A NEW DETERMINATION OF THE CAPACITY OF THE ELECTRICAL DOUBLE LAYER.

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The capacity of the electrical double layer is very important for every quantitative theory of the distribution of ions around a solid particle, but up to the present there has been a rather puzzling discrepancy between various estimations of this quantity. In the case of a mercury electrode the capacity can be calculated by means of the Lippman-Helmholtz equation from surface tension data. Calculations of this kind have been carried out with a high degree of accuracy by Gouy.[1] They give a minimum value of ca. 17 μF/cm.^{2} in the region of the descending branch of the electrocapillary curve, *i.e.*, at considerable cathodic polarisations. We owe the first reliable direct determination to Krüger,[2] who made his observations with a cathodically polarised surface, using alternating current and obtained values between 7 and 10 μF/cm.^{2}. In a later paper[3] Krüger and Krumreich considered 13 μF/cm.^{2} as the most probable value for a potassium nitrate solution. More recently, Bowden and Rideal[4] found that in the region of hydrogen overvoltage 6×10^{-7} coulombs per square centimetre caused a change of 100 millivolts in the electrode potential at a mercury surface in sulphuric acid. The capacity of the double layer should be therefore only 6 μF/cm.^{2} Erdey Gruz and Kromrey[5] made extensive measurements with different electrolytes and compared the experimental results with the values calculated by Gouy. As a rule, the observed values were much too low, in the case of normal sulphuric acid the minimum value being, for instance, only 3 to 6 μF/cm.^{2} The discrepancy between the electrocapillary data and the measured values of the capacity attracted the attention of many authors, but no adequate explanation has been proposed until now. This fact was especially striking, as measurements of the electric charge per unit surface, carried out by expanding the mercury surface at constant potential,[6] gave values in fair agreement with the theory of electrocapillarity. It seemed therefore advisable to take up this question once more.

The experimental procedure will be described in detail elsewhere; in this paper we mention only the most important features.

The solution was carefully saturated with hydrogen and freed before the measurements from the last traces of oxygen and mercury ions by electrolysis. The apparatus was made exclusively of glass, the ground joints being wetted only with water, without any lubricants. In order to lessen the errors caused by contamination and by the creeping of the solution between the mercury and the glass, the experiments were made with a rather large mercury surface of 5·1 cm.^{2} This was formed in a glass cup, which could be filled with mercury from underneath through

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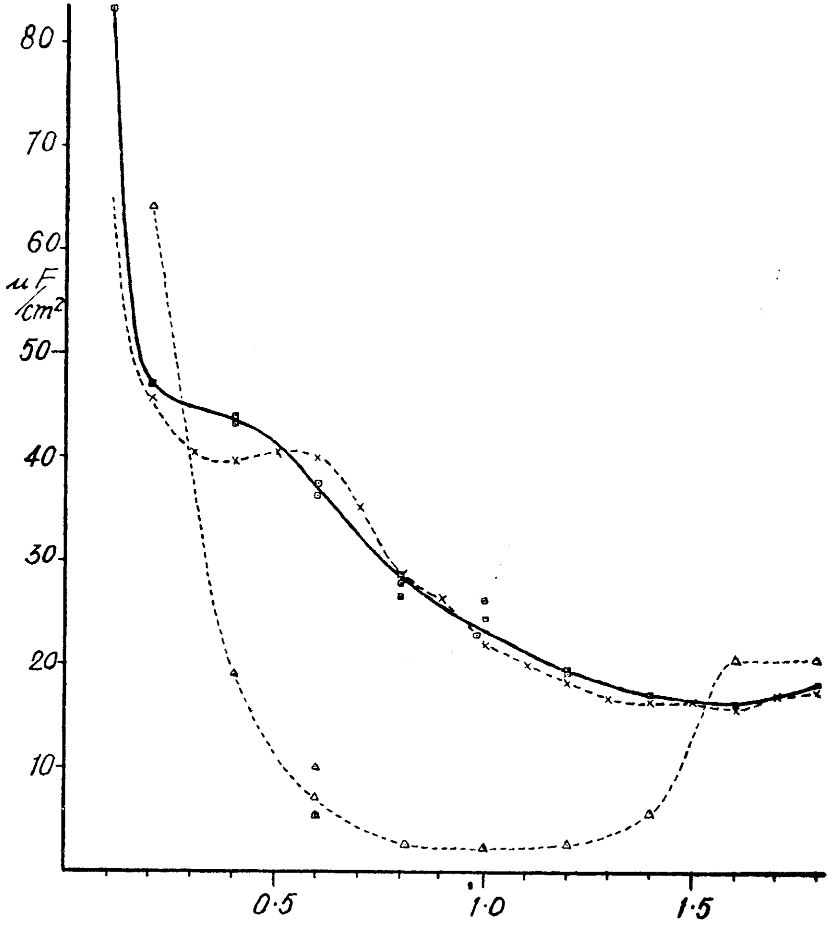
[1] *Ann. chim. physique*, (7), **29**, 159, 1903.
[2] *Z. physik. Chem.*, **45**, 1, 1903.
[3] *Z. Elektrochem.*, **19**, 620, 1913.
[4] *Proc. Roy. Soc.*, **120A**, 59, 1928.
[5] *Z. physik. Chem.*, **157A**, 213, 1931.
[6] Frumkin, *Z. physik. Chem.*, **103**, 55, 1922; Philpot, *Phil. Mag.*, 775, 1932.

