

THEORY OF THE STABILITY OF LYOPHOBIC COLLOIDS

THE INTERACTION OF SOL PARTICLES
HAVING AN ELECTRIC DOUBLE LAYER

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PREFACE

The present work is the result of theoretical investigations and calculations which were performed, with some interruptions, in the years 1940—1944. As conditions during the occupation of our country prevented earlier publication, and as a description of the collected results seemed to exceed the limits set to articles in periodicals we decided to present them in book form after the war.

The science of colloids appears to be entering upon a new stage, which is less empirical, and where the experimental study of better defined objects will be guided rather by more quantitative theories than by qualitative "rules" or "working hypotheses". The theory of the stability of lyophobic colloids, as developed in this book, may serve as an example of this development. This stability problem has been placed on a firmer physical basis by the introduction of the concept of Van der Waals—London dispersion forces together with the theory of the electrolytic or electro-chemical double layer. In the present work, too, these theories form the starting points of our considerations.

For the main part this book gives an account of our own work on the interaction of colloidal particles. It has not been written, however, on the assumption that the whole of the relevant literature is known to the reader. Accordingly we have added a number of chapters which may serve as an introduction to the main problem of the book. These chapters contain, for instance, a brief survey of some aspects of lyophobic colloids, a concise summary of the theory of the double layer, and a short introduction to the subject of Van der Waals—London forces.

At the time of writing this work (1944/'45) the literature which has appeared during the war in the countries fighting on the side of the Allies was not at our disposal. To some of the Chapters a few paragraphs were added later on (1947) in order to bring the text in accordance with recent developments.

We desire to acknowledge the assistance we received, in a considerable part of the numerical calculations, from Mr K. van Nes, chem. doct., now once again of the laboratory of the Bataafsche Petroleum Maatschappij, Amsterdam, to whom we are also indebted for valuable contributions in the final presentation of the results of the theory of Part II.

Eindhoven, June 1947.

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SUMMARY

The purpose of this book is to explain the stability of hydrophobic colloids and suspensions and to develop as far as possible a quantitative theory of this stability.

The basic concepts of this theory were the mutual repulsion consequent upon the interaction of two electro-chemical double layers, and the attraction by the London—Van der Waals forces. The principal facts of stability could be explained by combining these two forces. Among other things, a quantitative explanation of the rule of Schulze and Hardy has been given. For this purpose it was essential to use the unapproximated Gouy—Chapman equations for the double layer. The approximation of Debye and Hückel, however useful in the theory of electrolytes, appears to have only a very limited applicability in colloid chemistry.

The introduction of several refinements was necessary to explain various details. The quantitative agreement between theory and experiment, and the deviations from the rule of Schulze and Hardy (lyotropic effects) made it necessary to reckon explicitly with dimensions and the specific adsorbability of the ions. To this end, Stern's theory has been introduced.

Repeptization phenomena cannot be understood without the introduction of the Born repulsion, which, however, apart from this, is of very minor influence on the stability properties.

The London theory also needed a certain rectification in the form of a relativistic correction, because the uncorrected theory led to conflicts with the experiments in the case of coarse suspensions.

Part I deals with the single double layer, Part II with the interaction of two flat plates, and here most of the fundamental results of the theory already come to the fore. Part III gives a treatment of the interaction of spherical particles, which serves to clarify various details, especially the influence of particle dimensions and of the kinetics of flocculation.

In an introductory chapter I, a survey is given of the known facts and of the fundamentals of the theories to be applied. The stability rules and the mechanical properties of sols and suspensions, as far as they are related to stability, are stated fairly extensively. Chapter II gives the mathematical treatment

of the electro-chemical double layer. In Chapter III, the free energy of the double layer is dealt with at length, because it served as a basis for the theory of interaction. There have been some controversies in the literature on this point, but we believe we have cleared up the difficulties, especially by the consistent separation of the chemical and the electrical contributions to the free energy. Cf. also the Appendix on pp.

In Chapter IV and V the charge, the potential, and the interaction energy of two parallel flat double layers are represented. The interaction is proved to be fundamentally a repulsion for all distances between the plates.

Chapter VI gives a short treatment of London-Van der Waals forces and its application to flat plates. In this chapter the relativistic correction mentioned above is also dealt with.

