fact that $y^2$ becomes approximately a linear function of $t$ as thickening proceeds indicates that the process is largely controlled by the rate of diffusion through the film. The effect of concentration indicates that the molecular state of the excess iodine in the film is not lower than $I_2$, but the small temperature coefficient excludes the idea of gaseous diffusion through large apertures. The effect of varying the solvent indicates that we are not dealing with pores through which the solvent can enter. It is concluded that the iodine passes through pores of a few molecular diameters in loose union with the silver iodide—a process intermediate in character between diffusion in solid solution and gaseous leakage through definite cracks. This idea agrees with conclusions drawn from work on films other than iodides.

The Electrical Conductivity Caused by Insoluble Monomolecular Films of Fatty Acid on Water.

By Prof. James W. McBain, F.R.S., and Dr. C. R. Peaker.

(Received June 24, 1929.)

Introduction.

The well-known researches on thin films of insoluble fatty substances on water have brilliantly demonstrated that such films are monomolecular and that the molecules are oriented with their polar groups in contact with the water. Thus stearic acid spreads on water with its carboxyl groups on the water surface. No one, however, has as yet investigated the possible dissociation of such fatty acids with formation of free hydrogen ions in the water, leaving the fatty ions behind in a monomolecular film on the surface.

Such dissociation need not and probably should not involve more than a small fraction of the molecules on the surface. One of us* has pointed out the enormous voltages which would be caused between a complete monomolecular layer of free ions and the charges of opposite sign, vastly exceeding the electromotive forces of vigorous chemical reactions. This and many other lines of

evidence have led to the theory of "sparse surface dissociation,"* according to which a surface such as that of a colloidal particle may be largely covered or consist of undissociated molecules or adsorbed ion pairs, forming a double layer in the strict Helmholtz sense, but with a further portion of the surface covered only with unbalanced or singly adsorbed ions whose partners remain free and mobile somewhere in the solution.

The fact that colloidal electrolytes, such as soap, exhibit a high conductivity showed that at least a portion of the double layer, if any on these colloidal particles, must be dissociated into free and mobile ions existing independently in the solution, leaving behind highly charged colloidal particles which, like the mobile ions, exhibit high conductivity by virtue of their free charges. This conception invalidates the application of the classical formulæ of the Helmholtz double layer which are all derived on the assumption that there are no free charges on the surface in the interface. Indeed it is very possible that the electrical double layer has nothing to do with electrokinetic phenomena, although its ion pairs may be of importance in stabilising colloid surfaces as, for example, through induced solvation.

Films of insoluble fatty acid on water afford an opportunity of testing the essential aspect of this modern conception of the existence of free mobile ions within the solution corresponding to free, unbalanced charges on the interface. We have measured here the conductivity due to these mobile ions and find that only about one-ninth of the monomolecular layer of stearic acid on water is dissociated. This extra conductivity, introduced by the insoluble film of fatty acid, may be termed "surface conductivity." This constitutes the first actual measurement of surface conductivity in absolute units.†

The Experimental Method.

The object was to measure the extra conductivity in the neighbourhood of the surface after coating with insoluble fatty acid, and to distinguish it clearly from any conductivity due to slight solubility of the fatty acid or impurities introduced therewith. These purposes are accomplished through the use of a conductivity vessel of special design as shown in fig. 1.


† The absolute measurements of surface conductivity in the neighbourhood of optically polished glass surfaces in progress since 1919 (McBain and Darke, General Colloid Discussion, 'Trans. Farad. Soc.,' vol. 16, p. 150 (1921); 'Kolloid-Z.,' vol. 28, p. 239 (1921)) have now been completed by us for communication to the American Chemical Society.
The electrodes consist of two vertical platinum rings held concentrically by supports which in no wise tend to bridge the gap between them and which therefore do not introduce any surface conductivity of their own. It is a common fault in conductivity cells that they are partially short circuited by glass struts, or supports, or neighbouring glass walls, a source of error which seems never to have been suspected, even when cell "constants" have been recorded as varying appreciably with different solutions. The essential measurements are: (a) the conductivity of the water alone; (b) the conductivity of the water after introduction of the fatty acid but with the surface far removed from the electrodes; (c) the conductivity exhibited by the water when the surface is brought to the same level as the tops of the two electrodes; and (d) the conductivity with the surface in the same position after introduction of the fatty acid. In the design illustrated, measurements (a) and (c) could be repeated as often as desired until constant values were obtained before introducing fatty acid; thereafter the measurements (b) and (d) could be repeated indefinitely without opening the cell. This repetition is effected by pouring unwanted liquid into the side reservoir and pouring it back so as to fill the cell for such measurements as (a) and (b).

