Carrier Mobility Spectra of Spray Electrified Liquids

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The mobility spectrum of spray electrified salt solutions has been investigated with an Erikson mobility tube under conditions of high resolving power. In general there are no charged carriers of mobility greater than 1.7 cm/sec. per volt/cm. At about this value the curves rise sharply, and then level out, approaching a broad maximum in the region between 0.05 and 0.10 cm/sec. per volt/cm, and then very gradually decrease toward zero. Superposed on this "background" striking peaks are observed, indicating groups of unique mobility. For the spraying of distilled water the most prominent peaks occur at mobilities of 1.5 for the negatives and 0.9 for the positives. Carriers of both signs are produced in about equal quantities. For bubbling the negative predominate in the ratio of 2.5 to one, and the prominent peaks occur at 1.5 and 0.3 for the negatives, and 0.9 and 0.4 for the positives. The introduction of salts to the water increases the electrification from spraying up to a concentration of about 1.0×10^{-4} normal. At this value the electrification is about double that for distilled water, but at higher concentrations the electrification decreases so that for 0.2 normal it is only 10 percent of that for distilled water. The salt gives rise to very strong peaks at mobility 0.5. Investigations have also been made of the effects on the curves of age of the carriers and humidity of the air. It is concluded that the peaks represent stable groupings, the negative 1.5 group being due to a normal negative ion in moist air coming from an evaporated drop. The 0.5 peaks in the salt curve presumably come from carriers containing electrolytic ions. Probably all of the carriers are singly charged. It is impossible to calculate quantitatively the size of the small carriers in the faster groups from their mobility, but from the value of the potential difference of the double layer, and estimates on salt solutions, it is concluded that the separation of the double layer is 2.0×10^{-6} cm corresponding to an extra electronic charge for every 550,000 H_2O molecules.

THE electrification of liquid droplets produced by spraying, bubbling, and similar methods is well known.[1-8] These phenomena depend upon the surface condition of the liquid, the presence of an electrical double layer within the surface being the important factor.[4]

While water and aqueous solutions have been studied by various workers (particularly by Lenard), the nonaqueous liquids have received relatively little attention. Results obtained by the writer[8] who used the Millikan oil-drop method on organic liquid droplets of 3×10^{-5} to 5×10^{-4} cm radius were quite different from those of Lenard, who estimated that his droplets were of 10^{-6} to 10^{-7} cm radius. To correlate the two sets of results, the writer set up an Erikson mobility tube capable of covering a wide range of mobilities under conditions of *high resolving power*. The present paper reports the results obtained with water and salt solutions. A study of nonaqueous liquids is now in progress.

APPARATUS AND PROCEDURE

The apparatus is shown schematically in Fig. 1, which is, however, not drawn to scale. The spray is generated by a glass atomizer S, in the spray chamber M. The spray is led through the inlet I, into the Erikson tube. A blast of air from the air pressure regulator A_2 blows the spray down the tube, while the electric field between the plates P_1 and P_2 drives the charged carriers across the tube. The point at which they strike the plate P_2 will thus depend on their mobility. Hence by moving the electrodes E_1 and E_2 up or down the tube one can obtain a mobility spectrum, that is, a curve of current to the electrometer Q, as a function of electrode position.

The Erikson tube, made of poplar and coated on the inside with paraffin, has an over-all length of 3 meters. The air blast travels down the tube 80 cm before reaching the inlet I. The brass plates P_1 and P_2 are 140 and 200 cm long, respectively. The grounded plate (P_2) may be moved vertically over a range of 50 cm. Thus with the two electrodes E_1 and E_2, spaced 50 cm

[1] Lenard, Wied. Ann. 46, 584 (1892).
[2] J. J. Thomson, *Discharge of Electricity Through Gases* (1898), p. 17 *et seq.*
[3] Coehn and Mozer, Ann. d. Physik 43, 1048 (1914).
[4] Lenard, Ann. d. Physik 47, 463 (1915).
[5] Blackwood, Phys. Rev. 16, 85 (1920).
[6] Busse, Ann. d. Physik 76, 493 (1925).
[7] Bühl, Kolloid Zeits. 59, 346 (1932). A review.
[8] Chapman, Physics 5, 150 (1934).

apart, it is possible to cover a range of 100 cm in downstream distance from the spray inlet I. P_1 supported on hard rubber is spaced 1 mm from the walls of the tube. The spacing between P_1 and P_2 is 2.78 cm. The air blast thus travels down the rectangular area 6.10×2.78 cm.

