

THE ORIGIN OF THE CHARGE OF A COLLOIDAL PARTICLE AND ITS NEUTRALISATION BY ELECTROLYTES

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The origin of the charge of a colloidal particle is generally referred to the adsorption of ions. Regarding the mechanism of the adsorption we have no definite idea. In his theory of adsorption Langmuir* refers it to "chemical forces" due to the surface atoms. The adsorption of an ion gives a charge to the surface, and as a result introduces electrical forces. The recognition of this factor elucidates the influence of electrolytes on the precipitation of suspensoids on electro-osmosis and allied phenomena.

THE CHARGE OF SUSPENSIDS

It is well known that the stability and the charge of suspensoids are connected with traces of electrolytes. Table 1 shows that for most suspensoids the charge is of the same sign as that of the "ion" the substance has in common with the peptising or stabilising electrolyte. Most suspensoids (excepting colloidal metals and other elements) are included in the table.

TABLE 1

Suspensoid.	Stabilising Electrolyte.	Common Ion.	Sign of the Charge of the Particles.
¹ Insoluble silver salts	(a) Silver nitrate (b) Electrolyte with common anion.	Ag ⁺ Anion	Positive. Negative.
² Metal sulphides	Hydrogen sulphide or ammonium sulphide.	S ⁻ or HS ⁻	Negative.
³ Ferrocyanides of copper, and iron.	Potassium ferrocyanide	Anion	Negative.
⁴ Hydroxides of iron, aluminium, etc.	Nitrate or chloride of the corresponding metal.	Cation	Positive.
⁵ Hydroxide of iron	Alkali hydroxide	Hydroxidion	Negative.
⁶ Barium carbonate	Barium nitrate	Barion	Positive.

REFERENCES

- ¹ Lottermoser, *Koll. Zeitsch.*, 1910, **6**, 78 (see also earlier papers).
² Linder and Picton, T., 1892, **61**, 114; T., 1905, **87**, 1914; Mukherjee, *J. Amer. Chem. Soc.*, 1915, **37**, 2024; Young and Goddard, *J. Phys. Chem.*, 1917, **21**, 1; Mukherjee and Sen, T., 1919, **115**, 461.
³ Duclaux, *Compt. Rend.*, 1904, **138**, 144, 571; *J. Chim. Phys.*, 1909, (vii), 405.
⁴ Pauli and Matula, *Koll. Zeitsch.* 1917, **21**, 49; Duclaux, *J. Chim. Phys.*, 1907, **5**, 29.
⁵ Powis, T., 1915, **107**, 818.
⁶ Perrin, *J. Chim. Phys.*, **2**, 1904, 601.
 Compare also for "stannic hydroxide" Biltz, *Ber.*, 1904, **37**, 1095 and Glixelli, *Koll. Zeitsch.*, 1913, **13**, 194.

The relationship shown in Table 1 makes it possible to define the chemical forces involved in this particular case. The fixation of a common ion is due to the same causes that bring about the growth of a crystal in its solution.

* *J. Amer. Chem. Soc.*, 1916, **38**, 2221; *ibid.*, 1917, **39**, 1848.

The growth of a crystal in its solution shows that the surface atoms of a solid attract the molecules of which it is composed, and that the "atoms" or "groups" in the molecule are attracted most strongly at specific points in the surface. The "attached" molecule thus conforms to the structure of the crystal. As an example one may say that at the surface of a crystal of sodium chloride there are "places" where the chlorine ion in salt solution can be held by chemical forces. The specific nature of chemical forces requires that the same attraction will be present when the crystal is in contact with any other solution of an electrolyte, which gives a "chlorine ion" in an aqueous solution. Thus on the addition of hydrochloric acid the chloridions will be attracted. If "N" be the number of "places" per unit surface where the chloridions are attracted chemically, then the number remaining "attached" to the surface (at any instant) will be dependent:—

(1) On the concentration of the "ion," and

(2) "A" the work necessary to separate the "ion" from its position in the surface. "A" is evidently the measure of the chemical affinity acting on the "ion," and $e^{-A/kT}$ is a

measure of the stability of the "fixation" where $k = \frac{R}{N_0}$, R

being the gas constant, N_0 the Avogadro number, and "T" is the absolute temperature. For a stable union it is necessary that "A" should be great compared to kT . In this case a small amount of an electrolyte with an adsorbable "ion" will be sufficient to lead to the adsorption of an appreciable amount of the "ion." Since the molecules of sodium chloride and hydrochloric acid do not combine with each other in their entirety this sort of "fixation" of the chloridion will impart a charge to the surface.

