CCA-582 541.18.046.7
Conference Paper

Ion Exchange Theory of Coagulation and its Experimental Verification

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Contribution No. 149 of the Laboratory of Physical Chemistry.

On the basis of the discrete (fixed) ion charge double layer model the principles of the derivation of the discrete charge double layer potential equations

$$\Delta\varphi = \Delta^{\circ}\varphi + [z\,\mathbf{a} + \ln (a_M/x\sigma)]\,(RT/F) \text{ and}$$

$$\Delta\varphi' = \Delta^{\circ}\varphi + \{z'\,\mathbf{a} + \ln [a_M/(1 - x)\,\sigma]\}\,(RT/F)$$

are reviewed. The discrete charge double layer potential is used as the basic electric parameter of the theory, and the corresponding potential equations are valid when two counter ions or a counter ion and a dipole are in equilibrium with fixed constituent ions in the system »colloidal ionic particle—solution«.

From the discrete charge potential equations, the equations of the classical thermodynamics of ion exchange have been obtained: the separation factor equation, the equilibrium constant (mass action law) equation using activities and equivalent ionic fractions and Strickland's equation for the determination of ion valencies by the ion exchange method.

Furthermore, the linear Schulze-Hardy rule has been derived for coagulation, for electrokinetics, for counter ion exchange and for adsorption in the general form

$$\ln (a_M/a_{M^{\circ}})_{coag} = \ln \; (a_M/a_{M^{\circ}})_{\xi\,=\,const} = \ln (a_M/a_{M^{\circ}})_{x\,=\,const} = -z\mathbf{a}$$

The equation defining the theoretical variation in the electrokinetic potential with the adsorbed amount of stabilizing particles is given in the form

$$1/\zeta = 1/\zeta_{H_2O,\,layer} - (1/\zeta_s) \ln (1 - x)$$

where the variation of the fraction of adsorbed stabilizing particles $1 - x$ and of the counter ions x, with activity a_M ($a_{M^{\circ}}$ = constant) and valency z of the counter ions is defined by:

$$\ln [x/(1 - x)] = \ln [a_M/(a_{M^{\circ}})_{x\,=\,0.5}\,] + z\mathbf{a}$$

The proportionality constant **a** of the linear Schulze-Hardy rule is defined by:

$$\mathbf{a} = \Delta^{1}\varphi\, F/RT = \mu_{A^{z-},\,ads}\,/RT\,z^{-}$$

It is thus proportional to the chemical potential of the fixed constituent ions.

The regularities and rules governing isoelectric coagulation and mutual isoelectric and counter ion coagulation in the three silver halide systems have been incorporated into the theory.

A review of published experimental results is given, showing that all the derived equations and rules have been satisfactorily confirmed by experiment.

A review of the published criticisms of the ion exchange theory is also given and some of the points of the criticism are discussed.

The main and basic differences, in principle, between the ion exchange theory and the various versions of the Derjaguin-Landau-Verwey-Overbeek theory are pointed out. Instead of the surface or Nernst potential of the latter theory the discrete charge double layer potential is used as the basic electric parameter. The discrete charge potential is defined thermodynamically by the basic experimental parameters: the valency, the activity, the fraction or the amount of the adsorbed counter ion and the valency and the chemical potential of the adsorbed constituent ion. The Nernst potential is defined by the ratio of the activities of the oxidized and reduced states of the constituent ion and by the difference of their oxidation numbers. At least one of the latter activities is not defined in the colloidal system. The cited experimentally justified parameters have been introduced into the DLVO theories using experimentally not proved and thermodynamically not justified assumptions.

A. INTRODUCTION

The theory of the double layer of ionic solids in contact with electrolyte solutions described in this review is based on the concept of discrete charges, known in the theory of ion exchange as the concept of fixed or discrete charges. The theory is derived from the point of view of classical thermodynamics. It will be shown that a large number of experimental results on coagulation and stabilization, on counter ion and constituent ion adsorption, on potentiometry and electrokinetics of silver halide and other colloidal systems may be quantitatively or semiquantitatively explained by the ion exchange theory of coagulation.[1-8]

Experimental and theoretical data on which the ion exchange theory is based have been published in the course of the last 15 to 20 years. The name ion exchange (IE) was chosen after the observation has been made that the classical model system of colloid chemistry, the silver iodide system, is an ideal counter ion exchanger, and that an exchange mechanism should be made responsible for the stabilization-coagulation process. It is the purpose of this review to describe and explain the IE theory systematically and to predict on the basis of the IE theory the typical colloidal phenomena of ionic solids. Subsequently a comparison of the predicted rules with experimental observations in silver halides will demonstrate the versatility of the IE theory. In this way a strong support for its basic correctness will be given. Some sporadic data from other systems suggest that the IE theory is applicable, besides to the silver halide and similar ionic systems, also to other colloidal systems.

The IE theory based on a single double layer model was originally developed step by step as a result of attempts to explain various experimental findings. In Chapter B of this review the whole theory will be derived in a systematic way. The discrete charge double layer and its electric parameter will be described first. Its basic electric parameter — the discrete charge double layer potential — will subsequently be used to derive the main rules and equations of the theory.

In Chapter C a comparison between theoretical postulates obtained in Chapter B and published experimental results obtained in various laboratories are presented. In this way it is shown that the theory is capable of explaining the majority of observations made in various experimental fields of the silver halide systems. The silver halides are the most investigated model system of colloid chemistry.

Chapter D gives a discussion on the published criticism of the ion exchange theory of coagulation.

Chapter E is a comparative discussion of the Derjaguin-Landau-Verwey-Overbeek double layer theory and its extensions by Levine, and by Lyklema and Overbeek.

B. THEORETICAL PART

1. *Discrete Charge Double Layer*[1]

The theory of the discrete charge double layer is based on the assumption that discrete charges in the form of constituent ions A^{z-} (*e. g.* I^-) or B^{z+} (*e. g.* Ag^+) of valency z^- or z^+ or charged surface active agents (in ion exchangers the chemically bound charges of dissociated active groups) are situated at the interface of colloidally dispersed ionic or other solids, in an amount determining the specific surface charge density of particles having an average surface area A. Furthermore, it is assumed that the surface charge density σ is so small that the electrostatic potential φ around a single charge is not influenced by other charges of equal sign. In other words, surface electric charges are considered as discrete independent charges fixed at the surface of the particles.

On the other hand, the counter ions, although attracted by the electrostatic coulombic forces, due to the thermal motion and electrochemical equilibrium, are in a statistical distribution around the fixed ions. An elementary treatment analogous to that of the ion distribution around the central ion by the Debye-Hückel theory should be applied, also in the present case, to the counter ions. The variation in the electrostatic potentials and counter (an)ion densities with distance r from a central (cat)ion is shown in Fig. 1. The units are: $\varkappa r$ for distance, $z^+e\varkappa/D$ for potential, and $z^+e\varkappa^3/4\pi$ and $z^+e\varkappa$ resp. for charge density. $\delta = 1/\varkappa$ is the Debye-Hückel radius. The same plots, however, symmetrical with the $\varkappa r$ axis would be valid for a fixed central anion.

The curve

$$\varphi_+ = (z^+e\varkappa/D)\,(1/\varkappa r) \tag{1}$$

shows the variation of the electrostatic potential φ_+ according to the Coulomb's equation. The elementary electron charge is e and D is the dielectric constant. The Debye-Hückel anion (»volume«) density $\bar{\varrho}_-$ function reads

$$\bar{\varrho}_- = (D\varkappa^2\bar{\varphi})/4\,\pi = (-\,z^+e\varkappa^3/4\,\pi)\; e^{-\varkappa r}/\varkappa r \tag{2}$$

$\bar{\varphi}$ is the average potential equal to the electrostatic potential of the central cation plus the anion density potential, and is given by

$$\bar{\varphi} = (z^+e\varkappa/D)\; e^{-\varkappa r}/\varkappa r \tag{3}$$

The anion density function $\bar{\varrho}_-$ multiplied by the sphere surface $4\,r^2\pi$ gives anion »distance« density function $\bar{\varrho}_-(r)$, *i. e.* it indicates the probability that an anion could be found at the distance $\varkappa r$:

$$\bar{\varrho}_-(r) = 4\,r^2\pi\bar{\varrho}_- = -\,(z^+e\varkappa)\,(\varkappa r)\; e^{-\varkappa r} \tag{4}$$

The »distance« density function $\bar{\varrho}_-(r)$ is a plot with a maximum in absolute values at the distance $\delta = 1/\varkappa$. It follows therefore that, according to the Debye-Hückel theory, the radius of the ionic atmosphere $1/\varkappa$ is in fact the statistical mean distance δ between the ions of a binary electrolyte and at the same time the most probable distance between the ions of opposite charge.

The same relations can be assumed also in the case when the central ion is fixed at an interface, while the value $\varkappa$ for the fixed ion-counter ion pair is in general different from the $\varkappa$ value of the same ions in the liquid phase. However, the value $\delta = 1/\varkappa$ for the ions in the layer will depend on the electrochemical potential of the same ions in the liquid phase (see eq. 6).

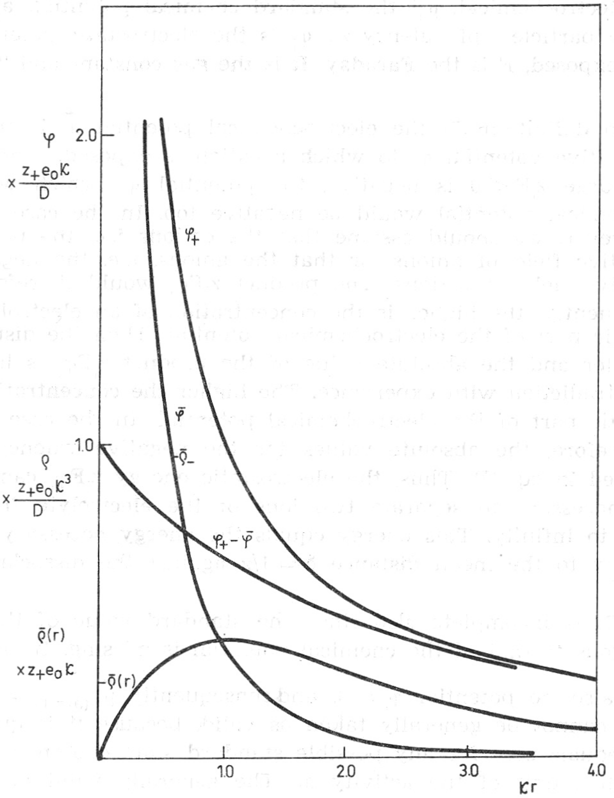

Fig. 1. Debye-Hückel potential and charge density functions. φ_+ electrostatic potential due to a cation at $\varkappa r = 0$, $\bar{\varphi}$ average potential due to the electrostatic potential φ_+ and the ion (anion, counter ion) atmosphere potential, $-(\varphi_+ - \bar{\varphi})$ ion (anion, counter ion) atmosphere potential, $\bar{\varphi}_-$ anion charge density(volume), $\bar{\varrho}_-$ (r) anion »distance« charge density with a maximum at $\varkappa r = 1$.

The average potential exhibited by the counter ion atmosphere upon the central cation at $r = 0$, can be calculated from eq. (4) in the following way:

$$\bar{\varphi}_- (r = 0) = \int_0^\infty [\bar{\varrho}_- (r)/Dr] \, dr = -\int_0^\infty (z^+ e \varkappa^2/D) \, e^{-\varkappa r} \, dr = -\mathbf{z^+ e \varkappa / D} \tag{5}$$

This result is equivalent to that obtained by the classical expansion of the equation for the average anion atmosphere potential $\bar{\varphi}_- = \bar{\varphi} - \varphi_+$ into infinitesimal series for $r = 0$.

One can also assume that the same potential, however of the opposite sign, is the average potential to which the counter ions are exposed in the double layer and that their electrochemical potential $\tilde{\mu}_{M,\,\mathrm{layer}}$ is defined by it.

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

$$\tilde{\mu}_{M,\,\mathrm{layer}} (r = \delta) = \tilde{\mu}_M (r \to \infty) \tag{6}$$

The electrochemical potentials are conventionally defined by:

$$\tilde{\mu}_i = \mu_i^o + RT \ln a_i + z_i F \varphi_i \tag{7}$$

Here $\tilde{\mu}_i$ is the electrochemical, μ_i^o the standard chemical potential, a_i the activity of an elementary particle i of valency z_i, φ_i is the electrostatic potential to which the particle i is exposed, F is the Faraday, R is the gas constant and T the absolute temperature.

According to definition (7) the electrochemical potential $\tilde{\mu}_i$ is the higher the higher is the positive potential φ_i to which a cation is exposed. Since in the case of anion the charge $z_iF < 0$ is negative, the potential φ_i which would cause a higher electrochemical potential would be negative too. In the case of dissociated electrolytes, however, we should assume that the cations *i. e.* the positive charges are in the negative field of anions, or that the anions, *i. e.* the negative charges, are in the positive field of cations. The product $z_iF\varphi_i$ would therefore be always negative. Consequently, the higher is the concentration of an electrolyte the lower is the electrostatic part of the electrochemical potential. Then the distance between the ions is smaller and the absolute value of the product $z_iF\varphi_i$ is higher. This is obviously in contradiction with experience. The higher the concentration the higher is the electrostatic part of the electrochemical potential. In the case of dissociated electrolytes, therefore, the absolute values for the negative valency or potential should be inserted in eq. (7). Thus, the electrostatic energy $z_iF\varphi_i$ can be explained as the energy necessary to separate two ions of the electrolyte from the mean distance $\delta = 1/\varkappa$ to infinity. This energy equals the energy necessary to bring two ions from infinity to the mean distance $\delta = 1/\varkappa$ against the dissociating forces of the solvent.

Definition (7) is incomplete also since the standard value of the electrostatic potential, analogous to that of the chemical potential is missing. It can be assumed that for $a_i = 1$ also the potential $\varphi_i = 0$, and consequently $\tilde{\mu}_{i\,(a_i=1)} = \mu_i^o$. However, this assumption cannot be generally taken as valid, because it is quite impossible that φ_i always equals zero for any possible standard state chosen, *i. e.* for any, by agreement selected, unit of the activity a_i. The generally valid definition of the electrochemical potential in a phase should therefore read

$$\tilde{\mu}_i = \mu_i^o + RT \ln a_i + z_i F (\varphi_i - \varphi_i^o) \tag{8}$$

in which the constant standard electrostatic term φ_i^o was inserted. Then for $\tilde{\mu}_i = 0$ and $\mu_i = \mu_i^o + RT \ln a_i = 0$ or for

$$\tilde{\mu}_i = \mu_i^o + RT \ln a_i \tag{9}$$

$\varphi_i = \varphi_i^o \neq 0$. Thus φ_i^o is a standard electrostatic potential independent of the chemical potential of the particle i, and

$$\tilde{\mu}_{i\,(a_i=1,\ \varphi_i=0)} = \mu_i^o - zF\varphi_i^o = \tilde{\mu}_i^o \tag{10}$$

can be, for $a_i = 1$ and $\varphi_i = 0$ considered a standard electrochemical potential.

For the counter ion in the layer and in the solution phase the electrochemical potentials should therefore be defined by:

$$\tilde{\mu}_{M,\,\text{layer}} = \mu^o_{M,\,\text{layer}} + RT \ln (x\sigma/z) + zF (\varphi_{\text{outer}} - \varphi^o_{\text{outer}}) \tag{11}$$

and

$$\tilde{\mu}_M = \mu_M^o + RT \ln (a_M/z) + zF (\varphi_{\text{liquid}} - \varphi^o_{\text{liquid}}) \tag{12}$$

Here $\tilde{\mu}_{M,\,\text{layer}}$ and $\tilde{\mu}_M$ are the electrochemical potentials of the counter ion M in the layer and the liquid respectively, $\mu^o_{M,\,layer}$ and μ^o_M the standard chemical potentials, σ is proportional or equal to the average number of dissociated ions adsorbed per single colloidal particle, or per unit surface area, or per surface area per liter of the system, in equivalents. x is the equivalent ionic fraction of the counter ion M_{layer} present in the layer at the average potential φ_{outer} and at the mean distance δ:

$$\varphi^o_{outer} = \varphi_{outer} \text{ when } \tilde{\mu}_{M,\,layer} = \mu^o_{M,\,layer} + RT \ln (x\sigma/z)$$

and

$$\varphi^o_{liquid} = \varphi_{liquid} \text{ when } \tilde{\mu} = \mu^o_M + RT \ln (a_M/z).$$

Most conveniently a_M can be expressed in equivalents per liter of system, z is the valency of the counter ion and $x\sigma/z$ and a_M/z are the quantities of M in the layer and the liquid phase in moles and proportional to the corresponding molar ratios or activities. The difference of eqs. (11) and (12) reads

$$z\,(\varphi_{outer} - \varphi_{liquid}) = (\mu^o_M - \mu^o_{M,\,layer})/F + z\,(\varphi^o_{outer} - \varphi^o_{liquid}) + (RT/F) \ln (a_M/x\sigma) \quad (13)$$

We define

$$\Delta\varphi = z\,\Delta\varphi_M = z\,(\varphi_{outer} - \varphi_{liquid}) \quad (14)$$

as the actual average potential to which the counter ions are exposed in the layer relative to the potential of the electroneutral liquid phase φ_{liquid}. If the counter ion in the layer were replaced by ions of valency one, the latter ions would be at the potential $\Delta\varphi = z\Delta\varphi_M$, while their electrochemical potential would remain constant.

The potential $\Delta\varphi$ is called the »discrete or fixed charge double layer potential«.

We can define

$$\Delta^o\varphi = (\mu^o_M - \mu^o_{M,\,layer})/F \quad (15)$$

as the standard electrostatic potential determined by the standard free energy, *i. e.* the difference of standard chemical potentials for the counter ion distribution between the layer and solution phase. It is assumed constant for all ions because these are considered ideal charged particles equal in all properties except in charge. Namely, all the specific effects like specific adsorption, ion polarization, ion hydration, hydrolysis and others are neglected.

The equality

$$\Delta^1\varphi = \varphi^o_{outer} - \varphi^o_{liquid} \quad (16)$$

defines the variation in $\Delta\varphi$ caused by the variation of the valency of the counter ion by unity at its constant distribution coefficient $D_M = x\sigma/a_M$ *i. e.* when the counter ion is replaced in a fictive experiment by a second counter ion with its valency differing by one, while their chemical potentials in the layer and liquid phase remain the same.

If a second counter ion M′ of valency z′ is present in the same system its equivalent ionic fraction in the layer must be $1 - x$ because it must be

$$x\sigma + (1 - x)\,\sigma = \sigma \quad (17)$$

Since we assume that both ions are ideal charged particles equal in all properties except in charge $\Delta^o\varphi = \Delta^o\varphi'$.

Then the »discrete or fixed charge double layer potential« equations for two ions read:

$$\Delta\varphi = \Delta^o\varphi + z\Delta^1\varphi + (RT/F) \ln (a_M/x\sigma) \quad (18)$$

and

$$\Delta\varphi = \Delta^{\circ}\varphi + z'\Delta^{1}\varphi + (RT/F) \ln [a_{M'}/(1 - x)\,\sigma] \tag{19}$$

In both eqs. σ can be replaced by γ or $\gamma - \sigma$ with a corresponding change in $\Delta^{\circ}\varphi$ if the assumption is made that the total specific adsorbed amount of the not dissociated + dissociated counter ion γ and the amount or activity of the not dissociated part of the counter ion-constituent ion electrolyte $\gamma - \sigma$ are constant.

Then the sum

$$(\Delta^{\circ}\varphi + z\Delta^{1}\varphi)\, F = \Delta\tilde{\mu}^{\circ}_{M} \tag{20}$$

can be considered the standard electrochemical potential difference — the standard free energy — for the counter ion distribution between the solution and the layer phase at $a_M/x\,\sigma = 1$.