The spray chamber M is a virtually air tight brass box 13×25×40 cm. The spray is led through the brass inlet I, 0.5×4.0 cm in cross section and 6 cm long. At the entrance to the tube, the inlet is bent over as shown, allowing an entrance of 4.0×0.25 cm. The inlet makes electrical connection between P_1 and M.

The solution to be studied is placed in the supply vessel G, and is siphoned into the reservoir J, which maintains constant level. The sprayer S and all the supply system is constructed so that, except for the platinum electrode D, the solution comes in contact only with glass. The top of the glass sprayer capillary tube is shielded on the outside with platinum foil connected to D. The sprayer is placed so that at least a large part of the spray generated goes into the inlet I.

The electrodes E_1 and E_2 are 0.5 ×4.0 cm with an air space 1 mm wide between them and the grounded plate P_2. The electrodes are supported by the sulphur block II, and protected by the spray guard K. A stream of filtered air dried over P_2O_5 comes from the filter N, and ventilates the electrode. This electrode ventilation was particularly necessary when working with concentrated salt solutions. It might be supposed

FIG. 1. Diagram of Erikson mobility apparatus.

that the ventilating stream would blow the charged carriers away from the electrode, but this is not so, as is proved by the fact that curves for weak solutions made with and without ventilation are found to be identical.

The air pressure regulators will be described elsewhere. The pressures of A_1 and A_2 are held constant within 1 percent, that of A_3 to $\frac{1}{2}$ percent. Throughout this experiment the air through A_2

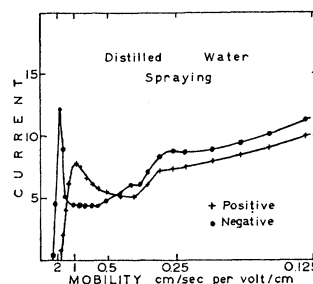
FIG. 2. Mobility spectrum of spray electrified distilled water.

was held at 2900 cm³ per sec., the value being obtained by use of a gas meter and water manometer. The air supply to the spray chamber M was 200 cm³/sec. This auxiliary supply doubled the number of carriers in the main blast. The air to the sprayer (60 cm³/sec., pressure equivalent to 19 cm of Hg) was filtered through the glass wool and cotton filter F. The average velocity of the air down the tube was 186 cm/sec. No turbulence was observed through a glass window when smoke was sent down the apparatus.

The electrometer (sensitivity 400 mm/volt) was shunted with a resistance of 3×10¹⁰ ohms so that the currents of 10⁻¹¹ amp. could be easily measured. A transformer and rectifier supply the high voltage to the terminals T. A compensating circuit is introduced to permit a continuous variation of the voltage from zero to ±4600 volts without inducing disturbing charges on the electrometer.

The mobility of the ions is given by the equation

$$k = dT/Vwl$$

where k is the mobility of carriers in cm/sec. per volt/cm; d is the (average) distance that the ions travel across the tube; T is the volume of air in cm³/sec.; w is the width of the tube; l is the distance downstream to the collecting electrode;
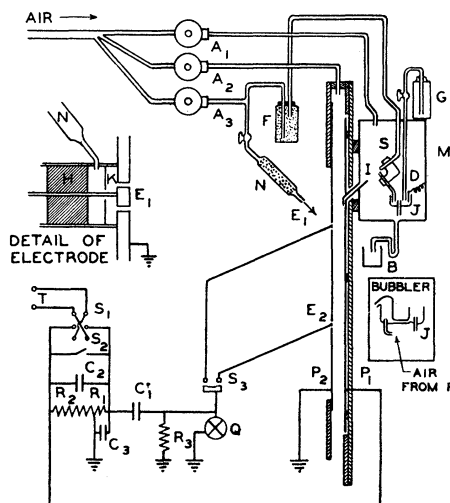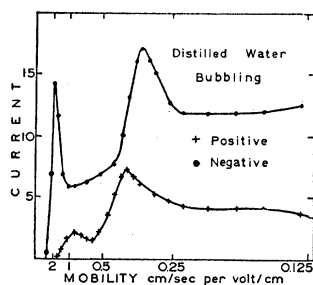
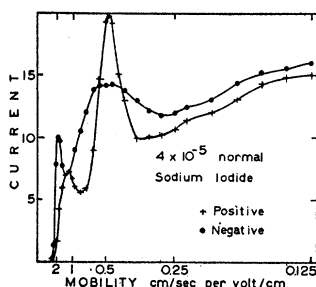FIG. 3. Mobility spectrum by bubbling distilled water.

