Interpretation of Carrier Mobility Spectra of Liquids Electrified by Bubbling and Spraying

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The homogeneous group of negative carriers of mobility 1.8 cm/sec. per volt/cm, produced by bubbling distilled water, consists of a normal negative ion in moist air. The positive and negative groups at mobilities $+1.0$ and -0.95 appear to be due to carriers containing an extra H^+ and OH^- ion, respectively. It is likely that the other distilled water groups are formed partly by the breaking of the thin bubble film in uniform fashion, and partly by the evaporation of larger carriers. The presence of electrolytic ions in the bubble film seems to cause irregular rupture, and thus a wide distribution of mobilities. With increasing concentration in solutions more concentrated than 10^{-3} mole per liter, the reduced vapor pressure of the carriers containing solute causes the main maximum to shift gradually to lower mobilities (i.e., larger drop sizes). Presence of sucrose in the bubble film appears to provide "nuclei" so that a greater number of droplets are formed than is the case with distilled water. Thus more total charge and more types of carriers are produced. When distilled water is bubbled more violently than usual, the bubble films are more extensively torn into thick fragments by the air blast, so that the positive charges (which on Lenard's theory are in the under layer of the electrical double layer) are more frequently torn off. Hence the proportion of positive charge produced relative to the negative is greater. The less turbulent breaking of the bubble film in the case of gentle bubbling seldom exposes positive charges, so that no positive carriers are produced. The use of supersaturated air in the bubbling blasts inhibits evaporation so that only a wide distribution of carriers of all sizes is observed.

IN the preceding paper the author has reported the results of an investigation of the electrification of droplets produced by bubbling water and various aqueous solutions. It is the purpose of this paper to interpret these results on bubbling, and to correlate them with some results previously observed on spraying.[1] Although all the conclusions are interrelated, the paper is divided into sections. In general, each one primarily relates to the interpretation of a particular set of experiments, or to the nature of a particular group of carriers.

EXISTENCE OF CARRIER GROUPS

The striking peaks in the curves of the preceding article showing current as a function of mobility indicate the existence of homogeneous groups of carriers of nearly unique mobilities. The formation of these groups (some of which are labelled with Roman numerals in the figures) is conditioned by the mechanism of breaking of the bubble film. It is known from high speed motion picture studies of the formation of drops from tips[2] that, in general, primary drops of a certain size are formed along with a number of smaller secondaries. It is thought likely that when the thin bubble film breaks a similar type of droplet formation occurs, except that in this case the droplets are much smaller. The charged droplets thus formed account for the existence of the various groups discussed in greater detail below.

According to the electrical double layer theory of liquid surfaces first proposed by Lenard,[3] the electrical nature of molecular forces causes a stratification of charge at the liquid surface. The *negative* charge at the outer surface of water (corresponding to one electron for about 10^5 H_2O molecules in the surface region) is composed partly of polarization charge, and partly of electrons which have migrated to the surface.

Under ordinary conditions the breaking up of a polarized medium produces no separation of charge. The structure of the molecules in water, however, is such as to permit it to form an extended electropolar complex.[4] It is not impossible that a mechanical tearing apart of such a surface of polar molecules as H_2O in H_2O, in which there are strong linkage forces (hydrogen

[1] Chapman, Phys. Rev. **52**, 184 (1937).
[2] Edgerton *et al.*, J. Phys. Chem. **41**, 1017 (1937). Hauser *et al.*, J. Phys. Chem. **40**, 973 (1936).
[3] Lenard, Ann. d. Physik **47**, 463 (1915).
[4] Bernal and Fowler, J. Chem. Phys. **1**, 515 (1933).

bonds) between adjacent molecules, can occasionally[5] produce a separation of charge either by breaking off electrons (see discussion of group I, below) or by actually splitting up the molecular complex giving rise to groups containing H^+ or OH^- (see discussion on group II, below). Positive electrolytic ions, if present, will migrate into the outer negatively charged component of the double layer, while the negative *ions* will be found further down in the liquid.[3] Thus one would expect that the smallest charged droplets might contain electrons; larger droplets, H^+ or OH^-; and still larger droplets, single electrolytic ions. Droplets of radii greater than about 10^{-6} cm might contain electrolytic ions of both signs in about equal quantities.

