

Electrification Associated with Breakup of Drops at Terminal Velocity in Air

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ABSTRACT

The electrification accompanying the breakup of large drops falling in air in the absence of an electric field has been studied. A closed circuit vertical tunnel has been used, and the chemical composition of the drops has been carefully controlled. The results obtained for the average charge separation between the large and small fragments are non-specific regarding the nature of the ions present (except for surface-active species), but strongly dependent on the electrolytic conductivity. The magnitude of the effect goes from about $+10^{-2}$ esu per breakup (5×10^{-2} esu cm^{-3}) for pure water to -10^{-2} esu for concentrated solutions, reversing sign at about $10^{-5} \Omega^{-1} \text{cm}^{-1}$ (concentrations $\sim 10^{-4} N$). It was shown that these results can be interpreted on the basis of two competing processes, one of which is the shearing of the electrical double layer on the water-air interface while the air develops the characteristic liquid film bag or bubble.

1. Introduction

The breakup of water drops equal to or larger than ~ 6 mm of equivalent spherical diameter in free fall has been studied by a number of authors (see, for instance, Blanchard, 1950; Margarvey and Taylor, 1956; Mathews and Mason, 1964; Cotton and Gokhale, 1967). It has been shown that when a drop becomes unstable due to collision with another drop or to turbulence in the air stream, it may break up either by dividing in two or more large fragments with eventual formation of smaller satellite droplets, or by developing a characteristic bag or bubble formed by a film attached to a toroid containing most of the liquid. In the last case the film disintegrates into a fine spray and the toroid into larger fragments.

Electrical effects are associated with the breakup, and these have been the object of several studies. The larger fragments produced in the breakup of pure water drops have been found to possess a positive charge, while the corresponding negative charge remains in small droplets or in the ions left by their evaporation. The results of measurements of this charge separation are hardly comparable, because the experimental conditions have differed widely from one worker to another. Simpson (1909) and Hochschwender (quoted by Lenard, 1921) measured the charges on the large fragments. Simpson, Zeleny (1933), Chapman (1952) and Muchnik (1954) conducted experiments where the ions of one or the other sign were captured electrostatically and their charges measured. The methods for producing the breakups differed, and the chemical composition of the liquid, which has a strong influence on the effect, has not always been controlled sufficiently.

In the present research we have endeavored to measure the charge separated between the large and

the small fragments resulting from the breakups, in the absence of an electric field and with particular consideration of the chemical composition of the liquid.

2. Experimental arrangement

a. Tunnel

In order to be able to control and maintain the purity of the air, as well as that of the drops, a closed circuit wind tunnel has been used, with a vertical section where the drops could be suspended freely floating. Fig. 1 shows the general arrangement. The blower, driven by a motor with variable regulated speed, sends air upward through the vertical section. Honeycomb and wire meshes were inserted to minimize turbulence. Just below the breakup section, two wire meshes, one a small disc 3 cm in diameter at the center, were found to give an appropriate well in the profile of vertical velocities and a good stability for the drops suspended in the air stream. The average speed of the air was ~ 10 m sec^{-1} . The breakup section is followed by a conical section ending in a wide rectangular conduit leading the air first sideward and then downward to a metallic box connected to the entrance to the blower. At this point the air passed over the surface of a tray with concentrated NaOH (except during the CO_2 experiments) to keep a low concentration of CO_2 , and through a filter of cotton wool and plastic fiber. The vertical cylindrical section is a perspex tube, 14 cm in internal diameter and 60 cm high. The conical section is also of perspex and has an angle of 6° and an upper diameter of 24 cm. The rectangular conduit is made of wood and varnished. The whole tunnel is reasonably air tight, except for a small opening at the breakup section

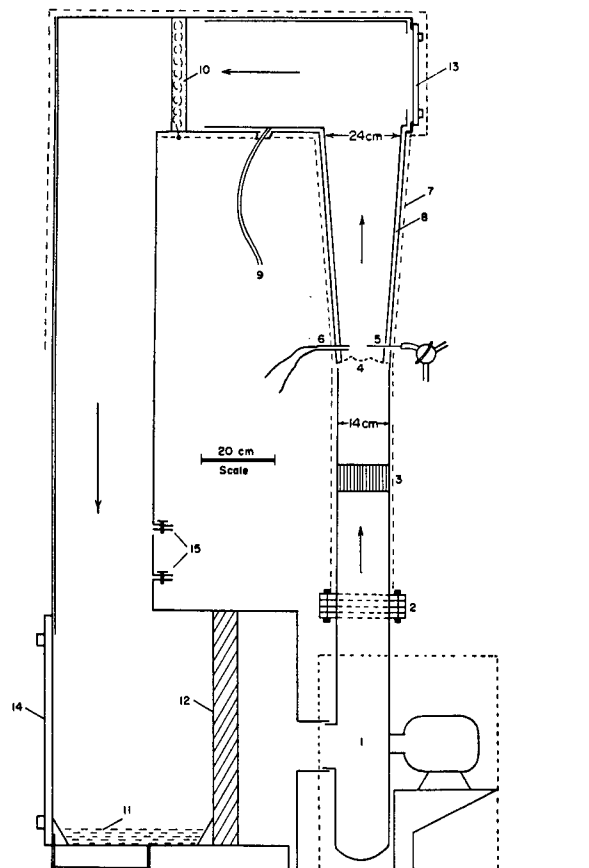


FIG. 1. Diagram of the closed circuit wind tunnel: 1, blower; 2, wire screens; 3, honeycomb; 4, shaped wire screens; 5, needle; 6, conductivity cell; 7, external shielding; 8, copper plates; 9, connection to electrometer; 10, steel wool filter; 11, tray with concentrated sodium hydroxide solution; 12, cotton wool filter; 13, door with window; 14, door; 15, inlet and outlet.

through which the drop producing needle can be inserted.