In Chapter VII, as a further extension of the general considerations of J. H. De Boer and more especially Hamaker, the stability of colloids is discussed on account of potential curves, which are formed by a combination of the London-Van der Waals attraction and the double layer repulsion. A criterion is given for distinguishing potential curves as belonging to either stable or flocculated systems, and we investigate the way in which the transition from the stable to the flocculated state is influenced by the potential of the particles, the concentration and valency of the ions, and the attraction constant. All these quantities are shown to influence the stability. In order to get a good accord with experiments the attraction constant must be taken at about 1 or $2 \cdot 10^{-12}$, in good agreement with other theoretical and experimental values.

The influence of the valency and the concentration of the electrolytes agrees with experimental data as expressed by the rule of Schulze and Hardy. As a first approximation following from the theory we find that the flocculation values for monovalent, bivalent and trivalent electrolytes are in the proportion

$$c_1 : c_2 : c_3 = \frac{1}{1^6} : \frac{1}{2^6} : \frac{1}{3^6}.$$

The deviating stability conditions of emulsions are dealt with in a separate section. The basis of this treatment is laid in a number of sections in the preceding chapters, where the double layer at the interface of two liquids is considered.

The ground plan of Part III (Chapters VIII—XII, spherical particles) resembles that of Part II. All concepts used in Part II return in Part III. The treatment of the stability conditions (Chapter XII) deviates in so far as the Brownian motion of the particles is here explicitly incorporated in the theory. For a good understanding of stability it was necessary

to give a thorough treatment of the kinetics of coagulation, especially of slow coagulation.

The results of Part III agree in most respects with those of Part II. Quantitative agreement with experimental evidence is also satisfactory. Different effects known from experiment, as there are: instability of very small particles, the increase of stability during the flocculation process, and the influence of the concentration of electrolytes on the rate of coagulation, can be explained without the introduction of new hypotheses.

Finally, the Appendix gives a critical survey of the work of other investigators in this field.

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PART I

Theory of a single double layer

I. INTRODUCTION

§ 1. *Lyophobic and lyophilic colloids.*

Colloid science is generally understood to be the study of systems containing kinetic units which are large in comparison with atomic dimensions. Such systems may be systems in which the particles are free to move in all directions, or they may be derived systems (as a coagulum, a gel, etc.) in which the particles have lost their mobility either partially or entirely, but have maintained their individuality.

It is customary to distinguish two classes of colloids whose general behaviour is entirely different. These classes are generally called *lyophobic* and *lyophilic* colloids, respectively; hence it is assumed that in the colloids of the second kind there is a strong affinity between the particles and the molecules of the dispersion medium which, in the colloids of the first kind, is either weak or absent. This assumption is expressed, for instance, by the concept of Kruyt, according to which the stability of lyophobic colloids is governed by only one factor (the electric charge of the particles) and that of lyophilic colloids by two factors (charge and solvation). Examples of lyophobic colloids are: a gold sol, a silver iodide sol, a quartz suspension (in water or in an organic liquid), and strictly speaking also the emulsions (although the stability conditions of this group are apparently different). An example of a lyophilic colloid is the gelatin sol. Typical for lyophilic colloids are, for instance, the swelling phenomena illustrating the great affinity between the gelatin and the water molecules (hydration).

The kinetic units mentioned above in lyophobic colloids are rigid particles (either amorphous or crystalline) or small liquid droplets. The crystalline nature of the particles of a gold sol, for example, may easily be proved by investigating a coagulum with the aid of X-rays: it is seen that the particles are very small crystals of the same crystal structure as the metal itself.

A clear notion of the nature of the kinetic units in lyophilic colloids has been lacking for a long time. Modern investigations, however, especially in the fields of cellulose and protein chemistry, have revealed that the "particles" consist either of a single large molecule or of a cluster of such molecules dissolved

in the dispersion medium. This "macromolecule" may be either an extremely long threadmolecule, or a molecule of a more complicated form, with long side-chains, etc., and the molecules may either be more or less stretched, or rolled up to a complicated clew, or folded together. But a common property of the "particles" will be that they are entirely open to the dispersion medium in that each "link" or atom group of the chain system is in contact with the solvent molecules. Moreover, each link of the molecular threads or chains is subject to thermal motion, so that the spatial configuration of the dissolved macro-molecule or molecular cluster varies continually. The „hydration" of a hydrophilic colloid is therefore partially a direct adsorption of watermolecules at the polar groups throughout the entire macro-molecule (accompanied by a gain in energy) and partially an imbibition or enclosure of water due to the thermal expansion of the macro-molecule (accompanied by a gain in entropy).