All the ion groups observed have doubtless evaporated to equilibrium sizes determined by their age, charge, surface tension, vapor pressure, and the conditions of humidity. These observed groups are characteristic then, not so much of the surface layer, but of the configurations (about an electrically charged nucleus) that are stable under the existing conditions.

GROUP I

The figures (of the preceding article) show that by bubbling solutions weaker than 10^{-4} mole per liter, there is produced a very prominent group of negatively charged carriers (labelled group I), having a mobility of 1.8 cm/sec. per volt/cm. [All mobilities in this paper are expressed in this unit.] The corresponding positive group I is very weak and is generally lost in the tail of the adjacent group II$^+$, although it may be distinctly seen in Figs. 14 and 15 for spraying. Since the mobility of group I$^-$ is identical with that of the normal negative ion in moist air, it has been concluded[1] that the carriers of this group consist of single electrons attached to at least one and probably not more than three water molecules.

Since the outer component of the double layer is negative,[3] the chance of creating a *small* drop containing an excess of positive charge is very slight. Thus the fact that the positive group I is very weak shows that the carriers in the group I must have come from the *smallest* droplets

originating at the surface (radii less than 10^{-7} cm). These droplets, subsequent to their creation, must then have evaporated down to the configuration of a stable normal negative ion in pure, moist air.

NORMAL IONS IN MOIST AIR

In conjunction with the group I carriers, it is desirable to discuss the ions ordinarily observed in air. For conditions of high purity and very dry air, the accepted values of mobility are[6] 2.21 for the negative ions, and 1.60 for the positive ions. Since the air used in the present experiments always contained some water vapor, one would expect the values of mobilities to be less than these, and indeed, the observed mobilities of group I were -1.8 and $+1.5$, values which are consistent with those obtained by other workers for normal ions in pure, moist air.[7]

In attempting to test the apparatus on "normal ions" from a radioactive source, such intense ionization from polonium was used in order to give convenient currents, that the air was contaminated by ionization products such as nitric oxides. The ions formed in the presence of these impurities gave broader peaks and lower mobilities than the pure bubbler produced ions from water.[8]

GROUP II

The effects of acids, bases, and salts on the bubbling curves are essentially similar to one another with but one exception: Although salt is approximately equally effective in reducing the amount of charge associated with both the II$^-$ and the II$^+$ groups, acids and bases are strongly selective in their action on these II groups. With dilute acid the II$^+$ peak is strongly enhanced, while the II$^-$ peak is suppressed. With dilute base, the opposite effect occurs. These facts suggest that the II$^+$ group probably contains an H^+ ion and the II$^-$ group contains an OH^- ion. As shown from their mobilities, the

[5] It can be estimated from the magnitude of the currents observed that only a very small fraction (perhaps 10^{-4}) of the droplets with radii less than 5×10^{-7} cm are charged.

[6] Bradbury, Phys. Rev. **40**, 508 (1932).

[7] Tyndall and Grindley, Proc. Roy. Soc. **A110**, 341 (1926), **A110**, 358 (1926); Mahoney, Phys. Rev. **33**, 217 (1929); Erikson, Phys. Rev. **33**, 403 (1929); Zeleny, Phys. Rev. **34**, 310 (1929).

[8] For discussions on mobility spectra of normal ions, see Loeb and Bradbury, Phys. Rev. **38**, 1716 (1931); Varney, Phys. Rev. **42**, 547 (1932).

II⁻ group is slightly larger in size than the II⁺ group. This can be ascribed to secondary valence linkage (the hydrogen bond) favoring a smaller size in the case of the carrier containing H⁺ than in the case of the carrier containing OH⁻. These group II carriers originate in droplets that come from thicker portions of the bubble film than do the droplets that account for the group I carriers. It is in the thicker portions of the film that ions are to be expected.[3]

Size of Carriers

For radii less than 6×10^{-8} cm, theory is incapable of giving the *actual* radius of the carrier from its mobility. The reason for this is that the mobility depends on the mean free path of the carrier, and it is impossible to distinguish the effect of polarization forces in changing the mean free path, from the forces affecting cluster formation. Despite the effectiveness of Langevin's theory[9] (as modified by Hassé) for large radii (see next paragraph) and its effectiveness in accounting for the mobility in the case of monatomic ions, the probable inapplicability of the normal value of the dielectric constant at distances of about 3×10^{-8} cm makes this theory indeterminate in the case of carriers of radii less than about 6×10^{-8} cm. ·

For larger radii the dielectric forces of attraction become inappreciable and Langevin's equation reduces to the form of a solid elastic equation:

$$k = 76 \times 10^{-16}/s^2, \tag{1}$$

where k is the mobility of the carrier in cm/sec. per volt/cm, and s is the sum of the radii in cm of the carrier and of a molecule of the gas in which the measurement is made (in this case air at atmospheric pressure and 20°C). In this paper the sizes of large carriers have been based on Eq. (1).