Fig. 2 represents graphically the functions discussed in the present Chapter.

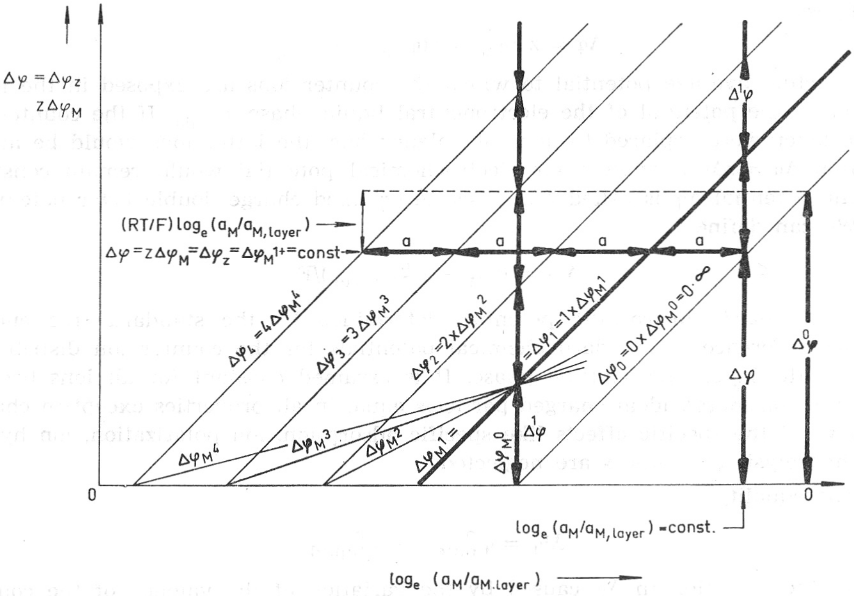

Fig. 2. Plots of $\Delta\varphi = z\,\Delta\varphi_M$ and $\Delta\varphi_M$ against $\log_e(a_M/a_{M,\,layer})$ for ions M of valency z=1, 2, 3, 4.

2. *Thermodynamics of Counter Ion Exchange*[9]

The ion exchange equilibria can be expressed by the following constants defining equilibrium concentrations or activities: the thermodynamic equilibrium constant K_a (see eq. 22) using a suitable unit for activity, or the analogous equilibrium constant using activity ratios K_α (see eq. 23), and the separation factor S (see eq. 21). The equilibrium constants K_a and K_α were normally derived thermodynamically using the chemical potentials and not the electrochemical ones. A theoretical explanation of S as well as the interrelation between K_a, K_α and S has not been given as yet. In this chapter a suggestion is given how to explain theoretically the difference between the cited constants and their meaning on the basis of the fixed charge model of ion exchangers using instead of the chemical the electrochemical potentials, and the fixed charge double layer potential equations (18) and (19).

When two counter ions M and M′ are in equilibrium in the double layer their electrostatic and chemical free energies must be equal, namely $z\Delta\varphi_M = z'\Delta\varphi_{M'}$ and therefore $\Delta\varphi = \Delta\varphi'$. Then by elemination of $\Delta\varphi$, $\Delta\varphi'$ and $\Delta^o\varphi$ one obtains from eqs. (18) and (19) the equation

$$S = \exp (z' - z)\, \Delta^1\varphi\, F/RT = a_M (1 - x)/a_{M'}\, x = \alpha (1 - x)/x (1 - \alpha) \qquad (21)$$

S is the well known separation factor or selectivity coefficient of ion exchange. It is explained here as a constant for a pair of ions determined by the standard electrostatic potential $\Delta^1\varphi$ of the discrete charge double layer.

The separatioin factor S equation was derived empirically in the AgI, I system (See Chapter C 2).

Assuming that the sum of the activities of both counter ions in the liquid equals the mean activity of all anions Y^- present, namely that $a_M + a_{M'} = a_{Y^-}$, one can write $a_M = \alpha\, a_{Y^-}$ and $a_{M'} = (1 - \alpha)\, a_{Y^-}$ where α and $1 - \alpha$ are the equivalent ionic fractions of the counter ions in the liquid.

By elimination of $\Delta^1\varphi$ from eqs. (18) and (19) one obtains two definitions of the ion exchange equilibrium constant: K_a and K_α, depending on whether the activities are expressed on the normality or the molarity scale, or as equivalent ionic fractions, namely:

$$K_a = \exp (z' - z)\, (\Delta\varphi - \Delta^o\varphi)\, F/RT = [a_M/x\gamma]^{z'}\, [(1 - x)\, \gamma/a_{M'}]^z \qquad (22)$$

and

$$\mathbf{K}_\alpha = \exp (z' - z)\, [(\Delta\varphi - \Delta^o\varphi)\, F/RT - \ln (a_{Y^-}/\gamma)] = [\alpha/x]^{z'}\, [(1 - x)/(1 - \alpha)]^z \qquad (23)$$

In the conventional definitions of the ion exchange equilibrium constants the electrostatic term $\Delta\varphi$ was neglected because the latter constants were derived from the chemical potentials only and defined by the standard chemical free energy (see eq. (15)). If we consider the fixed charge model of ion exchange as correct in principle the electrostatic term $\Delta\varphi$ should also be applied and the electrochemical potentials should be used for the derivation of the various equilibrium constants. The result are eqs. (22) and (23).

According to eq. (18) the parameter K_a would be constant for an ideal ion exchanger only if $\Delta\varphi$ were constant. The latter can be constant only if the total electrolyte activity in the liquid a_{Y^-} were constant.

On the other hand, in an ideal exchanger the parameter K_α would be constant for any a_{Y^-} value because according to eqs. (18), (19) for α/x = const and $(1 - \alpha)/(1 - x)$ = const. the difference $\Delta\varphi\, F/RT - \ln a_{Y^-}$ should be constant for all values of a_{Y^-}.

Since in many practical ion exchangers the parameter K_a does not display a very great variation, its tendency to constancy should be explained by the constancy of $\Delta\varphi$. The electrostatic potential $\Delta\varphi$ could be assumed constant and independent of a_{Y^-} in ion exchangers of high charge density, because its values is always higher than the reversible value derived from eqs. (18), (19) and (22), (23) resp.

Parallel to this explanation of high $\Delta\varphi$ potentials in high capacity ion exchangers, the explanation given by a high degree of association of the »fixed charge-counter ion« electrolyte can be considered. Then is the free energy of the associated and adsorbed electrolyte determined by its chemical potential only, and the exchange equilibrium constant is determined by the free energy for the transition from the dissociated electrolyte in the bulk to its associated and adsorbed state in the layer. The product $\Delta^{\circ}\varphi F$ (eq. (15)) is then the standard free energy for the transport of one mole of the electrolyte »fixed constituent ion — counter ion« from its dissociated state in the liquid to its associated, therefore electroneutral adsorbed state in the layer.

The potential $-\Delta\varphi$ corresponds to the potential of the ionic atmosphere of the Debye-Hückel theory at $r \rightarrow 0$. It is the potential exhibited by the statistical distribution of all ions surrounding the fixed ion. However, for a dissolved electrolyte, the variation of the ionic atmosphere potential with the concentration represents a minor part of the total (chemical plus electrostatic) free energy variation, while for the electrolyte »fixed ion — counter ion«, the chemical free energy is essentially constant, because the charge density is constant when $x = \text{const}$. The variation of the activity of the counter ion in the liquid causes therefore primarily the variation of the electrostatic energy, *i. e.* of the potential $\Delta\varphi$.

From the same ion exchange equilibrium constant expression (22) Strickland's[27] expression for the experimental determination of ion charges can be derived. If the chemical activity of the ion M is very low, *e. g.* a tracer concentration of a radionuclide of a high specific radio activity, and the chemical activity of the ion M′ is systematically varied, then $a^{z}_{M'} > a^{z'}_{M}$, $x^{z'} < 1$ and $1 - x = 1$, and eq. (22) can be written in the form

$$\ln (1/D_M) = \ln (a_M/x\gamma) = (z/z') \ln a_{M'} - (z/z') \ln (K_a^{1/z}/\gamma) \qquad (24)$$

The distribution coefficient of the radioactive ion $D_M = x\gamma/a_M$ can be determined by the ratio of radioactivities in the exchanger and the liquid, as a function of the logarithm concentration of the ion M′. The slope of the plot, z/z', determines the unknown valency z' supposing that z is known.

3. *The Linear Schulze-Hardy Rule in Counter Ion Exchange and Coagulation*

The importance of the valency of counter ions present in sols was found very early as a major factor determining the stability or the coagulation of the sol. It was found namely that the higher is the valency of the ion the lower is its concentration causing the coagulation or the same constant adsorbed fraction. The analogous observation in ion exchange is that the higher is the valency of the exchanging ion the higher is the amount of the ion in the exchanger. Many efforts were made to formulate the quantitative influence of the valency of the coagulating counter ions upon the minimum concentration necessary to induce coagulation *i. e.* upon the coagulation value. The above qualitative relation is known as the Schulze-Hardy rule. The theoretical influence of the valency of the exchanging ions upon the adsorption and the exchange can be derived as follows:

One can assume, as the basis for thermodynamic considerations, that the adsorbed electrolyte »counter ion — constituent ion« is partly associated and the association — dissociation equilibrium can therefore be represented by the equations

$$(A_z M_{z^-})_{ads} \leftrightharpoons z\,A^{z-}_{ads} + z^- M_{layer} \qquad M_{layer} \leftrightharpoons M$$

$$(A_{z'} M_{z^-})_{ads} \leftrightharpoons z' A^{z-}_{ads} + z^- M'_{layer} \qquad M'_{layer} \leftrightharpoons M'$$

A^{z-}_{ads} are the adsorbed negative (or positive) constituent ions for which we assumed in the preceding section that they represent discrete point charges fixed on the surface of the solid by a mechanism which is not electrostatic. These are firmly bound in such a way that the variation in a broad range of the counter ion concentration and the constituent ion concentration does not cause any variation of their amount in the surface. Consequently their chemical potential can be assumed as having a constant limiting value. The zero free energy condition at equilibrium is defined by the equalities:

$$\mu^{o}_{AM,\,ads} + RT\ln\left[(\gamma - \sigma)x/zz^{-}\right] = z\,\mu_{A,\,\overset{z-}{ads}} + z^{-}\mu^{o}_{M} + z^{-}RT\ln(a_M/z) + zF\,\Delta\varphi_M \tag{25}$$

and

$$\mu^{o}_{AM',\,ads} + RT\ln\left[(\gamma - \sigma)(1 - x)/z'z^{-}\right] = z'\mu_{A,\,\overset{z-}{ads}} + z^{-}\mu^{o}_{M'} + \\ + z^{-}\,RT\ln(a_{M'}/z') + z'F\,\Delta\varphi_{M'} \tag{26}$$

In the preceding section an explanation for the assumption of the equality $\mu^{o}_{M'} = \mu^{o}_{M}$ was given and analogously, with the same explanation, also the equality $\mu^{o}_{AM',\,ads} = \mu^{o}_{AM,\,ads}$ should be valid. Also $zF\Delta\varphi_M = z'F\Delta\varphi_{M'}$. Then for a simpler case of $z^{-} = 1$ the difference of these two eqs. gives

$$RT\ln S = RT\ln\left[a_M(1 - x)/a_{M'}x\right] = (z' - z)\,\mu_{A,\,\overset{-}{ads}} \tag{27}$$

represented by Fig. 3.

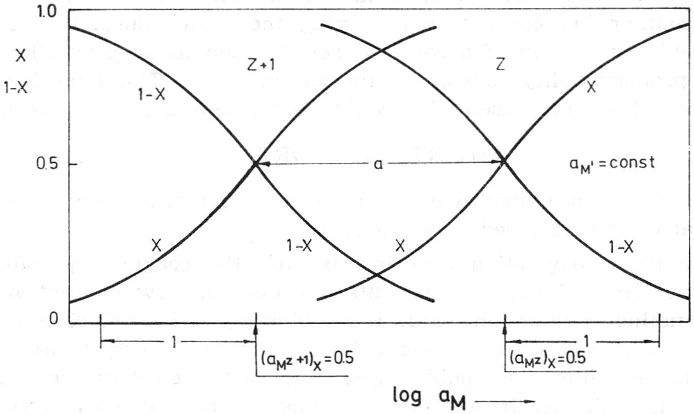

Fig. 3. Plots of x and 1—x against $\log_{10}a_M$ (Eqs. 27, 29, 30, 32) for ions of valency z an z+1 shifted for the parameter **a**. The activity of a counter ion $a_{M'}$ = const in both cases.

The parameter $\mu_{A,\,\overset{-}{ads}}$ should bo assumed constant for an ionic solid of a constant dispersity and at least for experimental conditions in which the activity of the excess constituent ion A^{z-} is kept constant. This supposition is supported by the following description of experiments. In experiments with coarse AgI sols the charge density σ and, under certain experimental conditions in coagulated suspensions also γ, the total adsorbed amount per mole of AgI were found constant. The constancy of $\mu_{A,\,\overset{-}{ads}}$ is justified also because the chemical potential $\mu_{A,\,\overset{-}{ads}}$ can be defined by

$$\mu_{A,\,\overset{-}{ads}} = \mu^{o}_{A,\,\overset{-}{ads}} + RT\ln\gamma = \mu^{o}_{A,\,\overset{-}{ads}} + RT\ln\sigma = \text{const.} \tag{28}$$

and σ and γ were found constant under reproducible conditions. Thus, experimental evidence suggests that for the purpose of theoretical interpretation the chemical potential $\mu_{\mathrm{A},\,{}^{-}_{\mathrm{ads}}}$ can be assumed a constant limiting value. In this way the constancy of the separation factor S for a given pair of ions is explained.

We assume two fictive experiments in which $x = \mathrm{const}$, $1 - x = \mathrm{const}$, $a_{M'} = \mathrm{const}$ and $z' = \mathrm{const}$. In the first experiment the counter ion added has the valency $z_1 = z$ and in the second experiment $z_2 = z + 1$. The difference of two corresponding eq. (27) for z_1 and z_2 gives the possibility of defining the experimentally accessible parameter a by (See Fig. 3)

$$a = \ln (a_{M^{z}}/a_{M^{z+1}})_{x=\mathrm{const},\ a_{M'}=\mathrm{const}} \tag{29}$$

For a pair of ions $z_1 = z$ and $z_2 = 0$ one obtains

$$\ln (a_M/a_{M^o})_{x=\mathrm{const},\ a_{M'}=\mathrm{const}} = -za \tag{30}$$

The ion of valency $z = 0$ is of course nonexistent, but it is used here to define physically the constant of the equation a_{M^o}. This constant can be derived from experimental adsorption or exchange values by extrapolation to $z = 0$. Its definition follows for $x = \mathrm{const}$ and $1 - x = \mathrm{const}$ as

$$\ln a_{M^o} = (\ln a_M + z\,a)_{x=\mathrm{const}} = (\ln a_{M'} + z'\,a)_{x=\mathrm{const}} \tag{31}$$

The equation (30) represents the linear formulation of the Schulze-Hardy rule for counter ion exchange. According to this formulation of the rule the logarithm of different counter ion concentrations giving the same constant fraction of an adsorbed second counter ion of a constant activity, should be proportional to their valency. The proportionality constant is the parameter a. This experimental parameter is explained by the present theory (because of eqs. 21, 27, 29, 30) by

$$a = \Delta^1\varphi F/RT = \mu_{\mathrm{A},\,{}^{-}_{\mathrm{ads}}}/RT \tag{32}$$

i. e. it is defined by the standard electrostatic potential difference and/or the chemical potential of the adsorbed constituent ion.

In the simplest coagulation experiments only the coagulating counter ion is present. In the ion exchange experiments, however, at low concentration of the counter ion, another counter ion enters the double layer. In a stable sol, where the coagulating counter ion is not present in a significant concentration, the only particle which can enter the double layer, due to the electrostatic attraction by the fixed ion, is a dipole. In aqueous solutions the only dipoles present are the water molecules[62]. Consequently, they are the only particles which can be used in the explanation of the stable state of liophobic colloids. They can be attracted and oriented in the electrostatic field of the fixed constituent ion. A decrease in the concentration of the counter ion causes a decrease in the potential $\Delta\varphi$ (eq. 18). Thus the tendency of the oriented dipoles to take the positions of the counter ions in the electric field of the fixed ion will gradually increase. The measured adsorbed amount of counter ions will still remain the same and equal to the adsorbed amount of fixed ions. However, they will not be in the double layer under a reversible electrostatic potential, but outside of the double layer at the potential of the electroneutral liquid phase. The equivalent ionic fraction of various counter ions in the liquid and that of the adsorbed ones will be equal. A defined factor z′ by which the dipole replaces the counter ion in the layer can also be assumed. For example, in the case of water molecules, perhaps because they are quadrupoles, it can be assumed that $z' = 2$. The reaction of the dipoles in the layer with adsorbed constituent ions can be presented by the equation

$$2\,z\,I^-_{ads} + 2\,M_{layer} + z\,H_2O = z\,[(I^-_{ads})_2\,(H_2O)_{layer}] + 2\,M$$

The reaction of dipoles is stoichiometric. This is the only implication as to the real nature of this reaction. It is possible that the reaction is of a purely electrostatic character, or that the entity given as $(I^-_{ads})_2\,(H_2O)_{layer}$ is a chemical compound. In any case eq. (18) can be assumed valid for the present counter ion and eq. (19) for the dipole. It is necessary to assume that $z' = 2$ in order to explain the experimental result described in Chapter C 5 which is defined by the theoretical eq. (57) in Chapter B 5.

If we assume that oriented dipoles in the layer cause the colloidal stabilization, and if we assume as a consequence that coagulation starts at a critical value of the chemical potential of the dipoles in the layer, namely when a critical fraction x_{coag} of the stabilizing dipole is replaced by the counter ion, we obtain the two eqs. defining the value of the potential $\Delta\varphi_{coag}$ in coagulation

$$\Delta\varphi_{coag} = \Delta^{o}\varphi + \{z'\,\mathbf{a} + \ln\,[a_{M'}/(1 - x)_{coag}]\}\,RT/F \tag{33}$$

by the dipole, and

$$\Delta\varphi_{coag} = \Delta^{o}\varphi + \{z\,\mathbf{a} + \ln\,[(a_M/x)_{coag}]\}\,RT/F \tag{34}$$

by the counter ion.
Defining

$$\ln a_{M,\,{}^{o}_{coag}} = z'\mathbf{a} + \ln a_{M'}\,[(1 - x)/x]_{coag} \tag{35}$$

one obtains from the difference of eqs. (33) and (34)

$$\ln\,(a_M/a_{M^o})_{coag} = -\,z\mathbf{a} \tag{36}$$

$a_{M,\,coag}$ is the critical coagulation activity or the coagulation value. The parameter $a_{M,\,{}^{o}_{coag}}$ is a constant of the equation and can be obtained from experimental coagulation values by the extrapolation to $z = 0$ (Fig. 4). Physically it can be explained as the coagulation value of a nonexistent particle having zero charge. It is justified to assume that the critical coagulation activity will be determined by the equality of the values $x = 1 - x = 0.5$ namely by the equality of the amount of the adsorbed counter ion and the stabilising particle. Then the coagulation value is represented by that activity of the counter ion at which its $\Delta\varphi$ value for $x = 1$ becomes higher than the value $\Delta\varphi_{H_2O,\,layer}$ for $1 - x = 1$.

Surveys of the influence of the valency of the counter ion upon the coagulation values in various systems strongly support the validity of the linear formulation of the Schulze-Hardy rule according to eq. (36). (See Charter C 3).

