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THE ELECTRIC CHARGE OF PAPER SURFACES IN WATER

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THE electrokinetic euphoria which gripped the paper industry a few years ago gradually subsided when it became clear that the zeta potential is not the panacea many people, particularly instrument manufacturers, had hoped it to be. This may have the salutary effect that electrokinetic phenomena, which undoubtedly occur in papermaking, are seen to be part of a complex of physico-chemical processes to which they make different contributions under different circumstances. It may well become the order of the day in the immediate future to study case histories in the hope that one day some more general rules may emerge. This is one of the reasons why the second half of this session is given to a number of short contributions, unusual for these symposia but a step we decided to take because it seemed the right thing to do.

The purpose of my own short contribution to this first and more academic half of the session is not to provide one of those case studies but to report on a simple observation in the laboratory which, if our interpretation is correct, would be very much at variance with the established concept of the electric double layer and the various models built around it.

Hermann Helmholtz is usually given the credit for the formal introduction of the electric double layer as a physical reality around 1853.(1, 2) In his later article in 1879 he quotes two estimated values of its thickness, namely, W. Thomson's value of 'one millimeter divided by 30 million' (0·33 Å or one tenth of an atomic diameter), and F. Kohlrausch's value of 'the 2 475 000th part of a millimeter' (about 4 Å). This difference by a factor of ten is not only of historical interest but is an early example of the discussions, or speculations, which have continued to this day, about the thicknesses of the various layers which separate the bulk of one phase from the bulk of another phase with which it is in contact. These speculations are not only about the thickness of those layers but also about their structures. A number of very detailed models

Under the chairmanship of A. A. Robertson have been built and analysed in considerable depth and many of them bear the names of their creators, but they cannot in my opinion disguise the fundamental arbitrariness and artificiality of the concept of the electric double layer and its inherent imprecision. The responsibility presumably falls back on Helmholtz who, we must remember, did not know ions and electrons and to whom electricity was a kind of fluid spread evenly over the available surface.

What is left when all model building and speculating is ignored is the fact that if a solid particle moves in a liquid to which an electric field is applied (referring to the specific phenomenon of interest here), it bears an electric charge. Quite apart from special circumstances, such as the adsorption of ions or the presence on the surface of dissociating molecular groups, this is a perfectly normal and universal phenomenon. Whenever two chemically different and not miscible substances are in contact with each other the electrons prefer one of the two substances to the other. The contact surfaces therefore develop opposite charges. When a rod of zinc touches a rod of copper the electrons prefer the copper to the zinc. The copper surface is therefore negatively charged where it touches the zinc surface, and the zinc surface has a positive charge. When the rods are separated the charges disappear because of the conductivity of the two metals. When two insulators are brought into close contact and then separated the charges accumulating at the surfaces stay there and can be detected and measured. The rubbing of an ebonite rod with a cat's fur and of a glass rod with a silk cloth are the classical examples with which to demonstrate static electricity. (The effect has, of course, nothing to do with friction, which merely increases the chance of intimate contact, and the term triboelectricity is purely historical.) The rubbing together of many pairs of objects led, incidentally, to the discovery that there are only two kinds of electricity and not, for example, three or four. In 1777 the physics professor, Georg Christoph Lichtenberg at Göttingen University, proposed to call the glass electricity positive and the ebonite electricity negative, and this is still the convention today. Shortly before the beginning of our century Alfred Coehn,(3) also from Göttingen University, observed that as a rule the substance with the higher dielectric constant assumes a positive charge, which explains why most natural substances have a negative charge against water.(3)

One of the successors of Professor Lichtenberg on the chair for physics at Göttingen University was my own physics teacher, the late Professor Robert Wichard Pohl, and quasi as an introduction to the film you will see shortly I would like to repeat two of his instructive lecture demonstrations.(4)

For the first we use a mixture of very fine lead shot and sulphur powder. The sulphur has the higher dielectric constant and is therefore positive, the