The resulting separation of electricity will be opposed by the electrical attraction exerted by the cations in the surrounding liquid.

THE ELECTRICAL ATTRACTION ON IONS OF OPPOSITE CHARGE

We shall speak of the "ions" fixed to the surface by chemical forces as "chemically adsorbed." *In the following discussions it is assumed that there is no chemical affinity acting between "ions" of opposite charge.* This assumption is obviously made to investigate the effect of the electric forces alone.

In consequence of the charge, ions of opposite sign will be drawn near the surface. In the liquid there remains an equivalent amount of ions of opposite sign. The electrical energy will be minimum when these ions are held near the surface so that the distance between the oppositely charged ions has the minimum value possible under the conditions, and they will be held opposite to the ions chemically adsorbed. An "ion" so held will not be "free" to move if its kinetic energy is less than "W", the energy required to separate the ion from the oppositely charged surface.

The number of such "bound" ions determine the diminution in the charge of the surface. When the concentration of ions of opposite charge in the liquid is small the number of ions "held" to the surface by electrical attraction will be small. The equilibrium conditions will be discussed more fully later.

If the chemically adsorbed ions have a valency equal to " n_1 " and " n_2 " is the valency of the oppositely charged ions in the liquid in contact with the surface then

$$W = \frac{n_1 n_2 E^2}{D x} \quad \dots \quad (1)$$

where E = the electronic charge, x = the distance between the centres of the "ions" at the position of minimum distance, and " D " is the dielectric constant of water. Since "ions" have probably an envelope of water " x " has a value of the order of 10^{-7} cm (the diameter of the molecules of water is about 4×10^{-8} cm.). The probability of an ion remaining fixed is given by $1 - e^{-W/kT}$ where " k " and " T " have the same significance as before. The values of $1 - e^{-W/kT}$ for different values of n_1 and n_2 are given below.

TABLE 2.

$x = 10^{-7}$ cm. $D = 81$. Values of $1 - e^{-W/kT}$

$T = 27^\circ\text{C} \cdot k = 1.37 \times 10^{-16}$
 $E = 4.77 \times 10^{-10}$ C.G. S units.

	$n_2 = 1$	$n_2 = 2$	$n_2 = 3$	$n_2 = 4$
$n_1 = 1$.501	.751	.875	.938
$n_1 = 2$.751	.938	.984	.986
$n_1 = 3$.875	.984	.998	X

Since the value of " x " is not known definitely, Table 2 conveys a rough idea of the order of magnitude of $1 - e^{-W/kT}$.

A consideration of the values given above will show that the electrical attraction is sufficiently strong to account for the adsorption.

THE DOUBLE LAYER

Depending on the concentration of the oppositely charged ions in the liquid near the surface at any instant a certain number of the "chemically adsorbed" ions are "covered" by "ions" of opposite charge. In the liquid near the surface there are always a number of free "ions" equivalent in amount to the "uncovered" chemically adsorbed ions on the surface. The total amount of ions of opposite sign both "bound" and "free" is equivalent to the amount of ions "chemically adsorbed." These "free" ions form the second sheet of the double layer. It is evident that as a result of their thermal motion the mean distance between the two layers will be greater than " x ."

CONDITIONS WHEN EQUATION 1 HOLDS GOOD

" W " has the value given in Equation 1 when the mean distance between the chemically adsorbed ions is considerably great compared to " x ," i.e., molecular dimensions. The two oppositely charged ions can then be assumed to be uninfluenced by neighbouring ions on the surface. The considerations set forth below show that for practical purposes we can treat the charge of the surface as due to discrete charged particles widely separated from each other compared to molecular dimensions.