A large copper plate internally covers the walls of the conical section of the first part of the horizontal conduit, with appropriate insulation from the wood, and is connected to the electrometer. In the lowest portion, the plate is connected to the metallic mesh just below the needle, so that by grounding the electrometer before every breakup, the event occurred in a field-free environment. The vertical portions and the upper horizontal conduit are externally shielded with wire mesh.

The temperature inside the tunnel was between 25 and 29C for all the experiments.

b. Control of air and water purity

The influence that air impurities might have on the suspended drops was checked by means of a small auxiliary conductivity cell through an opening in the breakup section. The cell was open at one end and could

be filled with high purity water through a needle while the air was flowing. Readings of the conductivity were then taken as a function of time. It was observed that a quick increase in the conductivity during the first seconds was followed by a slower increase at a steady rate, suggesting a rapid absorption of gases to an equilibrium, followed by a steady pollution due to aerosol particles. The pollution rate was strongly diminished both by a previous flushing of the tunnel with pure air and by reducing the CO_2 with the NaOH solution. In these conditions, an initial conductivity below $10^{-7} \Omega^{-1} \text{cm}^{-1}$ increased to about 3×10^{-7} in 5 sec, to 5×10^{-7} in 20 sec and to 10^{-6} in about 80 sec. The pollution rate should be somewhat higher for a suspended drop as it is better exposed to the surrounding atmosphere than the liquid in the conductivity cell. The time interval necessary in a measurement to produce the drop and wait until it bursts (see below) was less than 5 sec, usually 3-4 sec. Therefore, in the experiments with pure water, a conductivity of $\sim 1-3 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ may be assumed at the time of the breakup.

c. Production of drops: Control of solutions

The drop-producing setup (see Fig. 2) included a column of ion-exchange resin to remove traces of CO_2 or other electrolytic impurities. The resulting water has a conductivity of $0.6-0.8 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ at the exit of this column. This water could be used directly for the breakups or for preparing solutions in a graduated separating funnel with protection from CO_2 and into which concentrated solutions could be introduced through a hypodermic needle. The liquid to be tested passed through a small conductivity cell, and a 1-ml syringe graduated to 0.01 ml was used to introduce the desired volume through a needle into a fixed position near the center of the testing section of the tunnel. The circuit could be flushed with the liquid to be tested. Drops of ~ 6 mm equivalent diameter could be suspended for long periods in the air stream. Larger drops of 7.3 ± 0.5 mm equivalent diameter ($\sim 0.20 \pm 0.05$ ml) broke up within 1-2 sec after falling from the tip of the needle, indicating a certain amount of turbulence in the tunnel (drops of this size will remain longer without bursting in a less turbulent air stream). This was the procedure adopted to produce the breakups. The concentrations of the solutions were derived from the conductivity measurements. When the effect of CO_2 concentration was being studied, the caustic soda tray was removed from the tunnel and when necessary (for the more concentrated solutions) CO_2 was introduced into the tunnel at the proper concentration to maintain approximately the equilibrium partial pressure corresponding to the solution to be tested. Any variations in concentration due to exchange of CO_2 during the drop life should not exceed a factor of 2.

d. Droplet size cutoff

The experiment was designed to measure the charge separated between the resulting larger fragments and the finer spray. The former mostly fell sideward onto the copper plates in the air-decelerating conical section of the tunnel. Some of the fragments reached the upper part, even the top plate. The smaller droplets were carried by the air stream and filtered away before the air was cycled again.

It is important to determine the approximate size limit between the two groups of particles ("larger fragments" collected by the copper plates, and "spray") that results from the experimental arrangement. Glass slides covered with magnesium oxide were placed at different points on the final downstream border of the bottom, sides and top copper plates, in the upper section of the tunnel. They were left in place during a series of measurements (with pure water and NaCl solutions, involving about 1600 breakups) and were then analyzed under the microscope, using May's (1950) factor (0.86) to relate the diameter of the droplets to that of the impressions. The great majority of the impressions were found on the bottom plate, and very few on the sides and upper plate, showing that at this stage of the circulation the droplets are being separated from the stream by gravity. The results are shown in the histogram of Fig. 3. It may be seen that about two-thirds of the droplets were in the 100–200 μ diameter range, while more than 90% were between 50 and 270 μ . This seems an appropriate range for the size limit between larger fragments and spray when the possibility of gravitational separation and subsequent growth in a cloud are considered.

e. Charge measurement

An electrometer of the vibrating reed type was used in connection with a strip chart recorder. The electrometer measured the difference of potential across an input capacitance including the inner capacitance of the instrument plus the external connections, which included the copper plates. Thus, any charge transferred to the plates by the drop fragments (the group of larger fragments produced by the breakup) was observed as a sudden change in the potential. The total input capacitance was 77 pF (where the real attached capacity is divided by a feedback factor of 100).