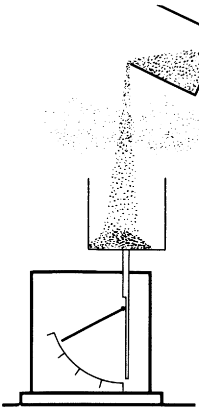

Fig. 1—Separation of charge carriers by the different velocities with which they fall

lead negative. When I pour the mixture into the Faraday box which is connected to a static voltmeter the lead particles fall faster and reach the bottom of the box first because of their lower air resistance. The sulphur powder forms a more slowly sinking cloud. The charges are thus separated, and therefore a voltage develops between them which is indicated by the instrument, see Fig. 1. The full scale deflection of this instrument is 1 600 volt. Even when poured from moderate heights several thousand volts can be achieved. This is similar to one of the mechanisms that produce lightning in a thunderstorm when charged layers are sheared off falling raindrops, forming a charged mist above the faster falling cores of the drops.

This experiment cannot easily be quantified, but the next one can. Here the two insulators are distilled water and paraffin. When I immerse the paraffin block briefly in water it assumes a negative charge and when the block is held inside the Faraday box the instrument reads about 250 volt (Fig. 2a). We can modify the experiment and place the beaker with the water inside the box. If now the paraffin block is again immersed and then withdrawn from the water it takes negative charges with it and leaves positive charges behind. The voltage is again about 250 volt (Fig. 2b). In this demonstration the instrument functions as a condenser. The capacity is $7{\cdot}2\times10^{-12}$ F, the charge was therefore $1{\cdot}8\times10^{-9}$ C or, after division by the electron charge ($1{\cdot}6\times10^{-19}$ C), $1{\cdot}1\times10^{9}$ elementary charges. The dimensions of the block are $5{\cdot}5\times3{\cdot}0\times2{\cdot}5$ cm, i.e. the surface area is 75 cm^2. The charge density is therefore about $1{\cdot}5\times10^{8}$ electrons per cm^2.

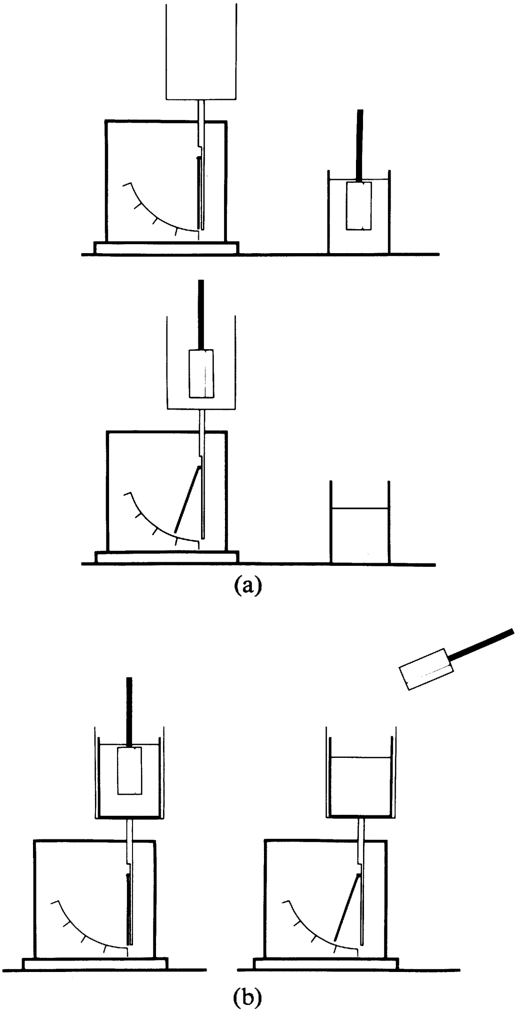

Fig. 2—Demonstration of the electric charge of paraffin in contact with water

In order to measure the charge of paper in water we used circular discs of 0·5 cm diameter as they are produced with an office punch. We chose the method of electrophoresis in distilled water and used the Electrophoretic Mass Transport Analyzer made by Micromeritics, Norcross, Ga., U.S.A. The cell we used is shown schematically in Fig. 3. The lines on the centre tube are 1 cm apart. The experimental technique was described in some detail in

