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Concept of Discrete Charges in the Theory of Electrokinetic Phenomena

M. Mirnik

*Institute »Ruđer Bošković, Zagreb and Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia, Yugoslavia**

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A structure of the electric double layer, based on the concept of discrete ion charges fixed on the surface of the solid in the system »ionic crystal — liquid«, is given. Applying elementary principles of (electro) chemical thermodynamics, electrostatics of elementary particles and the principle of electroneutrality of the systems, and considering the fact that water molecules are dipoles, an equation relating electrokinetic tension with counter ion concentration was deduced. Some available experimental results on electrokinetic phenomena of AgI were interpreted in the light of the present theory and were shown to confirm it quantitatively in the limits of experimental errors. For other existing theories of the electric double layer similar results were not yet shown to confirm them.

The theoretically requested linear Schulze-Hardy rule with the same proportionality constant which was shown up to now to be valid in coagulation and counter ion exchange and adsorption was shown to be valid in electrokinetics too.

The obtained definition of the discrete (fixed) charges tension given by the formula:

$$\Delta\varphi = \Delta^0\varphi + z\,\Delta^1\varphi + (RT/F)\ \ln(a_M/x)$$

is different from the tension defined by the Nernst formula:

$$\psi = \psi^0 + (RT/nF)\ \ln(a_O/a_R)$$

The latter one can be valid only for an electrode of a three- or multi-phase Galvanic cell; it is without physical meaning in a two phase colloidal system.

INTRODUCTION

In the present paper the ion exchange (IE-) theory[1] of coagulation and adsorption will be extended for the interpretation of electrokinetic phenomena because the same theory and the same principles should be applied for the explanation of different phenomena observed in the same system.

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory in its original version could not explain the existing experiments and therefore it was recently modified in different ways[24,25]. Different extended theories include different principles and are based upon quantitatively different double layer structures. Neither theoretical nor satisfactory experimental indications were cited which would have proved the correctness of the extended versions.

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The theory as applied for the interpretation of electrokinetic tensions[25] with 1—1 electrolytes was not compared with any experiments and the influence of the valency of counter ions was not investigated.

Therefore in the present paper the IE-theory will be applied in deducing the influence of the counter ion concentration and valency upon the electrokinetic tension.* In this way a theoretical explanation of the double layer processes will be given and a method of the treatment of the double layer processes will be suggested. The theoretical predictions will be checked with some representative experimental results. To deduce the theory of electrokinetic phenomena no new concepts or ideas will be introduced. The classical thermodynamics of ion exchange[12], the concept of discrete (fixed) charges in the double layer and the concept of the electrochemical, rather than chemical potential of ions and dipoles in the double layer are the basic principles upon which the theory is deduced. The principle of electroneutrality of the system is also maintained. The electrokinetic tension is that deduced by the classical Helmholtz-Smoluchowsky equation (eq. 11). It was possible so far to show that the results of coagulation and counter ion adsorption in the Ag-halide systems confirm the IE-theory. Experimental observations used in proving or deducing this theory are:

1) the counter ion exchange properties of coagulated AgI[2],

2 the linear Schulze-Hardy rule of coagulation[3,4,5,8,9],

3) the decrease in quantity of the adsorbed counter ions with counter ion concentrations lower than the coagulation value (Fig. 1 ref. 5),

4) The linear decrease of the logarithm of coagulation value when plotted *vs.* the reciprocal dielectric constant of water — solvent additive mixtures[6,7]. It followed from this theory that the silver ion activity limit of stability should be independent of the particular halide[8] and equal for the three halides, which was observed experimentally before (Fig. 4 ref. 9).

5) The experimentally established equality of the coagulation values of bivalent ions for all the three halides[10] is also in accordance with the theory (Table 1. ref. 5). It also proves that the stabilizing particles are bivalent.

Although the electrokinetic experimental evidence used is not the ideal one it is certainly representative and based upon the results of two laboratories. This evidence together with the remaining cited results of the most different experimental fields justify the consideration of the IE-theory based upon the concept of discrete ionic charges in the double layer as a possible explanation of the double layer processes on ionic solid-liquid interfaces.

THEORETICAL PART

1. *The discrete charges double layer*

This theory is based upon the assumption that discrete charges in the form of constituent ions (or charged surface active agents, in ion exchangers the charges of the dissociated surface groups) are adsorbed at the interface of the colloidally dispersed ionic solid in an amount determining the surface density of the double layer charges. This density is low and therefore the distance between the like charges is sufficiently large that these can be considered as totaly separated and treated as discrete

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* The use of this term is in accord with the proposal of P. Van Rysselberghe[11].

charges. The electrostatic tension caused by an adsorbed constituent ion at the position of the second is considered as negligible.

In the case of negative AgI the adsorbed constituent ions are I^- ions. The character of this adsorption is of secondary importance if the energy of the adsorption may be considered as large, *i.e.* if the changes of the system, which cause the observed phenomena cited in the introduction, do not alter appreciably the adsorbed quantity of these ions. Thus, the adsorbed quantity of constituent I^- ions can in the theoretical interpretation be assumed as practically constant in the region of *p*I values encountered in the experiments ($1 < p\mathrm{I} < 9$, Fig. 2 ref. 2a, Fig. 1 ref. 2b). The observed decrease of the adsorbed quantity of counter ions with *p*I, if expressed in gramequivalents per grammole of AgI, is small and of the same order of magnitude as the decrease of the adsorbed quantity of I^- ions as observed potentiometrically (Fig. 1 ref. 25b, Fig. 4 ref. 26).