This peculiar difference between the structure of the kinetic units in lyophobic and lyophilic colloids yields a second criterion used to distinguish between the two classes of colloids, namely the contrast: *irreversible* and *reversible* colloids. A protein "crystal" or dry gelatin, when brought into contact with water, is converted spontaneously into an apparently homogeneous gel, or, if the amount of water is sufficient and the temperature is not too low, into a stable sol. A gold crystal brought into contact with water, however, is a system with a much lower free energy than a gold sol, and the former will never generate the latter spontaneously. A lyophobic colloid is therefore never stable in the sense of thermodynamics; the subdivision of the gold crystal into small particles can be performed only by supplying a considerable amount of work. The total free energy of the gold/water interface is a positive quantity. The small gain in entropy accompanying the formation of more kinetic units is negligible (even a colloidal particle still contains a large number of gold atoms).

There is a third and important difference between the two classes of colloids. Lyophobic colloids may be *flocculated* or *coagulated* by comparatively small amounts of electrolyte added to the system, and the effective amounts depend characteristically on the valency type and the nature of the electrolyte. What we observe when a lyophobic sol is coagulated is that the at first apparently homogeneous liquid becomes turbid and distinctly non-homogeneous. On examination with the microscope or ultramicroscope it appears that before the flocculation each individual particle is subject to thermal motion (Brownian movement), but that afterwards the particles cluster together and form larger agglomerates. In the coagulum the particles have maintained their individuality in that they hold together

at a few points only (at any rate immediately after coagulation) by comparatively weak forces. Sometimes, by removing the electrolyte from the system, the coagulum may easily be peptized again, i.e., the regular distribution of the particles through the dispersion medium, as present in the original stable sol or suspension, may be re-established.

Because of this sensitivity of the stability of lyophobic colloids towards electrolytes (stability with respect to coagulation) Freundlich used the term of *electrocratic* colloids for this class of colloids.

Actually, lyophilic colloids do not, as a rule, show the phenomenon of flocculation under the influence of small amounts of electrolytes in a way analogous to the behaviour of lyophobic colloids. In special cases, however, very similar phenomena may be observed, for instance in an aqueous gelatin sol to which a sufficient amount of alcohol has been added; and the work of Kruyt and Bungenberg de Jong¹ has given a great many examples of lyophilic colloids in which the physical properties (though not always the stability with respect to flocculation) are influenced by electrolytes in much the same way as is typical for lyophobic colloids. One of the oldest examples is the electroviscous effect shown by many lyophilic colloids: a considerable decrease in viscosity, effected by the addition of small amounts of electrolyte. This effect suggests that the electrolyte greatly influences the spatial configuration of the dissolved macro-molecules. It may even be said that the influence of electrolytes upon lyophilic colloids is more or less analogous to that upon lyophobic colloids. For, as will be argued in the following sections, an electrolyte added to a lyophobic colloid destroys the potential barrier existing between the particles, thus enabling their mutual approach and final agglomeration. In the case of the lyophilic colloid the electrolyte obviously has a similar effect with respect to different parts of the same macro-molecule or molecules of the same cluster, again allowing their mutual approach, and, therefore, a folding together or curling up of the molecule to a less stretched form.

In the present treatise we will confine ourselves to the study of the stability of lyophobic colloids and a number of kindred problems relating to this type of colloids; only occasionally shall we refer to analogous points in the behaviour of lyophilic colloids. The above considerations may suffice, however, to show that a treatment of the fundamental aspects of the stability of lyophobic colloids must also be important for a better under-

¹ H. R. Kruyt and H. G. Bungenberg de Jong, *Kolloidchem. Beihefte*, 28 (1928) 1 and other papers by Kruyt and coworkers in the same journal under the title „Zur Kenntnis der lyophilen Kolloide”.

standing of the rather complex set of phenomena in the field of lyophilic and bio-colloids.