The outside platinum electrode was 1 cm. high and about 2 cm. in diameter, with about 1 or 2 mm. between it and the inner electrode, so that the area in square centimetres of the annular space between them is about equal to the volume between them in cubic centimetres. The platinum wires leading to the electrodes were covered with glass. A very great advantage of supporting the inner electrode from the ground-in joint at the top of the cell is the ease with which the electrodes may be taken apart for platinising and cleaning operations which otherwise were found to consume many weeks. Three cells were successively used, fig. 1 showing the final design for use with especially pure conductivity water which has not yet been available. The electrodes were well platinised, were reduced by using each as cathode, and were washed until the resistance of conductivity water placed in the cell remained constant.

The stearic acid used was a sample of stearic acid "Kahlbaum." This was extracted several times with hot conductivity water, allowed to dry on a filter paper in a desiccator, and finally recrystallised from distilled ether. The melting point of the stearic acid was 69.2° C.

The arrangement of the conductivity bridge was similar to that described by Jones and Josephs* with some modifications. Instead of the fixed-ratio slide wire used by them, we used a Kohlrausch type slide wire (Leeds and

Northrup). The grounding resistance was another slide wire of the same type. The slide wire in the bridge circuit proper was carefully calibrated, and the necessary corrections applied to the bridge readings. The resistance of the box was adjusted so that the readings came about the centre of the slide wire.

The resistance box was of the five-dial type made by Leeds & Northrup. Coils of 1000 ohms and above were of the Curtis design. A Vreeland oscillator (Leeds & Northrup), supplying alternating current at a frequency of about 1000 cycles per second to the bridge network, was used. The oscillator was at a distance of 40–50 feet from the bridge. A one-stage vacuum tube amplifier was used in conjunction with the telephones. Two variable air condensers (caps. 0.001 and 0.00012 mfds.) were used to balance the capacity of the cell, the one of smaller capacity being used as a vernier. The region of silence in the telephones could be fixed very accurately (to 1/10,000 part of the length of the bridge wire).

**Procedure and Calculation.**

The cell was first filled with conductivity water to the point marked (a) in the figure and immersed in a thermostat, containing distilled water maintained at $25 \pm 0.005^\circ$ C. When the resistance became constant ($R_1$), water was spilled over into the side bulb until the tops of the electrodes were just in the surface. When the resistance again became constant ($R_2$), the water in the side bulb was run back into the main part of the cell, and another set of measurements on the resistance obtained. After obtaining a consistent series of values for $R_1$ and $R_2$ in this way, we were ready to start the second part of the experiment. After obtaining the last value for $R_2$, a small amount of stearic acid was put on the surface of the water through the side tube (A), thus not disturbing the electrodes at all. When the resistance became constant ($R_3$), the water in the side bulb was spilled back to fill the main part of the cell to point (a), and measurements taken until a constant resistance was obtained ($R_4$). Care was always taken to have visible crystals of stearic acid on the surface when measuring ($R_3$).

$R_1$ = resistance of cell filled with conductivity water; $R_2$ = resistance of cell filled to top of electrodes with conductivity water; $R_3$ = resistance of cell filled to same position with fatty acid present; this includes the resistance of the water, of the dissolved stearic acid, and any surface effects; $R_4$ =
resistance of cell filled with contaminated water; this includes the resistance of the water and of the dissolved stearic acid.

\[ \frac{1}{R_3} = \text{conductivity of water} + \text{conductivity of dissolved stearic acid} + \text{“surface conductivity”} (S). \]

Hence

\[ \frac{1}{R_3} = S + \left( \frac{1}{R_2} \cdot \frac{R_1}{R_4} \right). \]  

