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Original Scientific Paper

Experimental Electrokinetic Systems and the Point Charge Double Layer Model*

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The Coulombs, Ψ_{Cp} ionic cloud, Ψ_{icp} and the average Ψ_{DHp} potentials of the Debye-Hückel theory, in the space adjacent to spherical particles, charged with a given number of elementary point charges, can be calculated using the equations

$$\Psi_{Cp} = (1/2\, r_{max}\, \pi) \sum_{-n}^{+n} \sum_{-p}^{+p} 1 / r \qquad \text{(A1)}$$

$$\Psi_{DHp} = -(1/2\, r_{max}\, \pi) \sum_{-n}^{+n} \sum_{-p}^{+p} e^{-r} / r \qquad \text{(A2)}$$

$$\Psi_{icp} = (1/2\, r_{max}\, \pi) \sum_{-n}^{+n} \sum_{-p}^{+p} (1 - e^{-r}) / r \qquad \text{(A3)}$$

The Gouy-Chapman potential, Ψ_{GCh} at planar surfaces is defined by

$$\Psi_{GCh} = e^{-x} \qquad \text{(A4)}$$

Here: $r = \{x^2 + l_{ic}^2\,[(n + y)^2 + (p + z)^2]\}^{0.5}$, $r_{max} = l_{ic}\, n_{max}\, \sqrt{2} = \lambda_{ic}\, p_{max}\, \sqrt{2}$, the latter being predetermined; n, p integers. The intercharge distance is l_{ic}; x, l_{ic} $(n + y)$, l_{ic} $(p + z)$ are the coordinates of any point in the layer, while $0 < y, z < 1$. The distance of points on the axes from the surface is x. All symbols are multiples of κ, *i.e.*, $x = x'\kappa$, $y = y'\kappa$, $z = z'\kappa$, $l_{ic}\, l'_{ic}\kappa$, and $\Psi_{Cp} = \Psi'_{Cp}/\Psi_o, \Psi_o = z\, e_o\, \kappa/4\, \pi\, \varepsilon$. The intersections of the $\Psi_{Cp}x$ = var., n, p, $y, z = 0$) plots with the $\Psi_{icp}(x \to 0) = 1$ horizontal line define $x = 1/\kappa_p$, which is valid for given particles and ionic strength. The calculations prove that Ψ_{icp} is higher than Ψ_{GCh}. Consequently, the introduction of the slipping

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plane and of the Stern layer necessarily results in too low ζ potentials. The author (1963) proposed and supported the proposal with experiments, that the reciprocal electrokinetic quotients, q are proportional to log I, or to the logarithm coagulating counterion concentration (q = »transported volume/current strength«, »streaming current/streaming rate«, »streaming potential/pressure«, »mobility/field strength«). Then, one obtains the function

$$q = q_m - | s \log (I/I_m) | \qquad (A5)$$

This is represented by two straight lines, one increasing, the other decreasing, with the intersection at $I = I_m$ and at $q = q_m$. Parameters q_m and the slope, s, are adjustable and they depend on the technique applied. Several published experimental plots by Hidalgo-Alvarez and colls. (1986) and Midmore and Hunter (1988) can be approximated as two straight lines intersecting at log I_m. The cited experiments are certainly a strong support for the correctness and usefulness of the DHT, as applied for the point charge double layer modelorts to calculate ζ potentials were generally unsuccessful because l_{ic} and $1/\kappa_p$ are not included in the homogeneous charge, electrical double layer models, which, for these reasons, should be abandoned.

INTRODUCTION

Motto:

»... though in reality it is a charge consisting of point charges, it is customary to consider it, as first approximation, as a homogeneous surface charge spread over the surface of the particles.«

» ... and in default of preciser data, we shall, in the following considerations, generally assume the surface charge to be homogeneous«, Overbeek.[1]

» ... the disparity between the total potential (Nernst potential) as determined by the potential determining ions and the ζ potential calculated from electrokinetics led to the introduction of the slipping plane...«, Overbeek.[2]

Practically all current double layer theories in electrokinetics are concerned with the calculation of the ζ potential from experimental results. As a rule, the basic and starting are either von Smoluchowski's or Henry's equations. Strictly, the former equation is applicable to macroscopic capillaries or large rodlike particles only, and the latter to spherical particles of various sizes charged with a homogeneous charge.

Some workers calculate ζ potentials by multiplying the measured electrokinetic quotient with the constant factor of von Smoluchowski's equation. Some corrections or extensions of Smoluchowski's equation have been proposed. All of them, in high ionic strength, give the same ζ potentials as Smoluchowski's equation. It can be stated that as many ζ potential equations exist as many theories have been proposed, while only a single one can be correct: The latter is a fact which should be beyond any discussion. *E.g.*, there exists only one Nernst-potential equation. Also, the smallest AgI stable particles are charged with one single ion only of charge number one, while in the membranes of coagulated AgI 150 primary particles are charged with a single ion charge.

The electrokinetic quotients are q = »transported volume / current strength«, »streaming current / streaming rate«, »streaming potiential / pressure«, »mobility /

field strength«. Very seldom is the measured electrokinetic quotient multiplied by conductance, even in experiments with variable conductance. Since the colloidal particles are never large rodlike cyclinders, neither are there large cylindrical channels in membranes, the values of ζ potential obtained in this way are simply numbers proportional to experimental electrokinetic quotients of no quantitative physical significance. Namely, the Smoluchowski's equation is based on the supposition that big rodlike particles constitute the movable particles, or, that the electrolyte is transported through big cylindrical channels in membranes. In reality, neither such particles nor membranes exist.

An evident disparity between the total electric potential measured between two metallic electrodes of the first or second order (Nernst potential) and determined by potential-determining ions (PDIs) and the ζ potential, calculated from electrokinetics, was observed very early.[1,2] For this reason, the idea of the not measurable but speculatively adjustable distance of the slipping plane was introduced and the potential in the slipping plane was taken to represent the ζ potential. The same idea was retained also for polymeric colloids (latices), despite the fact that on polymeric colloids, which are insulators, no electric potential analogous to the Nernst potential, is possible in principle. Also, the Nernst potential is measurable only in galvanic cells having two metallic electrodes, possibly covered with an ionic solid.