A fraction of the total adsorbed amount of counter ions, which is equal to the total amount of adsorbed I^- ions, will be associated with the former and will form ion pairs (electrically neutral associates). Another fraction will be dissociated and their energy will be defined by their electrochemical potential. The energy distribution will follow the Boltzman statistics. Therefore they will be statistically located around the adsorbed constituent ions at a mean distance. The adsorbed or fixed constituent ions cause their surroundings to have a decreasing electrostatic field following Coulomb's law. The dielectric properties of the medium and the energy of thermal motion of the molecules and ions in the liquid phase are responsible for this behaviour. The electrical attracting forces between counter ions and fixed $I^-_{\mathrm{ads.}}$ ions are equal to the repelling forces originating from the thermal energy. The dielectric properties of the liquid cause the dissociation of the strong electrolyte »adsorbed constituent ion — counter ion« in the same manner as they cause the dissociation of the same electrolyte if its constituent ions are not adsorbed. Positive counter ions, at sufficiently low concentrations, will be replaced by the positive charges of oriented solvent molecules if these are dipoles as in the case of water as solvent. The replaced counter ions will be therefore in the liquid at large distances having the electrochemical potential of the same ions in the liquid phase.

Equations representing the reversible reactions in the double layer can be given in the following form (for notation see the end of the paper):

$$\text{(a)}\quad (\mathrm{A_zM_{z^-}})_{\mathrm{ads.}} \rightleftarrows \mathrm{z\,A^{z-}_{ads.}} + \mathrm{z^-M_{layer}}$$

$$(\mathrm{I_zM})_{\mathrm{ads.}} \rightleftarrows \mathrm{zI^-_{ads.}} + \mathrm{M_{layer}}$$

$$\text{(b)}\quad (\mathrm{A_2^{z-}} \cdot \mathrm{z^-H_2O})_{\mathrm{ads.}} \rightleftarrows \mathrm{2A^{z-}_{ads.}} + \mathrm{z^-H_2O_{layer}}$$

$$(\mathrm{I^-_2} \cdot \mathrm{H_2O})_{\mathrm{ads.}} \rightleftarrows \mathrm{2I^-_{ads.}} + \mathrm{H_2O_{layer}}$$

$$\text{(c)}\quad \mathrm{M_{layer}} \rightleftarrows \mathrm{M}$$

$$\mathrm{La^{3+}_{layer}} \rightleftarrows \mathrm{La^{3+}}$$

$$\text{(d)}\quad \mathrm{H_2O_{layer}} \rightleftarrows \mathrm{H_2O}$$

The experimentally established counter ion exchange properties of the negative AgI[1] could be well explained by equations of the type(a). The interrelation between the coagulation value and the adsorption of counter ions[1,2] and the influence of the dielectric constant of the medium[6] can be explained by equations of both types (a) and (b).

Figure 1. shows schematically the variation of the electrostatic tensions with the distance r from fixed positive constituent ions. The plot φ_+ gives the variation of the electrostatic tension due to the presence of a positive ion of valency z at r = 0. The variation of the tension due to the statistical energy and density ϱ distribution of counter ions at the mean distance δ is shown schematically by the plot φ^-.

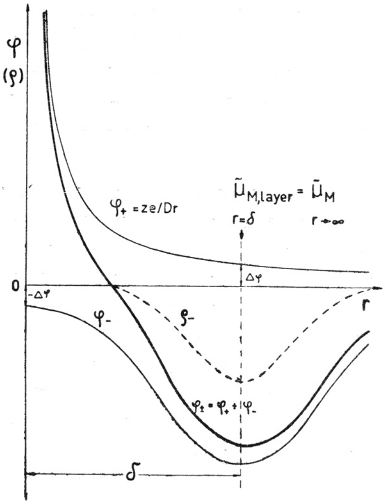

Fig. 1. Electric tension functions of the fixed charges double layer, and the counter ion density function. (Schematic, see text!)

The condition of electrochemical equilibrium between the counter ions in the double layer and in the solution phase is given by:

$$\tilde{\mu}_{M,\mathrm{layer}\ (r\,=\,\delta)} = \tilde{\mu}_M{}^{(r \to \infty)}$$

When these equilibria are established the actual variation of the tension with the distance from fixed ions in the surface is given by the plot $\varphi_\pm = \varphi_+ + \varphi_-$.

In this way the fixed charges double layer tension $\Delta\varphi$ and the counter ion distance δ are defined thermodynamically. From these values the electrokinetic tension will be deduced assuming that the distance of the slipping plane or rigid boundary is negligible as compared with the counter ion distance.

At the interface the following particles can be found:

1. associated ion pairs $(A_zM_{z^-})_{\mathrm{ads.}}$ or $(KI)_{\mathrm{ads.}}$ in an amount $x(\gamma - \sigma)$
2. hydrated adsorbed constituent ions $(A_2^{z^-} \cdot z^-H_2O)_{\mathrm{ads.}}$ or $(I^-_2 \cdot H_2O)_{\mathrm{ads.}}$ in an amount $(1 - x)(\gamma - \sigma)$ whose counter ions are in the liquid phase under the chemical potential determined by their own activity.

3. Free, unassociated constituent ions $A^{z^-}_{ads.}$ or $I^-_{ads.}$ in an amount $x\sigma$, whose counter ions in an equivalent amount are under an electrochemical potential $\mu_{M,layer}$ in the outer layer at a mean distance δ.
4. Free unassociated constituent ions $A^{z^-}_{ads.}$ or $I^-_{ads.}$ in an amount $(1 - x)\ \sigma$, whose counter ion charges are replaced by an equivalent amount of positive charges of oriented water molecules at a distance δ. The positive charges of oriented H_2O dipoles are under an electrochemical potential $\tilde{\mu}_{H_2O,\, layer}$.

The counter ions, in an equivalent amount, are in the liquid phase under the chemical potential μ_M determined by their activity.

The amounts γ and σ should be given in gramequivalents of the solid per litre.