a glass tube. To clean the surface the mercury was allowed to overflow the borders of the cup. In order to maintain a definite potential at the surface, the latter was polarised with the help of an auxiliary anode with direct current and its potential measured against a non-polarisable electrode separated from the cell by a siphon.

To determine the capacity, the mercury surface was polarised with an alternating current of 50 periods with the help of a second auxiliary electrode situated above the mercury surface. The variations of the potential difference between the mercury and a reference electrode (platinum ring round the cup on a lower level than the mercury surface) were amplified about 3000 times with a two tube amplifier and measured with a cathodic oscillograph. To check the value of the capacity we used a standard capacity equal to 8·92 µF. The amplitude of the potential oscillations as a rule did not exceed 15 millivolts. A special filter practically prevented the alternating current from entering the circuit formed by the mercury cathode and the auxiliary anode.

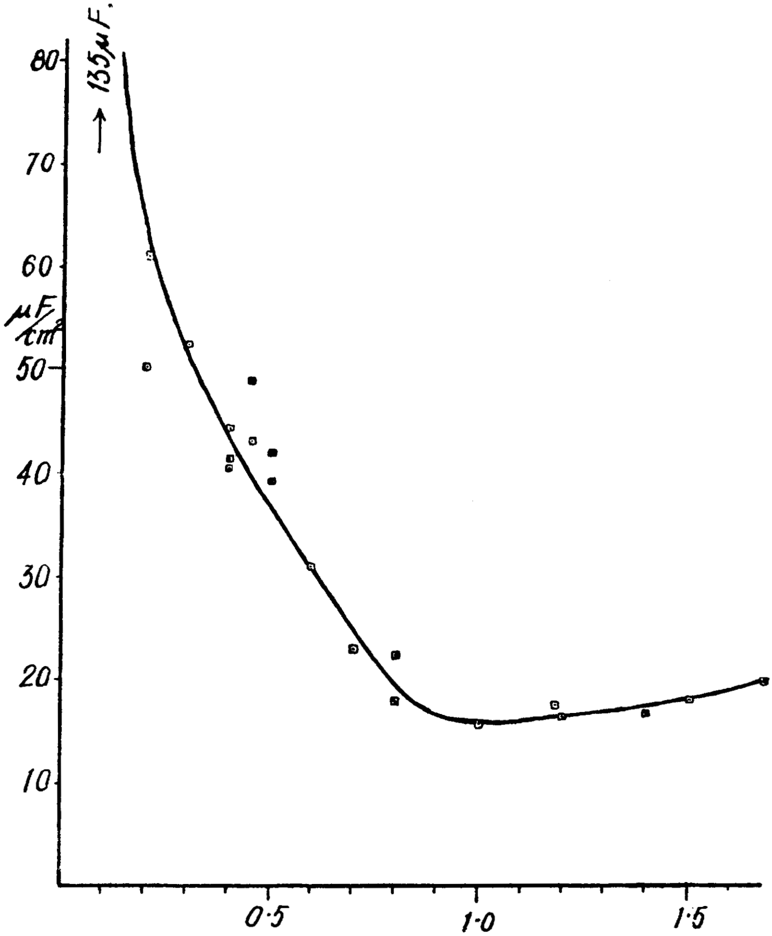


Norm. Na_2SO_4. ⊡ Observed values, clean surface. △ After contamination with picein. × Calculated from electrocapillary curve.

FIG. 1.

Measurements have been carried out with normal solutions of Na_2SO_4, KCl, NaOH, H_2SO_4 and Na_2SO_4 saturated with octyl alcohol, and the values of the capacity plotted against the cathodic polarisation. The zero point on the potential scale corresponds to the saturation of the solution with the respective mercury salt, *i.e.*, Hg_2SO_4 in Na_2SO_4 and H_2SO_4, HgO in NaOH and Hg_2Cl_2 in KCl.