The idea of Nernst potential was dropped by many scientists after experimental and theoretical arguments had showed that electrokinetic measurements of ionic solids do not depend on the concentration of PDIs, as it was expected in many examples, the electrokinetic quotients are in a broad region practically independent of [PDI] or ionic strength. In latex sols, the counter ions do not physically determine an electrical potential analogous to the potential determined by PDIs.

However, despite the fact that: (a) it is impossible to prove the existence of the Nernst potential on colloidal particles, (b) the Nernst potential on the same electrode can be positive or negative, depending on the reference electrode, and (c) its existence is impossible on insulator (polymeric latex, organic, biochemical) particles, the idea of the slipping plane and its ζ potential has been retained in practically all current double layer and electrokinetic theories.

A colloidal system of two adjoining defined phases is completely defined with a minimum of four experimental basic parameters (a) particle size and form, (b) charge density, or elementary charge per particle number or inter charge distance, (c) particle number concentration and (d) ionic strength of, if present, the (1–1) electrolytes. If coagulating counter ions or surfactants are present, the additional unavoidable parameters are: (e) the concentration of the coagulating counter ion of charge number $z \geq 1$ and (f) surfactant concentration. Consequently, theories in which all the cited parameters are not included, cannot be applied to the theoretical explanation of experimental or real systems for the definition of which the same parameters are unavoidable.

THEORETICAL CONSIDERATIONS AND DISCUSSION

The Point Charge Double Layer Model

According to the elementary version of the DHT, the following potentials are effective in the vicinity of ions: the Coulombs, Ψ_C, the ion cloud, Ψ_{ic}, and the average DHT, Ψ_{DH}. The same potentials, in the vicinity of stable or coagulating particles charged with many adsorbed ions or chemically bound ionogenic radicals, can be calculated as the sums of the same potentials originating from the adsorbed ions on

the surface, considered as point charges, and the counter ions statistically distributed in the adjacent electrolyte layer forming the ion cloud.

Potentials on small stable particles charged with one elementary ion charge and primary particles twice the radius of the stable particles and possibly initially charged with eight point charges, as well as potentials in aggregates of many primary particles, are described in reference[3].

There is no reason whatsoever why the adsorbed ions or chemically bound ionogenic radicals on colloidal particles should not be theoretically treated as they are treated by the generally accepted DHT of ionic interactions in electrolytes. Also, there is no reason whatsoever why the law of superposition of potentials should not hold for the three cited potentials exhibited by adsorbed or chemically bound ions. An argument supporting the same claim is the fact that the homogeneous charge potential, *i.e.*, the Gouy-Chapman potential, for $x \to 0$, can be calculated as the sum of an infinitely big number of ion cloudpotentials of infinitesimally small point charges on a plane surface of unit area. In reality, the Gouy-Chapman potential arises only on polarized electrodes charged from an outside battery. Its charge is either a surplus or lack of electrons. Consequently, only the point charge model can be valid for interfaces charged with ions or ionogenic radicals.

The Debye-Hückel Potentials at Planar Surfaces

The DHT potentials, in the vicinity of stable or coagulating plane surfaces, charged with a given number of adsorbed ions or chemically bound ionogenic radicals, can be calculated as the sums of the same potentials originating from point charges in a quadratic pattern by the following equations.[4]

The electrostatic or Coulombs potential, Ψ_{Cp}, by

$$\Psi_{Cpl} = (1/2\, r_{max}\, \pi) \sum_{-n}^{+n} \sum_{-p}^{+p} 1 \,/\, x \tag{1}$$

Analogously, the average Debye-Hückel potential, Ψ_{DHp}, is defined by the formula

$$\Psi_{DHpl} = -\,(1/2\, r_{max}\, \pi) \sum_{-n}^{+n} \sum_{-p}^{+p} e^{-x} \,/\, x \tag{2}$$

The sum of the two potentials is the ion cloud potential, Ψ_{icp}. Its equation reads

$$\Psi_{icpl} = (1/2\, r_{max}\, \pi) \sum_{-n}^{+n} \sum_{-p}^{+p} (e^{-x} - 1) \,/\, x \tag{3}$$

Here: $r = \{x^2 + l_{ic}^2\,[(n + y)^2 + (p + z)^2]\}^{0.5}$; $l_{ic}\,(n^2 + p^2)^{0.5} \leq r_{max} = l_{ic}\, n_{max}\sqrt{2} = l_{ic}\, p_{max}\sqrt{2}$. The latter circular surface should be equivalent to the particle surface of any form. The intercharge distance is l_{ic}; x, $l_{ic}\,(n + y)$, $l_{ic}\,(p + z)$ are coordinates of the points in the interface, while $0 \leq y < 1$, $0 \leq z < 1$; $l_{ic}\, n$, $l_{ic}\, p$, are coordinates of the points on the surface. The perpendicular distance of the points from the interface is x. All symbols are multiples of $1/\kappa^o$, *i.e.*, $x = x'\,\kappa^o$, $y = y'\,\kappa^o$, $z = z'\,\kappa^o$, $l_{ic} = l_{ic}'\,\kappa^o$, $\Psi = \Psi'/\Psi^o$. The symbols marked with ' are absolute values and

$$\Psi^{o} = z\, e_0\, \kappa^{o} / 4\, \pi\, \varepsilon\, \varepsilon_0 \tag{4}$$

The latter is a standard electrostatic potential determined by a defined standard ionic strength, $I = I^{o}$, which determines κ^{o}. All plots are valid for any selected constant I.

Upon the surface charge, the ion cloud exhibits the ion cloud potential $-\Sigma\ \Psi_{icp}\ (r, x \rightarrow 0)$. It is equal to the Gouy-Chapman potential at $x \rightarrow 0$ if, in both cases, the charge density is constant.