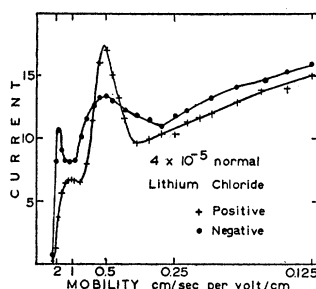FIG. 4. Mobility spectrum of spray electrified sodium iodide solution.

FIG. 5. Mobility spectrum of spray electrified lithium chloride solution.

and V is the voltage difference between the plates. It is possible to vary T, l, or V but in each run V only was varied. The usual effective downstream distance was 2.5 cm but measurements were made from 1.0 to 100 cm, which range permitted measurements of mobilities above 0.003 cm/sec. per volt/cm. Corrections as determined by auxiliary experiments with a model in a salt water trough were made for the distortion of the field near the inlet.

The distance of 2.5 cm downstream was chosen as the optimum value because for longer distances the sharp peaks disappeared due to diffusion, attachment of impurities, etc. Shorter distances gave a reduced resolving power. The

time spent in the tube was thus $2.5/186 = 1/75$ sec. and the total time for the collection of the carriers after their production was certainly less than 0.2 sec., possibly less than 0.04 sec. Blackwood[5] mentions no time less than 2 sec.; dimensions of Bühl's[7] apparatus indicate times of at least 1 sec. The short time interval has an important bearing on the results obtained.

EXPERIMENTAL RESULTS

The experimental results are given in Figs. 2–14. The ordinates are given in the same arbitrary units. The abscissae are indicated in terms of mobility although the voltage is the factor determined directly in the experiment. While an air-blast method gives good relative values of mobility, the absolute magnitude may be in error by as much as 20 percent.[9] The curves rise sharply at a mobility of about 1.7 cm/sec. per volt/cm and then level out with some peaks superposed on this general background.

Spraying

Figure 2 shows the type of curve obtained for ordinary fresh distilled water. The striking feature of the curve is the strong negative peak at mobility 1.5 cm/sec. per volt/cm. The high mobility positive peak is not so strong, nor so sharp, and comes at mobility 0.92. There are weaker negative peaks at 0.39 (very weak, but definite as shown by duplicate runs) and 0.25; and a weaker positive peak at 0.29. Except in the immediate vicinity of the peaks the amounts of positive and negative electrification are about the same.

Bubbling

Figure 3 shows a curve made the same day by bubbling. In bubbling the breaking up of the surface is much less extensive in depth than in spraying since the film of water comprising a bubble is less than a wave-length of light in thickness just before bursting. Accordingly there should be a preponderance of negatives, since these come from the outer surface of the double layer. This is seen to be the case, the ratio of negatives to positives being about 2.5 to one. Variation in the bubbling pressure by a factor

[9] *Footnote added in proof:* Recalibration of static voltmeter indicates that all mobilities should be increased by 7 percent.

of four did not change this ratio, nor does the one to one ratio for spraying change over a limited (factor of 3) pressure range. Bühl[7] has observed a variation, which may have been due to working in a different pressure range, or to the fact that his carriers were of greater age.

With bubbling the same high mobility peaks, occur as with spraying, but the lower mobility peaks are much more prominent in the case of bubbling. However, with very low spraying pressures the lower mobility peaks become more prominent. Fig. 3 is the only curve made by bubbling, all others were made by spraying.

Salt

Figure 4 shows a typical curve obtained for salt solutions, in this case the solution being 4×10^{-5} normal sodium iodide. In addition to the high mobility peaks previously observed by bubbling and spraying distilled water, there are very prominent peaks at mobilities of 0.5. Fig. 5 for LiCl is almost identical with that for NaI, showing that the nature and size of the electrolytic ion are not of great importance in determining the mobility of the carrier (unless these electrolytic ions are hydrated to the same size).