Težak[17,18] has derived for the same rule the equation $\log\,(c_{coag}/c_{fix}) = -\,z({}_{c}d/{}_{s}d)$. Here are ${}_{c}d$ and ${}_{s}d$ distances derived from Bjerrum's theory. Replacing in this equation c_{coag} by $a_{M,\,coag}$, c_{fix} by $a_{M,\,{}^{o}_{coag}}$ and ${}_{c}d/{}_{s}d$ by $\mathbf{a}$ one obtains eq. (36). One can define $\Delta^1\varphi = z^+e/D\delta_1$ and $\Delta^s\varphi = RT/F = z^+e/D\delta_s$. The latter definitions inserted in eq. 32 give $\mathbf{a} = \delta_s/\delta_1$. The Schulze-Hardy proportionality constant $\mathbf{a}$ can be defined according to the present theory also as a ratio of two characteristic mean distances. Thus, Težak's formulation of the Schulze-Hardy rule and its definition of the parameter $\mathbf{a}$ can be considered formally identical with the definitions derived by the ion exchange theory.

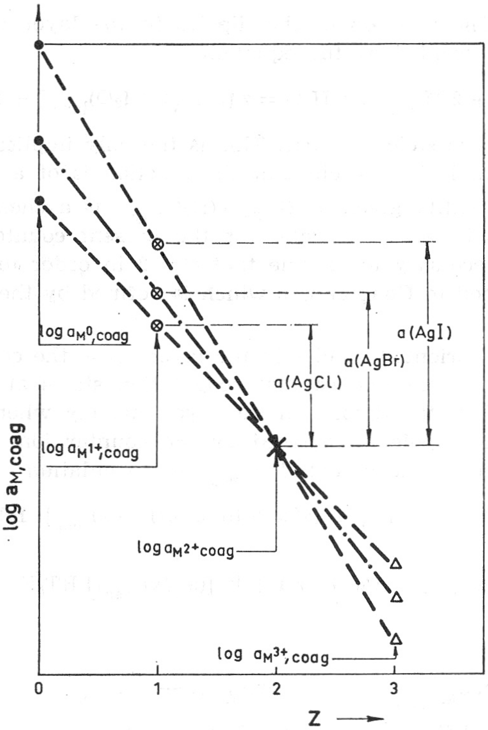

Fig. 4. Plots of $\log_e a_{M,\,coag}$ against z for AgI, AgBr, and Ag Cl. (Eqs. 36, 57).

4. *Electrokinetic Potential in Dipole Liquids*

By the classical Helmholtz-Smoluchowsky equation the electrokinetic potential

$$\zeta = 4\,\pi\,\sigma\,\delta/D = 4\,\pi\,\eta\,\varkappa\,\mathbf{b}/D \tag{37}$$

is defined as a calculated potential between the metallic plates of an imaginary elongated cylindrical condenser which would have the electron surface charge density σ equal to the surface charge density of the real system. $\varkappa$ is the conductivity of the electrolyte. The conducting plates in the medium of dielectric constant D of the cylinder would be separated by the calculated distance δ. The factor $6\,\pi$ is used instead of the factor $4\,\pi$ for a spherical condenser model. η is the viscosity coefficient. This imaginary cylindrical condenser would produce the same value for the factor **b** as that obtained from experiment. The electrokinetic factor **b** is equal to the experimentally determined ratios »transported volume to current strength«, »streaming current to streaming rate« »streaming potential to pressure« or »migrated distance (= mobility) to field strength« depending on whether the observation is made by electroosmotic, streaming current, streaming potential or electrophoretic techniques. For any other geometrical array of the same charge density $\sigma = \gamma/A$, if the charges were separated by the real mean distance δ, the electrokinetic potential might analogously be defined by

$$\zeta = \text{const.}\ \sigma\,\delta/D = \text{const.}\ \eta\,\varkappa\,\mathbf{b}/D \tag{38}$$

The proportionality constant depends on the geometrical array of charges and on the geometry of the particles. For practically all polydisperse crystalline lyophobic sols this constant cannot be derived theoretically. The cylindrical or the spherical model are rough approximations and the proportionality constants 4π or 6π cannot have any real or even a semiquantitative significance. It can be however anticipated that the relative range of the values of this constant cannot be very great and it may vary between $4/4 = 1$ to $6/4 = 1.5$ approximately.

It follows that the ζ — potentials calculated on the basis of the Helmholtz-Smoluchowsky equation with the proportionality constant 6π or 4π have no physical significance nor do they represent a physically meaningful exact quantitative parameter for real systems. Eq. (37) is physically insignificant and no quantitative comparison with electrokinetic results obtained with different material systems of different dispersity is possible on a scale of electric potential units (*e. g.* volts). In each different real system the constant of eq. (38) has a different value, and this value cannot be derived either theoretically or experimentally. This value is also different for each particle of different shape and size. The practice of calculation ζ -potentials from experimental data, namely from the experimental value for the product $\varkappa \mathbf{b}$, is therefore superfluous. The ζ -potential is simply a value proportional to the experimental parameter **b**, while the proportionality constant is arbitrarily taken equal for all systems and particles. This constant is certainly different for the particles in the coagulated and stable state of the same sol. The experimental electrokinetic results given as ζ -potentials yield no advantage over the directly measured **b** values. On the contrary, their disadvantage is that usually, when the conductivity is not explicitly stated, they cannot be compared in different systems with each other. Except perhaps for macroscopic capillaries in electroosmotic experiments the constant of eq. (38) is in all colloidal systems unknown and there is no justification for using the value 4π or 6π or any corrected value (See Chapter E 3) for any real system unless its dispersity (size, shape, modification of particles) and array of charges can be represented by a useful model. We are sure that colloidal particles are not of such a geometrical form that they could be in all cases approximated as long and narrow cylinders forming a radially homogeneous condenser composed of two electrically conducting cylinders with a continuous »smeared out« charge distribution.

In many present day theoretical efforts to explain the phenomena of colloid chemistry, instead of the cylindrical, or spherical, the infinite parallel plate condenser model was usually used, and applied to the same material model systems. It is obvious that for a given material a single double layer model should be used for the explanation of all phenomena depending or governed by double layer processes and observed by various experimental techniques. This model should be therefore equal for the explanation of the results of electrokinetics, adsorption, ion exchange, coagulation and others. In the following derivations the fixed charge model is used.

Theoretical equations defining the variation of δ and **b** (or ζ) with the counter ion activity, for systems of constant and variable conductivity, can be derived as follows.

The water molecules are assumed quadrupoles with a constant activity and a factor $z' = 2$, also if the activity of the counter ion is varied. If we assume that the geometry of the charges remains constant, during this variation of the counter ion activity we can write (*e. g.* (19))

$$\Delta\varphi' = \Delta^{\circ}\varphi + \{2\,\mathbf{a} + \ln\,[a_{H_2O}/(1 - x)\,\sigma]\}\,RT/F \qquad (39)$$

as the equation valid for the water dipoles, where $z' = 2$, $a_{H_2O} = \mathrm{const.}$ For

$$\Delta\varphi_{H_2O,\ \mathrm{layer}} = \Delta^{\circ}\varphi + [2\,\mathbf{a} + \ln (a_{H_2O}/\sigma)]\ RT/F = \mathrm{const} \tag{40}$$

one obtains

$$\Delta\varphi' = \Delta\varphi_{H_2O,\ \mathrm{layer}} - (RT/F) \ln (1 - x) \tag{41}$$

as the eq. defining the variation of $\Delta\varphi'$ with $1 - x$ of the oriented dipoles in the layer. With decreasing concentrations of the counter ions $x < 1$ and $1 - x \rightarrow 1$ and therefore $\Delta\varphi' \rightarrow \Delta\varphi_{H_2O,\ \mathrm{layer}}$ *i. e.* the fixed charge double layer potential tends to a constant minimum value determined by the activity of the water dipoles. Then the latter replace all counter ions in the layer. The counter ions are still adsorbed; however, they are not at a reversible potential in the layer but at the potential of the electroneutral liquid phase. At the same potential of the electroneutral liquid phase are also the opposite charges of the water dipoles. In the double layer plus surroundings the condition of electroneutrality remains preserved. Since we assume that the constituent ions of a given charge sign are fixed on the surface of the solid and separated by distances which are large enough so that the electrostatic potential of one ion at the position of the second can be neglected, the variation in the electrostatic potential around the fixed ions at a mean distance δ at which the adsorbed counter ions are in equilibrium with the counter ions in the liquid (eq. (6)) follows from Coulomb's law:

$$\Delta\varphi = z^{-}e/\delta\, D \tag{42}$$

The following definitions inserted in eq. (41)

$$\Delta\varphi_{H_2O,\ \mathrm{layer}} = z^{-}e/\delta_{H_2O,\ \mathrm{layer}} D \tag{43}$$

and

$$RTD/z^{-}eF = 1/\delta_s \tag{44}$$

give as the result

$$1/\delta = 1/\delta_{H_2O,\ \mathrm{layer}} - (1/\delta_s) \ln (1 - x) \tag{45}$$

The distance δ is not accessible to direct measurement and we can transform with the aid of eq. (37) the latter eq. into

$$1/\varkappa\, \mathbf{b} = 1/\varkappa\, \mathbf{b}_{H_2O,\ \mathrm{layer}} - (1/\varkappa\, \mathbf{b}_s) \ln (1 - x) \tag{46}$$

for $\varkappa$ variable, or into

$$1/\mathbf{b} = 1/\mathbf{b}_{H_2O,\ \mathrm{layer}} - (1/\mathbf{b}_s) \ln (1 - x) \tag{47}$$

for $\varkappa$ constant with the counter ion activity. The third form of the same eq. reads

$$1/\zeta = 1/\zeta_{H_2O,\ \mathrm{layer}} - (1/\zeta_s) \ln (1 - x) \tag{48}$$

The last three eqs. were derived from eq. (45) using the following definitions based upon the eqs. (38) and (42)

$$\delta = \eta\varkappa\, \mathbf{b}/\sigma = D\, \zeta/\mathrm{const.}\ \sigma \tag{49}$$

$$\delta_{H_2O,\ \mathrm{layer}} = \eta\varkappa\, \mathbf{b}_{H_2O,\ \mathrm{layer}}/\sigma = D\, \zeta_{H_2O,\ \mathrm{layer}}/\mathrm{const.}\ \sigma \tag{50}$$

and

$$\delta_s = \eta\varkappa\, \mathbf{b}_s/\sigma = D\, \zeta_s/\mathrm{const.}\ \sigma \tag{51}$$

Eqs. (46, 47, 48) represent the theoretical variation of the experimental parameters $\varkappa\,\mathbf{b}$, $\mathbf{b}$ or ζ with $1 - x$. A graphical representation of eqs. (46, 47, 48) is given by Fig. 5. However, since no method is known by which the constant of eq. (38) can be established from any experimental characterization of real systems with polydisperse, or even monodisperse, particles of various geometrical shape, it is better to avoid calculating ζ-potentials on the basis of the value 4π or 6π of the proportionality constant of eqs. (37), (38) and use instead of eq. (48) eqs. (46) or (47).

From the separation factor S in eq. (27) the following relationship for the variation in $(1-x)$ in eqs. (46, 47, 48) with a_M for different valencies z can be obtained (Fig. 5)

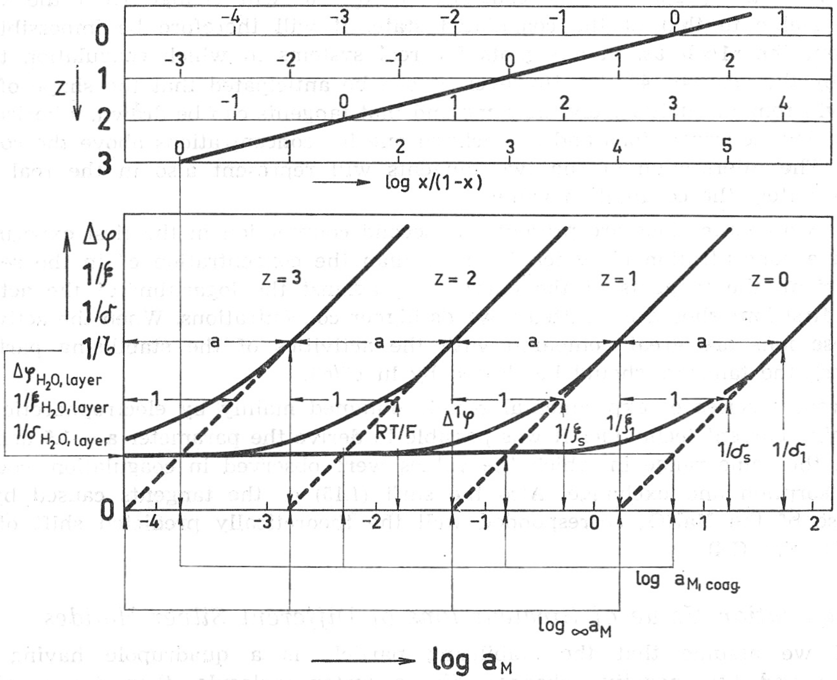

Fig. 5. Theoretical Δφ, 1/δ, **1/b**, 1/ζ against $\log_{10} a_M$ plots in dipole liquids and the scalar variation of $\log_{10}[x/(1-x)]$ with $\log_{10} a_M$ for ions of a different z (Eqs. 19, 46, 47, 48, 27, 54).

$$\ln [a_M/(a_M)_{(x=0.5)}] = \ln (a_{M^\circ}/(a_{M^\circ})_{(x=0.5)}] = \ln [a_M/(a_{M^\circ})_{(x=0.5)}] + \mathbf{za} = \ln [x/(1-x)] \tag{52}$$

For an easy graphical evaluation this function can be transformed into

$$1/x - 1 = (a_M)_{(x=0.5)} / a_M \tag{53}$$

When $1-x < 1$, $x \rightarrow 1$ and $a_M > (a_M)_{(x=0.5)}$ eq. (46) becomes the equation of the tangent of the »$1/\mathbf{b}$ *vs.* $\log a_M$« curve with the slope $1/\varkappa b_s$. This eq. reads

$$1/\varkappa\,\mathbf{b} = 1/\varkappa\,\mathbf{b}_{H_2O,\ layer} - (1/\varkappa\,\mathbf{b}_s) \ln [a_M/(a_{M^\circ})_{(x=0.5)}] - \mathbf{za} \tag{54}$$

Its graphical representation (for $\varkappa$ = const.) is given in Figs. 5 and 9, upper part. (An analogous eq. for ζ-potentials can also be used).

The tangents of the »$1/\varkappa\,\mathbf{b}$ or 1/ζ *vs.* $\log a_M$« curves for high concentrations of counter ions of different valencies should be shifted for the product **za**. This theoretical conclusion is analogous to that for coagulation (eq. 36) and counter ion exchange (eq. 30) and can therefore be considered the linear formulation of the Schulze-Hardy rule for electrokinetics.

The intersection of the horizontal and inclined tangents should define the coagulation value, in the ideal case. For the ideal case it is assumed (See Chapter 3) that the adsorbed amount of the coagulating counter ion and of the stabilising dipole are equal, namely that $x = 1 - x = 0.5$.

Because of the transition of the dispersed solid from the stable state to the coagulated state, it is impossible to measure the electrokinetic effects with the same technique in counter ion concentrations lower and higher than the coagulation value. Also the proportionality constant of eq. (38) will change from the value of the stable to that of the coagulated state. It will therefore be impossible to represent the »$1/\varkappa\,\mathbf{b}$ *vs.* ln a_M« plots for real systems in which coagulation takes place by the eqs. (46, 47, 48). However, it can be anticipated that the shape of the plots will remain qualitatively the same and that tangents can be drawn, a horizontal one for low concentrations and an inclined one for concentrations above the coagulation. The intersection of the two tangents will represent also in the real case approximately the coagulation value.

If two counter ions are present, the second counter ion in the first experiment having a concentration c', which is lower than the concentration c'' in the second experiment, the tangents of the curves »$1/\zeta$ against the logarithm of the activity of the first ion« should be shifted towards higher concentrations. When the activities of these ions are great compared with the activities of the stabilising particles (dipoles), the tangents should be shifted by $\ln(c''/c')$.

From a series of experimental results obtained mainly by electrophoretic and streaming current techniques it was possible to derive the parameter $\mathbf{a} = 1.5$ and 1.8, *i. e.* in the same range in which the values were observed in coagulation, counter ion adsorption and exchange. Also the shift (1.15) of the tangents caused by an increase of the $NaNO_3$ corresponded well the theoretically predicted shift of 1.2. (See Chapter C 4).

5. *Coagulation Value of Bivalent Ions of Different Silver Halides*

If we assume that the stabilizing particle is a quadrupole having two positive and two negative charges, like a water molecule, then for a critical $(1 - x)_{coag.}$ value, the critical fixed charge double layer potential for coagulation is determined by the eq. (39). It is equal to the same potential of a bivalent counter ion determined by

$$\Delta\varphi_{coag} = \Delta^{\circ}\varphi + [2\,\mathbf{a} + \ln(a_{M^{2+}}/x\,\sigma)_{coag}]\,RT/F \tag{55}$$

Then the coagulation value of a bivalent ion is determined by

$$a_{M^{2+},\,coag} = a_{H_2O}\,[x/(1 - x)]_{coag} = \text{const} \tag{56}$$

From the difference of the eqs. (39) and (55) one obtains the relationship (**Fig.** 4) (for $\Delta\varphi' = \Delta\varphi_{coag}$)

$$\ln(a_M/a_{M^{2+}})_{coag} = (2 - z)\,\mathbf{a} \tag{57}$$

The coagulation value of ideal bivalent counter ions should be independent of the type of the solid and of the adsorbed constituent ion, *e. g.*, it should be identical for silver chloride, bromide, and iodide. The constant **a** should be different for each halide because, by eq. (32), this constant was defined as being proportional to the chemical potential of the adsorbed constituent ion, which is different in each case.

A comparison of coagulation values of different silver halides gave as the result linear relationships as predicted by eq. (57) and Fig. 5 with an intersection of the lines at the coagulation value of the bivalent ions (See Chapter C 5).

6. *Adsorption Isotherm in the Region of the Coagulation Value Activities and the Free Energy of Coagulation*

The total adsorbed amount of constituent ions γ should depend on the dispersity of the solid oversimplified represented by the A value. When the counter ion activity is much lower than the coagulation value, the dispersity of the solid is higher than the dispersity at high concentrations at which the sols are coagulated (See ref. 58, Figs. 6, 7, 8 and 12, representing electron micrographs).

Thus the adsorption isotherm of constituent ions passing through the coagulation value cannot be the elementary one as given by eq. (52).

It should therefore be expected that the value γ_{stab} of the isotherm of the stable state is higher than the value γ_{coag} measured in coagulation concentrations (Fig. 9). It is most probable that the experimental isotherm for I^- ion adsorption will be more or less a continuous transition from the isotherm valid for the stable form of the solid to that valid for its coagulated state.

For concentration $a_M < a_{M,\,coag}$, when $x < 1$ and $1 - x \rightarrow 1$, the logarithm of the activity $x\gamma$ of the adsorbed counter ions should become proportional to the logarithm of the counter ion activity according to eq. (52) which becomes the equation of the tangent of the same isotherm:

$$\ln x = \ln \left[a_M/(a_{M^o})_{(x\,=\,0.5)} \right] + z\mathbf{a} \tag{58}$$

It follows that the tangents of the curves »logarithm of the activity of the adsorbed ion *vs.* logarithm of the activity of the counter ion« should be shifted in the stable region $a_M < a_{M,\,coag}$ for ions of different valencies and the shift should be proportional to the valency. The proportionality constant should be equal to the value **a** of coagulation and exchange.

The decrease from γ_{stab} to γ_{coag} value in sols of small primary particles can be explained as follows.

The activities of the adsorbed iodide and counter ions of valency z are equal, and defined as

$$a_{I^-,ads} = a_{M,\,layer} = \gamma/AX_\delta = \sigma/x_\delta \tag{59}$$

The product $AX_\delta = V$ has the dimension of a volume. Since γ is here proportional to the number of A^-_{ads} ions on the surface area, this volume is proportional to the number of solvent molecules, and the activity equals the molar ratio as required. (Fig. 6). For a given system the activity has the same property as the free energy: it tends to a minimum value.

