ELECTRICALLY CHARGED DROPS FROM BUBBLES IN SEA WATER AND THEIR METEOROLOGICAL SIGNIFICANCE

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ABSTRACT

A modification of Millikan's classic oil-drop experiment was used to determine the electric charge and radius of drops that were ejected from a bursting bubble at an air-sea water interface. Charge measurements were made of both the natural and the induced charge. Drops of 2 to 20 microns in radius carry natural charges of at least $2 \times 10^3$ to $5 \times 10^3$ elementary units, respectively. The induced charges are considerably higher, reaching $10^4$ elementary units on drops of 50 microns radius. The sign of the natural charge is positive on drops $< 4$ microns. For larger drops both the sign and magnitude of the charge appear to be a function of the depth of water through which the bubble rises.

The meteorological significance stems from the fact that rain and snow, as well as whitecaps, can produce great numbers of small bubbles in the surface waters of the oceans. Both laboratory and field work suggest that the majority of these bubbles produce positively charged drops that contribute to the atmospheric space-charge. Of special significance is the fact that, for positive induction fields less than about 25 $v$ cm$^{-1}$, a positive charge is found on the small drops. For fields greater than 25 $v$ cm$^{-1}$ the induced negative-charge exceeds the natural positive-charge and so the drops carry a net negative-charge. Consequently, small bubbles breaking at the surface of the sea in the presence of the earth's fair-weather positive field of about 1 $v$ cm$^{-1}$ will produce drops that carry a positive charge. Observations based on measurements of the bubble spectrum produced by whitecaps indicate that the charge on the drops may, under some conditions, provide a countercurrent of the same order of magnitude as the fair-weather conduction current. Thus the sea may be a source as well as a sink for the charge that maintains the earth's positive electric-field.

1. Introduction

The origin of the sea-salt particles that are so numerous in marine atmospheres [1, 2, 3] is most likely to be found in the bubbles that are produced in the water near the sea surface. The production of these bubbles can be modified by many factors including precipitation, wind force, and supersaturation of the surface waters [4]. If the evolution of rain in marine clouds is intimately connected to the salt-particle distribution in the free air [5], then the physical and chemical properties of these bubbles and their disintegration products should be of the utmost concern to the cloud physicist. This paper will be concerned with the electric charge that is carried from the water surface by the drops that are ejected from the bubble as it bursts at the air-water interface [6].

A number of papers have dealt with the charging of the aerosols that are produced by bubbling air through various liquids, but none of these investigations was aimed at a determination or understanding of the charge production from a single bubble. Chapman [7, 8, 9, 10], in a series of careful researches, determined the carrier mobility spectra of liquids electrified by bubbling and spraying. Köhler [11] obtained the charge on individual drops that were created by directing an air blast tangentially at a sea water surface. These drops apparently were formed by mechanical disruption of the water surface. Dinger and Gunn [12], who were interested in the electrical effects associated with the freezing and melting of water, measured the charge given off to the air by bubbles that were released from a melting block of ice. Aliverti and Llovera [13] carried out a laboratory study of the charge given off to the air by a disintegrating foam patch on a sea-water surface. Only the latter investigation appeared to be concerned mainly with the production of charged particles by the ocean surface and the resultant modification of the earth's electric field.

2. Experimental technique

Before attempting to discuss the methods used for charge determination, it might be well to describe just how the charged drops that we will be concerned with are ejected from the sea-water surface. Stuhlmann [14], in a study of effervescence, had observed the breaking of bubbles at the surface of fresh water and the subsequent ejection of several small drops. He postulated that the drops came from the breakup of a vertical jet of water that rose from the bottom of a

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collapsing bubble. This hypothesis was verified in this laboratory by taking high-speed motion pictures of the collapse of bubbles [15]. Fig. 1a shows a side view of the collapse of a 1.7-mm-diameter bubble and the formation of the jet. The bottom photo of the sequence shows a drop just at the point of separating itself from the jet. Fig. 1b shows the final stages of collapse of a 1-mm-diameter bubble with three drops detached from the jet. The time interval from the initiation of the collapse of the bubble to the separation of the five or six drops from the jet is of the order of $10^{-3}$ sec. The drops from bubbles <100-μ diameter are ejected with speeds that exceed 30 m sec$^{-1}$. This high ejection speed precludes visual observation of the upward flight of the drops and they only become visible when frictional retarding forces stop the upward motion and allow them to fall at a speed defined by Stokes' law.

Each of the several drops is ejected to a characteristic height which is a function of bubble size. The experimental study illustrated in fig. 2 shows how the ejected height of the top drop is roughly 100 times the bubble diameter up to the maximum of about 18.5 cm at a bubble diameter of 1.9 mm. The diameters of the top two drops coming off the jet are approximately 0.1 the bubble diameter while the lower drops are somewhat larger. For a given bubble size, the drop diameters and the heights to which they are ejected are amazingly reproducible. In fact, this reproducibility provides a very simple method for the production of homogeneous water drops down to one-micron radius [16]. More important, perhaps, it implies identical chemical and electrical properties of drops from similar positions on the jets from bubbles of similar size.

The first observations of a charge on the drops were made by simply holding a charged comb a few cm above an area where bubbles were breaking. All of the ejected drops were attracted to the comb regardless of the sign of the charge on the comb. This, of course, indicated that charging by induction was taking place. Electrostatic induction occurred

![Fig. 1a. Composite photograph of high-speed motion pictures illustrating some of the stages in the collapse of a 1.7-mm-diameter bubble and the formation of the jet. The time interval between top and bottom frames is about 2.3 milliseconds. The angle of view is horizontal through a glass wall. The surface irregularities are due to meniscus.](image1.png)

![Fig. 1b. Oblique view of the jet from a 1-mm-diameter bubble. The diameter of the smallest drop shown is 0.09 mm. The exposure time was 30 μsec.](image2.png)

![Fig. 2. Illustration of the heights of ejection of the several drops from the jet of a bubble bursting in sea water. Stuhlman's (14) findings are shown by dotted lines for drops from bubbles bursting in distilled water, while the solid lines represent the data obtained by Dr. C. Keith from bubbles bursting in sea water.](image3.png)
when the jet (bottom photo, fig. 1a) rose in the electric field of the charged comb, and induction charging took place as the drops were separated from the jet. It was desired to determine the magnitude of not only the induction charging but of any natural charging that might occur as the drops separated from the jet in a field-free region.

