ON THE THICKNESS OF THE HELMHOLTZ DOUBLE LAYER

HELMHOLTZ and Lamb assumed the double electric layer around colloid particles to be of molecular dimensions, but Gouy calculated it to be greater and to increase with dilution of the solution. Whereas the diameter of a water molecule is about 0.03×10^{-6} cm, Gouy calculated the distance (a) between the surface of a colloid particle (having 10 electrostatic units of charge per sq. cm of surface) and the center of gravity of the excess ions of opposite sign in a 0.1 N solution of monovalent salt at 18° to be 0.096×10^{-6} cm, and in a 0.001 N solution 0.96×10^{-6} cm. Gouy assumed a dielectric constant of 80. Burton showed that Gouy's a was equal to Debye's $\frac{1}{K}$. Burton and Currie showed experimentally that the Helmholtz double layer was thick enough to account for repulsion between colloid particles as well as larger bodies (shot) and that its thickness increases with dilution. They account for the discharge of colloid particles on the addition of salts by the thinning of the double layer to the point of break-down of the dielectric.

In previous papers (McClendon-1926) it has been shown that the double layer acts as a condenser and becomes thicker the greater the dilution of the solution. It was hoped that a method might be found to measure its thickness.

Since the surface of a charged metal electrode (immersed in an electrolyte solution) and the layer of excess ions of opposite sign act as the plates of a condenser whose capacity may be measured, knowing the dielectric constant, the thickness of the Helmholtz double layer may be calculated. The capacity in microfarads, $C = 0.0885 \times 10^{-6}\frac{KS}{T}$, where S is the surface area of the electrode in cm², T is the thickness of the dielectric (Helmholtz double layer) and K the dielectric constant. The conductivity vessel contained two bright gold electrodes each of 10 cm² surface (5 cm² face and 5 cm² back) and acted as two condensers in series, equivalent to one condenser with double the thickness of dielectric. Assuming $K = 80$ the equation becomes

$$T = \frac{7.08}{C} \times 10^{-6} \text{ cm}$$

and the thickness of the Helmholtz layer will be $\frac{T}{2}$.

The capacity is most easily measured using alternating current, but since it changes slightly with frequency the electrostatic value can only be approximated.

As will be seen from the table the thickness of the Helmholtz layer as measured is for 0.1 N solution 0.194×10^{-6} cm whereas Gouy calculated 0.096×10^{-6} cm, a fairly close agreement particularly in view of the uncertainty of the dielectric constant. The measured value for 0.001 N solution, 0.325×10^{-6} cm, is far from Gouy's value of 0.96×10^{-6} cm, but the change is in the right direction, *i.e.*, increase in thickness of the Helmholtz layer with dilution of the electrolyte.

Frequency in cycles per second	Normality KCl	Capacity microfarads	$\frac{T}{2}$ Unit 10^{-6} cm	Normality KCl	Capacity microfarads	Unit 10^{-6} cm $\frac{T}{2}$
436	0.0002	11.3	0.313	....	....	....
640	"	10.7	....	....	....	....
885	"	10.2	....	0.001	11.0	....
1000	"	9.7	0.365	"	10.9	0.325
1375	"	9.5	....	"	10.5	....
1720	"	....	....	"	10.3	....
1950	"	8.4	....	"	9.8	....
2820	"	6.7	....	"	9.2	....
4420	"	4.2	0.843	"	7.3	....
1000	0.002	15.3	0.231	0.01	14.2	0.249
1000	"	....	....	0.1	18.3	0.194

The fact that the thickness of the Helmholtz layer increases with frequency of the alternating current might be explained by lack of time for the ions to migrate to their definitive positions.[1]

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