The specific surface area, A can be assumed constant for coarse particles. X_δ is a calculated mean thickness of the layer of the solvent molecules defining the saturation activity. X_δ is at a minimum at equilibrium, and there is a limiting number of solvent molecules defining the saturation activity. The dilution of the bulk solution and/or peptization of the precipitate (or coagulate) does not cause any variation in V and consequently in the activity of the ions adsorbed in the double layer, in accordance with the assumption of their specific adsorption. This is in other words, the postulate for a limiting value of $a_{A^-,\,ads} = \text{const}$ and $\mu_{A^-,\,ads} = $ $= \text{const}$. (eq. 28). In systems in which A and AX_δ are constant, also σ and γ are constant in equilibrium. The decrease in σ below the limiting value does not

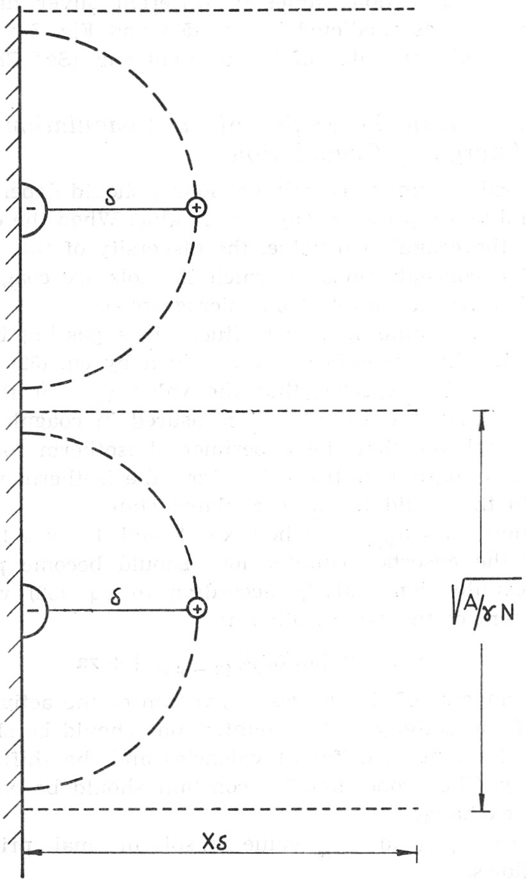

Fig. 6. Saturation charge density and saturation activity of an adsorbed electrolyte. Statistical mean distance δ between the fixed anion and the counter ion, Xδ limiting thickness of the double layer, A/γN limiting surface area per adsorbed ion pair.

cause any variation of the activity of the adsorbed ion, because any increase of the surface which is at disposal to single adsorbed ions A/γ N, beyond the limiting value established prior to the variation in *p*A, does not cause any decrease of the activity of the single adsorbed constituent and counter ions (See Fig. 6). This conclusion is analogous to the conclusion that any increase of the thickness of the solvent layer beyond the limiting value X_δ does not cause any decrease of the same activity. N is the Avogadro's number.

The increase in the concentration of the counter ion above the coagulation value induces coagulation. This is due to the tendency to increase $a_{M,\ \mathrm{layer}}$. This increase, however is virtually impossible since it would violate the postulate $a_{M,\ \mathrm{layer}} = a_{A^-,\ \mathrm{ads}} = \mathrm{const.}$ The system will yield to the force by decreasing $V = AX_\delta$, and consequently γ.

Physically, this means that the solvent molecules will be expelled from the double layer of small primary particles. Secondary aggregates will be formed with the intermicellar liquid volume at a minimum value. This value will be mainly dependent on the geometrical shape of the particles, but independent of pI and counter ion concentration (above the critical coagulation concentration). The volume of the intermicellar liquid will then define the number of adsorbed A^-_{ads} in order to satisfy the postulate of a constant activity proportional to the ratio γ/AX_δ .

As a consequence of this model, the value of γ_{coag} must be smaller than $\gamma_{stab} = A_{stab}\,\sigma$ for sols with sufficiently small primary particles. It is easily understood that for larger particles the difference between the two values is less. Considering the shortcomings and the ultimate obtainable precision of adsorption and coagulation experiments it is quite possible that there is a limit in the particle sizes when observable differences disappear (See Shapter C 6).

The tendency to expel solvent molecules from the double layer volume corresponds to the tendency to attract the colloidal particles. The former tendency in fact represents the attractive forces between the particles. It is possible that the attractive forces, due to the reduction of the double layer volume, act independently of any other possible forces, as perhaps the Van der Waals forces which are supposed to act between the particles. However, the latter forces even if they do act accross liquid layers, they are certainly always under the influence of the interaction of the layers on the particles. It is also very probable that the Van der Waals forces are much smaller than the forces caused by the interface films, *i. e.* by double layers.

7. *Neutralization of Adsorbed Constituent Ions with Constituent Ions of Opposite Sign*

The neutralization of adsorbed constituent ions A^{z-}_{ads} (simplified as A^-_{ads}) with ions of opposite sign B^{z+} (B^+) dissolved in the solution phase can be represented by the reaction

$$z^+A^{z-}_{ads} + z^-B^{z+} = (A_{z^+}B_{z^-})_{ads} \quad \text{(simplified as } (AB)_{ads})$$

Then, for a simpler case when $z^+ = z^- = 1$, the relation

$$\mu_{A^-,\,ads} + \mu_{B^+} = \mu_{(AB)ads} \tag{60}$$

is valid. If the total originally adsorbed activity of A^- is γ, the activity of neutralized $(AB)_{ads}$ is $(1-\beta)\,\gamma$ and the activity of the unneutralized A^-_{ads} is $\beta\gamma$, where β is a fraction, then

$$\mu^o_{A^-,\,ads} + RT\ln(\beta\gamma) + \mu^o_{B^+} + RT\ln a_{B^+} = \mu^o_{(AB)\,ads} + RT\ln[(1-\beta)\,\gamma] \tag{61}$$

and we obtain

$$\ln[\beta/(1-\beta)] = \ln(a^o_{B^+}/a_{B^+}) \tag{62*}$$

---

* R. Matejec and R. Meyer[63] derived the corresponding adsorption isotherm in the form

$$B^-_A \approx \frac{N}{1 + A^+_{L''}\sqrt{K^+_{L,\,A}\cdot K^-_{L,\,A}/K_{L,\,G}\exp(-e\,\Delta\varphi_{L,\,A}/kT)}} \tag{40^{63}}$$

Our eq. (62) can be written in the form

$$\beta = 1/(1 + a_{B^+}/a^o_{B^+}) \tag{62a}$$

Since B^-_A /N is identical with the fraction β of the not neutralized A^-_{ads} and A^+_L with

Here

$$\ln a^{o}_{B^+} = (\mu^{o}_{(AB)\,ads} - \mu^{o}_{A^-,\,ads} - \mu^{o}_{B^+})/RT \tag{63}$$

is the logarithm activity of the constituent ion in which half of the originally adsorbed ions is neutralized, *i. e.*, when $\beta = 1 - \beta = 0.5$.

The activities of the adsorbed ions should decrease bilogarithmically and become zero practically within two logarithmic units of activity of the neutralizing constituent ion B^{z+}. The intersection of the tangent of the bilogarithmic plot through the inflection point with the logarithm activity axis is a characteristic constant called the zero point of adsorption.

Actually, the experimental results obtained when the equilibration was allowed at each measured *p*Ag value, can be interpreted in this sense (See Chapter C 7).

In the case where $pA = -\log_{10} a_A$ is varied, by the addition of B^+ ions to a sol consisting of coarse particles initially in a dispersion equilibrium, A and X_δ will remain constant. In this case we can assume that the volume of the intermicellar liquid is greater for aggregates consisting of coarse particles than the limiting volume AX_δ (Fig. 7b). The variation of *p*A causes then a change in σ but not in the activity of A^-_{ads} and of counter ions in the layer, *i. e.* of the limiting volume $AX_\delta/\sigma N$ in the actual interaction with a single ion pair. The equilibrium condition between the adsorbed electrolyte and the electrolyte in the liquid is given by

$$\tilde{\mu}_{M,\,layer} + z\,\tilde{\mu}_{A^-,\,ads} = \tilde{\mu}_M + z\,\tilde{\mu}_{A^-} \tag{64}$$

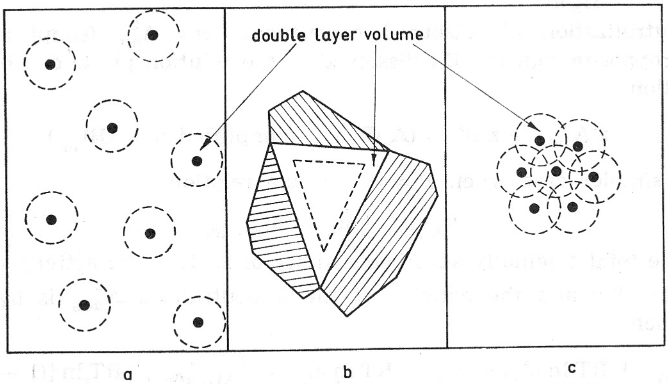

Fig. 7. The double layer volume and the intermicellar liquid volume: (*a*) in stable sols of small particles; (*b*) in coagulated aggregates of coarse particles; (*c*) in coagulated aggregates of small particles.

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a_{B^+}, eq. (40)[63] and our eq. (62a) are identical. The »Ersatzkonzentration« $A^+_{L''}$ is defined namely by

$$A^+_{L''} = \frac{A^+_L}{N_G}\sqrt{\frac{K^-_{L,\,A}}{K_{L,\,G}\cdot K_+}} \qquad (32a)^{63}$$

and therefore our standard activity $a^{o}_{B^+}$ by

$$a^{o}_{B^+} = \frac{N_G\,K_{L,\,G}}{K^-_{L,\,A}}\exp\,(e\,\Delta\varphi_{L,\,A}/kT)$$

When $\Delta\varphi_{L,\,A}$ is constant our eq. (62) is a symetrical bilogarithmic plot.

Here are $\tilde{\mu}_{M,\,layer} = \mu_{M,\,layer} + zF\,\varphi_{layer}$ and $\tilde{\mu}_{A^-,\,ads} = \mu_{A^-,\,ads} + F\,\varphi_{inner}$ the electrochemical potentials of counter ions with the electrostatic potential in the outer layer, φ_{layer}, and of A^- ions in the inner layer with the electrostatic potential φ_{inner}. The electrostatic potential φ_{liquid} in the liquid phase is set to be the zero reference potential.

Defining $\Delta\varphi = \varphi_{inner} - \varphi_{outer}$ and

$$-RT \ln a^{o}_{A} = p^{o}_{A} \cdot RT = (\mu^{o}_{A^-} - \mu_{A^-,\,ads}) - (\mu_{M,\,layer} - \mu_{M})/z \tag{65}$$

and $pA = -\ln a_{A^-}$ one can derive the equation

$$\Delta\varphi = (pA^{o} - pA)\, RT/F \tag{66}$$

This derivation assumes that in addition to the already postulated $\mu_{A^-,\,ads} = \text{const.}$, and $\mu_{M,\,layer} = \text{const.}$, μ_M has a constant value. This is a special, experimentally feasible condition if $pA > 3$ and when pA is changed *e. g.* by addition of a M′A electrolyte, with M′ different from M. The additional requirement is that $z' = 1 < z$ and $a_{A^-} = a_{M'} < a_M$ or simply that $a_{A^-} < a_M = \text{const}$. The place of counter ion can be taken over by the positive pole of a dipole (water molecule) at very low values of a_M. This could be the case in stable sols due to $a_M < a_{M,\,coag}$.

One can consider the »counter ion-adsorbed constituent ion« pair as an elementary condenser.* The sum of these elementary condensers over the surface is equi-

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* The basis of the derivation of the electric potential in the theory of the electric double layer on ionic crystals proposed by R. Matejec and R. Meyer[63] is represented by the eq.

$$\varphi = \varphi_0 + (1/4\,\pi\,\varepsilon\,\varepsilon_0) \sum_i Q_i/r_i \tag{1}^{63}$$

The following equalities between the symbols of both theories are valid:

$$\varphi - \varphi_0 = \varphi - \varphi_L = \Delta\varphi_{L,\,A} = \Delta\varphi, \; \sum_i Q_i = \gamma F, \; r_i = \delta.$$

The summation according to the concept of discrete charges gives the eq.

$$\Delta\varphi = \gamma F/4\,\pi\,\varepsilon\,\varepsilon_0 \delta$$

in place of the eq. obtained by Matejec and Meyer which reads

$$\Delta\varphi_{L,\,A} = [A^{+}{}_{A} - B^{-}{}_{A}]\; e\delta_1\,\delta_2/\varepsilon\,\varepsilon_0 \tag{9}^{63}$$

Since the concentration $[A^{+}{}_{A} - B^{-}{}_{A}]$ can be considered equal our $\gamma/X_\delta\, A = \gamma/4\, a^2 \pi X_\delta$, the latter eq. $(9)^{63}$ can be written in the form

$$\Delta\varphi_{L,\,A} = \gamma\,\delta_1\,\delta_2\; e/\varepsilon\,\varepsilon_0 X_\delta\; 4a^2\,\pi$$

It follows that our capacitance C is defined by

$$C = 4\pi\,\varepsilon\,\varepsilon_0\;\delta/\gamma\,F = 4a^2\,\pi\,\varepsilon\,\varepsilon_0\,X_\delta\;/\delta_1\,\delta_2\,\gamma\,e$$

and the interrelation between the distance parameters a, δ_1 and δ_2 and our distance parameters X_δ and δ is given therefore by

$$X_\delta\;/\delta = \delta_1\,\delta_2/a^2\,N$$

The parameter $(\Delta\varphi_{L,\,A})_{max}$ in eq. $(36)^{63}$ is defined therefore using our X_δ and δ by

$$(\Delta\varphi_{L,\,A})_{max} = N^2\, X_\delta\;\; a^2 e/\delta\,\varepsilon\,\varepsilon_0$$

while according to the concept of discrete charges it is defined by

$$\Delta\varphi = F/4\,\pi\,\varepsilon\,\varepsilon_0\,\delta \qquad \text{for } a_M = \text{const.}$$

valent to a hypothetical continuous double layer with an average capacitance C in farads/cm^2. Then is $\Delta\varphi = \sigma F/C$ and $\sigma^\circ = CRT/F^2$ and we obtain:

$$\sigma = \sigma^\circ (pA^\circ - pA) \tag{67}$$

In other words this is the expression defining the proportionality of charge density σ and pA for coarse sols of a constant surface area. $\sigma = \sigma^\circ$ for $pA^\circ - pA = 1$.

In stable sols consisting of small primary particles there is a minimum possible number of adsorbed ions per particle. In the whole stability region no increase in pA will produce a decrease beyond that one as long as the primary stable particles are homogeneously dispersed (Fig. 7a). The particles will aggregate instead and retain the same activity of the adsorbed electrolyte mole per mole solution (Fig. 7c). This can occur only if the aggregation is accompanied by a decrease of the double layer volume AX_δ. Assuming that the basic nature of the counter ion-colloidal particle interaction remains the same, instead of a variation in σ we shall have a variation in γ and $V = AX_\delta$. Using the notation

$$\sigma = \gamma/A^\circ \text{ and } \sigma^\circ A^\circ = \gamma^\circ \tag{68}$$

where A° is the surface area and γ° the adsorbed amount at $pA^\circ - pA = 1$ we obtain

$$\gamma = \gamma^\circ (pA^\circ - pA) \tag{69}$$

which indicates the linear decrease of the adsorbed amount, mole per mole solid, with pA. The decrease in the specific surface area is visualized in a process of agglomeration when successively larger parts of the double layer volume are involved in forming the intermicellar liquid between the small particles. The intermicellar liquid volume becomes smaller than the original double layer volume. This intermicellar volume depends on the geometry of the particles in the coagulated state.

In stable sols consisting of small particles the adsorbed amount *e. g.* of $A^- = I^-$ per given amount of the solid (*e. g.* per gram mole AgI) should decrease linearly with $pA = pI$ because of a decrease in the specific surface, resp. of the total double layer volume. The coagulation accompanied by a decrease in A could be explained by van der Waals attraction forces between the particles in direct contact. There is little probability that these forces could be acting accross solvent layers of several molecules[56] separating the particles before the contact between the particles in the collision has been established.

In sols of coarse, aged, or preformed AgI particles the decrease of the adsorbed amount should be approximately linear with pI. Since here the specific surface area can be assumed essentially constant, the decrease can be assumed as the decrease of the adsorbed amount per unit surface area, *i. e.* as the decrease of the charge density (See Chapter C 7).

8. *Isoelectric (constituent ion) Coagulation*

In stable sols when increasing the concentration of the second constituent ion, *e. g.* in negative AgI sols when adding ions of opposite charge B^{z+} (Ag^+), we may expect that this ion like the counter ion, will show a tendency to replace the stabilizing particle (dipole) in the layer, and to react with the originally adsorbed constituent ion of opposite charge, in our example with A^{z-}($=I^-$), so as to form an electrically neutral unit in the surface of the solid. This reaction was discussed in the preceding section. The resulting isoelectric coagulation will be therefore induced at a limiting value of the activity of this ion. This value was observed experimentally in the negative silver halide systems and called the »negative« activity limit of stability[5,31,36].

It is justified to assume that the energy of this neutralized ion B^{z+} in the lattice of the surface of a homologous series of ionic solids with different A^{z-} but the same B^{z+} *e.g.* AgCl, AgBr, AgI is constant and independent of the second constituent ion A^{z-} and that the difference in their properties is caused completely by the different energies of the different A^{z-} in the surface layer and in the solid phase. Thus we may expect that coagulation will start at the value $a_{B,\overset{+}{l}imit}$ when a given fraction x_{coag} of A^{-}_{ads} is neutralized by B^{z+}_{ads}. Thus

$$(\mu_{AB,\,ads})_{limit} = \mu_{B,\overset{+}{l}imit} + \mu_{A,\overset{-}{a}ds} \tag{70}$$

and

$$pB_{limit} = -\ln a_{B,\overset{+}{l}imit} = \mu^{o}_{B^{+}} + \mu_{A,\overset{-}{a}ds} - (\mu_{AB,\,ads})_{limit} = \text{const.} \tag{71}$$

Hence the negative activity limit of stability, *i.e.* the coagulation value of the constituent ion- the pAg_{limit} -should be constant and equal for silver chloride, bromide and iodide. This was in fact the actual experimental observation (See Chapter C 8).

9. *The Influence of Dielectric Constant on the Coagulation Value*

Eq. (33) and (34) determine the value $\Delta\varphi_{coag}$, which is constant and independent of the valency of the coagulating ion because $x_{coag} = \text{const}$, $a_{H_2O} = \text{const.}$ and $z' = 2 = \text{const.}$ Thus, because of eq. (42), $\Delta\varphi_{coag}$ should be a linear function of 1/D, since δ_{coag} can be assumed independent of D at least in a limited region. Then because of eq. (34) the logarithms of the coagulation values of ions of different valencies should also be linear functions of the reciprocal dielectric constant.

In fact linear plots »$\ln c_{coag}$ *vs.* 1/D« were observed in the AgBr system for three different ions of different valencies. The variation in 1/D was achieved by the addition of solvent additives to water (See Chapter C 9).