§ 2. *The electric double layer surrounding the particles*

From several phenomena observed in colloidal systems it has been inferred that the dispersed particles carry an electric charge. Since the system as a whole is electrically neutral, the dispersion medium must contain an equivalent charge of the opposite sign. These charges are carried by ions, i.e., by an excess of ions of one sign at the particle surface and an excess of ions of the opposite sign in the solution. We will consider, as a fairly simple example, the AgI sol¹ in which the nature and magnitude of these charges have been extensively investigated. In a dialysed AgI sol the particles carry a negative charge. It is possible to determine this charge analytically. The particles are small AgI crystals of about $50\text{ m}\mu$ (or $5 \cdot 10^{-6}\text{ cm}$), containing about 10^6 AgI "molecules", and carry a charge of the order of 10^3 elementary charges per particle. This particle charge is caused by an excess of I^- ions in the crystal faces of the particles; each particle, therefore, contains, per 1000 AgI "molecules", about one I^- ion in excess. In a well dialysed AgI sol the negative ions in the intermicellar liquid are almost entirely removed, and, especially if the sol is not too diluted, the aqueous solution phase contains practically none but positive H^+ ions; these ions (or, more exactly, the excess of H^+ ions over the negative ions still present in the liquid) are therefore responsible for the positive charge neutralizing the negative charge of the particles.

The positive charge carried by the H^+ ions in the dialysed AgI sol is not distributed uniformly through the intermicellar solution, as the H^+ ions are strongly attracted by the negatively charged AgI particles. Conversely, however, the H^+ ions will not be adsorbed all on the surface of the AgI particles, as the electrical attraction is counteracted by the thermal motion of these ions. The result is that these ions, or at least part of them, are still "free" ions, being dissolved in the solution and subject, individually, to progressive thermal motion; but on the other hand they are forced by the electric attraction to remain in the neighbourhood of the particles, so that each particle charge is screened off by an equivalent swarm of H^+ ions surrounding the particle.

Hence, if we consider one particle separately, immersed in the liquid, it is surrounded by an *electric double layer*.

¹ E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, A 167 (1933) 137, 149, 312.

E. J. W. Verwey, *Chem. Rev.*, 16 (1935) 363.

One layer of this double layer is formed by the charge in the surface of the particles. (Strictly speaking this assumption of a *surface* charge is only more or less justified if the particles are crystalline or amorphous; in the case of liquid droplets things may be different). Though in reality it is a charge consisting of point charges, it is customary to consider it, as a first approximation, as a homogeneous surface charge spread over the surface of the particles. This may be rather a rough approximation, as it seems possible that the excess of I^- ions present in the AgI surface of a negative AgI particle will be concentrated around certain active spots, edges, and corners of the crystal faces, etc. In many problems, however, we are interested in the action of the surface charge at some distance from the particle surface, where its detailed structure is much less influential; often moreover, only its time average is material. We must also bear in mind that an excess of one elementary charge is generally carried by a group of surface ions, as it is often impossible to point to the ion which may be called the excess-ion (except in the case of an I^- ion adsorbed upon a complete crystal plane; rather an improbable case). For all these reasons, and in default of preciser data, we shall, in the following considerations, generally assume the surface charge to be homogeneous.

The second layer of the electric double layer (the outer layer) is formed by the excess of oppositely charged ions in the solution; hence, in the case of the AgI sol, by the H^+ ions (more general: by the counter-ions of the colloid). In consequence of their thermal motion the electric charge carried by this layer (or at least part of it) extends over a certain distance from the particle surface, and dies out gradually with increasing distance (diffuse layer). Though again carried by discrete ionic charges, this charge may very often be approximated by regarding it as a continuous space charge, since, in many problems, we are again interested only in its time average. The "thickness" of this diffuse layer appears to be of colloidal dimensions; in very diluted electrolytic solutions it may be of the order of 10^{-5} to 10^{-4} cm; in more concentrated solutions (especially if the counter ions are polyvalent) the extension is much less. In a dialysed AgI sol the particles are therefore smaller than the thickness of the double layer; in suspensions, especially when some electrolyte is present, the double layer extension is generally small in comparison with the size of the particles.

§ 3. *The stability of lyophobic colloids*

After this introduction into the properties of the electric double layer surrounding colloid particles we may now return to the problem of the stability of lyophobic colloids.