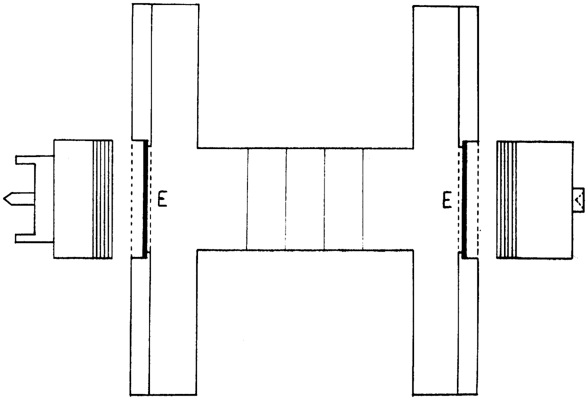

Fig. 3—Schematic of the measuring cell for the electrophoresis of paper discs

an earlier publication.(5) Briefly, the cell is filled with distilled water so that the chambers at either end of the tube are about three-quarter full. A few paper discs are placed into that chamber from which they are expected to migrate. The instrument is switched on and the cell rotates with 20 rmp until the first disc has entered the tube. Then the rotation is stopped. The disc sinks to the bottom of the tube and, viewed from above, appears as an ellipse since the water-filled tube has the effect of a cylinder lens. The disc moves along the bottom towards the other chamber and its velocity is measured with a stopwatch. When it has reached the end of the tube the polarity is reversed and the movement is now in the other direction. This is done several times and the velocities are averaged.

Fig. 4 is a section of 30 frames from the film I showed. The film speed was 25 frames per second. The disc is from a paper that had been coated with an aqueous solution of a highly cationic polymer (a polyamine-epichlorohydrine resin). The excess was washed off twice with distilled water. The paper then assumed a positive charge against water. The disc in Fig. 4 therefore moves, progressing from top left to bottom right, towards the cathode. 1 cm is covered after about 22 frames, i.e. in just under one second.

When discs of ordinary paper, having a negative charge, are placed into the cathode chamber and discs having a positive charge into the anode chamber they move in the tube in opposite directions and every now and then two of them collide. If the collision is head-on, i.e. with the line connecting the centres in the direction of the field, one disc is usually the stronger of the two (in most cases this is the positive disc) and pushes the other one along in front of it. If the collision is askew the discs perform a little dance: they slide