10. *Mutual Counter Ion and Constituent Ion Coagulation*

If the concentration of a constituent ion determining the charge is decreased by the addition of the second counter ion, while the concentration of the counter ion is constant in each experiment and lower than the coagulation value, one may expect that in a limiting idealized case the counter and the constituent ions will cause the coagulation additively, *i.e.* they will cause the sum of the ratios between the actual concentrations and the coagulation concentrations of both ions equal one. In this case it should be valid namely the relation

$$a_M/a_{M,\,coag} + a_{B^{z+}}/a_{B,\overset{z+}{l}imit} = 1 \tag{72}$$

Here, the concentrations a_M and $a_{B^{z+}}$ are the concentrations in which both ions cause the coagulation additively. After transformation, the logarithmic form of the same eq. reads:

$$\ln (a_M/a_{M,\,coag}) = \ln (a_{B,\overset{+}{l}imit} - a_{B^{+}})/a_{B,\overset{+}{l}imit} \tag{73}$$

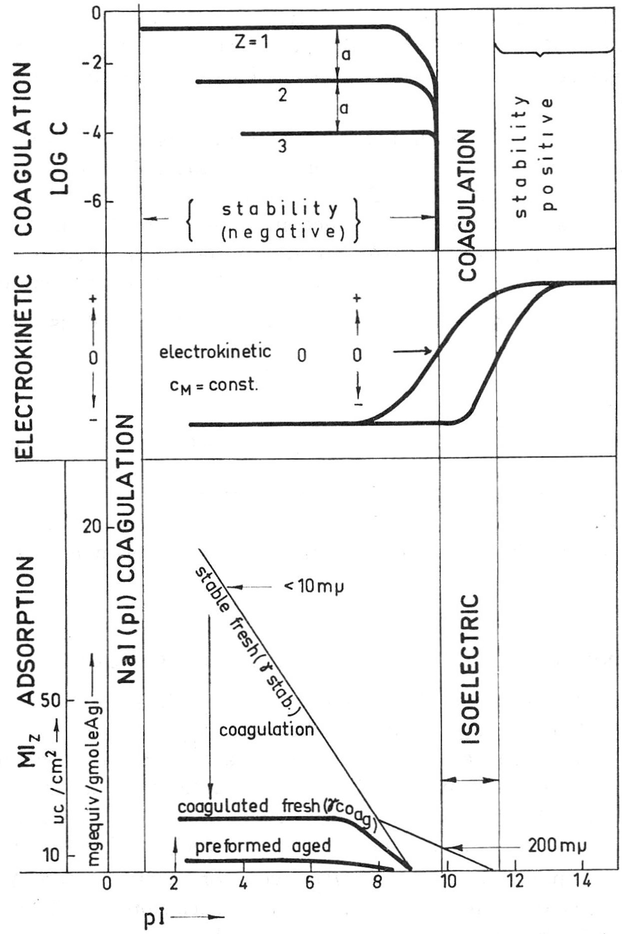

Fig. 8. A comparison of: (1) coagulation values (2) electrokinetic potential or mobility, and (3) MI_z, *i. e.* counter ion + constituent ion electrolyte adsorption as a function of $pI = 16 - pAg$, under the influence of different preparation techniques (schematic !).

The graphical representation of the theoretical plot is given in Fig. 8. upper part by the plot for ions of valency 2 of the AgI system. The plot for ions of valency 1 is drawn under the assumption that a sensitization takes place, namely, that the actual values are lower than the theoretical. The plot for the ion of valency 3 is drawn under the assumption that both ions do not affect each other's coagulation values.

It follows that the plots of the coagulation values of counter ions should be practically constant with pI in the region up to $\log_{10} c_{M,\,coag} - 1$ and that the pAg_{limit} value should be practically constant with $\log_{10} c_{M,\,coag}$ up to the value $pAg_{limit} + 1$.

The experimental observation on AgI was in accordance with the idealized case for the case of Ba^{2+}, a sensitization was observed in the case of Na^{+} and no interaction in the case of La^{3+} as schematically presented in Fig. 8 (See Chapter C 10).

11. *Negative Adsorption of Co-Ions*

The negative adsorption, as opposed to the positive adsorption, can be observed occasionally as an increase of the concentration of a species, *e. g.* it was observed in the negative AgI system[37] by an increase in the bulk liquid of the concentration of bivalent co-ions like HPO_4^{2-} or SO_4^{2-}.

Theoretically, the same phenomenon could be predicted as follows. We assume that the co-ions Y^- are excluded, or expelled out of the double layer volume because of the adsorbed A^-_{ads} ions. This volume is determined by the amount of the adsorbed ions A^-_{ads} and therefore it is constant and independent of the co-ion, concentration. We assume that in this volume, the co-ions — if not expelled — would have a given chemical potential $\mu_{Y,\overset{-}{des}}$. In equilibrium, the sum of the chemical potentials of Y^-_{des} and A^-_{ads}, multiplied by the valency of the co-ions z^-, equals the chemical potential of the co-ions in the liquid. It is valid namely the equality:

$$z^-(\mu_{A,\overset{-}{ads}} + \mu_{Y,\overset{-}{des}}) = \mu_{Y^-} \tag{74}$$

and

$$z^-(\mu_{A,\overset{-}{ads}} + \mu^o_{Y,\overset{-}{des}} + RT\ln a_{Y,\overset{-}{des}}) = \mu^o_{Y^-} + RT\ln a_{Y^-} \tag{75}$$

The factor z^- in the above eq. could be explained by the electrostatic repulsion between the two ions in the layer and the liquid where the co-ions are influenced by the chemical potential only.

The sum of the constant terms defines the standard activity of the desorbed co-ions by the following eq. valid when $a_{Y^-} = 1$:

$$RT\ln a^o_{Y,\overset{-}{des}} = \mu^o_{Y^-} - z^-(\mu_{A,\overset{-}{ads}} + \mu^o_{Y,\overset{-}{des}}) \tag{76}$$

The resulting equation reads

$$RT\ln(a_{Y,\overset{-}{des}}/a^o_{Y,\overset{-}{des}}) = (1/z^-)\ln a_{Y^-} \tag{77}$$

The activity of the co-ion can be measured as its concentration $a_{Y^-} = c_1$, the activity in the layer of its desorbed part by

$$a_{Y,\overset{-}{des}} = \Delta c_1/AX_\delta \tag{78}$$

and the corresponding standard activity by

$$a^o_{Y,\overset{-}{des}} = \Delta c^o_1/AX_\delta \quad (\text{for } c_1 = 1) \tag{79}$$

where Δc_1 is the increase of the concentration of the co ion in the liquid, and Δc^o_1 the standard increase when $c_1 = 1$. A is here the surface per liter of the system. These definitions inserted in the eq. (77) give the final result as

$$\ln(\Delta c_1/\Delta c^o_1) = (1/z^-)\ln c_1 \tag{80}$$

If the thermodynamic principle was applied to the correct process assumed as causing the negative adsorption, the plot logarithm desorbed amount *vs.* logarithm co-ion concentration should be a straight line and the slope should be inversely proportional to the co-ion valency.

In the case of two valent co ions the slope of the plots was measured as being equal 1/2. A final experimental proof for the correctness of this explanation of the negative adsorption might be obtained by experimental plots for co-ions of valency three having a slope equal 1/3 (See Chapter C 11).

12. *Phase Scheme and Basic Thermodynamic Equilibria in the Negative AgI System*

For a review, and as an example of the application of the described principles to a concrete case, the phase scheme of the negative AgI model system can be set up with the ion distribution in the different phases (Table I, line 0). The different

TABLE I

Phase Scheme and Basic Equilibria of Elementary Particles in the Negative AgI System

(0) Elementary particle distribution in the phases; *(1)* Solubility product; *(2)* Adsorption capacity; *(3) Counter ion (or dipole) exchange; (4)* Neutralization of I^-_{ads} with Ag^+; *(5)* »Negative« adsorption of the co-ion — counter ion electrolyte.

	Solid	Layer		Solution
		inner	outher	
0	$AgI \quad Ag^+ \quad I^-$	I^-_{ads}	$M_{layer} \quad M'_{layer}$	$I^- \quad Ag^+ \quad M \quad M' \quad Y^{z-} \quad H_2O$
1	$AgI = Ag^+ + I \rightleftharpoons$			$\rightleftharpoons I^- + Ag^+$
2	$nAgI + \overset{}{\longrightarrow}$ $\downarrow$	$\longrightarrow$	$\longrightarrow$	$+ I^-$
	$\leftrightharpoons (AgI)_n$	I^-_{ads}		
3		$z\, I^-_{ads}$	$M_{layer} \quad \rightleftharpoons$	M
			$\rightleftharpoons$	
		$z'\, I^-_{ads}$	M'_{layer}	$M' (= H_2O)$
4	$AgI \rightleftharpoons$	I^-_{ads}		$+ Ag^+$
5		$z^-\, I^-_{ads} \quad +$	$z^-\, Y^{z-}_{des} \quad \rightleftharpoons$	Y^{z-}

ions are at defined energy levels in the electroneutral solid and liquid phases, and in the double layer phase. The fixed $\bar{I}_{ads}$ form the inner part of the double layer, giving rise to coulombic discrete electric fields. The counter ions are under an electrostatic potential at a mean distance from the former and form the outer layer. They have at the same time a defined chemical potential. The most probable equilibria are at the same time those which were observed experimentally, namely (See Table I, lines 1—5): (1) ionic solubility, (2) fixation of I^- ions on the surface by a complexing mechanism or by crystal lattice forces, (3) counter ion exchange, (4) neutralization of the fixed $\bar{I}_{ads}$ ion with Ag^+ ions, and (5) co-ion Y^{z-} exclusion observed as their negative adsorption.

The electrochemical, and chemical potentials respectively, of the present elementary particles in the different phases (Table II, line 0), can serve for the derivation of the different isotherms, rules and laws valid for equilibrium conditions.

The solubility product K_{AgI} follows from the zero free energy change, *i. e.* the standard free energy, given by the equality in line 1 and is defined by

$$\ln K_{AgI} = \ln (a_{I^-} \cdot a_{Ag^+}) = (\mu_{AgI} - \mu^{o}_{Ag^+} - \mu^{o}_{I^-})/RT \qquad (81)$$

TABLE II

Basic Thermodynamic Relations of Electrochemical Potentials: $\tilde{\mu}_i = \mu_i + z_i F \varphi_i$ *and Chemical Potentials* $\mu_i = \mu_i^o + RT \ln (a_i/z_i)$; $\mu_i(a_i/z_i = 1) = \mu_i^o$ *of Elementary Particles*

	Solid	Layer			Solution
		inner		outer	
0	$\bar{\mu}_{AgI}$ $\bar{\mu}_{Ag^+}$ $\bar{\mu}_{I^-}$	$\mu_{I,\bar{a}ds}$	$\tilde{\mu}_{M,\text{ layer}}$	$\tilde{\mu}_{M',\text{ layer}}$	μ_{I^-} μ_{Ag^+} μ_M $\mu_{M'}$ $\mu_{Y^{z-}}$ μ_{H_2O}
1	$\bar{\mu}_{AgI} = \bar{\mu}_{Ag^+} + \bar{\mu}_{I^-} =$				$= \mu_{I^-} + \mu_{Ag^+}$
2	$n\,\bar{\mu}_{I^-} +$	$\mu_{I,\bar{a}ds}$			$\neq \mu_{I^-}$
3				$\tilde{\mu}_{M,\text{ layer}}$	$= \tilde{\mu}_M$
				$\tilde{\mu}_{M',\text{ layer}}$	$= \tilde{\mu}_{M'}$ $(= H_2O)$
4	$\bar{\mu}_{AgI} =$	$\mu_{I,\bar{a}ds}$			$+ \mu_{Ag^+}$
5		$z^- \tilde{\mu}_{I,\bar{a}ds}$	$+$	$z^- \tilde{\mu}_{Y,\overset{z-}{des}}$	$= \tilde{\mu}_{Y^{z-}}$

The following thermodynamic derivations are not less evident than the derivation of the solubility product.

In systems in which the dispersity (A) is constant, the constant adsorption capacity γ and the average charge density σ follow from the equality in line 2. The chemical potentials of the I^- and Ag^+ ions in the solid are constant, since we assume that the solid AgI is in internal equilibrium. The tendency to form complexes of the general type $(AgI_{solid})_n I^-_m$ on the surface is assumed to explain the basic process. In sols of small particles used in the experiment n/m is of the order of several hundred and is inversely proportional to the observed constant capacity γ.

The equations in line 3 can serve as the basis for the derivation of the ion exchange isotherms described in Chapter 2.

The electrical parts of the electrochemical potentials of the counter ions serve as the basis for the derivation of the electrokinetic potential equations described in Chapter 5.

The three different adsorption isotherms for the variation in I^-_{ads} with *p*I follow from the equality in line 4 and are discussed in Chapter 7.

The negative adsorption derived in Chapter 11 follows from the equalities in line 5.

C. EXPERIMENTAL VERIFICATION WITH SILVER HALIDES

1. *Adsorbed Amount of the Electrolyte »Constituent Halide Ion — Counter Ion« and Double Layer Models*

An analysis[10] of the available experimental results published so far on electrolyte adsorption on silver halides has shown that the adsorbed amount of the constituent and counter ions is small and independent of *p*I in a range of up to

5 units (if the dispersion equilibrium is established after the final pI value is reached in the system.), that the variation in the ion charge on colloidal particles with pI cannot be continuous (analogy with Millican's experimental proof of the elementary electron charge by the oil drop experiment), that the distances between the adsorbed ions as derived from the estimated charge density should be of the same size as those for small primary particles forming aggregates and greater than the maximum possible straight line on any one surface. These distances are also much greater than the thickness of the flat plate or sphere condenser double layer models. On the basis of these results it has also been demonstrated that only a few ions of valency one can be adsorbed on small primary colloidal particles forming the aggregates (not more than one or two on the smallest primary particles).

From the fact that the adsorbed counter ions are easily exchangeable when their concentration ratio is varied by a factor of 100 in a critical region while the adsorbed amount of iodide ion is constant and independent of the activities of these ions in the range of over five powers of ten[10-15], the conclusion has been made that constituent ions are fixed on the surface by other than electrostatic forces whereas counter ions are bound to them by Coulombic electrostatic forces. The adsorbed electrolyte is dissociated in the same manner as it would be dissociated if the constituent ions were not fixed on colloidal particles. Accordingly, the double layer may be described as the sum of a finite number of discrete charges in the form of constituent ions fixed on the surface of a finite number of particles and of counter ions statistically distributed in time and space at a mean distance from the fixed ions forming the outer layer. Such a model should be considered as a more probable and simpler aproximation to the real physical state than the model given by a homogeneous flat plate, a spherical or a cylindrical condenser. The continuous flat plate or the spherical condenser model has usually been applied in the current double layer theories of coagulation, while in electrokinetics the cylindrical condenser model has been used. It is obvious that one single model only should be used for a given material system, or a group of analogous systems.

2. *Counter Ion Exchange on Silver Iodide*

In a series of papers using the radioactive tracer technique[10-15] it was demonstrated that coagulated silver iodide might be considered as an ideal counter ion exchanger in which the sorption and swelling might be neglected. From the same experimental results the separation factor equation (21) was derived empirically.[11,12] Consequently, eqs. (18) and (19), from which eq. (21) was derived, should be considered as experimentally confirmed.

For seven counter ion pairs of different valencies it was shown that the constant **a** amounts to 1.5—1.8. Since no activity coefficient corrections were made, the maximum range of the results of ± 0.15 indicates the very probable constancy of this parameter and in this way eq. (32) may be considered as also confirmed.

Furthermore, it was demonstrated that the total amount of adsorbed counter ions (γ) lies between 3 and 2 grammequivalents per 1000 moles of coagulated AgI (prepared in a reproducible way) in the negative stability region where $2 < pI < 7$. This value was practically independent of the concentration of the counter ions when the concentration was higher than the coagulation value by a factor of up to ten. The variation in this value with pI was small ($\doteq$ 0.25 mg. equivalent/g.mole AgI per $\Delta pI = 1$ or 10%) and could be explained by the observed (by light scattering) increase in the primary particles with an increase in pI. This proves that the mean charge density, *i. e.* the chemical potential of the I^- ions and counter ions in the intermicellar liquid in the aggregates is constant. The result[42] that the specific adsorbed amount of I^-_{ads} in $\mu C/cm^2$ is independent of the specific surface area in the range of 1 to 5 m^2/g should be considered as additional, direct support for the assumption that the chemical potential of I^-_{ads} is a characteristic constant according to eqs. (28) and (32).

From the cited results it was concluded that the constituent I^- ions cannot be in a Nernst distribution equilibrium (c_{bulk}/c_{layer} = const.), for which an elementary thermodynamic isotherm of the Nernst type is valid. They also indicate that the excess constituent ions are much more strongly adsorbed than the counter ions. It is therefore justifiable to assume, for the AgI system, that the total amounts of adsorbed constituent and counter ions, and therefore their chemical potentials are constant and independent of the excess concentration of the constituent ions and that the constituent ions are irreversibly adsorbed as was suggested by eqs. (28) and (32).

3. *The Linear Schulze-Hardy Rule Constant* **a** *in Counter Ion Exchange and Adsorption in Electrokinetics and in Coagulation*

A comparison of the observed values for the linear Schulze-Hardy rule constant **a** (ref. 2 Table II) demonstrated that this value varied between 1.5 to 1.9 in the silver iodide system: It was measured in ion exchange seven times, in ion adsorption in stable sols once, in counter ion coagulation at least 80 times, and in electrokinetics twice. This value was also found constant in the $AgCl/Cl^-$, $AgBr/Br^-$ and $AgBr/Ag^+$ systems. (See also ref. 8. p. 213).

The scatter of the results between 1.5 and 1.9 should not be considered too high because no activity coefficient corrections of the concentration were made and because various ions and various criteria for the determination of the coagulation values were used. Dialized and aged sols as well as fresh sols *in statu nascendi* were used in the experiments. The experiments were performed using different techniques in different laboratories and at different times.

In addition, the constancy of **a** was especially well confirmed when extrapolated coagulation values were used. Ions of the same valency group showed a practically linear »logarithm coagulation value against ion size« plot from which the extrapolated coagulation value for zero radius could be derived.[16]

Težak, Matijević, Schulz, and collaborators have repeatedly claimed that the linear formulation of the Schulze-Hardy rule follows from experiment.[16-26] On the basis of this formulation a method for the determination of ion charges has been developed. Thus Strickland's[27] ion exchange method and Težak's coagulation method for the determination of ion charges can be considered to be based on the same ion exchange mechanism for which the same thermodynamic principles are valid.

Apart from the silver halide colloidal systems, at least four other systems may be quoted as having **a** values in coagulation approximately constant: the gold sols, the silver rhodanide sols, and the cross linked polystyrene gels,[2] and synthetic latexes[8,28]. The various hydrolized species of counter ions[20,21] of various charges also suggest the constancy of **a**.

4. *Electrophoretic, Electroosmotic and Streaming Current Measurements of Electrokinetic Potentials on Silver Iodide*

Electrokinetic mobilities measured on silver iodide and published from two laboratories were transformed into »$1/\zeta$ or $1/u$ against logarithm concentration« plots (u = mobility) (ref. 1 Figs. 2 and 3). The shape of the plots is as predicted by the theory (eq. 47 or 48) and the tangents are shifted for the values **a** = 1.5 and 1.8 as required by eq. (54). Thus the **a** values are in the same range as those obtained in counter ion adsorption and exchange and in coagulation.

The shift in the tangent of the plots of ref. 1 Fig. 3 and those obtained from ref. 29 Fig. 1, using the same value for the slope $1/\zeta_s$, was 1.15. The main difference between the former and the latter results was in the concentrations of Na^+ which were $2 \cdot 10^{-3}$ (pI = 3, $c_{NaNO_3} = 10^{-3}\,N$) and $3.1 \times 10^{-2}\,N$ respectively. This measured shift of 1.15 compares well with the theoretically required shift of 1.2 if due consideration is given to the fact that in different concentrations of electrolytes the conductivity and the dispersity are not constant, causing a variation in the value of the constant and in $\varkappa$ in eqs. (38) and (46). The observed constancy of the ζ-potential suggesting the constancy of σ with pI (ref. 30, Figs. 4 and 5) is also in accordance with the observed constancy of γ, and both are in accordance with the theory.

