PART II.—THEORETICAL TREATMENT OF THE DOUBLE LAYER AND ITS IMPLICATIONS.

INTRODUCTORY PAPER.

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As this second part of our Discussion includes (*a*) the theoretical treatment of the electric double layer ; (*b*) electrokinetics ; and (*c*) their bearing for the stability of colloids, it seems to be useful to consider why these problems are central problems in present day colloid chemistry.

Any material, colloidally dispersed, is characterised by the facts that it does not tend to molecular dispersity (true solubility) and at the other hand that it is inhibited from forming a coherent phase. Though the possibility has been discussed, whether the cohesion energy would be negative in colloidal systems, it is taken for granted that such is not the case, at least with hydrophobic colloids, but that, in addition to the tendency to cohesion, there exists in these systems a repulsive factor which counterbalances the cohesion tendency.

It was William Hardy who, in 1900, pointed out that there is a relation between electrophoretic mobility and colloidal stability. It is now generally accepted that an electric repulsion inhibits coalescence of the particles in what is called a stable colloidal solution. Though other repulsive factors may interfere also in colloidal solutions, we shall now consider only this electric repulsion.

As mentioned, Hardy had called the attention of colloid-chemist to the close relation between an *electrokinetic* phenomenon and stability ; since then, electrokinetics have become a main chapter of colloid-chemistry. Consequently the subject has been treated mostly for the special purpose of explaining colloidal phenomena, and theories have been given, which often accounted in sufficiently for results obtained in other fields of electrochemistry. It will not be necessary to give an account of many errors made in this domain ; I want to confine myself only to the remark, that it is psychologically understandable that in the beginning colloid chemistry went its own way with regard to electro-kinetics. Helmholtz had given already in 1879 a profound discussion of the electrokinetic phenomena ; Gouy in 1910, von Smoluchowski in 1914, and Stern in 1924, on the sound basis of the electric double layer of the Helmholtz paper, developed the theory further. Later, many authors tried to reconcile the data of colloid-chemistry with those of general electrochemistry, and this meeting is a manifestation of that desire.

Now what is the general trend of our now prevailing point of view ? We think it can be put in this way :

An electric double layer arises at the boundary of two phases as soon as an ion is distributed unequally in these two phases. When one of the

phases is a crystalline phase, the chemical potential of an ion constituting that crystal has a constant value $[\mu_i]_{cr}$ at a given temperature. When the same ion is in a solution in contact with the crystal, it will have there another chemical potential $[\mu_i]_{liq.}$, and ions will be transported from one phase to the other until an electric potential $\Delta\psi$ between the two phases has arisen

$$\Delta\psi = \frac{[\mu_i]_{liq.} - [\mu_i]_{cr}}{z_i F} \qquad .$$

and according to a well-known relation

$$\Delta\psi = \frac{-[\mu_i]_{cr}}{z_i F} + \frac{RT}{z, F} \ln a_i,$$

where z_i is the ions valency and a_i its activity in the solution.

In colloid-chemistry we are accustomed to write this equation as

$$\epsilon = E_o + \frac{RT}{z_i F} \ln a_i \quad . \qquad . \qquad . \qquad . \quad (1)$$

ϵ, the " total potential (difference) " of the double layer * is governed only by the activity of the " potential-determining " ions, *i.e.* ions distributed unequally over colloid particle and intermicellar liquid. As the double layer is caused by these ions, the notions " peptising ions " and " potential determining ions " are closely related.

The double layer is built up by the ions adhering to the solid wall and an electrically equivalent amount of counter-ions. We shall take silver iodide in HJ solutions as an example ; iodide ions give the particles a negative charge, hydrogen ions being the counter-ions.

According to the Helmholtz-Gouy theory, the latter are distributed according to Boltzmann-principle. When the liquid moves with respect to the wall (or the reserve) only part of this ionic atmosphere moves, either because a certain water layer is fixed to the wall (von Smoluchowski) or because the first layer of counter-ions is fixed by great electric or adsorptive forces (Stern). The potential difference located in the mobile part of the double layer, ζ, thus, is alone electrokinetically active. According to Hardy's principle, this ζ potential governs colloid stability.