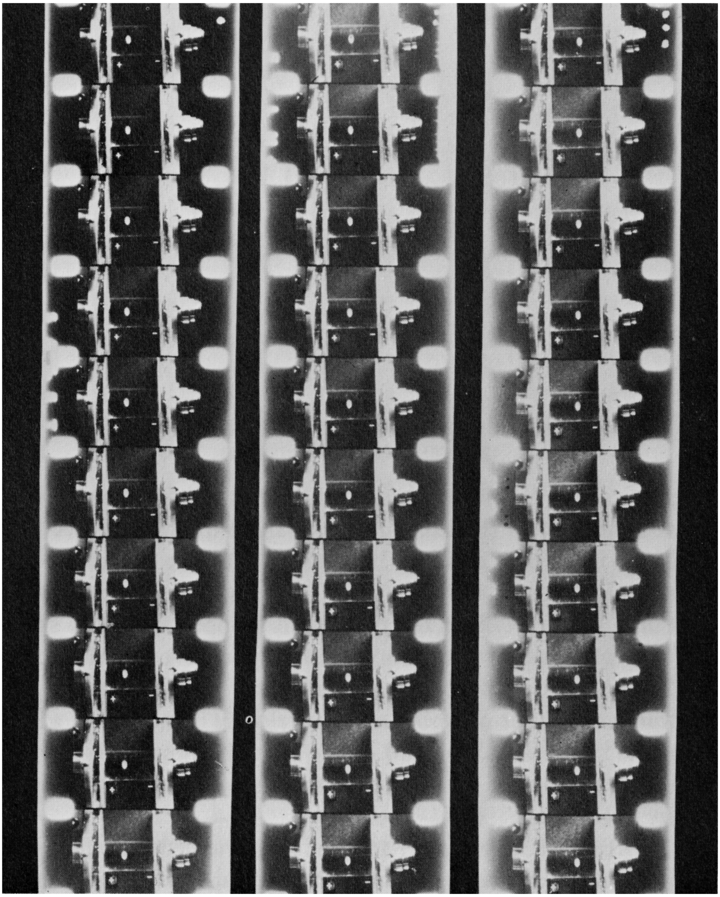

Fig. 4—Section of the film shown

round each other until the position is the mirror image (with respect to the horizontal perpendicular to the tube axis) of the configuration at the moment of collision, and then part. This phenomenon has a certain similarity to that observed by Manley and Mason(6) for spheres colliding in a sheared viscous liquid.

The evaluation of the charge of the paper discs is based on equating the driving force, eE(e = charge, E = field strength), and the frictional force according to Stokes's law for discs moving edge-on, $\frac{32}{3}\eta w r$ (η = viscosity of the water, w, r = velocity and radius of the discs).(7, 8) It is handicapped by two factors. One is the electro-osmotic movement of the water in the (perspex) tube. Since the discs are probably not moving in the stationary zone but nearer the wall of the tube they move against the current when they are negative and with the current when they are positive. The observations showed that on average positive discs moved indeed somewhat faster than negative discs, by a factor of 2 to 4, although it is impossible to say to what extent this is caused by the positive charge being on average higher than the natural negative charge. The absence of any dramatic differences in all of about 100 observations leads me to believe, however, that the effect of the electro-osmotic water movement does not alter the order of magnitude of the charge calculated from the observed disc velocities. The second factor will be referred to later. Ignoring it for the moment the charge is calculated from the (relatively high) velocity of 1 cm/sec for the disc shown in Fig. 4 and the following experimental data: $E = 85$ V/cm, $r = 0{\cdot}25$ cm, $\eta = 0{\cdot}01$ Poise. The result is a charge density of 5×10^8 elementary charges per cm^2. This is the highest value measured so far. Most of the others were around $1–2 \times 10^8$ and the lowest was 5×10^7. The typical charge density of untreated paper is thus 10^8 electron charges per cm^2.

It is possibly coincidence that this value is similar to the one found for the paraffin block in Fig. 2, but it is worth considering what it means. If one cm^2 is on average occupied by 10^8 electrons each of these has an area of 10^{-8} cm^2 available. If the area were a square the side length would be 10^{-4} cm or 10^4 Å or 3 000 atomic diameters. In other words, each electron charge is on average 3 000 atomic diameters away from the next. This is 'as the crow flies'. The paper surface is uneven and the 'walking' distance is therefore a multiple of this value. A surface so sparsely populated with electrons can hardly be called a continuous electric layer.

Current theory makes provision for this, however, by postulating that the double layer, like an ionic cloud, retards the movement of the object so that the charge density calculated when this 'brake' effect is taken into account, would come out higher. This is the second factor affecting the calculation of the charge density referred to above. Professor J. Th. G. Overbeek very kindly calculated the charge density of the disc shown in Fig. 4 for two values of the thickness of the double layer, 10^{-5} cm and 10^{-6} cm.(9) The result was $10^4–10^5$ times the value quoted above. Stokes(7) derived his formula when he investigated the motion of a pendulum in air, driven by the gravitational field of the earth. The same formula applies if the object falls in water, provided that the velocity is not too high. If in such a case the gravitational field is replaced by an electric field the movement is slowed down according to the current theory, by a factor of 10^4 to 10^5. This is an extraordinary brake effect which, expressed as an increase of the apparent viscosity of the liquid, would make the paper disc feel as though it were moving through something like centrifuged honey instead of through water.