Following Helmholtz and Lamb (*Brit. Assoc. Rep.*, 1887, p. 495; *Phil. Mag.*, 1888, p. 60) it is usual to consider the thickness of the double layer to be of the order of molecular diameters. McTaggart (*Phil. Mag.*, 1914, [6], 27, 297) calculates the "density" of the charge at the surface of gas bubbles to be 1.5×10^4 C.G.S. units (from the well-known Lamb-Helmholtz equations). He assumes that a layer of water of thickness of about 10^{-8} cm. separates the opposite charges. Since the electronic charge is 4.77×10^{-10} C.G.S. units (Millikan's value) the number of univalent "ions" which must be adsorbed per unit surface (cm^2) is equal to about 10^{18} . The mean distance between the "ions" will be about 3×10^{-6} cm. The

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distance is greater if the charge is due to adsorbed polyvalent "ions." For a thickness of the double layer of the order of 10^{-6} cm. the mean distance is 3×10^{-5} cms. Similar values of the "density" of the charge are obtained from other data (cp. Lewis, *System of Physical Chemistry*, 1916, Vol. 1, p. 407). Thus we find that the "ions" imparting the charge to the surface are situated wide apart compared to molecular dimensions. Under these conditions the neighbouring ions have comparatively little effect on an oppositely charged "ion" at its position of minimum electrical energy and "W" as given in Equation 1 can for practical purposes be taken to be the measure of the stability of the electrical adsorption of ions of opposite charge.

THE MAXIMUM ELECTRICAL ADSORPTION ON THE ADDITION OF AN ELECTROLYTE

It will appear from Table 3 that the addition of an electrolyte with univalent "ions" of opposite sign to the charged surface seldom produces a reversal in the original charge. If, however, the electrolyte has a bivalent ion of opposite sign reversals are sometimes observed. On the other hand, with electrolytes having multivalent ions of opposite sign a reversal of the charge is more frequent.

TABLE 3

Substance.	Sign of Charge.	Electrolytes.	
		No Reversal.	Reversal.
¹ CrCl ₂ -	Made "positive" by the addition of acid.	Ca(NO ₃) ₂ - - - MgCl ₂ - - -	K ₃ Fe(CN) ₆ , K ₄ Fe(CN) ₆
² CrCl ₃ -	Made negative by the addition of alkali.	MgCl ₂ - - -	Ba(NO ₃) ₂ , Ca(NO ₃) ₂
³ Al ₂ O ₃ -	"Positive" with acid.	MgSO ₄ - - - Ca(NO ₃) ₂ - - -	K ₄ Fe(CN) ₆ .
⁴ Al ₂ O ₃ -	"Negative" with	x	Ca(NO ₃) ₂ .
⁵ Mn ₂ O ₃ -	"Negative" with base.	x	Ba(NO ₃) ₂ .
⁶ Carborundum.	"Negative" with base.	x	La(NO ₃) ₃ .
⁷ Glass -	Negative -	K ₂ SO ₄ , KNO ₃ , NaCl HNO ₃ , Ce(NO ₃) ₃ , UO ₂ (NO ₃) ₂ , AgNO ₃ , Al ₂ (SO ₄) ₃ , BaCl ₂ , CaCl ₂ .	Thorium nitrate.
⁸ Quartz -			Thorium nitrate.
⁹ Copper hydroxide.	Positive -	KCl, K ₂ SO ₄ , Al ₂ (SO ₄) ₃	K ₃ PO ₄ , K ₃ Fe(CN) ₆
¹⁰ Gas bubbles	Negative -	HCl, HNO ₃ -	La(NO ₃) ₃ , Th(NO ₃) ₄ , Zr(NO ₃) ₄ , Al ₂ (SO ₄) ₃ .
¹¹ Silver, gold	Negative -	x	Al ₂ (SO ₄) ₃ .
¹² As ₂ S ₃ -	Negative -	KCl, BaCl ₂ , Al ₂ (SO ₄) ₃	Th(NO ₃) ₄ .
¹³ Emulsions -	Negative -	KCl - - -	BaCl ₂ , Al ₂ (SO ₄) ₃ , Th(NO ₃) ₄ .
¹⁴ Gas bubbles	"Positive" with thorium nitrate.	x	K ₃ Fe(CN) ₆ , K ₄ Fe(CN) ₆ .

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- ^{1,6} Perrin, *loc. cit.*
- ^{7, 8} Elissiaoff, *Zeitsch. Physikal. Chem.*, 1912, **79**, 385.
- ^{9, 11} Burton, *Physical Properties of Colloidal Solutions*, 1916, 151, 153.
- ^{10, 14} McTaggart, *Phil. Mag.*, 1914(6), **27**, 297, 12; Powis, T., 1916, **109**, 734.
- ¹³ Powis, *Zeitsch. Physikal. Chem.*, 1914, **89**, 91, 186; also T., 1915, **107**, 818.

