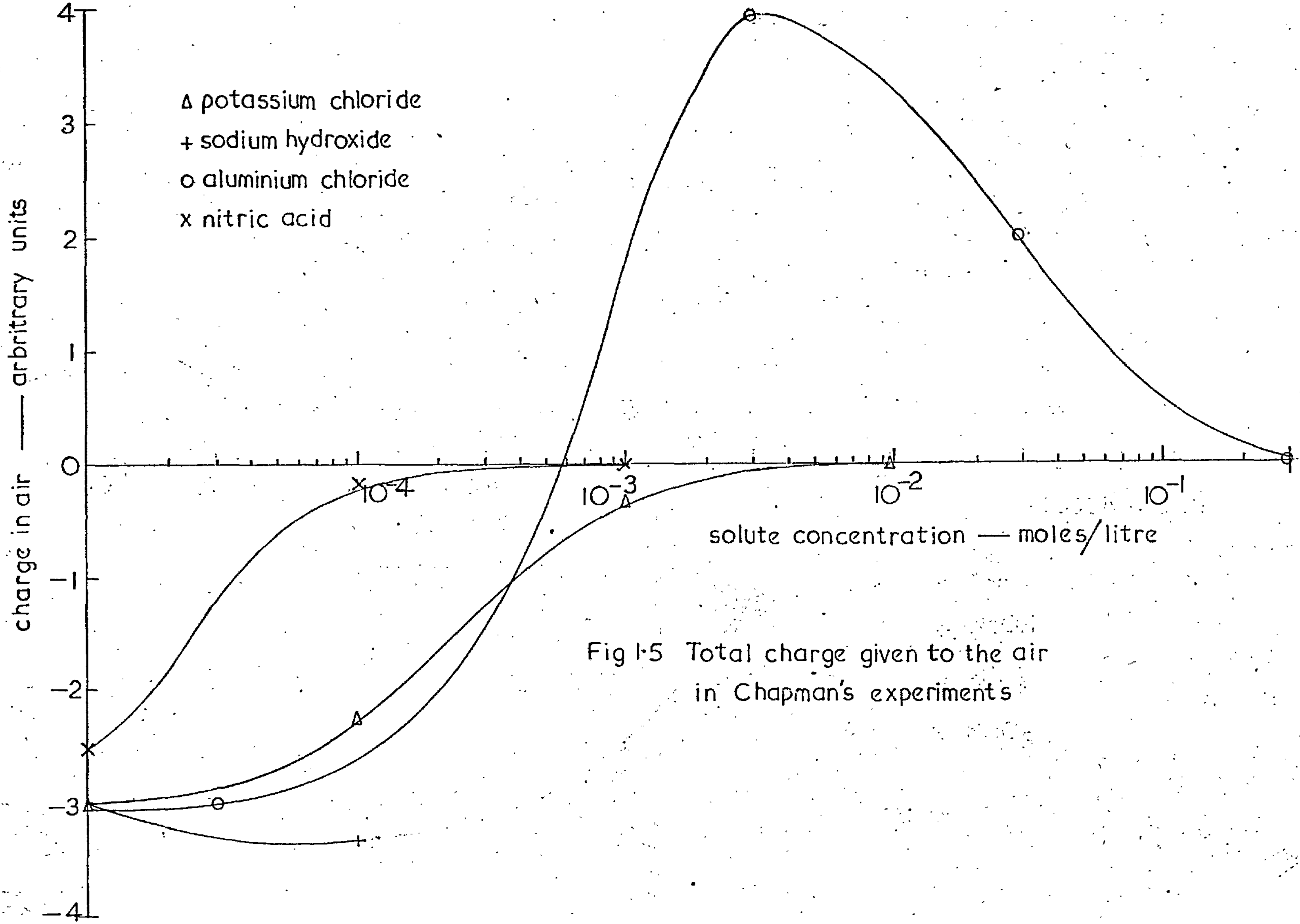


Fig 1·5 Total charge given to the air in Chapman's experiments spraying, splashing off a plate, and by allowing two jets of liquid to impact on each other and break up. The charge on the large drops was positive for distilled water but negative for sodium chloride solutions. The reversal occurred at 2.5 x 10^{-2}% sodium chloride for violent atomisation and at 5 x 10^{-5}% sodium chloride for the weaker impaction of the two jets.

Banerji also used some organic liquids. Amyl alcohol, acetone, methyl alcohol, and ethyl alcohol gave little or no charging to the large drops. The air however contained ions of both sign of charge but which had a total charge almost zero. Ether and turpentine, on the other hand, gave charges on the drops larger than those observed with distilled water. Banerji found that applying a charge to the liquid produced no other effect than the division of the extra charge between the drops. The additional charge did not affect the charge separation process.

The results of Banerji's experiments are difficult to interpret, especially the dependance of the reversal of charge in sodium chloride with the violence of the break up. The violence of the break up could alter the magnitude of the charge separated since it alters the geometry of the break up. It could hardly affect the polarity of the double layer however, and the disruption of this was believed to be the cause of the charge separation. The most plausible explanation is that the charging is the resultant of two or more distinct processes, which give opposite charging, and whose relative contribution is a function of the violence of the break up. The small charging with some organic liquids was most probably due to a different charging mechanism, statistical charging, which will be considered later in more detail.

1.4.2 Contact potential charging

We have considered charge separation to occur when the charged layer at the liquid-air interface is broken up. In many experiments there is however another interface, between the liquid and some metal surface, across which a potential difference exists. Some authors believe that the charging of drops can be explained simply by considering that they are charged by induction, at the moment of formation, in the fields of these, 'contact potentials'.

Gill and Alfrey (1952) atomised liquids in an air blast. The blast drove the fragments onto a target connected to an electrometer. The apparatus is shown in fig 1.6 together with graphs showing the variation of the charge with the pressure of the air blast. The graphs show the total charge separated for each drop broken up by the blast.

The charging was independant of the target used, if this was of metal. If the target was coated with wax however the charging was reversed and the target became negatively charged. The magnitude of the charge increased by a factor of 3 for a coating of sealing was, and 9 for paraffin

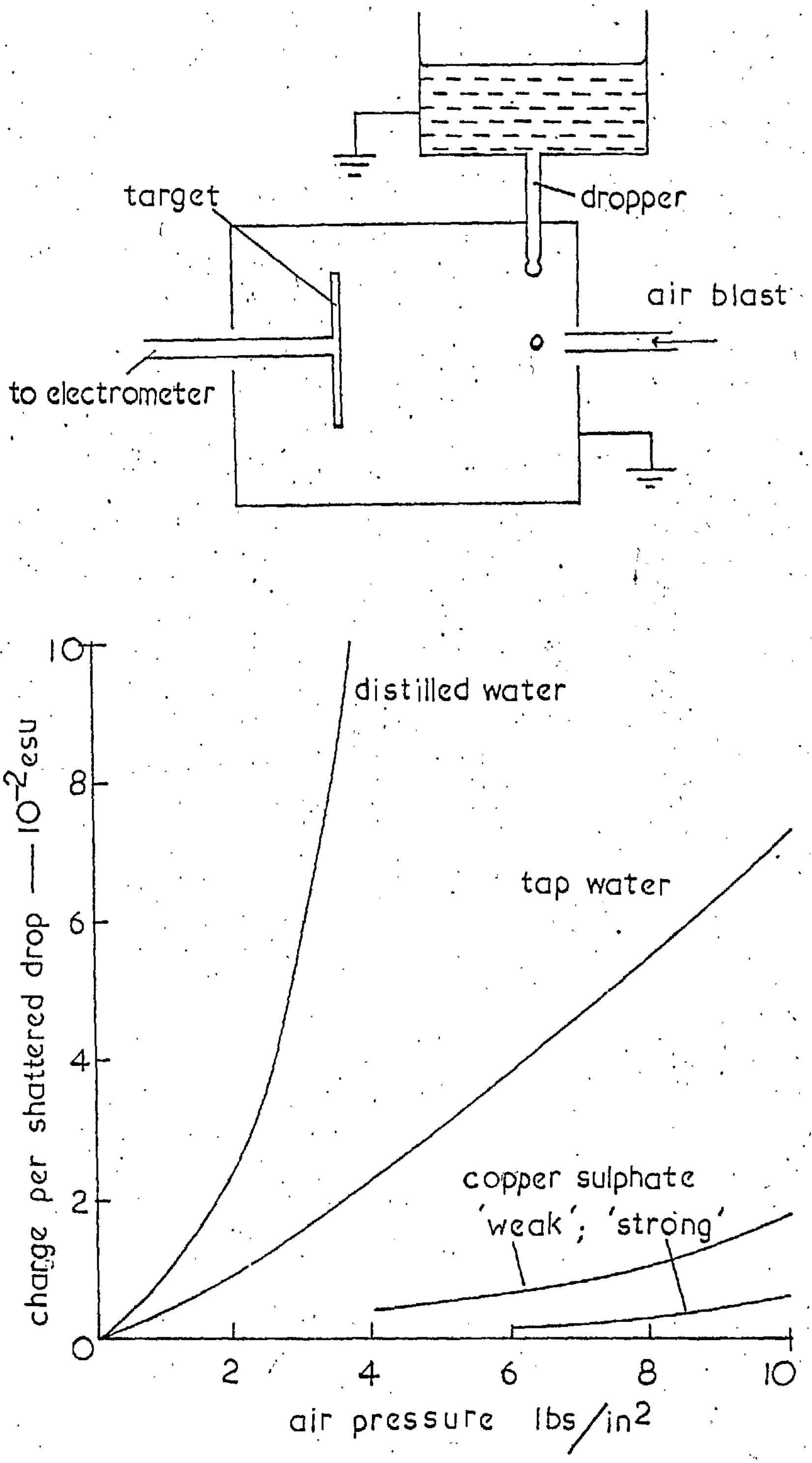


Fig 1·6 Apparatus and results of Gill & Alfrey (1952) wax. The authors suggested that the drops became charged in the field of the metal-liquid contact potential when they hit the target. When they splash they carry negative charge from the metal targets. Gill andAlfrey assumed that waxes have opposite contact potentials to metals. They accounted for the decrease in charging at high concentrations by saying that the increasing conductivity decreases the capacity of the liquid near the surface, the drop therefore carries away less charge for the same value of the contact potential. In reaching this conclusion Gill and Alfrey consider a previous experiment of theirs (1949) in which the charges on the fragments produced by breaking drops in an electric field were measured. The charging was proportional to the field except that the drops had zero charge for a field of a few tens of millivolts per centimeter. The drop charging obeyed the normal laws of induction, the residual charge being due to induction charging in the field of a contact potential of about 100 mv.

The conclusion reached by these authors can be criticised however. The behaviour of a drop splashing on metal and wax targets will be completely different. Also, although the experimental curves pass through the origin considerable charging can occur when dry air is forced past a target at speeds above 10 m/s (Drake, private communication). Gill and Alfrey used velocities in excess of this for almost all of their measurements so that some of the charging may have been due to this.

The most convincing evidence against contact potential charging is an old experiment by Bloch (1911). He measured the charges on droplets produced by bubbling. In a field free volume the bubbling produced drops with both signs of charge. If a field was applied, however, only one sign of charged drops was detected. Surely if applied fields could produce drops of one sign so would the field of the contact potential! The contact potential could only play a small part, if any, in the chargingin this particular situation.

1.4.3 Statistical Charging

We have considered that small charged droplets might be produced from charged parts of the double layer. Charged regions can also exist in liquids owing to random statistical variations of the ion concentrations in the liquid. Drops formed from a region in which there was a momentary excess of ions would be expected to be charged.

This statistical charging has been studied extensivly by Dodd (1953), the theory of the charging process being mainly due to Bateman (1911). Dodd sprayed non-conducting organic liquids in an ordinary glass spray. The droplets produced were allowed to fall between two vertical charged plates and the trajectories photographed using intermittant illumination. The velocity could then be measured from these photographs. Knowing this, and the field strength, the charge and the size of the drops could be calculated, assuming that the drops obeyed Stokes Law. The liquids used were di-n-butyl sebacate, specially purified dibutyl phthalate, oleic acid, distilled paraffin (mostly dodecane) and nitrobenzene. The droplets were of diameter between 1 and 50 microns.

The size range was divided into 11 intervals and it was found that in each range the numbers of positive and negative charged drops were equal and the net charge in each range was zero. The resultant charge distribution is described as symmetrical and net neutral. Gaussian curves were easily fitted to the results, fig 1.7. Using the theory of statistical charging, which predicts such a charge distribution, the mean numbers of ions in the liquids was calculated. This was about 2.3 x 10^{12} per cm^3. This is in reasonable agreement with the number expected in organic liquids of low dielectric constant.

Using the same statistics Dodd calculated the charging expected for various drop sizes in different solutions. The table (page 47) is taken from Loeb (1958).

It seems that considerable charging could result from producing large drops from highly conducting solutions. We have however neglected the large fields which would occur due to the charge density variations, during the formation of the drop. These fields will cause conduction in the liquids which will reduce the charge separated. The reduction will depend on the way in which the liquid breaks up but will be considerable in the highly conducting solutions. Nevertheless,

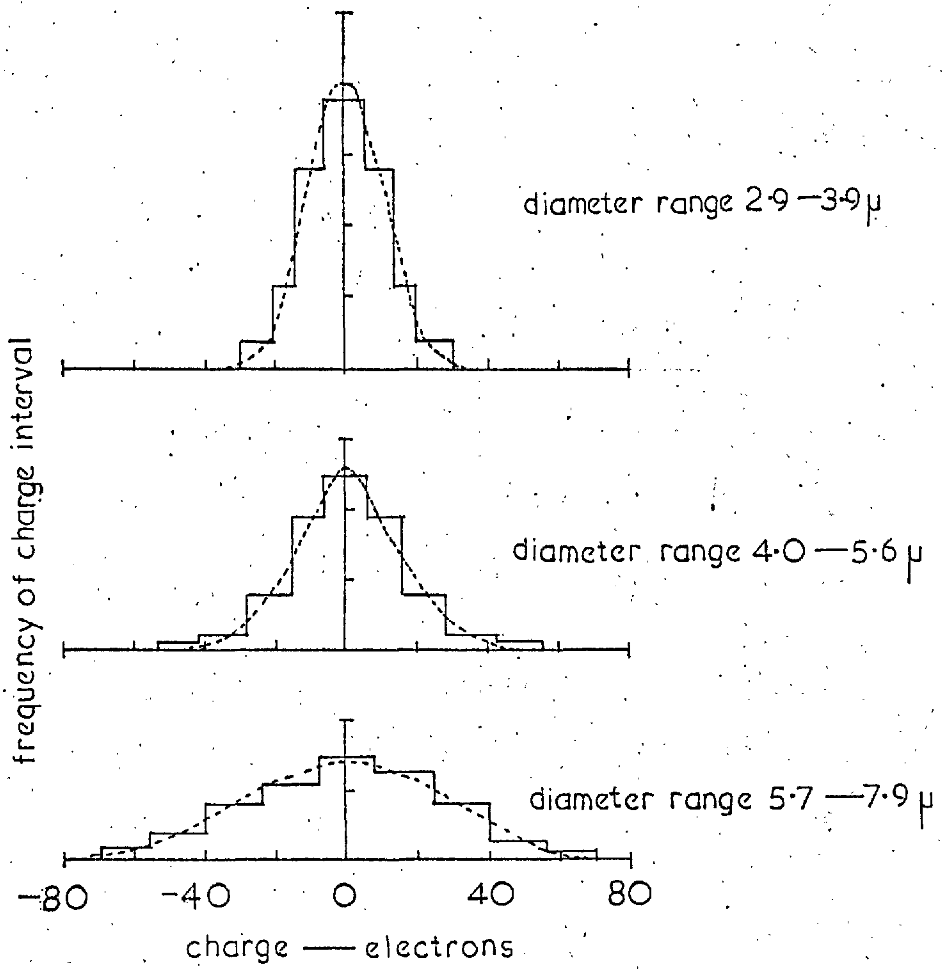


Fig 1·7 Charges on drops of di-n-butyl sebacate produced by spraying (Dodd, 1953)

molar concentration	ion pairs per unit volume	drop diameter microns	mean probable charge-electrons
1	$6.0\text{x}10^{20}$	1.0	$2.0\text{x}10^{4}$
1	$6.0\text{x}10^{20}$	0.1	$6.3\text{x}10^{2}$
10^{-2}	$6.0\text{x}10^{18}$	1.0	$2.0\text{x}10^{3}$
10^{-2}	$6.0\text{x}10^{18}$	0.1	63
10^{-4}	$6.0\text{x}10^{16}$	1.0	$2.0\text{x}10^{2}$
10^{-4}	$6.0\text{x}10^{16}$	0.1	6.3
$2.1\text{x}10^{-6}$ (a)	$1.3\text{x}10^{15}$	1.0	29
$2.1\text{x}10^{-6}$	$1.3\text{x}10^{15}$	0.1	$9.1\text{x}10^{-1}$
10^{-8} (b)	$6.0\text{x}10^{12}$	1.0	63
$2.5\text{x}10^{-10}$(c)	$1.5\text{x}10^{11}$	10.0	10

(a) High purity conductivity water

(b) Many organic liquids including di-n-butyl sebacate

(c) Ameroil

Table showing charges separated by the statistical mechanism

Dodds calculations show that considerable charging by the statistical process can occur in some liquids. This process will, of course, tend to mask anyother charging process.

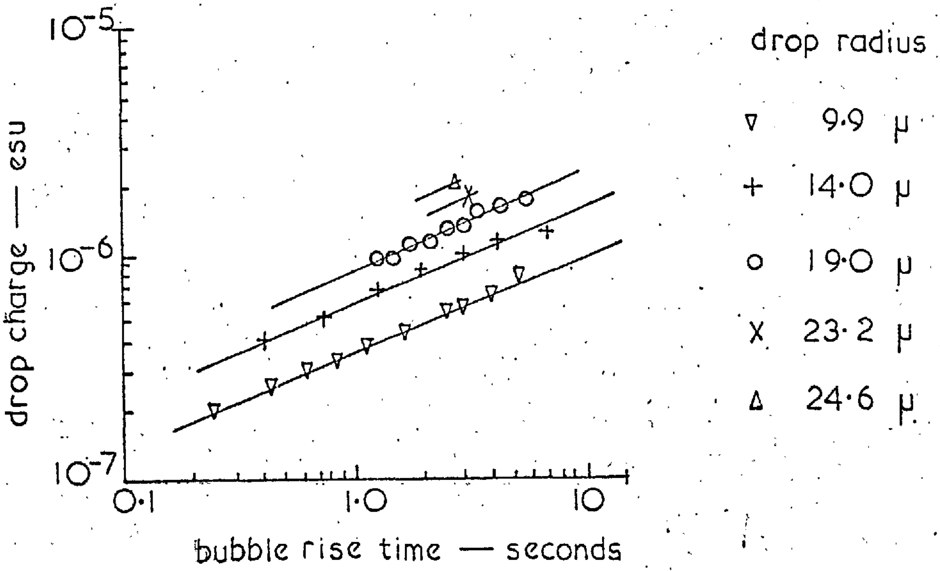
An experiment by Harper (1953), while not designed to investigate statistical charging shows results which would be expected from Dodds observations. He measured the charges produced by a bubbler. The liquids used were specially purified organic, non polar, liquids. As the purity was increased (i.e. as the number of ions was reduced) the charging decreased to zero. The conductivities quoted were of the order of $10^{-14}-10^{-13}$ohm^{-1}cm^{-1} which would correspond to ion concentrations of about 10^4ions/cm^3. This would produce negligible charging even for 10 micron drops.

1.4.4 Recent measurements and the charge separation mechanism

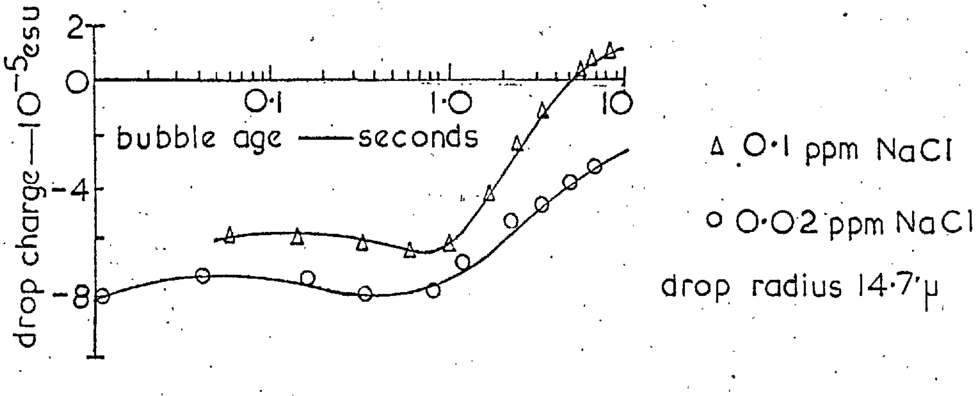
The observations of the authors mentioned above have all been the results of experiments in which violent, uncontrolled atomisation of liquids has occurred. It is necessary, in order to postulate the true nature of the charging mechanism, to consider the results of recent experiments in which the atomisation of the liquids has been closely controlled. These experiments have both concerned the electrification produced by single bursting bubbles. Blanchard (loc.cit.) was concerned with the charge separation at the surface of the sea, while Iribarne and Mason (1967) were concerned with the physics of the charging mechanism.

Blanchard used single bubbles in sodium chloride solutions to produce drops which passed into an electric field between charged plates. The motion of the charged drops was observed with a telescope, and the charge calculated from their deflection in the field. The charges on the drops formed from the breaking jet, for sea water, were of the order of $+10^{-6}$ esu per drop. The drops from the bursting film had charges small compared with this, being less than 3×10^{-8} esu. Blanchard also noticed a variation of the charge with the time taken for the bubble to rise through the liquid. A few experiments were made using lower salt concentrations in order to try to find the charging mechanism. Some of Blanchard's results are shown in fig 1.8. He found that the charges for solutions of 10^{-1} or 2×10^{-2} ppm of sodium chloride were about 100 times greater than those for solutions of 1 or 5 ppm. The variation of charge with bubble age, in the more concentrated solutions was, however, similar to that in the dilute solutions.

Blanchard suggested that the charge separation occured during the time of formation of the jet. He considered that the flow of liquid down the cavity sides and into the jet caused the diffuse part of the double layer to be carried up into the jet, giving it, and the drops, the observed positive charge. He used the observations of Worthington and Cole (1900) who had traced the flow near the cavity produced by dropping a solid object into a liquid, with small bubbles. A diagram taken from one of their photographs is shown in



Charge on jet drop using sea water



Charge separation with dilute solutions

Fig 1·8 Charge on drops produced by a bursting bubble
(Blanchard, 1963)

fig 1.9. It seems that the liquid near the surface does in fact drain down the cavity sides. Blanchard suggested that the flow of the water layers was resisted by the drag of the air, so that only the inner layers were taken into the jet. This charging mechanism is illustrated in fig 1.10. The theory cannot explain the negative charging of the drops at low concentration or the variation of charge with bubble age. It also seems improbable that the drag of the air would be sufficient to cause shearing in the surface layers of the liquid.

Iribarne and Mason used ion exchange resins to produce water of high purity, in fact the conductivity was close to the intrinsic conductivity of water. Pure water and dilute aqueous solutions were used in a bubbling experiment. A range of different solutions and bubble sizes were used and extreme care was taken to prevent the contamination of the surface by impurities. The charge on the debris was measured by sucking it into a copper filter connected to an electrometer. Some results for the bursting of nitrogen bubbles in sodium chloride solution are shown in fig 1.11. This shows the total charge on the debris, but it was thought from Blanchards observations that most of the charge was on the jet drops.

Iribarne and Mason suggest that there are two distinct charging mechanisms. These are the skimming off of the surface layers of liquid during the formation of the jet,

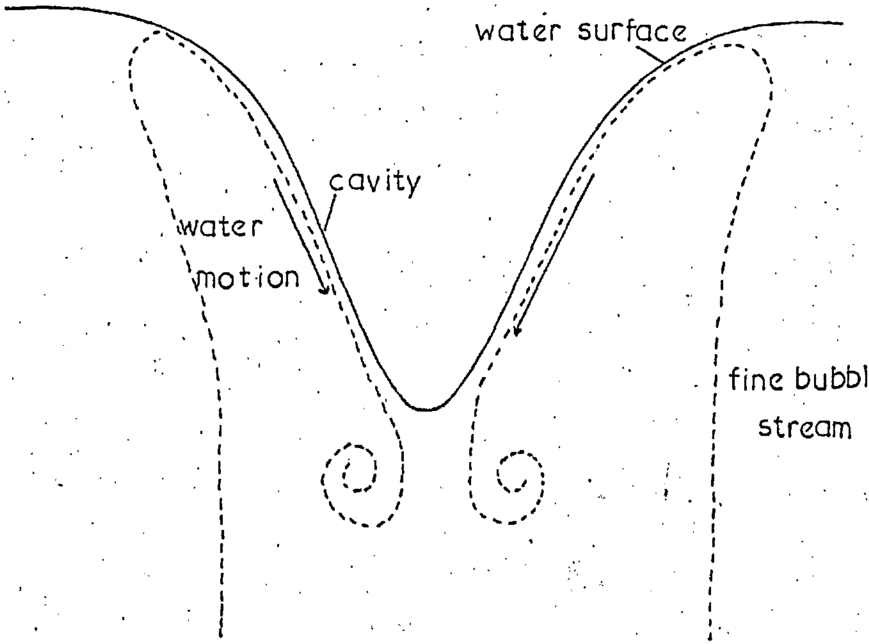


Fig 1·9 Water flow near surface cavity traced with fine bubbles (Worthington & Cole, 1900)

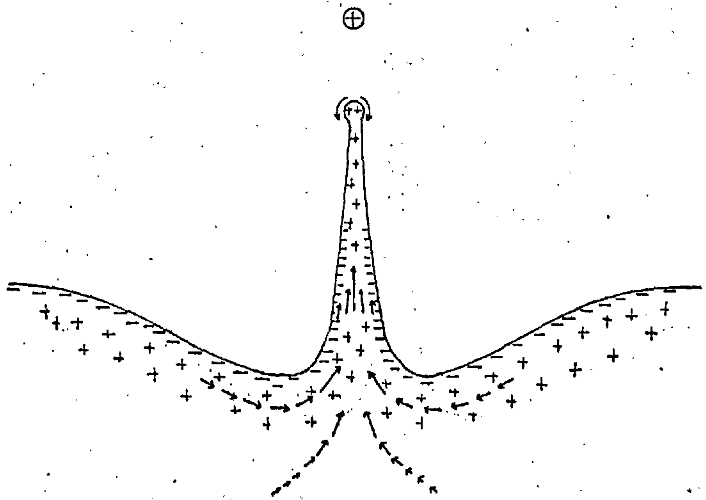


Fig 1·10 Charge separation mechanism proposed by Blanchard

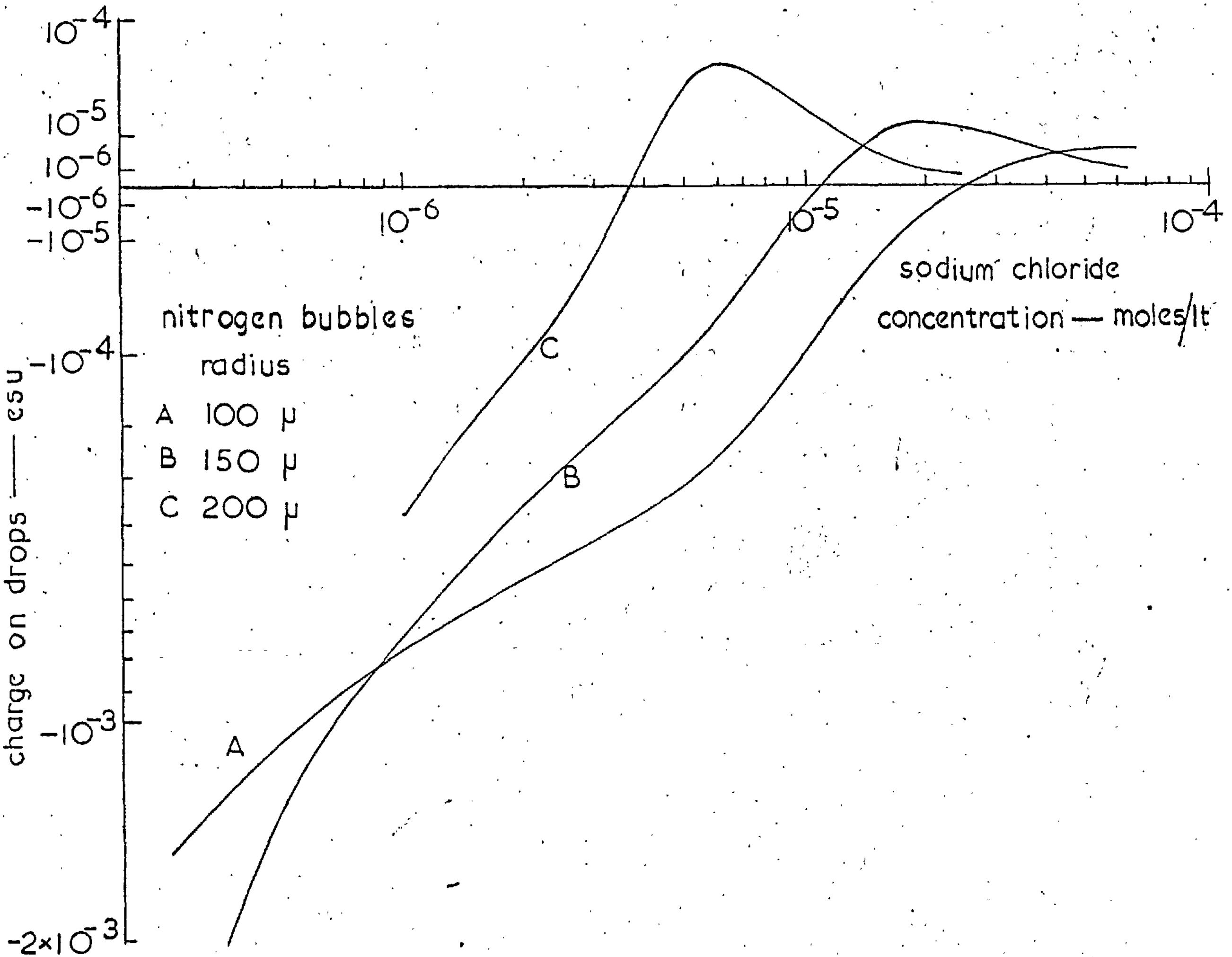


Fig 1·11 Charge on drops produced by a nitrogen bubble bursting in sodium chloride solution (Iribarne & Mason, 1967) and the squeezing of the bulk liquid through the neck as the jet breaks. The former would give a negative drop charge and the latter a positive charge. The processes are shown in fig 1.12. Calculations showed that the former process would be dominant at low solute concentrations while the squeezing of the neck would give a higher charge separation at high concentrations. The calculations show that the results can be explained using this theory.