Other Groups

The IIIa, IIIb, and IV groups observed in bubbling distilled water are stable configurations of molecules, probably formed partly by the breaking of the thick portions of the bubble film in a uniform manner as discussed in the section "Existence of Carrier Groups," and partly by the evaporation of carriers that were large when created. [See also the section on "Humidity Effects," below.] If the diameter of a water molecule is assumed to be 3×10^{-8} cm, Eq. (1) gives the diameters of the droplets comprising the IIIa, IIIb, and IV groups as 8, 9–10, and 12 molecules, respectively. Of these groups, IIIb is definitely the most stable, for experiments on variation of humidity show that for high humidity (see Fig. 11 of the preceding article) IIIa⁻ is nearly lost, and IV is greatly enhanced, as might be expected if IIIa⁻ were formed by evaporation of a layer of molecules from IIIb⁻, and IV⁻ were formed by condensation of a layer on IIIb⁻.

Although, with bubbling, few carriers are found with mobilities less than 0.1, with spraying the greatest portion of the charge comes from the slow carriers of mobilities less than this value. These large heterogeneous carriers are unstable droplets formed by the spraying and are in the process of evaporating. In general it can be seen from the curves of the preceding article that the ratio of negative to positive electrification approaches unity for carriers of mobility less than 0.1. These carriers are so large (diameter greater than 20 molecules) that, although the outer component of the double layer is negative, one would expect little sign preference. These results are consistent with previous observations on visible droplets measured by the Millikan oil-drop method.[10]

Violence of Bubbling

When the bubbling is more "violent" than usual, there are two changes in bubbling mechanism: (1) More surface is brought into play because of the fact that more bubbles are formed, thus resulting in an increase in the charge produced (see Table I of the preceding article); (2) The bubble films are more extensively torn by the air blast. Consequently the number of large carriers of mobility less than about 0.1 is increased (see Fig. 10); and in addition, the positive charges residing in the body of the liquid[3] are more frequently exposed and torn

[9] Langevin, Ann. Chim. Phys. 8, 238 (1905). Hassé, Phil. Mag. 1, 139 (1926).

[10] Chapman, Physics 5, 150 (1934).

off, so that the ratio of the number of positive carriers to the number of negative carriers is increased (see Table I of the preceding article).

When the bubbling is more gentle than usual, the above changes are reversed. The amount of charge produced is considerably reduced (as shown in Table I of the preceding article). The bubbles are larger than usual and are drawn out into thinner films before bursting. There is also less turbulence in the bubble stream. Hence the bubble film is not so extensively torn into thick fragments, and no large carriers are produced. Whether the electrification by bubbling arises from electron migration to the surface or from splitting of the polar structure of the water, or both, it would be expected that the relatively nonviolent breaking off of small droplets from the outer surface of the bubble film would produce no positively charged droplets. Experimentally none are observed.

SALT

In the bubbling of salt solutions, two prominent effects are noticed: the reduction of magnitude of groups I and II, and the appearance of large numbers of carriers of both signs with mobilities less than 0.1. Both effects may be attributed to the presence of electrolytic ions in the double layer. The concentration of electrolytic ions in the bubble film as it becomes thin just before bursting may differ by some orders of magnitude from the concentration in the body of the liquid. It appears as if the cations such as K^+, which are attracted to the negative outer surface of the double layer,[3] become associated with the electronic charges there, so that any small droplets which are formed are neutral, thereby accounting for the disappearance of groups I and II.

The concentration of electrolytic ions in the thin film is probably irregular (statistical fluctuations of small numbers). The ions disturb the normal cohesive forces in the film, thus affecting the mechanism of film-breaking so that uniform sizes of carriers are no longer produced. As a consequence one obtains a wide distribution of mobilities of carriers (as shown in Fig. 4 of the preceding paper, for instance).