It is difficult to reconcile these facts with the specific nature of the "adsorption" of ions. They are, however, a necessary consequence of the view advanced here. Let us suppose that the "primary ions" which are chemically adsorbed are all univalent. An ion of opposite sign entering the "double layer" will be driven towards the surface by the strong electric field. An "ion" of the same sign will rarely strike the surface. The oppositely charged ions will be held to the surface by electrical forces near each primary ion. The maximum number of ions which can possibly be held in this manner per unit surface is equal to the number of primary ions in the same area. If the oppositely charged ions are univalent it is evident that when the maximum adsorption has been reached the surface is neutral. In general when the primary ions are univalent the maximum possible charge per unit surface is equal to—

$$NE(1 - n_2) \dots \dots \dots (2)$$

where "N" is the number of univalent "primary" ions per unit area, E, the electronic charge and "n" the valency of the oppositely charged ions.

For the general case the possible maximum charge is given as

$$NE(n_1 - n_2) \dots \dots \dots (3)$$

where "n₁" is the valency of the "ions" chemically adsorbed and N, E and n₂ have the same significance as before.

Thus a reversal of charge by "electric adsorption" is theoretically possible only when the added electrolyte has an oppositely charged ion with a valency greater than the primary ions. For univalent "ions" of opposite sign reversal is impossible by electrical adsorption. In considering particular cases it should be remembered that "chemical action" is quite possible. It is satisfactory to note that in Table 3 there is not a single case of reversal with univalent ions of opposite sign.

Actually, however, the maximum adsorption will coincide with the neutralisation of the surface. The collisions of "ions" of opposite sign are mostly due to the electrical field of the double layer, and the collisions due to "diffusion" are comparatively negligible. The number of collisions will diminish rapidly with increased electric adsorption, and will have a small value at the neutral point. Farther adsorption will impart to the surface a charge of the same sign as the "ion" and the double layer will now repel the "ion" from the surface. The number of collisions will decrease rapidly and will soon be negligible. Thus a reversal of charge is only possible when the valency of the oppositely charged ion is very great, so that $1 - e^{-W/kT}$ has a considerable value. Even then the theoretical maximum adsorption is not possible, and the reversal in charge can proceed only to a small extent. In the majority of cases, therefore, the maximum adsorption will correspond to a neutralisation, or reversal to a slight extent.

EQUILIBRIUM CONDITIONS

In discussing the equilibrium conditions we shall deal with the case when the maximum adsorption corresponds to the neutralisation of the charge. The "maximum" amount of an ion of opposite sign that can be adsorbed per unit area is thus equivalent to the charge per unit area. If the charge of the surface is due to "N" ions of valency n₁ per unit area, then the maximum number N of an

“ion” of valency “ n_2 ” and of opposite signs which can be adsorbed electrically is given by the relation

$$N_m = N \cdot n_1 / n_2 \quad \dots \dots \dots (4)^*$$

Let “ θ_1 ” denote the fraction of this maximum which has been adsorbed when equilibrium has been reached in presence of ions of opposite sign having a concentration “ c ” in the liquid. For equilibrium the number of electrically adsorbed ions becoming “free” in any interval per unit area must be equal to the number re-adsorbed in the same time.

Considering unit surface the rate at which the adsorbed ions of opposite charge become “free” is evidently given by

$$k_1 \cdot N_m \cdot \theta_1 \cdot e^{-W/kT} \quad \dots \dots \dots (5)$$

since $N_m \theta$ is the number of “ions” adsorbed per unit surface k_1 is a constant.

The rate of adsorption depends on two factors: (a) the rate of collision of oppositely charged ions, and (b) the number of “places” where adsorption is possible; that is, the number of primary “ions” that remain “uncovered” and unneutralised by oppositely charged ions at any moment. (Cf. Langmuir.) This is given by

$$N - N_m \theta_1 = N \left(1 - \frac{n_1}{n_2} \theta_1\right) \quad \dots \dots \dots (6)$$

The rate of collisions (a) is determined by the concentration of ions of opposite sign in the liquid in contact with the surface and the forces driving the ions towards the surface. Each “ion” is urged to the surface by two forces:—

(1) *Its thermal agitation to which its osmotic pressure is due.*—

According to Einstein this force is equal to $\frac{RT}{No}$.