A. The Millikan-type chamber.—A device embodying the principle of Millikan’s classic experiment on the charge of the electron was constructed and used to obtain both the charge and radius of an individual drop. A schematic sketch of the apparatus is shown in fig. 3. The bubbles were created by forcing air under 10- to 30-psi pressure through a finely drawn-out section of glass capillary tubing. The bubbles rose through the sea water in the inner container A, broke at the water surface, and ejected electrically charged drops into the observation region between A and the horizontally mounted, rectangular (5.7×8 cm) brass plate B. Plate B was rigidly attached to, but electrically insulated from, a rectangular open-bottomed plexiglas housing C. This housing sealed the observation region off from room air by making contact with the sea water in the cylindrical (12-cm diameter) outer container D. The electric field E could be controlled by varying the voltage on the plate or by changing the plate-water distance. A simple switching circuit, not shown in fig. 3, allowed the plate to be at any desired ±DC voltage up to 12 kv with respect to the grounded sea water in A. The plate-water distance could be varied from 0 to 2.5 cm by raising or lowering C.

The observations leading to the charge and radius of an ejected drop were made in the following way. The air-supply value (not shown in fig. 3) was turned on and bubbles began to issue from the glass tip. With clean, filtered sea water and a bubble production rate of 3 to 10 sec⁻¹ most of the bubbles would break as they reached the surface and eject charged drops into the air. If a voltage of the proper sign is now applied to the plate while one is observing a particular drop as it falls toward the water surface, the resulting vertically-oriented electric field will exert an upward-directed force on the charged drop. The air supply is turned off and the plate voltage adjusted until the upward-directed electric force just balances the gravitational force and the drop remains stationary in the electric field. At this point we can write

\[ \frac{4}{3} \pi R^3 \rho g = E_o Q, \]

(1)

where \( R \) is the drop radius in cm; \( \rho = 1.025 \), the density of sea water; \( g = 980 \) cm sec⁻², the acceleration of gravity; \( E_o \), the electric field in esu cm⁻¹; \( Q \), the drop charge in esu. As both \( R \) and \( Q \) are unknown in (1), more information is required. This may be obtained by turning off the plate voltage and, with a stopwatch and a cathetometer, determining the fall speed \( V \) of the drop from the time it takes to fall a known distance to the water surface. With the cathetometer telescope, the drop is easily followed and its entry into the water can be anticipated by watching the drop approach its reflection from the water surface. While the drop is falling, the gravitational attraction must be balanced by the frictional force as given by Stokes’ Law and so we obtain

\[ \frac{4}{3} \pi R^3 \rho g = 6 \pi \eta RV \]

(2)

where \( \eta = 1.83 \times 10^{-4} \) g sec⁻¹ cm⁻³, the viscosity of the air; \( V \), the fall velocity of the drop in cm sec⁻¹. With the observed value of \( V \), equation (2) can be solved for \( R \) and, with this value, (1) may be solved for \( Q \). The validity of this method depends upon using sufficiently small drops such that Stokes’ Law will apply and that the time required for the drop to attain terminal velocity is negligible compared to the total time of fall to the water surface. In regards to the latter requirement, calculation indicated that drops as large as 10 microns radius essentially attain terminal velocity within about 0.2 sec after starting from rest. As this time is sufficiently small compared to the total fall-time of several seconds, the drop may be assumed to be at terminal velocity during the entire fall. Drops of this size are well within the range where Stokes’ Law applies.

Drops > about 10 microns radius fall much too rapidly to enable one to obtain an accurate value of

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Fig. 3. A schematic sketch of the apparatus that was used to determine the charge and radius of small drops from bursting bubbles. The charged drops were suspended, as shown, in the electric field \( E \). See text for details.
the terminal velocity over the short fall path that is available. Thus after the drop has been suspended in the electric field \( E_s \), and (1) applies, the voltage on the plate is not turned off but only decreased a slight amount. The electric field is now \( E_m \) where \( E_m < E_s \) and the drop will move slowly downward. The gravitational force is balanced by the frictional force plus the upward-directed force due to the field \( E_m \) and we can write

\[
\frac{4}{3} \pi R^3 \rho g = 6 \pi \eta RV + E_m Q.
\]

This equation can be solved simultaneously with (1) to obtain an expression for \( R \)

\[
R^3 = \frac{9 \eta V}{2 \rho g} \left( \frac{E_s}{E_s - E_m} \right).
\]

Note that the \( 9 \eta V/2 \rho g \) term follows directly from Stokes' Law when (2) is solved for \( R^2 \). As \( E_m \) approaches zero, (4) approaches Stokes' Law.

The production of bubbles by a glass tip provides a simple way to produce any desired bubble size, but it obviously is not the manner in which bubbles are produced on the open sea. In an attempt to approach this natural method of bubble production, the glass capillary tip was removed and the inner container A of fig. 3 was extended downward about 35 cm and closed off at the bottom. Housing C was removed and sea water was allowed to fall down the extension tube in such a way as to produce as much splashing as possible. By the time A was full of water, many hundreds of minute bubbles were distributed through the entire water column. Housing C was replaced immediately with a minimum of plate-water separation (<1 cm) to insure rapid saturation of the chamber. The saturation process is undoubtedly hastened by the partial evaporation of the hundreds of drops that are ejected into the chamber during the first few minutes after the chamber is sealed. At the end of about four minutes, only a relatively small number of minute bubbles remain and these, upon bursting, produce drops that rise a maximum of about 0.3 cm. With the techniques already outlined, the charge and radius of the drop are easily determined.