The physical picture of the electric double layer being defined once, all the remaining deductions ,and conclusions of this series of papers have to be accepted for double layers of the same type. (Because they were obtained using the chemical ,respectively electrochemical thermodynamics and the electrostatics of elementary particles.)

However, it should be stressed that such a double layer structure may be considered as valid only for the two-phase system »ionic crystal-liquid« or »resin-liquid«. The present discussion is not concerned with the theory of the electric double layer of polarizable or not polarizable electrodes with electric fields applied externally or originating from a second electrode immersed in the same electrolyte. The interrelation between the double layer structure of polarizable or unpolarizable electrodes of galvanic cells and the proposed structure of simple two-phase systems was not investigated.

2. *Concentration functions of double layer tension, counter ion distance and ζ-tension.*

The force between an adsorbed constituent ion and a counter ion is determined by the well known equation

$$F = z\, z^-\, e^2 / D\delta^2 \qquad (1)$$

and, respectively, for all charges in the double layer of the system by

$$F_{layer} = (z^-\, e/D\delta^2) \sum_{N\sigma/z} z\, e = \sigma\, N\, z^-\, e^2/D\delta^2 = \text{const.}/D\delta^2 \qquad (2)$$

The electrostatic (coulombic) energy of counter ions in the outer layer is

$$E_{M,layer} = \sigma\, N\, z^-\, e^2/D\, \delta = \sigma\, F\, \Delta\varphi \qquad (3)$$

where $\Delta\varphi$ is defined by

$$\Delta\, \varphi = z^-\, e/D\, \delta \qquad (4)$$

For high concentrations of a counter ion in the liquid or when no dipoles are assumed to be present, *i.e.* when $x = 1$, the energy of the double layer will be determined only by the energy of counter ions, and therefore their electrochemical potentials in the liquid and in the layer are equal:

$$\overleftharpoonup{\mu}_{M,layer} = \overleftharpoonup{\mu}_M \qquad (5)$$

Then for

$$\overleftharpoonup{\mu}_M = \mu_M{}^0 + RT \ln(a_M/z) + \varphi_{liquid}\, F \qquad (6)$$

$$\overleftharpoonup{\mu}_{M,layer} = \mu^0{}_{M\ layer'} + RT \ln(x\sigma/z) + \varphi_{outer} F \qquad (7)$$

$$\Delta\varphi = |\varphi_{\text{outer}} - \varphi_{\text{liquid}}| \qquad (8)$$

$$\delta_s = z^- \text{N } e^2/\text{DRT} \qquad (9)$$

$$\delta_s/\delta = \Delta\,\varphi\,\text{F/RT} \qquad (10)$$

$$\zeta = \text{const. } \sigma\,\delta/\text{D} \qquad (11)$$

$$\zeta_s = \text{const. } \sigma\,\delta_s/\text{D} \qquad (12)$$

$$\zeta_s/\zeta = \delta_s/\delta \qquad (13)$$

and

$$\ln {}_{\infty}a_M = \ln \sigma + (\mu^{0'}_{\text{M,layer}} - \mu^0_M)/\text{RT} \qquad (14)$$

one obtains

$$0.4342\,\Delta\varphi\text{F/RT} = \delta_s/\delta = \zeta_s/\zeta = \log a_M/{}_{\infty}a_M\,(x = 1) \qquad (15)$$

The classical Helmholtz — Smoluchowsky equation (11) defining the electrokinetic tension of the rigid Helmholtz double layer is used for the deduction. The dimension and value of the proportionality constant were discussed recently in ref. 13. The distance of the slipping plane is assumed as infinitesimal compared with δ. It follows from this equation that, if only one charged species (counter ion) is assumed to be present ($x = 1$) the reciprocal counter ion distance, the reciprocal electrokinetic tension and the double layer tension are linear functions of the logarithm of counter ion activity. (Tangents on the plots of Figs. 2. and 3.)

3. Counter ion valency influence upon ζ — tension

It follows from adsorption measurements[1,2] that the counter ion valency and activity influence upon the adsorbed quantities of two counter ions of valency z' and z can be expressed by ($\mathbf{a}$ = const.)

$$\log[a_M/x\gamma] + z\mathbf{a} = \log[a_{M'}/(1-x)\gamma'] + z'\mathbf{a} \qquad (16)$$

Assuming that x = const., $1 - x$ = const. and $a_{M'}$ = const. we obtain from the difference af two corresponding equations (16) valid for two ions M^z and M^{z+1}

$$\log\,(a_M{}^z/a_M{}^{z+1})_{x\,=\,\text{const.}} = \mathbf{a} \qquad (17)$$

The change $\Delta^1\varphi$, δ_1, and ζ_1 of $\Delta\,\varphi$, δ and ζ which corresponds to a $10^{\mathbf{a}}$ fold change in counter ion activity can be defined by

$$\mathbf{a} = 0.4343\,\Delta^1\varphi\text{F/RT} = \delta_s/\delta_1 = \zeta_s/\zeta_1 = \log\,(a_M{}^z/a^{z+1})_{\zeta\,=\,\text{const.}} = \\ = \log\,({}_{\infty}a_M{}^z/\,{}_{\infty}a_M{}^{z+1}) \qquad (18)$$

It was obtained from eq. (17) and the difference of two corresponding eqs. (15), when in the second a_M is replaced by $a_M{}^{z+1}$.