1.4.5 Summary of the charging mechanisms

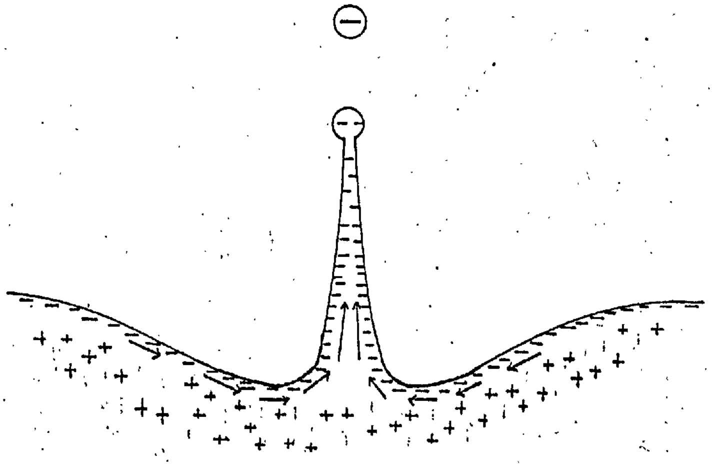
We have seen that there are three possible charging mechanisms which can separate charge when liquids are broken up. These are:

(i) Partial or complete separation of the components of the double layer.

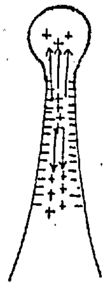
(ii) Contact potential charging.

(iii) Statistical charging.

Statistical charging, while being important in the case of organic liquids of high purity, will not separate much charge with aqueous solutions and will not concern us in this thesis. The formation of small charged drops from parts of the double layer is quite well documented and the charges seem to be in agreement with those expected. These charged drops are however very small, of radius comparable with the thickness of the double layer. The formation of larger charged drops of aqueous solutions can only be due to either contact potential charging, or to a shearing of the double



Charging during jet formation



Charging during jet break-up

Fig 1·12 Charging mechanisms proposed by Iribarne & Mason layer during the formation of the drops. Calculations show that this latter process could occur as the charging mechanism for the drops produced from the jet of a bursting bubble.

1.5 Conclusions

This chapter has shown that although some parts of the charging mechanism are understood there are still some unknown factors. The only experiments which have considered the sh shearing of the double layer have been those using bursting bubbles. The bursting of a bubble is however a very complicated process which is difficult to analyse. It is desirable therefore, in order to study the electrification accompanying a breaking jet to measure the charge separation occuring when a single jet breaks up without any possible influences of a bubble. The study of a single jet is essential if the charging due to shearing of the double layer is to estimated quantitativly, as it is only in this case that the geometrical factors can be estimated.

This thesis is an attempt to study the charge separation in a breaking jet of liquid. It will be shown that this is consistant with the ideas of shearing the double layer. An outline of the thesis is given below and shows how the various experiments and theories have been linked to present a picture of the breaking jet.

After a chapter on the purification of the solutions used in the experiments follows a chapter on the electrification produced by partial coalescence of a drop with a liquid surface. This produces a situation very similar to that when a bubble bursts but without any influence from the bubble.. Chapters follow investigating the charging produced when a jet is pulled out from a plane liquid surface, and on the charging when an isolated jet breaks up. In each of these chapters the sign of the charging process is shown to be consistant with the ideas of the shearing of the double layer. Chapter 6 is perhaps slightly different in that it shows how charging can occur in some situations by virtue of the contact potential mechanism. It shows also how these effects can be reduced and suggests the situations where this effect is likely to be troublesome. The masking effects of this charging process are very well demonstrated! Chapter 7 is a theoretical chapter discussing the shearing process and the double layer, and calculating the charges which can be separated.

The results of all the experiments are considered together in the final chapter and it is shown that, not only are they consistent, but that they agree with the calculated charges for this separation mechanism.

The thesis shows that the charging mechanism is linked very closely to the way in which jets break up and that the complicated processes which occur in many types of atomisation can only be estimated by considering the break up to occur by the break up of jets of liquid.

CHAPTER TWO

Water Purification

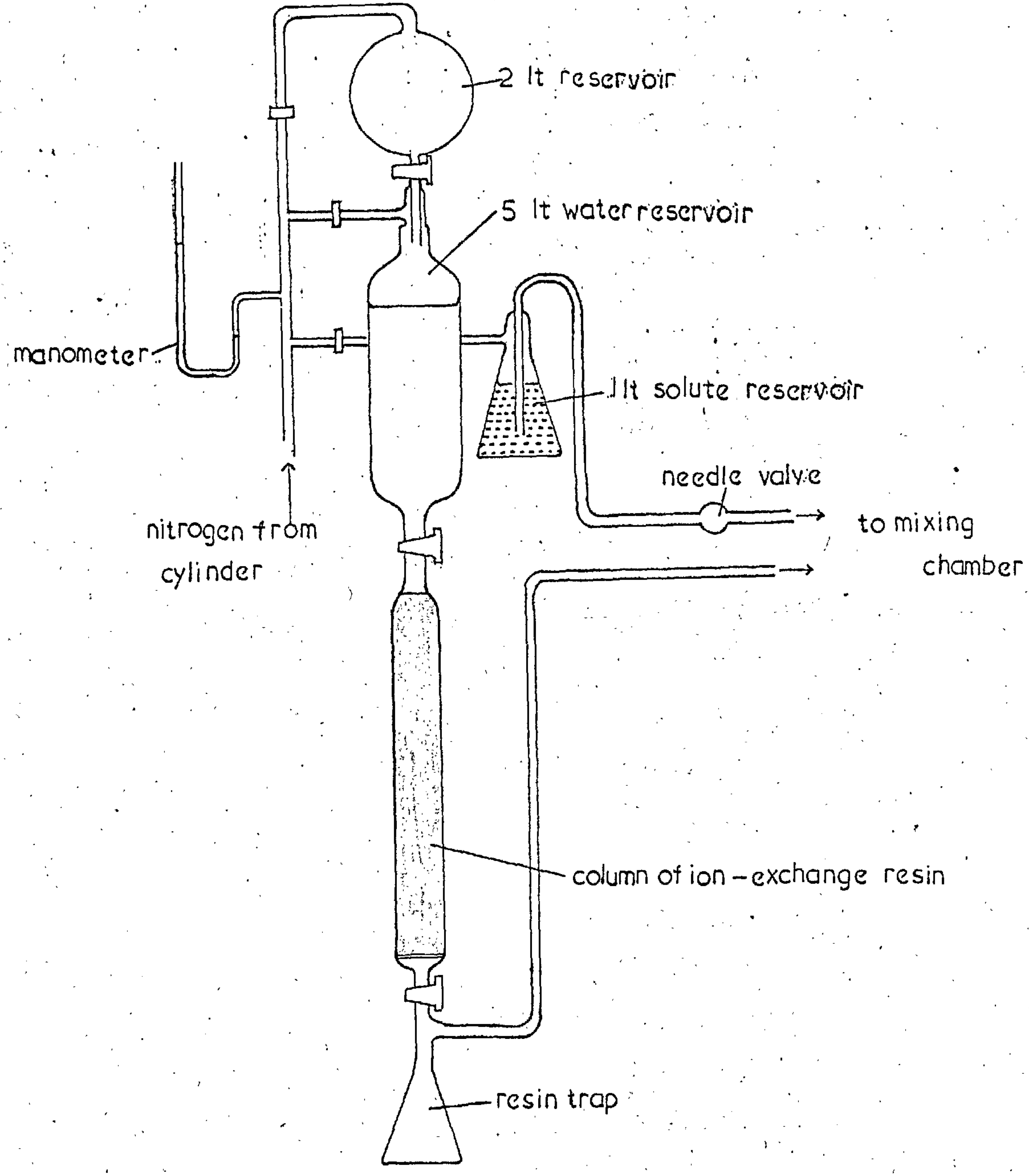
2.1 Introduction

Many of the experiments quoted in the previous chapter have shown that the charging of drops, particularly those of aqueous solutions, are very dependent on the concentration of solute. Iribarne and Mason have shown that the charges on drops produced by bursting bubbles decreased by two orders of magnitude as the concentration of sodium chloride was increased from 10^{-7}molar to 10^{-4}molar. Banerji and Thomson found that although there was not such a wide spread in the magnitude of the charge separated, small concentrations of some solutes were sufficient to reverse the sign of the charging. It was decided therefore that for all the work described in this thesis the utmost care would be taken when using aqueous solutions to prevent contamination by unknown impurities, and to measure accurately the concentrations of known solutes.

2.2 The water purification apparatus

It was decided that the best method of producing solutions of pure chemicals was to start with very pure water and to add a concentrated solution of the solute to this, in variable amounts. A diagram of the apparatus used is shown in fig 2.1.

A mixed bed ion-exchange resin was used to remove ionic



Fig·2·1. Diagram of the water purification apparatus impurities from the water. This was of a type suitable for the production of high purity water. The resin was packed in a glass column shown in the diagram. The apparatus was made of standard glassware using conical ground glass joints and individually ground, greaseless, glass taps. The conical flask at the base of the column was to catch any small pieces of resin which passed through the sintered glass filter on which the resin was supported.

Before the apparatus was assembled, all the glass was thoroughly cleaned. Hot soapy water was used first and, after rinsing, the apparatus was allowed to stand in cold chromic acid for 24 hours. This oxydised and removed any organic films which may have been present on the glass. From this point the apparatus was always handled by parts which would not come into contact with water when the column was in use. Traces of chromic acid were removed by a thorough rinsing in fresh distilled water after which the column was assembled and packed with resin. The apparatus was kept full of water to prevent possible contamination of the glass by dirty air entering the reservoirs.

The concentrated solute solutions were to be kept in a conical flask clamped to the column stand. This was arranged so that the bottom of the flask was level with the reservoir so that the mean liquid levels were at about the same height. The outlet at the base of the ion-exchange column was connected to a small mixing chamber with glass tubing. The solute supply was also connected to the chamber, through a small stainless steel needle valve. All the connections between glass tubes were made with polythene tubing which had been soaked in water for a while to remove any traces of plasticiser. The polythene tubing and the needle valve were also steamed before being used. The glass tubing was cleaned in a similar manner to that used for the ion-exchange column.

The mixing chamber is not shown in the diagram since it varied between different experiments, but it consisted basically of a small chamber where the pure water and the solute could mix. This was connected to a small conductivity cell so that the solute concentration could be continuously measured. The cell was calibrated using standard solutions before it was incorporated in the apparatus. In order to obtain a sufficient liquid flow rate through the apparatus, it was necessary to pressurise the reservoirs. This was done by using a cylinder of compressed nitrogen, the connections being as shown in the diagram. The use of the two reservoirs made it possible to fill the column while maintaining a high pressure to force the liquid through the resin. The water was introduced into the upper reservoir by removing the adaptor connecting it to the gas supply.

The column was filled with specially purified water. This had been distilled in a conventional laboratory still and then further purified with an 'Elgastat' ion-exchange column.

The solute reservoir was usually filled with about 10^{-2} molar solutions of the required solutes. These were made up in an environment free from carbon dioxide using 'Analar' grade reagents dissolved in the high purity water from the 'Elgastat' column.

2.3. The purity of the solutions

The solutions from the column could possibly contain three types of impurity in addition to that deliberately introduced. These are ionic impurities, surface active impurities, and non-ionic impurities. The first of these could easily be detected using the conductivity measurements.

The column was normally set up to give a flow rate of several cm^3/min. When the solute supply was shut off the conductivity of the water could be reduced to 4.5×10^{-8} ohm^{-1} cm^{-1}. This would correspond to an impurity concentration, assuming it to be carbon dioxide, of less that 5×10^{-8} molar, the conductivity of pure water being takenas about 4×10^{-8} $ohm^{-1} cm^{-1}$ at the temperatures normally encountered in the laboratory. These low conductivities could only be achieved after a long period of continuous running of the apparatus, the purest water easily obtainable having a conductivity of about 6×10^{-8} $ohm^{-1} cm^{-1}$. After the column had been turned off for a short while the conductivity of the water immediatly after the apparatus had been turned on again was observed to have risen to about $5 \times 10^{-7} ohm^{-1} cm^{-1}$. This was probably due to the solution of impurities from the glass tubing and could be reduced by flushing through the apparatus for a few minutes.

The manufacturers of the ion-exchange resin did not guarantee that water from such a column would be free of pyrogens from the resin. It was thought that these might be present in sufficient quantities to affect the surface properties of the water even though they would not affect the conductivity. Surface active contaminants can easily be detected by the fact that if a liquid containing them is shaken, then persistant frothing to the surface is observed. This is a result of the stabilisation of the thin bubble caps as mentioned in the previous chapter. This test was therefore used on the water from the column. No frothing was observed with water taken from the column after it had been run for some time showing that no surface active contaminants were present. Samples taken soon after the column had been turned on however did exhibit frothing when shaken. This was probably due to the absortion of impurities from the polythene connecting tubing. The column was always flushed through before use for about 15 minutes after the water had reached a minimum conductivity in order to remove any pockets of contaminated water.

These tests did not detect the presence of any non-ionic, non surface active impurities. It was thought that many of these would have been removed during the distillation although the passage through the resin may have introduced some more.

These impurities would not affect the electrical properties of the water unless they were sufficiently concentrated to distort the surface structure of the water, that is in concentrations of about 10^{-2} normal. It is difficult to suggest any mechanism by which such absorbtion could have occurred. No tests were made for non ionic impurities but it was thought that their effect, if present, would be negligible.

2.4 The concentration of solutes

Using the needle valve and the flow rate of several cm^3/min it was possible to control the conductivity of the solution leaving the mixing chamber quite well. Lower flow rates however resulted in very erratic variations in the conductivity. When the conductivity had been increased by the addition of a solute it took some while to decrease it again by flushing the mixingchamber with pure water. For this reason all experiments at varying concentrations were made with the concentration increasing. This gave a much more reliable measurement of the concentration, and more reproducible results, especially at low concentrations.

The conductivities were measured using a conductivity bridge. During the course of the work two bridges were used, one working at about 1000 c/s using an oscilloscope as a detector and the other working at 50 c/s with a 'magic eye' detector. Both of these were capable of measuring the conductivities to within about 5%, errors arising in finding the balance point and in the calibration of the conductivity cell. The concentration of the solutes were calculated from the conductivities using data extracted from the International Critical Tables. The conductivities were calculated at low concentrations assuming that the water contributed the intrinsic conductivity due to the OH^- and H^+ ions.

Using this method the concentration of various ionic solutes could be controlled and measured between less than 10^{-7}molar and 10^{-3} molar. The method prevented the absorbtion of carbon dioxide which might have occurred had various solutions been made up and then stored. The stock solutions used would be considerably diluted so that if these absorbed some carbon dioxide this would also have been diluted. The solutions were not kept however for more than a few days in order to prevent contamination by the glass.

The apparatus proved a highly successful method of producing high purity solutions which enabled the variations of the charge separated in various processes to be accuratly related to the concentration of the solution used.

CHAPTER THREE

Charging associated with the partial coalescence of drops with a plane liquid surface

3.1 Introduction

Iribarne and Mason (loc.cit.) measured the charges carried by drops ejected from nitrogen bubbles bursting at the surface of water and aqueous solutions, for various concentrations of the solutions and several bubble radii. Drops ejected from pure water and solutions of concentration less than about 10^{-4} molar carried a negative charge, the magnitude of which decreased as the solution concentration was increased, becoming vanishingly small at concentrations of about 10^{-4} molar. For more concentrated solutions the drops carried a small positive charge. Several of the results were shown in fig. 1.11.

The negative charging was explained by a thin film of water rising from the surface of the bubble cavity to form a jet, which broke up to form the drops, the charge resulting from the rupture of the electrical double layer at the surface of the cavity. The depth of the double layer decreases at higher concentrations so that this would account for a reduction of the charge. The positive charging of the drops at higher concentrations was believed to be due to separation of charge as the jet was broken into drops, the water containing an excess of positive ions being forced into the swelling regions of the jet which formed the drops.

Several observers have noted that a single jet can be produced by the splashing of a drop onto the surface of a deep liquid. Day obtained photographs of the formation of a jet using millimetre sized drops. Jayaratre and Mason (1964) made a detailed study of the oblique impact of small water drops (100μ - 200μ radius) on a water surface. They noticed that for some impact angles and velocities bouncing occurred with no contact between the drop and the surface, but with higher velocities, or more normal incidence, the drops coalesced. Between these two regimes there was a region of partial coalescence in which a secondary drop, smaller than the impacting drop, was ejected from the surface. These secondary drops were formed by the rupture of a jet of liquid extending from the surface. If the impacting drops formed a stream, each moving in an identical manner, the secondary drops also formed a stream, showing the regularity with which the jet broke into drops.

Partial coalescence forms a very reproducible method of producing a small rising jet from a plane surface and for this reason it was decided to use partial coalescence to study the electrification associated with a breaking water jet. A series of photographs of partial coalescence taken during these experiments is shown in fig 3.1. The incident drops were observed to have constant spacing on the photographs so that their velocity was constant. It was possible to calculate the times between succesive photographs by

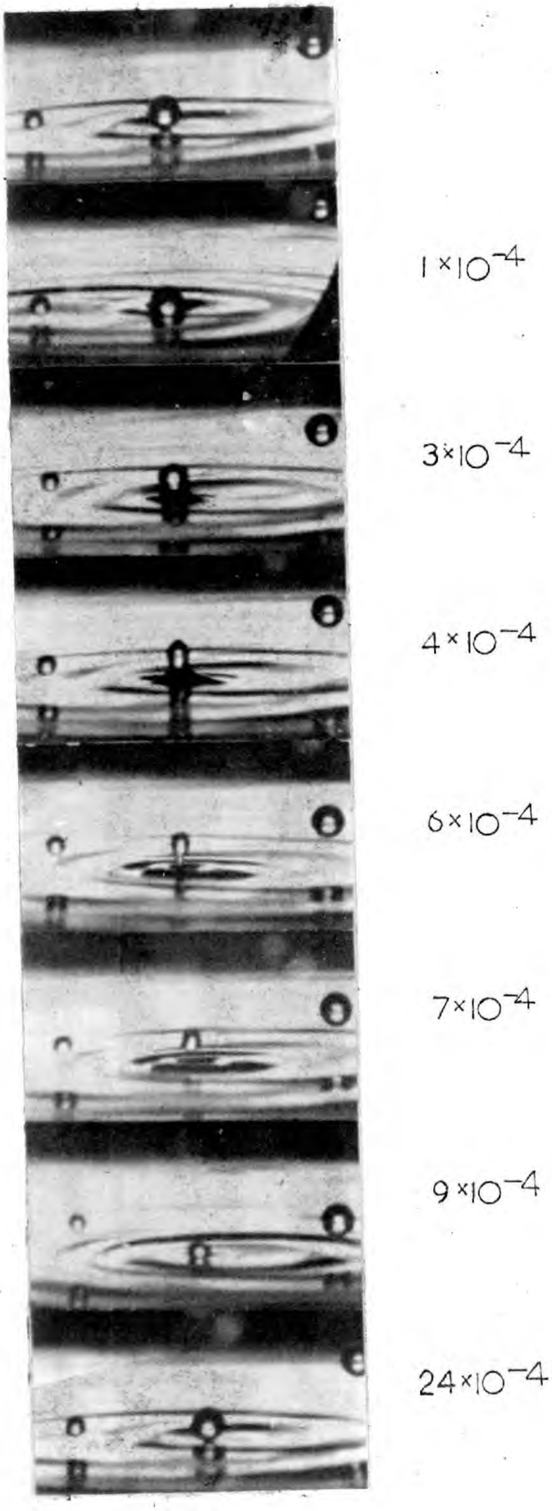


Fig 3·1 Drop formation by partial coalescence

(showing times in seconds after first photograph)

1mm

measuring the distance moved by one drop from some fixed reference point not shown in fig 3.1.

3.2 Design of the apparatus

It was necessary to design the apparatus so that it was suitable for use with very pure water and solutions of varying concentration. Although the method was similar to that described by Jayaratre and Mason, the vibrating needle atomiser, (Mason, Jayaratre, and Woods, 1963) used to produce the impacting drops was considerably modified.

The modified apparatus is shown in fig 3.2 The machined perspex block forming the mixing chamber and conductivity cell was fitted with stainless steel electrodes, and the hypodermic needles (1½", 30 swg) were forced through a polythene plug at the lower end after the brass fitting had been removed. Liquid inlets and an overflow were fitted as shown in the diagram. The resonant length of the needle could be altered by sliding the apparatus vertically, locking it to a stand clamped to the headphone which drove the needle. The locking screw also provided an electrical connection to the needle which was otherwise insulated by the perspex stand and a perspex insert in the driving spigot. The parts of the apparatus which would come into contact with the water were cleaned by steaming, followed by a prolonged soaking in pure water, before assembly.

The headphone assembly was mounted on an adjustable stand in a foil lined perspex box as shown in fig 3.3.

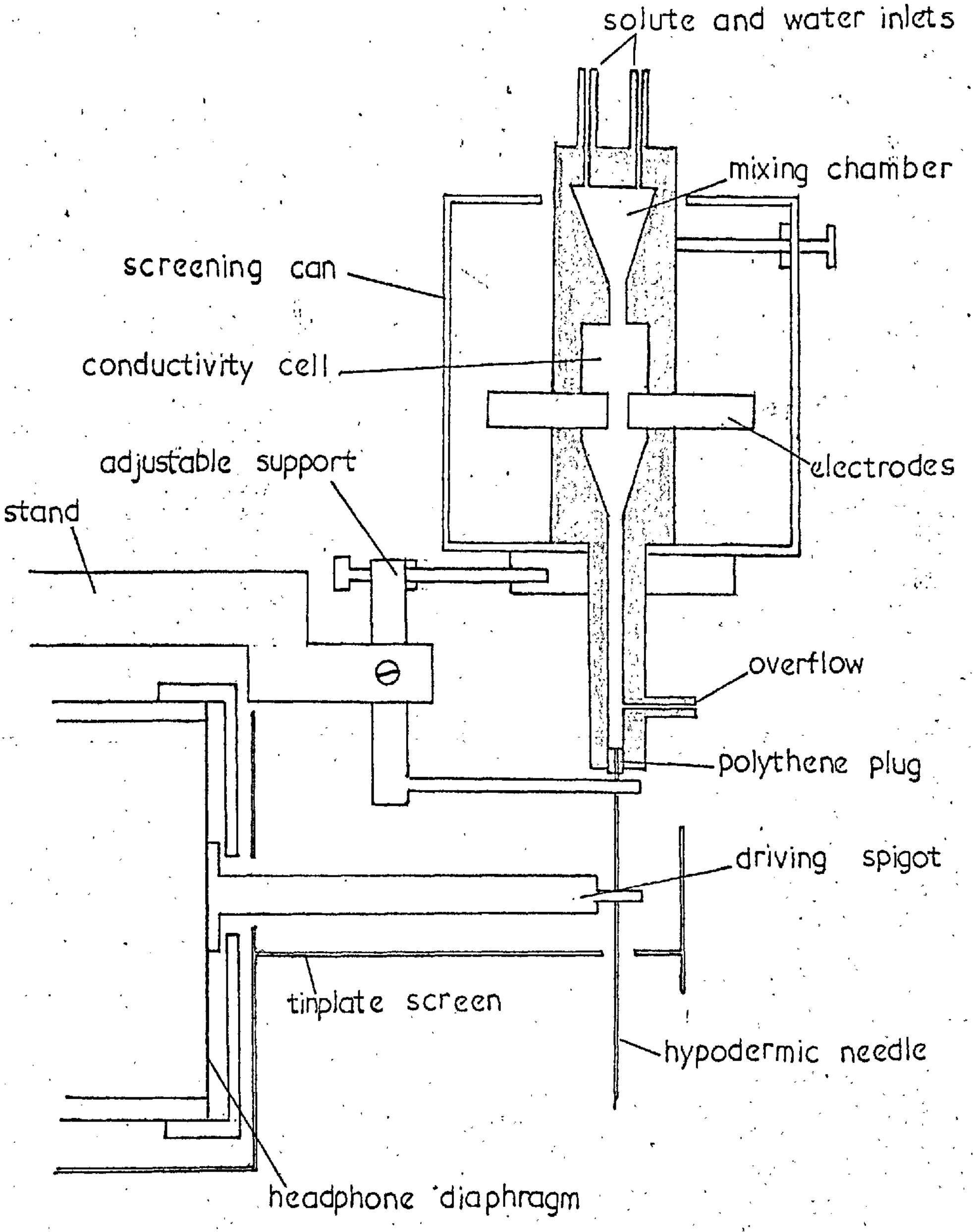


Fig. 3·2 Diagram of the modified vibrating needle apparatus. (about full size)

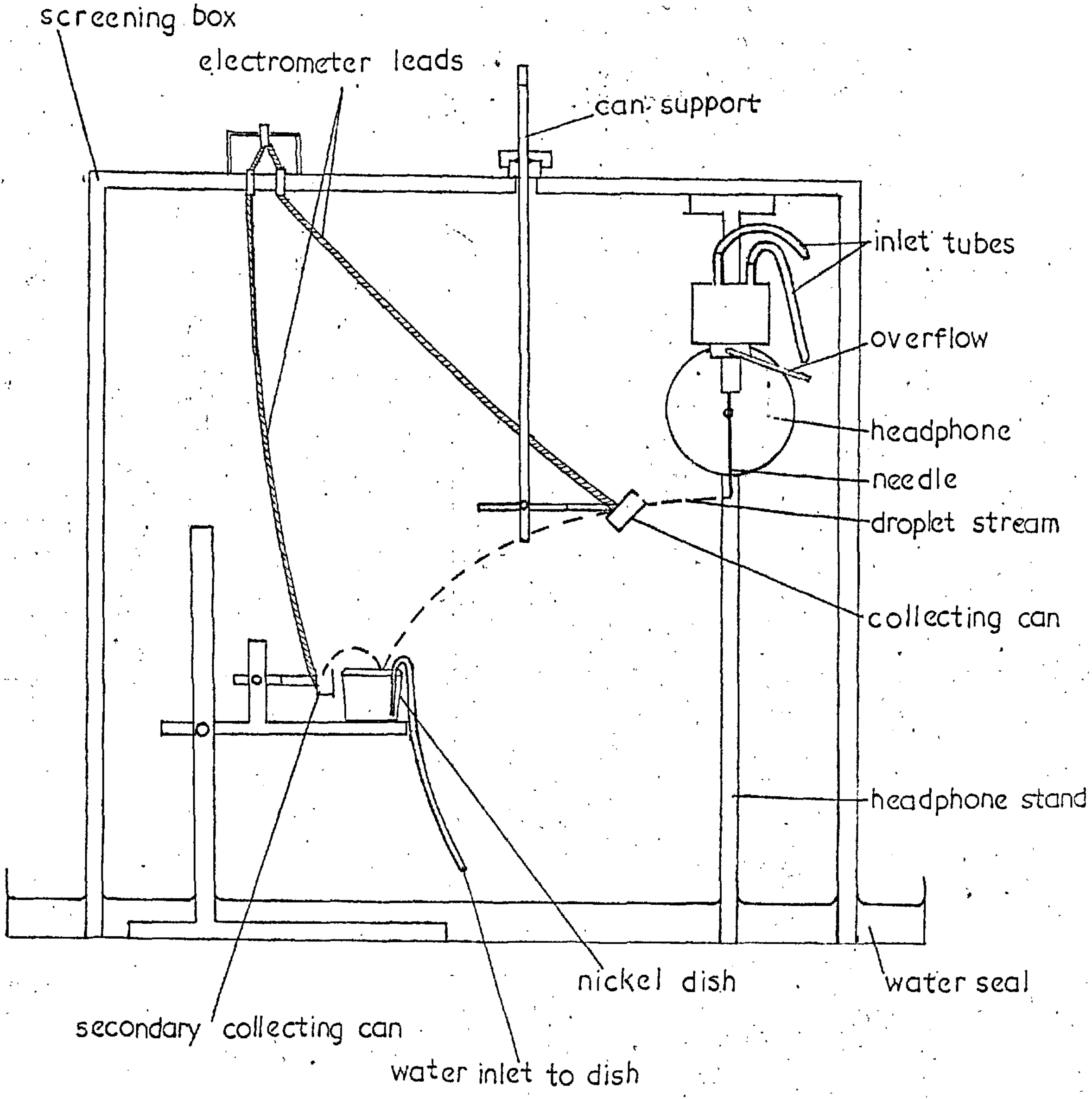


Fig 3·3 Apparatus to measure the charge separation associated with partial coalescence (about 1/3 size)

(tinplate screen and electrical connections not shown)

Specially cleaned glass and polythene tubing was used to supply the liquids and screened cable for all the electrical connections. The conductivity of the liquid entering the needle was measured with a conductivity bridge, the screening around the cell preventing pick up which otherwise reduced the sensitivity of the instrument. The needle was connected to a resistance network which could raise the potential to between ± 9 volts with an accuracy of ± 10 mv. The liquid overflow was connected to a needle valve to adjust the flow and the outlet could be run to waste or connected to the liquid supply to the surface.

The liquid which was to form the surface was contained in an earthed nickel crucible on an adjustable stand. The liquid was supplied to the bottom of the reservoir, the overflow cleaning the surface.

An insulated collecting can, connected to an electrometer was mounted from the roof of the box so that it could be moved from outside to catch the drops as they left the tip of the needle. A similar can caught the secondary drops as they dropped over the edge of the reservoir.

3.3 Adjustment of the apparatus and preliminary experiments

3.3.1 The purity of the water.

It has been noted by Jayaratre and Mason that it is difficult to obtain partial coalescence unless the incident drop radius is between about 140μ and 200μ, which limits the flow rate through the needle. The flow rate through the needle was very slow and it was thought that this might have resulted in the absorbtion of impurities into the water from the perspex and from the needle. In order to check this it was necessary to compare the conductivity of the water from the needle with that measured by the cell just above the needle. A J shaped conductivity cell was used with the electrodes about half-way up the longer arm. The tip of the needle was forced through a polythene plug in the shorter arm and the liquid passed between the electrodes, overflowing at the top. The long outlet helped reduce the absorbtion of carbon dioxide into the water between the electrodes.