B. Qualitative charge measurements.—The Millikan-type chamber that was just described was used to obtain the charge and radius of drops that were

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**Fig. 4a.** A schematic sketch of the apparatus used to determine the sign of the charge on the drops from large bubbles. The vertical line rising up through the pillbox represents the upward motion of the drop, and the arrows at the top indicate its direction of fall in the horizontal electric field that exists between the vertical plates. The charged drop is deflected to one side or the other depending on the sign of the voltage \( V \).

**Fig. 4b.** Similar to 4a with the exception that here the drop is suspended between the upper two plates by the electric field \( E \) and the pillbox has been replaced by a flat metal plate.
ejected from small bursting bubbles to heights of about 2 cm or less. It was not feasible to use this apparatus for the larger drops that were ejected to heights >2 cm as the plate-water distance became too great. This, plus the increased drop mass, required prohibitive plate voltages far in excess of the available 12 kv to produce the necessary electric fields for drop suspension. In addition, such high plate voltages produce corona and sparking at the regions of sharp curvature on the plate. It is thus perhaps fortunate that these large drops have such a high settling rate that they have little probability of remaining air-borne over the oceans and, therefore, will contribute little to the net separation of charge at the air-water interface. More details of this will come later. At any rate, a knowledge of the qualitative and semi-quantitative nature of the charge of the large drops would certainly be of interest in attempting to understand the fundamentals of the charging process.

It was pointed out earlier that the detection of any natural charge on the drops by their attraction or repulsion for a charged probe is overshadowed by an induced charge that is obtained during the jet to drop evolution. It is evident that the jet from the bursting bubble must be shielded from the electric field of the "test" charge. Two very effective yet simple experimental setups for this purpose are shown schematically in fig. 4. In fig. 4a, the region in which the bubbles burst is covered by an open-bottom, 9-cm diameter, 3-cm deep, brass cylinder. Any electric fields within the cylinder due to potentials at the brass-water interface are eliminated by lining it with blotting paper which is then saturated with sea-water [17]. To minimize the penetration of lines of force through the 3-mm hole at the top of the cylinder a 6-cm square, blotting-paper-lined brass plate was placed horizontally above the cylinder. The drops from the bursting bubbles passed up through the hole in the cylinder and a similar hole in the brass plate and entered the horizontal electric field between two vertical plates. If no field was present the drops would fall vertically down between the plates, but in the presence of a field they experienced a deflection to the left or right depending on the sign of their charge.

The apparatus shown in fig. 4b is similar in principle to that of fig. 3 except that here a grounded plate takes the place of the water surface. By moving the upper plates close together, a relatively low voltage \( V \) can produce a sufficiently high electric field to suspend the charged drop. The two grounded lower plates prevent induction charging of the drop. It is apparent that the rapid evaporation of the drops will allow only a crude estimate of the magnitude of the charge.

As some of the experiments with the drops from the smallest bubbles were aimed at obtaining only the sign of the charge, a far simpler device than those discussed so far was used. This consisted of nothing more than a large (11×21 cm) insulated copper plate that was lined on the bottom side with sea-water-saturated blotting paper and placed horizontally about 1 cm above the area where small bubbles were breaking. During the instant a bubble broke and drops were being ejected into the air, a copper wire was used to short-out the plate and the water surface. Thus, no electric fields could be formed due to sea water-copper potentials. While the drop was still in the air, the wire was removed and a voltage applied to the plate. The motion of the drop in the resultant electric field indicated the sign of the charge.

**C. Space charge measurements.—** If bursting bubbles at the sea surface are ejecting charged drops into the overlying air, then any net charge should be amenable to measurement by some type of space-charge measuring device. Although a number of methods are available for measuring space charge [18], the method used here, first suggested by Kelvin [18], consists of measuring a potential due to the space charge. The air containing the space charge is allowed to flow through a cylindrical cage made of 14-mesh copper window screening, on the axis of which a small amount of radioactive material is attached to a conducting rod. The space charge will create a potential difference between the cage and the radioactive point. The function of the radioactivity is rapidly to bring the rod to which it is attached to the potential of the center of the cage with respect to the periphery. Assuming a uniform distribution of space charge it can be shown that

\[
V = \pi R^2 \rho. \tag{5}
\]

With (5), the space charge \( \rho \) can be determined from the radius of the cage \( R \) and the voltage \( V \).

**3. Results**

**A. Natural charge from artificially created bubbles.—** By artificially created bubbles we mean bubbles that are produced by forcing air through fine glass tips as contrasted to bubble production on the open sea by the entraining of air by breaking waves. The apparatus shown in fig. 3 was used for the measurements discussed here, and some results are shown in fig. 5 in the curves marked B, C, and D.

Most of these data were obtained with bubbles that were ejecting drops to heights of 5 to 15 mm although the drops used were not necessarily the ones that rose to these heights. It was usually the case that several drops were in the air when the electric field was applied, and the drop that was most nearly balanced was the one selected for the test. Consequently, nothing can be said of the initial position of
the drop in respect to the others rising from the same bubble.

Curve B is for the charge found on small drops that appeared to be ejected only a few mm above the water surface. Other larger drops that were created at the same time rose much higher. Curves C and D show the charge from experiments with larger drops. Note that curve B indicates higher charges for drops of 3 to 4μ than does curve C and that the data of curve D suggest a different grouping from that of curve C. The most probable explanation of this is based on the fact that the charge on the several drops from a bursting bubble is a function of the depth of water through which the bubble has risen (see section C). This fact was not discovered until after most of the work described in this paper had been done and therefore no record was made of the length of time that the bubbles existed before they arrived at the surface and broke. It is possible that the bubbles used to obtain the data of curves B, C, and D were released at different depths and thus the charge on a drop size common to two of the curves might be expected to be different. It will be shown in the next two sections that the data for the small drops (curve A) probably represent the maximum charge on drops from small bubbles and that curves C and D most likely represent charges that are less than the maximum charge that could be obtained on drops from large bubbles.