Due to the large dimensions of the plates and the vibration from the motor, the noise level was high and it was difficult to avoid a certain amount of drift in the electrometer. In order to improve the sensitivity of the readings, an auxiliary potentiometric circuit was used to compensate the drift. Under these conditions, the sensitivity of the measurements was $\sim 2 \times 10^{-3}$ esu.

The drops had a small initial charge when breaking off from the needle. This was checked by lowering the

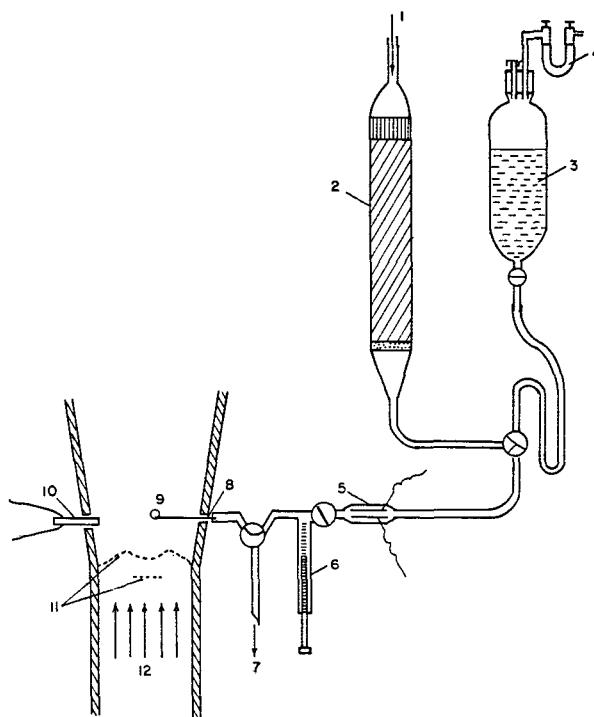


FIG. 2. Arrangement for drop production: 1, distilled water; 2, ion-exchange resin (Elga); 3, solution; 4, soda lime; 5, conductivity cell; 6, syringe; 7, waste; 8, needle (grounded); 9, drop; 10, conductivity cell; 11, wire screens; 12, air stream.

air speed so that a number of drops could be let to fall onto the metallic mesh underneath it, which was connected to the copper plates and electrometer. The average charge was found to be from -4 to -6×10^{-4} esu, depending on the concentration of the solution. The average values obtained in the experiments were corrected by this amount.

Tests were made to check on the possibility that splashing of drops on the plates could contribute to the readings. The needle was put in such a way that smaller drops broke off from its tip, were carried upward by the air stream and fell onto the plates. No charging effect could be detected under these conditions. Also, observation of breakups from above, by means of an inserted mirror, showed that the large fragments, or at least most of them, fell on the plates

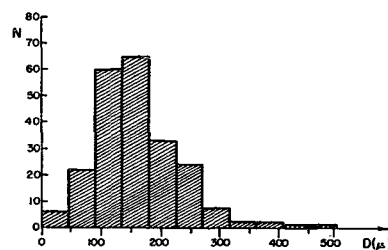


FIG. 3. Size distribution for the cutoff between large and small fragments: N , number of drops (fragments); D , diameter of drops. Histogram intervals are in arbitrary units.

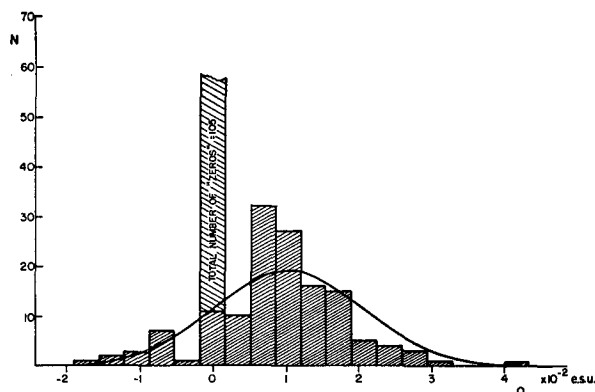


FIG. 4. Distribution of separated charges for pure water: N , number of breakups; Q , charge of large fragments. The fitted curve is the normal error law. The 105 "zeros" include 11 "random zeros" and 94 "non-random zeros" (NRZ). Histogram intervals are in arbitrary units.

with small velocities. We therefore concluded that splashing did not play any significant role in our measurements.

f. High-speed photography

For reasons that will become apparent in the description of the results, it was considered necessary to perform a series of experiments where the breakup mode could be identified and related to the occurrence of charge separation. For that purpose a high-speed camera (HYCAM) was used, at 300 frames per second. This speed is enough to detect the formation and burst of a bag, a process lasting about 10 msec for the drops used in the experiments.

The illumination requirements prevented in this case the use of the same arrangement for measuring the separated charges. A filter of steel wool was then installed in the upper horizontal section of the tunnel and connected to the electrometer. Thus, the charge of the spray caught by this filter was measured, although presumably a fraction of the total charge might escape detection by leaking through the filter. This was considered satisfactory, as only qualitative information was required in this experiment.

3. Results

a. Statistical distribution of readings. Averaging procedure. Pure water

A considerable spread of the results was found for each particular composition of the liquid, and this made it necessary to perform a large number of experiments to obtain a reasonably accurate result. The statistical distribution was very similar in all cases, and will be here exemplified with the case of pure water.