It was found that, using water flow rates which would produce drops of 160μ radius when the needle was vibrated, the conductivity measured with this cell was the same as that measured with the cell above the needle. The purest water having a conductivity of 6 x 10^{-8}ohm^{-1}cm^{-1} after flushing for about one hour. Minor alterations of the needle valve in the overflow which altered the flow rate through the needle did not affect the conductivity unless the total flow rate was reduced below about 3 cm^3/min. It seemed that no impurity was absorbed during the passage of the water through the needle.

3.3.2 Adjustment of the water surface.

The onset of partial coalescence depends on the size of the incident drop and its impact velocity. The resonance of the needle was adjusted so that a stable stream of drops of about 160 μ radius was produced and this was fired across the box onto the surface of the water in the reservoir. The height of the reservoir was adjusted so that partial coalescence occurred and the secondary drops fell into the collecting can. The incident stream was always adjusted so that only one stream of secondary drops was produced.

The various impact angles and velocities were measured on photographs similar to those of fig 3.1, which were taken using a Shackman automatic camera with an 8" lens and a 3' extension tube. Four or five photographs were sufficient to calculate all the information required.

3.4 Measurements of the charges on the secondary drops

The mean charge on the drops in a stream was measured by collecting the drops in a can connected to an electrometer, the potential across the known input impedance of the instrument giving the current carried by the droplet stream. The mean drop charge was found by dividing this current by the frequency of droplet production, which was assumed to equal that of the head phone oscillator.

Jayaratre and Mason mentioned that a charge of about 10^{-6} esu was found on drops produced by the atomiser, which was thought might affect the charge on the secondary drops. This charge was removed by applying a potential to the needle and this was varied until no charge was detected when the drops were caught in the can mounted on the roof of the screening box. This meant that the average charge was less than 10^{-8}esu per drop. The can was moved out of the stream and the uncharged drops allowed to fall onto the surface, the secondary drops being caught in the other can.

The experiment consisted of allowing a stream of uncharged drops to impact on the surface, and to measure the charges on the secondary drops. The solute concentration in the drops could be varied without altering the drop size by adjustment of the needle valve in the solute supply so that a large number of different concentrations could be used. Three different experimental arrangements were used. The surface was either stationary, of pure water in equilibrium with the air, while the drop concentration was varied, or else the liquid was of the same concentration as the drops and allowed to flow continuously over the edges of the reservoir. The accumulation of water from fragments of the impacting drops was prevented in the first case by occasionally blowing a stream of nitrogen over the surface. A few experiments were also made in which the concentration of the drops was kept constant while the concentration in the reservoir was changed.

It was possible, by accurate adjustment of the needle valves to obtain very reproducible experimental conditions so that the mode of breakup of the jet into secondary drops was constant. Solutions of sodium chloride, thorium nitrate, and ammonium chloride, were used and the variation of the charges on the secondary drops with concentration, for surfaces of the same concentration, are shown in figs 3.4, 3.5, 3.6. All these curves were obtained with

incident drop	radius	$180 \pm 5\mu$
	velocity	140 ± 5 cm/sec
	angle of impact	$50 \pm 3^\circ$
secondary drop	radius	$64 \pm 4\mu$
	velocity	36 ± 3 cm/sec
	angle of impact	$31 \pm 2^\circ$

A comparison of the results for stationary and moving surfaces is shown in fig 3.7. These results are typical, there being only a small decrease of the charge at low drop concentrations. Similar results were obtained if the drop concentration remained constant while the concentration of the bulk liquid was altered. The charge on the secondary drops was independant of the concentration of the bulk liquid, except for a slight reduction if the impacting drops were of concentration less than 10^{-5} molar. The charge therefore is dependant only on the concentration in the incident drop unless the drops are of pure water.

Fig 3.8 shows that there is also a small but systematic increase in the charge separated as the incident drop energy is increased. The range of energies used was quite small however and over this range there was an increase in the secondary drop radius from 40μ to 70μ as the energy was increased.

The errors shown on some of the graphs were obtained from the uncertainties in balancing the conductivity bridge and from errors introduced into the electrometer readings

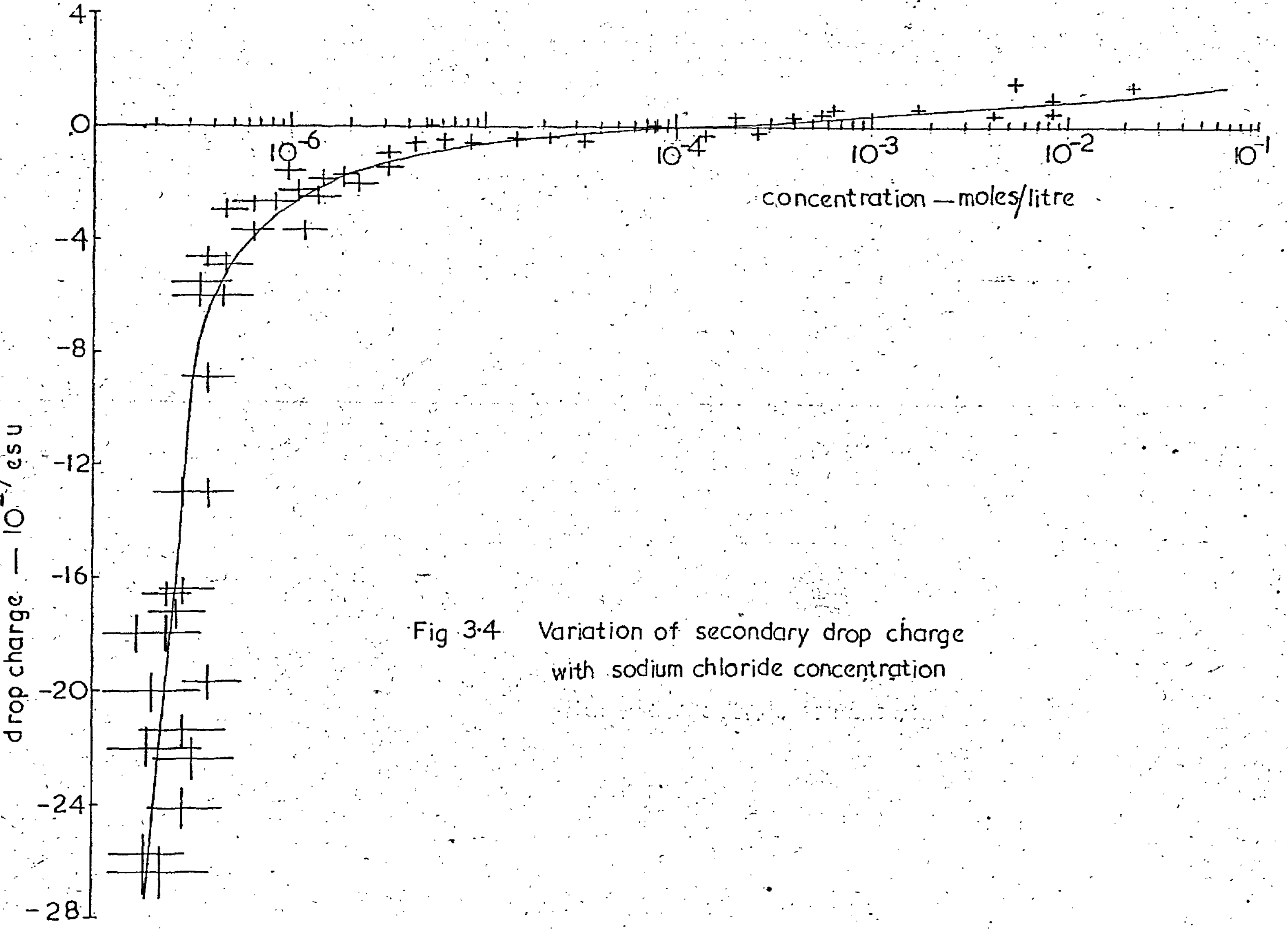


Fig 3·4 Variation of secondary drop charge with sodium chloride concentration

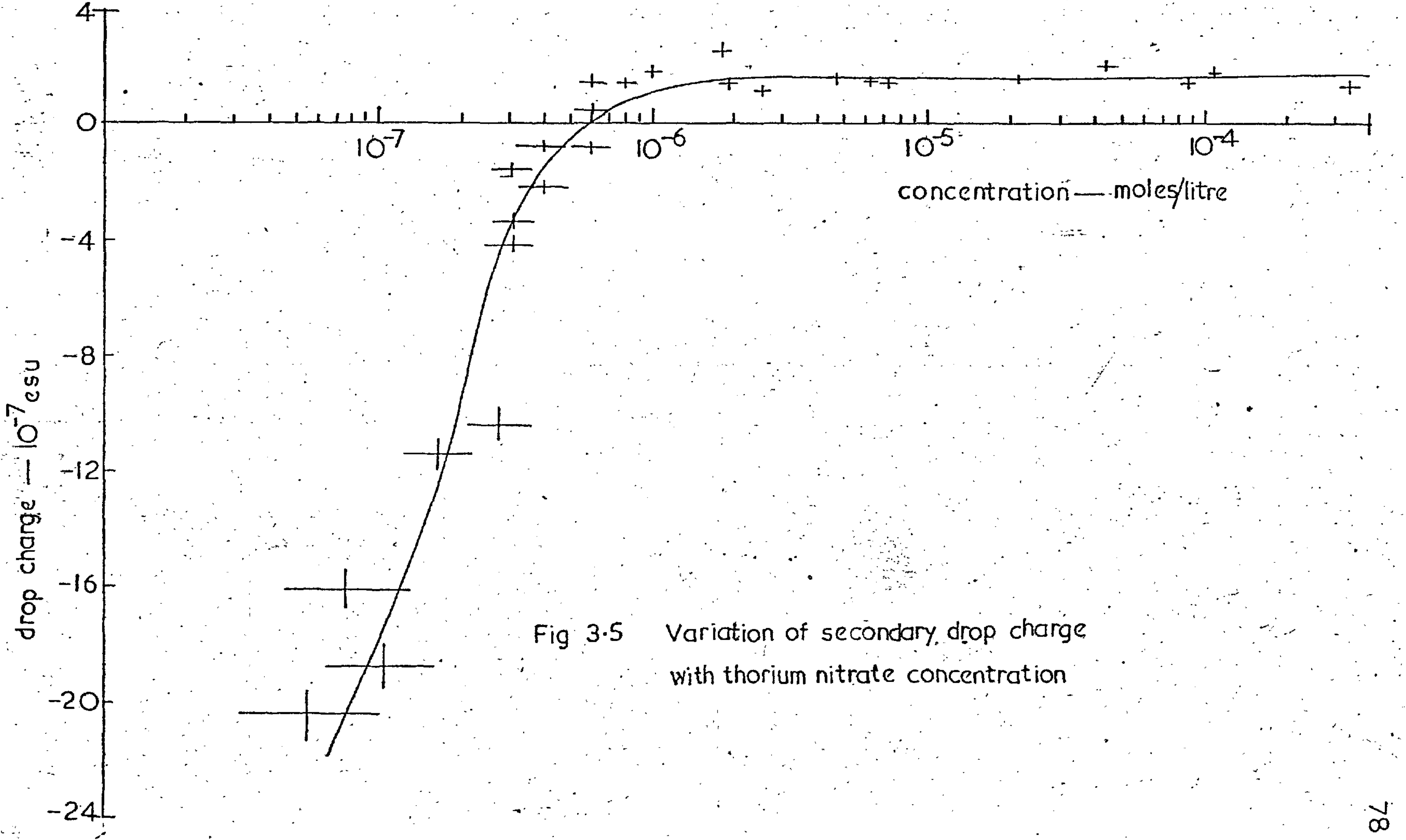


Fig 3·5 Variation of secondary drop charge with thorium nitrate concentration

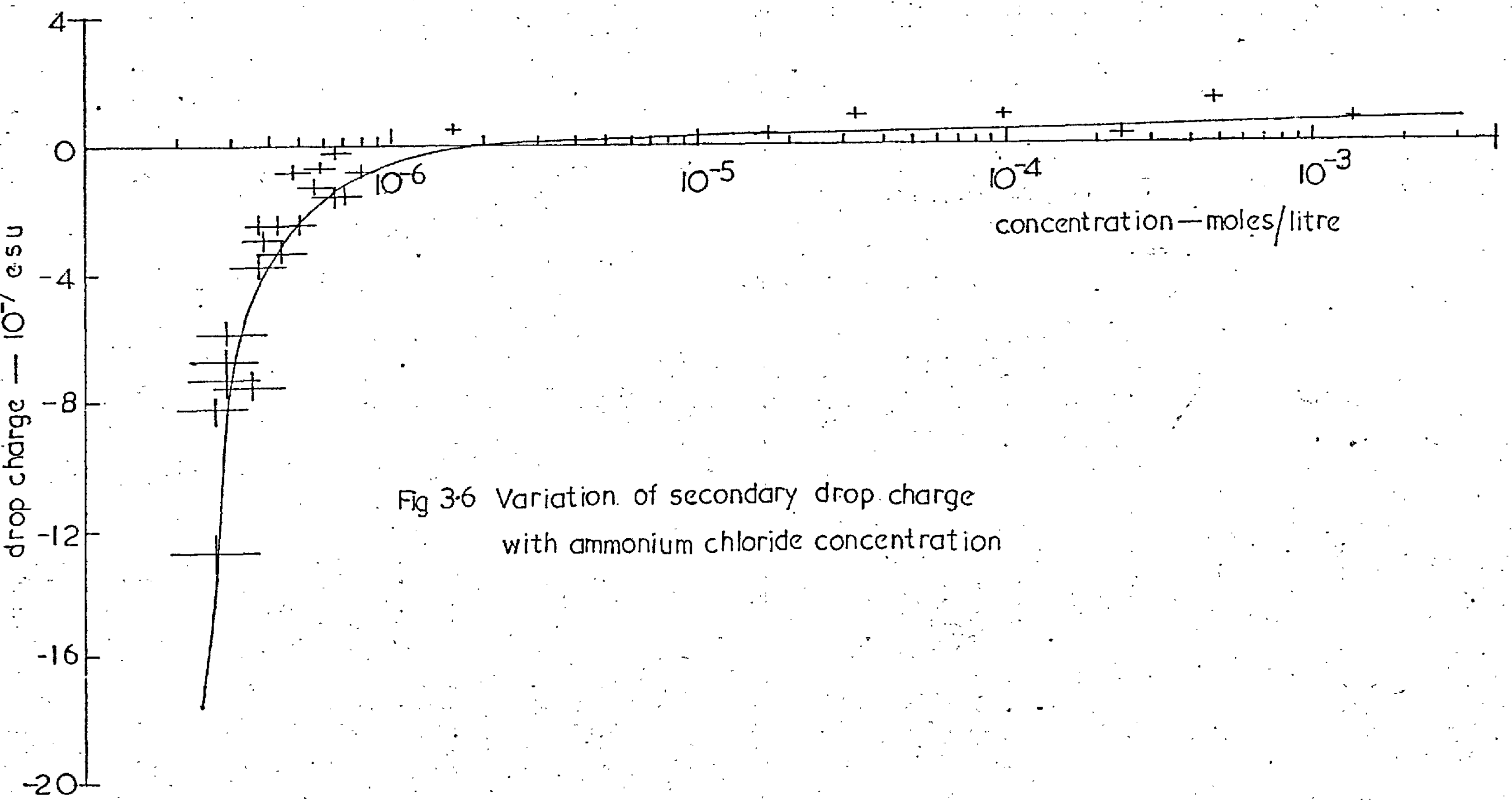


Fig 3·6 Variation of secondary drop charge with ammonium chloride concentration

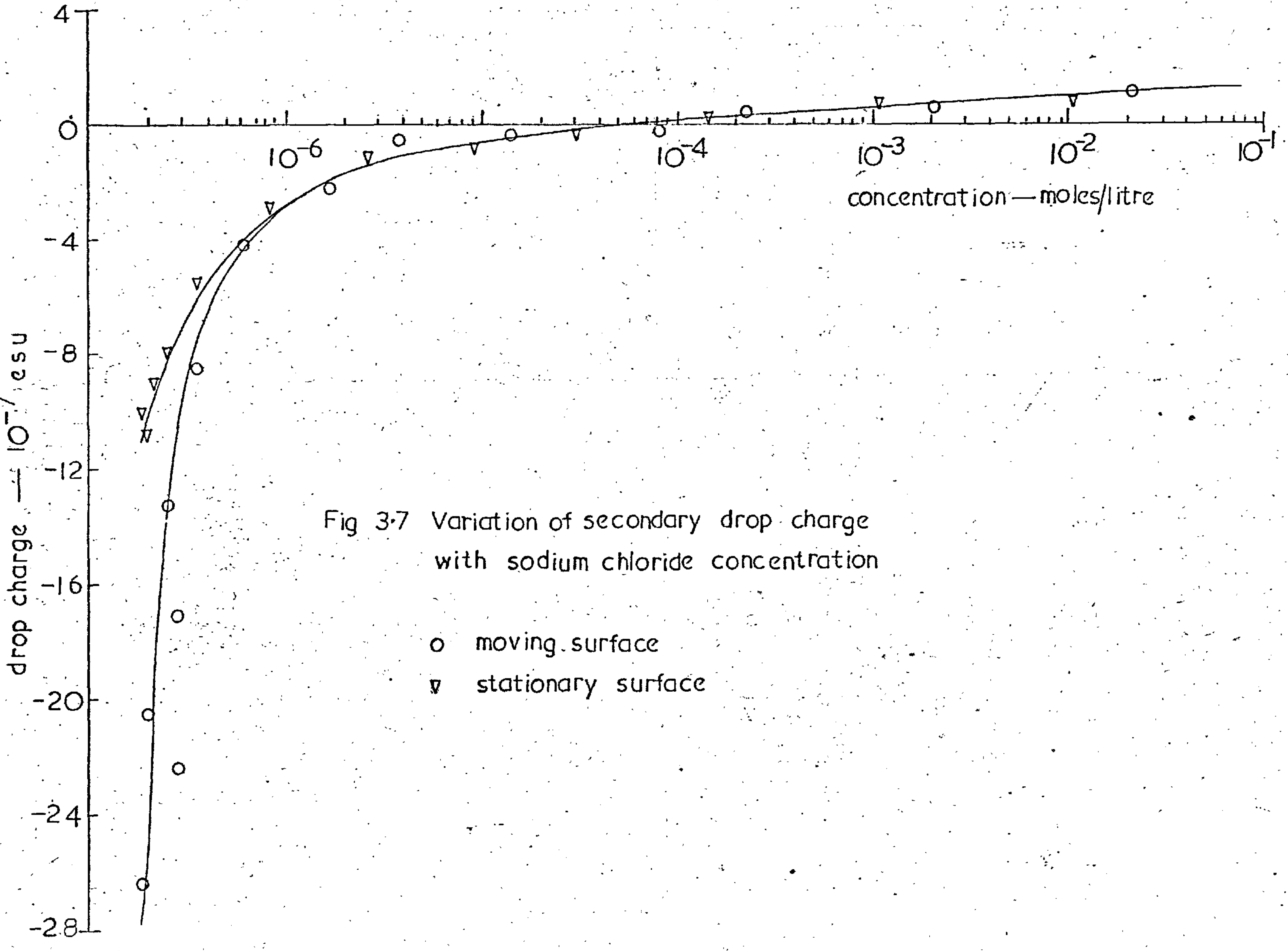


Fig 3·7 Variation of secondary drop charge with sodium chloride concentration

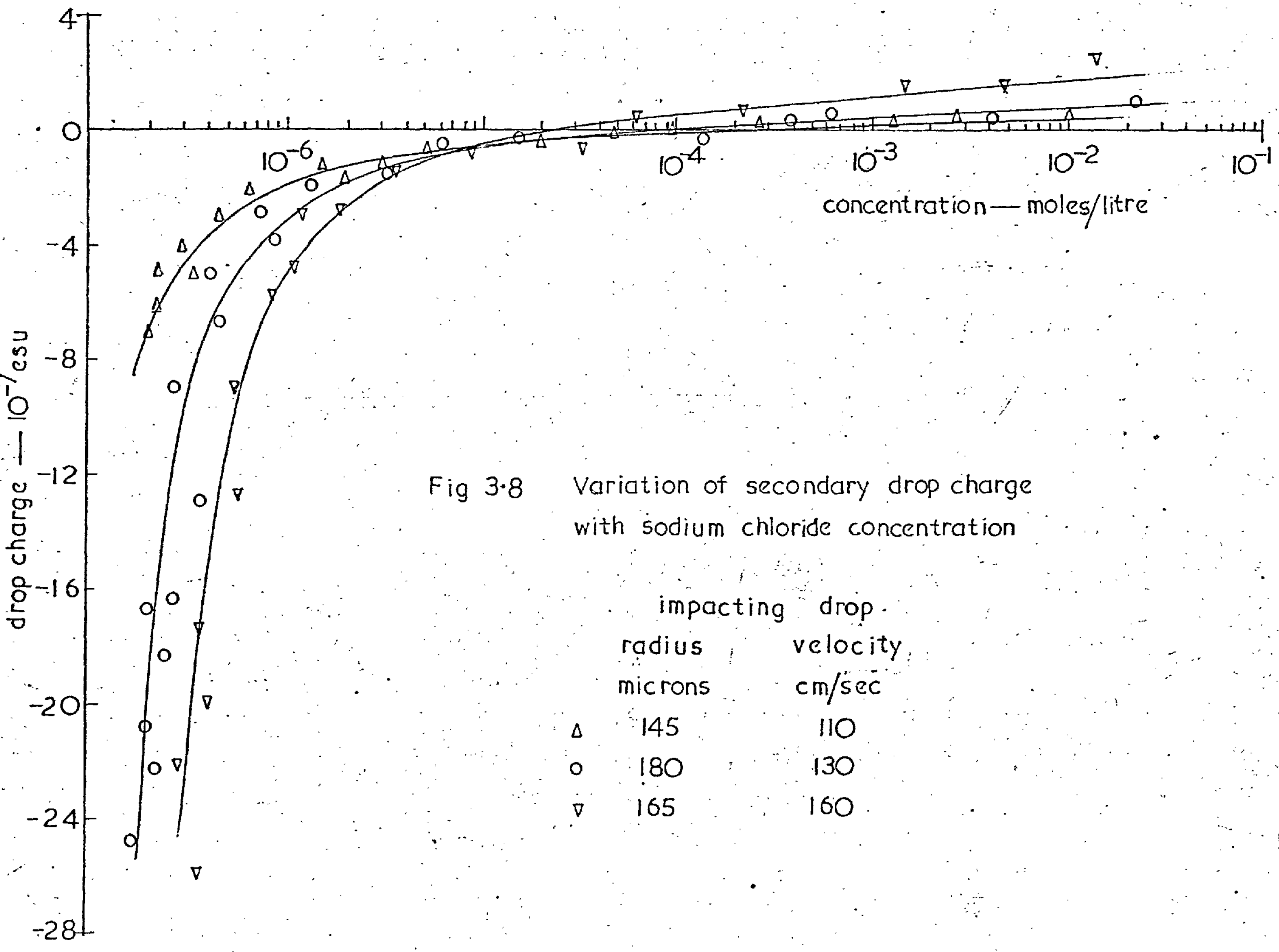


Fig 3·8 Variation of secondary drop charge with sodium chloride concentration

by random pick-up. The former errors were most important at low concentrations when a large change in the solute concentration causes a very small change in the conductivity. The errors on graphs where these are not shown are comparable with those on the earlier graphs.

3.5 The origin and motion of the secondary drops

It was necessary, in order to clarify the significance of the results, to investigate the origin of the water forming the secondary drop. For this purpose drops of pure water were splashed on a surface of a 10^{-2} molar solution of sodium chloride. The secondary drops were collected in a glass tube and analysed using silver nitrate solution. No trace of chloride was detected, showing that the concentration in the secondary drop was less than 10^{-6} molar. Similar results were obtained with a range of incident drop sizes and velocities, and with stationary or moving surfaces. It seems therefore that the secondary drop is formed almost entirely from the water of the original drop which was also suggested by the dependance of the charge on the concentration of the drop and not of the surface.

It was noted that the secondary drop was not, as was first thought, ejected upwards, but downwards so that the trajectory of the secondary drop stream was determined by the velocity with which the drops bounced off the surface. This bouncing did not separate any charge so that it did not affect the results, but in the discussions of the geometry of the breaking jet it is important to consider this point.

3.6 The charging mechanism

The measurements show that charges of the order 10^{-6} esu can be separated at low solute concentrations, the drops being negatively charged. An increase in the concentration reduces, and finally reverses the sign of, the charge, the drops of higher concentrations having charges of the order of + 10^{-7}esu. This variation of the charge with concentration is similar to that found by Iribarne and Mason, except that the charges measured in their experiments were larger, especially the negative charges at low concentrations.

We shall consider the way in which the jet is formed and breaks up, from information obtained from the photographs. The processes involved are shown in fig 3.9. The incident drop flattens as it hits the surface and a crater is formed beneath it. The kinetic energy ofthe incident drop is expended as a larger surface area is formed and the crater deepens. At some point the drop, oscillating about its spherical shape, becomes elongated vertically and the air film between it and the surface ruptures. The liquid then begins to drain out of the drop but, as it does so, the surface tension forces attempt to reduce the area of the cavity, kinetic energy being given to the now jet shaped drop. The jet is forced upwards and the surface layers of liquid from the cavity are forced up behind it. Eventually the equilibrium position of the jet is passed and its velocity is decreased and reversed. During

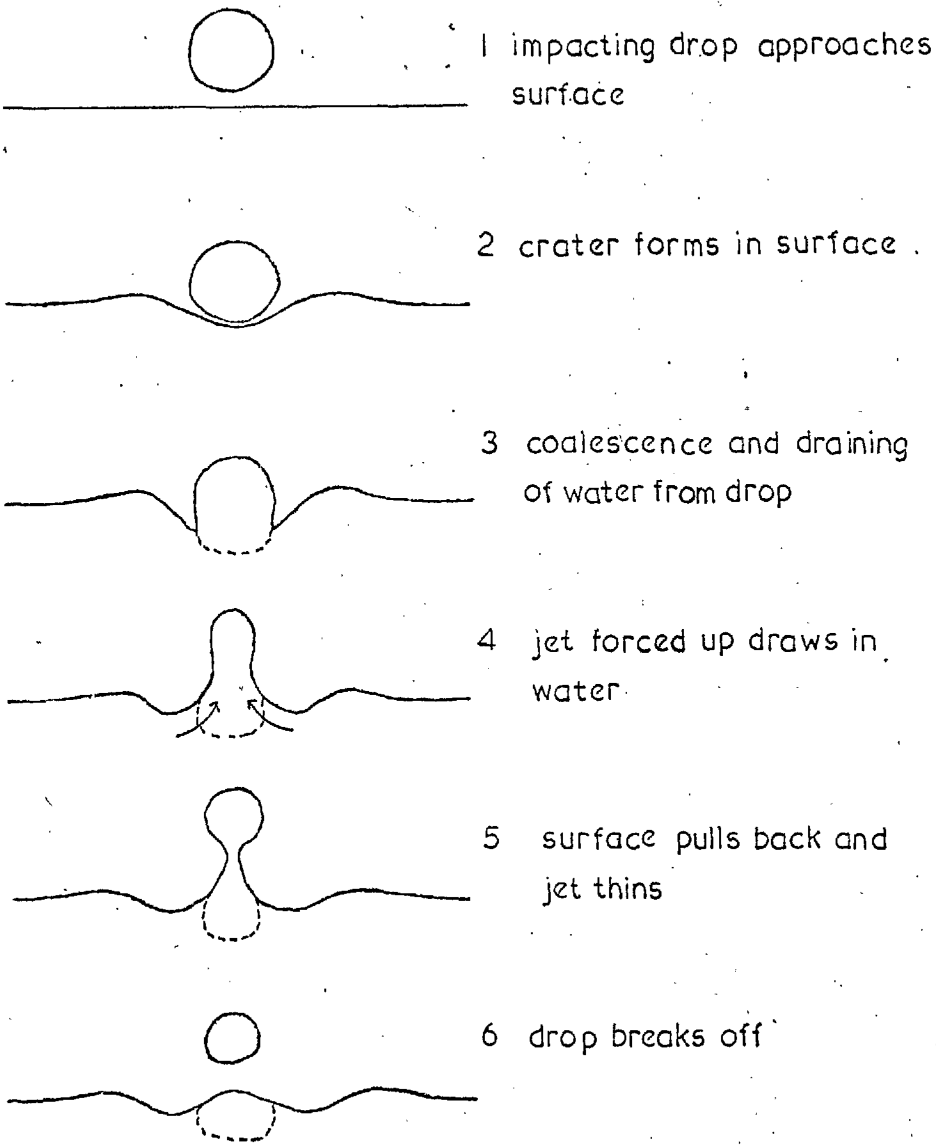


Fig 3·9 Formation of a secondary drop by partial coalescence this downward motion of the surface the jet elongates and breaks to form the secondary drop which bounces off the surface.

It was noted that only water from the incident drop was found in the secondary drop and this can be explained by considering the diagram. It is seen that the water which is forced up behind the rising jet is in fact water which earlier drained out of the incident drop.

Having considered the flow of liquid during the formation of the jet it is seen that this is very similar to that in the case of the jet formed by a bursting bubble, except that in the latter case all of the jet is forced up from the surface, while in this case only a small part, at the bottom of the jet, is so formed. It seems probably therefore that the same theory that was used by Iribarne and Mason to explain the charging of the drops produced by a bursting bubble will explain the charges separated in this experiment.

It is believed that negative charging of the jet occurs asthe surface layer of liquid are drawn up into the jet but that a positive charge is given to the drop as it becomes detached from the jet. The former is the important mechanism at low solution concentrations but decreases at higher conentrations due to the thinning of the electrical double layer. The positive charging is then more important and is much less sensitive to the concentration. The drops produced by the break up of the jet formed by the bursting bubble were comparable with those in this experiment so that it seems difficult to explain the difference in the magnitudes of the charges separated. Iribarne and Mason suggested that water from a layer about 1μ thick was drawn into the jet but in the present experiments the depth was probably much greater.

The liquid drawn into the jet must have originated in the volume of water which drained from the incident drop. We suppose that this water exists in a cylinder of liquid of radius R equal to the radius of the incident drop. We suppose that a surface layer of depth d is drained off this cylinder into the jet so that the volume entering the jet is then $\pi R^2 d$. Now Iribarne and Mason calculated that the charge σ in the surface layer of liquid extending to a depth d, was given by

$$\sigma \approx -7 \times 10^4 c^{\frac{1}{2}} \exp\left\{-\tfrac{1}{2} - 10^8 c^{\frac{1}{2}} d/3\right\}$$

where c is the concentration of the solution.