The charge for the drops of curves B and C is mostly positive and reaches about 10⁸ fundamental units while that for curve D is negative and attains a value of several thousand fundamental units. It will be shown presently that the charge is positive on drops from small bubbles and either positive or negative on drops from large bubbles. In the case of the large bubbles, the sign of the charge is a function of bubble age and the position of the drop in the bubble jet.

B. Natural charge produced by bubbles created by splashing.—One might argue that the charge of the drops of fig. 5 is a direct result of a charge-separation process that occurs as the bubble is formed and detached from the capillary tip. To investigate this effect, bubbles were created, as described earlier, by the splashing of water to simulate bubble formation at sea. As the drops from these bubbles were all <5-μ radius, the bubbles from which they originated were probably <50-μ. The charge-radius correlation that was found was not significantly different from that obtained with drops of similar size from bubbles from capillary tips (see curve B, fig. 5). The sign of the charge for all of the drops investigated here was positive, and it appeared that most, if not all, of the drops from bubbles of this size carried a positive charge.

It was conceivable that the existence of surface films and the concomitant lowering of surface tension might play a major part in the drop-charging process. To check this, data were obtained from sea water with surface tensions varying from 40 to 74 dynes cm⁻¹. The surface films were produced by oleic acid, unknown contamination on the water container, Aerosol OT, and by simply touching the water surface with one's finger. Several surface-tension values were made at the end of each run with a standard du Nouy tensiometer but, as errors of an uncertain magnitude were associated with this method [19], these values can only be considered approximate ones. Although in general it was found that the nature of the surface film has little effect on the magnitude of the charging and no effect on the sign of the charge, at least one experiment showed a
reversal of charge which appeared to be a result of surface film effects.

It can be simply and convincingly demonstrated that the positive charge is most likely characteristic of a majority of the drops from small bubbles created by splashing sea water. When many tens of bubbles are breaking sec⁻¹, the stratum of air in the first millimeter or two above the water becomes filled with a "haze" of drops. If a strong field is applied, the drops move up or down depending on the direction of the field and the sign of the charge on the drop. It appears that all of the drops that are ejected from these small bubbles are positively charged. Consecutive observations on twenty breaking bubbles showed no exception to this. These observations have been repeated on many occasions with the same results.

C. Natural charge on drops from large bubbles.—It was pointed out earlier that the apparatus shown in fig. 3 could not be adapted easily for the large drops that were ejected more than about 2 cm from the water surface. As only a semi-quantitative knowledge of the charge was desired, the experimental setups of fig. 4 were used. All bubbles were produced by a capillary tip as it was not feasible to produce large bubbles by splashing and expect them to break directly beneath the holes in the cylinder and horizontal plates of fig. 4.

The drops from various-sized bubbles were ejected from 0.4 to 8 cm. Fig. 2 shows that the drops ejected to the maximum height, 8 cm, came from bubbles of about 700-μ diameter. In using the apparatus shown in fig. 4a, the drop that rose the maximum height from each bubble indicated a negative charge. To eliminate the possibility that this negative charge was being caused by surface films or by some other action of the cylinder-blotter-water contact, the apparatus of fig. 4b was used. After the 5-cm plastic cylinder was full, the sea water was allowed to drain over the paraffined edges to remove surface films. A clean platinum wire was used to ground the water.

Observations were made of the electric field that was required to suspend the top drop as a function of the depth of water through which the bubble rose. As the field required to suspend a given drop is inversely proportional to the charge, it is a simple matter to obtain the relative charge of the drop as a function of bubble depth. It was found that the charge on the top drop of a jet was positive if the bubble rose from a depth of at least a centimeter and increased with the bubble-release depth. Some preliminary experiments indicate that, with bubbles that produced jets of 30 to 40 mm, the top drop from a bubble released at a depth of 100 cm carried a positive charge at least ten times as great as the same drop from a bubble released at a depth of only 1 cm. In most of the experiments where the bubble release depth was <0.2 to 1 cm, the top drop was weakly charged either positive or negative. This appeared to be true for the top drop from jets not only in the 30- to 40-mm range but in the entire range studied to date; i.e., 6 to 50 mm.

The second drop in the jet in the 30- to 40-mm range is strongly negative if it comes from bubbles that are released near the surface but becomes increasingly less negative and finally positive as the depth of bubble release is increased. The point at which the charge on the second drop goes positive is not well known but it appears to be for bubble-release depths in excess of 5 cm. At the present time nothing can be said of the variations of charge on the lower drops of the jet as a function of the bubble-release depth.

With these findings in mind, it is unlikely that the positively charged drops of curve C or the negatively charged drops of curve D, fig. 5, represent the maximum possible charge for drops of this size that originate from bubbles in sea water. If we carry this reasoning to the small bubbles, it is puzzling to find that the charge on drops from bubbles released near the surface (curve B, fig. 5) is similar to that from bubbles that rose from much greater depths (section B). No explanation can be given at the present time, but this point will be considered in future work.