Then the equation determining the counter ion valency influence upon $\Delta\varphi$,δ and the ζ-tension reads ($x = 1$).

$$\log\,(a_M/\,{}_{\infty}a_M{}^0) + z\mathbf{a} = 0.4343\,\Delta'\varphi\,\text{F/RT} = \delta_s/\delta = \zeta_s/\zeta \qquad (19)$$

To simplify this equation a hypothetical non existent particle M^o of valency $z = 0$ is introduced as a mathematical aid with properties analogous to properties of other charged particles. ($_\infty a_M{}^0 = {}_\infty a_{M'} - z'a = \text{const.}$)

It follows that the linear Schulze-Hardy rule equation should be valid in electrokinetics to, namely

$$\log(a_M/a_M{}^o)_{\zeta\,=\,\text{const.}} = \log({}_\infty a_M/{}_\infty a_M{}^0) = -za \tag{20}$$

If two charged species are present in the system eq. (15) should read

$$0{\cdot}4343\,\Delta\varphi F/RT = \delta_s/\delta = \zeta_s/\zeta = \log(a_M/x\,{}_\infty a_M) \tag{21}$$

From eq. 19 for $(RT/F)\ \ln \infty\ a_M{}^0 = -\Delta^0\varphi$ as a standard value we obtain

$$\Delta\varphi = \Delta^0\varphi + z\,\Delta^1\varphi + (RT/F)\ \ln(a_M/x) \tag{22}$$

respectively

$$\Delta\varphi' = \Delta^0\varphi + z'\,\Delta^1\varphi + (RT/F)\ln[a_M{}'/(1-x)] \tag{23}$$

By these quations the counter ion valency, adsorbed fraction and activity influence upon the double layer tension are determined.

Equations 2 and 3 ref. 1 were special cases of eqs. (22) and (23) if we set $\Delta^0\varphi = (RT/F)\ \ln{}^0D$ and $\Delta^1\varphi = (\mathbf{a}RT/F)\,/\,0.4343$ for $\Delta\varphi = 0$. Therefore for the general case in ref. 1 eq. 5, $K_c = \alpha^0 D^{(z''-z')}$ when $\ln\alpha = \Delta\varphi\, F/RT$.

From the difference of eqs. (22) and (23) one obtains for $a_M{}' = \text{const.}$ $\Delta\varphi = \Delta\varphi'$ and $\ln(a_M)_{x\,=\,0.5} = (z' - z)\,\Delta'\varphi F/RT + \ln a_M{}'$

$$\log[a_M/(a_M)_{x\,=\,0.5}] = \log[a_M/(a_M{}^0)_{x\,=\,0.5}] + z\mathbf{a} = \log[x/(1-x)] \tag{24}$$

The constant **a** is the proportionality constant of the linear Schulze-Hardy rule[1]. The constituent ions are adsorbed at the interface of the solid and the counter ions in an equivalent constant amount are at a given mean distance δ separated from the former. The variation of the concentration of the counter ions in the solution phase causes the variations of δ and $\Delta\varphi$, namely it causes the variation of the electrical part of the electrochemical potential of constituent and of counter ions, while the chemical potential (their amount!) of the adsorbed constituent ions remains constant. Therefore the definition of the constant **a** as given in ref. 1.

$$\mathbf{a} = \mu_A{}^{z-}_{\text{ads.}}\ 0.4343/z^- RT = \text{const.} \tag{25}$$

implies that the constituent ions are irreversibly adsorbed in a constant amount, as found experimentally, and it does not imply that the activity of constituent ions in the solution phase should be independent of their concentration, which conclusion was incorrectly drawn by Levine and Matijević[14].

4. *The dipole influence upon $\Delta\varphi$, δ and ζ — tension*

A consequence of the presence of dipoles in the system is that the outer layer will partly be formed by their oriented species. Their charges, whose sign is opposite to the sign of adsorbed constituent ions, will be at a given distance from the latter. Charges of a sign equal to the sign of adsorbed constituent ions will be oriented towards the liquid phase and will remain under its potential.

If M' is a dipole present in a constant concentration, then for concentrations practically smaller than $(\log a_M)_{x=0.5} - 1$ the outer layer will be mainly formed by oriented dipoles $(1 - x \to 1)$, while for concentrations larger than $(\log a_M)_{x=0.5} + 1$ it will mainly be formed by counter ions $(x \to 1)$ the range in between being the transition region. When two or more charged particles are present, the double layer tension and counter ion distance will be equal for all particles having to satisfy eqs. (22) and (23).

$$\text{For } z' = 2 \quad M' = H_2O \quad a_{H_2O} = \text{const.}$$

and

$$\Delta\varphi_{H_2O,\text{layer}} = \text{const.}/\delta_{H_2O,\text{layer}} = \text{const.}/\zeta_{H_2O,\text{layer}} = \\ = \Delta^0\varphi + 2\Delta^1\varphi + (RT/F) \ln a_{H_2O} \tag{26}$$

we obtain

$$\Delta\varphi = \Delta\varphi_{H_2O,\text{layer}} - (RT/F) \ln (1-x) \tag{27}$$

$$1/\delta = 1/\delta_{H_2O,\text{layer}} - (1/\delta_s) \log (1-x) \tag{28}$$

$$1/\zeta = 1/\zeta_{H_2O,\text{layer}} - (1/\zeta_s) \log (1-x) \tag{29}$$

These equations should be valid in aqueous systems. Since $\Delta\varphi$ and δ are not measurable by any direct method eq. (29) renders the only possibility for an experimental check of the theory in respect with the electrochemical entities characterizing the double layer.

On the log a_M-scale the values $\log(1-x)$ are functions of z and a_M and can be evaluated from eq. (24).