Now in this experiment we have charges on drops of 5×10^{-7} molar solutions of the order of 10^{-6} esu so that $\sigma \pi R^2 = 10^{-6}$

Hence for $R = 150\mu$ $\quad d \sim 5\mu$

The volume of liquid entering the jet is then about 3×10^{-7} cm^3 or about 30% of the volume of the secondary drop.

It is seen that if the negative charging is to be explained by the theory of Iribarne and Mason it must be assumed that a much greater depth of liquid is drawn into the jet in this case than into the jet produced by a bursting bubble. This is reasonable however in the light of the fact that any liquid drawn up in this way, is liquid from the original incident drop, which limits the area over which the liquid is drawn up. The positive charging of the drops at higher concentrations could again be the result of charge separation as the jet of liquid is broken up and it is this problem which will concern us in the remainder of this thesis.

CHAPTER FOUR

Charge separation in a jet

4.1 Introduction

In chapter three it was suggested that some of the charge separation when a bubble bursts, or during partial coalescence, is caused by the break up of the jet of liquid rising from the surface. It has also been noted that some authors have observed that the charge separation when drops are broken up depends on the violence of the break up. It was decided to investigate this by measuring the charge separation as a jet of liquid was extended by a mechanical force, the rate of extension being variable. The charge separated when a single jet was broken was measured, instead of the mean of a large number of events.

4.2 The apparatus

The method was to allow a capillary to touch the surface of liquid contained in a reservoir connected to an electrometer. The surface tension forces caused the liquid to rise up the capillary to form a column of liquid extending from the surface. Withdrawl of the capillary from the surface resulted in the formation of a neck of liquid, between the capillary and the surface, which would become unstable and break as the capillary was moved further. The charge separation was measured as a potential on the electrometer.

The apparatus is shown in the diagram fig 4.1 A lever,

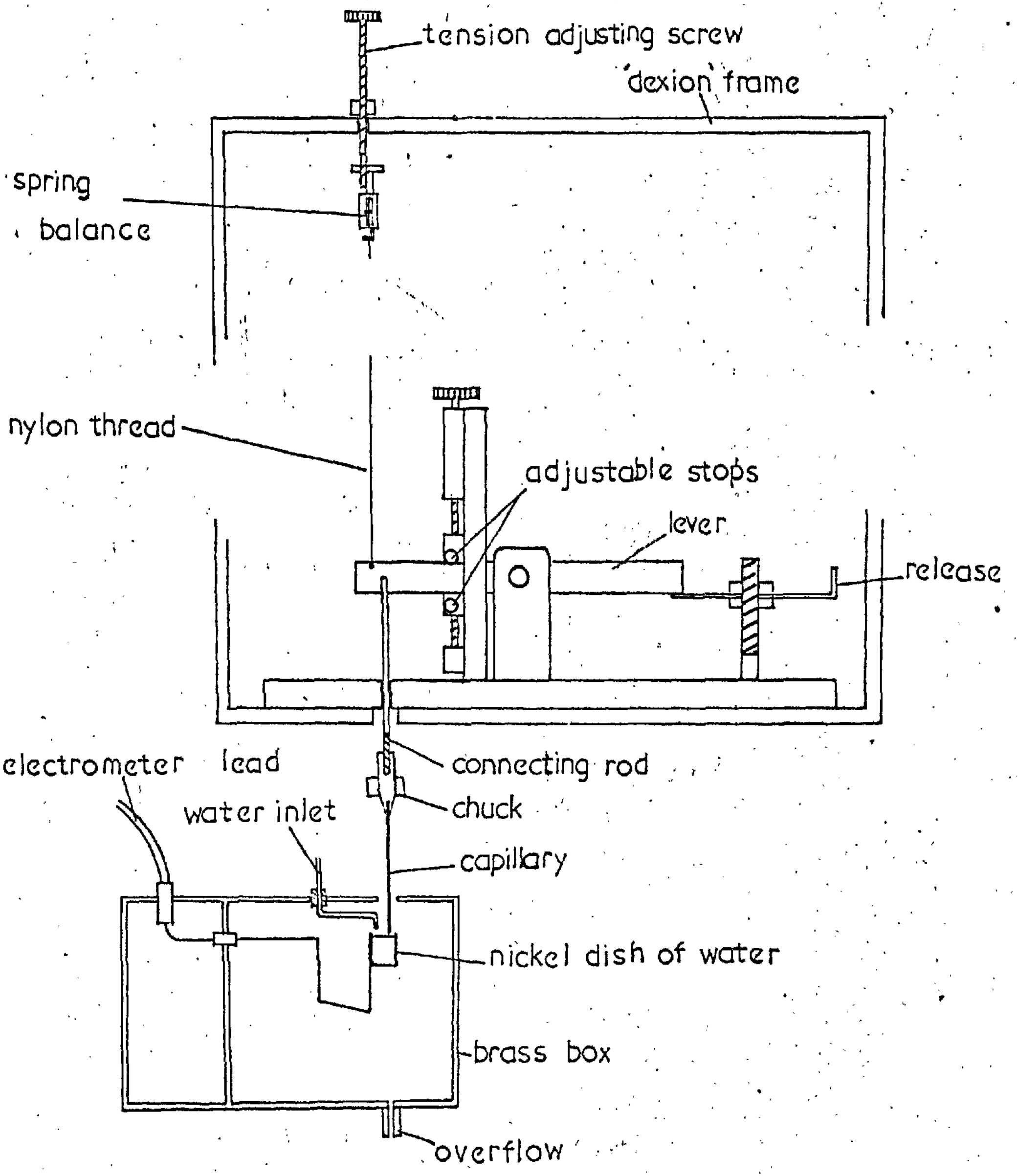


Fig 4·1 Apparatus to withdraw a capillary from a liquid surface about 7 cm long, 1 cm deep, and 0.2 cm thick was pivoted at its mid point and a 2 mm diameter rod about 5 cm long hung from a short bolt near one end of the lever. The rod could slide through a vertical hole in the lever base plate so that a small movement of the lever caused a vertical movement of the lower end of the rod. Two stops, one just below the lever when it was horizontal, and the other just above it, allowed about 2 mm movement of the end of the rod. The height of the stops could be adjusted but not their separation. The lever could be held down onto the lower stop with a small catch shown in the diagram.

A spring balance, mounted on an adjustable stand about 1 metre vertically above the connecting rod, was connected to the lever with a length of nylon thread. The screwed mounting allowed the thread to be strained so that if the lever was forced against the lower stop and then released, it drew the connecting rod upwards very rapidly. A small chuck was screwed onto the end of the rod to hold a range of different capillaries.

The water, forming the surface under test, was contained in a reservoir about 1 cm in diameter, made of nickel plated copper foil. The reservoir was mounted in a brass screening box 1.5 cm vertically below a 3 mm hole in the roof of the box, the wire support also making the electrical connection to the electrometer. A jet of the liquid could be forced into the reservoir through a tube, but when the flow was stopped there was no electrical connection between the inlet and the reservoir. The screening box was mounted on an adjustable stand so that when a capillary was mounted in the chuck it dipped into the reservoir through the hole in the box.

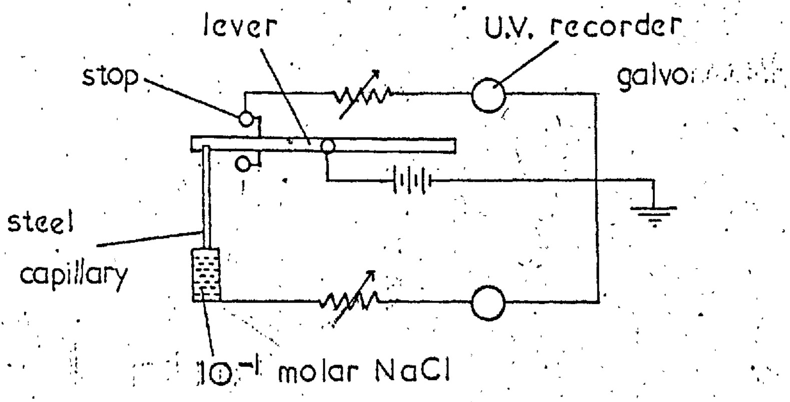
The liquid was supplied from the apparatus described in chapter two, a glass mixing chamber and conductivity cell being incorporated in the supply near the connection to the liquid inlet. All of the apparatus which would be in contact with the liquid was cleaned, the glass in chromic acid and the metal in soapy water followed by steaming, and the assembled apparatus was flushed with pure water at about 20 cm^3/min to remove any impurities.

4.3 Preliminary experiments

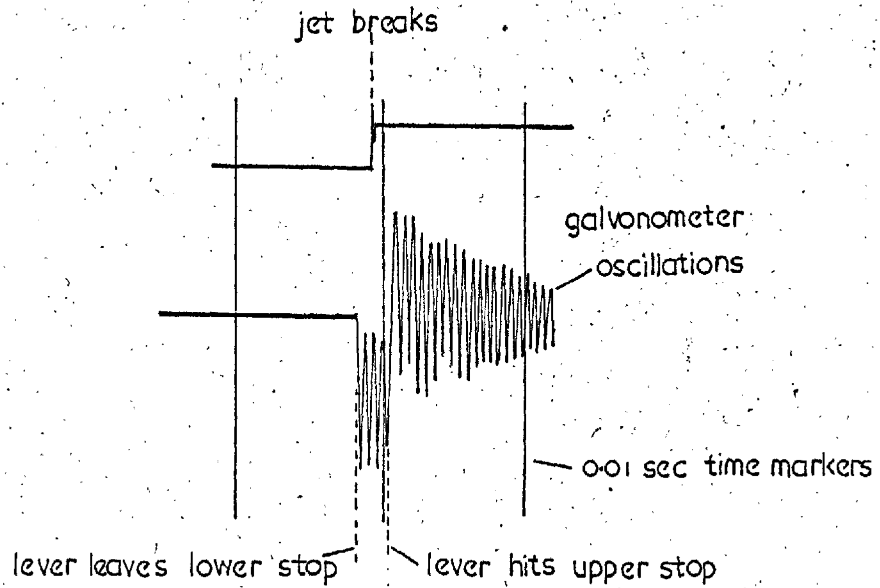
4.3.1 Measurement of the capillary velocity.

It was necessary to measure the capillary velocity at the instant when the neck between the capillary and the liquid surface was broken. This was done electronically using the circuit shown in fig 4.2a. The steel capillary of 250 μ just touched the surface of a sodium chloride solution of conductivity 10^{-2} ohm^{-1} cm^{-1} contained in the reservoir, when the lever was in its lowest position.

When the lever was in contact with either stop a current flowed through the galvonometer, the resistance being adjusted to give about ½ full scale deflection. A current flowed through the other galvonometer only when there was a



a) Circuit diagram



b) Copy of a typical U.V. recorder trace

Fig 4·2 Measurement of capillary withdrawal speed liquid connection between the capillary and the surface. If the cord was strained and the lever released a pulse was recorded by one galvonometer while the lever was moving and a step in the other trace indicated the instant when the jet ruptured. A tracing of a typical trace is shown in fig 4.2b. The oscillations in the speed measuring trace are due to oscillations of the galvonometer which occurred since only one very high speed galvonometer was available.

The distance moved by the tip of the capillary was measured with a cathetometer. The acceleration of the lever was assumed to be uniform as there was only a small change in the thread tension during the movement, so that the maximum capillary velocity could be calculated. This is shown in fig 4.3 The liquid connection was found to break in all cases after about 70 ±5% of the time taken for the lever to complete its movement so that the capillary was moving at about 70% of the maximum speed at this instant. This velocity will be called the capillary velocity throughout the remainder of this chapter.

4.3.2. Preparation of the capillaries

The capillaries used in the experiments were either stainless steel hypodermic needles with the ends ground square or drawn pyrex capillary tubes with ground and polished ends. The tubes were carefully cleaned and stored in sealed tubes of pure water until required for use.

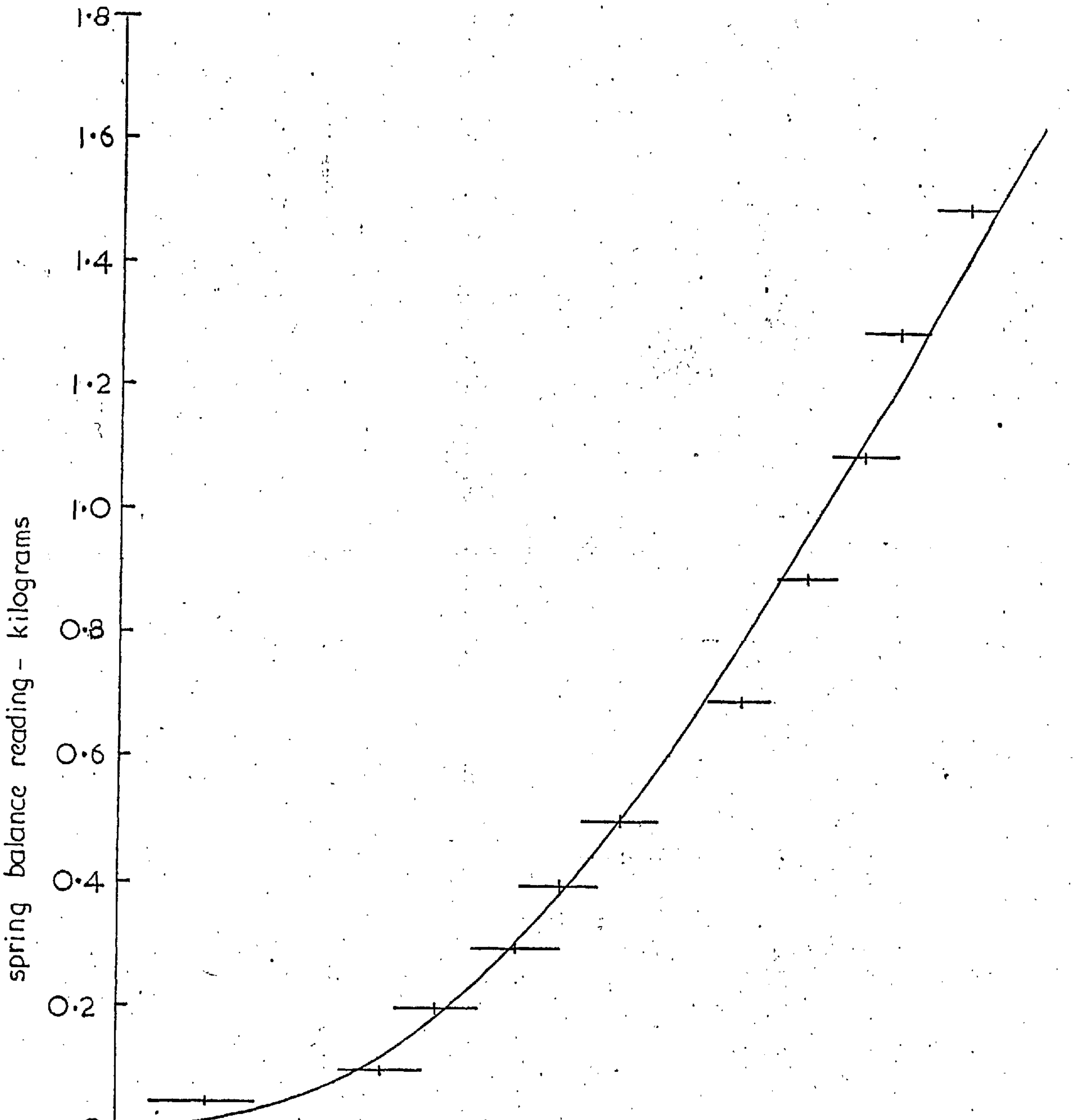


Fig 4·3 Calibration of capillary withdrawal speed

4.3.3 Calibration and use of the electrometer

. The charge separated was to be measured by noting the change of potential of the reservoir which was connected to the electrometer, so that it was necessary to know the imput capacity of the system and to reducd this to a minimum for increased sensitivity. The time constant of the system was measured by applying a small potential to the reservoir and noting how this decayed away. With the instrument set on a voltage measuring range the external capacity, estimated at 50 - 100 pf was dominant but this was degenerated by a factor of 100 on the current range so that it was comparable with the input capacity of the instrument. The results are shown in fig 4.4 and from these it was calculated that the input capacity on the current range was 1.60 ± 0.05 pf. A change in the potential of the input of 1 mv corresponded to a charge of 6 x 10^{-6}esu. Charges as low as 10^{-6}esu would be detected although random noise and pick up made accurate measurements below 5 x 10^{-6}esu very difficult.

It was noted as the capillary was dipped into the liquid in the reservoir a potential was recorded on the electrometer. This was due to the metal-liquid contact potential for earthed steel capillaries or to surface charges on the insulated glass capillaries. To reduce these effects the lever was insulated and connected to earth through a large knife switch. With the lever insulated and an electrometer input capacity of 10^{13} ohm, the potential would build up very slowly, so that

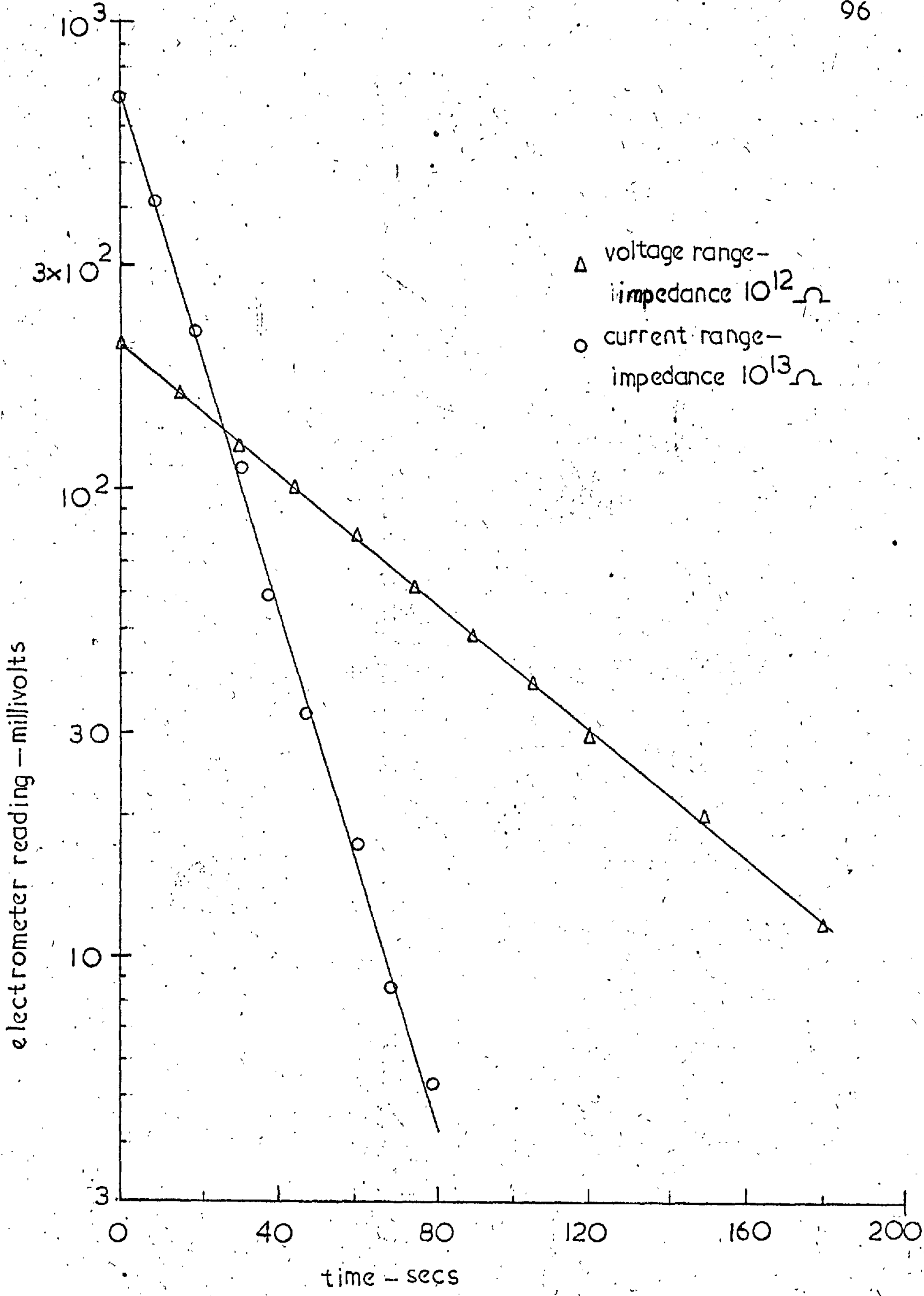


Fig 4·4 Calculation of electrometer input capacity if the experiment was performed quickly the electrometer could be used on a sensitive range, the change in potential being due to the removal of the capillary.

The changes of capacity due to the removal of the lever were shown to be negligible by applying a large charge (10^{-3}esu) to the reservoir and removing the capillary. No change in the measured potential was observed.

4.4 Experimental details

The experiment consisted of measuring the charge separation which occurred when various capillaries were withdrawn from the surface of water and sodium chloride solutions at different speeds. The liquid was flushed through the apparatus for about 5 min before each experiment, the conductivity being kept constant. The lever was adjusted so that it just touched the surface when the thread tension was the required value and the change potential noted as the capillary was withdrawn.

The results were found to be quite reproducible except for a few cases when charged drops were shaken from the capillary as it hit the upper stop. It was also essential that the capillary only touched the surface before withdrawal, or charge was separated as it was drawn up through the liquid.

The apparatus was not designed to prevent contamination of the liquid by carbon dioxide but since it was possible to complete the experiment within a few seconds of turning off the supply of fresh liquid the effect of absorbtion was believed to be small. If the same sample was used several times a slow decrease of charge amounting to about an order of magnitude in 3 - 4 min was recorded. This would only result in an error of 10-15% in the first measurement after one or two seconds, which was comparable with the other experimental errors.

4.5 Results of the experiments

In order to assess the reproducibility of the results a series of measurements was made using a solution of given concentration and a constant capillary withdrawal speed. These results are shown in the histogram in fig 4.5. The error in each result is about 10% due to uncertainties in reading the electrometer caused by the contact potential drift, and about the same amount due to random pick up. The results are shown to be very reproducible within this experimental error.

Graphs ofthe variation of charge separation with capillary velocity for various solutions are shown in fig 4.6 and fig 4.7. Each point is the mean of two or three individual measurements. The results for the very concentrated solutions were very inaccurate owing to the electometer being used on the limits of its sensitivity with considerable pick up. These results are the means of about six readings.

Complete curves were obtained for several different capillaries and the results for these are shown in fig 4.8.

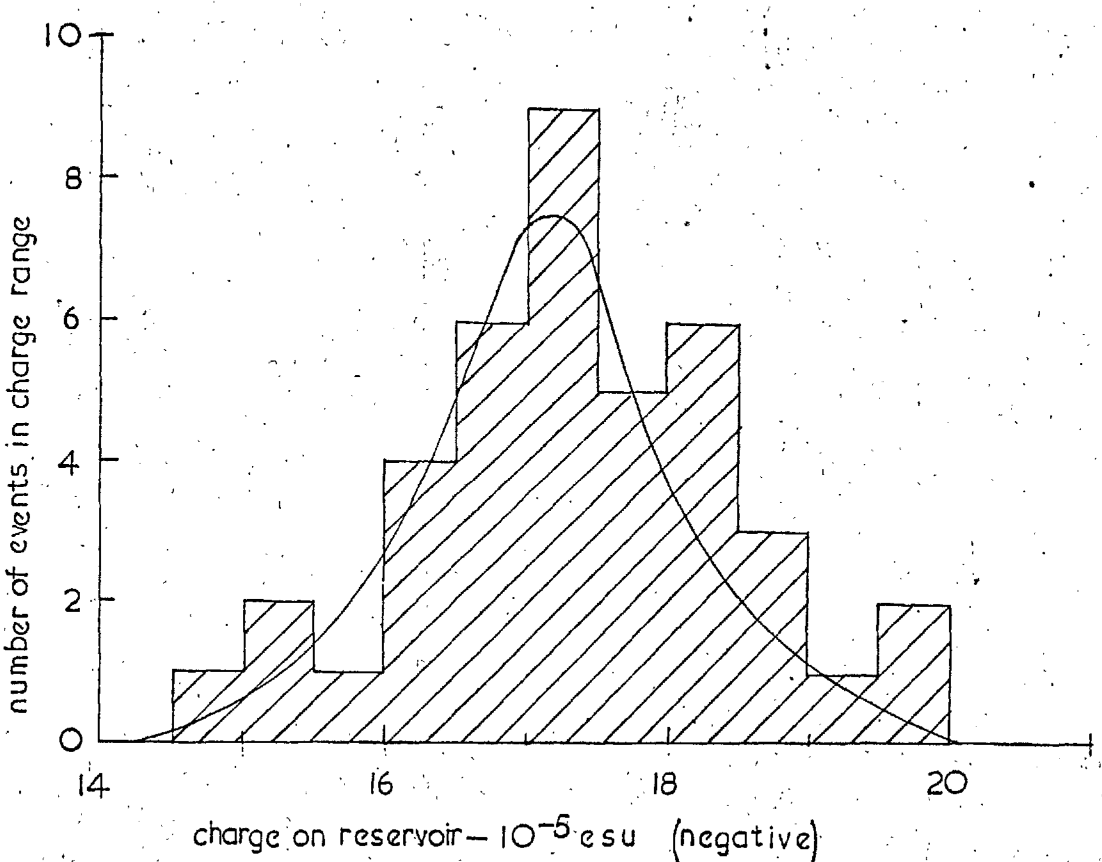


Fig 4·5 Charge separated by the withdrawal of a steel capillary from $1{\cdot}5\times10^{-7}$ molar sodium chloride at 130 cm/sec