(2) *The electrical attraction exerted on the particles by the charged surface.*—An ion in the double layer is acted on by its electrical field. The intensity of the field is proportional to the “density” of the charge on the surface, and is, therefore, given by:

$$k'_2 (1 - \theta_1) n_1 N \cdot n_2 \quad \dots \dots \dots (7).$$

Since “ n_1 ” and “ N ” are constants for the same surface we may write (7) as—

$$k_2 (1 - \theta_1) n_2 \quad \dots \dots \dots (7a) \text{ where } k_2 \text{ is a constant.}$$

The thickness of the surface layer is small and the rate of fall in the potential, that is, the intensity of the electric field, is enormous. A simple calculation will show that RT/No is negligible in comparison to $k_2 (1 - \theta_1)$. Under the conditions the rate of collision is given by—

$$k_3 n_2 (1 - \theta_1) \cdot C \cdot u \quad \dots \dots \dots (8),$$

where “ C ” is the concentration of the “ions” in the liquid in contact with the surface, “ u ” is the “mobility” of the “ion” (under unit force), k_3 is a constant, and “ n_2 ” and “ θ_1 ” have the same significance as before.

* Equation “4” holds when n_2 is equal to or greater than n_1 . When $n_1 > n_2$ more than one “ion” of opposite charge should be adsorbed for each chemically absorbed “ion” to neutralise its charge. The mutual repulsion of these “ions” brings in complications which will not be considered in the present paper.

From (6) and (8) we find that the rate of adsorption is given by—

$$k_4 \cdot N \left(1 - \frac{n_1}{n_2} \theta_1\right) \cdot n_2 (1 - \theta_1) \text{ C.u.} \dots \dots \dots (9).$$

Finally, for equilibrium we get

$$k_1 N_m \theta_1 e^{-w/kT} = k_4 N \left(1 - \frac{n_1}{n_2} \theta_1\right) n_2 (1 - \theta_1) \text{ C.u.} \dots \dots \dots (10).$$

Putting $N = \frac{N n_1}{n_2}$ and remembering that N_1 , n_2 , u and $e^{-w/kT}$ are constants for the same ion we can write equation (10) in the form

$$\theta_1 = k_0 \frac{n_2}{n_1} \text{ C.} \left(1 - \frac{n_1}{n_2} \theta_1\right) (1 - \theta_1) \dots \dots \dots (11)$$

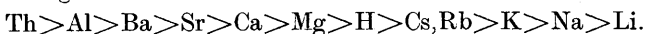
where $k_0 = \frac{k_4}{k_1} n_2 \cdot u \cdot e^{-w/kT}$.

[It may be stated that k_4 contains the term “ $n_1 N$ ” (*cf.* equation 7).]

Since “ θ_1 ” denotes the “fraction” of the original charge neutralised by adsorption the charge of the surface is proportional to

$$1 - \theta_1 = \theta_2 \dots \dots \dots (12).$$

Equations (1) and (10) show that the “electrical” adsorbability of an “ion” of opposite charge is dependent on its mobility and its valency. Thus for a “negative” surface the order of adsorption of the following cations should be



(Rubidium and Caesium have practically the same ionic mobility.)

It should be remembered that all along we have assumed that the surface does not exert any chemical affinity on the “ions.” Clearly this is not likely to be the case always, and the order given above cannot be expected to hold good in such instances. The following section will show, however, that the above order holds good in a large number of cases.

THE PRECIPITATION OF A SUSPENSOID BY AN ELECTROLYTE

It was first pointed out by Hardy that the precipitation of suspensoids by inorganic electrolytes is due to a diminution in the electric charge of the particles. The “ion” having a charge of the same sign on the colloid has very little influence on the precipitation and the precipitating power of an electrolyte is determined by the “valency” of the “ion” which has a charge opposite in sign to that of the colloid. The same results have been observed in experiments on cataphoresis and electro endosmosis (*cp.* the works of Perrin, Burton, Elissafoff, McTaggart, Ellis, Powis, &c.). These regularities are not consistent with the specific nature of the adsorption process as it is ordinarily understood, and they show that the process of “adsorption” in these cases is “electrical” in nature.

Whetham (*Phil. Mag.*, 1899, **48**, 474) recognised the electrical nature of the process, and considering the probabilities of a charged particle meeting an equivalent amount of electrical charge of opposite sign in the form of ions deduced his interesting relation between the precipitating powers of “ions” of different valency.

In the application of his equation of adsorption isotherm to this process Freundlich (*Zeitsch. Physikal. Chem.*, 1910, **73**, 404) assumed that different ions are equally adsorbed at equal concentrations, the constants in the equation being independent of the nature of the “ion.”