Fig. 4 shows a histogram of the values of Q (charge remaining in the large fragments) obtained for 235 breakups of pure water drops. A striking feature is

given by the large number of readings with no detectable charge, corresponding to the interval around zero. This strongly suggests two types of events, one producing no electrification and the other giving a random distribution of charges around a certain value. We accordingly fitted a normal error law curve, as shown in the diagram, around the average value obtained by simultaneously subtracting the excess zeros over the curve. This excess we shall call hereafter the "non-random zeros" (NRZ). In this example there were 105 zeros, from which 11 were considered as "random zeros" and 94 as NRZ. Thus, from the total 235 breakups, 40% were NRZ.

The proportion of NRZ depended strongly on the location of the tip of the needle in the air stream. Thus, in the previous example and in a series of experiments using NaCl solutions, from 40–60% of NRZ were obtained in each case. The arrangement was then modified and for all other experiments, including new measurements with pure water and with NaCl solutions, the proportion of NRZ varied from 5–25% (mostly 10–15%).

Histograms were prepared for all experiments as in the above example for pure water. The number of NRZ was subtracted in every case and the average charge separation \bar{Q} and the standard deviation σ were computed from the remaining random distribution. In the example of pure water, $\bar{Q} = +1.05 \times 10^{-2}$ esu, the sign referring to the large fragments, and $\sigma = 1.0 \times 10^{-2}$ esu. The rms error of \bar{Q} in this case was $\sigma/\sqrt{N-1} = 0.8 \times 10^{-3}$ esu, N being the number of breakups. In all the series of experiments, σ was found to be between 0.6 and 1.7×10^{-2} esu, mostly around 1.0×10^{-2} esu. Since N varied between 150 and 200, the rms error of the averages ranged between 0.6 and 1.3×10^{-3} esu.

The proportion of NRZ, considered as indicating a difference in the conditions of the breakup, seemed immaterial for the \bar{Q} computed as described, as the pure water and NaCl solutions repeated with the two arrangements mentioned above gave similar results. For instance, the second series with pure water gave the value $\bar{Q} = 1.03 \times 10^{-2}$ esu.

b. Meaning of the NRZ

A total number of 144 experiments were analyzed with the high-speed film technique, with drops of pure water. The film revealed three main types of events:

1) The drop rises and goes out of the field of view without breaking up.

TABLE 1. Percentage of occurrence of different types of events.

Type of event	Charge	No charge
Drop does not break up	0%	6%
Division	5%	3%
Bag bursting	83%	3%

2) The drop divides into two major fragments. Sometimes the neck linking the fragments during the process of division is long (several diameters of the major fragments) and leaves satellite droplets when it collapses.

3) "Bag bursting." This usually occurs with the whole drop, but also quite frequently just after division of the drop, on one or sometimes on both of the major fragments.

Due to the quickness of the events, it is impossible to realize with the naked eye what type has occurred.

Regarding the relation of the type of event with the charge separation, Table 1 gives the percentages obtained for the three types, with and without charge detected. All charges were negative as measured on the spray. It appears from these results that the NRZ are the result of experiments in which the drop did not break at all or divided into large fragments only. Most of the charge separations detected are due to the bag bursting, and a small percentage to divisions in which satellite droplets are produced. These conclusions justify the procedure adopted for computing the average values, as described in the previous section.

c. Carbon dioxide and salt solutions

Fig. 5 represents the results obtained with solutions of CO₂, NaCl, KCl and (NH₄)₂SO₄. All curves show a similar behavior. For very dilute solutions they start from a value close to that of pure water (~10⁻² esu), and then decrease, reverse sign for a concentration around 10⁻⁴ N, and tend to level off to a negative value around -10⁻² esu. This similarity becomes more evident when the charges are plotted as a function of the conductivity rather than concentration, as has been done in Fig. 6. The NaCl appears to deviate somewhat from the other curves at high concentrations, and (NH₄)₂SO₄ gives an exceptionally high value at low concentration, but otherwise the data coincide practically on the same curve within the experimental errors.

d. Surface active cations

Two quaternary ammonium salts were also tested, in order to have an independent check on the basic assumptions of the theoretical interpretation (see Section 4). These were the tetrabutylammonium chloride, (C₄H₉)₄ NCl, and the tetrapentylammonium chloride, (C₅H₁₁)₄ NCl. The results are plotted in Fig. 7. Both salts produce a distinctly different type of curve, with negative values at low concentrations, increasing to a maximum and then decreasing again for increasing concentration. A very similar curve was obtained when instead of solutions of pure (C₄H₉)₄ NCl, this salt was added in the constant concentration of 10⁻⁶ N to varying concentrations of NaCl; these results are also plotted in the figure.

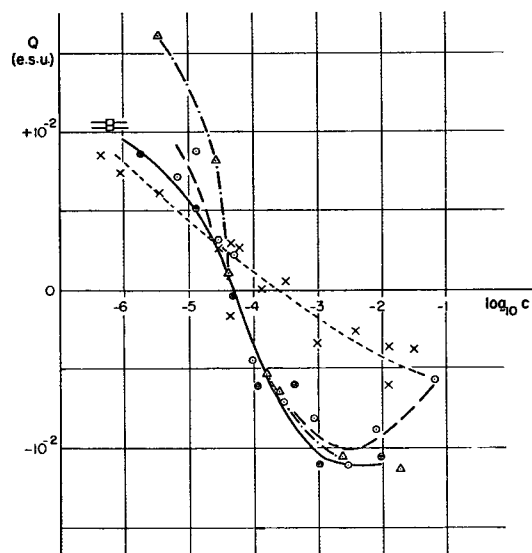


Fig. 5. Average separated charge per breakup (sign of large fragments) as a function of electrolyte concentration *c* (normality; for CO₂, molarity): solid circles, KCl; open circles, NaCl; triangles, (NH₄)₂SO₄; crosses, CO₂; squares, pure water, considered as CO₂ solution.