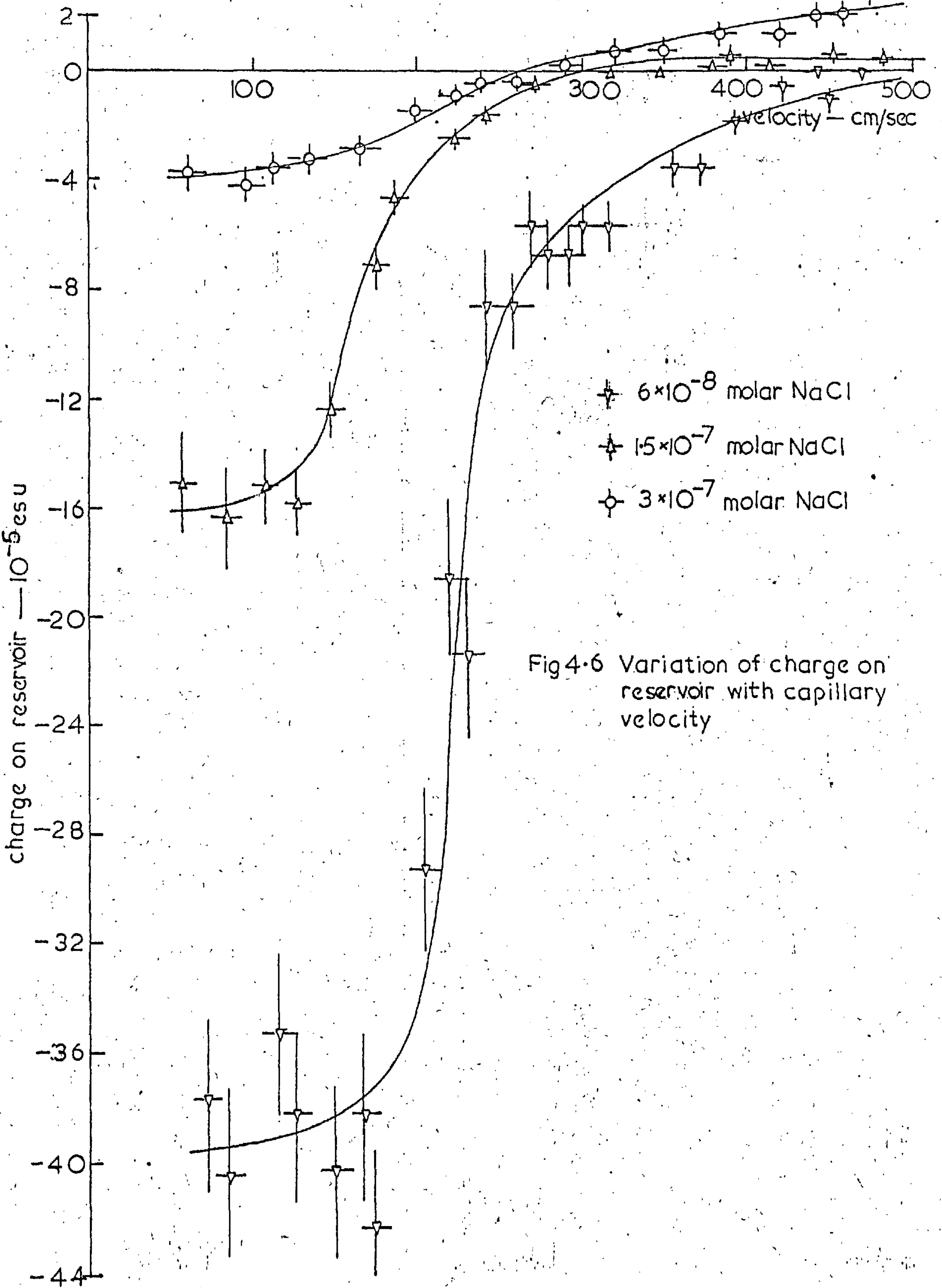


Fig 4·6 Variation of charge on reservoir with capillary velocity

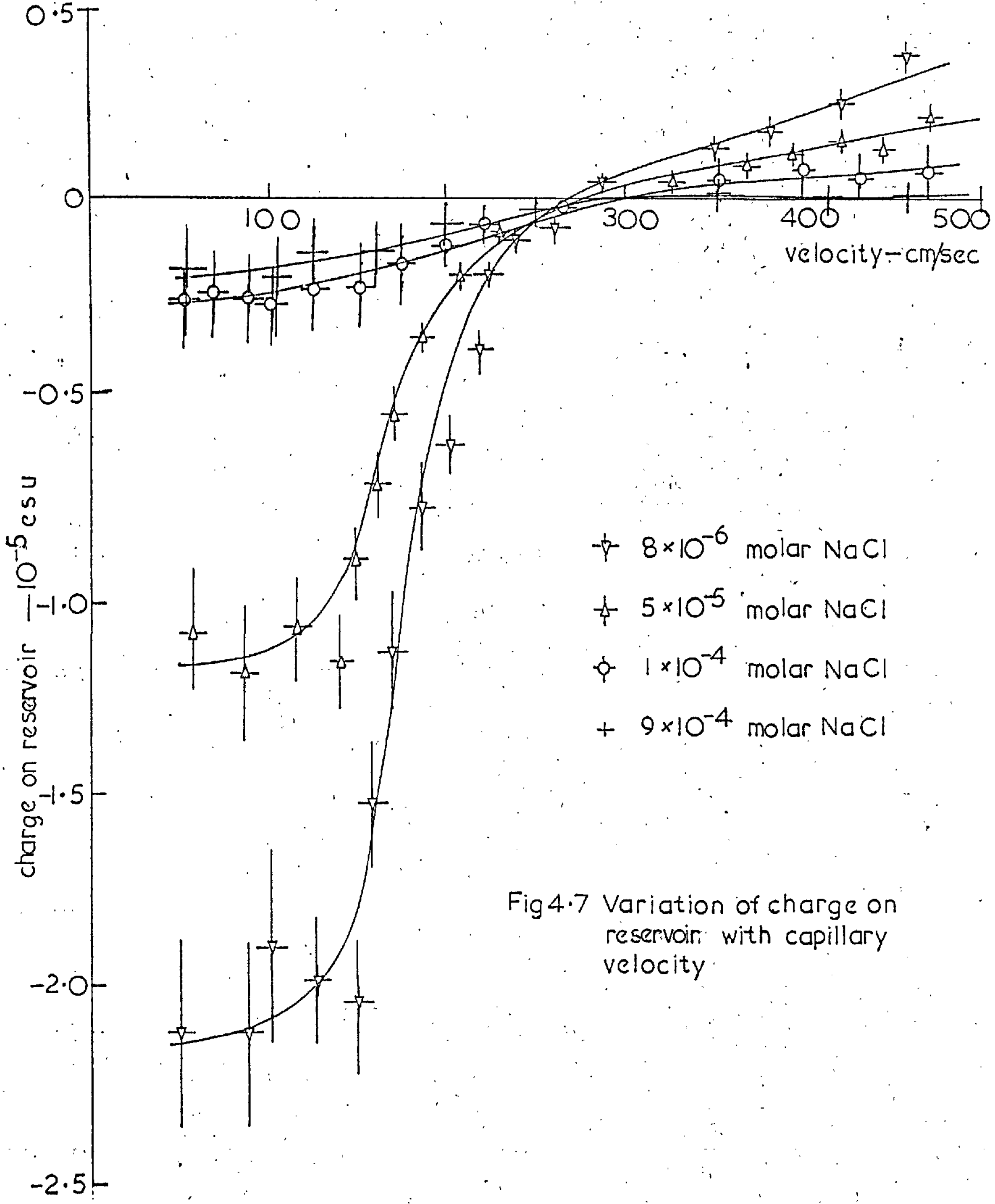


Fig 4·7 Variation of charge on reservoir with capillary velocity

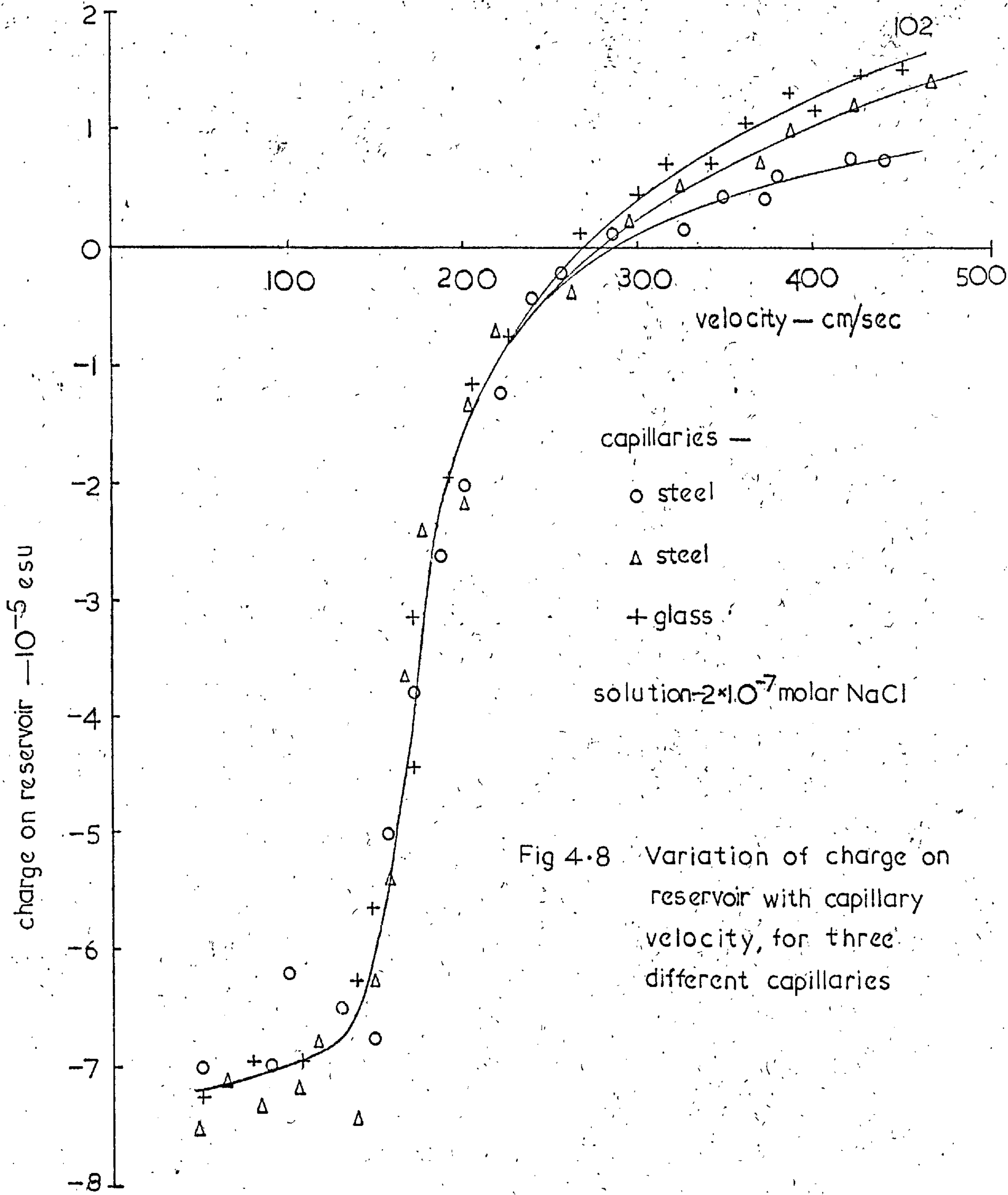


Fig 4·8 Variation of charge on reservoir with capillary velocity, for three different capillaries

The errors, which are not shown on this graph for clarity are comparable with those in fig 4.6. The variation of charging with capillary diameter is shown in fig 4.9.

The results show that the reservoir becomes negativoly charged for capillary speeds less that about 250 cm/sec. The charge separation is independant of the capillary diameter and also of the velocity below 200 cm/sec. Positive charging of the reservoir occurs at higher speeds, the charge increasing with increasing speed or capillary diameter. In both cases the magnitude of the charge separated decreases with increasing sodium chloride concentration except for very small positive charging for dilute solutions. The variation of the negative charge with concentration is shown in the graph, fig 4.10 on which two points are plotted in addition to those of figs 4.6 and 4.7.

4.6 Conclusions and the charge separation mechanism

The results of this experiment are believed to be consistant with the idea that the charge is separated by the shearing of the double layer during the breaking of the jet. The outer layers of water in the jet are drawn up as the jet is elongated. For low velocities however the bulk liquid is forced through the neck by surface tension forces at a faster rate so that the break up of the jet is dominated by Rayleigh instability. At higher velocities, when the capillary is moving faster than the mean liquid velocity, the dragging up of the outer layers by the capillary will be the

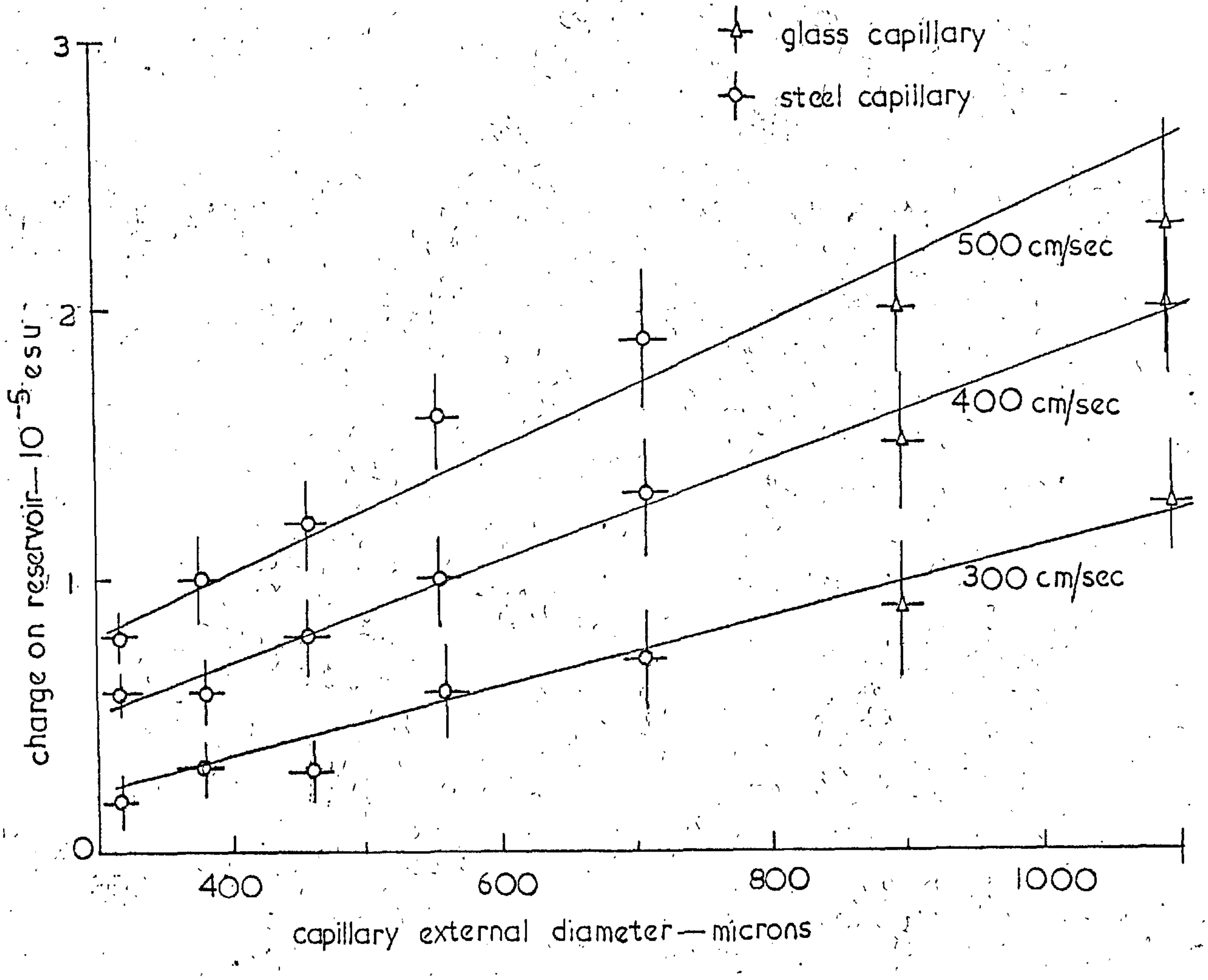


Fig. 4·9 Variation of charge on reservoir with capillary diameter

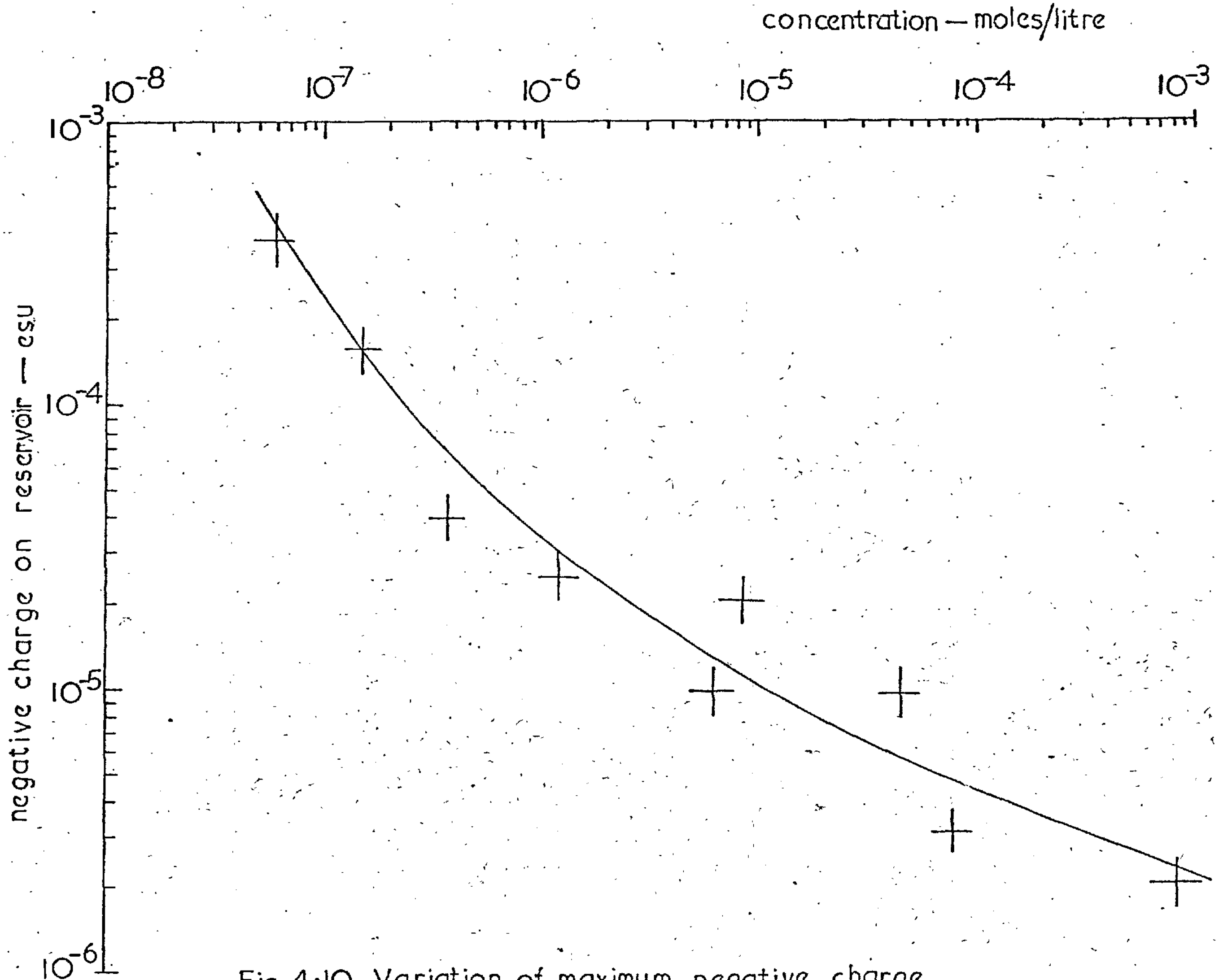


Fig 4·10 Variation of maximum negative charge with sodium chloride concentration dominant charge separation mechanism. We can calculate an order for this critical speed.

Consider a cylindrical neck of liquid of surface tension γ with length 2 l and radius a. The mean velocity $\bar{u}$ due to the excess pressure in the neck, caused by surface tension forces, will be given by

$$\bar{u} = \frac{\gamma a}{8\eta l}$$

where η is the viscosity

For Rayleigh instability $l = \pi a$

$$\therefore \bar{u} = \frac{\gamma}{8\pi\eta}$$

Hence for water $\bar{u} \sim 300$ cm/sec

This is in agreement with the critical velocity at which a sudden decrease in the charge occurred. When the velocity is in excess of 300 cm/sec the charge is not separated by a Rayleigh instability mechanism.

For these high velocities we would expect the charge on the reservoir to be positive because the surface negative layer is drawn up by the capillary. We would also expect the charge to increase with increasing capillary radius because the increase in the circumference of the ring of liquid drawn up will increase the area over which the shearing of the double layer occurs. These ideas are both in agreement with the experimental results. The observed decrease of charge with increasing concentration is probably due to the thinning of the double layer at high concentrations which will decrease the charge separated by shearing over a plane at some fixed depth below the surface.

It will be shown in chapter seven that the charge separated when a jet breaks by Rayleigh instability is almost independant of the initial radius of the jet. The charge is separated so that the ends of the jet would become positively charged, which would leave a negative charge on the reservoir in these experiments if the jet broke with the breaking point displaced towards the capillary. Unfortunately it was not possible to photograph the breaking jet to verify this assumption but it seems probable that the greater volume of liquid would be left at the lower end of the breaking jet.

This theory explains the reversal of the charge at some critical velocity of the capillary and also correctly predicts the sign of the charge and the variation with capillary radius. The magnitude of the charge which is separated by Rayleigh instability will be calculated in chapter seven where it is shown that the charge separated at low capillary velocities is in good agreement with both theoretical and experimental results for the charge separated by Rayleigh break up of a jet.

The low positive charges for the dilute solutions were due to the double layer not completely formed in the time available. The time of formation and break up of the jet at high velocities is less than 0.5 ms but for these concentrations the time of formation of the double layer will be shown to be about 1 ms so that incomplete formation is probable at speeds greater than 100 cm/sec.

These experiments have shown that very complicated variations in the charge separated can only be explained by considering the flow of liquid in a breaking jet. This is in common with the results of other of the experiments by the author where several different charge separation mechanisms are found. It is only by considering the results of these individually that the total charge separation can be explained.

CHAPTER FIVE

The break up of free drops

5.1 Introduction

Gill and Alfrey (loc. cit.) have suggested that measurements of the charge separation resulting from the atomisation of large drops in an air blast have been affected by charging in the field of contact potentials invariably present. It was decided to use the hypodermic needle atomiser, decribed previously, to attempt to produce drops which would break up in free space. It was hoped to measure the charges on the fragments so that the charging associated with the break up of isolated drops could be determined.

5.2 Break up into two drops

5.2.1 Experimental method.

The vibrating needle was mounted in a screened box similar to that used in the experiment described in chapter three and connected to the pure water apparatus. A high power telescope was used to study the flow of liquid from the tip of the needle under stroboscopic illumination. When the needle was vibrated a large drop of lquid was formed initially joined to the needle by a neck of liquid. This neck separated from the drop and then from the needle to form a small satellite drop. It was observed that if the liquid flow rate was increased, by increasing the pressure in the liquid reservoirs, and if the amplitude of the vibraion of the needle was increased, then the neck of liquid was much longer. These necks also became detached at either end but the detached jet was unstable and broke up into two or three drops. This was the type of break up which was desired with an isolated volume of water breaking up into small drops. These particular modes of break up were not very stable or reproducible but were useable, with some care. Two main types of neck were observed, some were almost parallel throughout their length and broke up near one end as shown in fig 5.1. The other mode of break up produced a very tapering neck usually with the thinner end near the main drop from the needle. These necks broke up to produce two drops of widely differing radii there sometimes being a factor of 5 difference, while the parallel jets produced drops of almost equal radii.

The experiment was to allow the jet to break into two drops using solutions of varying concentrations of sodium chloride. The charges on the two streams of drops were measured by catching the drops in small cans connected to an electrometer. The rate of droplet production was taken from the frequency of the oscillations of the needle. The mean drop charge could then be calculated from the steady current into the can.

5.2.2 The initial charge on the jet

It was found that the charges on the two fragments were not equal and opposite due to the charge which was present on the jet before it broke up. The results of Banerji (loc.cit)

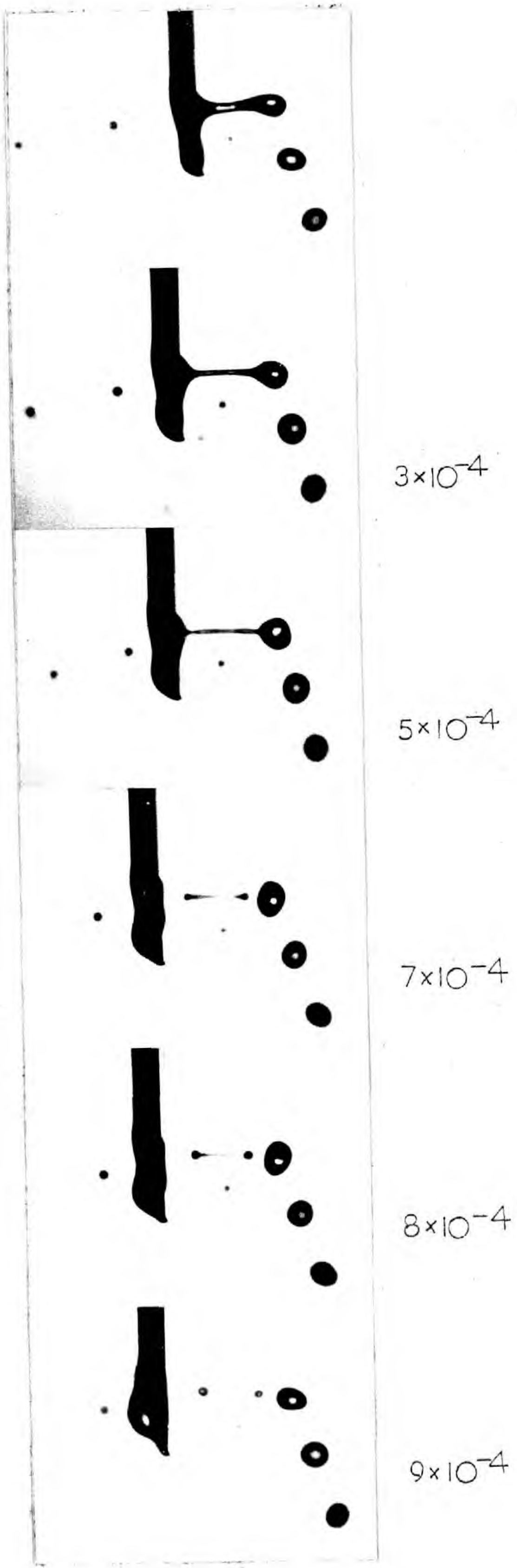


Fig 5·1 Jet break-up into two drops

(showing times in seconds after first photograph)

1mm

would suggest that this charge would be divided between the two fragments and would be added to any charge separated during the break up of the jet.

Suppose that the charge on the jet was Q which will be assumed to be divided between the drops in the ratio of their radii. If the drop radii are r_1 and r_2 then the charges due to the initial charge on the jet are

$$\text{on (1)} \qquad \frac{r_1 Q}{r_1+r_2}$$

$$\text{on (2)} \qquad \frac{r_2 Q}{r_1+r_2}$$

Now suppose that a charge q is separated during the break up. The charges will then be

$$\text{on (1)} \qquad \frac{r_1 Q}{r_1+r_2} + q = q_1$$

$$\text{on (2)} \qquad \frac{r_2 Q}{r_1+r_2} - q = q_2$$

Hence

$$q = \frac{r_2 q_1 - r_1 q_2}{r_1 + r_2} \qquad (5.1)$$

Another method of finding the charge separated by the break up would be to neutralise the charge on the jet by applying a potential to the needle. The collecting cans were connected in parallel to the electrometer and arranged to catch both streams of drops. The potential applied to the needle was adjusted until there was no detectable current.

It was found necessary, to prevent any changes in capacity caused by moving the cans, to fire the drops into the cans through a hole in an earthed screen. One can was then moved and only one stream caught so that the charges on these drops wereequal and opposite tothose on the other drops.

Another method of adjusting the potential to neutralise the jet charge was also possible in some cases. The amplitude of the oscillator could be adjusted so that while there was very little change in the formation of the jet the two drop streams could be altered and made to coalesce. This altered the charge separated by the break up of the jet but not the original charge on the jet. The potential could then be adjusted so that the single stream was uncharged. When the amplitude was altered to produce two streams the charges on the two streams were again equal and opposite but the magnitude of the charge depended on the amplitude.

These three methods were compared in detail for one particular case. A 5×10^{-6} molar sodium chloride solution was used with drops produced at 325 $\sec^{-1}$. The charges on the two streams of drops, of radii $21 \pm 2\mu$ and $30 \pm 2\mu$, were measured as the potential applied to the needle was increased. With the needle earthed the charge on the smaller drop was $+ 2.1 \times 10^{-6}$ esu and on the larger drop $- 4.2 \times 10^{-6}$ esu. Formula (5.1) gives a charge separation due to the breaking of the jet of 2.9×10^{-6} esu, the smaller drop receiving the positive charge. The variation of the charges with the applied potential is shown in fig 5.2. The results indicated that the charges were equal and opposite for an applied potential of + 160 mv, the charge separation being 2.6 x 10^{-6} esu. When the two streams were combined a potential of + 165 mv gave an uncharged stream. When the streams were again separated the charge on the smaller, positively charged, drops varied from 1.3 x 10^{-6} esu to 3.4 x 10^{-6} esu, depending on the amplitude. When this was adjusted to the same value as before the charge separated was 3.0 x 10^{-6} esu. All of these measurements were estimated to have an error of ± 10% so that the agreement between the three results is very good.

It was decided that the easiest method, to be used in future experiments, was the second described above. Measurement of the drop sizes essential for the first method was best accomplished by tedious photographic methods, while the last method was only applicable in certain cases.

5.2.3 Experimental results.

The streams of drops from the needle were not sufficiently stable in many cases to allow a detailed study of the variation of the charge with the solute concentration to be made. Several concentrations were used for one mode of break up, producing drops of radii 23 ± 2μ and 37 ± 2μ and the results are shown in fig 5.3. The smaller drop was positively charged.