Owing to the finite size of the inlet and the electrode, a group of unique mobility will be made evident by a peak of finite width on the mobility curve. One may calculate the exact shape of such a peak. In practice the "corners" of the curve are rounded somewhat, but with this exception the theoretical curve for the LiCl positive peak at mobility 0.52 coincides with the experimental curve within the accuracy of drawing the curves. Similar remarks apply to most of the very strong peaks observed, particularly those of mobility 0.5 for the positives, and 1.5 for the negatives. The striking sharpness of the strong peaks confirms the smoke test for the absence of turbulence in the Erikson tube.

Change of concentration

Figures 6 to 11 show the curves obtained for KCl for various strengths of solution. Fig. 6 shows the curves for 0.2 and 0.04 normal. No peaks are seen for the 0.2 normal, and the amounts of electrification are very small. For 0.04 normal there is some definite structure to
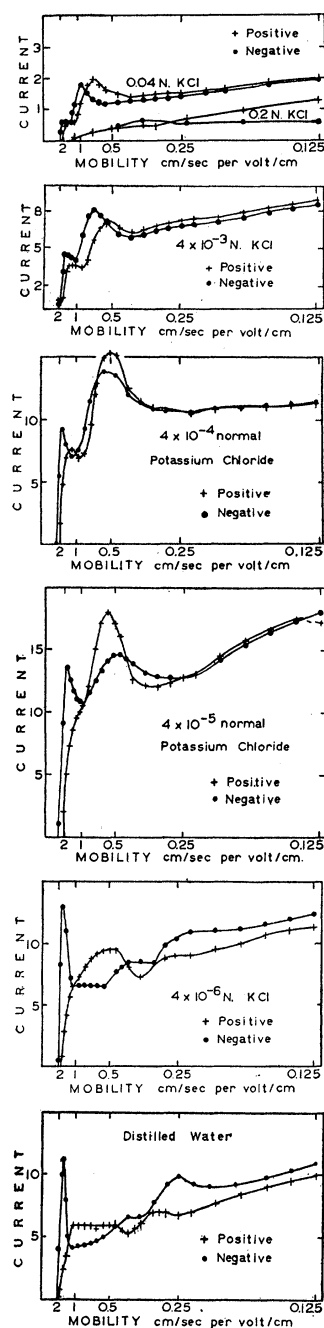
FIGS. 6–11. Mobility spectra of spray electrified potassium chloride solutions with varied concentrations.

the curves. With decreasing concentration the peaks increase in strength, and the amount of electrification increases until a strength of about 10^{-4} normal is reached. With further dilution the curves approach those for distilled water,

shown in Fig. 11. It is interesting to notice how the mobility of the peaks changes with concentration, particularly in the case of the 0.5
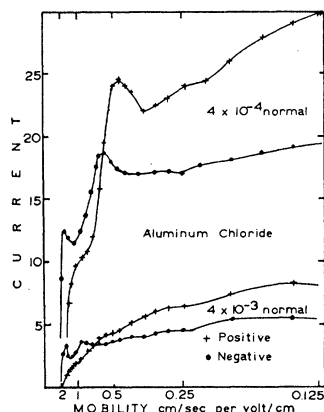

FIG. 12. Mobility spectrum of spray electrified aluminum chloride solutions.

negative group which changes from 0.4 for weak solutions to 0.9 for strong ones. Fig. 12, for AlCl$_3$, is similar to the other salt curves. Even HCl and NaOH give curves similar to those for salt.

The fact that the amount of electrification from salt solutions decreases with increasing concentration (above 10^{-4} normal) 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.

Effect of age

Figure 13, for MgSO$_4$, is also similar to the other salt curves. The dotted curve is the curve for the negative carriers when the electrode was downstream 5.5 cm instead of the usual 2.5 cm. Thus the carriers had an additional 0.016 second to age. Even in this short time the high mobility carriers have become definitely less numerous, although the position of the peaks has remained unchanged. The positives behave similarly to the negatives, although to include the positive curve in Fig. 13 would be confusing.

Figure 14, for distilled water, was made by pointing the sprayer directly away from the inlet I, so that it was a matter of seconds before the carriers reached the Erikson tube. Comparison with Fig. 2 shows that most of the high mobility particles have disappeared due to the

longer time for aging in moist air. It is not surprising therefore that previous workers who worked over long time intervals of several seconds should have failed to find high mobility carriers.