4. Discussion

It has been recognized by several authors that the breakup mode of a large drop in free fall depends on the method of disruption—in particular, on the degree of turbulence of the air stream, the oscillations of the drop, and the suddenness and strength of the jet they encounter, if they are made to break up with such a device [see, for instance, Hinze (1955)]. In the present experiments the air stream had a speed of ~10 m sec⁻¹ and the "bag" mode is by far the most frequent, al-

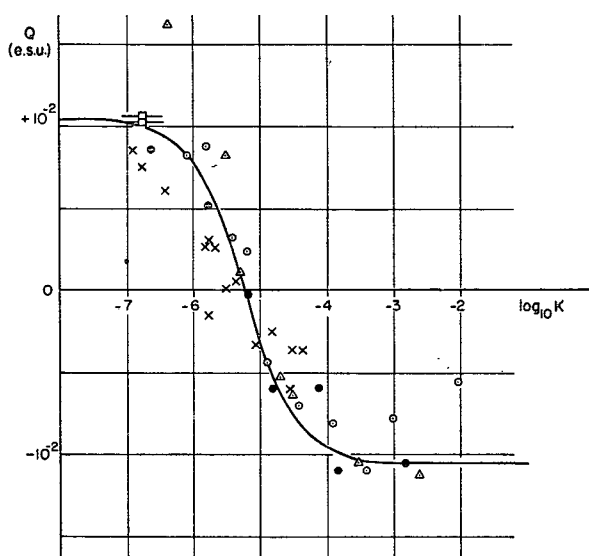


Fig. 6. Average separated charge per breakup (sign of large fragments), as a function of conductivity *K* (Ω⁻¹ cm⁻¹): solid circles, KCl; open circles, NaCl; triangles, (NH₄)₂SO₄; crosses, CO₂; squares, pure water. Full line is the theoretical curve.

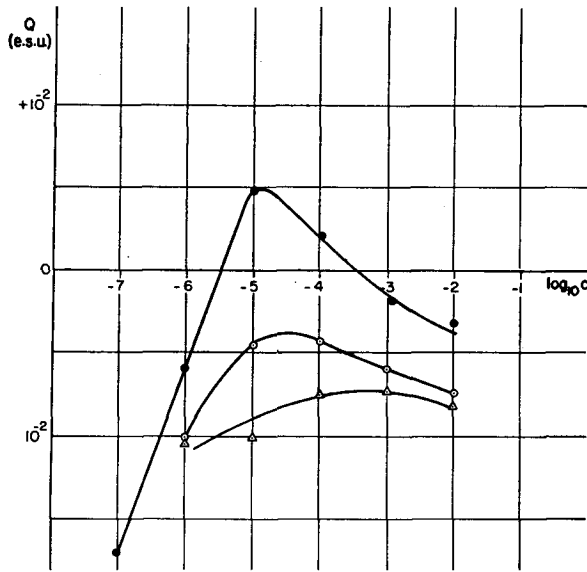


FIG. 7. Effect of surface active cations showing the average separated charge per breakup, as a function of electrolyte concentration c (normality): solid circles, tetrapentylammonium chloride; open circles, tetrabutylammonium chloride; triangles, $10^{-6} N$ tetrabutylammonium chloride in varying concentrations of sodium chloride.

though division in several fragments also occurred in an appreciable percentage of cases, as shown by the high-speed film investigation. The proportion of NRZ, eliminated from consideration, was very sensitive to changes in position of the drop-producing needle. Both these circumstances and the differences in the methods used to measure the charges (ions or charged droplets, and effective cutoff between large and small fragments in the last case) make difficult any comparison with the results of previous authors. We may remark, however, that our results agree very well with the early measurements by Simpson (1909), if we assume that his distilled water had a conductivity of $\sim 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. It is interesting that Chapman (1952), in his measurements of ionization production, where he let 4-mm diameter drops fall through 5 cm in a protecting tube and onto an updraft of $\sim 10 \text{ m sec}^{-1}$, also found that many drops gave no electrification.