Fig 5.4 shows the results from a large number of experiments using different modes of break up. There is only a spread of a factor of 3 in the charges at a given concentration,

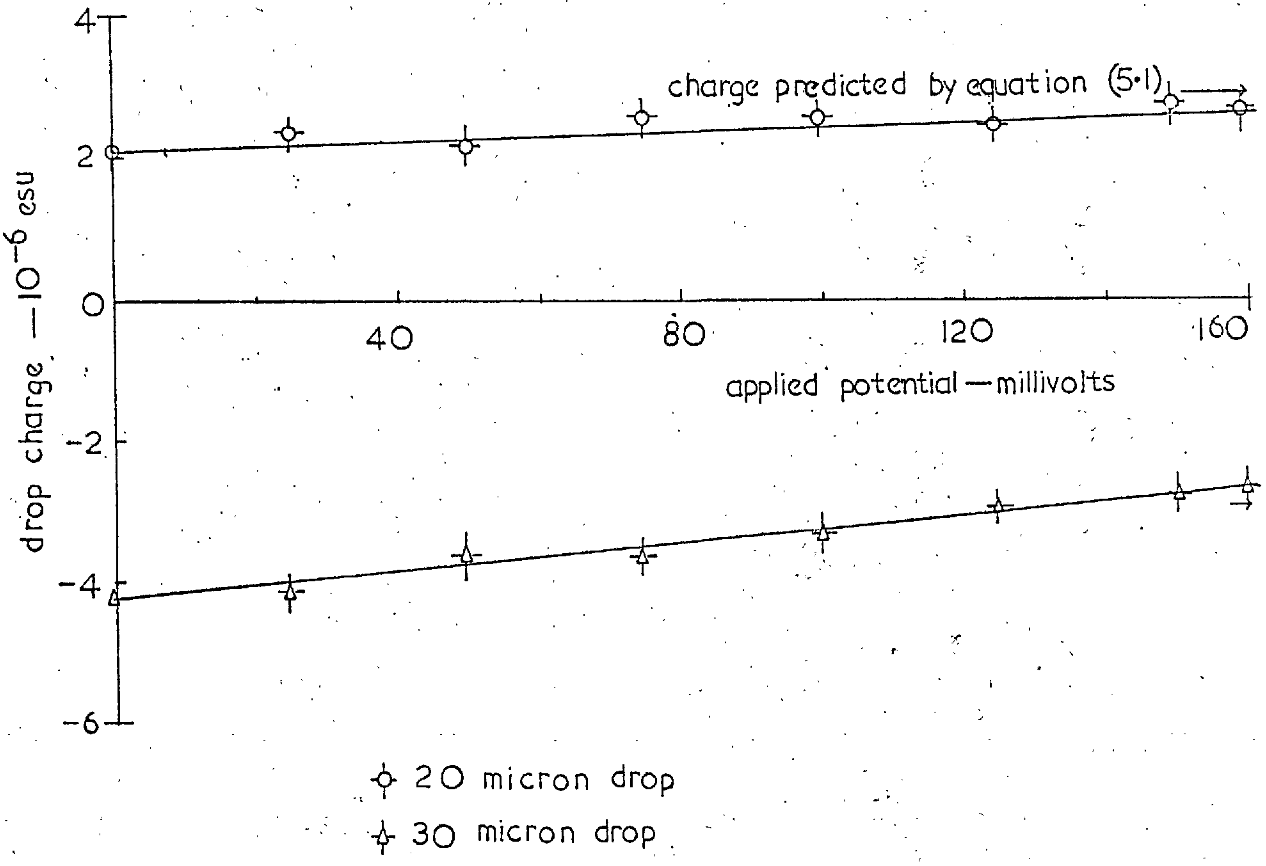


Fig 5·2 Variation of drop charges with needle potential

Charge calculated from equation 5·1 — $2{\cdot}9\times10^{-6}$ esu
Charge when potential gives zero total — $2{\cdot}6\times10^{-6}$ esu
Charge when zero charge on combined drops — $3{\cdot}0\times10^{-6}$ esu

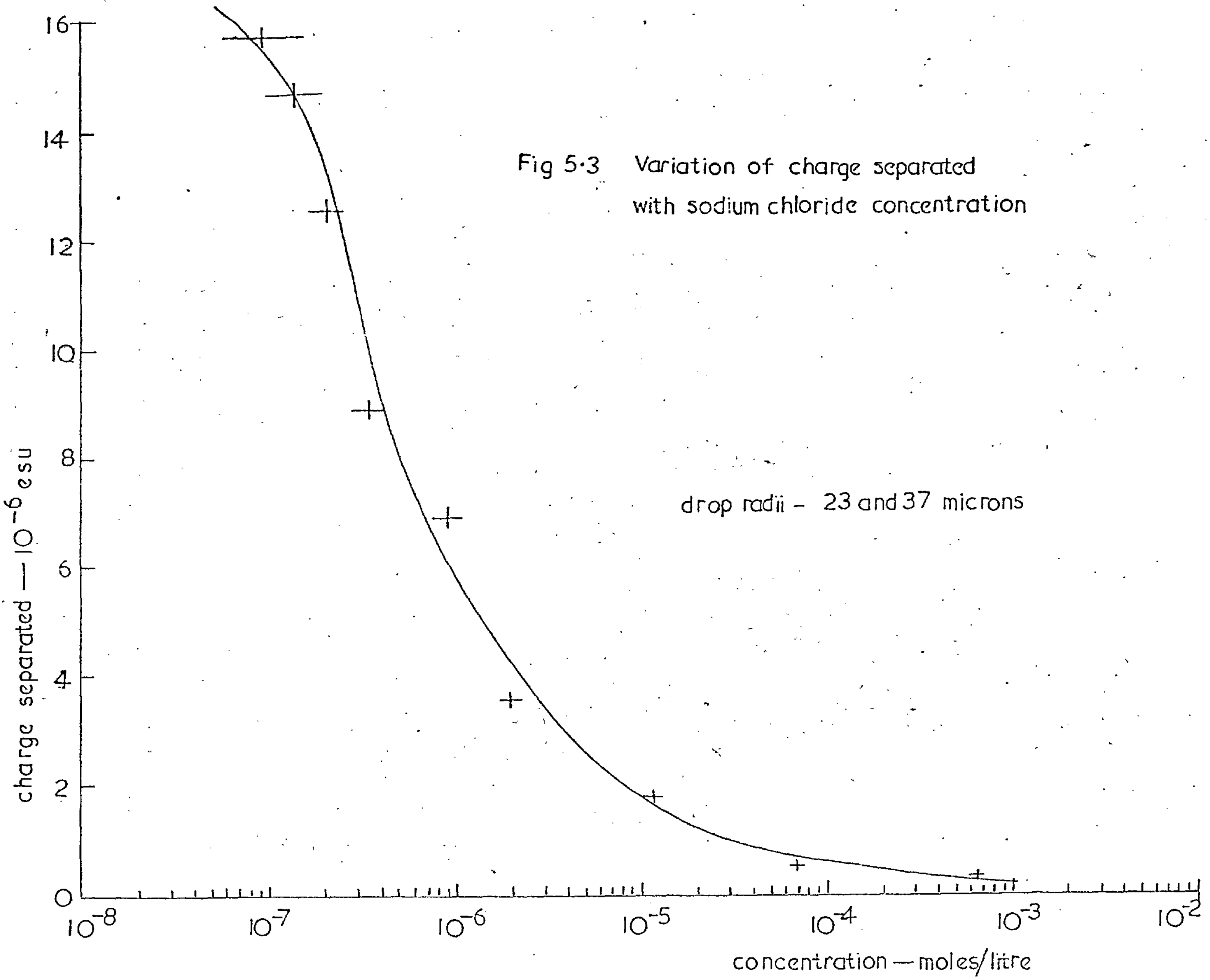


Fig 5·3 Variation of charge separated with sodium chloride concentration

drop radii - 23 and 37 microns

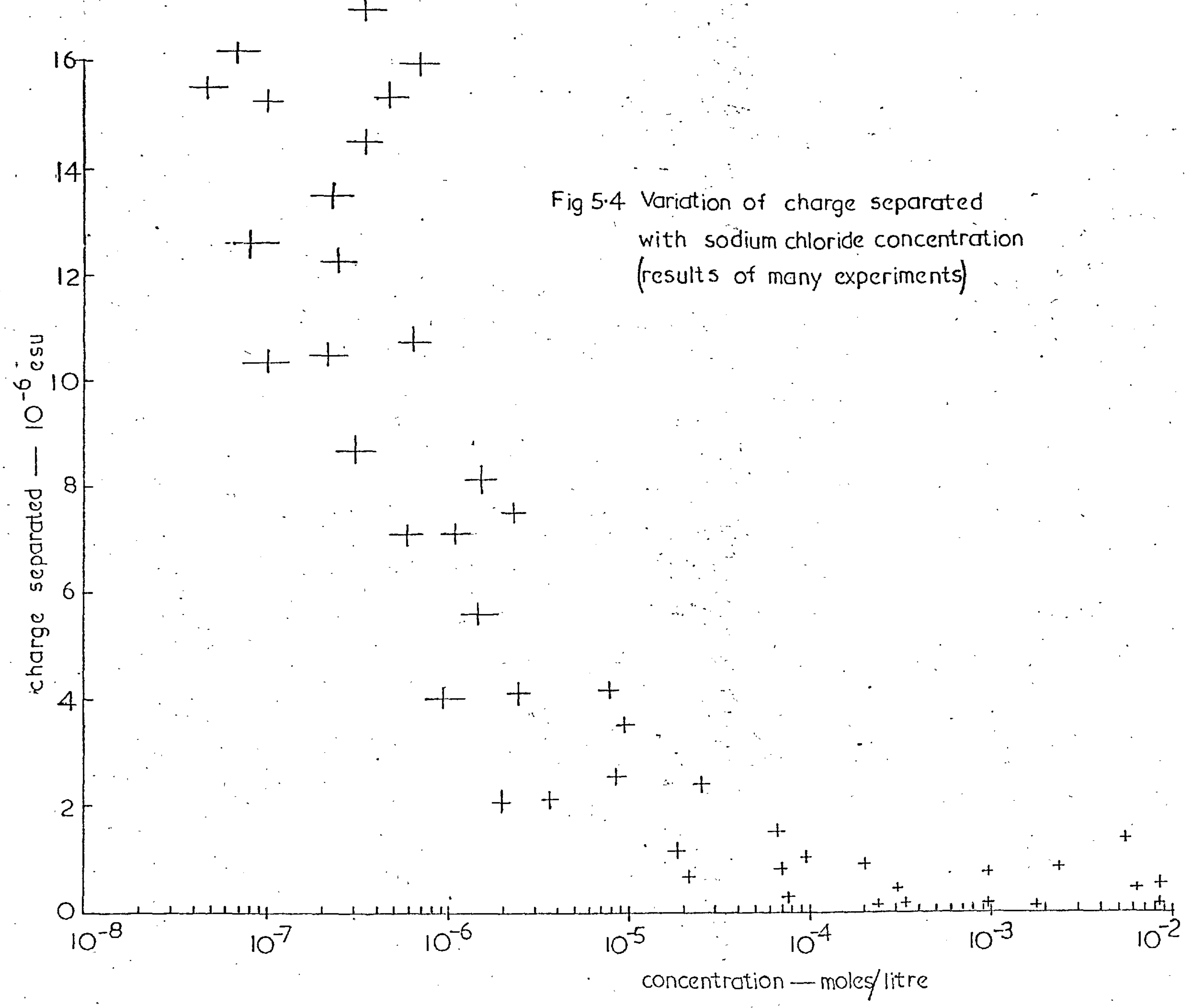


Fig 5·4 Variation of charge separated with sodium chloride concentration (results of many experiments) while the charge decreases by at least an order of magnitude over the range of concentrations used. The separation mechanism is therefore not very sensitive to the mode of break up of the jet of liquid. In ALL of these cases the smaller drop was positively charged and the ratio of the drop radii was less than 1:2.

5.2.4 Results of experiments with asymmetrical jets.

As has been mentioned it was possible to produce drops where radii differed by more than a factor of two by the break up of tapering jets. Under these circumstances the charging was reduced, the table below indicating that the charge decreased as the ratio of the radii increased. The limit of detection was 5 x 10^{-8} esu per drop.

drop radii microns		ratio of radii	concentration molar	charge 10^{-6} esu	sign of large drop change
21	53	2.5	2.0×10^{-7}	8.1	-ve
15	41	2.7	5.0×10^{-6}	1.1	-ve
29	84	2.9	1.0×10^{-4}	0.6	-ve
10	42	4.2	4.0×10^{-7}	1.1	-ve
14	61	4.2	9.0×10^{-6}	0.2	+ve
11	50	4.5	8.0×10^{-5}	<0.05	---

It should also be noted from this table that with the break up of highly asymmetrical jets the smaller of the drops produced was not always positively charged.

5.3 Break up into three drops

In a few cases it was possible to obtain a mode of break up where the jet broke up into three drops. Drops of radii 30μ - 40μ were formed from each end of the jet while the centre became detached to form a drop of about 20μ radius. This mode of break up was not very stable so that detailed experiments were not possible but a few results were obtained and these are shown in fig 5.5. The points show the charges on the larger drops, the potential on the needle being adjusted so that the charge on the smaller drop was equal and opposite to the sum of these. Both of the large drops were positively charged with a slightly larger charge on the larger drop.

5.4 Experiments using other chemicals

Iribarne and Mason (loc. cit.) noted that the charge separated by the bursting of bubbles at the surface of aqueous solutions was approximately the same for comparable concentrations of various inorganic salts. A few experiments were made with jet break up into two drops using solutions of thorium nitrate, ammonium chloride, and dilute hydrofluoric acid. The results are shown in fig 5.6 and it is seen that they are comparable with those using sodium chloride.

Attempts were made to repeat the experiments with solutions of surface active chemicals. When these were used they had no effect on the charging until the concentration was sufficient to affect the surface tension of the solution. In this case the break up became very unstable and measurements

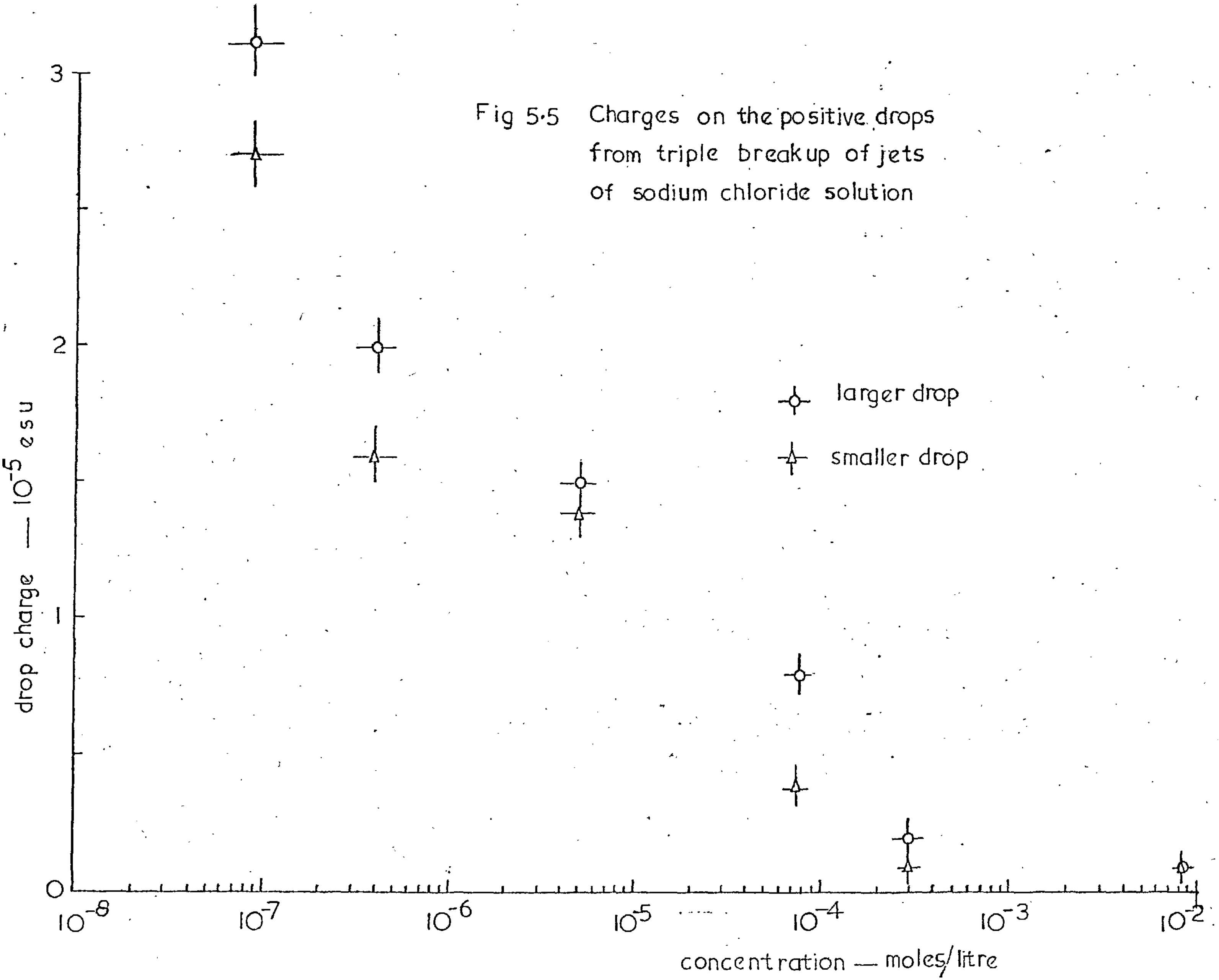


Fig 5·5 Charges on the positive drops from triple breakup of jets of sodium chloride solution

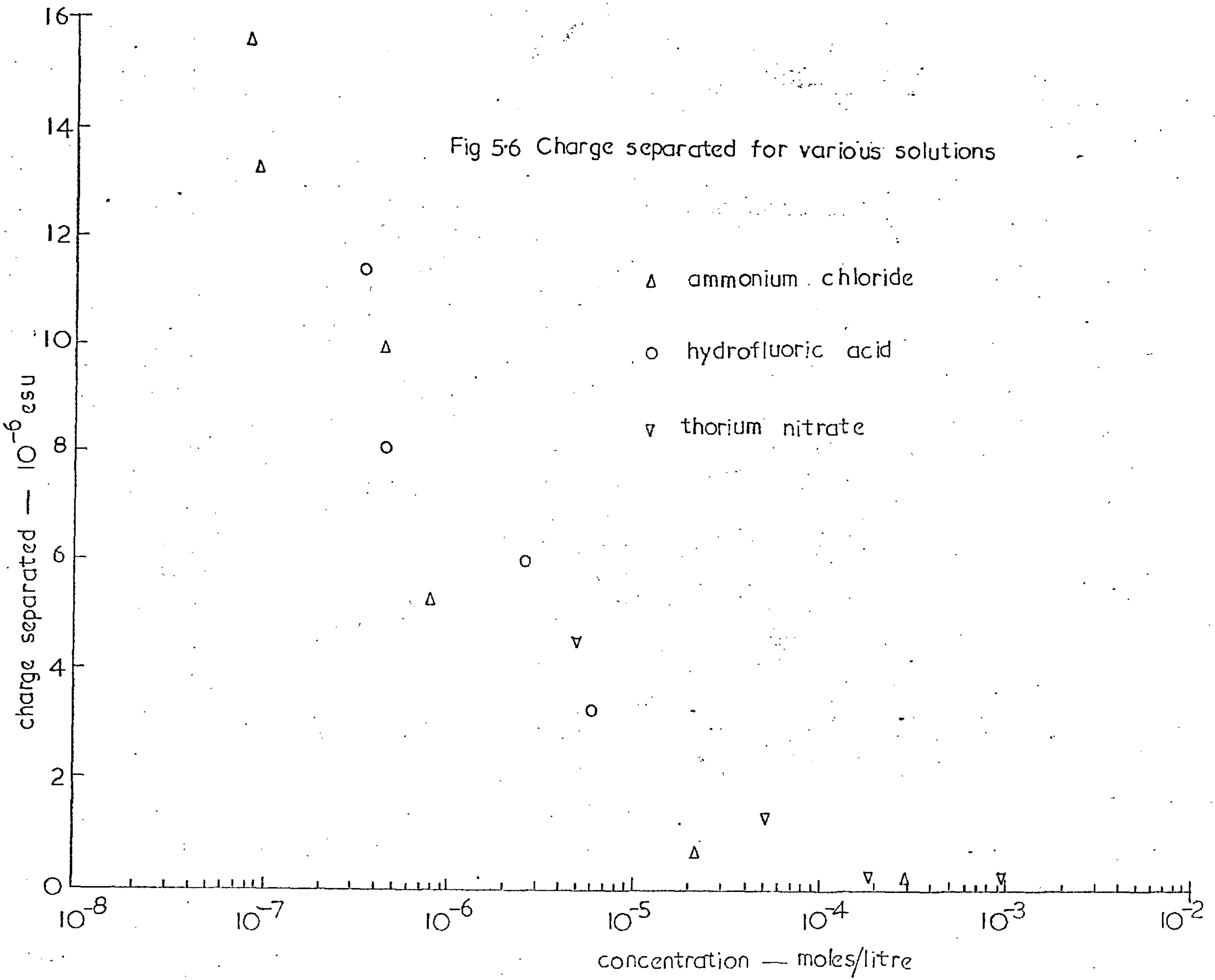


Fig 5·6 Charge separated for various solutions of the charge could not be made.

A few experiments were also made using the non-polar liquids, benzene, carbon tetrachloride, and a solution of stannic iodide in benzene. In all of these cases there was no detectable charge on the drops. Paraffin produced drops of small but erratic charge. The paraffin however was an ordinary commercial grade which could not be further purified.

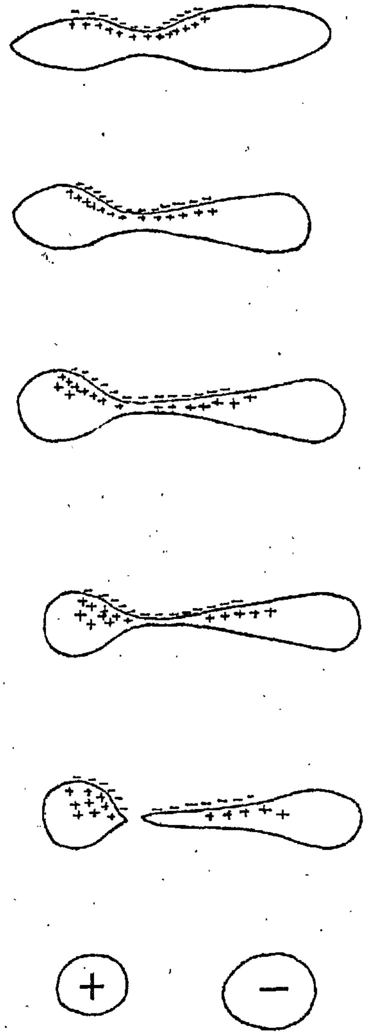
5.5 Explanation of the results

The results show that it is possible to separate charge by breaking up a jet of a polar liquid in a region free from any electric field. There is no possibility of the charging being due to any contact potentials. Statistical charging may have been present but this would have given a zero mean charge to the large number of drops sampled. This mechanism could not be responsible for the separation of the large charges measured. This leaves the possiblity of charge separation by the break up of the electrical double layer as the only mechanism by which the charge could have been separated. This idea would also predict that the drops of non-polar liquids would not be charged, as was found in this experiment. (The charge on paraffin drops was probably due to the formation of a surface charged layer by the impurities, which was subsequently broken.)

The measurements of the charge separated with the break up of the jet into three drops suggests that the central, thinnest, part of the breaking jet becomes negatively charged with the positive charge being separated towards the ends of the jet. This would also result in a negative charge being given to the larger drop when only two drops are formed from the break up of a symmetrical jet since it is this drop which absorbs most of the central part of the jet. The positive charge is therefore separated in the same direction as the liquid is forced when the jet thins at the centre and breaks. It seems probable therefore that it is the movement of the liquid which separates the charge, the sign of the charge being consistant with the idea that the interior of the liquid contains the diffuse region of positive charge. It is the development of the constriction in the jet and the break up by Rayleigh instability which forces liquid, and charge, to the ends of the jet, so that charged drops are produced when the jet finally breaks. This is shown in fig 5.7.

The break up of highly asymmetrical jets will separate charge again as rupture of the jet occurs, but in this case the larger drop may not absorb all of the thinnest part of the jet and may not therefore be negatively charged.

The results indicate qualitatively that the charge separation mechanism is the shearing of the double layer at the surface of the breaking jet. The magnitude of the charging which is to be expected is calculated later and is in good agreement with the experimental results. In particular the variation of the charge with the solute concentration is explained.



1 neck begins to form

2 neck elongates

3 asymmetrical constriction forms

4 constriction forces positive charge to wider end of neck

5 neck breaks at one end

6 larger drop with negative charge

Fig 5·7 Charge separation in breaking jet

CHAPTER SIX

Charging in the field of contact potentials

6.1 Introduction

It has been mentioned in section 1.4.2 that some authors believe that the charge separation when liquids splash off metal surfaces may be due to induction in the field of the metal-liquid contact potential. The first experiment which the author attempted in order to measure the charge separated when a liquid jet is broken showed how charging resulting from the disruption of the liquid could be obscured by charging due to contact potentials.

One of the most reproducible methods of producing, and breaking, a jet of liquid is utilised in the vibrating needle atomiser. The break up of the liquid jet emerging from the needle is perfectly regular and may easily be studied by stroboscopic methods. It was thought that measuring the charges on the drops produced by this method would be a simple way of measuring the charge separated when a jet of liquid is ruptured. The apparatus was convenient to set up so that the influence of such factors as the gaseous environment could be determined.

The effects of charging due to contact potentials were so great, however, that the experiments led to a calculation of the magnitude of the effect and a discussion of the methods of reducing these effects is included in this chapter.

6.2 The apparatus and experimental method

The apparatus consisted of the modified vibrating needle atomiser described in section 3.2. This was mounted in an air-tight screened box. Access being through a port which could be sealed. The apparatus was connected up as previously mentioned with the needle connected to the variable potential network. Water was supplied from the pure water apparatus and the break up of the jet at the tip of the needle could be studied using stroboscopic illumination.

It was possible to alter the concentration of solute in the water without altering the mode of break up, as observed with the telescope, provided that there was a flow rate of a few cm^3/min through the overflow to ensure thorough mixing. As has already been mentioned this flow rate was also necessary to prevent the absorbtion of impurities from the connecting tubing. The apparatus was very suitable for the production of a controlled jet of water containing various solute concentrations.

In all of the experiments described in this chapter the frequency and amplitude of the needle oscillations were adjusted so that a single stream of drops of radius about 100μ was produced. This type of break up occurred either if any satellite drops were captured by the larger drops, or if the liquid flow rate was just sufficient to prevent the formation of any small drops.

The drop charges were measured by allowing the drop stream to fall into an insulated can connected to an electrometer which measured the steady current carried by the drop stream. Division of this current by the drop production rate gave the mean charge on each drop. The drops were fired through a hole in an earthed screen between the needle and the can to prevent any movements of the can affecting the capacity of the drop as it was formed.

6.3 Experimental details and results

6.3.1 Experiments with pure water

The apparatus was flushed through with a stream of pure water until no further decrease in the conductivity was noted. A series of measurements of the drop charges was made using drops of radius 80μ - 120μ produced at rates from 665 per sec to 980 per sec. The drop sizes were obtained using a calibrated graticule in the telescope and the production rates from the frequency of the headphone oscillator. The charges on these drops varied from -5×10^{-6} esu to $+1.7 \times 10^{-5}$ esu. There appeared to be no connection between either the drop size or the frequency, and the sign or magnitude of the charge.

The experiment was repeated with the air in the screening box replaced by a non polar gas. Helium, nitrogen, and oxygen were used and a similar spread of drop charges found as with air. Replacement of the air by the gas while the mode of break up remained constant produced no significant change in the charge on the drops.

6.3.2 The uniformity of the charge on the drops

It has been noted that the jet break up was very regular and it was thought that the charges on the drops would also be regular. To investigate this it was necessary to measure the charges on the drops individually. This was most easily carried out by attempting to deflect the drop stream in an electric field between two parallel plates.

Some difficulty was experienced with this because of the very high polarisability of water in electric field. The force on water drops due to very slight inhomogeneities in the field was very large and exceeded the force due to the charge in the uniform field except with very low fields. It was therefore necessary to use very carefully aligned plates and finally a pair were obtained which were sufficiently accurate. The drops were fired through a small hole in an earthed plate into the 5 mm gap between the plates where the field was 4 kv/cm. The trajectory of the stream was observed with a telescope with the field of either sign or with both plates earthed. In all cases the stream followed a single path so that the drops must have been uniformly charged. The magnitude of the charge was not calculated, as the deflections when the field was reversed were not equal and opposite. This was presumably due to slight inhomogeneities in the field, the effect of which is independent of the direction of the field.

6.3.3 Experiments with sodium chloride solutions

A series of experiments was made in which the charge on the drops was measured as a function of the sodium chloride concentration in the water. The mode of break up of the jet being constant throughout the experiment.

It was found that the experimental results could be divided into two groups of which the graphs in fig 6.1 are examples. Some of the curves showed charges exceeding $+ 10^{-5}$esu per drop with pure water, the charging decreasing as the sodium chloride concentration was increased. The charge reversed sign at concentrations of between 10^{-6} molar and 10^{-5} molar and then the magnitude increased slowly with increasing concentration up to concentrations of about 10^{-2} molar. For some modes of break up of the jet the charges on drops of dilute solutions were smaller and negative. The charge decreased at concentrations from 10^{-6} molar to 10^{-5} molar, passed through a negative minimum and then increased slowly as the concentration was increased. All of the results showed the same variation of charge with concentration at concentrations above 10^{-4} molar, the negative charge increasing by about 3×10^{-6} esu for each order of magnitude increase in the concentration.

The variation of the charge with concentration did not appear to depend on the drop size or the production rate, but those modes of break up which produced positively charged drops of pure water gave charges which were a monontonic

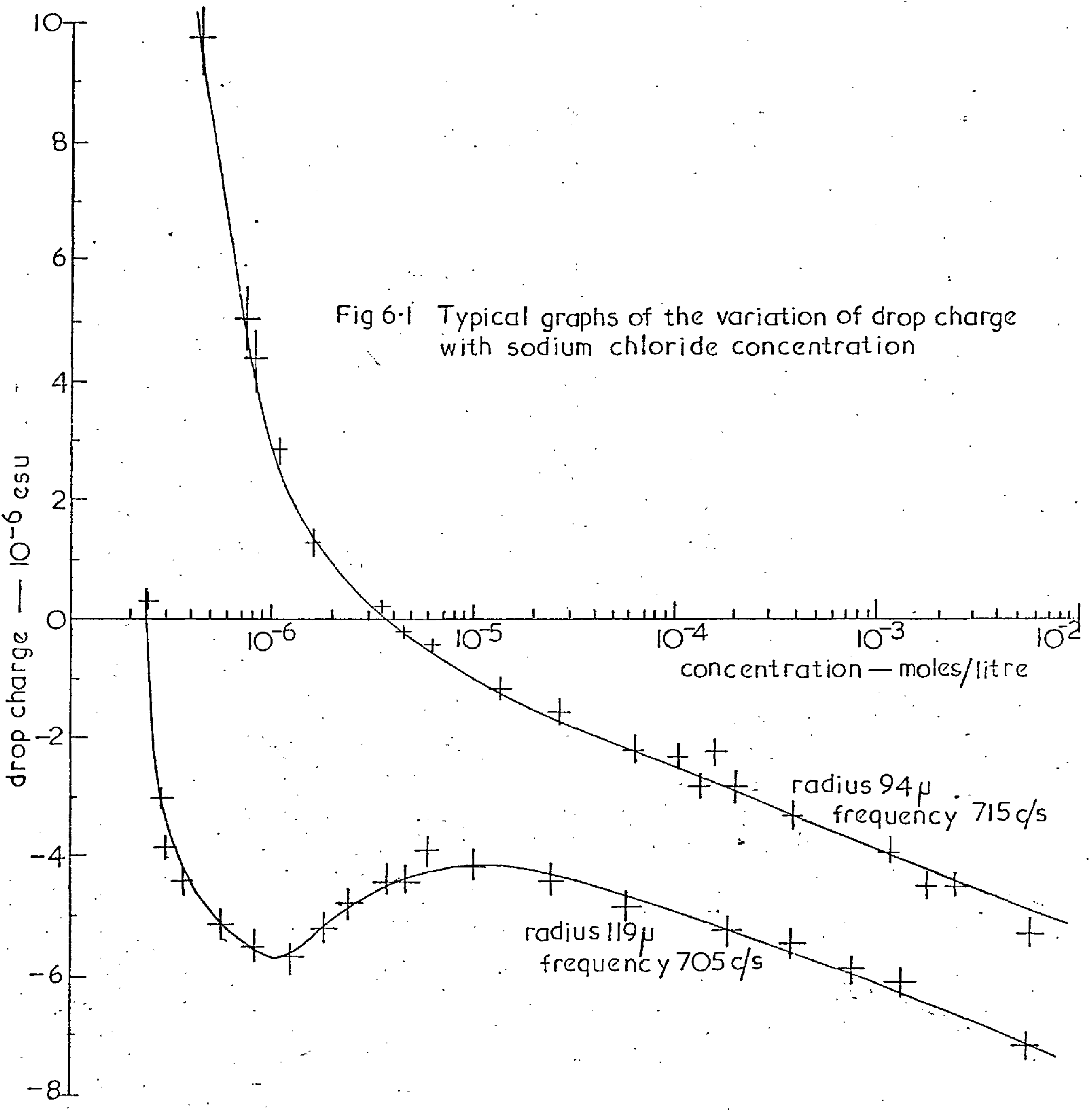


Fig 6·1 Typical graphs of the variation of drop charge with sodium chloride concentration function of concentration. The shapes of the experimental graphs indicated that probably two separate factors were responsible in separating charge and that the relative variation of each with concentration could produce either experimental curve. It was thought that in addition to charging as the double layer at the surface of the jet was broken, there was charging due to the field of the contact potential between the water and the needle.

6.3.4 The application of a potential to the needle

All of the experiments so far described were made using an earthed needle. It was decided to apply a potential to the needle and to measure the additional charge on the drops due to the potential. It was hoped that this would simulate the charging produced by a contact potential. It had been noted by Woods (private communication), using 10^{-4} molar solutions, that the application of about 5 volts to the needle in the atomiser produced drops with charges which were one third to a quarter of the product of the drop radius and the applied potential. The apparent capacity of the system was about one third of the drop radius. In Woods' experiments the additional charge was at least an order of magnitude larger than the charge on the drops produced using an earthed needle.