INTERPRETATION OF THE RESULTS

Distilled water peaks

The carriers comprising the negative 1.5 mobility peak have come from droplets which have evaporated down to nearly zero radius, since they are measured in relatively dry air. There is left one extra electron with a few water molecules or molecules from the air attached to it. Thus one has a "normal" negative ion in moist air. The same mechanism accounts for the high mobility positive peaks, except that there is less chance of spraying a *small* positive droplet since the outer surface of the double layer is negative. Thus the magnitude of the initial positive peak is less than that of the negative.

Salt peaks

The definite appearance of the positive and negative groups of mobility 0.5 with the addition of salts to the water is difficult to explain. These
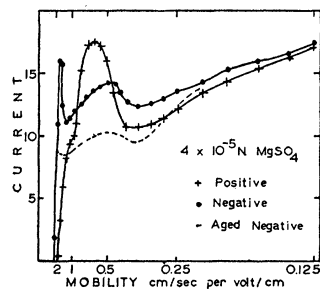

FIG. 13. Mobility spectrum of spray electrified magnesium sulphate solution. The dotted curve represents an aged curve for the negative carriers (see text).

groups may be "ionic" rather than "electronic." Apparently the presence of a Cl$^-$ ion instead of an electron inside a few water molecules changes the mobility from 1.5 to 0.5. It is known that ions are hydrated in solution, although the exact nature of an hydrated ion is not certain. It may be that these experiments offer evidence for certain stable groupings of molecules about ions in solutions.

The cations such as K$^+$ will migrate into the outer negatively charged layer of the double

layer, leaving the anions such as Cl^- behind in the inner layer. Thus one would expect the $+0.5$ peak to be higher and narrower than the -0.5 peak in the same way that the -1.5 peak is higher and narrower than the $+1.0$ peak, since the higher and narrower peaks will come from the outer layer. Reference to a typical salt curve such as Fig. 4 for NaI confirms these conclusions.

Bühl[7] and others have pointed out that with increasing concentration the greater numbers of electrolytic ions present tend to neutralize the double layer so that it becomes more difficult to get charged carriers. This explains the decrease in electrification with increasing concentration of salt. The shift in the mobility of the -0.5 peak to higher values with increasing concentration may be due either to this neutralization or to the relative decrease in the number of water molecules available to each K^+ ion, thus decreasing the size of the carrier and increasing the mobility of the group.

Other peaks

In the past it has been customary to calculate the radius of the carrier from its mobility using one of the many mobility equations.[10] It is true that there are a number of mobility equations of various degrees of reliability and applicability, but unfortunately there is at the present time no rigorously derived single equation which covers a wide range of mobilities.[11] There are equations deduced for point charges, in which the dielectric forces between th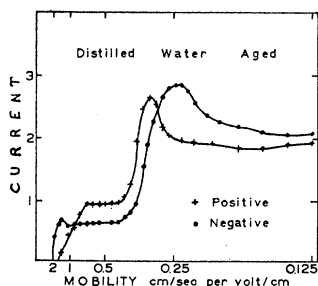e ions and the molecules in the gas are predominant in determining the mobility. These agree fairly well with experiment for small ions (of high mobility). There are "solid elastic sphere" equations (which neglect the effect on the surrounding molecules of the charge on the ion) in which the physical radius of the ion is predominant. This type of equation is applicable to large particles (say of radius 10^{-6} cm or larger). For water, which is particularly polarizable, the region in which it is desired to obtain the size of the carriers (mobility 0.1 or greater) is just that where the two effects are both important. Apparently the most reliable equation which is in a form in which it can be readily applied, and which takes into account both of these effects, is the theory of Langevin.[12] In this equation, however, the size of the carrier enters in such a way that the mobility is relatively insensitive to variations of size in the region where the radius is about 10^{-7} cm. As a result it is not possible to arrive at a *quantitatively* accurate knowledge of the size of the carriers whose mobility may be of the order of 0.5 or less. Consequently the nature of the other peaks observed cannot be definitely established beyond the fact that they too represent more or less stable groupings.

Double layer

From the size of the carriers deduced from mobility measurements Lenard (see discussion on page 512, reference 4) has concluded that the negative layer extends to 80×10^{-8} cm and the positive layer to 150×10^{-8} cm below the surface, corresponding to a separation of 75×10^{-8} cm. Bühl quotes Lenard as saying that one extra electron per 50,000 molecules will account for the electrification.