The equation can then be solved for \( S \), since everything else is known. The calculations from a typical experiment are given in detail as follows: \( R_1 = 14,438 \) ohms; \( R_2 = 16,129 \) ohms; \( R_3 = 13,949 \) ohms; and \( R_4 = 12,816 \) ohms. Substituting in equation (1), \( S = 0.000001841 \) mhos. Conductivity of water = \( \frac{1}{14,438} = 0.00006200 \) mhos. Then per cent. increase in specific conductivity is

\[ \frac{0.000001841}{0.00006200} \times 100 = 2.7 \text{ per cent.} \]

The cell constant of this cell was 0.0226, so the conductivity of the surface is

\[ 2.7 \times 0.0226 = 0.0000000422 \text{ mhos.} \]

It is of great interest to calculate the surface conductivity in absolute units. Volume conductivity is always indicated by specific conductivity; that is, the conductivity in reciprocal ohms of a cube of solution placed between parallel electrodes 1 cm. square and 1 cm. apart. Similarly we must invent a specific surface conductivity in two dimensions instead of three (as regards the actual surface area), defining it as the conductivity in reciprocal ohms between two parallel electrodes 1 cm. long, placed 1 cm. apart on the surface. Hence, from the determination given above, since the area of the film between the electrodes is to the volume of liquid between the electrodes very nearly as 1:1, the specific surface conductivity (for 1 cm.\(^2\)) is

\[ \frac{0.0000000422}{1} = 0.0000000422 \text{ mhos./cm.}^2 = 4.2 \times 10^{-8} \text{ mhos./cm.}^2. \]

**Results and Discussion.**

The following table records the results obtained with the different cells used.

The results demonstrate conclusively the existence of a conductivity in the neighbourhood of the monomolecular film of insoluble fatty acid. This is the first apparently unambiguous system that has been investigated. Surface conductivity has been surmised from the data of Stock, Miss Laing, Fairbrother, Briggs and Stamm, but in every case alternative explanations were possible.
Insoluble Monomolecular Films of Fatty Acid on Water.

Table I.—Specific Surface Conductivity in mhos./cm.$^2$ of a Surface of Water Carrying a Film of Stearic Acid at 25°00° C.

<table>
<thead>
<tr>
<th>Cell</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
<th>Cell constant</th>
<th>Per cent. increase</th>
<th>Specific surface conductivity.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4,618</td>
<td>4,805</td>
<td>4,409</td>
<td>4,289</td>
<td>0.00877</td>
<td>1.33</td>
<td>$4.2 \times 10^{-8}$</td>
</tr>
<tr>
<td>2</td>
<td>14,438</td>
<td>16,129</td>
<td>13,949</td>
<td>12,816</td>
<td>0.0226</td>
<td>2.70</td>
<td>$4.2 \times 10^{-8}$</td>
</tr>
<tr>
<td>3</td>
<td>10,137</td>
<td>10,576</td>
<td>10,153</td>
<td>9,964</td>
<td>0.00976</td>
<td>2.30</td>
<td>$2.2 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Mean .......... $3.5 \times 10^{-8}$

and plausible. We have completed absolute measurements of surface conductivity of salt solutions in contact with known areas of optically polished glass. There excess conductivities likewise could equally well be explained as being merely due to a concentration of salt in the neighbourhood of the surface rather than as here unmistakably due to mobile ions complementing unbalanced charges in the surface proper. N. K. Adam* found that with palmitic acid, which is presumably far more soluble than stearic acid, not $\frac{1}{2}$ per cent. of the molecules of palmitic acid placed upon his trough left the film to go into the water. This can only have been possible because of the acidity of his "water." Even with the more insoluble stearic acid, as will be seen, the amount which would dissolve in really pure water in a trough of the depth which Adam describes would be equal to the amount required for a monomolecular film upon the surface. Adam does not state the $p_H$ or conductivity of the "water," but he does describe the clear cut results obtained when the acidity exceeded $p_H$ 5.5.

Approximate evaluation of the true solubility of stearic acid is afforded by the data of Table I.† For example in cell 3, where the dissolved stearic acid raised the concentration of the water 980/963 fold, if the conductivity of the water ($0.963 \times 10^{-6}$) is ascribed to $H^+$ and $HCO_3^-$, then the concentration of $H^+ = 2.2 \times 10^{-6}$ N and of the stearate ion $= 7 \times 10^{-8}$ N, the solubility product being $15.4 \times 10^{-14}$. If the dissociation constant be taken as $0.8 \times 10^{-8}$, the dissociation is practically complete at this dilution and the total solubility is $4.1 \times 10^{-7}$ N at 25° C.