D. Induced charge.—The technique of the measurement of an induced charge involves the use of the apparatus of fig. 3 to measure the charge and radius of drops that originated from bubbles that burst at an air-water interface above which existed a known electric field. Electric fields from about 100 to nearly 300 volts cm⁻¹ were used, and the major results are shown on curve A of fig. 5. The data fall on essentially a straight line and indicate that charges reaching 10⁶ elementary units can be obtained on drops of 50-μ radius. With the exception of one point, all of the data for drops >20μ were obtained with fields of 225 to 280 volts cm⁻¹ while the data for drops <20μ, plus the above exception, were obtained in fields of 110 to 135 volts cm⁻¹. The linearity of the graph and the merging of one set of data into another suggests that the induction charging is fairly independent of field strength within the above-mentioned values. The drops >20μ probably are amongst the last of the several to arise from a breaking bubble. These are known to be the largest and are observed to rise only a small fraction of the distance attained by the other drops. When the electric field is high enough to induce charges sufficient to suspend these large drops, the smaller drops are carried rapidly to the upper plate. Using the data of curve A, one can calculate that a field of 200 to 300 volts cm⁻¹ will suspend the largest drops while only about 50 volts cm⁻¹ are necessary for the drops of about 3μ.

E. Induced charges and "buckling" fields at low field strengths.—The results of part B of this section
showed that the small bubbles produced by the splashing of water will burst at the water surface and eject positively charged drops into the air. As this process occurs in the absence of an electric field, induction charging cannot be the cause and, therefore, we must assume that some type of charge separation process is occurring at the air-water interface. Inasmuch as part D shows that induction charging can be appreciable, it is reasonable to suspect that a field strength of the proper value could be found such that an induced negative charge would be equal to the naturally occurring positive charge. Thus the drop will have a net-zero charge. In other words, there should exist a positive electric field such that, for fields smaller or larger, small bubbles will eject positively or negatively charged drops, respectively. By a positive field we mean one in which the potential increases with distance from the water surface.

This hypothesis was tested in the following way. Bubbles were produced by splashing water in a manner already described. An electric field, either positive or negative, was produced in the region above the breaking bubbles so as to insure an induced charge on the drops. While the drops were still in the air, a much larger electric field, of the order of several thousand volts cm\(^{-1}\), was applied. The observed motion of the drops in this test field was used to indicate the sign of the charge. Now the bubble spectrum created by splashing water is such that only a relatively few bubbles eject drops as high as a centimeter while the great majority eject drops <2 mm. These later drops are <5-\(\mu\)m radius and are the ones that we shall discuss below.

Let us consider the charging effects of these small drops. For all negative induction fields, the induced charge plus the natural positive charge gives, as must be the case, a net positive charge. This was shown by a pronounced up-and-down motion in a negative and positive test field, respectively. This same behavior was indicated for positive induction fields less than about 15 volts cm\(^{-1}\), thus indicating that the induced negative charge is not sufficiently great to exceed the natural positive charge. As the induction field went from negative to positive, the upward motion of the drops in a negative test field became progressively less pronounced until, at about +15 volts cm\(^{-1}\), the cloud of drops was observed to rise very slowly, if at all. At an induction field of >30 volts cm\(^{-1}\), the induced negative charge exceeds the natural charge and a net negative charging occurs. A reversal of the motion of the drops in the test field is observed, and they are now accelerated up or down in a positive or negative test field, respectively. Consequently, it is to be expected that the critical field necessary to produce a net-zero charge will vary, depending on drop sizes and charge, from about 15 to 30 volts cm\(^{-1}\).

These findings do indeed show that drops can leave the water surface with a net positive charge in spite of the existence of a positive bucking electric field. It would seem that the induced charge is a function of only the induction field and is independent of the natural charge. With this assumption, one can build up a simple qualitative model of the charge variation with induction field. This is shown in fig. 6 where the net drop charge is represented by the ordinate and the induction field by the abscissa. The graph of fig. 6 can be considered to represent the relative contributions of the natural and induced charge for a given small drop. The origin of the natural positive charge is not known but as it is most likely a manifestation of the chemistry of the bubble-water interface plus the manner in which the drops are formed, it can be represented by the arbitrarily placed horizontal line showing it to be independent of induction fields. The induced charge, shown as a dashed line through the origin, is here assumed, at least for positive or negative fields whose absolute value does not exceed 50 volts cm\(^{-1}\), to be a linear function of the field.

This is in accord with the usual classroom experiments to demonstrate the existence of an induced charge. By algebraically adding the two charges, the net charge may be obtained and is shown as the solid line. This model is in agreement with the basic findings discussed above in that the net charge is increasingly positive as the electric field algebraically decreases from a certain positive value but is increasingly negative for larger positive fields. It should be noted that the field for which the net charge is zero was selected to be in agreement with the observational data.

**F. Space charge above the surf.**—If, as the present work indicates, positively charged drops are ejected from the small bursting bubbles and if the bubbles...
formed at sea by natural processes are predominantly of this size, then it is reasonable to suspect that one should be able to find a positive space charge in the atmosphere over the sea. This should be especially true over regions of intense bubbling. Using the space charge apparatus described earlier, the writer, in connection with the field studies of Project Shower [20], carried out several experiments over large surf-producing regions on the east coast of the island of Hawaii. The results of one such experiment, shown in fig. 7, indicate that a large positive space charge was found downwind from regions where breaking waves had produced such great numbers of bubbles that the water appeared a milky white. In this case, the wind was blowing nearly parallel to the surf line and across a shallow inlet about 100 m in width. Large waves were breaking about 50 m offshore and produced foam and bubble-filled water that were carried nearly into the beach. The space-charge measurements were made on the downwind side of the inlet and curve A of fig. 7 shows the time variation of space charge near the beach where little bubbling had occurred. This is somewhat higher than the readings that were found inland away from the surf. Curve B shows how the positive space charge rises to average values of nearly 2000 fundamental units cc\(^{-3}\) as one approaches the area just downwind from the region of pronounced bubbling produced by the breaking waves. Curve C, obtained directly downwind, indicates even higher values and rapid fluctuations reaching peak space charges of about +5000 units cc\(^{-1}\). Here the high concentration of drops from bursting bubbles produced a marked salt haze that was easily visible against the dark vegetation near the shore.