The plots showing eqs. (15) resp. (19) and eqs. (27), (28) or (29) are given in Fig. 2. where a scalar representation of eq. (24) is also shown for ions of different z. The plots $1/\delta$, $1/\zeta$ or $\Delta\varphi$ (eq. 15) vs. log a_M should be parallel

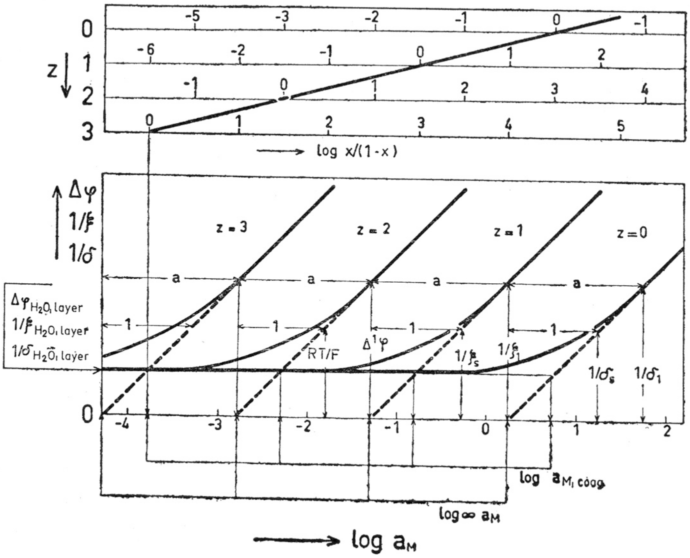

Fig 2.. Theoretical plots $\Delta\varphi$, $1/\delta$ or $1/\zeta$ (ordinate vs. log a_M (abscissa) according to eqs. 15, 19, 27, 28 and 29, and the variation of the function log $[x/(1-x)]$ (abscissa of the upper part) with log a_M (abscissa of the lower part) (eq. 24) for counter ions of different z.

lines with a slope $1/\delta_s$, $1/\zeta_s$ or 0.4343 RT/F for ions of different valencies. The vertical distance between the plots for ions whose valency difference is equal to 1 is equal to $1/\delta_1$, $1/\delta_1$ or $\Delta^1\varphi$ and the horizontal distance should be equal to **a**.

Eqs. (27), (28) and (29) are transitions from the tangents of eq. (15) to the horizontal $\Delta\varphi_{H_2O,\text{layer}} = 1/\delta_{H_2O,\text{layer}} = 1/\zeta_{H_2O,\text{layer}} = \text{const.}$ Eq. (15) is the tangent on eqs. (27), (28) or (29) for high a_M values when $(1 - x) \ll 1$ and $x \to 1$.

5. *Experimental verification*

An experimental check of the above equations is given in Fig. 3. which was drawn from the results of Fig. 57 in ref. 15, of Fig. 5. ref. 16 and of Fig. 4. ref. 18. The results of ref. 16 and 18 were plotted in the figure in such a way that the points in $10^{-2}N$ solutions matched the plot for $z = 3$ of ref. 15.

The former of these results were obtained by an electrophoretic technique, and no corrections of the ζ-tension for conductivity were probably made. The particles changed from the stable to the coagulated ones in the range of the concentrations varied. The latter results were obtained by a streaming current technique and the AgI were in the coagulated form since the concentrations were larger than the coagulation value. This figure confirms the present theory more than it could have been expected. The linear Schulze-Hardy rule constant **a** is equal to 1.5 for the difference between the log a_M values of bi- and trivalent ions, while for the valency of three and four it amounts to 1.75. The larger value for the latter ions may be explained by the tendency of Th^{4+} to recharge the negative AgI. Both values are practically equal to the values 1.5 to 1.8 which followed from adsorption and coagulation measurements[1,2,3,4,5].

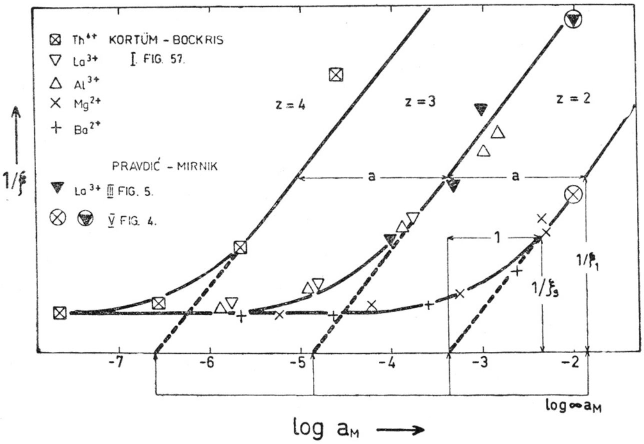

Fig. 3. Experimental plots $1/\zeta$ $(=1/u,\ u = \text{mobility})$ (arbitrary units, ordinate) vs. $\log a_M$ $(= \log c_M)$ obtained from refs. 16, 17 and 18.

DISCUSSION

The Galvani tension ψ defined by the Nernst formula

$$\psi = \psi^0 + (RT/nF) \ln (a_O/a_R) \tag{30}$$

is proportional to *p*I and the counter ion valency *z* and activity is not explicitly appearing in it (n is the difference of the oxidation numbers of 0 and R and not the valency of one of them, *e.g.* of I^-, ψ^0 is the standard tension.) No significant influence of neutral electrolytes upon the tension »Ag/AgI — reference electrode« couple could be observed, the variation of which is proportional to *p*I[23]. Contrary to this observation, log $a_{M,coag}$, ζ and γ are practically constant with *p*I (*p*Ag) in the negative stability region, and they are determined directly by the valency and concentration of counter ions as requested by the present theory. The first order influence of the valency of counter ions upon the ζ — tension is well demostrated by Fig. 4. ref. 16 and by Fig. 9. ref. 17. Therefore it is more logical to use the fixed charges double layer tension as a basic parameter of the theory than the total double layer tension ψ as derived from the Nernst formula. The constancy of the ζ — tension, log c_{coag} and the adsorbed quantity γ of counter ions with *p*I could be obtained from this tension only by introducing theoretical corrections of constant which are generaly accepted as invariable.[24,25]

Besides of these arguments, according to ref. 19 the physical existence of this double layer tension on a particle immersed in a solution is impossible. The thermodynamics on the basis of which the Nernst equation can be derived requires, that the electronic charge be produced on the particle by a redox reaction, while at the same time an equivalent charge has to be removed from the solution by redox reaction of opposite direction at the second electrode.