Sodium Sulphate (Fig. 1). The salt was heated to 550° in a platinum crucible and dissolved in twice distilled water. The capacity was independent of the age of the surface. The agreement with the values calculated by Gouy is quite satisfactory, especially on the descending branch of the electrocapillary curve, the minimum being 16·5 $\mu F/cm.^2$. The value of the capacity is very sensitive to surface contamination : touching the surface with a picein stick caused, as shown by Fig. 1, an enormous decrease of the capacity in the middle part of the curve.

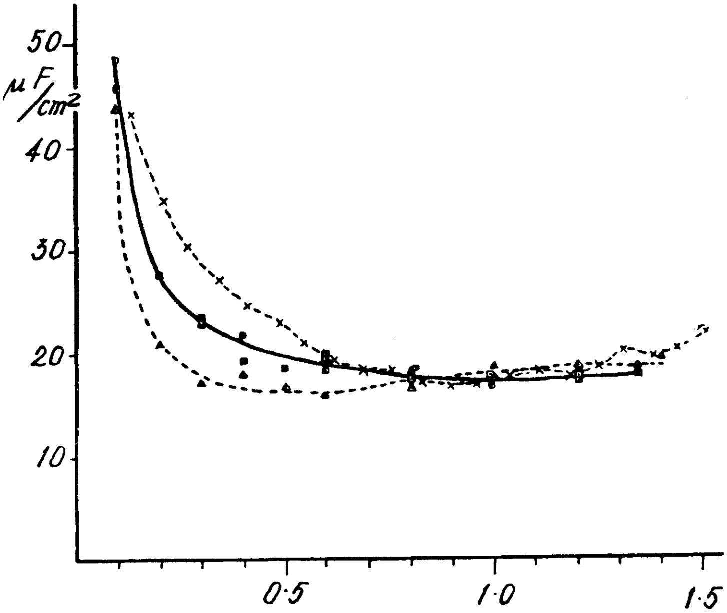


Norm. KCL. Observed values.
FIG. 2.

Potassium Chloride (Fig. 2). The constancy of the capacity was satisfactory ; unfortunately, calculated values of sufficient accuracy are not available.

Sodium Hydroxide (Fig. 3). *Natriumhydroxid aus Natrium* was used. For all values of cathodic polarisation which did not exceed 0·8 V. the capacity showed a marked decrease with time. For instance at a polarisation of 0·4 V. the capacity of a fresh surface, measured about thirty seconds after its formation was 21·2, after five minutes—19·4 μF/cm.[2] Renewal of the surface restored the original value. The same effect was observed after a strong cathodic polarisation (1·5 V.) during a few minutes. The full drawn curve refers to surfaces which were forty-five seconds old, but some points were taken after a cathodic polarisation. Nevertheless, as shown by Fig. 3, the effect of contamination could not be completely avoided. In the region of the ascending branch of the electrocapillary curve, the observed values are distinctly lower than the calculated ones.