The reasoning does not apply to the paraffin block of Fig. 2, however, since Stokes's law does not enter the picture. There it cannot be disputed that the charge density is as low as the voltage between the parts of the condenser which a known capacity directly indicates. There is to my knowledge no theoretical device which would augment the thinly spread charge to form something like a coherent electric layer.

These are only two isolated observations but they reveal a serious discrepancy between the fashionable and sometimes elaborate mathematical constructs devised to describe electrokinetic phenomena, and the elementary laws of electrostatics which we have learned at school. I prefer to trust the latter for the time being. A statement that a macroscopic object moving in water is slowed down by a factor of 10^4 or 10^5 simply because it is driven by an electric field, is not good enough. It will have to be *proved.* While such proof is missing the concept of the electric double layer and, directly connected with it, that of the zeta potential, must remain highly questionable, at least for macroscopic objects. MacBain and Laing-MacBain(10) showed that the entire complex of electrokinetic phenomena can be described without such concepts and, at the end of their article, call the established theory 'a pure figment of the imagination' (ein reines Gedankenbild). As far as macroscopic objects are concerned I find it difficult to disagree with them. It is still a matter of future experimentation and reasoned argument to determine at what size an object ceases to be macroscopic in the sense that continuum concepts, such as the viscosity, begin to lose their meaningfulness; and how the 'simplest possible description' (Sommerfeld) of their behaviour in an electric field can be achieved.

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Discussion

Prof. J. T. G. Overbeek My first remark is about the apparent absence of any gross effect of electro-osmosis in the experiment you have shown. Your paper discs move so much faster in the electric field that most ordinary particles do. A normal velocity for an ion or an electrophoretic particle is in the order of 5 μm cm $V^{-1}s^{-1}$, and in your case velocities in the order of 20 or 100 of these units has been seen for the paper discs. Therefore, if it is just plain electrophoresis the velocities that you have measured are an order of magnitude higher than other people have found on other objects. It would, I think, be very important to see if very much smaller pieces of paper, that could easily be prepared, move with the same high velocity or not. The fact that electro-osmosis does not come in your experiment is simply because glass electro-osmosis is in that low order of magnitude.

My second remark is about the electrometer experiment with the lead shot and the sulphur or the paraffin and the water. They are remarkably beautiful experiments but one should realise that you have obtained surface charges in the order of 10^{-5} micro-coulomb per square centimetre, and double layer charges on mercury, silver iodide and most oxides are in the order of 1 to about 10 micro-coulomb per square cm, so that is roughly a million times as large as the charges you have found. Now this is not so astonishing because when you draw out the paraffin from the water most of the double layer will be neutralised before you break the contact and only a very small unequal distribution will remain in the last moment. I think the same is true for the lead shot-sulphur experiment.

My question is, do you have an explanation why, in your experiment, the paper discs are moving with an order of magnitude higher velocity than one finds in any electro-osmotic or electrophoretic experiments that I know of?

Corte No I have not, but I told you that this is the highest velocity we observed and it was just coincidence that when we made the paper positive by coating it with a cationic polymer, we found this velocity. It is the highest

Under the chairmanship of A. A. Robertson velocity; the lowest is one tenth of this or none at all. They don't always do us the favour of moving at all. Also, after a while they get tired and stop, this 'while' is typically 20 minutes, and when we then measure the conductivity of the water we find that it has gone up by a factor of 5 or 6 because all technical pulps, including the sheets we made from distilled water contain electrolytes which gradually dissolve. As the conductivity increases the discs will eventually stop. If you remove the water and replace it with fresh water they move again, so it is not the discs which change but the water. I don't know why the velocity is so high; it surprised me as a matter of fact. If the velocity were as low as that for most small objects, the charge density would be even smaller. This is not a very easy experiment to quantify, unfortunately, because you have no control over where the discs move, you just have to replace quality by quantity, do it often enough and apply statistics. We certainly intend to try small discs and indeed, with such a separation of the charges we should find bits of paper with none at all. The electrons are so widely spaced that there must be areas which have no charge.