Additional evidence for the production of a positive space charge from the bursting of bubbles was obtained in the same area by Schaefer [21] who made observations of the current flow into a grounded radioactive point. He found that the positive current increased when the point was held near the breaking surf and observed the current "to have a definite relationship to the mass breaking of bubbles following the shoreward rush of foam from a breaking wave." This increase of positive current with bubble breakage seems certain to be the result of an increase in positive space charge.

4. Discussion

A. Origin of the drop charge.—At this point it will be well to review some of the literature to show that the charging described in this paper cannot be explained by existing hypotheses. The charging of drops created by spraying or other disintegration methods has usually been explained by the Lenard [22] spray-electrification mechanism in which it is postulated that the charge arises from a rupture of the double layer [19] that is believed to exist at the surface of most liquids. This double layer, in the case of pure water, consists of a negatively charged surface layer of a depth of about 20 molecules with an underlying positive layer of similar depth [23]. During a spray-disintegration process the smallest drops, considered to originate from the outer negative layer, should be charged negative. Other drops, although relatively few, are positive and originate from the deeper positive layer. According to this mechanism, the charging of drops >0.1-micron diameter should not occur for then the drop should be composed of water from both layers. This hypothesis failed when Chapman [7, 10], using the Millikan oil-drop method and an Erikson mobility tube, found relatively high charges of both signs on drops up to 5 microns radius.

In 1953, Dodd [23] found analogous results when he showed that charged drops that were created by spraying various nonconducting liquids had a net neutral Gaussian distribution. Dodd carried out an investigation to find out if this asymmetrical charging might be expected to result "from statistical fluctuations of the electrolytic ion concentrations of both signs present in relatively low concentrations compared to those in aqueous solutions." The results indicated that this hypothesis could indeed be used to explain the charging that was not predicted on the basis of the Lenard theory but it appears that it cannot account for the large charges that were found by Chapman [7].

The present findings of charge on micron-sized drops cannot be explained by the Lenard mechanism...
and as the charge on a collection of drops is, for the most part, either positive or negative but not both, we cannot appeal to statistical fluctuations of charge within the bulk water. The writer will attempt to show that the charge originates from some action at the bubble-water interface and is apparently independent of the inductive charging process that occurs when the bubble breaks in a region containing an electric field.

After the preliminary findings [6] were published, Prof. L. B. Loeb, aware that they could not be explained on the basis of existing theories, suggested2 that stray fields or voltages caused by electrode potentials might possibly account for the charging. The writer devised the type of experiment as illustrated in fig. 4a to eliminate any such effects. The continued occurrence of charged drops with this setup plus the production of positively charged drops in a bucking electric field removed any doubt that the drops could become charged by processes other than by induction.

Experiments with bubbles produced in a more natural manner by splashing were carried out to determine if any bubble charging was occurring at the capillary tip. As reported earlier in the paper, no significant difference in drop charge was found. The charge mechanism either was controlled by some double-layer phenomena at the bubble surface or else at the surface of the bulk water in the immediate vicinity of the bubble. These latter effects, although present, do not appear to be the main charging mechanism. The finding of a large increase of drop charge as a function of bubble-release depth definitely precludes bulk water surface effects as a major charge-producing mechanism and strongly suggests that the charge arises from phenomena at the bubble-water interface.

The charging of a gas bubble in water and its relative motion or cataphoresis during the application of an electric field is well known [24]. In this and later work, McTaggart [25] showed that a bubble in distilled water behaved as if it carried a net negative charge but, with concentrations as low as $8 \times 10^{-8}$ N thorium nitrate, the charge appeared to be positive, and in the region of $6 \times 10^{-8}$ N a bubble initially negative became positive as the bubble decreased in size. After experimenting with various gases, Alty [26] concluded that the composition of the gas plays very little part in surface electrification. In attempting to explain the charging, he presented a model that postulated the existence of a double layer that formed as a result of selective absorption of ions of one sign on the bubble. Polar water molecules were considered to be partly or completely orientated at the bubble surface and to attract negative ions from the water.

These ions gave the bubble its negative charge. A partial "covering up" of the negative ions by a diffuse cloud of positive ions was considered to extend some distance from the bubble surface.

During an investigation of the electrification accompanying the melting of ice, Dinger and Gunn [12] observed that ice made from distilled water showed electrification upon melting only if bubbles were present within the ice. They concluded that the bubbles on being released from the ice would carry a negative charge to the surface of the water and, upon bursting, somehow transfer this charge to the air and leave the water with a positive charge. The observed charge transfer was in the right direction to lend support to Alty's hypothesis. In general, they found that only bubbles coming from melting ice made from distilled water indicated a negative cataphoresis charge. If the same experiment was performed with ice made from tap water or aqueous solutions of HCl or NaOH such that the pH was <2.5 or >10, no electrification was noted. These significant observations are analogous, in some respects, to the findings of workers in spray electrification [8, 27, 28] who, in general, found that the addition of various contaminants to distilled water greatly reduced the net spray electrification. Chapman [8] stated "the fact that the amount of electrification from salt solutions decreased with increasing concentration (above $10^{-4}$ N) makes it impossible to account for much of the ionization observed over the oceans by a spray electrification process, since sea water is about 0.7 normal and even with 0.2 normal KCl the electrification is very slight."

To return now to the cataphoresis of bubbles, it would be well to consider the increase of charge of the drops (part 3, section C) as a function of bubble-release depth in the light of the findings of an appreciable bubble-charging time [26, 29, 30, 31]. Now inasmuch as the present work indicated that an increase in bubble-release depth showed no significant changes in bubble size, as evidenced by no change in the ejection heights of the drops, it seems reasonable to suppose that the effects of bubble-release depth are actually effects of the age of the bubble. Thus if the charge of the drops is a result of the charge of the bubble, then the present findings would indicate that a bubble-charging time is to be expected. Although the writer is unaware of any similar experiments with bubbles in sea water, other investigators have observed bubble charging in relatively pure water. Currie and Alty [30] found that bubbles of the order of 2-mm diameter required about 2000 seconds before an equilibrium charge had been obtained. Whybrew, Kinzer, and Gunn [31] observed that bubbles of about 300-microns diameter in water of a resistivity of from 0.8 to $5 \times 10^6$ ohm cm carried

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2 Personal communication.
about four times the surface charge after 15 min of existence as compared to less than 20 sec.