5. *Comparison of Coagulation Values of Silver Halides*

A comparison of the measured coagulation values of different silver halide systems was published in ref. 24. The results were reproduced in ref. 2 Table I. From these data it may be concluded that the linear Schulze-Hardy rule constant **a** is different for each halide and that the coagulation values of the ions of valency two are equal for the silver chloride, bromide and iodide. This results, which may be expressed in the form of equation (57), can be considered as a direct indication that in the double layer one bivalent counter ion replaces one stabilizing particle. It is therefore assumed in the theory (eqs. 40—50) that water molecules can only be considered as stabilizing particles having $z' = 2$. They are the only particles which can be attracted in an electric field by orientation and which are present when, in the stable sols $a_M < a_{M,coag}$, and the only particles which can be assumed to react in the double layer as dipoles (quadrupoles) carrying two positive and two negative charges. They can also act stabilizingly on positive sols, but oriented in the opposite direction.

If it is assumed in the theory that in the coagulation value the energy of the counter ions is equal to the energy of the stabilizing particles then the coagulation value should be equal to the logarithm activity in which $x = 1 - x = 0.5$. Therefore the intersection of the 45^0 tangent on the »$\log \gamma - \log a_M$« plot with the $\log a_{M,\,coag}$ ordinate should determine the γ_{stab} value. In this way a value of about 20 mg. equiv. per g. mole of AgI has been obtained[2,14]. This value compares well with the value of about 15 estimated from potentiometric measurements for pI 3 from ref. 31 Fig. 2. Practically the same value was also obtained by an analogous treatment of the results on counter ion desorption with increasing concentration of Ag^+ ion. (Ref. 15 Fig. 10).

6. *Counter Ion Adsorption Isotherm in the Region of Coagulation Values*

Results on the adsorption (see ref. 14 Fig. 1) of counter ions in the region of concentrations lower than the coagulation value have shown that the adsorbed amount decreases with decreasing concentration.

Earlier potentiometric[31] measurements show that, in analogous systems, the activity of I^- ion is higher in the dense sedimented fraction of a stable sol than in its supernatant liquid.

Consequently it should be concluded that there are adsorbed I^- ions on stable colloidal particles but the decrease in the adsorbed labelled counter ions is due to their replacement by the dipole molecules, which are adsorbed or oriented in increasing amounts with decreasing concentrations of the counter ions. As a consequence the counter ions will not be adsorbed specifically according to their valencies (eqs. 21, 27, 32) but in the ratio of their concentration in the liquid phase, in which there is always, in addition to the labelled ion, at least one unlabelled ion present (e. *g.* Na^+, H^+) in a relatively high concentration ($\doteq 10^{-3}$ *N*). Thus, the amount of adsorbed, labelled, and therefore measured, counter ion will be negligible in comparison with the (not measured) amount of unlabelled and therefore not measured, adsorbed counter ion of valency one.

On the same plots »logarithm adsorbed amount against logarithm counter ion concentration«, tangents of 45° slope were drawn. When the valency of the counter ion was changed by one, the shift of the tangents was 1.85, in the range of values for the measured constant **a**, as required by eq. (30).

From the same plots and from the coagulation values it may be concluded that the adsorbed amount of I^- ions in stable sols (γ_{stab}) is approximately ten times greater than the amount (γ_{coag}) of these ions on the primary particles which were coagulated by the counter ions. Assuming a constant specific adsorption, the specific surface should be, in coagulated suspensions, about ten times smaller than in stable sols.

7. *Neutralization of Adsorbed Iodide Ions with Silver Ions*

An investigation into the adsorption of the counter ions in the equivalency region[15] showed that the adsorbed amount remained essentially constant from *p*I 2—3 up to about *p*I 6—7 and that the main decrease to zero occurred between *p*I 7 to *p*Ag 7 (*p*I 9) if, in fresh sols having small particles, the final *p*I was obtained prior to the final dispersion equilibrium brought about by coagulation. The intersection of the tangent on the steep part of the plot with the *p*Ag axis gave an extrapolated zero point of adsorption of *p*Ag 7.1. Thus it may be concluded that the essential correctness of eq. (62) is experimentally confirmed and that the neutralization of adsorbed I^- ions with silver ions is the mechanism which decreases the I^- charge. Furthermore, it has been shown that the adsorption-desorption equilibrium between the I^- ions adsorbed on the surface and those dissolved in the liquid cannot be held responsible for the decrease in the adsorbed I^- ions to zero. Of course this neutralization can be considered equivalent to a desorption caused by the increase of *p*I. The small deviation of the experimental plot from the theoretical bilogarithmic plot (Eq. 62) can be explained by the assumed constancy of the electrostatic energy term $\exp[-\Delta\varphi F/RT]$ (See the footnote on p. 182, Chapter B 7), while in reality this energy probably decreases with the *p*I value.

If the I^- adsorption was determined on pre-formed coarse AgI suspensions, the specific adsorbed amount of I^-_{ads} in $\mu C/cm^2$ decreased approximately linearly with *p*I (= *p*A)[32,33]. The specific surface area A can be here assumed constant because, even if the coarse particles coagulate, the contacting surface remains relatively small and the intermicellar volume great as compared with $V = AX_{\delta}$ · This result therefore seems to confirm eq. (67).

Particles of size 10 mμ grow, by aggregation, to a size of about 150—200 mμ if the pI of 5 of a stable sol is increased to pI 9.8 by the addition of Ag^+ ions. The adsorption capacity γ_{stab} expresed in m. equivalents per mole simultaneously decreases. This decrease is linear with a slope of ≐ 3 mequiv/mole · pI. At pI 3, the adsorbed amount by extrapolation obtained is 15—20 mequiv/mole. The decrease in the adsorption capacity is observed also in suspensions coagulated by the counter ions (slope 0.6 mequiv/mole · pI)[31]. This result supports the validity of eq. 69. The decrease in the value $\gamma_{stab} = 15—20$ to a value $\gamma_{coag} = 2—3$ (Chapter C 5) is also in accord with the theoretical conclusion of Chapter B 6.

8. *Isoelectric (Constituent Ion) Coagulation*

Investigations of coagulation in the isoelectric region of the activities of the constituent ions[31] have demonstrated that the onset of isoelectric coagulation occurs at a constant limiting value of $pAg_{limit} = 6.2—6.5$ depending on the experimental conditions within these limits. This value has been shown to be practically independent of the concentration of the coagulating counter ions if this concentration is lower than approximately $\log a_{M, coag} - 1$ for monovalent and bivalent ions. It is independent of the concentration of trivalent ions if this concentration is lower than the coagulation value. Ref. 36 Fig. 4 also shows that this value is equal for silver chloride, bromide and iodide. An explanation of this equality is given by the present theory in Chapter B 9.

9. *The Influence of the Dielectric Constant on the Coagulation Value*

In refs. 34 and 35 results were published on the variation in the coagulation value with the variation in the dielectric constant of the liquid phase, which was achieved by addition of methanol, ethanol, *n*-propanol and isopropanol and with supstances of high dielectric constants. The first results are presented in ref. 4 as plots »logarithm coagulation value against reciprocal dielectric constant«. A statistical analysis confirmed the high significance of the linearity of these plots, and a linear relationship is required by the present theory (Chapter B 8).

10. *Mutual Counter Ion and Constituent Ion Coagulation*

The constancy of the coagulation value in the AgI system in the region from $p\text{I} = 2$ to $p\text{Ag} = 6{,}2$ in the presence of counter ions of valency three and of ions of valency two and one in the region $p\text{I} = 1$ to $p\text{Ag} = 7$ and 8 respectively, in pure water, was demonstrated in ref. 36. With small additions of acetone, ethanol, glycine the constancy was observed in the region from $p\text{I} = 2$ to $p\text{Ag} = 3$, 4.5, 3.5 respectively, that is, in the range of up to 11 units in the pI—pAg scale[5]. The precision of the plots in the vicinity of both limiting coagulation values (c_{coag} and $c_{Ag^+, limit}$) is not very high and there are many experimental influences by which the plot of the transition from the logarithm coagulation value (horizontal part) to the pAg_{limit} value (vertical part) can be varied. The plots for ions of valencies one and two are an approximate or semiquantitative confirmation of the plots required by eq. (62), and in this way they confirm the present theory (Chapter B 10). From the plot for the trivalent ion it follows that the Ag^+ ion does not influence the La^{+++} coagulation and *vice versa* in both concentrations lower than the coagulation values.

11. *Negative Adsorption of the Co-ion-Counter ion Electrolyte*

Experiments on the negative co-ion-counter ion adsorption in the AgI—I^- system have been reported[37]. From these it follows that the logarithm desorbed amount is a linear function of the logarithm co ion concentration with a slope $^1/_2$ for co-ions of valency 2 as derived thermodynamically by eq. (80). From the same paper it follows that negatively adsorbed amount is independent of *p*I in a broad range. In the same range the adsorbed amount is independent of the *p*I also. This confirms the assumption that the chemical potentials of the adsorbed I^- ions is constant, and that the adsorbed amount of I^- ions and that of the negatively adsorbed co-ions are proportional.

12. *Review of some Experimental Observations in the Silver Iodide System*

Some of the main experimental findings used and cited in the subchapters C 1 to 11 can be summarized by the following two simplified and schematized Figs. 8 and 9, (ref. 8, p. 210, 211).

Fig. 8 gives a review of the influence of *p*I (abscissa) upon the coagulation values, electrokinetic mobilities, and adsorbed amount of the MI_z electrolyte (ordinates).

The upper section illustrates the logarithm coagulation value plots of counter ion valencies $z = 1$, 2, and 3. These are mainly horizontal showing a transition to the vertical part which is defined by the coagulation value of the Ag^+ ion at *p*Ag 6.2 (the negative stability limit, Chapter 8). The horizontal branches are shifted for the value **a** — the Schulze-Hardy rule constant — when $\Delta z = 1$ (Eq. 32, 36).

The middle section describes the constancy of the electrokinetic mobility in the positive and negative stability regions. The range of isoelectric coagulation $6.2 > p\text{Ag} > 4.5$ coincides with that of the electrokinetic zero points *i. e.* the range where the positive mobilities change to negative ones. The actual zero points depend on experimental details such as age, dispersity, counter ion concentration, technique *etc.*

The lower section demonstrates: (*1*) the linear decrease of the adsorbed amount of stable sols with *p*I when by aggregation the particles grow from sizes of less than 10 mμ to about 200 mμ at *p*Ag 6.2 where visible flocks are formed abruptly (Eq. 69). (*2*) The constancy of the adsorbed amount γ_{coag} of 2—3 m. equivalents per mole of coagulated AgI in the range $p\text{I} > 7$ with the transition to zero at *p*I 9 (Eq. 62). (*3*) The decrease of the adsorbed amount in μ coulombs per cm^2 with *p*I of preformed aged AgI preparations. If this amount is measured in m. equivalents per mole, the hight of the plots depends on the specific surface area. The values in m. equivalents per mole of aged AgI are about 100 times lower than those of fresh stable sols (Eq. 67). (*4*) The limits of the isoelectric coagulation between $6.2 > p\text{Ag} > 4.5$ and the coagulation value of Na^+ from NaI (for the *p*I variation) at approximately *p*I 1 are also inserted.

Fig. 9 represents, in its upper part, a schematic demonstration of the influence of the logarithm concentration (abscissa) of two counter ions of valencies z and $z + 1$ upon the reciprocal $1/\xi$ of the electrokinetic potentials or mobilities or the reciprocal $1/\mathbf{b}$ of the electrokinetic effect (Eqs. 48, 54). The arbitrary zero on the logarithm concentration scale is at the coagulation value of the z valency ion.

The lower section illustrates experimental increase of the logarithm adsorbed amount $x\gamma$ with $\log a_M$ for stable sols of small particles (cca 10 mμ). By the

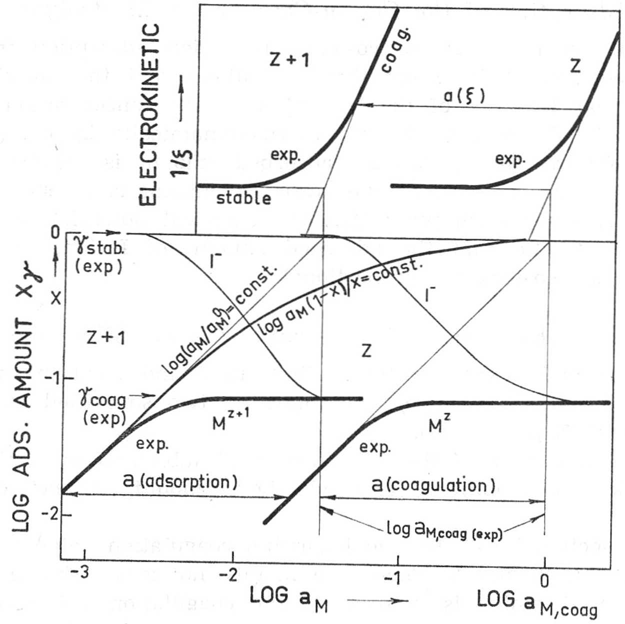

Fig. 9. Plots of $1/\zeta$ or $1/b$ and logarithm adsorbed amount $x\gamma$ against the logarithm activity of the counter ion of valency z and z + 1 for sols of small particles. Experimental transition of the adsorption isotherm of counter ions M and M^{z+1} from the theoretical isotherm defined by γ_{stab} to the isotherm defined by γ_{coag}. The probable isotherm of the adsorbed I^- ions determined by the experimental γ_{stab} and γ_{coag} values (schematic!).

horizontal part of the plot the γ_{coag} value is determined. The intersection of the inclined tangent with the ordinate at the $\log a_{M,\,coag}$ value defines the γ_{stab} value; the latter cannot be measured directly. The hypothetical transition of the total adsorbed amount of I^-_{ads} connects the γ_{stab} with γ_{coag} value.

The shift of the tangents on the $1/\zeta$ or $1/b$ and logarithm $x\gamma$ against $\log a_M$ plots for $\Delta z = 1$, as well as that of the logarithm coagulation values, equals the Schulze-Hardy constant **a**. The value γ_{coag} is determined by the adsorbed amount of M at high a_M, the value γ_{stab} by the intersection of the tangents on the $\log x\gamma$ plots *vs.* the $\log a_{M,\,coag}$ ordinate. The $\log a_{M,\,coag}$ value coincides theoretically with the intersection point of the horizontal and inclined tangents on the $1/\xi$ plots.

D. CRITICISM OF THE ION EXCHANGE THEORY

Several papers criticising the ion exchange theory and its basic concepts have been published[38-43]. Three different groups of objections against the theory have been quoted. One group concerning the interpretation of experimental results, the second claiming errors and inconsistencies in the theoretical assumptions and thermodynamic conclusions and the third the inapplicability of the concept of discrete charges. The aim of the replies[2,8,44] to this criticism was to demonstrate its incorrectness in all points. One of its aims was to prove that no error was made in the interpretation of the quoted results. All objections against the interpretation of results were either based on deviations in the experimental results from the theoretical postulates due to statistical variations on the results, or on the fact, that, these deviations could be corrected by activity coefficient corrections to the concentrations and ascribed to influences not included in the model. Deviations of this kind are normal and not significant enough to invalidate the conclusions. At the same time no simpler, and possibly more correct interpretation of the majority of the same results, has been suggested. It will be demonstrated in Chapter E that the majority of the results which were used for the interpretation or for the deduction of the ion exchange theory were not interpreted by the Derjaguin-Landau-Verwey-Overbeek theory and its extensions, nor by any other theory while those results which were interpreted could not be considered as confirming it. Before considering the Derjaguin-Landau-Verwey-Overbeek theory as accepted, all the results of the various experimental fields should be interpreted in the same rigorous manner as here, and the interpretation should be based on a single double layer model. The basic assumptions and parameters of a theory should not be modified for each group of experiments performed in identical systems (*e. g.* electrokinetics, coagulation, adsorption in $AgI\text{-}I^-$ system) in different ways.

One of the arguments against the theoretical assumptions of the theory is that, in eqs. (21), (28), and (32), the value $\mathbf{a} = \mu_{A^{z-}, ads}/RTz^- = \mu^{o}_{A^{z-}, ads}/RT + \ln\sigma$ (or γ instead of σ) cannot be constant with pI ($= pA = -\log a_{A^{z-}}$) because according the thermodinamic principles, we should have $\mu_{A^{z-}, ads} = \mu_{A^{z-}}$, $\mu_{A^{z-}}$ being variable[39,40,41] in all cases including the present one. This equality follows the Nernst distribution rule (Not the Nernst potential eq.).

According to this rule we should have:

$$\gamma/a_{A^{z-}} = \gamma/a_{I^-} = \text{const.}$$

However, this relationship was not observed for I^- ions in the AgI system. Namely, if the application of the equality of chemical potentials were correct here, then for a variation from pI 7 to 3 the adsorbed amount of I^- ions would increase 10,000 fold. At pI 7 to 3 the adsorbed amount was measured as equal to approximately 2 (up to 3) mg equiv. per mole of a given preparation of AgI[11,12]. Consequently at pI 3 the adsorbed amount of I^- ions should be approximately 20 equiv. per mole and not only 3 mg equiv. per mole as was observed experimentally. Thus, the requirement for the application of the equality of the electrochemical potentials $\mu_{A^{z-}, ads} = \mu_{A^{z-}}$ is absurd in the present case and experiment suggests that $a_{A^{z-}, ads} = \text{const}$, $\mu_{A^{z-}, ads} = \text{const} \neq \mu_{A^{z-}} = \text{var}$. (See Table II, line 2) because this equality contradicts the solubility product principle which follows from the equality in Table II, line 1.

Apart from the fact (see Chapter C 2, 3, 4) that **a**, γ and σ (because of eqs. 28, 37, 38 and 59 as indirectly indicated by electrokinetics, see Chapter C 4) can, according to experimental evidence, be assumed constant with pI, there is no general thermodynamic principle known according to which only one mechanism for adsorption would be possible and this mechanism should follow the Nernst distribution rule.

Even if **a** were a function of $a_{A^{z-}}$, it would still be possible to perform the experiments at a chosen $a_{A^{z-}}$, *i. e.* at a chosen pI value. In fact, the constancy of **a** was first observed in coagulation experiments performed with a constant excess concentration of I^-, Br^-, Cl^- ions which has been found by experience to be reproducible and representative.

According to the second main argument cited against the theory, it is incorrect to assume that:

$$\mu^{o}_{M} = \mu^{o}_{M'}, \mu^{o}_{M,\,layer} = \mu^{o}_{M',\,layer}$$

and

$$\mu^{o}_{A_zM_{z-},\,ads} = \mu^{o}_{A_{z'}M'_{z-},\,ads}$$

In reply[2] to this criticism, several examples have been quoted proving that the above terms should be equal according to the classical theory of ion exchange, as well as according to the elementary theory of electrolyte solutions if rational units for activities are used. *E. g.* according to the Debye-Hückel theory, all activity coefficients of ions of the same valency group are equal and, therefore, also their activities and chemical potentials. The ions are assumed elementary particles equal in all properties except in their charges.

Apart from that, the standard values can be chosen by chosing by agreement the standard states. According to the most elementary definition of ideal ions, they should differ only in charge, and therefore their thermodynamics should only depend on their number (= activity = molar ratio) present in a system. If present in equal numbers, as they are in chosen standard concentrations, their chemical potentials should be equal. Thus the standard chemical potentials of different ideal ions are equal if the activities are expressed in molalities or molarities.

One of Lyklema's and Bijsterbosch's[42] arguments against the discrete interpretation of charges is that, on coarse particles, thausands of I^{-}_{ads} may be adsorbed and not only one or several as has been concluded for extremely small particles. However, even if the number of adsorbed ions is large, these can be considered discrete like those on small particles, in a way similar to the central ions in the derivations of the Debye-Hückel theory.

Levine's opinion that the charge can also be considered continuous on the smallest particles, since the ions can be considered statistically oscillating and a partition function can be assigned to them, seems to be superfluous and unnatural. There are many indications known from which it follows that the mobility *e. g.* of I^- ions is not large in AgI, consequently there is no reason to assume that the I^- ions oscilate on the surface of the AgI particle, as they virtually remain in the same positions in the AgI crystals. The selfdiffusion of halide ions is for orders of magnitude lower in crystals than in solutions.