The intersections of the decreasing $\Psi_{Cpl}\ (x,\ 0 = n,\ p,\ y,\ z)$ plots (1) with the $\Psi_{Cpl} = 1$ horizontal line determine $1/\kappa_{pl}$, which, in turn, is determined by I and l_{ic}. A standard $I = I^{o}$ can be selected, which determines the standard $1/\kappa^{o}{}_{pl}$, which is valid for given particles characterized by $(a\ \kappa^{o}) \gg r_{max}$ and a given l_{ic}. In variable I, the three potentials are variable, because Ψ^{o} depends on I^{o}. The smaller is l_{ic}, the bigger is $1/\kappa^{o}{}_{pl}$. The Coulombs potential, for $1/\kappa^{o}{}_{pl}$, or for Ψ^{o}, in equation (1) is equal, for $x \rightarrow 0$ and for $r_{max} \rightarrow \infty$ in equation (4), to the ion cloudpotential of opposite sign, *i.e.* $\Psi_{Cpl}\ (x = 1/\kappa_{pl}) = -\Psi_{icpl}\ (x \rightarrow 0) = 1$. It suffices, therefore, to estimate $1/\kappa_{pl}$ for $\Psi_{Cpl} = 1$ to obtain the average distance, $1/\kappa_{pl}$, of the ion cloudpotential in a given interface.

The explanation of the distance $1/\kappa_p$, $1/\kappa_{pl}$ on the particles, also with planar surfaces, is analogous to the explanation of $1/\kappa$ for the central, or reference ion of the DHT: two surfaces or particles (two ions) of the same sign, at distances bigger than $2/\kappa_p$, $2/\kappa_{pl}$ $(2/\kappa)$, attract each other, at smaller distances, they repel each other and at $2/\kappa_p = 2$, $2/\kappa_{pl} = 2$, $(2/\kappa = 2)$ they are in equilibrium with respect to electrostatic forces and to statistical distances determined by concentration.

However, the calculation for plane surfaces is not applicable to small particles if their size and form are not defined.

Besides this argument, the author has proved that the charge density function is, if the size and form of particles are unknown, undetermined.[3,15]

The Debye-Hückel Potentials on Spheres of Various Size

Figure 1 represents schematically a quadrant of a particle of unit radius $r_{max} = r'_{max}\ \kappa = 1$. The axis x along which the potentials are calculated passes from the centre, C, across a selected point charge (0,0). The coordinates of any point on the surface are $(0, 0) \leq (n, p) \leq (n_{max}, p_{max})$ where $n_{max} = p_{max}$. The arcsinus values of the angles A_n and A_p between two lines $C - (0, p) -$
$x \rightarrow$, $C - (n, p) \rightarrow$ and $C - (n, 0) \rightarrow$, $C - (n, p) \rightarrow$ are

$$\arcsin A_n = n\, \pi/2\, n_{max} \tag{5}$$

$$\arcsin A_p = p\, \pi/2\, p_{max} \tag{6}$$

The calculation of distances r_1 and r_2 of points $(\pm n, p)$ from points (x) follows from Figures 1 and 2, the latter representing the plane $(-n, 0) \leftrightarrow (-n, p) \leftrightarrow (n, p) \leftrightarrow (x)$

$$r_1 = \{[x + r_{max}\ (1 - \cos A_p)]^2 + h^2\}^{1/2} \tag{7}$$

$$r_2 = \{[x + r_{max}\ (1 + \cos A_p)]^2 + h^2\}^{1/2} \tag{8}$$

Here, $r_{max} = a/2$ is the particle radius and

$$h = r_{max} \sin A_n \tag{9}$$

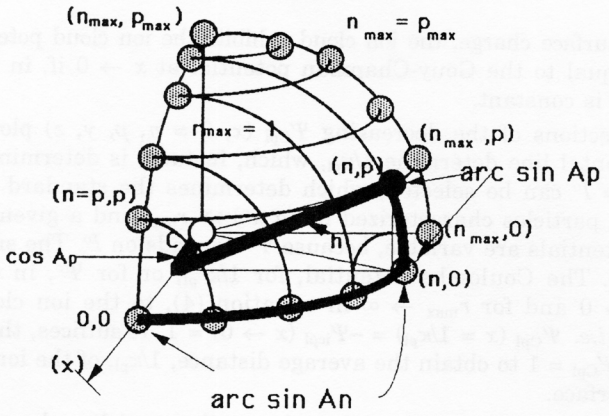

Figure 1. Quadrant of a sphere of radius $r_{max} = 1$, charged with $n_{max} = p_{max} = 6$ point charges. Angles, An, between lines »$C - (0,0)$ and $C - (n,0)$« and Ap, between »$C - (n,0)$ and $C - (0,p)$«. Distance, x, between a point (x) on the axis and point »$(0,0)$«.

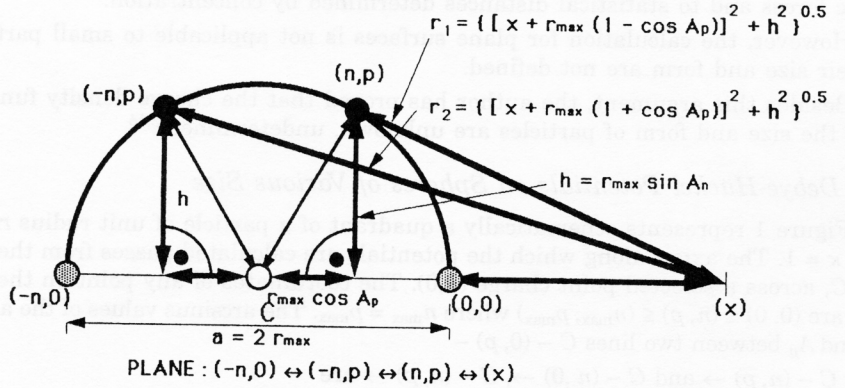

Figure 2. Crossection across the points $(-n,0) \leftrightarrow (-n,p) \leftrightarrow (n,p) \leftrightarrow (x)$ of a spherical particle of diameter $a = 2\ r_{max}$. Distances r_1 and r_2 follow from the figure and the text.