The system consisting of a particle under the reversible Galvani tension, which is determined by the Nernst equation does not include an excess of ionic charges in the liquid or in the outer layer. Therefore this excess of ionic charges could be removed only by a reaction of opposite direction[11] at the second electrode. If the second electrode is not present, as in the present case, the excess ions would remain in the liquid and the state of the system would not correspond to that upon which the thermodynamic deduction of the Nernst equation is based.

Equation (15) can be written in the form

$$\Delta\varphi = (RT/z^-F)\,[\ln(a_M/x) - \ln a_{A,z^-ads.}] + \Delta^0\varphi \tag{31}$$

For $\tilde{\mu}_{A^{z-},ads.} = \tilde{\mu}_{A^{z-}}$ it can be transformed into

$$\Delta'\varphi = (RT/z^-F)\,[\ln(a_M/x) - \ln a_{A^{z-}}] + \Delta^0\varphi \tag{32}$$

($\Delta^0\varphi$ are the corresponding standard values). Despite of the term $\ln a_{A^{z-}}$(for a_M and x = const.) this equation should not be considered as the Nernst equation because it was not deduced on the basis of a redox reaction but on the basis of adsorption processes. This latter equation is however in contradiction with experiments because neither method of measurement of the quantity of adsorbed constituent ions (in the AgI system) gave a proportionality between the logarithm adsorbed quantity and logarithm activity of constituent ions.

Otherwise the double layer tension derived from the Nernst equation could be defined by

$$\psi = \varphi_{\text{solid}} - \varphi_{\text{liquid}} \qquad (33)$$

contrary to the definition of $\Delta\varphi$ given by eq. (8). (φ_{solid} = inner electric potential of the solid phase).

The main and principal difference in the deduction of the IE-theory and of the extended DLVO-theory of Levine and Bell[24] as well as of that of Lyklema and Overbeek[25] is in the definition of the electric tension of this latter theory and in the calculation of actual values of the tension as a function of the activity of constituent ions. In these theories the tension defined by the Nernst equation is used.

The present double layer concept of fixed charges is based upon the assumption that the inner layer is formed by constituent (or surface active) ions which are strongly adsorbed. This assumption is justified by the experimental observation that the largest adsorbed amount of counter ions, which is supposed as being equal to the amount of adsorbed constituent ions, is independent of counter ion concentration when the latter is larger than their coagulation value[2]. On the other hand, the amount of adsorbed counter ions is diminished by only 10 to a maximum of 20% for an increase of 1 *p*I unit. At the same time a decrease of the specific surface of the particles *in statu nascendi* can be observed tyndallometrically. Therefore, it is concluded that in the region from *p*I = 1 to *p*I = 9 the amount of adsorbed constituent ions (as deduced from equivalency with the measured amount of adsorbed counter ions) is approximately independent of the activity of the constituent ions. This justifies the theoretical suppositions that the adsorption of constituent ions is due to a free energy change which is large compared to the changes for processes in the outer layer which are caused by variations of the activity of counter or constituent ions in the liquid.

Equations 17 and 18 are equivalent in respect to δ and $\log a_M = \log a_{M,\text{coag}}$ for $x = x_{\text{coag}}$ to eqs. (9) and (10) given by Težak[20] in 1949 resp. 1942 in order to explain the linear Schulze-Hardy rule of coagulation. By that time sufficient experimental evidence was already collected indicating the validity of this rule. Ideas of fixed charges and asosciation-dissociation equilibria similar to the present ones served as a basis for the deduction.

Težak used the concept of ion pairs in the double layer regarding them responsible for the stability and coagulation. In the present description Težak's ion pairs are the equivalent amounts of adsorbed constituent and counter ions in the inner and outer layers which are under an electrostatic tension.

Težak's designation »existence of ion pairs« should be considered as equivalent to the existence of nonuniformly distributed ion charges in the double layer and to the requirement of the present theory, that both kinds of ions (constituent and counter ions) in the double layer have to be present in equivalent amounts.

The same equation was repeatedly claimed as theoretically justified and confirmed experimentally by Matijević and coworkers[3,4,21].

Figures 2. and 3. explain why it is impossible to obtain illustrative results on ζ — tensions with ions of valency 1. The measured electrokinetic effect (transported volume, mobility, streaming potential, streaming current, sedimentation potential) is small here. Because of the high conductivity in high concentrations ($> 10^{-2}N$) it is impossible to increase sufficiently the factors causing the electrokinetic effect, namely the tension between the electrodes in electrophoresis and electroosmosis experiments, or the pressure in the case of streaming current measurements. In addition the ζ — tension at this concentration ($10^{-2}N$) is mainly determined by oriented dipoles and not by counter ions of valency one.

The measured coagulation values lie in the vicinity of the intersections of the $1/\zeta_{H_2O,layer}$ horizontal line with the $1/\zeta$ tangent in high concentrations of counter ions. A strict and quantitative check of the theory would require however a knowledge of the proportionality constants in eq. (11) for the stable and coagulated state. The same, a correction of the conductivity influence upon the evaluated ζ — tension would be necessary. For this purpose, the graphic method for the evaluation of such a corrected value, — of the »true« ζ — tension — as proposed by Ghosh and coworkers[22] could be recommended.

The same authors use for the determination of the »true« ζ — tension systems at »equicoagulating« concentrations. While the actual values of these concentrations were not cited by the authors, they can be considerd as those concentrations in which ions of different valencies cause equal rates of coagulation. Therefore these »equicoagulating« concentrations can be considered as equivalent to our coagulation values.