Your explanation of the electrometer experiments sounds to me a little *ad hoc*. According to it, when paraffin is separated from water or when a sulphur particle detaches itself from a sphere of lead most of the charges are neutralised when the contact is broken. How does this happen? I cannot think of another physical phenomenon where charges are neutralised upon separation. Besides, if we assume a double layer between the paraffin block and the water to form a plate condenser its capacity would be $\varepsilon_0 A/1$ (ε_0 = absolute permittivity, A = area (75 cm^2), 1 = distance). Assuming 1 to be an atomic diameter, 3×10^{-8} cm, we find a capacity of $2{\cdot}2 \times 10^{-4}$ Farad. The voltage (or the zeta potential) would then be charge/capacity $= 1{\cdot}8 \times 10^{-9}/2{\cdot}2 \times 10^{-4} = 0{\cdot}8 \times 10^{-5}$ Volt, which is not far from values quoted in the literature for other system.

But to me the whole exercise seems to be like juggling with numbers. So far nobody has with a voltmeter (like the one used in the demonstration) measured a voltage across the interface at a solid object immersed in water. Until this has been done the zeta potential and the double layer will remain to me, as they did to the MacBains, 'figments of the imagination'.

Overbeek I base my explanation of the electrometer experiments on the accepted explanation of frictional electrification (contact electrification). When two different materials are in contact the electrochemical potentials of electrons and all ionic species tend to become equal by transfer of charge and, if possible, material from one phase to the other. The amount of charge transferred is proportional to the capacitance between the two materials. In breaking the contact the capacitance becomes smaller, but there is a phase in which the contact area is still sufficiently conducting to allow the charge to adjust itself. When the distance between the materials becomes too large, the remaining charge is blocked and it is this remaining charge that is detected with the electrometer. This charge is expected to be only a small fraction of the charge needed to establish a potential difference of the order of 0·1–1 Volt between different phases when they are in close contact over a sizeable area.

I agree that the voltage across the interface of a solid and water (galvani-potential difference) cannot be measured with a voltmeter. The change in such a voltage with changing circumstances (concentration, applied voltage etc.) can and has been measured. These changes are of the order of 1 Volt and form the basis of electrochemistry.

I agree that the zeta potential cannot be measured directly with a voltmeter. But this does not affect the reality of ionic atmospheres and electrical double layers. There is nothing against giving the results of electrokinetic experiments in terms of surface charge, rather than in terms of surface potential, but explaining such experiments without taking ionic atmosphere effects into account is incorrect (except in electrophoresis in non polar media where the extension of the ionic atmosphere is often much larger than the particle size).

Dr D. A. I. Goring It seemed to me that the discs were always aligned flat and were moving edge on.

Corte This is true. The 5 mm discs sink to the bottom of the 25 mm tube. They then appear elliptical by virtue of the water lens. But they stay flat and move edge on.

Goring My point is that they are moving edge on like an aeroplane wing and are not subject to Brownian motion as are colloidal particles which rotate. This might explain the higher than usual electrophoretic mobility.—Another question, which is a deeper one, what causes the charge on cellulose?

Corte We don't know, apart from Coehn's rule which I quoted. This is an entirely different problem.

Goring All right. Perhaps I can ask Dr Overbeek that question. In your paper you emphasised ionisation but yet you do measure zeta potentials on cellulose which don't seem to have any chemical opportunity to ionise.

Overbeek There cannot be any electrokinetic mobility without a separation of charges between the two phases. With cellulose this may be ionisation of (a few) COOH groups generated by oxidation or of some sulphate groups or it may be due to perferential adsorption of negative ions. Finally, some noncellulosic amionic material might be present.

Corte We intend to perform experiments with modified cellulose. The simplest modification is oxidation of course. We would expect a change in the charge. I showed a paper with a positive charge where we had coated it with a polymer. I would expect modified cellulose to have a different charge.

Goring But you found a charge with plain, ordinary cellulose that hasn't got any carboxyl groups.

Corte That's true, but it is always negative.

Dr A. A. Robertson Just before moving on to the next paper it may be worth noting in passing that air bubbles have a negative charge in water.