In section 1 it has been mentioned that one of the typical aspects of lyophobic colloids is the sensitivity of their stability towards electrolytes added to the sol medium. As a matter of fact, in the development of the chemistry of lyophobic colloids, the stability has been the central problem during the last half century.

According to section 2 stable lyophobic colloid systems (including suspensions) may be considered as systems containing a great number of particles each surrounded by an electric double layer. In section 2 we only considered one separate particle with the double layer surrounding it. In actual sols or suspensions, however, we are facing with an additional problem, namely that of the interaction of two or more double layers. This problem arises in the first place in concentrated systems, in which the average distance of the particles is of the same order of magnitude as the "thickness" of the double layer, or even smaller. But also in more diluted systems (sol or suspension) particles meet continually, and the stability of the colloid depends entirely on the physical result of such an encounter. This interaction problem will therefore be one of the basic problems in a theory of colloid stability.

As will be evident from the brief survey of the main experimental facts relating to the stability of lyophobic colloids, to be given in the present section, this opinion is in complete accordance with colloid chemical evidence.

In discussing colloid stability, it is necessary to distinguish between two different factors influencing this stability¹.

1. A sol or suspension *primarily* acquires stability by the formation of a double layer of sufficient strength to prevent agglomeration. This process is called peptization and depends on the presence of small amounts of specific ions in the system.

2. *Secondarily*, the stability of the sol or suspension once formed can be affected and eventually completely destroyed (coagulation or flocculation) by the addition of all kinds of electrolytes to the system.

Some colloids peptize spontaneously when a finely divided substance and a liquid are brought together under suitable conditions. A stable suspension of quartz, for instance, in water, ethanol, acetone (in general: in liquids of a sufficiently electrolytic dissociating power) may be prepared by simply shaking the pure powder with one of these liquids. Some precipitates, such as V_2O_5 , or a number of insoluble metal sulphides, may be brought to peptization by washing them thoroughly with pure water. In other cases, however, we know that small quan-

¹ E. J. W. Verwey, *Chem. Rev.*, **16** (1935) 391.

tities of specific electrolytes are necessary for peptization. In the case of the AgI sol, a small excess of either Ag^+ or I^- is necessary to obtain stable sols; sulphides need a small excess of S^{--} or SH^- to build up the double layer, which sometimes has to be added deliberately to the system for peptization; oxides and metals may often be peptized by H^+ or OH^- . This stabilizing rôle is strictly reserved for very special ions; if these ions are not formed by the materials themselves (in the case of spontaneous peptization this occurs to such an extent that the resulting double layer is already sufficient for stability), they are, at any rate, closely related to the materials of the particles.

The inverse process, too, may occur; i.e., a sol can sometimes be coagulated by depeptization. Thus, unlike a negative AgI sol (where the peptizing I^- can be withdrawn from the sol as far as this is possible by dialysis without affecting the stability), a positively charged AgI sol can easily be brought to flocculation by dialysing the sol. Several other sols show the same behaviour. To this class of phenomena must also be reckoned the flocculation occurring when a diluted solution of AgNO_3 is added to a negative AgI sol. In this case the small excess of I^- ions building up the double layer is neutralized and precipitated by the Ag^+ ions added to the sol. (An excess of AgNO_3 , if mixed sufficiently rapidly with the sol, would convert the negative sol into the stable positive sol, without coagulation).

In the phenomena discussed in the preceding paragraph the flocculation is actually effected by reducing the particle charge.

Usually, however, coagulation is obtained by quite different methods, in which the concentration of the peptizing or stabilizing ions is not — at any rate not purposely — changed. Indeed, coagulation in lyophobic systems is mostly effected under the influence of "indifferent" electrolytes added to the systems. On determining the amount of electrolyte necessary to bring about a practically complete coagulation under specified conditions, adapted to the type of sol under consideration, the following values were found for different sols (see p. 8 and p. 9). The corresponding concentration is called the limiting or flocculation value.

The flocculation values united in Tables I and II clearly demonstrate the well-known rule of Schulze and Hardy stating that the flocculation value is first of all determined by the valency of the ions which are oppositely charged to the particles of the sol, whereas the specific nature of these ions is far less important. The influence of the valency and the nature of the ions bearing the same charge as the particles is of subordinate importance.