There seem no other probable explanations of our measurements than that they are due to independent mobile hydrogen ions dissociated from the fatty

† Compare the corresponding calculation for palmitic acid at 90° by McBain and Taylor, Z. phys. Chem., vol. 76, p. 179 (1911).
film. If so, the fatty film is left with an equal and opposite electric charge. It is to these free charges, the mobile ions on the one hand and the sum of the unbalanced sessile charges on the other, that we ascribe all electrokinetic effects.*

Since the conductivity of the surface has been ascribed to the "mobile" ions of the double layer, it is of interest to calculate the number of such "mobile ions" per square centimetre. Considering the results for cell J2 in detail, let us assume that the conductivity of the water used in this experiment was due to (monobasic) carbonic acid. Then from the relation that \( \Lambda = 1000 \frac{k}{C} \), where \( \Lambda \) = equivalent conductivity of \( \text{H}_2\text{CO}_3 \) solution (sum of mobility of \( \text{H}^+ \) (350) and \( \text{HCO}_3^- \) (70) at 25° C. = 420), \( k \) = specific conductivity of the water used, and \( C \) = concentration of hydrogen ion in gram equivalents per litre, we can calculate the value of \( C \). This is

\[
C = \frac{1000 \times 0.0226}{14,438 \times 420}.
\]

Then the number of mobile hydrogen ions per square centimetre is given by

\[
2.7 \times 1000 \times 0.0226 \times 6.06 \times 10^{23} = 6.08 \times 10^{13}.
\]

The total number of stearate molecules and ions per square centimetre for a "close-packed" monomolecular film, if each occupies 25·1 \( \times \) 10^{-16} sq. cm. is 4 \( \times \) 10^{14}. Thus the number of mobile hydrogen ions corresponds to about one-seventh of the stearate in the monomolecular film. (The number of mobile hydrogen ions per square centimetre, calculated as given above, is 3·64 \( \times \) 10^{13} and 3·20 \( \times \) 10^{13} for cells J1 and J3, respectively.)

The average value for the number of "mobile" ions, from the results of Table I, is 4·64 \( \times \) 10^{13}, corresponding to about one-ninth of a monomolecular film for a solution of \( p_H \) corresponding to a specific conductivity of about 1·2 \( \times \) 10^{-6} mhos, at 25° C.

For the study of materials which do not spread spontaneously, a somewhat different design of cell could be used, consisting of two concentric rings of platinum, clamped between glass plates, coated with the substance to be studied. Such a cell would be perfectly general in its application to the measurements of "surface conductivity."

Summary.

A monomolecular film of insoluble fatty acid on water consists partly of fatty ions whose corresponding hydrogen ions have dissociated into the aqueous layer. These free mobile hydrogen ions are revealed through the electrical conductivity which they impart to the aqueous layer in the neighbourhood of the surface. The specific surface conductivity at 25°C. in the neighbourhood of the monomolecular film of stearic acid is $3.5 \times 10^{-8}$ mhos., corresponding to a dissociation of about one-ninth of the total stearic acid in the monomolecular layer on water of conductivity $1.2 \times 10^{-6}$. The existence of the surface conductivity with its corollary of free mobile ions and corresponding charges left upon the interface lends support to the opinion that the Helmholtz double layer is not responsible for the electrokinetic phenomena, and that the classical formulae are not strictly applicable, owing to the existence of unbalanced charges upon the interface.

A Quantitative Study of the Reflexion of X-Rays from Crystals of Aluminium.

By R. W. James, M.A., G. W. Brindley, M.Sc., and R. G. Wood, B.Sc.,
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1. It has already been shown* that the observed variations with temperature of the intensity of reflexion of X-rays from crystals of rock-salt and sylvine agree closely with those predicted by the theory of Debye,† as modified by Waller,‡ from the lowest temperature at which experiments have been made, that of liquid air, up to about 500°C abs. Moreover, the absolute intensities of reflexion agree closely with those calculated theoretically, if the atomic scattering factors, F, are calculated from the Schrödinger charge-distributions for the atoms, obtained by the method due to Hartree.§ To obtain agreement, it is

† 'Ann. Physik,' vol. 43, p. 49 (1914).
‡ Upsala Dissertation, 1925.