The great problem for colloid chemistry, therefore, is to know the ζ potential. Many years the classical equations of Helmholtz were used :

for electrophoresis :

$$\zeta = \frac{4\pi\eta}{HD}u,$$

for streaming potentials

$$\zeta = \frac{4\pi\eta}{D} \times \frac{E}{P}.$$

These calculations, however, were very uncertain with regard to the values for η and D (viscosity and dielectric constant within the double layer). These were, moreover, not the only difficulties which arose in the interpretation of electrokinetic measurements. When the influence of electrolytes on electrokinetic phenomena was studied, results were obtained that did not agree with the stability of colloids. One of us, *e.g.*, had found when measuring streaming potentials at glass capillaries,

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* E. Lange has called attention for the fact that there are still other potential differences (so called χ potentials) in consequence of dipole orientation. As these represent only a constant value in weak electrolyte solutions, such as play a rôle in a hydrophobic colloid system, we shall disregard them in this paper.

that neutral (*i.e.* potential non-determining) electrolytes in small concentration caused the ζ value calculated according to Helmholz to increase. As κ the specific conductivity of the electrolyte solution was taken. Now Gortner and his pupils have pointed out that surface conductance played an important rôle with streaming potentials, and a short time ago Rutgers (Ghent), by an ingeneous method, took this surface conductance into account and showed that an increase of ζ by neutral electrolytes did not exist.

However, this question of high conductivity at the surface is only a detail from a much more important difference between the Helmholz theory and our modern conception of the double layer.

It has been shown by Bikermann, Henry, Hermans and others, that the electrophoresis equation needs corrections in many respects. In Helmholtz's equation surface conductance was not taken into account, nor was the difference in conductance between the colloidal particle and the surrounding liquid.

Hermans evaluated the influence of the relaxation terms in the complete electrophoresis equations, and found them surprisingly high. In some cases the correction terms for the relaxation effect were even
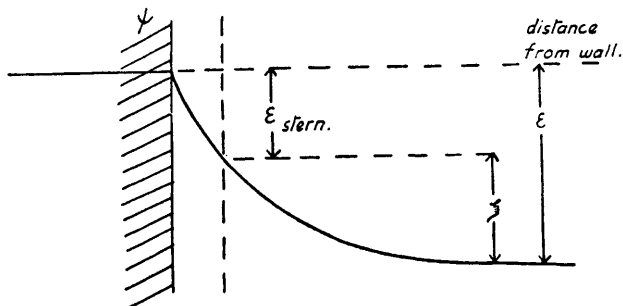

FIG. I.

larger than the main term itself. The evaluation of all these corrections entails very large mathematical difficulties.

So that we do not as yet possess an electrophoresis equation which takes all factors into account.

Owing to these difficulties, one was never certain whether the values calculated for ζ were right or not; many authors preferred, therefore, to use the electrophoretic u-values as a relative measure for ζ. Happily last year Dr. H. de Bruyn found a method to determine ζ-values not from electrokinetic phenomena, but from mere potential measurements.[1] As his work has not yet been published, we think it desirable to give a short survey of his method and results.

The course of the potential in the double layer may be represented schematically by Fig. I.

Next to the wall (solid phase) there is a steep potential difference ϵ_{Stern} determined by the total charge and by the capacity (c) of the Stern layer.

$$\epsilon_{Stern} = \frac{\text{total charge}}{c_{Stern}}.$$

[1] Recently we found that Levina and Sarvisty (*Acta Physicochim.*, 1937, **7,** 485, have also made an estimation of ζ by measurements of one voltage.

The course of the potential in the diffuse part of the double layer is determined by Gouy's theory. The potential difference in this Gouy layer will be called ξ. This may be equal to, or a little bit larger than ζ according to where we locate the first layer of liquid which may be sheared along the wall.

Now Dr. de Bruyn's method for measuring ξ is based upon equation (1).

$$\epsilon = E_o + \frac{RT}{ZiF} \ln d_i. \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

The absolute value of the " total potential difference," ϵ, may be found by determining the activity of the potential determining ions in the liquid phase provided E_o or the value of the zero-point of charge is known.

When a neutral electrolyte is added to the liquid phase, in the first instance the Gouy-layer will become less diffuse, the potential difference ξ will diminish. The total potential $\bullet$ will decrease with the same amount, so that equation (1) is no longer satisfied. This process is represented in Fig. 2 by the arrow 1.
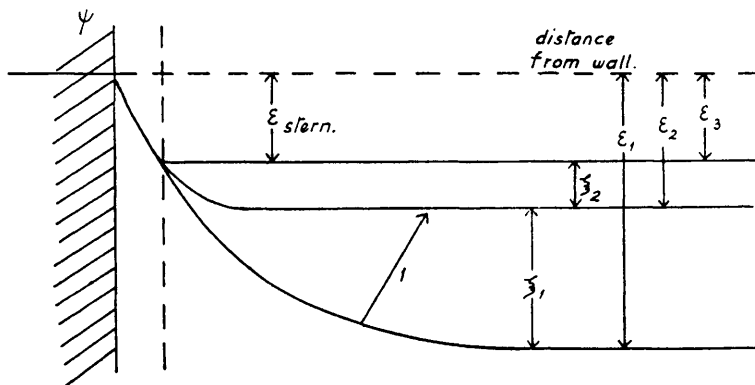

FIG. 2.