For obvious reasons Levine's opinion that extremely small particles should not be used for a check of double layer theories can also not be accepted. Extremely small particles are the most characteristic for the colloidal state.

It can be also concluded from a comparison of the I. E. theory with Levine's claims given in ref. 41, p. 216 that none of his contentions holds: *e. g.* the valencies z and z′ were not omitted in the derivation from eqs. (18) and (19) but used in a rational way, the constant **a** was not defined by the standard chemical potentials of counter ions which cancel out, because of eqs. (14) and (18) $\Delta\varphi_M$ and $\Delta\varphi$ are variables and not constant, as required by the definition of Levine's a*, the electric field around a fixed constituent ion is assumed decreasing according to Coulomb's formula and not constant (See Eqs. (1) and (42). If the charge density $\gamma(\sigma)$ is low as proved experimentally the field of the neighbouring constituent ions must become negligible, and $\Delta\varphi_M$ or $\Delta\varphi$ must not depend on *p*I since γ does also not depend on *p*I, $x = 1/2$ does not mean a high charge density since the total charge density $\gamma(\sigma)$, for x = 1 is low. The activity of divalent ions may have any value because it is variable, therefore it may acquire the value which is equal to the constant activity of water dipoles for the attraction in the electric field and this can be the coagulation activity. Any charged particle, also a charge of a dipole, if placed in an electric field must have an electrochemical potential. Water molecules are quadrupoles and therefore it is most probable that in the electrostatic interaction two fixed I^-_{ads} ion charges react with one water molecule which replaces in the layer the equivalent of a two valent ion.

(For a discussion on the remaining points of the criticism the reader is referred to refs. 1, 2, 8, 44.)

E. A COMPARATIVE DISCUSSION OF THE DERJAGUIN-LANDAU-VERWEY-OVERBEEK DOUBLE LAYER THEORY

1. *Introduction*

The most recent efforts to explain the electrokinetic and coagulation phenomena are based on modifications and extensions of the Derjaguin-Landau-Verwey-Overbeek[32,33,45,46] (DLVO) double layer theory. Obviously, these extensions are proposed because the original versions[47-49] can not satisfactorily explain the existing experimental observations.[43,50,51,56]

The original and the extended versions of the DLVO theory are based on the Stern-Gouy double layer model and they use, as the basic electric parameter, the total potential drop across the double layer, called the »surface« potential ψ^0. The actual value of this potential drop is calculated by the Nernst potential formula from the activity of the constituent ion in excess. The electrokinetic potential was deduced from it on the basis of suppositions concerning the charge densities of the constituent ions, the Boltzman distribution of the counter ions, in the Stern -Gouy layer the position of the slipping plane, te zero point of charge, the value of charge, the value of the dielectric constant and of the viscosity in various parts of the double layer, the discreteness of the charge effect and of others. All these suppositions were totally hypothetical and therefore uncertain.[10,33,43] Also, there is hardly any probability that by adjustment of many different hypothetical parameters, correct approximations for the actual values can be found. This probability would be poor even if the physical picture of the double layer were assentially correct and, despite of the known fact that »a function with five parameters can be fitted to the shape of, say, and elephant« (ref. 9, p. 100).

In the DLVO theories the stabilising action was assumed as being caused by repelling forces originating from the interplay of electric double layers on colloidal particles. The long range van der Waals forces were considered as attractive forces between the particles causing coagulation. The assumed values for the Van der Waals constant A were used[50]. These values were not obtained from directly measured values in the same »solid — liquid — solid« systems for which experimental data on coagulation, electrokinetics and ion adsorption are at present known. For all these reasons a discussion of some of the parameters and their variables will be presented here.

The recent discussions of Overbeek[46], Lyklema[43], and Derjaguin[59] can be considered as a direct support of the cited views.

According to Overbeek[56], in the interactions of double layers, the solvent molecules should be included and much refinement should still be made on the theory before the situation is satisfactory. Thus the situation has not changed in this respect, since 1954. when the same opinion was expressed[52]. As the best source on information on van der Waals forces Overbeek considers the flocculation experiments and experiments on thin liquid films, but direct measurements in the non-retarded range as still being highly inaccurate. In 1954, direct measurements of the van der Waals forces were expected to serve as the basis for the solution of the problem. In the meantime he suggested also the transmission of the Van der Waals forces through a medium may be a more serious error than is usually assumed.

2. *The Potential Drop accross the Double Layer and Double Layer Models*

In the DLVO theories the electric parameter is the so called surface potential ψ^o. On one side it is assumed to represent the total potential drop accross the double layer and it could be defined by the difference of the inner electric potentials of the solid and liquid phase, namely by the difference

$$\psi^o = \psi_{\text{solid}} - \psi_{\text{liquid}}$$

On the other side, in the case of metallic electrodes, bare or covered with an ionic solid, the surface potential is assumed to be defined by the Nernst potential equation of electrodes of the first or second order of reversible galvanic cells[47]. Consequently, the surface potential of Ag, or AgI for example, should be proportional to *p*I with an assumed *p*I° value at which the surface potential equals zero. In the monography ref. 47 at least, the surface potential has been explained by the Ag electrode potential, at which the charge formation process can be a redox process only. According to one of the newest claims of Lyklema[43] the proportionality of the potential with *p*I needs not to be based on redox processes while no other explanation for this proportionality has been offered.

In the following arguments are given demonstrating that the concept of the surface potential in colloids derived from the ideas on the electric potentials of galvanic cells is physically meaningless. The same opinion follows from the idea already expressed, first by Guggenheim and latter accepted by Grahame[61], according to which the electric potential difference between dissimilar phases is physically meaningless. Since the processes of electric conduction and charge formation are different in metals from those in ionic solids and electrolyte solutions, the inner electric potentials between dissimilar phases cannot be compared with each other and used as summands in mathematical equations.

To bring the potentials of two electrodes of a reversible galvanic cell to reversible values the formation of a positive and a negative electron charge is necessary, as well as the transference of the charge in the form of ions accross the electrolyte. Since in colloidal systems the second electrode is not present, the charge cannot be formed by simultaneous oxidation and reduction and it cannot be transported accross the electrolyte[6,53,54].

If the surface potential is considered to be the electric potential, or the electromotive force of a galvanic cell, or a part of it, then it is defined thermodynamically by

$$\varphi_{\text{ind}} - \varphi_{\text{ref}} = U = -E = \pm(RT/F)\,[(\mu_O - \mu_R)/n]_{\text{ind}} - [(\mu_O - \mu_R)/n]_{\text{ref}} + \Delta\varphi_{\text{diff}}$$

The subscripts designate the oxidized and reduced states of the potential determining species of the indicator and the reference electrode respectively. Both the charge formation processes can be given by

$$R \rightleftharpoons O + ne$$

one for each electrode but in opposite directions. Here R is the reduced and O the oxidized form of the potential determining species, n is the difference of their oxidation numbers. The symbol φ_{diff} stands for the diffusion or liquid junction potential. Formally it is the difference of the inner electric potentials of the reference and the indicator electrode electrolytes. According to latter equation U or E can only then have a defined value and be physically significant in a system when all species whose chemical potentials occur in the equation, are present in the system. In the colloidal system »ionic solid — electrolyte solution« the reference metallic electrode is absent and consequently the right hand side of the eq. is not defined either.

The process of charge formation on the Ag, AgI electrode can, for example, be presented by the reaction

$$I^- + Ag^o = AgI + e \ (n = 1)$$

and is of course different from the process of charge formation on colloidal AgI, which can be presented by

$$z\,m\,AgI + z\,I^- + M = z\,[(AgI)_m\,I^-_{ads}\,] + M_{layer}$$

Here m is the average number of AgI units per adsorbed I^- ion. In the DLVO theories the surface potential has always been explained as defined by the Nernst potential equation, which is applicable to electrode processes only. However, on the basis of adsorption processes no strict thermodynamic derivation of a potential which would be proportional to *p*I has been suggested so far.

In the colloidal AgI system no metallic Ag^0 is present as a defined phase and the charge represented by a given amount of adsorbed I^-_{ads} ions cannot be taken as equivalent or equal to the electronic charge of an electrode. The electronic charge of an electrode, which is always equal but of opposite sign from that of the second electrode, depends on the outside (integral) capacitance of both electrodes (connecting leads + instrument poles). It does not depend on the exposed electrode surface. The charge *i. e.* the adsorbed amount, on an ionic solid depends on its specific surface.

If the adsorbed electrolyte is assumed to represent the charge and to cause the potential on colloidal particles, then there would be several theoretical possibilities for the correlation between the charge and potential.

If we assume that the colloidal particle is a spherical condenser, then its capacitance, or the charge at a given potential would be proportional to the particle radius. The basic difference however between a spherical condenser in vacuum and a sphere with an adsorbed and disscociated electrolyte in a solution phase should be stressed here. In the first case the charge opposite to that of the sphere is at infinite distance, while on the colloidal sphere, the ionic charges are separated for a definite mean distance of the order of tens of millimicrons. No electric fields do arise at larger distances.

The ion charge located at the interface cannot be transported accross the connecting leads, as in the case of the electron charge.

If we assume that the charge density is constant under otherwise constant conditions, then the charge on a particle would be proportional to square of the radius. Since both principles cannot be applied, the charge density or the potential cannot be constant on particles of different size. In general, in the DLVO theories, it is difficult to conclude in which way the potential and the charge were correlated theoretically.

All these arguments indicate that the surface potential of the DLVO theories should be redefined and derived on the basis of straightforward thermodynamic principles.

The examples given in Fig. 10 describe some arguments leading to the conclusion that a »surface« potential determined by the Nernst potential equation, which would be characteristic for a given metal, does not physically exist and that even less such a potential exists on an ionic solid.

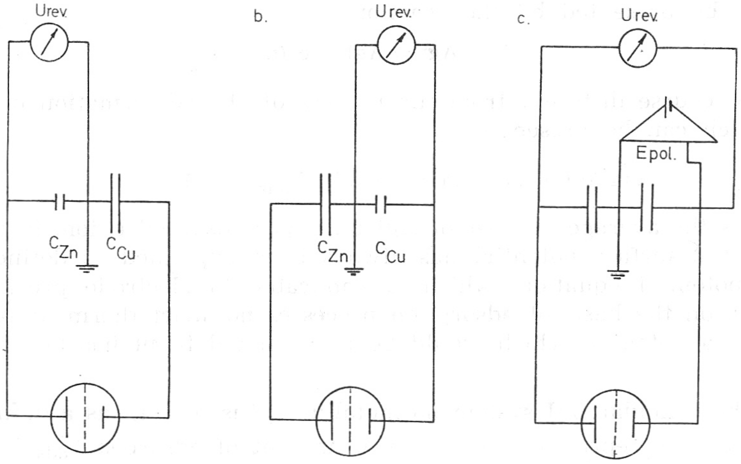

Fig. 10. A reversible Zn/Zn^{2+} — Cu^{2+}/Cu couple, liquid junction eliminated, when the capacitances connected to the electrodes are in (*a*) $C_{Zn} < C_{Cu}$, in (*b*) $C_{Zn} > C_{Cu}$ and (*c*) when a polarization potential is imposed upon one of the capacitances. In all cases is $U = U_{rev}$ measured by an electrometer or the like, with the electrometer connected to the smaller capacitance in (*a*) and (*b*) or to the electrodes in (*c*).

Cases (*a*) and (*b*) Fig. 10 show that the same reversible electromotive force $E_{rev} = —U_{rev}$ can be measured irrespectively of which of the electrodes is connected to the smaller condenser. The same is true for case (*c*). Irrespectively of how high or of which sign is the polarization potential, the measured electromotive force will be E_{rev}. Also the variation of the activity of the Cu^{2+} ion in scheme (*a*) will cause a variation of the potential of the smaller Zn electrode condenser, while the potential on the high capacitance Cu condenser will remain virtually constant and equal zero. In the case when the capacitances on both condensers are of the same magnitude the potential will vary on both electrodes depending on the ratio of their capacitances and not on the difference of their redox potentials. In case (*b*) the theoretical variation only of the Cu electrode potential would occur on the

Cu condenser, and in this particular case only the Nernst potential could be significant for the Cu electrode. Experiments performed in our laboratory with polarization potentials up to ± 1000 volts with a silver-calomel cell according to scheme (c) confirmed the above conclusions.

We assume now, that the Cu electrode is combined in one case with a Zn electrode to form a galvanic cell and in the other case with a Ag electrode. As a consequence of the ideas on absolute electrode potentials the Cu electrode would have the same potential, and the same charge in both cells. It is evident that in one case the charge formed is positive and in the other case it is negative. It follows that the electrode potential depends on its electron charge but not on its chemical composition whereas the electron charge depends on the second electrode present.

From the following an analogous theoretical argument can be deduced. Suppose that two metallic spheres, one being made of Zn, the other of Cu, are immersed in the solutions of their salts. Both solutions are in contact, the diffusion potential being eliminated. In one case the smaller is the Cu and in the other case the Zn sphere is the smaller. This means that the capacitances of electrodes are different in each case, while the integral capacitance of the pair of electrodes is the same in both cases. If the charge formation process is the redox process of Zn dissolution and of Cu^{2+} ion reduction, then again the difference of the inner electric potentials of both metals will be the same in both cases. Also the positive and negative electron charge on both electrodes will be the same. Consequently the charge density on the larger electrode remains after the charging process essentially unchanged, while practically the total potential drop in both cases occurs on smaller electrodes. Thus, the same reversible potential of the Zn—Cu couple would in one case occur on the Zn and in other case on the Cu colloidal sphere.

The assumption that the adsorbed electrolyte could contribute to the inner electric potential of a colloidal particle is impossible because of the following. The anions and cations are adsorbed in equivalent amounts. At distances which are large as compared to distances of their separation no electric fields can arise. We can assume that the inner of the colloidal particle is also at distances which are so large that no electric field do arise there.

An additional problem is that of the interrelation between the inner electric potentials of a metallic electrode and the ionic solid of second order electrodes. In the DLVO theories the assumption is made that the potential, or variation of the inner electric potential of the AgI equals the potential of the Ag electrode or to its variation. Obviously the proportionality between *p*I and the potential on AgI is based on this assumption. In general, conductors of different types in contact, like electronic conductors, semiconductors, ionic conductors, are always polarizable.

A combination of such conductors gives always a galvanic cell. There has been no explanation why the potentials in two different conductors in contact would be equal. The experimental evidence proves, however, that they are different, and cause the EMF of the cells.

On the other hand, the DLVO theories use also the Stern-Gouy double layer as the model for the double layer on colloidal particles. The Stern-Gouy double layer was worked out for the explanation of ideal polarized electrode interfaces. Here, the inner charge in the metal surface is assumed to be represented by an excess or deficiency of electrons. An excess of cations or anions in the liquid layer adjacent to the interface constitutes the outer layer of charges of opposite signs. An equivalent amount of ions was removed from the same layer by transference. This are the so called »ghost« ions of Grahame[61], which would be present in the same layer if the electrode had not been polarized. Also an equivalent amount of potential determining ions at the reference electrode was removed from, or formed in the electrolyte phase. It follows, that the double layer of adsorbed cations and anions on a colloidal particle is in principle different from the Stern-Gouy layer of a polarized electrode, and therefore the Stern-Gouy layer cannot be used for the explanation of phenomena in colloids. Also the source of energy for the formation of the Stern-Gouy distribution of ion charges is in the polarizing battery. Such an energy source is not present in the colloidal system.

The cited arguments prove that between the solid and liquid phase there is no electric potential difference characteristic for a metal, or an ionic solid in contact with solutions of their ions which is proportional to the logarithm of their activity. If such a potential existed, it would be different: (1) for each different electrode of a cell, (2) for different polarization and compenzation potentials, and (3) for different electrode capacitances (curvature, shape, size) and different capacitances connected to the electrodes. Consequently, for colloidal particles the capacitance and hence the potential would depend on their size. Also, in colloids the second electrode is missing. In polydisperse sols each particle would have a different potential and no explanation has been given as to the proportionality between the potential and *p*I.

Still less could such a potential be characteristic for solid-liquid systems where the solid is an insulator, semiconductor or ionic solid and not a metal. Yet, virtually identical colloidal properties were observed with all these categories of solids.

3. *Electrokinetic Potentials*

Interpretations of electrokinetic potentials suggested by Lyklema and Overbeek[32] are now indirectly declared as unsuccessful[43,56] by themselves and they expressed doubts on whether it will ever be possible to explain them by the DLVO theory. Overbeek considers, namely, the theoretical relationship between zeta and surface potential as being far from simple and that there is »no good understanding as to where the slipping plane (if it is a plane) is situated.«

Lyklema's recent opinion[43] is that neither of the theories (the ion exchange theory was not considered) can at present be used to relate the theoretical ψ_δ potential at the slipping plane and the experimental ζ-potential. Also the sole system for which the amount of specifically adsorbed counter ions in the Stern layer has been measured he cited the mercury system. As reliable data on the stability of mercury sols are scanty, this fact has little practical value. However, in our opinion, the chemical specificity of adsorption on mercury should be differentiated from the electrostatic one depending on the valencies of the adsorbed counter ions on silver iodide.

4. *The Schulze-Hardy Rule and the »Coagulation Value against* pI« *Plot*

There are two main experimental confirmations for the correctness of any of the theories of coagulation *i. e.* the quantitative variation in the coagulation values with the valency of the coagulating counter ions — the Schulze-Hardy rule — and the variation in the coagulation values with *p*I.

According to the original Derjaguin-Landau-Verwey-Overbeek theory[47,55,59] this rule should be formulated as the »inverse sixth power law«:

$$(a_{M^z}/a_{M^{1+}})_{coag} = z^{-6}$$

No experimental investigations have been published confirming this law, while the linear formulation has been repeatedly confirmed by experiment (Chapter C 3).[8] Thus in one of the extensions or modifications of this theory the proposal was given as how to »reconcile the linear formulation of the Schulze-Hardy rule and the inverse sixth power law.«[45]

The conclusion was that, at a discrete *p*I value the linear rule, and at another value the inverse sixth power law would be valid.

After the arguments[2] were published, from which it should be concluded that the inverse sixth power law cannot certainly be valid for the silver iodide system for any observed discrete *p*I value, and that the deduced theoretical »logarithm coagulation value against *p*I« plots are not in accordance with the experimentally observed plots, this theory was again modified[46]. The plots »logarithm coagulation value against *p*I« were deduced for trivalent ions only, and they were not compared with known experimental plots.

The final conclusion concerning the Schulze-Hardy rule was that »none of the simple formulas previously proposed for the variation in the coagulating electrolyte concentration with the valency can generally be valid« and that the »Schulze-Hardy rule must describe a range of coagulating concentrations dependent on the specific adsorption characteristic of the counter ions«.

From the experimental evidence cited in Chapter C 3 we may, however, draw the conclusion that the linear Schulze-Hardy rule and the constant resp. bilogarithmic »coagulation value against *p*I« plot represent formulations which are, in principle, most likely to decribe the experimental results correctly. The agreement between the cited formulations and experiment can be considered as sufficiently significant and therefore another better fundamental formulation is not necessary.

A characteristic of the two latest extensions of the theory is that more than ten values were adjusted arbitrarily without quoting any experimental evidence for the correctness of any of these adjustments. In the original theory six parameters were used in a similar way (ref.[50] p. 205).

Both (Lyklema's and Levine's) extensions of the Derjaguin-Landau-Verwey-Overbeek theory (Chapters E 3 and 4) are based on quantitatively different double layer models which cannot be valid for the same material system under practically equal experimental conditions. In one of the extensions, corrections for viscosity were introduced, in the other, corrections for the dielectric constant of water. It is evident that, for the same system, only one single structure of the double layer can be of physical significance. Thus these extensions exclude each other and at least one of them must be incorrect for the sole reason of principle.