Fig. 3. should be considered as a quantitative confirmation of the validity of the linear Schulze-Hardy rule in electrophoresis. The shape of the plots at the same time confirms the present theory semiquantitatively.

The constancy of the linear Schulze-Hardy rule constant **a** is confirmed in it for the negative AgI system for the third time: this constant (**a** $= 1.5$ to 1.8) was obtained by coagulation measurements, by counter ion adsorption measurements and now by electrokinetic measurements. Besides of the fact that the plots eqs. (15) and (19) are of the type predicted by the theory, this former fact alone should be considered as a sufficient proof of the correctness of the present theory. (*cf*. ref. 5. Table 2)

The experimental and theoretical plots of $1/\zeta$ *vs.* logarithm counter ion concentration (Figs. 2. and 3.) explain why attempts to measure directly a critical ζ - tension of coagulation failed up to now[22]. This critical value was sought for in the vicinity of the coagulation concentration in which the »ζ-tension-concentration« function is complex, and in which the values continuously change from those measured in colloidal systems to those having coarse particles. In the present paper the critical ζ - tension was explained to be a value which can best be obtained as the intersection of the tangent on the $1/\zeta$ - tension function at high concentrations of the coagulating electrolyte with the horizontal tangent at low concentrations. The actually measured value in the coagulation concentration is experimentally not well defined and therefore its actual experimental determination was up to now unsuccessful.

The deduction of the IE theory is based [Eqs. (5),(6),(7)] analogously as the extended DLVO-theory of Levine and Bell[24] on the equality of electrochemical potentials of counter ions in the double layer and in the bulk of the solution (eq. 8 ref. 24a). While in the IE theory the deduction is based upon the activity of the total amount of counter ions in the double layer, into the extended DLVO-theory only the activity of that part of the counter ions in the double layer was introduced which are supposed to form the outer Helmholtz layer. The counter ions in the diffuse part of the double layer and in the inner Helmholtz layer were left out from the calculation of equality. Namely, the double layer was arbitrarily divided in three different regions with counter ions of different energies and with two different values of the dielectric constant. These and many other assumptions of the theory have as a consequence that more than ten different parameters were adjusted arbitrarily, none of which can be experimentally checked by a direct independent method. In support of the theory not even a qualitative similarity between theoretical and experimental plots »logarithm coagulation values against logarithm activity of constituent ions« could be quoted.

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SYMBOLS USED

a	proportionality constant of the linear Schulze-Hardy rule
a_i, ∞a_i	activity of an elementary particle in gramequivalents per litre and its value for $\delta \rightarrow \zeta \rightarrow \infty$ or $\Delta\varphi \rightarrow 0$
A	surface of particles per litre of sol
A^{z^-}, $A_{z^-\,ads.}$	constituent anion of valency z^- in the liquid phase and adsorbed in the inner layer
$(A_z M_{z^-})_{ads.}$	adsorbed ion pair »constituent ion — counter ion«
B^{z^+}	constituent cation of valency z^+ in the solid phase
const.	proportionality constant for a given equation
D	dielectric constant in the bulk liquid phase
${}^0D = \gamma/a_{M^0,coag.}$	standard distribution coefficient of the hypothetical nonexistent counter ion M^0 for $x = 1$
${}^zD = x\,\gamma/a_M$	distribution coefficient of a counter ion M of valency z
e	electron charge
E	electrical energy of a counter ion — constituent ion pair in the double layer
$E_{M,layer}$, $E_{H_2O,layer}$	electrostatic energy of counter ions M and of oriented H_2O molecules respectively in the outer layer
F	Faraday
$F_{M,layer}$, $F_{H_2O,layer}$	force between adsorbed constituent ions in the inner layer and counter ions M (and oriented H_2O molecules respectively) in the outer layer per litre of the system
H_2O, H_2C_{layer}	H_2O molecule in the liquid phase and oriented H_2O molecule in the outer layer respectively
M, M′, M^0	counter ions, or dipoles of valency z, z′ and $z = 0$, respectively in the liquid phase

M_{layer} , $M_{coag.}$	counter ions in the outer layer, and in the coagulation value concentration respectively
N	Avogadro-Loschmidt constant
r	distance from a point charge
R	gas constant
S	selectivity coefficient of counter ion exchange and adsorption
T	absolute temperature
x, x_{∞}	fraction (of σ) of counter ions M in the outer layer, or fraction of adsorbed ion pairs (of $\gamma - \sigma$) and the same for $\delta = \zeta = \infty$ or $\Delta\varphi = 0$
$1\text{-}x$, $1\text{-}x_{\infty}$	fraction (of σ) of oriented H_2O molecules in the outer layer or of hydrated adsorbed constituent ions of $(\gamma - \sigma)$ and the value of the same for $\delta = \zeta = \infty$ or $\Delta\varphi = 0$. In ion exchange experiments the fraction of the second counter ion M′
z, z'	valencies of counter ions (= 0, 1, 2, 3, 4) or dipoles (for the H_2O dipole $z' = 2$)
z^-	valency of the negative constituent ion present in excess
γ	total adsorbed amount of constituent ions in gram equivalents per litre of sol
δ, δ_{H_2O}	mean distance between the constituent ions in the inner layer and counter ions (or the positive charges of oriented H_2O molecules) in the outer
$\delta_{coag.}$	counter ion distance in the coagulation value concentration
δ_1, δ_s	decrease of the counter ion distance for a 10^a-fold and for 10-fold, respectively increase of concentration
ζ, ζ_1, ζ_s	electrokinetic tension: 1) variable, 2) correspoding to a 10^a-fold and 3) to a 10-fold variation of the concentration respectively
$\zeta_{H_2O,layer}$	electrokinetic tension measured in low concentration of counter ions when $(1-x) \rightarrow 1$
μ_i, $\mu_{i,ads.}$, $\mu_{i,layer}$	chemical potential of an elementary particle i (ion, ion pair, molecule) 1) in the liquid phase, 2) adsorbed in the inner layer, and 3) adsorbed in the outer layer respectively
μ_i^0	standard chemical potential of an elementary particle i
$\tilde{\mu}_i$, $\tilde{\mu}_{i,ads.}$, $\tilde{\mu}_{i,layer}$	electrochemical potential (free energy change) of an elementary particle 1) in the liquid phase, 2) adsorbed in the inner layer and 3) in the outer layer respectively
σ	quantity of adsorbed constituent ions which are neither hydrated nor associated with counter ions (in gram equivalents per litre of sol)