The Coulombs potential, Ψ_{Cp}, exhibited by all charges upon the points $(x,0,0)$ on the axis, equals

$$\Psi_{icp} = (4 / F_p) \left(\sum_{p=n-1}^{n_{max}-1} \sum_{n=1}^{n_{max}-1} 1/r_1 + \sum_{p=n+1}^{p_{max}-1} \sum_{n=-1}^{-n_{max}+1} 1/r_2 \right) + 1/xF_p \tag{10}$$

The average Debye-Hückel potential, Ψ_{DHp}, can be calculated by

$$\Psi_{DHp} = (-4/F_p)\left(\sum_{p=n-1}^{n_{max}-1}\sum_{n=1}^{n_{max}-1} e^{r1}/r_1 + \sum_{p=n+1}^{p_{max}-1}\sum_{n=-1}^{-n_{max}+1} e^{-r_2}/r_2\right) + e^{-x}/xF_p \qquad (11)$$

The ion cloud potential function, Ψ_{icp} for particles is then defined by

$$\Psi_{icp} = \Psi_{DHp} + \Psi_{Cp} \qquad (12)$$

The factor, F_p is constant for systems of constant I and it replaces $2\, r_{max}\, \pi$ in (3). The corresponding Gouy-Chapman, Ψ_{GCh} potential function reads

$$\Psi_{GCh} = e^{-x} \qquad (13)$$

Figure 3 shows the plots of the four discussed potential functions calculated for $r_{max} = n_{max} = 6$ and $F_p = 57.703$ along the axis $C - (0,0) - x \rightarrow$. The sums (10) and (11) were divided by F_p. Then, the values $\Psi_{icp}\ (x \rightarrow 0) = \Psi_{Cp}\ (x = 1/\kappa_p = \Psi_{GCH}(x \rightarrow 0) = 1$ were obtained. In this way, the charge densities of the spheres and the Gouy-Chapman plane are assumed equal if I = constant.

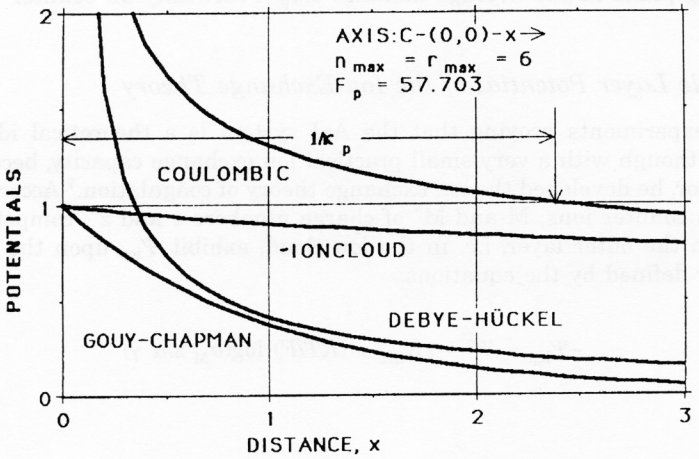

Figure 3. The Coulombic Ψ_{Cp}, ion cloud Ψ_{icp}, average Debye-Hückel Ψ_{DHp}, and Gouy-Chapman Ψ_{GChp} (ordinate) potentials at spheric particles as functions of the distance, x, (abscissa), along the axis »$C - (0,0) - x \rightarrow$«. $n_{max} = p_{max} = r_{max} = 6$, $F_p = 57.703$, Debye-Hückel distance $1/\kappa_p$, defined by $\Psi_{Cp}(x = 1/\kappa_p)/\Psi_{icp}(x \rightarrow 0) = 1$.

The remaining two characteristic axes are $C - (0.5, 0) - x \rightarrow$ and $C = (0.5, 0.5) - x \rightarrow$. Similar plots can be calculated along the two axes. The corresponding ones are $1/\kappa_p = 0.375$, 1.75 and 0.5. Obviously, if two particles are approaching by Brownian motion, an average charge density and potential distribution in the interface will be effective for repulsion.

The quotient $l_{ic} = r_{max} / n_{max}$ represents the intercharge distance. Theoretically, it can be calculated by any ratio r_{max} / n_{max}. Experimentally, it can be calculated from any I, charge density and size $a/2 = r_{max}$ of particles. The calculated variation of l_{ic} is equivalent to a variation of I, namely to a variation od $1/\kappa_p$. For feasible $30 \approx> (1/\kappa)/nm >\approx 3$, in $0.0001 < I_{stable} / \text{mol dm}^{-3} < 0.01$ in (1–1) electroytes, one can expect that $1/\kappa_p > 1$ is the average and effective for stability, while in the range $0.01 < I_{stable}/ \text{ mol dm}^{-3}\ 1 > 1/\kappa_p$ is effective for coagulation.

The main conclusion that follows from the present elementary geometrical analysis of spherical particles is the following: The ion cloudpotential function, $\Psi_{icp}(x)$, of the point charge double layer model corresponds to the Gouy-Chapman potential function, $\Psi_{GCh}(x)$, of the homogeneous or electrical, *i.e.* electron charge double layer model. The latter potential is physically impossible on colloids. The Ψ_{icp} functions of the point charge model are higher than the Ψ_{GCh} functions. This means that the calculated repulsion force of the point charge model is, for $0 < x \to \infty$, bigger than that of the homogenoeus charge model for any charge density and size of the particles. Any correction of the potentials, Ψ_{GCh}, by the introduction of the slipping plane and/or the Stern layer, or of the »triple« layer potentials, can only produce too low and irreal calculated ζ potentials. In addition, if the slipping plane were effective in reality, the majority of the counter charge ions would be inside of slipping plane and would cause a decrease of the effective inner charge and, consequently, of q. According to the point charge model, the majority of counter charge ions are outside the slipping plane at the average distance $1/\kappa_p$. Practically all counter charge ions increase q.

The Double Layer Potential of the Ion-Exchange Theory

After experiments proving that the AgI system is a theoretical ideal ion exchanger,[5,6] though with a very small practical ion exchange capacity, became known to the author, he developed the ion exchange theory of coagulation.[7] According to this theory, two counter ions, M and M" of charge numbers z and z", competing for the positions in the outer layer, *i.e.* in the ion cloud, exhibit Ψ_{icp} upon the ions in the inner layer defined by the equations:

$$-\Psi_{icp} = \Psi^o - zK_{SH} + (RT/F) \log(a_M\, z/\alpha\ \gamma) \tag{14}$$

and

$$-\Psi_{icp} = \Psi^o{}_{icp} - z"K_{SH} + (RT/F) \log[a_{M"}\, z"/(1 - \alpha)\ \gamma] \tag{15}$$

Here γ is the molar fraction, or the adsorption capacity, or the number of elementary charges per particle, or the concentration of charges divided by the concentration of the solid, α and $(1 - \alpha)$ are the equivalent fractions of counter ions M and M", a_M and $a_{M"}$ are their molar concentrations, z and z'' their charge numbers. The products $a_M\, z$ and $a_{M"}\, z''$ are »normal« concentrations.