These experiments consisted of measuring the charges on the drops as a function of the concentration, both with the needle earthed or raised to a small known potential. The difference in the two sets of results gave the additional charge as a function of concentration. Fig 6.2 shows a typical result where a potential of 100 mv was applied to the needle when a large positive charge was present on pure water drops formed at the tip of the earthed needle. The additional charge was independant of the concentration of the solute except perhaps at low concentrations where there was a slight increase. The results shown in fig 6.3 however are typical of those obtained when the charge on drops of pure water produced using an earthed needle, was negative. The additional charge increased rapidly as the concentration was reduced below about 10^{-4} molar. In these cases a potential, less than +350 mv removed the maxima and minima from the experimental curves. In the example shown this critical potential was about 100 mv.

6.4 Discussion of the results

The suggestion is that the charge on the drops was the resultant of the charge separated during the break up of the jet and charging by the contact potential between the water and the needle. We shall consider the resultant of two charging mechanisms both producing charges which decrease with increasing concentration of the solution. One of these mechanisms, which will be identified with the separation of charge during the break up of the jet, gives positive charges at low concentrations which become small at concentrations above 10^{-3} molar. The contact potential is assumed to give rise

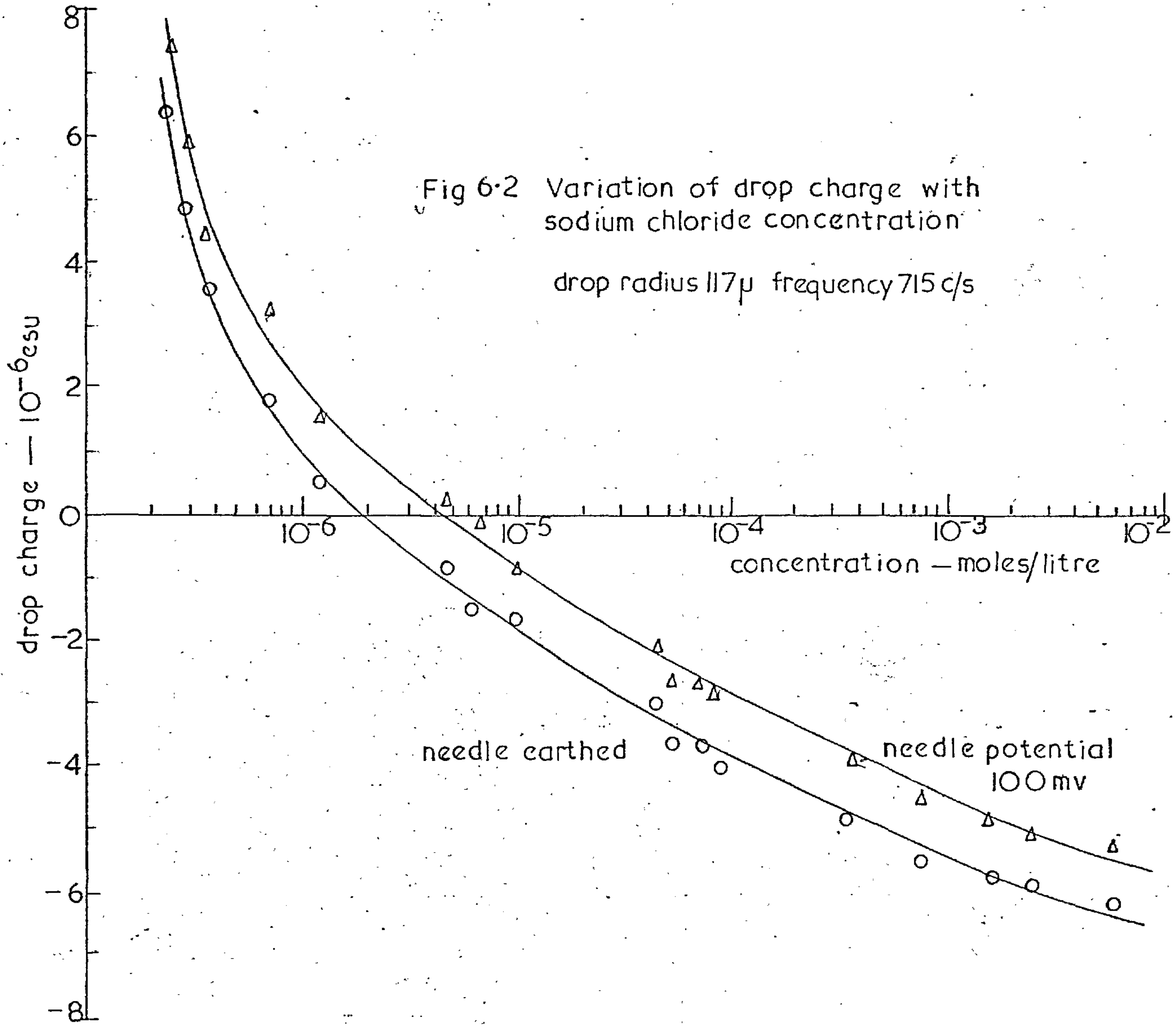


Fig 6·2 Variation of drop charge with sodium chloride concentration

drop radius 117μ frequency 715 c/s

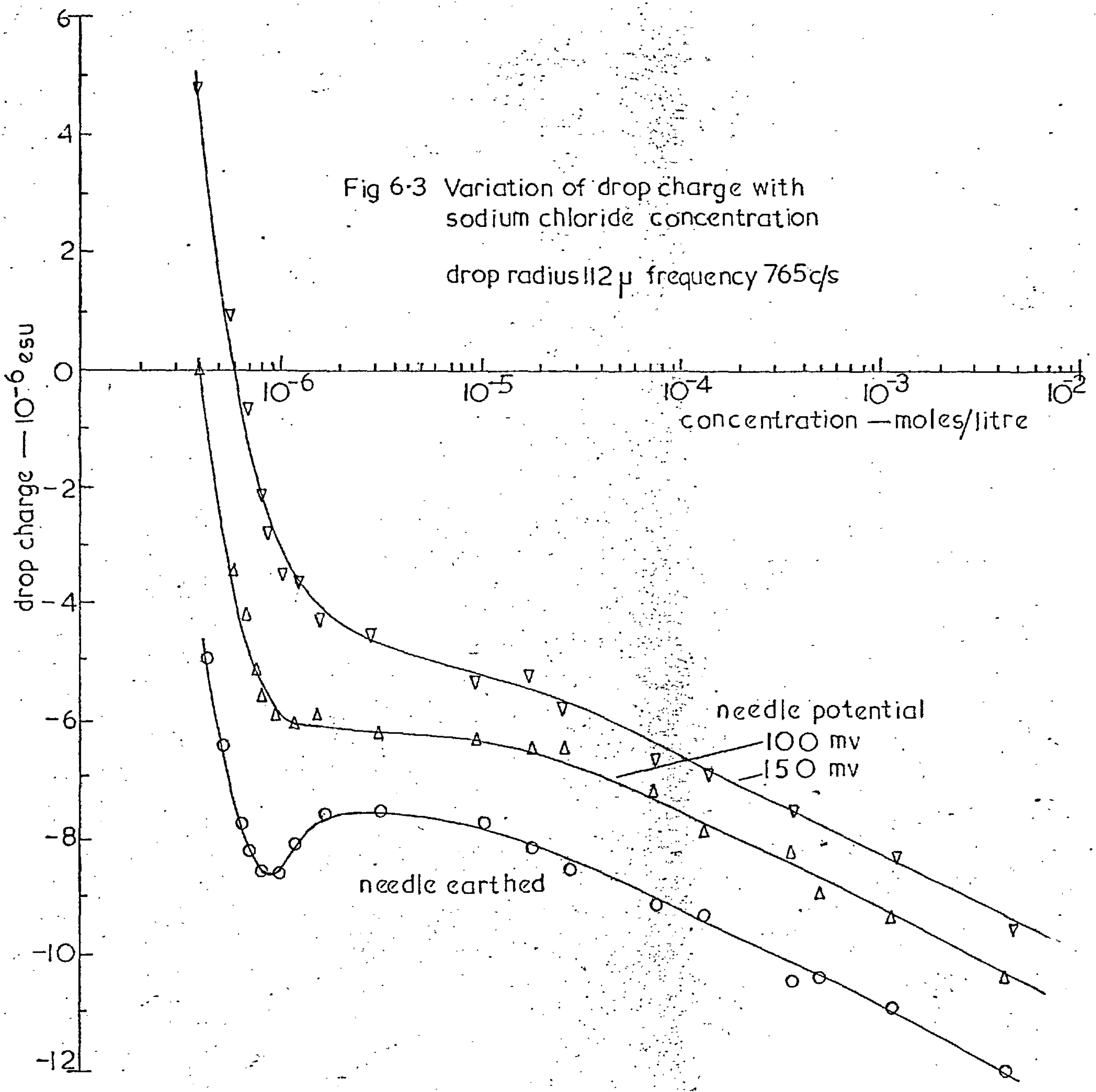


Fig 6·3 Variation of drop charge with sodium chloride concentration

drop radius 112 μ frequency 765 c/s

to negative charging of the drops, the magnitude being constant at high concentrations but increasing at low concentrations. The increase being appreciable below some critical concentration c_c which is between 10^{-7} molar and 10^{-3} molar. Fig 6.4a shows the resultant of the two mechanisms if c_c is about 10^{-4} molar and fig 6.4b the resultant if c_c is about 10^{-6} molar. It is seen that the variation of the resultant charge with solution concentration is similar to the two types of experimental results so that if the two charge separation mechanisms do separate charge as suggested above this will explain the experimental results.

The separation of charge in a breaking jet is considered in detail in chapter 7 where it is shown that this mechanism does separate charge as indicated above and this charge decreases as the solution concentration is increased.

The variation of the charges due to the contact potential with the concentration of the solution is more difficult to calculate and even the variation of the contact potential itself with the concentration is not well known. We shall consider in the first instance however that the potential is independant of the concentration. As the liquid emerges from the needle as a large drop it is charged by the contact potential, but as the drop is drawn out into a jet the capacity of the system decreases. Charge therefore flows back to the needle, the current depending on the geometry of the jet and the conductivity of the solution. If the

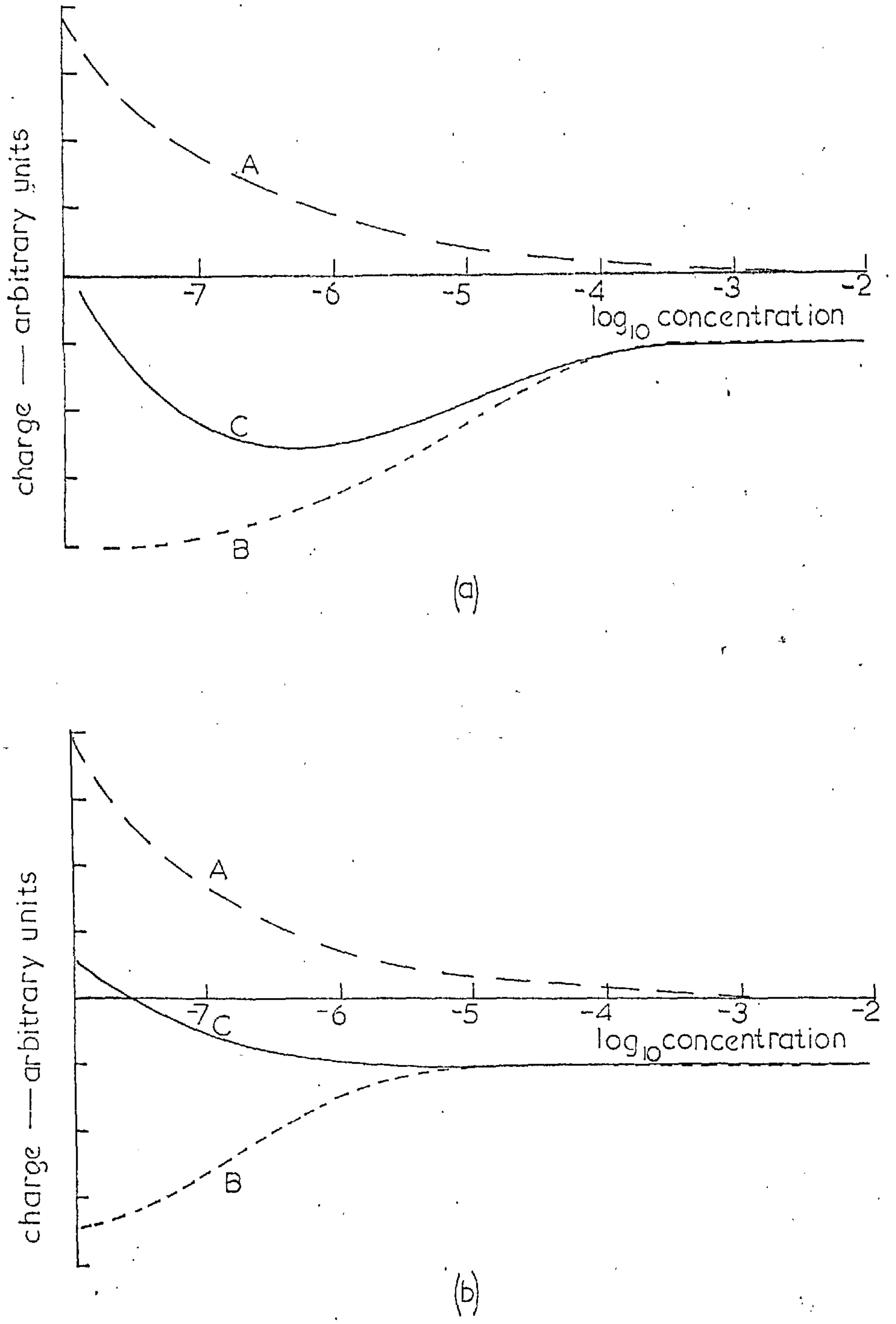


Fig 6·4 Variation of charging with solute concentration

A charge separated during jet break up
B charge due to contact potential
C resultant charge

conductivity is high the charge on the jet will tend to some constant value determined by the capacity of the system when the jet breaks, and the contact potential. The charge may not reach this constant value in the time available if the conductivity of the solution is low, so that we might expect in this situation, the contact potential charge to increase with decreasing solution concentration. The concentration at which this increase will become appreciable will depend on the geometry of the breaking jet. It is seen that the charge due to the contact potential could vary with concentration in either of the ways found for the charge due to the potential applied to the needle.

It was observed that the application of a potential of less than 350 mv to the needle removed the maxima and minima from the experimental results so that we would expect the contact potential difference to be less than 350 mv, the water being negative. This potential would produce charges about 3×10^{-6} esu on a system with a capacity of 3×10^{-3} cm. This is about one third of the capacity of an isolated 100μ drop which Woods showed was the capacity of the system when the drop breaks off from the jet. This charge is in reasonable agreement with the magnitude of the charge observed at high concentrations when charge separation in the breaking jet is small. The slight increase in the charge at very high concentrations was probably due to an increase in the contact potential, the value of which is not knownbut metal-water potentials are typically 250 mv - 500 mv.

We would expect those modes of break up where the jet remains of large radius for a considerable part of the drop formation time to give a contact potential charge independant of the concentration, but more slender jets would prevent the charge reaching the equilibrium value with low conductivity solutions. There is considerable evidence for this from the analysis of photographs taken of the breaking jets. The dividend of the jet length and the mean square radius, which determines the resistance of the jet, varies from 10^3 cm^{-1} for thicker jets to 10^4 cm^{-1} for the thinner jets.

In order to verify our hypothesis about the variation of the charge due to the contact potential with concentration, and how this depends on the geometry of the neck we will calculate the charge at least to within an order of magnitude.

6.5 Calculation of the charge due to the contact potential

We consider the charging due to the contact potential as the jet breaks, the water initially being charged to the potential V. At any instant the charge on the jet is q while the length and mean radius of the jet are l and r respectivly. If the capacity of the system is C and the resistivity of the solution is R, then

$$\frac{dq}{dt} = \frac{q\pi r^2}{l\ R\ c} \qquad (6.1)$$

For sodium chloride solutions $R \sim 10^{-11}/c$ where c is the molar concentration. Integrating (6.1) over the time of formation and break up of the jet, T.

$$q = q_f + q_o \exp - kc$$

where q_f is the equilibrium charge if $R = 0$

$$k = 10^{11} \int_0^T \frac{\pi r^2}{l\,C}\, dt$$

q_o is the original charge on the liquid at the needle tip.

Clearly k, q_f and q_o depend on the geometry of the breaking jet. Considering simple models of the breaking jet it can be shown that $5 \times 10^5 < k < 5 \times 10^6$. q_o can be shown to be less than 10^{-3} esu so that $q - q_f < q_f$ when $kc > 7$. With the range of values of k this gives critical concentrations in the range 10^{-6} molar to 10^{-5} molar. It is seen that the spread in the possible concentrations, below which the charge due to the contact potential increases as the concentration is reduced, is sufficient to explain the shapes of the various experimental graphs.

It seems probable therefore that the results obtained in this experiment can be considered as the resultant of a positive charge separation in the breaking jet, which has been charged by the contact potential.

6.6 Reducing the effects of charging due to contact potentials

This experiment has shown the importance of the contact potential as a charging mechanism and it is necessary to show how the effects could be reduced. Bloch (loc. cit.) showed that contact potential charging was small using an atomiser which used a large number of bubbles to break up water. This is to be expected because the change in capacity of the large volume of liquid, when a drop is formed, is very small so that the charges due to the contact potential are very small. Drops breaking in free space cannot be charged by this mechanism, but when a drop splashes from a metal plate covered by a thin liquid film the change of capacity may be sufficient for a large charge to be separated. This was probably the cause of the spurious results obtained by some early workers on splashing unless the surface was "well covered with the liquid". It is necessary, to reduce the charging due to the contact potentials, to ensure that the disrupting liquid surfaces are separated from any solid surfaces by a depth of liquid much greater than the radius of any drops produced by the disruption.

CHAPTER SEVEN

The Double Layer and Charge Separation

7.1 Introduction

The early experiments on electrification by splashing and on the catophoresis of gas bubbles gave results which led to the idea that there was a surface layer of charge on the surface of many liquids. The electrification was believed to be produced by the shearing of the components of this double layer, parallel to the surface, during the formation of thin films. The drops were then formed from parts of the charged film. Various theories have been proposed to explain the structure of the double layer and some of these have been very complicated. It seems possible to interpret many of the present experimental results in terms of a relatively simple model of the electric double layer.

7.2 The Structure of the Double Layer

It has previously been mentioned that the double layer is believed to consist of three parts. The surface layer of the liquid is believed to consist of a layer of partially oriented dipoles. Beneath this layer is a compact layer of charge which is tightly bound by the field of the dipoles. The compensating charge of opposite sign is in a more diffuse region of charge since the thermal disruptive energy is relativelymore important than the binding electrical forces. While it is difficult to separate the components of the double layer, it is believed that the motion of liquid past the surface will cause a shearing of the diffuse layer which will result in the transport of charge parallel to the surface. In the case of water and aqueous solutions the double layer is believed to consist of a negative compact layer and a diffuse region of positive charge. We shall consider the distribution of charge in this diffuse layer in an attempt to calculate the charge separation possible when the layer is sheared. Several theories of the layer have been summarised by Adamson (loc. cit.) together with extensions of the theories, and we shall follow the treatment of Gouy (1910) for the charge density beneath a plane charged surface.

We shall consider points at a distance x below the surface of the diffuse layer. This distance will be almost identical with the distance below the liquid surface since the compact layer is only a few tens of angstroms thick. At this point the charge density will be denoted by ρ and the potential by ψ. The origin of potential being taken so that $\psi \rightarrow 0$ as $x \rightarrow \infty$.

The concentrations, n, of the positive and negative ions of valency z at the point will be governed by the Boltzmann distribution law:

$$n_+ = n_0 \exp\left\{- \frac{z e \psi}{k T}\right\}$$

$$n_- = n_0 \exp\left\{+ \frac{z e \psi}{k T}\right\}$$

where, e is the electronic charge

k is Boltzmanns constant

T is the absolute temperature

n is the mean ion concentration

The total charge density ρ at the point is then given by

$$\rho = (n_+ + n_-)\, ze = -2\, n_o ze \sinh \left\{\frac{z\, e\, \psi}{k\, T}\right\} \qquad (7.1)$$

We will only have variations of charge density in the x direction so that Poisson's equation reduces to

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi\rho}{D}$$

Where D is the dielectric constant

$$\frac{d^2\psi}{dx^2} = \frac{8\pi n_o z\, e}{D} \sinh \left\{\frac{z\, e\, \psi}{k\, T}\right\} \qquad (7.2)$$

Integrating (7.2) with the condition for a neutral liquid,

$\left\{\frac{d\psi}{d\,x}\right\} \to 0$ as $x \to \infty$

$$\frac{d\,\psi}{d\,x} = \frac{8\pi n_o z\, e}{D} \sinh \left\{\frac{z\, e\, \psi}{k\, T}\right\} \qquad (7.3)$$

Further integration gives

$$\log \tanh \left\{\frac{z\, e\, \psi}{4\, k\, T}\right\} = -\left\{\frac{8\pi\, n_o z^2 e^2}{D\, k\, T}\right\}^{\frac{1}{2}} (x - x_o) \qquad (7.4)$$

With the usual notation for a solution of concentration c

$$\left\{\frac{8\pi\, n_o z^2 e^2}{D\, k\, T}\right\}^{\frac{1}{2}} = K \approx 3 \times 10^7\, c^{\frac{1}{2}}$$

Hence

$$\tanh\left\{\frac{z\,e\,\psi}{4\,k\,T}\right\} = \exp - K\,(x - x_0) \qquad (7.5)$$

Now for monovalent electrolytes at room temperature $z\,e\,\psi < k\,T$ so that

$$\psi \propto \exp\,(-\,K\,x) \qquad (7.5a)$$

We see that $(1/K)$ is the effective thickness of the double layer. It is also the radius of ionic influence calculated by Debye and Huckel.

It will be useful to evaluate the charge contained in a volume of unit cross section extending into the liquid from a depth x below the surface. This will be calculated in the general case.

We have

$$\rho = -\frac{D}{4\pi}\,\frac{d^2\psi}{d\,x^2}$$

The charge σ in the volume is therefore

$$\sigma = \int_x^\infty \rho\,d\,x = -\frac{D}{4\pi}\int_x^\infty \frac{d^2\psi}{d\,x^2}\,d\,x$$

$$= -\frac{D}{4\pi}\left[\frac{d\,\psi}{d\,x}\right]_x^\infty$$

But $\left\{\frac{d\,\psi}{dx}\right\} \to 0$ as $x \to \infty$

Substitution from (7.3) gives therefore

$$\sigma = \left\{\frac{2\,D\,n_0\,k\,T}{\pi}\right\}^{\frac{1}{2}} \sinh\left\{\frac{z\,e\,\psi}{2\,k\,T}\right\} \qquad (7.6)$$

7.3 The break up of the double layer

It is necessary, before calculating the charge which may be separated when the double layer is ruptured, to consider the ways in which this break up may be achieved.

When a thin film of liquid, such as a bubble cap, is formed it is observed to thin from the centre. The thinning causes the diffuse region of charge to be forced towards the edges of the film so that when it breaks up, charged drops of opposite sign are formed from the centre and the edges of the film. Although the film thins to 10^{-6} cm when it perforates the filaments are much larger and break to form drops of the order of 1μ radius which rapidly evaporate to form small ions.

A bubble of gas in an ionic liquid is observed to move as if charged when an electric field is applied across the liquid. This charge is due to the excess charge in the surface layers of liquid. The charge in the bulk liquid however, is opposite to that on the bubble surface so that it will move in the opposite direction under the applied field. This will give a region of high shear in the liquid at some point in the diffuse layer, the potential at this depth being called the electrokinetic or zeta potential. The binding in the layer between this depth and the surface is so strong that the layer can be regarded as being rigid.

Under the influence of a mechanical force however the interior of a liquid may be forced past the outer layers.

The outer layer will act as a solid boundary but below this the liquid velocity will increase with depth. This relative motion between the inner and outer parts of the liquid will separate charge. The shearing of the double layer will be resisted by electrical forces in addition to the normal viscous forces. Davis and Rideal (1961) have shown that if we are only considering depths greater than the thickness of the double layer the electrical forces are negligible compared with the viscous forces. It was also shown that to the same approximation the dielectric constant in the double layer could be treated as being the same as that in the bulk liquid.

The various velocity profiles in situations where shearing of the double layer occurs are shown in fig 7.1. These show the profile below a bubble surface in the presence of an electric field, the profile if the surface of a liquid is skimmed of at some depth d below the surface, and that in a pipe of liquid the walls of which are composed of the rigid outer layers of liquid.

We shall use this last case as being applicable to a breaking liquid jet. As the jet collapses the bulk liquid is forced from the thinnest point towards the ends, past the outer layers. Thus the diffuse charge is transported towards the ends of the breaking jet leaving a thin charged neck composed mainly of the compact layer. The flow of liquid will be due to the excess pressure at the centre of the neck resulting from the surface tension forces, and in order to

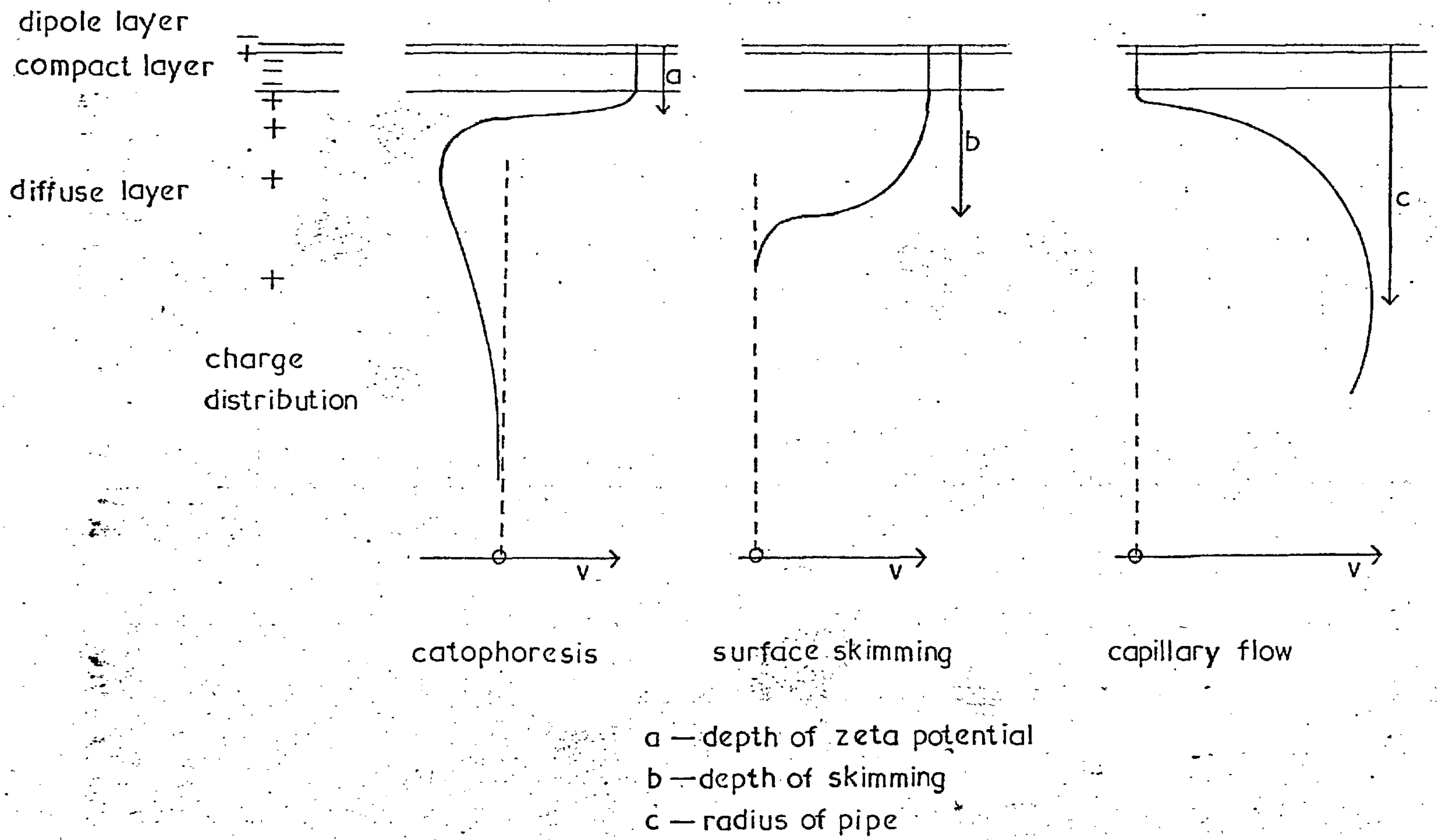


Fig 7·1 Diagram of charge distribution in the double layer, and surface velocity profiles (v) calculate the flow it is necessary to consider the shape of the neck while it is breaking up. Iribarne and Mason assumed that the neck had a sinusoidal profile and used this to calculate the charge separation. Goren however showed that the profile was not sinusoidal but approximated to a cylinder joining two almost spherical ends. It is seen from photographs, e.g. fig. 5.1, that even in the case of water jets breaking up there are considerable departures from a sinusoidal jet.

The excess pressure at the centre of a cylindrical jet of radius s and length 2 l is $P = \gamma/s$ where γ is the surface tension. In the case of a jet with a sinusoidal profile the expression is $P = 2\gamma\left\{\frac{1}{2a - s} - \frac{\pi^2 s}{l^2}\right\}$ where s is now the radius of the constriction, a the undisturbed radius, and the wavelength of the disturbance equals the length 2 l. This will not be appreciably different from the more simple expression unless $a \gg s$. Now a is a radius of the undisturbed jet not the radius of the drops produced, and it will be shown that most of the charge separation occurs before the amplitude of the disturbance is very large so that for the charge separation process the simpler expression may be used. It will be shown that this introduces errors which are small compared with other approximations which will be used.

We shall consider that the flow in the pipe due to this excess pressure is streamline and that the pressure at the ends of the pipe is small. The velocity u(r) of a cylinder of liquid of radius r will then be given by

$$u(r) = \left\{\frac{\gamma}{4\eta l s}\right\}(s^2 - r^2)$$

where η is the liquid viscosity

If the charge density in this ring is $\rho(r)$, the current i flowing is

$$i(r) = 2\pi r \, dr \, u(r) \, \rho(r)$$

so that the total current I is

$$I = \int_0^s \frac{2\pi r\gamma}{4\eta l s}(s^2 - r^2)\,\rho(r)\,dr \qquad (7.7)$$

We shall only consider the case where s K > 1 so that the charge density below the curved surface is approximatly that beneath a plane surface.