Subsequent work has shown that the simple relations indicated by these equations (of Whetham and of Freundlich) do not agree with observations. These theories do not attempt to elucidate the difference in the precipitating powers of "ions" having the same valency. Bancroft (*J. Phys. Chem.*, 1915, **19**, 363; *Rep. Brit. Assoc.*, 1918, Section B., pp. 2-16) and Wo. Ostwald (*Koll. Zeitsch.*, 1920, **26**, 28, 69) have admirably summarised the present position of the subject.

It is necessary to point out in this connection that the precipitation of a suspensoid by electrolytes is a complicated process. The diminution in the electric charge is undoubtedly responsible for the coagulation, but the precipitating concentration of an electrolyte is dependent on such other factors as the distance between the particles, their size, the total amount of colloid-liquid interface and "age." Ions of different valency (and hence different coagulating powers) are not all similarly affected by variations in these conditions. A diluted sol of arsenious sulphide requires a higher concentration of potassium chloride but a lower concentration of barium chloride than what the original sol requires. The ratio of the precipitating concentration of two electrolytes is thus variable (Mukherjee and Sen, T., 1919, **115**, 462; Mukherjee, T., 1920, **117**, 350; Kruyt and Duin, *Koll. Chem. Beihefte*, 1914, **5**, 269; Kruyt and Spek (*Proc. K. Akad. Wetenschap.*, Amsterdam, 1915, **17**, 1158). It is therefore clear that the precipitating concentrations (*i.e.*, the precipitating powers) of an electrolyte cannot be taken as a *quantitative* measure of the adsorption of the "ions." The discussion of such data from a quantitative point of view of adsorption is thus not possible. As a result no direct quantitative relationship is possible between the diminution in the electric charge of a colloidal particle and the coagulating concentration. The precipitating powers of different ions thus give a qualitative measure of their adsorbability.

It will be seen from Table 4 that the order of the precipitating power of cation (on "negative" suspensoids) is as follows:—

Th>Al>Ba>Sr>Ca>Mg>H>Cs,Rb>K>Na>Li
the same as deduced from equation (10).

TABLE 4

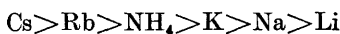
Order of Precipitating Power of Cations for various Suspensoid Systems

1. Arsenious sulphide under different conditions.	Th>Al>Ba>Sr>Ca>Mg>H>K>Na>Li.
2. Gold - - -	Al>Sr>Ca>Mg>H>Cs>Rb>K>Na>Li
3. Platinum - - -	Al>Ba>K>Na.
4. Copper ferrocyanide	Al>Ba>H>Cs>Rb>K>Na>Li.
5. Prussian blue - - -	Al>Ba>H>Cs>Rb>K>Na>Li.
6. Silver - - -	Al>Ba>Sr>Ca>H>Cs>Rb>K>Na>Li.
7. "Oil" emulsions -	Al>Ba>Sr>Ca>Mg>K>Na>Li.

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- Freundlich, *Zeitsch. Physikal Chem.*, 1903, **44**, 129; Mukherjee, *J. Amer. Chem. Soc.*, 1915, **37**, 2024; *loc. cit.* Other "sulphides" behave similarly.
Galecki, *Zeitsch. Anorg. Chem.*, 1912, **45**, 221; Westgren, *Arkiv Kem. Min. Geol.*, 1918, **7**, No. 6, 1-30.
Freundlich, *Kapillarchemie*, 1909, 352; 4, 5; Pappada, *Koll. Zeitsch.*, 1910, **6**, 83, 1911, **9**, 136, 6; Pappada, *Gaz. Chim.*, 1912, **42**, I., 263.

7. The series given refer to both the order of the de-emulsifying power and the effect on the inversion of phase (privately communicated by Mr. S. S. Bhatnagar, *see also* T., 1920, 117, 542. *Also* Bach (*J. Chim. Phys.*, 1920, **16**, 46) finds the series



for a number of cases).

It should be noted that in the experiments referred to in Table 4 inorganic "ions" only have been used, and that these cations have very little tendency to complex formation. The "alkali" metal cations have the least tendency for complex formation, and it is to be expected that they are most likely to be least affected by chemical affinity due to the surface atoms, and hence the "adsorption" should be mainly "electrical" in nature. The order of alkali cations as deduced from equation (10) determines the order of their precipitating powers in most cases. Pappada* first pointed out that the order of coagulating power of these ions is the same as the order of the mobility.