The statement made earlier to the effect that the net charge on a drop ejected from a bubble can be attributed to two independent charging mechanisms, that of induction charging and that of the natural charge, is based on two considerations. First, the findings of a positive charge in the face of a bucking electric field, as illustrated in fig. 6 make the idea appear qualitatively reasonable and, secondly, a similar phenomenon has been found by other investigators [27, 32]. For example, Banerji [27], in studying spray electrification, applied ± voltages to his atomizer (and hence to the water) and observed the net charge on drops that were sprayed from a given quantity of water. He obtained a net charge that varied linearly with the applied voltage in the same manner as shown on fig. 6.

It now seems quite evident that the electrification observed in the present study can be considered as arising from two independent processes with the most important being the charge separation as a result of double layer or other effects at the bubble surface. Any future work would do well to proceed along two separate lines. First, one should pay close attention to the work of Alty [29] but with considerations of the high conductivity of sea water. Secondly, it appears to be most important that we have a much better understanding of the details of the formation of the drops from the bubble jet. The high-speed camera studies [15] were quite inadequate to give any detail of the drop formation from bubbles of the order of 100-microns diam. A camera taking pictures at a rate of 10,000 sec⁻¹ or more would be necessary to give information on the manner in which the bubble jets are formed.

B. Possible atmospheric electrical effects.—If one is to make an attempt to evaluate the atmospheric electrical effects that might result from a collection of charged drops from bursting bubbles, it is apparent that in addition to a knowledge of the magnitude and sign of the charge on a given-sized drop one would have to have an idea of the size distribution and rate of production of the drops. This, in turn, implies an understanding of their source, the spectrum of bubbles in the sea. Recent experimental studies [4] have shown that whitecaps are a most potent mechanism for the production of a bubble spectrum in which, in the size range of about 70- to 500-microns diameter, the number of bubbles m⁻³ is inversely proportional to the fifth power of the bubble diameter. From these experimentally determined values it was computed, assuming that 10 per cent of the sea surface was producing bubbles, that over a given area the average production rate for bubbles <100-microns diameter was 3 cm⁻² sec⁻¹ while the production rate for bubbles from 100–200 microns was only about 0.3 cm⁻² sec⁻¹, or 10 times less. The production rate for bubbles >200 microns was negligibly small, being about 0.06 cm⁻² sec⁻¹. It is evident, assuming that bubbles are the source, that the great majority of the airborne drops that are observed over the open sea should be <20 microns diameter. (This is determined from the rule of thumb, mentioned earlier, of 10 as the ratio of bubble-to-ejected-drop diameter.) This agrees with the experimental work of Woodcock [1].

We can now make a rough but conservative estimate, based on the above and present studies, of the charge transfer that might be expected to take place at the sea surface. Let us assume that only one drop from each bubble remains airborne. If each of the drops from the 3 bubbles cm⁻² sec⁻¹ that are <100 microns carries a positive charge of 10³ fundamental units while each of the drops from the bubbles >100 microns transports an average negative charge of 3×10⁶ units (see fig. 5), then a net positive charge of about 2×10⁷ fundamental units will be transferred from the sea to the air cm⁻² sec⁻¹. This would appear to be a minimum value as the above assumptions of all drops from bubbles >100 microns remaining airborne and carrying a negative charge is most unlikely.

The production of a net positive space charge should not be confined to the breaking of bubbles that are produced solely by wave action. In addition to the obvious whitecaps, Blanchard and Woodcock [4] have found that snow, hail, and raindrops are capable of producing great quantities of bubbles, predominantly <100 microns, whose ejected drops should carry a positive charge. As all of these natural methods for the production of bubbles in the sea, and especially those involving precipitation, produce a spectrum of bubbles the majority of which are <100-microns diameter, it follows that most of the ejected drops, according to the present study, will be positive in charge and <10-microns diameter. The significance of the net positive charge of 2×10⁷ fundamental units cm⁻² sec⁻¹ that has been estimated to be leaving the sea as a result of breaking bubbles from wave action can be seen when we compare it to the average air-earth conduction current that prevails in areas of fair weather. The upward flow of a positive charge of 2×10⁹ fundamental units cm⁻² sec⁻¹ is equivalent to about 10⁻⁶ statamperes cm⁻² which is the same value that has been calculated to be flowing into the oceans wherever fair weather prevails [33]. Now it is generally assumed that the mechanism by which the atmosphere regains the positive charge that is lost as a fair weather conduction current has its origin only in thunderstorms while the sea has been considered only as a sink for the positive charge. In view of the above calculation, it appears that the sea, which
comprises about 70 per cent of the earth's surface, may be far from being a complete charge sink and might, during intense wave action or snow showers, contribute an appreciable net positive charge to the atmosphere. The positive space charge (fig. 7) found over the surf in Hawaii suggests that this is true for intense wave action. The calculated contribution of $10^{-4}$ statampsere cm$^{-2}$ of positive current from sea to atmosphere certainly cannot be considered as an average for the ocean as a whole but only for those regions where the above effects would cause moderate bubble formation. The transfer of charge from sea to atmosphere was discussed by Aliverti and Lovera [13] who bubbled air through sea water and found a net positive charge transferred to the air. They did not get their data from individual bubbles but from an artificially created foam patch that, in the opinion of the writer, is not representative of bubble phenomena on the open sea. Thus it is hard to interpret their results in a quantitative manner.