φ_{liquid}, φ	inner electric potential (absolute Galvani potential) in the liquid and solid phase
φ_{outer}	electrostatic potential arising at the mean distance $r = \delta$ from an adsorbed constituent ion
φ_+, φ_-, $\varphi_\pm$	electrostatic potentials arising from cations, anions and from both
$\Delta\varphi$, $\Delta^1\varphi$, $\Delta^s\varphi = RT/F$	double layer tension: 1) variable, 2) corresponding to a 10^a-fold, and 3) to a 10-fold change in concentration
ψ	Galvani tension defined by the Nernst formula

REFERENCES

1. M. Mirnik, *Nature,* **190** (1961) 689.
2. M. J. Herak and M. Mirnik, *Kolloid — Z.,* **168** (1960) 139; **179** (1961) 130.
3. B. Težak, E. Matijevič and K. F. Schulz, *J. Phys. Chem.* **59** (1955) 769.
4. E. Matijević, D. Broadhurst and M. Kerker, *J. Phys. Chem.,* **63** (1959) 1552.
5. M. Mirnik, *Nature,* **199** (1963) 555.
6. M. Mirnik, *Croat. Chem. Acta,* **34** (1962) 97.
7. J. P. Kratohvil, M. Orhanović and E. Matijević, *J. Phys. Chem.* **64** (1960) 1216.
8. M. Mirnik, F. Flajšman and B. Težak, *Kolloid — Z.* **185** (1962) 138.
9. M. Mirnik, F. Flajšman, K. F. Schulz and B. Težak, *J. Phys. Chem.,* **60** (1956) 1473.
10. E. Matijević and B. Težak, *Kolloid — Z.,* **125** (1952) 1.
11. P. Van Rysselberghe, *Electrochim. Acta,* **1961** 257.
12. F. L. Tye, *J. Chem. Soc.* **1961** 4784.
13. R. J. Hunter, *J. Colloid Sc.,* **16** (1961) 191.
14. S. Levine and E. Matijević, *Nature,* **197** (1963) 1196.
15. G. Kortüm and J. O'M. Bockris, *Textbook of Electrochemistry* Vol. II. p. 385. Elsevier Publishing Company, Amsterdam 1951.
16. M. Mirnik and V. Pravdić, *Croat Chem. Acta,* **30** (1958) 213.
17. V. Pravdić and M. Mirnik, *Croat. Chem. Acta,* **32** (1960) 1.
18. V. Pravdić and M. Mirnik, *Croat Chem. Acta,* **32** (1960) 75.
19. M. Mirnik, *Kolloid — Z.,* **185** (1962) 66.
20. B. Težak, *Z. Physik. Chem.,* **191**A (1942) 270, *Arhiv kem.* **22** (1950) 26.
21. E. Matijević, *Chimia,* **9** (1955) 287.
22. B. N. Gosh and P. K. De, *Kolloid — Z.,* **161** (1958) 107.
23. M. Mirnik and B. Težak, *Arhiv kem.,* **23** (1951) 14; M. Mirnik and R. Despotović, *Croat. Chem. Acta,* **32** (1960) 139.
24. S. Levine and G. M. Bell, *J. Colloid Sci.,* **17** (1962) 838; *J. Phys. Chem.* **67** (1963) 1408.
25. J. Lyklema and J. Th. G. Overbeek, *J. Colloid Sci.,* **16** (1961) 501; *Ibid.,* **16** (1961) 595.
26. M. Mirnik and B. Težak, *Trans. Faraday Soc.,* **50** (1954) 65.

IZVOD

Koncept diskretnih električnih naboja u teoriji elektrokinetičkih pojava

M. Mirnik

Opisan je model električkoga dvosloja sa diskretnim nabojima fiksiranim na površini koloidne čestice. Izvedena je kvantitativna veza između elektrokinetske pokretljivosti i koncentracije protuina uzimajući u obzir dipolni karakter vodenih molekula. Kod izvoda su primijenjeni elementarni principi kemijske i elektrokemijske termodinamike, elektrostatike i princip elektroneutralnosti sistema. Raspoloživi rezultati o elektrokinetičkoj gibljivosti interpretirani su u svijetlu predložene teorije te je pokazano da je kvantitativno potvrđuju. Za potvrdu ostalih teorija električnog dvosloja slični rezultati nisu upotrebljeni.

Pokazano je da teorijom traženo linearno Schulze-Hardy-jevo pravilo vrijedi i za koagulacione vrijednosti i izmjenu protuiona.

Izvedena je definicija električne napetosti dvosloja fiksnih naboja i pokazano je da se ta razlikuje od Galvanijeve napetosti elektroda koja je definirana Nernstovom jednadžbom.

INSTITUT »RUĐER BOŠKOVIĆ« I
FIZIČKO-KEMIJSKI INSTITUT
PRIRODOSLOVNO-MATEMATIČKI FAKULTET
ZAGREB

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