Another method of calculating the separation is as follows. A careful inspection of the curves shows that the maximum height for the 0.5 peaks for KCl comes at a concentration of about 1.0 $\times 10^{-4}$ normal, and that the mean ordinates at this concentration are about double those for distilled water. It seems reasonable to suppose that at this concentration the number of ions from the salt correspond to the number of extra electrons associated with the double layer in pure water. Then using the value of the potential

FIG. 14. Aged mobility spectrum of spray electrified distilled water.

[10] For instance Bühl, reference 7, refers to Lenard's equation. Lenard, Ann. d. Physik 61, 665 (1920).

[11] See Loeb, *Kinetic Theory of Gases*, second edition, Ch. XI where the subject is discussed in detail.

[12] Ann. Chim. Phys. 8, 238 (1905). See also Hassé, Phil. Mag. 1, 139 (1926).

difference of the double layer as 0.0055 volt as determined experimentally by Bühl,[7] one may calculate the separation of the double layer.

The energy of thermal agitation at room temperature (about 0.04 volt) is so much larger than the potential difference of the double layer, that one would not expect a large permanent excess of salt in the double layer due to electrostatic attractions. The Gibbs adsorption has been investigated experimentally by McBain and Swain[13] who find that the adsorption for salt solutions amounts to a surface deficiency of salt corresponding to the positive adsorption of only one or two molecular layers of water. Thus one may conclude that the concentration of salt in the double layer is about the same as in the body of the liquid.

Accordingly on this basis the surface region contains one extra electron for every 550,000 H_2O molecules, and the separation of the double layer is 2.0×10^{-6} cm. These values, while only very approximate, do not involve the calculation of the size of any carriers, and hence are probably more accurate than estimates based on mobilities.

Effects of humidity and age

Previous workers in this field have generally blown the carriers down their mobility tube by the same blast of air which generated the spray. Thus their humidity may have been 100 percent. In this work the humidity of the main blast was about 50 percent, a significant difference. When all *three* blasts were simultaneously humidified, difficulties were encountered with the insulation so that complete curves could not be obtained. However, several points were obtained. In particular, with 100 percent humidity (taking account of leakage) the negative 1.5 peak dropped to less than 10 percent of its former value. Thus it is clear that the appearance of high mobility particles is due to evaporation of small unstable droplets.

The disappearance of the high mobility particles (see Fig. 14 for distilled water aged) is due to recombination, diffusion, or attachment to slower carriers. Blackwood[5] has shown that for the slower carriers of several seconds age,

the shift of the maximum in the mobility curve (in these experiments, the broad maximum of the "background" at mobility 0.05 to 0.10) can be ascribed to a growth of the carriers at constant rate. Extrapolating from Blackwood's data, mobility 0.10 corresponds to an age of one second. Thus it is likely that the broad maximum observed in these experiments is due to particles which drifted in the spray chamber for about a second before entering the Erikson tube. The high mobility particles come from droplets sprayed directly into the inlet whose total age is 0.1 second or less.

There are four reasons why these groups of carriers have not been observed previously. Other work has been characterized by (1) lack of adequate resolving power, (2) moist air inhibiting evaporation, (3) ages of one second or more, and (4) in the case of salt solutions concentrations of 10^{-3} normal[6] or greater, while the concentration where the very strong peaks occur is an order of magnitude weaker.

Charge on carriers

Chapman[8] found with the Millikan method that the magnitude of the charge for the large carriers decreased with decreasing radius so that for drops of radius 10^{-6} cm or smaller, one would expect not more than one charge. In addition if the small carriers of fairly high mobility had many charges originally, they would tend to recombine readily, so that after 0.01 second or so, there would be few of them left. Thus it is likely that the carriers studied in this investigation are singly charged. The divalent and trivalent ions of $MgSO_4$ and $AlCl_3$ give the same typical curves as KCl. Unless the charge on very small droplets does not affect their mobility (see Langevin equation[12]), then the 0.5 carriers containing the Al^{+++} ion are still only singly charged (due to two extra electrons from the double layer). The preponderance of the positives for the slower $AlCl_3$ carriers is due to the three charges on each aluminum ion penetrating into the outer layer of the double layer.

[13] Proc. Roy. Soc. A154, 608 (1936). See also Harkins and McLaughlin, J. Am. Chem. Soc. 47, 2083 (1925).