The postulated net positive charge transfer from sea to atmosphere by breaking bubbles becomes especially significant in view of the fact expressed earlier in the paper that it can occur in the presence of bucking electric fields up to about 25 volts cm$^{-1}$. Inasmuch as the average fair-weather field over the oceans is about 1 volt cm$^{-1}$ [34], it is plain that the transfer of positive charge will be relatively unaffected by such small fields. Once airborne, the motion of the charged drops due to the electric field will be equally insignificant with respect to the motion due to gravity and turbulent processes. For example, a 3-micron-radius drop carrying a charge of $10^6$ fundamental units will have a mobility of only $1.6 \times 10^{-4}$ cm sec$^{-1}$, some three orders of magnitude less than that of the small ions in the atmosphere and 70 times less than the fall velocity due to gravity. Thus, in opposition to the force due to the earth's electric field, turbulent mixing and convective updrafts could carry the positive charge into clouds. Here the process envisaged by Vonnegut [35] may reverse the electric field at the top of the cloud and effectively cause a transfer of positive charge to the higher regions of the atmosphere where it spreads out and returns to the earth as a part of the fair-weather conduction current.

Let us consider the electric fields at the surface of these charged drops with the view that under some conditions they may be high enough to cause corona discharge and neutralization of the drop charge. Consider the case of a 3-micron-radius drop carrying 1000 fundamental units of charge (see fig. 5) when it leaves the sea and again when it is subjected to humidities $<75$ per cent. Using Gauss' Law we find that the electric field $E$ at the surface of a drop of radius $R$ carrying a charge $Q$ is $E = Q/R^2$ which, in the above case of the drop as it leaves the sea, gives a field of 1600 volts cm$^{-1}$. As the humidity of the air is decreased, the drops will become smaller and more saline. For humidities $>75$ per cent, an equilibrium drop size will exist where the vapor pressure of the saline drop is identical with that of the air. At about 75 per cent relative humidity the drop becomes a saturated salt solution and further reduction of the vapor pressure of the air will cause the NaCl to crystallize [36]. A spherical crystalline sea-salt nucleus has a radius about 25 per cent of the initial radius [37]. Gauss' Law shows that a 16-fold increase of the electric field will occur and, consequently, the above-mentioned field of 1600 volts cm$^{-1}$ will rise to 25,600 volts cm$^{-1}$. It might be well to note that the charge of a drop will diminish the tendency of the drop to evaporate [38]. It can be shown, however, that the effect is negligible when we consider magnitudes of charge and radius as given above.

If an electrical storm occurs that produces fields of 100 volts cm$^{-1}$ at the sea surface, it can be shown from the data of fig. 5 that all drops $<10$-microns radius will have a sufficiently high induced charge to enable them to be carried upward in the electric field. The field at the surface of these 10-micron drops, assuming a charge of $2.2 \times 10^4$ fundamental units, would be 3200 volts cm$^{-1}$, becoming about 51,000 volts cm$^{-1}$ on the crystalline nucleus at a humidity $<75$ per cent.

It has been assumed that the crystalline nucleus (not entirely crystalline as magnesium and calcium salts are still in solution long after the major salt NaCl precipitates out) is spherical, but this is not the case as examination under the microscope reveals many sharp edges and protuberances [39]. As the surface charge density will vary in direct proportion to the reciprocal of the radius of curvature [40], the edges and points will attain a proportionately higher surface charge $\sigma$. Consequently, the field strength $E = 4\pi \sigma$ may well attain values far in excess of those computed on the basis of a spherical drop.

Although in the case of phase change and at points of high curvature the surface electric field may well exceed 30,000 volts cm$^{-1}$ (the critical value for spark discharge in air at atmospheric pressure), it will not necessarily break down. The breakdown of an electric field results from ionization produced by the collision of ions with the molecules of the gas. In the case of spherical drops, the electric field falls off inversely with the square of the distance from the drop center. Thus, the smaller the drop the faster will the field decrease over a given distance from the drop surface. The probability of ionization by collision will, therefore, decrease, and the electric field required for corona will increase. This was shown by the investigation of Zeleny [41] and more recently by the work of Engle [42]. It appears then that the charge on
these drops will not experience a neutralization by electric-field breakdown. The only method by which charge can be lost is by the diffusion onto the drops of the small ions that exist in the atmosphere over the oceans [43]. The relaxation time for the charge on drops in the lower atmosphere will vary, depending upon the conductivity, from 5 to 40 min [44]. Thus, under some conditions it is to be expected that drops could be carried by air current into clouds and still retain much of their original charge. In any event, any decrease with time of the charge of the drops does not change the net charge per unit volume of space but merely transfers the charge to smaller carriers.

5. Conclusion

Probably the most significant aspect of the present findings is the charge-separation process that appears to be occurring at the bubble-water interface of a small bursting bubble which results in a positive charge on the ejected drops. The observations cannot be explained on the basis of known phenomena and make further work imperative.

The suggestion that the sea need not be considered as a complete sink for the atmospheric space charge, but also as a source, leads to consideration of the sea as a source of the supply current to maintain the earth's electric field. This should be followed up with more laboratory and field studies of the net charge transfer under various simulated and natural bubbling conditions. It would be well to investigate the charge transfer by the small drops that are created by the bursting of the films of the relatively few large bubbles that are produced by wave action [45].

Finally, it is well to keep in mind that the large electric fields, associated with thunderstorms and perhaps snow showers at sea, would induce high charges on the ejected drops from bursting bubbles. Due to an increase of local winds and precipitation in these storm areas, the bubble formation would be increased and a high local concentration of space charge should occur. It may be that such pronounced local effects will be of more importance in the atmosphere electrical balance than the charge transfer from a relatively quiet sea in areas of low surface winds and fair weather.

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