In pure 1–1 electrolytes, $z'' = 1$, $a_{M"}\, z'' = I$ and $\alpha = 0$. This means that the concentration is equal to the ionic strength, I. The linear Schulze-Hardy rule constant of coagulation, counter ion exchange or adsorption, and electrokinetics is K_{SH}.

These equations were first deduced[8] applying electrochemical potentials to the adsorbed and dissociated electrolytes (*e.g.*, NaI on AgI, or of the counter ions, M, M", in the layer and liquid phase). The electrochemical potential is the sum of the ion cloud electrostatic potential free energy and of the chemical potential (free energy) of the interface and bulk electrolyte. To point out the fact that the potential deduced is a thermodynamic difference and that it is not the Nernst potential, with the then conventional symbol, Ψ^{o}, the symbol $\Delta\varphi$ was used instead. In the present paper, the symbol used for the same entity is Ψ_{icp}. The same potential is named »discrete (also fixed) charge double layer tension«. An extended version and description of the theory is published.[9]

The role of the two equations in ion exchange and colloids is analogous to the role of two single electrode Nernst potential equations in galvanic cells: in both systems the equilibrium potentials and concentrations can be calculated.

Using the two equations and assuming the equilibrium condition $\Psi_{icp} = \Psi''_{icp}$ and by elimination of K_{SH}, it is possible to deduce K_{IE}, the thermodynamic ion exchange equilibrium constant

$$K_{IE} = \exp\,[(F/RT)\,(z - z'')\,\Psi^{o}_{cp}] = (a_M\, z / \alpha\, \gamma)^{z''}/[a_{M''}\, z''/(1-\alpha)\gamma]^{z} \qquad (16)$$

and by elimination of $\Psi''_{icp} = \Psi_{icp}$ only, one obtains the separation factor of ion exchange, S. Its definition reads

$$S = \exp[(F/R\,T)(z'' - z)\,K_{SH}] = a_{M''}\, z''\, \alpha/(1-\alpha)(a_M\, z) \qquad (17)$$

Potentials and Distances of the Debye-Hückel Theory on Spherical Particles in the Presence of Coagulator Ions

Various experiments in electrokinetics,[8] counter ion exchange and adsorption,[5] coagulation,[2,10] and PDI adsorption[11] have been published with coagulating counter ions of $z = 1, 2, 3, 4$, in a sufficiently low and constant concentration, $a_{M''} = I_{stable} < 0.001 - 0.01$ mol dm^{-3} of the counter ion of $z'' = 1$. In such a low I_{stable}, the adsorbed 1–1 electrolyte is certainly highly hydrated. An increase of $a_M\, z$ causes replacement of the highly hydrated $z'' = 1$ counterion at a large average $1/\kappa_p$ with M of $z \geq 1$ at a small $1/\kappa_p$ in sufficiently high concentrations.

The cause of coagulation can be explained by the destruction of the hydrated double layer ions in low I_{stable} with the coagulator ions in high $a_M\, z$. The same experiments can be interpreted in the following way:

From (14), one obtains for z = const.

$$\log \alpha \rightarrow (F/RT)\,(\Psi^{o} - \Psi_{icp}) + \log a_M\, z \qquad (18)$$

and from (15)

$$\Psi_{icp} = \Psi_{icp}(I_{stable}) - (RT/F)\,\log\,(1-\alpha) \qquad (19)$$

The shift of the plots, for $\Delta z = +1$ and $\Psi_{icps} = \text{const}$, follows from (15). It defines the linear Schultze rule constant K_{SH} by

$$(RT/F) \log a_M z - K_{SH} = (RT/F) \log(z + 1) a_{M1} \tag{20}$$

Figure 4 represents equations (17), (18), (19), (20) with four plots for $z = 1, 2, 3, 4$, with parameters adjusted in such a way that it, in principle, correctly explains the corresponding experimental plots in Ref. 18. The ordinate represents either ψ_{icp}, κ_p, or $1/q$. Log ($a_M z$ / mol dm^{-3}) is on the abscissa. Theoretical $1/q$-plots can be always fitted to any corresponding experimental plots. The intersections of the tangents on the plots with the horizontal tangent, $\Psi_{icp}(I_{stable})$, define the condition $1 - \alpha = \alpha = 1/2$. Equations (14) and (15) represent, for $a_M z \ll a_M z$ ($\alpha = 1/2$) and $a_M z \gg a_M z$ ($\alpha = 1/2$), the tangents on the horizontal and inclined parts of the plots.

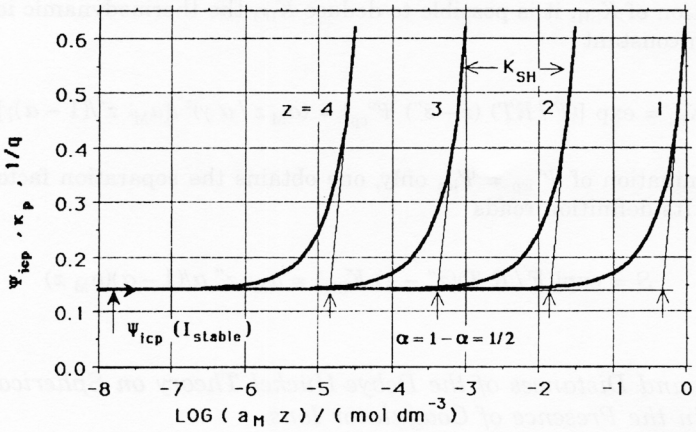

Figure 4. Variation of »Ψ_{icp}, κ_p, $1/q$ (ordinate) with log ($a_M z$/mol dm^{-3}) (abscissa)« for $z = 1, 2, 3, 4$. Schulze-Hardy rule constant K_{SH}.