It is characteristic of this random type of process that the values appear very widely spread. In this we also agree with Chapman, who mentions an average deviation of 78% of the average value in a series of 10 μ are set loose from the tip of a filament as the linking neck collapses. We assume that this may again be responsible for the high concentration branch of the curves in Figs. 5 and 6. For instance, from comparison with the results in bubble bursting, small droplets separating from the large fragments in the last stages of the breakup might carry charges of the order of 10^{-5} esu; about 10^3 droplets would be necessary to produce the observed values of -10^{-2} esu for breakups at high concentrations. No experimental evidence is available at present to support or contradict such

If we consider now the results as a function of concentration for different electrolytes (Fig. 5), two main points are to be stressed. First, the electrification appears very sensitive to the concentration, which also causes a reversal of sign. Second, plotting the results as a function of the conductivity rather than the concentration (Fig. 6), the action of the electrolytes appears to be independent of their chemical nature. We shall try to explain these features, although the lack of information about the dynamics of the process only allows a tentative model. This discussion will be based on the "bag" mode of breakup, and no consideration will be given to the fact that a small percentage of the charge separations was probably due to the "division" mechanism.

a. Charging mechanisms

Perhaps the most remarkable feature of our results is the reversal of sign with increasing concentration of electrolytes. This reversal cannot be due to changes in the dynamics of the process; the concentrations are too low to produce any appreciable variations of density, viscosity or surface tension. At the same time, if the electrification is attributed to electrokinetic effects where the electrical double layer plays the important role, the reversal cannot be attributed to a reversal of the value of the electrokinetic or zeta potential ζ at the water-air interface [see, for instance Kruyt (1952)]. A concentration of $10^{-4} N$ is far too low to expect this effect with uni-univalent electrolytes. Moreover, Bach and Gilman (1938) showed that KCl had no effect on the zeta potential for the range 10^{-5} – $10^{-3} N$. Thus, the conclusion is reached that two different processes with opposite electrification effects must be present here, so that the reversal of sign may be explained by a shift in their relative importance. This seems to be a regular feature in water disrupting processes [see, for instance, Coehn and Mozer (1914), spray produced by bubbler; Iribarne and Mason (1967), bubble bursting; Jonas and Mason (1968), several phenomena; Shewchuk and Iribarne (1970), splashing].

The electrification effect persisting at high concentrations in bubble bursting has been attributed by Iribarne and Mason to the very rapid process (occurring in 1–10 μsec) by which small droplets of the order of 10^{-5} esu; about 10^3 droplets would be necessary to produce the observed values of -10^{-2} esu for breakups at high concentrations. No experimental evidence is available at present to support or contradict such

an explanation; however, it does not seem unreasonable in view of the known facts.

Whatever the process responsible for the charge separation at high concentrations, we assume that as we go toward the dilute region, another process of opposite sign compensates at first, and then prevails, producing a net positive charge in the large fragments which reaches about 10^{-2} esu for our pure water. We shall demonstrate that this effect can be attributed to a shearing of the double layer during the bag formation, and that its decay for increasing concentration can be accounted for by the effect of a back current through the electrolyte solution.

Let us consider the formation and burst of the bag, as shown schematically in Fig. 8. The lower surface is blown up by the aerodynamic pressure, dragging a thin film of liquid, while most of the liquid remains in the toroid. The liquid in the film thus undergoes a sudden upward acceleration, and at the same time the external layers of the film must drain over the internal surface toward the toroid. We can compare this process with that of the withdrawal of a vertical plate from a liquid, while the plate is being accelerated (and the adhered liquid film with it). We are interested in calculating the shear stress at the internal surface of the liquid (as if it were at the surface of the plate). Let us consider the unit surface of lateral film; it is accelerated to a velocity v (referred to the toroid) that can be estimated by $v=L/T$, where L is the height of the bag and T the time it has taken to develop. The acceleration has taken place in a time interval of the same order. The unit surface of film has acquired a momentum mv , where the mass m is equal to $d\delta$, d being the density of the liquid and δ the thickness of the film. The change in momentum per unit time is equal to the accelerating force. The tangential component of this force (along the internal surface) is the shearing stress τ . Observation of the bag development by the high-speed films indicates that the magnitude of τ is comparable with that of the total force. Using an average proportionality factor of 0.5 as a rough approximation, we have

$$\tau \approx \frac{d\delta L}{2T^2}, \tag{1}$$

where L and T can be measured from the high-speed pictures. Their approximate values were $L \approx 2$ cm, $T \approx 10$ msec. Thus,

$$\tau \approx 10^4 \delta \tag{2}$$

in cgs units. We should add the gravity term due to the falling liquid film, $dg\delta \approx 10^3\delta$, but this can be neglected, being an order of magnitude smaller.

From the point of view of the charge separation, we are interested in the region close to the surface, the site of the electrical double layer. If we consider it as a diffuse or Gouy layer, its "thickness" is characterized

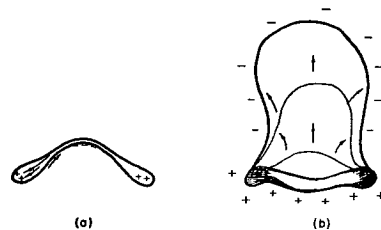


FIG. 8. Charge separation during breakup showing initial development (cross section) of bag (a), and later stage (b).

by the parameter $1/\kappa$, where

$$\kappa = \left(\frac{8\pi N e^2 c}{1000 \epsilon k T} \right)^{\frac{1}{2}} \approx \frac{10^8 c^{\frac{1}{2}}}{3}, \tag{3}$$

where N is Avogadro's number, e the elementary charge, ϵ the dielectric constant, k Boltzmann's constant, and T the absolute temperature [see, for instance, Kruyt (1952, Chap. 4)]. The concentration c is given in moles per liter. For theoretically pure water ($c=10^{-7}$ N at 25C) $1/\kappa \approx 1 \mu$, and for electrolyte solutions the thickness decreases as $1/\sqrt{c}$.