The carriers of mobilities less than 0.1 probably contain electrolytic ions. The presence of these

ions in the droplets reduces their vapor pressure, and tends to keep them from evaporating, so that they remain relatively large in size. The vapor pressure effect accounts for the decrease in mobility of the main maximum for solutions of 10^{-3} molal and greater.

In concentrated solutions (10^{-2} molal and greater) the ion densities in the surface layer become so great that it is increasingly unlikely that a droplet will be produced in which there is a numerical preponderance of one sign of ion over the other, because the association effects of ions in solution then tend to keep the positive and negative charges bound together. Hence at high concentrations the total amount of charge produced decreases with increasing concentration (see Table I of preceding paper).

The proportionally greater positive charge observed with $AlCl_3$ than with KCl is due to the fact that the Al^{+++} ion can still produce a charged droplet, even though there are as many as two Cl^- ions associated with it.

SUGAR

The reduction in magnitude of the I^- and II^- groups with increasing concentration is much *less rapid* with sucrose solutions than with salt, because the sugar is electrically *inert* and cannot act to neutralize the electronic charge of the double layer. With increasing concentration of sugar, however, the sugar in the bubble film may increase the surface tension enough so that fewer small droplets are formed, thus finally reducing the magnitude of the I^- and II^- groups. [For the opposite effect see the section on "Soap," below.]

Even in weak sugar solutions, more carriers are formed than is the case with distilled water. Thus the presence of sugar in the thin bubble film seems to provide "nuclei" so that an increased number of large droplets can be formed from the bubble film (i.e., effectively there is an increase in the amount of surface that is torn apart). The amount of charge thus produced is greater than with distilled water (see Figs. 6–9 and Table I of the preceding paper). The breaking of the surface of the sugar solutions is fairly uniform, as is shown by the number of discrete groups in Fig. 7 of the preceding paper.

With increasing concentration the reduction of vapor pressure of the large carriers containing sugar molecules shifts the main maximum (labelled group V in Fig. 9 of the preceding paper) to lower mobilities, just as in the case of salt. Although in the case of salt, the electrolytic ions may have caused a more extensive breaking of the surface (as above suggested for sugar), they also tended to neutralize the double layer, so that only for very low concentrations was there an increase in the total amounts of electrification with increasing concentration.

At high concentration when many large droplets are produced, fragments of some of the large neutral droplets may break off. These secondary droplets, if charged, will be negative (since the outer component of the double layer is negative) leaving the large droplet positively charged. This mechanism can account for the facts that in Fig. 9 of the preceding paper there are more fast negative carriers than positive ones, and that there is an equivalent excess of slow positive carriers.

HUMIDITY EFFECTS

Under the usual conditions of operation the relative humidity of each of the three air blasts is about 35 percent. Hence it is possible for any of the large droplets formed in the bubbling of distilled water to evaporate. As a result, very few carriers of mobilities less than 0.1 are observed, since most of the larger carriers have evaporated down to the stable IV and IIIb configurations before entering the Erikson tube. [Compare Figs. 1 and 11 of the preceding paper.]

When the humidity of the blasts is just less than 100 percent, evaporation of the larger carriers is inhibited. Consequently more of the charge is concentrated in the groups of low mobility than is the case with dry air (see Fig. 11 of the preceding paper). Since the carriers are larger than with dry air, they diffuse less rapidly to the walls, and hence the measured total amounts of electrification are greater. The humidity of the auxiliary blast is ordinarily the determining factor in the humidity experiments, because if the electrode is 2.5 cm downstream, the carriers spend about thirty times as long in the auxiliary blast as they do in the Erikson tube.

In the experiment of Fig. 11 of the preceding paper, in which the humidity of the auxiliary blast was just less than 100 percent, it is seen that the high humidity has caused the negative group II to become well smeared into the background. In previous bubbling experiments[1] where there was no dry auxiliary blast connected to the bubbler, the negative group II was for the same reason smeared completely out, so that it was not observed.

It is to be noted that high humidity affects the spectrum of the negative carriers much more than it does the positive, a fact which might be in conformity with the well-known preferential condensation of supersaturated water vapor on negative ions.

When the auxiliary blast is slightly supersaturated, evaporation in the auxiliary blast is retarded to such an extent that carriers of all sizes are observed. It can be seen in Fig. 12 of the preceding paper that as the length of time spent in the dry blast in the Erikson tube is increased (by increasing the downstream distance and decreasing the volume of the blast) there is an increased amount of evaporation of large carriers, so that the average mobility of the carriers becomes greater.