Now the wall of the solid phase will take up a number of potential determining ions. This causes ϵ to become larger and a_i to become smaller ; until a new equilibrium is reached in which equation (1) is satisfied. *The experimental conditions may be chosen in such a way* (small a_i, large adsorption capacity of the solid phase) *that while a_i does diminish, ϵ does not increase measurably.* In that case the value of a_i, after the new equilibrium establishes itself, determines immediately the value of ϵ_2, and the difference $\epsilon_1 - \epsilon_2$ just equals the amount $\xi_1 - \xi_2$ with which the potential in the diffuse part of the double layer has diminished. If the quantity of added salt has been great enough to suppress the diffuse double layer completely, the value of the potential ξ_1 of the Gouy layer may be set equal to the difference $\epsilon_1 - \epsilon_3$.

The value of $\epsilon_1 - \epsilon_2$ is given by

$$\epsilon_1 - \epsilon_2 = \frac{RT}{Z_i F} \ln \frac{a_{i_1}}{a_{i_2}}. \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

The activity of the i-ions may be determined by measuring the potential difference P between a reference electrode and an electrode which is reversible on the i-ion.

Than

$$P_1 = P_N + \frac{RT}{Z_i F} \ln a_{i_1}$$

$$P_2 = P_N + \frac{RT}{Z_1 F} \ln a_{i_2}.$$

From which follows

$$\frac{RT}{Z_i F} \ln \frac{a_{i_1}}{a_{i_2}} = P_1 - P_2. \qquad . \qquad . \qquad . \qquad (3)$$

Combining equations (2) and (3) one finds

$$\xi_1 - \xi_2 = \epsilon_1 - \epsilon_2 = P_1 - P_2 \qquad . \qquad . \qquad . \qquad (4)$$

The change of the potential difference in the diffuse layer is equal to the directly measurable change of the potential of the i-electrode.

To demonstrate the usefulness of this new method we will quote some examples from the work of Dr. de Bruyn.

We start with a fine suspension of AgI in a liquid in which the activity of the I′ ions equals $a_v = 10^{-10}$. At this a_v the AgI is uncharged ; ϵ and ξ are both equal to zero.

The potential difference between an AgI-electrode and a reference electrode (*e.g.*, a glass electrode or a calomel electrode) dipped in this system is measured and called P_0. A small quantity of a NaI solution is added now to the suspension and, after establishment of the adsorption equilibrium, the new potential difference P (and therewith the activity of the I′-ions) is determined.

The difference between P and P_0 is equal to the " total potential difference " after addition of the NaI.

The concentration of the suspension is chosen so large that the free I′-ions form only a very small fraction of the total quantity of I′-ions that has been added and we may identify the adsorbed I′ ions to the added quantity of I′-ions. In this way the total potential difference ϵ may be determined as a function of the amount of adsorbed I′-ions, that is of the charge of the suspension.
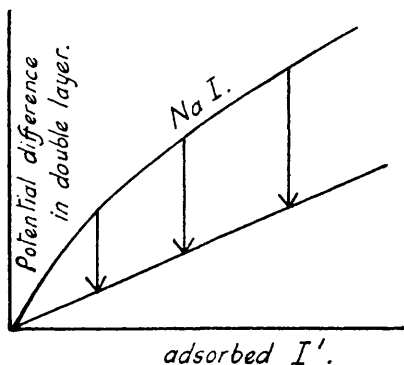

FIG. 3.

The curve marked NaI in Fig. 3 illustrates this relation

If neutral electrolytes are added to such a suspension, which has been charged by NaI, the accompanying changes in the diffuse double layer manifest themselves in the change of potential of the AgI electrode.

Fig. 4 shows the changes of double layer potential brought about by different electrolytes in a suspension of AgI which had been charged previously by NaI to a total potential difference of 230 mV.

Attention is called to the influence of the valency of the counter-ions but also to the fact that the final decrease of potential is independent of the valency-type, provided the quantity of added salt is large enough to suppress the diffuse double layer. The potential is not decreased until zero but the lowest value reached (130 mV in this case) represents the remaining potential difference of the Stern layer.

The difference 230 — 130 = 100 mV represents the ξ potential of the suspension before addition of the neutral salts. This value is somewhat

larger than the ζ-values found by electrophoresis measurements, but the difference may be probably fully accounted for by the imperfections of the electrophoresis-equation.