In such a shallow layer, the shear stress can be considered as constant, equal to the shear stress at the surface. We assume, therefore, a linear velocity profile perpendicular to the surface as a reference. If x is the distance from the surface, we set $V=0$ for $x=0$, and we have

$$\frac{dV}{dx} = \frac{\tau}{\eta} = \text{constant},$$

where η is the dynamic viscosity of the liquid (10^{-2} poise in our case), and

$$V = \frac{\tau}{\eta} x. \tag{4}$$

The effect of this velocity gradient is, as in other electrokinetic phenomena, that of a shearing of the double layer, which results in a charge separating current I . The value of this current can be computed from the electrokinetic potential ζ . According to the theory of electrokinetic phenomena (Kruyt, 1952, Chap. 5), the velocity V of the liquid becomes zero not exactly at the interface, but at some distance at which the potential of the double layer has decayed from its value at the interface to the ζ potential. The plane for which $V=0$ is the "plane of shear" or "slipping-plane." The flux of electric charge carried by the liquid per unit of transversal length can be computed from

$$F = \int_0^{\infty} V \rho dx, \tag{5}$$

where ρ is the net charge density. Here ∞ is written for a distance far enough from the interface to consider total decay of the double layer potential ($\gg 1/\kappa$).

We now substitute for V from (4), counting x from the plane of shear rather than from the surface itself (the very thin layer between the plane of shear and the actual surface is considered to have zero velocity gradient). The charge density ρ is related to the potential by Poisson's equation, $d^2\phi/dx^2=4\pi\rho/\epsilon$, where ϕ is the potential, ϵ the dielectric constant and the sign is disregarded. Therefore (5) can be written as

$$F = \frac{\epsilon\tau}{4\pi\eta} \int_0^\infty x \frac{d^2\phi}{dx^2} dx = \frac{\epsilon\tau}{4\pi\eta} \int_0^\infty x d\left(\frac{d\phi}{dx}\right).$$

The integral is solved by parts to give the potential ζ at $x=0$ (ϕ decreases exponentially to zero when x is large enough). Thus,

$$F = \frac{\epsilon\tau\zeta}{4\pi\eta}. \quad (6)$$

If we now consider this charge separation as occurring along the perimeter of the toroid πD , where D is the diameter, the charging current is

$$I = \frac{D\epsilon\tau\zeta}{4\eta}. \quad (7)$$

The maximum charge separated by this current, in the absence of a back current, would be

$$Q_{\max} = IT = \frac{D\epsilon\tau\zeta T}{4\eta}. \quad (8)$$

From the pictures, we can estimate D at ~ 1.5 cm and we know $\epsilon=80$. The potential ζ for the water-air interface is not well-known. The most reliable data for dilute solutions seem to be those of Bach and Gilman (1938), whose experiments on the electrophoresis of gas bubbles gave values of about 35 mV or 1.2×10^{-4} esu, with little or no variation due to the concentration of the electrolyte, except for surface active substances. Introducing these values into Eq. (8), we have

$$Q_{\max} \approx 4 \times 10^{-3} \tau \text{ [esu]}. \quad (9)$$

And if we replace Eq. (2) for τ , we obtain

$$Q_{\max} \approx 40\delta. \quad (10)$$

The thickness δ is unknown; comparison with the films formed during splashing of large drops (Shewchuk and Iribarne, 1970) or spray production suggest that δ might be of the order of 10μ , so that $Q_{\max} \approx 0.04$ esu.

This order-of-magnitude estimate of Q_{\max} may be checked by another model, independently of the value of δ . For that purpose we consider the flow at the internal surface of the toroid, from which the film is emerging upward. The relative motion of this liquid

region when referred to the air that penetrates and blows up the bag is compared with that of a liquid layer sliding over a flat plate. In that case the shear stress at the surface can be estimated from [see for instance, Bennett and Myers (1962)]

$$\tau = 0.332\eta V_0 \left(\frac{V_0 d}{\eta L}\right)^{\frac{1}{2}} = 0.332 \frac{\eta V_0}{L} \text{Re}^{\frac{1}{2}}, \quad (11)$$

where V_0 is the relative velocity between the bulk of the liquid and the interface, and the local Reynolds number Re is based on the distance L traveled by the liquid over the plate from a leading edge (here given by the height of the bag) and the velocity V_0 . The formula assumes laminar flow, being applicable for $2 \times 10^4 < \text{Re} < 5 \times 10^5$. In our case, setting $V_0 \approx L/(2T)$ (using $V_0/2$ as a rough average for the tangential component), $\text{Re} \approx 2 \times 10^4$ and $\tau \approx 20$ dyn cm^{-2} . Introducing this estimate for τ in Eq. (9), we obtain $Q_{\max} \approx 0.07$ esu, not far from the previous estimate.

In order to compare these estimates with our experimental results, we must consider the difference between the maximum positive charges (on the large fragments) for low concentrations and the final negative charges for high concentrations. This is about 0.02 esu. In view of the approximate character of the calculations, this order of magnitude agreement is satisfactory. It shows that the proposed mechanism is capable of producing the observed charge separations, and gives a plausible explanation of the process.