It is seen in the bubbling experiments that high humidity causes a slight decrease in mobility of many of the peaks. In the case of spraying, the humidity in the chamber and in the inlet to the Erikson tube is always 100 percent, so that one would expect the spraying groups to be slightly lower in mobility than the bubbling groups, as in fact they are. The spraying groups at mobilities +0.70 and +0.49 are the groups that shift into the strong positive group observed when spraying salt solutions.[1] Apparently these two groups are peculiar to spraying; no bubbling analogues have been detected with certainty.

SOAP

The results obtained with solutions of sodium stearate are *not unlike* the results on salt and sugar. Group I behaves as it does with salt solutions, and the slowest group behaves like the group V of sugar. The appearance of group II⁻ is almost exactly the same as that of group II⁻ of hot water, illustrated in Fig. 13 of the preceding paper. In both cases this effect is

probably due to the reduction of surface tension in the bubble film causing production of an increased number of small droplets. The increase in magnitude of the group II^- in the case of weak solutions of sodium stearate is not inconsistent with its alkaline nature (see discussion on "Group II," above). The increase in the total amounts of electrification with increasing concentration is similar to the case with sugar, and likewise may be due to the fact that an increasing amount of surface is brought into play.

Working with solutions of sodium oleate, Johonott[11] has observed films as thin as 6×10^{-7}

cm. In fact, the films he observed were *stratified* so that as many as five different thicknesses of film could be observed at one time. A carrier having a diameter of 6×10^{-7} cm has a mobility of 0.08. The fact that carriers discussed in this paper have mobilities ranging about equally on both sides of this value, coupled with the fact that the results on soap are not unlike the other results, is corroborative evidence in favor of the bubble-film-breaking mechanism advanced as a basis for interpretation.

In conclusion, the writer takes pleasure in expressing his gratitude to Professor L. B. Loeb for his helpful guidance and assistance in interpreting the results.

[11] Johonott, Phil. Mag. **47**, 501 (1899); Phys. Rev. **20**, 388 (1905).

The Magnetic Anisotropy of Copper Sulphate Pentahydrate, CuSO₄·5H₂O, in Relation to its Crystal Structure. Part II

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In Part I of this paper were reported some magnetic measurements on the crystal of $CuSO_4 \cdot 5H_2O$. The crystal, though triclinic, has nearly uniaxial magnetic symmetry, and the symmetry axis is the direction of minimum susceptibility for the crystal. This observed uniaxial symmetry and the negative sign of the anisotropy were shown to follow naturally from the known fine structure of the crystal, and the direction of the symmetry axis also is nearly that predicted from the structure. In the present paper are described further magnetic studies on the crystal, and a more detailed correlation with its structure. The magnetic data are also discussed in relation to the magnitude and the asymmetry of the internal electric fields acting on the Cu^{++} ions in the crystal. A general method is described for determining, for any triclinic crystal, the principal magnetic axes and susceptibilities, i.e., the constants of the magnetic ellipsoid.

1. EXPLANATION OF THE MAGNETIC ANISOTROPY OF PARAMAGNETIC CRYSTALS

IN some recent papers[1,2] we have discussed the magnetic anisotropy of several organic crystals in relation to the anisotropy of the constituent molecules and their relative orientations in the crystal lattice. When the molecular anisotropy is known, either from measurements on

the magnetic double refraction of the substance in the liquid state or in state of solution in suitable solvents, or theoretically from considerations of the structure of the molecules, we can utilize the observed data for the anisotropy of the crystal to obtain much useful information regarding the orientations of the molecules in the unit cell of the crystal. On the other hand, if the molecular orientations in the crystal are already known from x-ray analysis, the magnetic measurements on the crystal may be used for calculating the molecular anisotropy, which is an important molecular constant.

[1] Krishnan and Mookherji, Phys. Rev. **50**, 860 (1936), which is Part I of this paper.
[2] Krishnan, Guha and Banerjee, Phil. Trans. Roy. Soc. **A231**, 235 (1932); Krishnan and Banerji, Phil. Trans. Roy. Soc. **232**, 99 (1935); Zeits. f. Krist. **A91**, 173 (1935).