For the AgI-sol, for instance, the monovalent cations flocculate at a concentration of about 140 millimols/liter, the bi-

TABLE I
FLOCCULATION VALUES IN MILLIMOLS/LITER FOR NEGATIVELY CHARGED SOLS

Electrolyte	As ₂ S ₃ -sol *	Au-sol **	AgI-sol †
LiCl	58	—	—
LiNO ₃	—	—	165
NaCl	51	24	—
NaNO ₃	—	—	140
KCl	49.5	—	—
KNO ₃	—	25	136
¹ / ₂ K ₂ SO ₄	65.5	23	—
RbNO ₃	—	—	126
MgCl ₂	0.72	—	—
Mg(NO ₃) ₂	—	—	2.53
MgSO ₄	0.81	—	—
CaCl ₂	0.65	0.41	—
Ca(NO ₃) ₂	—	—	2.38
SrCl ₂	0.635	—	—
Sr(NO ₃) ₂	—	—	2.33
BaCl ₂	0.69	0.35	—
Ba(NO ₃) ₂	—	—	2.20
ZnCl ₂	0.685	—	—
Zn(NO ₃) ₂	—	—	2.50
UO ₂ (NO ₃) ₂	0.64	2.8	3.15
AlCl ₃	0.093	—	—
Al(NO ₃) ₃	0.095	—	0.067
¹ / ₂ Al ₂ (SO ₄) ₃	0.096	0.009	—
La(NO ₃) ₃	—	—	0.069
Ce(NO ₃) ₃	0.080	0.003	0.069
Th(NO ₃) ₄	—	—	0.013

* H. Freundlich, *Z. physik. Chem.*, **44** (1903) 129; **73** (1910) 385.

** H. Freundlich and G. Von Elissasoff, *Z. physik. Chem.*, **79** (1912) 385, H. Morawitz, *Kolloidchem. Beihefte*, **1** (1910) 301.

† H. R. Kruyt and M. A. M. Klompé, *Kolloidchem. Beihefte*, **54** (1942) 484.

valent cations at about 2.3 millimols/liter and the trivalent cations at about 0.07 millimols/liter.

The differences between electrolytes of the same valency type are comparatively small. Generally a negative sol is flocculated by large cations at a somewhat smaller concentration than by small cations of the same valency.

Organic ions often have an exceptional position in as much as they cause flocculation in a concentration which is much lower than would correspond to

TABLE II

FLOCCULATION VALUES IN MILLIMOLS/LITER FOR POSITIVELY CHARGED SOLS

Electrolyte	Fe ₂ O ₃ -sol *	Al ₂ O ₃ -sol **
NaCl	9.25	43.5
KCl	9.0	46
$\frac{1}{2}$ BaCl ₂	9.65	—
KNO ₃	12	60
$\frac{1}{2}$ Ba(NO ₃) ₂	14	—
K ₂ SO ₄	0.205	0.30
MgSO ₄	0.22	—
K ₂ Cr ₂ O ₇	0.195	0.63
K ₃ Fe(CN) ₆	—	0.080
K ₄ Fe(CN) ₆	—	0.053

* H. Freundlich, *Z. physik. Chem.*, **44** (1903) 151.** N. Ishizaka, *Z. physik. Chem.*, **83** (1913) 97.

their valency. This exceptional behaviour is evidently connected with the abnormal adsorbability of these ions. We have mentioned this point for completeness, but in the following we will mainly consider the normal inorganic ions.

It was originally assumed that the flocculating action of these electrolytes should be explained by an adsorption of the oppositely charged ions (Freundlich's adsorption theory). This theory was a direct result of the fact that in the more primitive stage of colloid chemistry one was satisfied with the picture of the agglomeration of the particles being prevented in stable sols or suspensions by the mutual repulsion of the particle charges. Later on it was recognized, however, that in reality we are not dealing with a pure Coulomb repulsion, but with the rather different and more complicated problem of the interaction of double layers. Moreover, Freundlich's adsorption theory, and therefore the simple conception that the coagulation by electrolytes is a matter of reduction of the particle charges, could not be affirmed by exact analytical measurements¹. There were even a number of experimental indications that the effect of an increase of the electrolyte concentration is generally

¹ H. Freundlich, K. Joachimsohn and G. Ettisch, *Z. physik. Chem.*, **141** (1929) 249.

E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, A **167** (1934) 312.