Analogously to (19), for the DHT reciprocal distance at particles, one can write

$$\kappa = \kappa_{icp} (I_{stable}) - \kappa_{sp} \log(1 - \alpha) \tag{21}$$

and for the electrokinetic quotient

$$1/q = 1/q_{icp} (I_{stable}) - s \log(1 - \alpha) \tag{22}$$

The slopes of the plots are RT/F, κ_{sp} and s. For $a_M z \ll a_M z$ ($\alpha = 1/2$), the corresponding values are $\Psi_{icp}(I_{stable})$, $\kappa_{icp}(I_{stable})$, $1/q_{icp}(I_{stable})$. The two values $1/q_{icp}(I_{stable})$ and s depend on the applied technique and, most probably, they cannot be predicted theoretically. They can be obtained from experiments.

The three equations containing K_{SH} represent the »linear« Schulze-Hardy rule, as applied to the double layer, *i.e.*, the ionic cloud potential, the reciprocal Debye-Hückel distance and the electrokinetic quotient.

It is reasonable to anticipate that concentrations $a_M z \approx< 0.1\ a_M z$ ($\alpha = 1/2$) cause coagulation. The three equations can be used also for $z = 1$ if $I >> I_{stable}$. Also, sufficiently high concentrations of (1–1) electrolytes cause coagulation.

The transition of the low I_{stable} to the coagulating concentration, $a_M z$ ($\alpha = 1/2)/10 \approx< a_M z$, or $I(\alpha = 1/2)/10 \approx< I$, can be explained as an exchange of the hydrated (1–1) double layer electrolyte in I_{stable} with the weekly or essentially unhydrated counter ions in high $a_M z$ or I.

Electrokinetics and the Quasi Crystal Model in Debye-Hückel Electrolytes

In Ref. 12, experiments are published on electrophoretic mobilities and streaming currents with positively charged polystyrene latices and, in Ref. 13, high frequency dielectric response and microelectrophoretic measurements on anionic and cationic styrene latices. The results are presented as »mobility« or »ζ potential« against »log I plots«, where the concentration of several (1–1) electrolytes is equal to the ionic strength, I. The ζ potentials were calculated by using different theories, all based on homogeneous charge double layer models. The plots can be approximated as a straight line increasing up to log (I_m/mol dm^{-3}) $\rightarrow$ –3 to –2.5 and a decreasing line with an intersection at log $I_m = -3$. The increasing line can be explained qualitatively by the conventional ζ potential theories, while the decreasing line is not explained. The theoretical explanation based on the point charge double model and the DHT follows below.

From definition (4), valid for electrolytes, it follows that, analogously, it must be valid for colloidal particles too

$$\Psi_{icp} = -e_0 \kappa_p / 4\pi\varepsilon \tag{23}$$

and

$$\log(\kappa_{pm} / \kappa_p) = (-1/2) \log(I / I_m) \tag{24}$$

The dependence of the edge length, l, of the cube which statistically contains 1 single ion of the (1–1) electrolyte on I, reads

$$\log(l / l_m) = -(1/3) \log(I / I_m) \tag{25}$$

where for $I = 1$ mol dm^{-3} one obtains the standard edge length $l = l^o = 9.399 \times 10^{-9}$ mol$^{1/3}$ of the cube and the standard reciprocal DHT radius, $\kappa^o_p = 3.286 \times 10^{-8}$ mol$^{-1/2}$. The Avogadro-Loschmidt constant is L in $I = I_m$ are $1/\kappa_{pm} = l_m = l_{pairm}$.

Equations (24) and (25) are linear (log – log) plots with the intersection at $I = I_m = (\kappa^o\ l^o)$.[6] They are represented in Figure 5.

In low $I < I_m = 1 \times 10^{-3}$ mol dm^{-3}, $1/\kappa_p > l$. At first sight, it is hard to explain how the average distance, $1/\kappa_p$ or $1/\kappa$, between the cations and anions can be bigger than the distance, l, which follows directly from concentration. An explanation can be given on the basis of the DHT of quasi crystals.

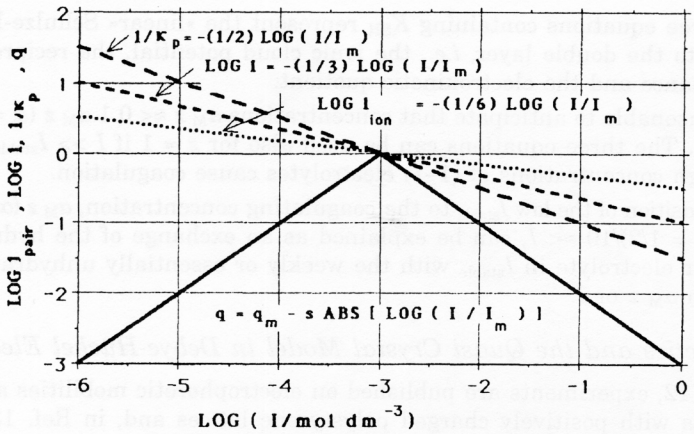

Figure 5. Variation of »$1/\kappa_p$, square root, l, cube root, l_{ion}, sixth power root, and q, (ordinates, relative units), with logarithm ionic strength, log (I/mol dm^{-3}), (abscissa)«.

It has been demonstrated[14] that, in order to obtain the DHT square root dependence on I, the electrolytes can be described as having a quasi crystal lattice, *i.e.*, the ideal disorder of the DHT electrolyte is replaced by the ideal order of an imaginary quasi crystal. Single ions of opposite sign at great distances, l_{cube}, are present in low concentrations and follow equation (25) and a great majority of ions are at small distances, $l_{ion} \approx 1$ nm, which is approximately equal to the size of one H_2O molecule. They can be considered to form ion pairs. The distance between the ion pairs is l_{pair}.

The following equation can be obtained for a sufficiently high value of the parameter I and constant, sufficiently small, κ_{ion}

$$\log(l_{pair} / l_{pairm}) = -(1/6)\ \log(I / I_m) \tag{26}$$

By summation of (25) and (26), one obtains the average electrostatic potential $1/\kappa$ or $1/\kappa_p$ and its square root dependence on I of equation (24).Then, as requested by the DHT, the requirement is fulfilled that in $I < I_m$ is $1/\kappa > l$ and in $I_m < I$ is $1/\kappa < l$. In $I = I_m$, $1/\kappa_{pm} = l_m = l_{pairm}$. Equation (26) is valid for the assumed, perfect order, quasi crystal lattice as well as for the total disorder of the DHT electrolytes.