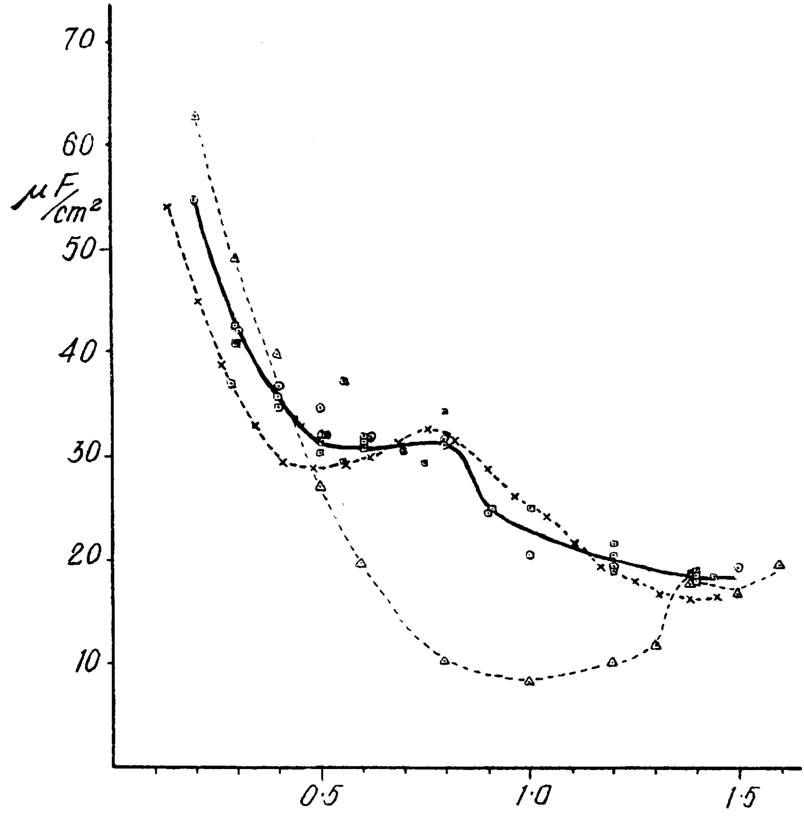
Sulphuric Acid (Fig. 4). Two specimens were used: one was H_2SO_4 *zur Analyse, mit Garantieschein* from Kahlbaum (I), and the other was obtained by distilling fuming sulphuric acid (II). The measurements with sulphuric acid were more difficult to carry out than those recorded above, except at the cathodic end of the curve. At polarisations above 0·6 V. the capacity decreases with time as in the case of NaOH. At lower polarisations, especially in the neighbourhood of 0·5 V., a fairly rapid rise of the capacity is observed, as if some capillary active anion was adsorbed. The deviations of the experimental curve from the calculated one show, that the influence of the contamination could not be completely avoided even with a fresh surface. The value of the capacity in the overvoltage region (18-20 μF/cm.[2]) is much higher than the values given by other investigators. Fig. 4 also shows the influence on the capacity of a contact with paraffin.



Norm. NaOH. ⊡ Observed values, fresh surface. △ After 5 mins.; × Calculated from electrocapillary curve of ca. 2 norm. KOH.

FIG. 3.

Sodium Sulphate Saturated with Octyl Alcohol (Fig. 5). The capacity curve shows two maxima and a strong depression in the middle part. The anodic and cathodic ends coincide with the sodium sulphate curve. This is what we ought to expect from the electro-capillary curve,[7] which shows that higher aliphatic alcohols are strongly adsorbed in the neighbourhood of the electrocapillary maximum and that the adsorption disappears rather abruptly in definite narrow intervals of the ascending and descending branch. In these intervals the amount adsorbed changes very strongly with the potential. This causes an increase of the capacity. The position of the capacity maxima is in a fair agreement with the form of the electrocapillary curve. A more detailed theory of these interesting phenomena will be given elsewhere.