Derjaguin[59] attempts to explain the divergence between the theoretical inverse sixth power law (z^{-6}) and the empirical linear formulation of the Schulze-Hardy rule by the arbitrary supposition that the product $z\psi$ (ψ being the surface potential) of the Derjaguin-Landau-Verwey-Overbeek theory has seldom a sufficiently high value for strongly adsorbable high-valency counter ions. Therefore, for a check of the theories only ions of valency $z = 1$ and 2 should be used. In our opinion[8], the experiments do not suggest any difference in the coagulation of ions of valency $z = 1,2$ and 3,4 and the coagulation values of ions with $z = 3$ (or even 4) are not less conclusive than those of $z = 1,2$. A physical explanation of the empirical linear rule is in the meantime given by the ion exchange theory, the latter was not considered by Derjaguin.

5. *Various Experimental Observations on the Constituent and Counter Ion Coagulation*

None of the remaining experimental findings reviewed in Chapter C, which were used for the derivation, or cited here as a confirmation of the ion exchange theory of coagulation have, so far, been either incorporated into these theories or used to check them. In the first place the results on the specific adsorption of constituent and counter ions have been completely neglected, especially the fact that the adsorption of different counter ions follows the classical thermodynamics of ion exchange. The Schulze-Hardy rules, the linear or the 6 log z rule have been investigated in coagulation only, and no attempts to deduce them in electrokinetics or in counter ion adsorption are known. The influence of the valency and concentration of the counter ion upon the electrokinetic potentials has not been investigated (see Chapter C 4), nor has an explanation been given as to why the coagulation values of bivalent ions are equal in the silver chloride, bromide and iodide systems. Similarly, no explanation has been given as to why the Schulze-Hardy rule constant is different in each of these systems (See Chapter C 5). The decrease in the adsorbed amount of counter ions below the coagulation value concentration has also been established[14] and has not yet been incorporated into these theories. (See Chapter C 6). No explanation has been given either for the linear variation in the logarithm coagulation value with the reciprocal dielectric constant (See Chapter C 7), or for the equality of the negative activity limit of stability (See Chapter C 8) in all the three silver halide systems. All these experimental observations also need to be explained by the DLVO theory, and this explanation should be based on a single double layer model which should not be different or should not be modified for each group of experiments in any way.

6. *Basic Parameters of Different Double Layer Theories*

The equations defining the discrete charge potential the coagulation value and the electrokinetic potential or mobility (eqs. 18, 19, 48, 54) include the following basic parameters: valency (z), activity in the liquid phase (a_M, $a_{M'}$) and the activity ($x\sigma$ and $(1-x)\sigma$) in the adsorbed counter ions, the activity (σ) and the valency (z^-) of the adsorbed or fixed constituent ions.

The quoted elementary and basic parameters, by which the discrete charge potential of the ion exchange theory is thermodynamically defined, are the same as those found in the empirical equations for the coagulation values, electrokinetic potentials, and counter ion adsorption and exchange. The cited parameters are the representative, quantitatively measurable parameters of the double layer and their properties predicted by the ion exchange theory can be considered as confirmed by experiments.

The basic parameters by which the Nernst potential is defined are: the ratio of the activities of the potential determining species in the oxidized and reduced states, a_O/a_R, the difference in the oxidation states of the potential-determining species, n, and the electronic charge, *i. e.* the potential of both electrodes. None of the cited parameters of the Nernst potential has any first order influence on the electrokinetic potential, on counter ion adsorption and coagulation. The Nernst potential, which is assumed proportional to *p*I, is the basic parameter of the DLVO theory.

Thus, one of the main advantages of the IE theory is that its elementary and basic parameters have an influence on the experimentally observed phenomena in coagulation, electrokinetics, and electrolyte adsorption and exchange as required by direct thermodynamic postulates. The same critical parameters were introduced into the DLVO theory by hypothetical, not proved suppositions, requiring a series of additional parameters and their quantitative adjustment. The introduced suppositions, which are not proved, either theoretically or experimentally are: the influence of the valency and activity of the counter ion on its quantitative Boltzman (Stern-Gouy) distribution in the double layer the actual value for the distance of the slipping plane and the quantitative variation in the dielectric constant and in the viscosity in the double layer as functions of the distance from the surface. At the same time it has not been experimentally proved that the viscosity and the dielectric constant vary in the double layer of the colloid in the supposed way.

An additional basic parameter of the DLVO theory is the van der Waals constant. Its role in coagulation has been anticipated without nay experimental evidence. Its actual value has not been determined for the system silver halide-electrolyte solution-silver halide. It is evident that the values obtained for other materials in vacuum are not applicable in the present case.

The Debye-Hückel thickness of the double layer has been arbitrarily taken as equal to the Debye-Hückel thickness of the bulk electrolyte.

In general, the actual values of the majority of parameters used in the DLVO theories were not directly derived from experiments on the same solids for which coagulation, adsorption, and electrokinetic data are available. No direct proof therefore for the correctness of their application in the DLVO theories is possible (see also Overbeek[56] and Lyklema[43]).

An additional theoretical parameter of the DLVO theory is the particle size for which it was shown that its influence upon coagulation is negligible while the DLVO theory requires significant quantitative influences. By this theory a marked difference between the coagulation of fresh (small particles) and aged sols (coarse particles) was predicted. However, such a difference was not reported for the AgI system. On the contrary it was repeatedly observed that fresh and dialized sols gave the same results in coagulation[8,20,22,57]. Analogously, fresh and aged sols, having small (~ 10 mμ) and coarse particles ($\sim$ 150 mμ) gave the same pAg value at which the Ag^+ ions cause the »isoelectric« coagulation (ref. 50 pp. 225 and 226). Also, the zero point of the I^- adsorption does not depend on the method of preparation of the AgI (fresh or aged) and on the direction of the activity change during the experiment. Analogous independence of the slope of the logarithm stability factor against logarithm coagulating counter ion concentration has been observed also by Ottewill and Shaw while the DLVO theory predicts a significant increase with particle size[60].

There is no doubt that the DLVO theory has been developed prior to the publication of many of the experimental data on coagulation, counter ion exchange, and electrokinetics. The premises used were brought into the theory from experimental observations on reversible galvanic cells, on polarized electrodes, on the attraction between solids in vacuum and others, which were latter found not to be connected with the colloidal phenomena in the supposed way. It is therefore not surprising that the conclusions obtained were latter not confirmed by new experiments. The present position of the DLVO theory with regard to its theoretical premises and its experimental confirmation does certainly not warrant its acceptance and it urges the search for other useful and acceptable theories of colloid stability and coagulation.

Acknowledgement. The ion exchange theory of coagulation is mainly the result of a large number of experimental investigations initiated by Prof. Božo Težak some thirty years ago and has been continued by a large group of investigators. Only a part of all papers dealing with the experimental aspect of this problem has been quoted in the literature of this article.

The valuable experimental contributions of my younger colleagues and students, cited in the papers where I am coauthor merit special acknowledgement. Without their collaboration the greater part of the experimental basis of the theory would not have been at my disposal.

I am grateful to Prof. Težak for introducing me into this field of investigation, for his being my teacher during the initial period of my research on this subject and for the many discussions we have held in the years that followed.

I would like to thank Prof. Velimir Vouk for the revision of a part of the manuscript and for a critical discussion and Mrs. Lidija Đačić and Dr. S. Carter for their help in the presentation of the manuscript.

GLOSSARY OF SYMBOLS

a	Proportionality constant of the linear Schulze-Hardy rule
a_i, $(a_i)_{x=0,5}$, $a_{i,\,coag}$, a_i^o	Activity of an elementary particle i in gram equivalents per liter, its value at x = 0.5, its critical coagulation value, and its standard value
A, A^o	Specific surface area in cm^2 per gmole or per liter of the solid, its value at $pA^o - pA = 1$
A^{z^-}, $A^{z^-}_{ads}$ (A^-, A^-_{ads})	Constituent anion of valency z^- in the solution phase and adsorbed in inner layer

$(A_{z^+} B_{z^-})_{ads}$ or $(AB)_{ads}$, $((AB)_{ads})_{limit}$	Adsorbed constituent ion neutralized with another constituent ion, at its limiting value for stability
$(A_z M_{z^-})_{ads}$, $(AM)_{ads}$	Adsorbed ion pair: constituent ion — counter ion
$\mathbf{b}$, $\mathbf{b}_s$, $\mathbf{b}_{H_2O,\ layer}$	Measured electrokinetic effect: 1) variable, 2) corresponding to a tenfold variation in activity and 3) constant when $a_M < (a_M)_{x=0.5}$
$B^{z^+} (B^+)$, $B^{z^+}_{limit}$ (B^+_{limit}), $B^{z^+}_{ads}$	Constituent cation of valency $z^+ =$ 1) in the solution phase, 2) in the limiting coagulation value activity, and 3) adsorbed in the double layer
c_1	Co-ion concentration
C	Capacitance of a condenser
const.	Proportionality constant of a given equation
D	Dielectric constant of the liquid phase
$D_M = x\gamma/a_M$ $D_{M'} = (1-x)\ \gamma/a_{M'}$	Distribution coefficient of two counter ions or of a counter ion and dipole M and M′ of valencies z and z′
e	Electronic charge
F	The Faraday
H_2O, H_2O_{layer}	Water molecule in the solution phase and oriented in the double layer
K_a, K_α	Thermodynamic equilibrium constant in counter ion exchange expressed by the aid of activities or their ratios resp.
K_{AgI}	Solubility product of AgI
$M\ (M^z,\ M^{z+1})$, M', M^o	Counter ions or dipoles of valencies z, (z + 1), z′ and z = 0
M_{layer}, M'_{layer}, M^o_{layer}	Counter ions of valencies z, z′ z = 0 adsorbed in the outer layer
M_{coag}, M'_{coag}, M^o_{coag}	Counter ions of valencies z, z′, z = 0 in the coagulation value concentration
n	Number of excess charges
pA, pA^o	Negative logarithm (basis e or 10) activity of the ion A^- and its critical value for σ (or γ) = 0
pB_{limit}	Negative logarithm activity of B^+ in the limiting coagulation value activity
Q	Charge of a condenser
r	Distance from a point (ion) charge fixed in the layer
R	The gas constant
S	The separation factor of counter ion exchange and adsorption
T	The absolute temperature
x, x_{coag}	Fraction (of γ or σ) of counter ions M in the outer layer and its value in the coagulation value concentration

$1-x$, $1-x_{coag}$	Fraction (of γ or σ) of oriented H_2O molecules in the outer layer and its value in the coagulation value concentration; in counter ion exchange, fraction of another adsorbed counter ion M′
X_{δ}	Mean double layer thickness
Y^-, Y^-_{des}	Anions of the liquid phase = co ions, desorbed or expelled from the double layer
z, z', z_i	Valencies of the counter ions M, M′, i
z^+, z^-	Valency of the positive or negative constituent ion forming the precipitate
α, $1-\alpha$	Fraction of the counter ion activity a_M and $a_{M'}$ of $a_{Y^-} = a_M + a_{M'}$ in the liquid phase
β, $1-\beta$	Fraction of the activity of 1) nonneutralized $a_{A, z^-_{ads}} = \beta\sigma$ and 2) neutralized $a_{(AB)ads} = (1-\beta)\,\sigma$ adsorbed constituent ion
γ, γ_{stab}, γ_{coag}, γ^0	Total adsorbed amount of constituent ions in the inner layer equal to the total adsorbed amount of counter ions in the outer layer for stable and coagulated states per liter; its value at $pA^\circ - pA = 1$
δ, $\delta_{H_2O,\,layer}$, δ_{coag} δ_s	The mean distance between the constituent ions in the inner layer and 1) counter ions in the outer layer, 2) the positive charges of oriented H_2O molecules in the outer layer, 3) same distances in the coagulation value concentration when they are in equilibrium with the same particles in the liquid phase, 4) the variation of δ for a 10-fold variation in a_M
Δc_1, Δc_1^o	1) increase in the bulk concentration of the desorbed anion Y^-, 2) its standard value at $c_1 = 1$
$\Delta\varphi$, $\Delta^o\varphi$, $\Delta^1\varphi$, $\Delta\varphi_{coag}$, $\Delta\varphi_i$	Double layer electrostatic potential: 1) variable, 2) standard, 3) corresponding to a 10^a-fold change in concentration, 4) in the coagulation value concentration 5) actual of an ion i
$\Delta\mu_i$, $\Delta\mu_i^o$, $\Delta\tilde{\mu}_i$, $\Delta\tilde{\mu}_i^o$	Difference of chemical and electrochemical potentials in the liquid and layer phase; their standard values
$\varkappa$	Electric conductivity in the solution phase
$1/\varkappa$	Debye-Hückel radius
ζ, ζ_s, $\zeta_{H_2O,\,layer}$	Electrokinetic potential 1) variable, 2) its value corresponding to a tenfold variation of a_M when $x \rightarrow 1$ and 3) its value for $a_M < (a_M^o)_{x=0.5}$
η	Viscosity constant
μ_i, $\mu_{i,\,ads}$, $\mu_{i,\,layer}$	Chemical potential of an elementary particle i (ion, ion pair, molecule): 1) in the solution phase, 2) adsorbed in the inner layer, 3) adsorbed in the outer layer

μ_i^o	Standard chemical potential of an elementary particle
$\tilde{\mu}_i$, $\tilde{\mu}_{i, ads}$, $\tilde{\mu}_{i, layer}$	The electrochemical potential (free energy change) of an elementary particle i: 1) in the liquid phase, 2) adsorbed in the inner layer, 3) adsorbed in the outer layer
$\tilde{\mu}_i^o$	Standard electrochemical potential of the ion i
π	Ludolf's number
$\bar{\varrho}_-$, $\bar{\varrho}_-$ (r.)	Average anion charge density, 1) per unit volume, 2) per unit distance
$\sigma \pm$	Counter ion charge density (anions or cations)
σ, σ^0	1) The quantity of adsorbed constituent ions which are neither hydrated nor associated with counter ions (in gram equivalents per liter of sol), 2) the same at $pA^o - pA = 1$
φ_{liquid}, φ_{solid}	Inner electric potential (absolute Galvani potential) in the solution and in the solid phase
φ_{outer}, φ_{liquid}, φ_{outer}^o, φ_{liquid}^o, $\varphi^\pm$, φ_i, φ_i^o, $\bar{\varphi}$	Electrostatic potential arising 1) at the mean distance r = δ from an adsorbed constituent ion, 2) in the liquid phase, 3) and 4) their standard values, 5) caused by the actual statistical counter ion distribution in the layer, 6) the potential to which the ion i is exposed, 7) its standard value, 8) average electrostatic + charge density potential
ψ^0	Galvani potential defined by the Nernst formula or the surface potential

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IZVOD

Teorija ionske zamjene koagulacije i njena eksperimentalna verifikacija

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Na temelju modela dvosloja diskretnih fiksnih naboja dan je izvod jednadžbi elektrostatskog potencijala tog dvosloja, koje za dva prisutna protuiona M i M′ glase:

$$\Delta\varphi = \Delta^{\circ}\varphi + [z\,\mathbf{a} + \ln(a_M/x\,\sigma)]\,(RT/F)$$

i

$$\Delta\varphi = \Delta^{\circ}\varphi + \{z'\,\mathbf{a} + \ln[a_{M'}/(1 - x)\,\sigma]\}\,(RT/F)$$

$\Delta\varphi$ je potencijal dvosloja fiksnih naboja, $\Delta^{\circ}\varphi$ je njegova standardna vrijednost definirana razlikom standardnih kemijskih potencijala iona u dvosloju i u otopini, z, z′ su valencije iona, **a** je konstanta proporcionalnosti linearnog Schulze-Hardyjevog pravila, a_M i $a_{M'}$ su aktiviteti iona u otopini, x i (1 — x) su njihove ekvivalentne ionske frakcije u dvosloju, σ je gustoća naboja u gramekvivalentima na mol (ili gram) krutnine, R, T i F imaju uobičajeno značenje. Te dvije jednadžbe vrijede kad su dva (protu) iona ili ion i dipol u ravnoteži s ionima drugog predznaka koji su fiksirani na površini neke krutnine. Potencijal fiksnih naboja koristi se kao osnovni električni parameter opće teorije ionske zamjene i njene primjene u koagulaciji i koloidnoj stabilnosti.

Dvije jednadžbe potencijala dvosloja fiksnih naboja služe za izvod jednadžbe faktora separacije, termodinamske konstante ravnoteže izražene aktivitetima, odnosno ekvivalentnim ionskim frakcijama, kao i Stricklandove jednadžbe za određivanje naboja u teoriji ionske zamjene.

U koloidnoj kemiji izvedena je jednadžba linearnog Schulze-Hardyjevog pravila za koagulaciju, elektrokinetsku pokretljivost, izmjenu protuiona, adsorpciju u općem obliku

$$\ln(a_M/a_M{}^{\circ})_{coag} = \ln(a_M/a_M{}^{\circ})_{\zeta = const} = $$
$$= \ln(a_M/a_M{}^{\circ})_{x = const} = -z\mathbf{a}$$

Tu su $a_{M^{\circ},\,coag}$, $a_{M^{\circ}\,(\zeta = const)}$ i $a_{M^{\circ}\,(x = const)}$ konstante.

Jednadžba koja definira teoretsku promjenu elektrokinetskog potencijala ζ ili produkta elektrokinetskog efekta **b** i vodljivosti ϰ s logaritmom frakcije stabilizacione čestice u dvosloju (1 — x) glasi:

$$1/\zeta = 1/\zeta_{H_2O,\,layer} - (1/\zeta_s)\ln(1 - x)$$

odnosno

$$1/\varkappa\,\mathbf{b} = 1/\varkappa\,\mathbf{b}_{H_2O,\,layer} - (1/\varkappa\,\mathbf{b}_s)\ln(1 - x)$$

Tu su $\zeta_{H_2O,\,layer}$, $\mathbf{b}_{H_2O,\,layer}$, ζ_s i $\mathbf{b}_s$ konstante.

Konstanta proporcionalnosti linearnog Schulze-Hardyjevog pravila **a** objašnjena je definicijom

$$\mathbf{a} = \Delta^1\varphi\,F/RT = \mu_{A^{z-},\,ads}/RTz^-$$

Prema tome, ta je konstanta proporcionalna kemijskom potencijalu fiksnih i adsorbiranih iona. Izvedena su također pravila za izoelektričku i istovremenu izoelektričku i protuionsku koagulaciju u tri argentum halidna sistema.

Dan je pregled objavljenih eksperimenata koji pokazuje da su sve izvedene jednadžbe i pravila potvrđeni eksperimentima.

Također je dan pregled objavljenih kritika teorije ionske zamjene i diskutirani su neki od argumenata kritike i odgovora na tu kritiku. Protuargumentima je pokazano za neke od tačaka kritike da je ova nepravilna.

Opisane su najvažnije principijelne razlike između teorije ionske zamjene i izvorne, kao i proširenih verzija Derjaguin-Landau-Verwey-Overbeekove teorije koagulacije i koloidne stabilnosti. Umjesto osnovnog električkog parametra te teorije, tj. površinskog ili Nernstovog potencijala, upotrebljen je i izveden u teoriji ionske zamjene potencijal dvosloja fiksnih naboja. Taj potencijal je definiran egzaktno termodinamski, na bazi jasno definiranih eksperimentalnih parametara: valencije, aktiviteta, adsorbirane frakcije protuiona, odnosno količine i valencije fiksnog konstitutivnog iona. Da se zadovolje eksperimentalni podaci u DLVO-teoriji, ti su parametri uvedeni putem eksperimentalno i teoretski neopravdanih pretpostavki. Nasuprot tome Nernstov, ili tzv. površinski potencijal, definiran je logaritmom omjera aktiviteta oksidiranog i reduciranog oblika konstitutivnog iona i razlikom njegovih oksidacijskih stanja. Od ovih dvaju aktiviteta bar jedan nije definiran u koloidnom sistemu.

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