The Effect of Electrolytes on Electro-Endosmosis

A verification of equation (10) is possible from the experimental work on electro-endosmosis. Unfortunately the experimental difficulties are considerable and the limits of error quite great. The most careful work is that of Elissafoff (*Zeitsch. Physikal Chem.*, 1912, **79**, 385) who considers the limits of error to be about 10 per cent. in his experiments. It will be seen from the following tables that the agreement is as good as can be expected.

In applying equation (10) or (11) it should be remembered that :

(a) Chemical action between the surface and the oppositely charged ion is not always negligible, and

(b) That the surface concentration is not always the same as that in the bulk of the liquid. Thus "adsorption" due to variation in surface energy in the sense of Gibbs' well-known equation is always possible.

The solid substances examined by Elissafoff are glass and quartz. We shall assume that the charge of the surface is due to the fixation of "hydroxyl ions" by chemical affinity.

From equations (11) and (12) we get

$$1 - \theta_2 = k_0 c \frac{n_2 - n_1}{n_1} \theta_2 + k_0 c \theta_2^2 \dots \dots \dots (13)$$

For hydroxyl ions $n_1 = 1$ and putting n_2 equal to 1, 2, 3, 4 successively we get the following equations for the adsorption of oppositely charged ions of valency 1, 2, 3 and 4 respectively.

$$k_0 c \theta_2^2 + \theta_2 - 1 = 0 \dots \dots \dots (13A).$$

$$k_0 c \theta_2^2 + \theta_2 (k_0 c + 1) - 1 = 0 \dots \dots \dots (13B).$$

$$k_0 c \theta_2^2 + \theta_2 (2k_0 c + 1) - 1 = 0 \dots \dots \dots (13C).$$

$$k_0 c \theta_2^2 + \theta_2 (3k_0 c + 1) - 1 = 0 \dots \dots \dots (13D).$$

There is only one unknown constant in these equations. For comparison the values of θ_2 calculated by Elissafoff from an empirical equation is also given. The unit of concentration is taken to be 10^{-6} gram-ion per litre.

* *Kolloid. Zeitsch.*, 1909, **4**, 56.

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TABLE 5

Electrolyte—sodium chloride $k_0 = \cdot 0076$.

Glass capillary concentration.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
22·5	43	43·4	42
68	37	36·4	34
136	31	30·6	29
225	26	26·4	26
2240	8	10·6	10
4500	5	7·8	5

TABLE 6

*Glass*Electrolyte—potassium sulphate $k_0 = \cdot 00875$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
22	41	42·8	38
67	36	35·2	32
134	27	29·5	29
224	26	25·2	26
470	23	19·4	22
800	21	15·7	19
4000	8	7·7	10
7900	5	5·6	7

TABLE 7

*Glass*Electrolyte—silver nitrate $k_0 = \cdot 059$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
4	42	41·2	39
7	35	37·3	35
10	32	34·5	34
20	29	28·6	30
50	27	21	25
1000	9	5·8	8

TABLE 8

*Glass*Electrolyte—barium chloride $k_0 = \cdot 0163$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13B).	50 θ_2 (Empirical equation).
2·2	47	46·7	—
4·4	46	44	—
6	41	42	39
22	28	31·5	30
110	15	15	20

TABLE 9

*Glass*Electrolyte—uranyl nitrate $k_0 = \cdot 0168$.

C.	$50 \theta_2$ obs.	$50 \theta_2$ (Eqn. 13B).	$50 \theta_2$ (Empirical equation).
3·5	52	—	—
7	45 (38)	41·1	39
10·5	38	38	36
14	36 (32)	35·4	33
28	29	28·5	27
56	23	21·3	21
112	14	14·5	15
140	13	12·6	13
238	5	8·7	9

The results of a second determination are given in brackets. For a concentration of 3·5 instead of a decrease a rise had been observed. These and other instances illustrate that the limits of error are considerable.

TABLE 10

*Glass*Electrolyte—nitric acid $k_0 = \cdot 059$.

C.	$50 \theta_2$ obs.	$50 \theta_2$ (Eqn. 13A).	$50 \theta_2$ (Empirical equation).
8	45	36·1	—
20	29	29·6	30
34	26	25	26
60	21	20·4	20
100	16	16·9	16

TABLE 11

*Quartz*Electrolyte—potassium nitrate $k_0 = \cdot 01$.