From a purely qualitative viewpoint, the results with the tetra-substituted ammonium salts give also support to the model. Gilman and Bach (1938) showed that these salts, due to the surface activity of the cations, change the sign of the ζ potential for concentrations between 10^{-6} and 10^{-3} M . This is in agreement with the reversal of sign for the low concentration branch of our curves. It is not clear on the other hand why a reversal should not occur also at higher concentrations; this problem has been discussed elsewhere, in connection with other electrokinetic processes (Iribarne *et al.*, 1970).

b. The neutralization current

The previous estimates have been made under the assumption that the charges separated by the shearing of the double layer would remain so until the breakup of the liquid film makes impossible any recombination. In fact, the field which these charges build up during the bag formation until its rupture, should produce a back or neutralization current I_n , proportional to the field and to the conductivity of the solution, i.e., proportional to its concentration. The time relations between these charging and neutralization processes will determine the amount of charge that can actually be separated. If q is the net charge being separated,

we can write

$$\frac{dq}{dt} = I - I_n = I - AK E, \tag{12}$$

where A is the total cross section of film through which the charges are leaking back (as obtained by a plane cutting the bag horizontally through its middle), K the conductivity, and E the field created by q , acting vertically from the film toward the toroid. Actually, E will vary with the position, and its dependence on q will be a function of the rather complicated geometry involved in the problem. It may be seen, however, that its order of magnitude should be around some units of $q/(ehD)$, where h is the vertical distance between the negatively charged region of the film and the positively charged toroid. In a general way, we may take $E = kq$, where k is a constant to be fixed, and write

$$\frac{dq}{dt} = I - AKkq, \tag{13}$$

where I can be taken as a constant during the process, and K is related to the concentration of the electrolyte by

$$K = \frac{0.9 \times 10^{12} \Lambda c}{10^3}, \tag{14}$$

where Λ is the equivalent conductivity ($\text{cm}^2 \Omega^{-1}$ equivalent-gram $^{-1}$), c is in equivalent-grams liter $^{-1}$ and the factor 0.9×10^{12} converts to esu. We may define the time τ' by

$$\tau' = \frac{1}{AKk} = \frac{10^3}{0.9 \times 10^{12} A \Lambda k c}. \tag{15}$$

The solution of (13) is then

$$q = I \tau' (1 - e^{-t/\tau'}), \tag{16}$$

and the maximum charge separation, at each concentration, should be given by

$$Q = I \tau' (1 - e^{-T/\tau'}), \tag{17}$$

where T is, as before, the total time taken by the process of bag development until breakup.

We can now use Eq. (17), after adjusting the constants I and τ' . For very low c , $Q \approx IT$, where $T = 10^{-2}$ sec according to our previous estimate. We write Q in that case as 2.1×10^{-2} esu, assuming that one-half of this value compensates the second constant charging mechanism, giving -1.05×10^{-2} esu. This would thus correspond to a charge measured at low concentrations of 1.05×10^{-2} esu. The current I should then be equal to 2.1 esu. With this value, τ' is then fixed so that $Q = 1.05 \times 10^{-2}$ esu (reversal of sign for the net charge) for a concentration of KCl equal to $4 \times 10^{-5} N$. Taking into account that $\Lambda = 150 \text{ cm}^2 \Omega^{-1} \text{ mole}^{-1}$ for KCl, this gives $\tau' = 3.4 \times 10^4 / K$ for Eq. (15), K in esu. With these

constants, the theoretical curve of Fig. 6 has been drawn, the second mechanism being assumed to produce a constant charge equal to -1.05×10^{-2} esu. It may be seen that the general behavior agrees well with the observed data. If we estimate the total cross section of the film A as $\sim 5 \times 10^{-3} \text{ cm}^2$ (10μ thick and a bag diameter of $\sim 1.5 \text{ cm}$), and take $h \approx 2 \text{ cm}$, we obtain from the previous value of the constant in (15), $k \approx 0.006 = 1.4 / (ehD)$, a reasonable value.

Thus, the shape of the curves can be understood under the assumption that two electrification processes compete in the breakup. The first, slower one gives a positive charge to the large fragments, which decays rapidly around concentrations of $10^{-4} N$ due to the neutralization or back current. The second process, quick enough to be unaffected by these electrolyte concentrations, gives a constant charge of opposite sign. The non-specificity of the curves supports the idea of the neutralization current, which depends only on the conductivity.

c. Drop breakup in the atmosphere.

Matthews and Mason (1964) already pointed out that charges such as obtained here are insufficient to explain not only the main electrification in thunderstorms, but also the subsidiary positive charge sometimes observed below the 0C isotherm. It may be interesting, however, to see what effect can be expected in the atmosphere due to the breakup of drops while the electric field is still low.

Data on chemical composition of rain (Junge, 1963) range over a wide interval of concentrations, roughly between 10^{-5} and 10^{-3} for the total normality of salt electrolytes, with Na^+ , Cl^- and SO_4^{2-} as prevalent ions. Typical average values would be $5 \times 10^{-5} N$ for continental air and $3 \times 10^{-4} N$ for maritime air. However, the effects of washout and evaporation should be taken into account; the range should therefore be shifted toward lower concentrations for raindrops in the cloud rather than at ground. CO_2 will always be present, in concentrations of the order of $10^{-5} M$. Thus, we can see from Fig. 5 that the range of concentrations in raindrops coincides with the region of rapid variation in the average charge separation. Any value between about 5×10^{-3} and -10^{-2} esu per drop breakup (or between 3×10^{-2} and -6×10^{-2} esu cm^{-3}) could be expected, with positive values (sign referred to large fragments) for the purer air and negative ones for the high range of concentrations in maritime atmospheres.

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