An analogous explanation can be suggested for particles. The majority of inner charges on the surface, in low I, are highly hydrated and they are separated from counter ions by the small distance, l_{ion} of one H_2O molecule. In high I or $a_M z$, they are at the average distance $1/\kappa_p$. The latter is the average between l_{pair}, l_{ion} and l.

Furthermore, one can suppose: if $I < I_m$, the ion pairs, equation (26), cause a retardation, *i.e.*, a decrease of q, while, if $I > I_m$, the cube root ions of equation (25) cause the retardation. In $I = I_m$, $q = q_m$. The retardations caused by the two kinds of ions are equal. Consequently, one can write the following equation which represents the experimental increasing and decreasing lines

$$q = q_m - |s\ \log\ (I / I_m)| \tag{27}$$

The q-plots depend on the applied technique and it is probably impossible to deduce theoretically the values of q_m and s. In $I = I_m$ is $q = q_m$. However, q_m and s can be obtained by fitting (27) to experimental values. Function (27) is also represented in Figure 5. All plots are adjusted for $1/\kappa_{pm} = l_m = l_{pairm} = 1$ and $I_m = 0.001$ mol dm^{-3}.

The counter ions in the outer layer form the ion cloud. In this way, the theoretical intersection of the increasing and decreasing q lines is at $\log I_m \approx 0.001$ mol dm^{-3}, as suggested by experiments.[14] Some higher I_m values obtained by some counter ions were explained by the authors as specific exceptions.

The Point-Charge and the Homogeneous Charge Double Layer Models

It should be stressed here that practically the only electrochemical methods by which the double layers have been investigated are the electrokinetic methods. The dielectric response method[14] is a recent exception. Experiments with polarizable Hg-electrodes (Gouy-Chapman double layer) or Nernst-electrodes cannot be used for a theoretical analysis. The Nernst electrodes serve solely for potentiometric determinations of log[PDIs] or log I (pH).

According to the point charge double layer model, the average counter ion volume charge density is at $x = 1/\kappa_p$ and, according to the homogeneous or Gouy-Chapman model, the biggest volume charge density is at $x \to 0$. According to the latter theory, at distances $x <$ »*distance of the slipping plane*« the majority of counter ions decrease the net charge of the moving particle and, consequently, q, while according to the former model, they all practically increase the net outer charge of the ionic cloud, and in this way, they all increase q. Possibly, even if the slipping plane, or the Stern layer, were of any real influence, the greatest part of counter charges would be in the outer layer and it would increase q. According to the point charge model, the average number of counter ions are in the moving parts of the electrolyte outside the possible slipping plane, at an average distance, $1/\kappa_p$, where they all increase the relative mobility of the liquid phase, *i.e.*, they all increase the actual q. The charges in question are proportional to the surface areas under the plots to the left and right from the slipping plane.

All efforts to calculate ζ potentials on the basis of the homogeneous charge double layer model have failed to date. One can conclude that as many ζ potentials have been obtained as theories proposed, introduction of the »triple«, to replace the double layer, did not solve the problem.

The homogeneous charge model was unsuccessfully used in the calculations of ζ potentials because this model does not include parameters l_{ic} and $1/\kappa_p$. The two latter parameters, as it is demonstrated above, are crucial for the deductions and postulates of all theoretical equations obtained by the point charge double layer model. The same theoretical equations explain, in principle correctly, all the experiments quoted in the present paper.

In addition, practically all, homogeneous charge, ζ potential theories are based on the charge density function, which has been proved by the present author to be underdetermined,[3,15] if the size and form or the particles, or the specific surface, are not known.

Also, in a broad region, when $q << 0 << q$, *i.e.*, outside the isoelectric region, $\pm q$ values are practically constant with log I (= pH) or log a_M or they asymptotically approach a saturation value.[17,19,21]

Electrokinetics of Small AgI Particles

Electrophoretic mobilities of freshly prepared AgI sols in the region 14 > pI < 9.5 or 2 < pI < 9.5 are essentially constant and negative in low concentrations (I = $[NaNO_3] \leqq 0.01$ mol dm^{-3}) of (1–1) electrolytes.[16] In the presence of counter ions in coagulating concentrations and in the same region of pI values, the electrosomotic mobilities are approximately constant with pI and they decrease with the $[La^{3+}]$, $[Ba2^{+}]$, $[Na^{+}]$ concentration.[17] The latter results were partly used in Ref. 18, which is theoretically analyzed by the present Figure 4. The constancy with counterion concentration of mobilities has also been demonstrated.[20]

The influence of z is elucidated also in Ref. 19. In the negative region, $[Ba^{2+}]$, $[Mg^{2+}]$ decreases q, as compared with the q of $[Na^{+}]$, while in the positive region, $[SO_4^{2-}]$ causes the same effect. The change of negative to positive q values, the recharging, was achieved by an increase of $10^{-5} \rightarrow$ [dodecylamine] / mol $dm^{-3} \rightarrow 10^{-4}$.

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LIST OF SYMBOLS

a	diameter of a spherical particle
a_M, $a_{M''}$	molar activity or concentration of ions M, M" of charge numbers z' z''
e_o	elementary charge
F_p	factor for transforming sums of distance functions into potentials
I, I_m, I^o, I_{stable}	ionic strength, of the maximal q_m, standard, in stable systems
K_{IE}	thermodynamic equilibrium constant of ion exchange
K_{SH}	Schulze-Hardy linear rule constant
L	Avogadro-Loschmidt constant
l_{ic}	intercharge distance
l, l_{cube}, l_m, l^o	side length of the cube containing 1 ion of the (1–1) electrolyte, the length of the lattice unit, in I_m, standard
l_{pair}, l_{pairm}	distance between ion pairs, in I_m
M, M"	counter ion of charge number z, z''
π	Ludolf's number
pAg, pI	negative logarithm of Ag^+, I^- concentration
q, q_{icp}, q_m	electrokinetic quotient of particles, in I_{stable} in I_m
r, r_{max}	radius on a circular charged plate to calculate the sum of reciprocal distances, radius of a plate or sphere
r_1, r_2	distance between a charge on a sphere and a point on an axis
S	selectivity coefficient of ion exchange
s	slope of the q plot
x	distance from the surface
y, y'	distance between two points n and n+1, at a charged particle, absolute
z, z'	distance between two points p and p + 1, absolute