C.	$50 \theta_2$ obs.	$50 \theta_2$ (Eqn. 13A).	$50 \theta_2$ (Empirical equation).
8	48	46·6	—
28	43	40·6	43
68	33	34	33
120	28	29	26
390 (?)	10	19	13

TABLE 12

Electrolyte—calcium chloride $k_0 = \cdot 043$.

C.	$50 \theta_2$ obs.	$50 \theta_2$ (Eqn. 13B).	$50 \theta_2$ (Empirical equation).
1·6	43	44·4	44
4·3 (?)	28	37·7	36
8·1	32	31·9	31
13·5	28	26·5	27
29·5	20	18·3	21
82 (?)	19	9·6	12

114 THE ORIGIN OF THE CHARGE OF A COLLOIDAL PARTICLE

Aluminium and thorium salts are hydrolysed to a large extent in such low concentrations as have been used by Elissafoff. The "hydroxide" has a positive charge in the colloidal state. Positively charged colloids can neutralise the charge of negatively charged colloids and equation (13) can no longer be applied.

From Table 7 we find that "silver nitrate" has a greater neutralising power than other monovalent ions. This should be attributed to chemical forces. Equation 13 holds good for the limiting case when there is no chemical attraction. In case of chemical action "W" as given in equation (1) no longer represents the stability of the adsorption of the ion. We can, however, put the energy required to separate the ion from the surface as equal to "W + B," where "B" is a measure of the chemical affinity acting on an ion. The form of the equation thus remains the same as in (13).

TABLE 13

	Ions.							Surface
	Na·	K·	Ag·	H·	Ca ^{..}	Ba ^{..}	UO ₂ ^{..}	Glass.
$k_0 \times 10^3$.76	.87	5.9	5.9	x	1.63	1.68	—
(Eqn. 13).	—	1.0	—	—	4.3	—	—	Quartz.

A discussion on the values of k given above is not possible unless we know " x " in Equation (1). If " x " has such a value that $-W/k.T$ for a univalent ion is less than 0.2, then $e^{-W/k.T}$ for a divalent ion will be only slightly different from that of an univalent ion. In this case " k_0 " in Equation (10) will be proportional to $n_2.u$, when n_2 and u denote the valency and the mobility of the ion respectively. For the three ions H·, K· and Na·, " k_0 " is approximately proportional to their mobilities, cf. equations 10 and 13 (a).

Considering the simplifying assumptions made and the experimental difficulties involved, the agreement is as good as can be expected. The neutralisation of the charge of a colloidal particle by electrolytes is thus mainly the result of electrical "forces."

At the surface, however, the oppositely charged ions which are attracted are subject to the chemical affinity of the surface atoms. The order of adsorption deduced from Equation (10) will not hold for these cases. The order will be determined by the chemical affinity of the surface atoms. The alkali metal cations conform best with the theoretical series. This is in agreement with the fact that they have the least pronounced tendency to form complex "ions," to enter into combination with other elements to form "groups" and to form insoluble salts—all these facts point to their being least affected by "chemical affinity." Their chemical activity is simply due to their tendency to pass into "ions."

SUMMARY

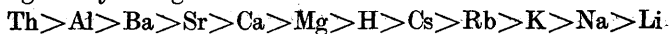
1. The charge of a number of suspensoids has been traced to the adsorption of a common ion. The nature of the chemical forces to which this adsorption is due has been defined.

2. The effect of the electrical charge of a surface (due to the disorption of ions) on "ions" of opposite sign has been theoretically investigated for the case when chemical action does not take place between the surface and the "ion." It has been shown that the "electrical" forces are sufficiently strong to account for adsorption.

The stability of the adsorption of an ion of opposite sign by electrical forces has been given a quantitative form assuming that the charge of the surface consists of "ions" which can be treated as "point" charges widely separated from each other. Actual calculations justify this assumption.

3. The reversal of the charge by electrical adsorption has been discussed.

4. The following series of the order of adsorbability of cations by a negatively charged surface has been deduced from the theory



5. This is the order of the precipitating power of these ions for a number of suspensions of widely different chemical properties

6. Equations deduced from the theory satisfactorily agree with the experimental observations of Elissaffoff on electro-endosmose.

7. The chemical affinity of the surface atoms is not always negligible. For this reason the series given in paragraph 4 cannot be expected to hold in all cases. Equation (10) is applicable to this case also and retains the same form.

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