Norm. H_2SO_4. ⊡ Observed values with fresh surface, specimen I. ⊙ Same, specimen II. △ After contamination with paraffin. Calculated from electro-capillary curve.

FIG. 4.

The results recorded in this paper show that the observed values of the capacity agree fairly well with the values calculated from electro-capillary data, which can be therefore considered as a sound basis for any further theoretical developments. The remaining discrepancies can be accounted for by traces of contaminations, which we could not avoid.

We cannot give at the present moment a definitive interpretation of the lower values which have been observed by previous authors. It

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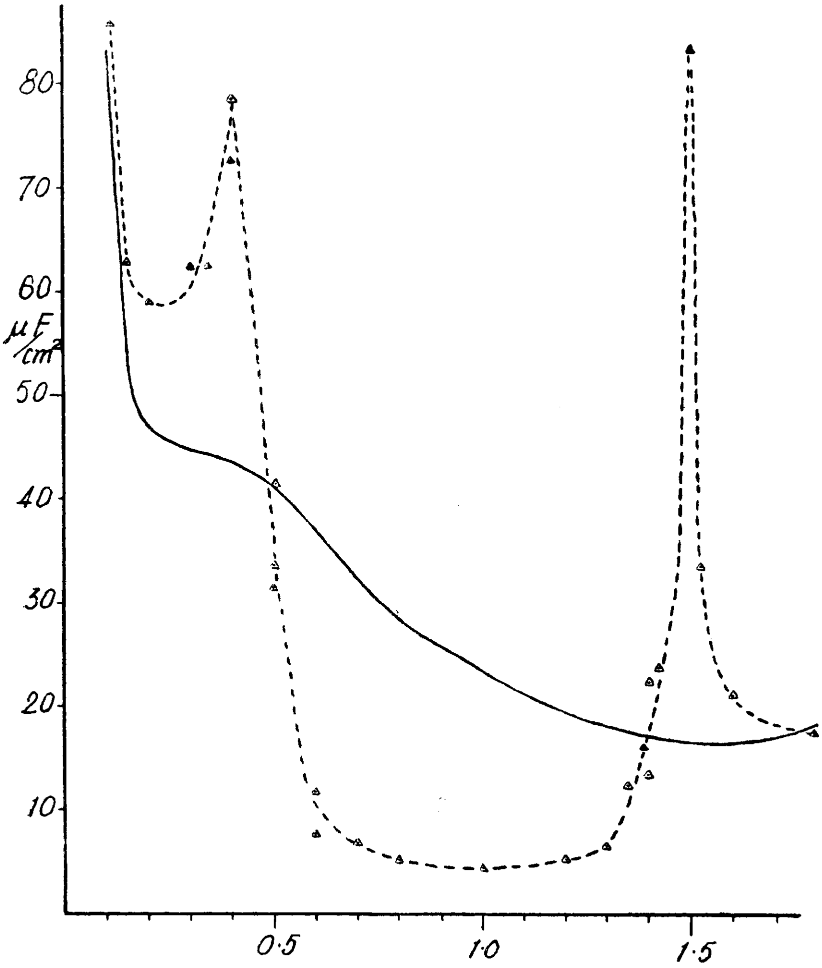
[7] Gouy, *Ann. physique*, (8), **8**, 291, 1906; Frumkin, *Z. Physik.*, **35**, 792, 1926.

appears however that the danger of contamination has not been realised to a sufficient extent. This applies especially to the apparatus of Erdey Gruz and Kromrey, as they introduced picein in the interior of their cell. The curves given by these authors are very similar to those which we observed with notoriously contaminated surfaces.



Full line — norm. Na_2SO_4. △ norm. Na_2SO_4 saturated with octyl alcohol.

FIG. 5.

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