The influence of neutral electrolytes has been investigated in various states of charge of the suspension, so determining which part of the total potential difference belongs to the Gouy-layer and which part to the Stern-layer. In Fig. 3 this has been represented by arrows departing from different points of the NaI curve. The heads of the arrows may be connected by a curve, which must represent the potential difference of the Stern-layer as a function of the amount of adsorbed I′ ions.

It is a strong support to the theory here developed, that this curve comes out to be a straight line, in full accord with the capacity of the Stern-layer (*i.e.*, total charge/e_{Stern}) being a constant.

Although, in many cases, colloid chemistry is more interested in the potential of the double layer than in its charge, a full knowledge of the structure of the double layer requires a knowledge of the charge as well. The theory of Stern, which we may say is generally accepted nowadays,
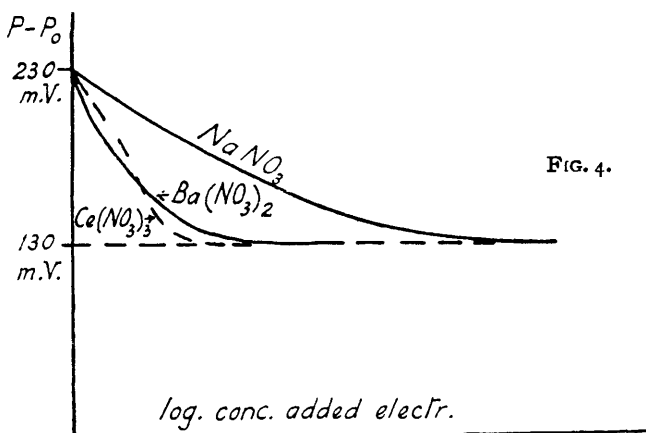

FIG. 4.

owes its existence to the fact that neither Helmholtz' nor Gouy's theory could account for the capacity of the double layer on mercury.

Determination of the charge of a double layer from electrokinetic phenomena is impracticable owing to the great mathematical difficulties. Moreover the charge determined in this way would only represent the charge of the mobile part of the double layer and would be smaller (in most cases much smaller) than the total charge.

Apart from that, determination of the charge generally presents less difficulties than the determination of the potential. The difficulties here are of a more experimental character, owing to the smallness of the charge.

The first values for the charge of the double layer have been obtained in the case of a mercury surface, during researches on the electrocapillary curve.

With colloids most determinations of the charge are based on chemical determinations of the bearers of the charge (*i.e.*, the ions). The most simple and convenient method is the titration of the counter-ions. Pauli was the first to show, that a great many negative sols may be dialysed so sharply, as to expel practically all foreign electrolytes and

replace all the counter-ions by H-ions. By direct conductometric or potentiometric titration of such a sol with NaOH the total charge may be determined with accuracy.

In other cases it is possible to determine directly the quantity of peptising ions (e.g., in the AgI sol the peptising I' ions may be titrated with $AgNO_3$). The determination of the maximum exchange capacity of the double layer may be mentioned as a third method.

In the case of the AgI sol these three methods have been used independently and have given results, that are completely concordant among each other. We may infer herefrom that the determination of the total charge of colloids rests on a very sound base.

In drawing theoretical conclusions from this total charge there arises, however, a very serious difficulty. It is not enough to know the total charge in a certain portion of a sol ; one has also to know the charge of a single particle or the charge per $cm.^2$ of surface ; and it is well known that determination of the dimensions of colloidal particles has always been affected by very large experimental errors.

So far the present considerations on the *capacity* and the *charge* of the double layer in colloids are attended with great uncertainty. In this field of research the mercury surface remains the ideal object.

On the other hand, we have available, for the measurement of *potentials* in the double layer, various methods, applicable to micro as well as to macro phase-boundaries, the results of which have been roughly concordant. It will be one of the tasks of the near future to compare these different methods in a more exact and systematic way.

From what we have said above, it will be obvious that our knowledge of the mechanism of the double layer is still very incomplete. It is evident that the problem of colloid stability, as determined by the electric protection of the double layer is still more complicated and uncertain. We do not doubt that Hardy's fundamental conception is in principle, right, but the numerous investigations of Burton, Powis, Freundlich, Limburg, Briggs and many others, indicate that a simple relation between electrophoretic mobility and colloid stability does not exist. This is clear if ζ governs stability ; for we have seen that the proportionality between ζ and u is mostly dubious. However, severe doubt has arisen whether ζ is a direct measure for stability. Eilers and Korff have pointed out from dimensional considerations, that ζ could not be the repulsive energy, that only ζ^2 multiplied by a length could play such a rôle. They assumed from the Debye theory to be that length ; several other scientists made other assumptions. At the moment, as we start this Discussion, the question is still unsolved.