Equation (7.6) gave

$$\sigma = \left\{\frac{2 D n_0 k T}{\pi}\right\}^{\frac{1}{2}} \sinh\left\{\frac{z e \psi}{2 k T}\right\}$$

and from (7.5)

$$\tanh\left\{\frac{z e \psi}{4 k T}\right\} = \exp - K(x - x_0)$$

Now for monovalent solutes at room temperature $e\psi > 4kT$

$$\therefore \sinh\left\{\frac{z e\psi}{2 k T}\right\} \approx \left\{\frac{z e\psi}{2 k T}\right\} \not\approx 2\tanh\left\{\frac{z e\psi}{4 k T}\right\}$$

Substitution in (7.6) gives

$$\sigma = \left\{\frac{8\ D\ n_0 k\ T}{\pi}\right\}^{\frac{1}{2}} \exp -K(x - x_0) \qquad (7.8)$$

Now $\rho = \dfrac{d\sigma}{d\ x}$

$$\therefore \rho(x) = -K \left\{\frac{8\ D\ n_0 k\ T}{\pi}\right\}^{\frac{1}{2}} \exp -K(x - x_0) \qquad (7.9)$$

Changing the notation we can identify (s - r) with x so that

$$\rho(r) = -K \left\{\frac{8\ D\ n_0 k\ T}{\pi}\right\}^{\frac{1}{2}} \exp -K(s-r-x_0) \qquad (7.10)$$

Substitution in (7.7) gives

$$I = -\frac{\pi\gamma K}{2\eta ls}\left\{\frac{8D\ n_0 k\ T}{\pi}\right\}^{\frac{1}{2}} \exp -K(s - x_0) \int_0^s (s^2 - r^2) \exp(Kr)dr$$

Which gives on integration

$$I = \frac{\pi\gamma K}{2\eta ls}\left\{\frac{8Dn_0 k\ T}{\pi}\right\}^{\frac{1}{2}} \exp -K(s-x_0) \cdot \left[\left\{\frac{2s^2}{K^2} - \frac{6s}{K^3} + \frac{6}{K^4}\right\} \exp(Ks) + \frac{s^2}{K^2} - \frac{6}{K^4}\right]$$

Now K $s > 1$ so that many of the terms can be neglected

$$I = \frac{\pi\gamma}{2\eta ls}\left\{\frac{8D\ n_0 k\ T}{\pi}\right\}^{\frac{1}{2}} \exp(K\ x_0)\frac{2s^2}{K} \qquad (7.11)$$

Davis and Rideal have shown that the value of ψ at the surface of dilute aqueous solutions is about 70 mv and independant of the concentration. Substitution of this value when $x = 0$ is equation (7.5) gives $Kx_0 = -0.5$. Also for Rayleigh instability $l = \pi s$. Substitution of these and the other constants in (7.11) gives a charging current

$$\underline{I = 10 \text{ esu/sec}} \qquad (7.12)$$

The charging current calculated by Iribarne and Mason was an order of magnitude smaller than this being given by

$$I = 37\,\frac{x^3(1 - x)}{(1 + x)}$$ where x varies from 0 to 1 during the break up

It is noted that to our approximation the charging current is independant of both the concentration and the jet radius. We would expect the theory to break down when Ks = 1. This happens for jets of radius less than 1 micron for pure water and for jets as thin as 10^{-6}cm for solutions of concentrations greater than 10^{-3} moles/litre.

7.4 Calculation of the charge separation

In order to calculate the charge separation it is necessary to know not only the charging current but also the break up time of a jet and the losses due to conduction.

Castleman (loc.cit.) has calculated the break up times for liquid jets. The amplitude of the disturbance was assumed to increase from some small value, perhaps 10^{-6}cm, to the radius of the jet. The break up times for aqueous jets of initial radius s was shown to be given by $t \approx 0.9 s^{3/2} \log s/\alpha$, where α is the initial amplitude. These results are plotted in fig 7.2. Newitt et al (1954) have obtained good agreement with this theory working with the jets produced by bursting bubbles. Crane et al (loc.cit.) obtained break up times of the order of 5×10^{-3} sec for 4×10^{-2}cm radius jets which is in good agreement with the theory as a large amplitude disturbance was used to break up the jet, even though the profile of the disturbance was not sinusoidal.

The losses due to conduction are difficult to calculate,

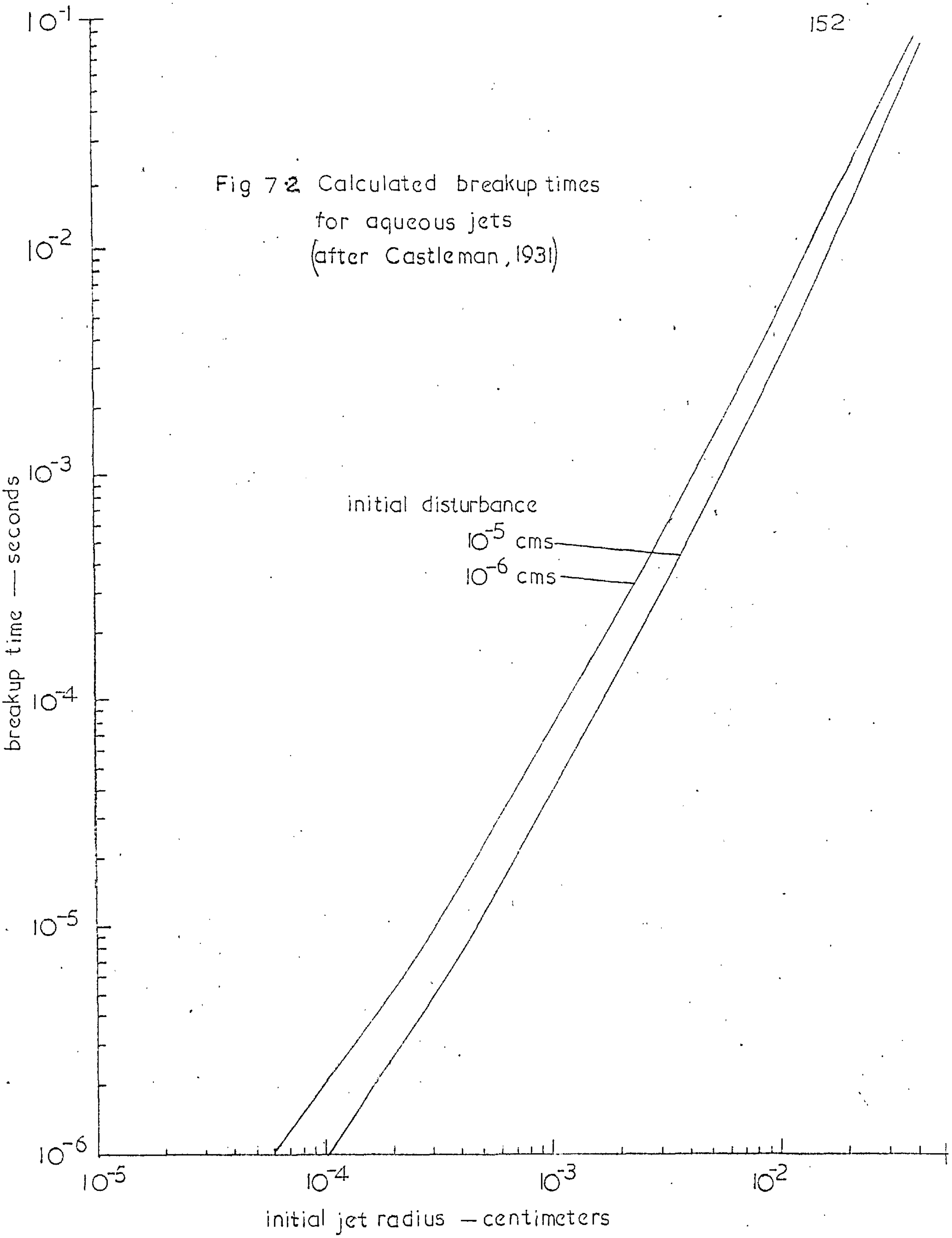


Fig 7·2 Calculated breakup times for aqueous jets (after Castleman, 1931) but the maximum charge which can be separated is found by equating the reverse conduction current to the charging current. Suppose that the capacity of the system is C and the maximum charge is q max, then with the same notation as before the reverse current is

$$I_r = \frac{\pi s^2 \; q \; \max}{2 \; R \; l \; C}$$

where R, theresistivity of the solution $\sim 10^{-11}/c$ for sodium chloride.

For Rayleigh instability $l = \pi s$ so that the maximun charge, when $I_r = 10$ is given by

$$10 = \frac{cs \quad q \; \max}{2.10^{-11} C}$$

$$q \; \max = \frac{2.10^{-10} C}{cs}$$

We see that although the charging current is independant of the jet radius, the maximum charge increases as the radius decreases. It should also be noted that the maximum charge is proportional to the capacity of the system.

The charge separated as the jet thins from some initial radius can be calculated, and is shown in fig 7.3 together with the maximum charge, as a function of radius for a capacity of 10^{-2}cm. While the maximum charge depends on concentration, the total charge separated depends only on the initial radius of the jet. Initially there is a rapid increase in the charge separated and, depending on the concentration,

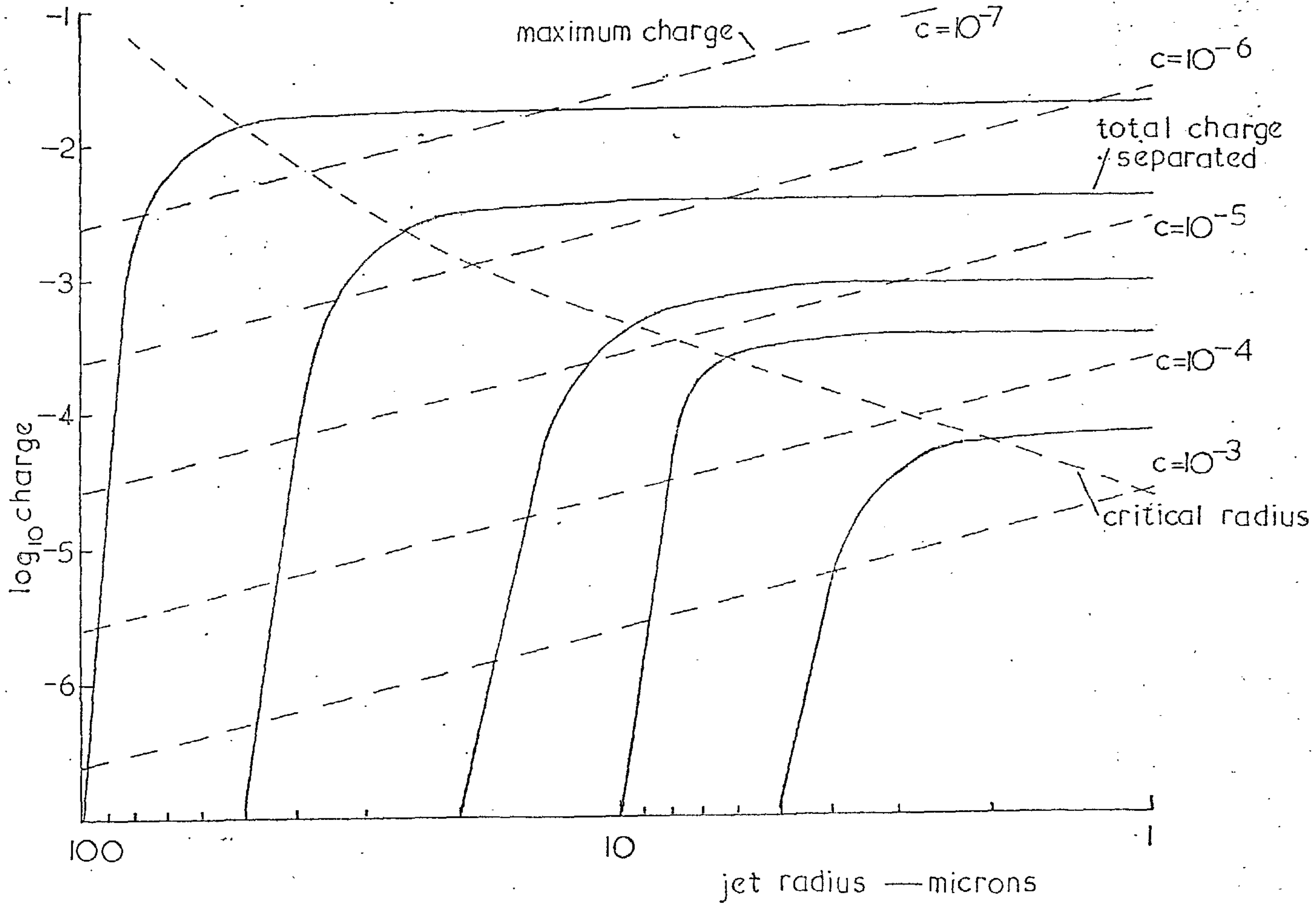


Fig 7·3 Charge separation against jet radius this may reach the maximum. If this would occur, however the charging rate decreases due to the high reverse current, and the charge tends to the maximum, increasing as the radius decreases. At some critical radius the charging current cannot maintain the increase in the maximum charge so that the charge then departs from the maximum and continues to increase at a rate depending on the charging current. This produces very little additional charge separation, owing to the short life of the jet after reaching the critical radius. The critical radius is shown on the graph plotted as a function of concentration. In some cases the charge does not reach the maximum, particularly for initially thin jets and dilute solutions. In this case the charge is dominated by the charging current and is independant of concentration. The variation of the charge separated with concentration, as calculated from this graph for various initial jet radii, is shown in fig 7.4. It is seen that the charge for a breaking 30μ jet is about 2 x 10^{-3} esu for pure water and about 10^{-5} esu for concentrated solutions, the charge remaining independant of concentration for concentrations below 10^{-6} molar. In the case of high capacity systems this constancy may be extended to higher concentrations, if the capacity is 10^{-1} esu the charge separated will be independant of concendtration below 10^{-5} molar.

7.5 The formation of the double layer

In the derivation of the theory it has been assumed

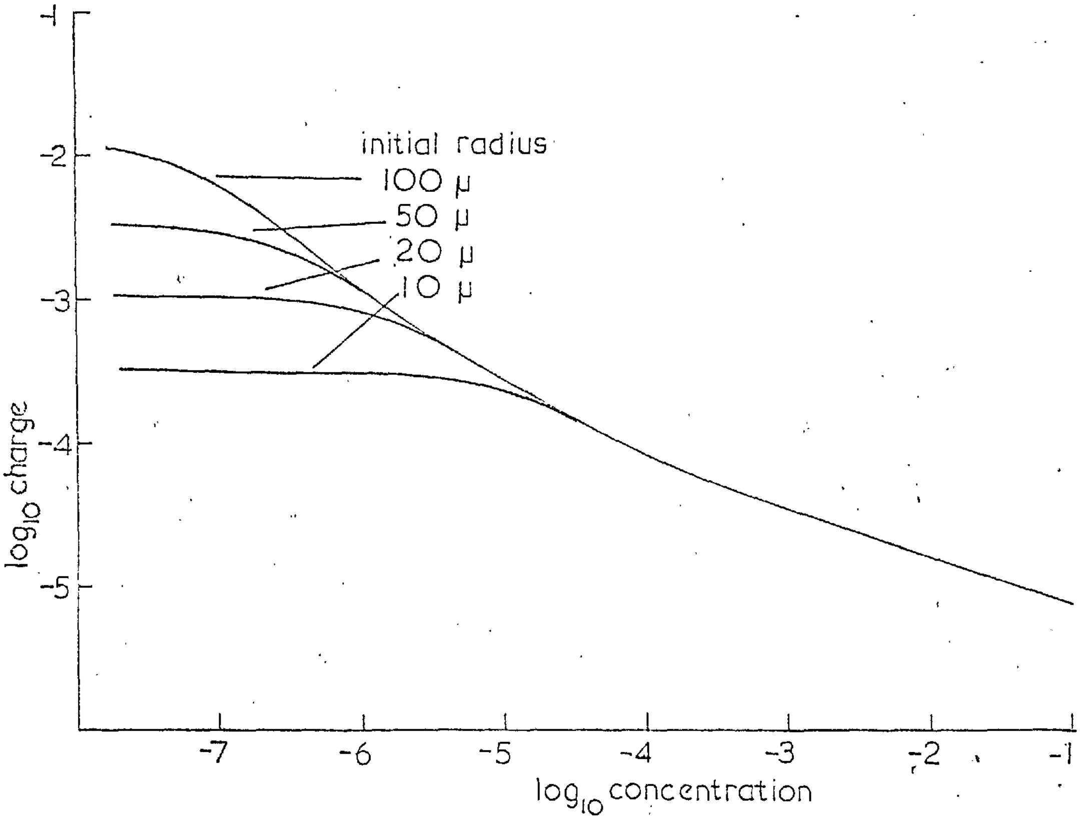


Fig 7·4 Variation of charge with concentration calculated from fig 7·3 that if the double layer is broken it is reformed instantly. Although it is true that the dipoles will be reorientated in a very short time, about 10^{-11} secs, the formation of the diffuse layer takes an appreciable time. It seems reasonable to suppose that this time will be of the same order as the time taken to set up local order in a liquid and Debye (1923) calculated this time to be

$$\tau \sim 10^{-10}/c \quad \text{seconds.}$$

The time of formation of the double layer will vary from about 10^{-3} seconds for pure water to 10^{-8} seconds for concentrated solutions. The assumption of instantaneous formation will be justified for solutions of 10^{-5} molar or stronger but it may give rise to considerable errors for more dilute solutions so that the charges measured for pure water may be less than those calculated.

7.6 Comparison of results and the theory

In the experiments in this thesis it has been suggested that the charge measured on the drops was in many cases separated when a jet of liquid was ruptured. The results of these experiments, together with the theoretical curve for a breaking 30μ jet are shown in fig 7.5. The following points should be noted;

1) All the points are taken from results where the main cause of charge separation is believed to be Rayleigh break up of the jet.

ii) The result for partial coalescence is the only one where

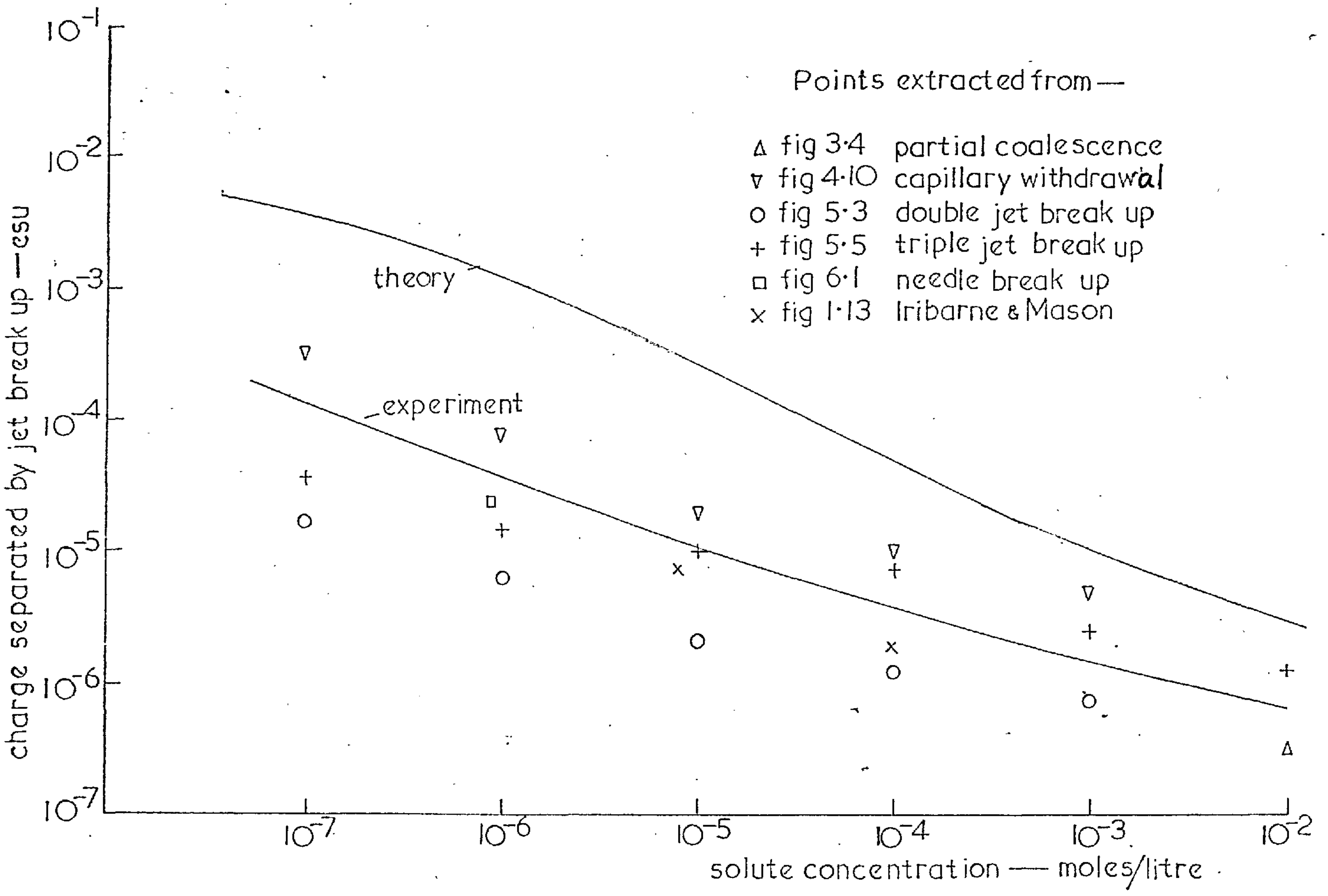


Fig 7·5 Summary of experimental and theoretical results it can be certain that the charge separation during the formation of the jet is unimportant.

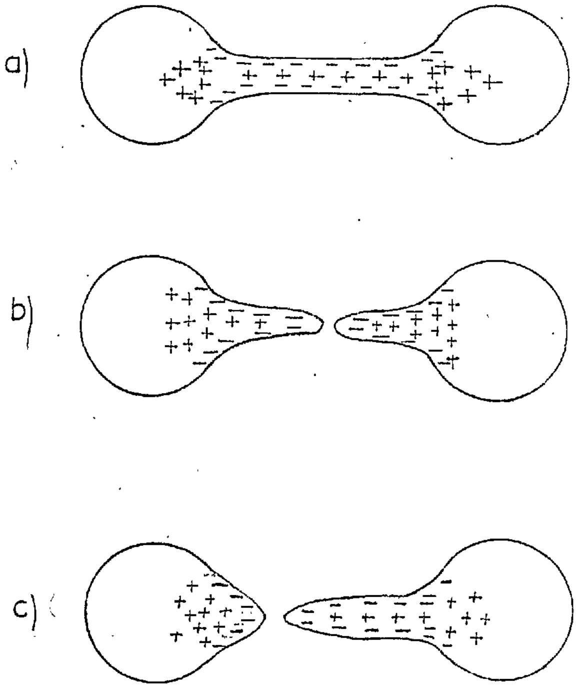
iii) The charge for triple jet break up is the charge on one large drop.

iv) The result for the break up at the tip of a vibrating needle is corrected for estimated contact potential charging.

All of the experimental values are less than the calculated charges although the spread between the results from different experiments is less than an order of magnitude. The difference between the theory and the experimental results decreases at higher concentrations which is probably due to neglecting the time of formation of the double layer. The charge separation is also reduced by the presence of concavities in the breaking jet, and variations in these probably gives rise to the spread of the results. We have also calculated the charge transfered by the moving liquid. The total separation will be less than this by an amount depending on the exact position of the point of rupture of the jet, see fig 7.6. However charge separation can occur in a breaking jet and that to within an order of magnitude the charge separated is given by the experimental curve

$$\underline{q \sim 10^{-7} c^{-\frac{1}{2}} \text{ esu}}$$

It was noticed that while the results of many of the experiments indicated a large variation of the charge separated with the concentration of the solution, the positive charge separation in partial coalescence or bubble bursting



a) positive charge forced from centre to ends of jet

b) jet breaks at centre — no charge separated

c) jet breaks at one end — charge separated approximately equal to charge transported to ends of jet

Fig 7·6 Charge separation in a breaking jet was to a great extent independant of concentration. Some of this is probably due to negative charge separation while forming the jet, at low concentration, but it is probably also due to the very large capacity of a drop being formed close to a large surface. As mentioned earlier this will reduce the conduction losses and remove some of the concentration dependance of the charge at these concentrations.

CHAPTER EIGHT

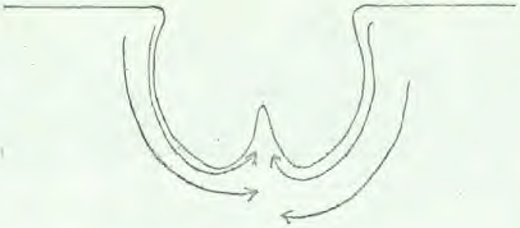
The charging of small drops and atmospheric electrification

8.1 The charging mechanisms

The experiments in this thesis have been designed to investigate the charging of small drops produced by the breaking up of liquid jets, and in particular, of jets of aqueous solutions. It has been shown that the electrification of drops produced by various atomisers was the resultant of charges separated during the break up of many such jets. The measurements of Iribarne and Mason, of the charges on drops ejected by bursting bubbles, suggested that the electrification was the result of the separation of the components of the electrical double layer at the surface of the bubble cavity as the jet, from which the drops were formed, was created. It was also suggested that charge separation also occurred during the break up of the jet, but this was negligible compared with that separated during the formation of the jet except if solutions of concentration greater than 10^{-4} molar were used.

An experiment on the electrification accompanying the partial coalescence of drops with a liquid surface and the formation of secondary drops showed that the variation of the secondary drop charges with the concentration of the aqueous solutions used was similar to that observed by Iribarne and Mason. Differences between the two results were due to different geometrical factors in the two experiments. This confirmed the idea that the charge separation did not depend on the presence of the bubble but only on the presence of a cavity in the liquid surface which would result in a flow of the liquid under surface tension forces.

The later experiments showed that charge could be separated during the break up of an isolated liquid jet. This charge was measured and was shown to be consistant with the charges expected if the liquid motion in the jets caused a separation of the double layer at the surface of the jet. It was also shown that the break up of jets of similar size produced by various techniques separated comparable charges. This was expected from theoretical considerations. The experiments showed that while the charge separated during the break up of a jet from a bursting bubble was independant of the concentration of dissolved solutes, the charge separated by a breaking isolated jet decreased as the solute concentration was increased. It is thought that the large capacity of the jet close to the bubble cavity reduces the loss of charge in the jet due to conduction, and that it is this conduction loss which gives the variation of charge with concentration for isolated breaking jets. Fig 8.1 shows the motion of the liquid near a bubble cavity and in a breaking jet. Also shown are the areas of positive and negative charge for aqueous solutions and from these it is seen how the jet rising from the bubble cavity becomes negatively charged while the ends of a breaking jet become positively charged.



liquid flow near a bubble cavity

charge distribution near a bubble cavity

liquid flow in a breaking jet

charge distribution in a breaking jet

Fig 8·1 Liquid flow and charge separation in breaking aqueous solutions

We have shown that the breaking of the double layer gives rise to charges which are in both qualitative and quantitative agreement with the experimental results. These theories would predict that drops formed by atomising non-polar liquids would have no charge due to the break up of the double layer and that any statistical charging would give a zero mean charge to the drops. This is also in agreement with the experimental observations. The experiments have also shown that in some circumstances charging due to contact potentials may occur and that these charges may mask any charges due to other separation mechanisms.

The various charging mechanisms are so some extent dependant on the geometry of the breaking jet so that if liquids are atomised in an uncontrolled manner, the drops may have varied charges. This occurs in many atomisers. Even in cases where the drops are of almost equal size there is often a wide spread of charges, and examination of the breaking liquid shows the break up to be very irregular. These atomisers also often produce many small ions from the evaporation of drops produced by the rupturing of thin liquid films. The charging of these small drops, which was studied by Chapman (loc.cit.), gives rise to a considerable charge on the atomised liquid.

It is seen that the charging of small drops is a very complicated process and the charge separated by any atomiser is difficult to calculate. It can however be estimated if the geometry of the atomising liquid is known but this has not been studied except in the case of atomisation by bubble bursting. The case of electrification by splashing is very complicated owing to the complicated geometry of the process.

8.2 Breaking liquid and atmospheric electricity

There are three main ways in which water drops are disintegrated in the atmosphere. Large drops may break up while falling at their terminal velocity, drops may splash off solid hydrometeors, and air bubbles burst at the surface of the sea and during the melting of hail and snow.

Large drops are found at the base of large cumulo-nimbus clouds, particularly just below the 0°C level, and usually break up in this region. In such clouds there is often an electric field present and the main charge separation mechanism is by induction in this field (Matthews and Mason, loc. cit.). The field is normally associated with the presence of the solid phase in the cloud, but some observers have claimed to observe lightning from clouds below the 0°C level (Alpert, 1964).

The splashing of drops off the liquid surface of hailstones near the 0°C level may also be a cause of electrification although again it seems possible that induction effects due to the fields invariably found in clouds containing hail will be dominant.

Drake (loc. cit.) has shown that the bursting of bubbles at the surface of melting hailstones produces sufficient electrification to explain the positive pocket of charge at the base of many cumulo-nimbus clouds. The bursting of air bubbles at the surface of the sea produces sufficient electrification to be a major mechanism for transfering charge from the earth to the atmosphere, and it is here that the electrification of breaking jets is most significant in the atmosphere.

The charging of solid objects in the atmosphere by the splashing of drops off them is probably not important in atmospheric electrification but it does raise practical problems with the charging of aircraft flying through rain. This is a result of the drops, which usually have a small charge, impacting on the aircraft. The water is shed as much larger drops which will be charged to the potential of the aircraft. When a small number of very large drops are shed a large potential may be built up before equilibrium is reached.

8.3 Conclusions

The work in this thesis has shown how the electrification of small drops can be explained as a result of charge separation during the breaking up of liquid jets to form the drops. The charging is an extremely complicated process but the charging mechanisms have been clarified and the charges obtained with single breaking jets have been explained quantitatively. Simple double layer theory is useful to calculate the charge separation but unknown geometrical factors are probably one of the largest sources of error. There is still much work to be done in the examination of the various atomisation mechanisms particularly the complicated phenomenon of splashing.

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