z, z''	charge number (valence) of counter ions M, M"
α, $1 - \alpha$	equivalent fraction of two counter ions M, M" in the double layer
$\Delta\varphi$	point or discrete charge double layer potential of the ion exchange theory of coagulation
ε, ε_0	relative, permittivity of free space
γ	equivalent ion exchange capacity of ion exchangers
κ, κ_m, κ°	reciprocal Debye-Hückel radius of electrolytes, in I_m, standard
κ_p, κ_{icp}, κ_{sp}	reciprocal Debye-Hückel radius on particles, in I, reciprocal slope of the plot (21)
κ_{pl}, κ°_{pl}	reciprocal Debye-Hückel radius at planar surfaces, standard
π	Ludolf's number
Ψ_C, Ψ_{ic}, Ψ_{DH}	double layer potentials of the Debye-Hückel theory: Coulombs, ion cloud, their sum, *i.e.*, the Debye-Hückel average
Ψ_{Cp}, Ψ_{icp}, Ψ_{DHp}	double layer potentials of the Debye-Hückel theory at particles: Coulombs, ion cloud, their sum, *i.e.* the Debye-Hückel average
Ψ_{Cpl}, Ψ_{icpl}, Ψ_{DHpl}	double layer potentials od the Debye-Hückel theory at planar surfaces: Coulombs, ion cloud, their sum, *i.e.*, the Debye-Hückel average
Ψ°	standard electrostatic potential
ζ	hypothetical electrokinetic double layer potential

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SAŽETAK

Eksperimentalni elektrokinetički sistemi i model dvosloja točkastih naboja

Mirko Mirnik

Potencijali: coulombski, Ψ_{Cp}, ionskog oblaka, Ψ_{icp} i prosječni, Ψ_{DHp}, Debey-Hückel-ove teorije, u prostoru u blizini okrugle koloidne čestice, koja je nabijena određenim brojem ionskih naboja, mogu se izračunati s pomoću jednadžbi:

$$\Psi_{Cp} = (1/2\, r_{max}\, \pi) \sum_{-n}^{+n} \sum_{-p}^{+p} 1 / r \qquad \text{(A1)}$$

$$\Psi_{DHp} = -(1/2\, r_{max}\, \pi) \sum_{-n}^{+n} \sum_{-p}^{+p} e^{-r} / r \qquad \text{(A2)}$$

$$\Psi_{icp} = (1/2\, r_{max}\, \pi) \sum_{-n}^{+n} \sum_{-p}^{+p} (1 - e^{-r}) / r \qquad \text{(A3)}$$

Gouy-Chapman-ov potencijal, Ψ_{GCh}, uz ravnu površinu definiran je jednadžbom

$$\Psi_{GCh} = e^{-x} \qquad \text{(A4)}$$

Značenje simbola: $r = \{x^2 + l_{ic}^2\,[(n + y)^2 + (p + z)^2]\}^{0.5}$, $r_{max} = l_{ic}\, n_{max}\, \sqrt{2} = l_{ic}\, p_{max}\, \sqrt{2}$, n, p cijeli su brojevi. Udaljenost među nabojima je l_{ic}, x, $l_{ic}\,(n + y)$, $l_{ic}\,(p + z)$ su koordinate točaka u sloju, dok $0 < y, z < 1$. Udaljenost točaka na osima od površine je x. Svi simboli su višekratnici parametra κ, tj. $x = x'\kappa$, $y = y'\kappa$, $z = z'\kappa$, $l_{ic} = l'_{ic}\,\kappa$, a $\Psi_{Cp} = \Psi'_{Cp}/\Psi_{o}$, $\Psi_{o} = z\, e_o \kappa / 4\, \pi\, \varepsilon$. Presjecišta krivulja Ψ_{Cp} (x = var., n, p, y, z = 0) sa horizontalom $\Psi_{icp}(x \to 0) = 1$ definiraju $x = 1/\kappa_p$, a taj je određen vrstom čestica i ionskom jakošću. Računi pokazuju, da je $\Psi_{icp} > \Psi_{GCh}$. Iz toga slijedi, da uvođenje klizne plohe i Stern-ovog sloja nužno prouzrokuje preniske ζ potencijale. Autor je 1963. predložio i prijedlog opravdao eksperimentima, da su elektrokinetički kvocijenti, q, proporcionalni log I, tj. logaritmu koncentracije koagulirajućih protuiona ili ionskoj jakosti (q = »prenesen volumen / jakost struje«, »električna struja strujanja / brzina strujanja tekućine«, »potencijal strujanja / tlak«, »gibljivost / jakost električnog polja«). Time se dobije funkcija

$$q = q_m - |\, s \log (I/I_m)\,| \qquad \text{(A5)}$$

Ta je predstavljena prelomljenim pravcem, prvi dio raste, drugi pada sa log I, a presjecište je kod log I = log I_m i $q = q_m$. Parametri q_m i nagib, s, mogu se uskladiti s eksperimentima i ovise o primijenjenoj tehnici. Nekoliko grafova koje su objavili Hidalgo-Alvarez i suradnici (1986) i Midmore i Hunter (1988), mogu se aproksimirati sa dva pravca koji se sijeku kod log $I_m \approx -3$. Prvi raste, a drugi pada s log I. Navedeni eksperimenti predstavljaju presudnu potvrdu za ispravnost i korisnost primjene Debye-Hückel-ove teorije u modelu ionskog dvosloja točkastih naboja. Općenito, svi su pokušaji računanja ζ potencijala na bazi modela homogenih naboja električnog dvosloja bili neuspješni, jer u njih nisu uključeni međuionska udaljenost, l_{ic} i ionski radius Debye-Hückel-ove toerije, $1/\kappa_p$. To je dovoljan razlog zbog kojeg valja odbaciti Gouy-Chapman-ov model električnog dvosloja u koloidnoj kemiji.