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Fixed Charge Double Layer Potential Equations — a Derivation*

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Assuming equality of electrochemical potentials

$$\tilde{\mu}_M = \tilde{\mu}_{M,\ \mathrm{layer}}$$

of a counter ion M or M′ in the layer and the liquid phase of the system »solid-liquid«, and assuming that:

$$\tilde{\mu}_M = \mu^o_M + RT\log_e(a_M/z) + z(\varphi_{\mathrm{liquid}} - \varphi^o_{\mathrm{liquid}})F$$

$$\tilde{\mu}_{M,\ \mathrm{layer}} = \mu^o_{M,\ \mathrm{layer}} + RT\log_e(a_{M,\ \mathrm{layer}}/z) + z(\varphi_{\mathrm{outer}} - \varphi^o_{\mathrm{outer}})F$$

$$\varphi_{\mathrm{outer}} - \varphi_{\mathrm{liquid}} = \Delta\varphi_M$$

$$\varphi^o_{\mathrm{outer}} - \varphi^o_{\mathrm{liquid}} = \Delta^1\varphi = \mathbf{a}RT/F$$

$$z\Delta\varphi_M = \Delta\varphi$$

$$\mu^o_{M^0} - \mu^o_{M^0,\ \mathrm{layer}} = \Delta\mu^o_{M^0} = \Delta^0\varphi F$$

the two fixed charge double layer potential equations

$$\Delta\varphi = \Delta^0\varphi + [z\,\mathbf{a} + \log_e(a_M/x\gamma)]\,RT/F$$

and

$$\Delta\varphi = \Delta^0\varphi + \{z'\,\mathbf{a} + \log_e[a_M{}'/(1-x)\gamma]\}\,RT/F$$

are derived.

The symbols have the following meaning: μ^o_M and $\mu^o_{M,\ \mathrm{layer}}$ are standard chemical potentials, **a** are activities in equivalents per litre, $\Delta\varphi_M$ is the actual electrostatic potential under which counter ions M, M′ of valency z, z′ are exposed in the outer layer relative to the potential $\varphi_{\mathrm{liquid}}$ of the liquid phase, and it depends on z, $\Delta^0\varphi$ is the standard chemical potential expressed as electrostatic potential, $\Delta\varphi$ is the variable potential per elementary charge of ions of different valencies independent on z, $\Delta^1\varphi$ is the difference of the standard electrostatic potentials in the outer layer and the liquid, *i. e.* $\varphi^o_{\mathrm{outer}}$ and $\varphi^o_{\mathrm{liquid}}$. $a = \Delta^1\varphi F/RT$ is the proportionality constant of the linear Schulze-Hardy rule which defines the separation factor S of ion exchange by:

$$\log_e S = (z' - z)\,\mathbf{a} = \log_e(a_M\, a_{M',\ \mathrm{layer}}/a_{M,\ \mathrm{layer}}\, a_{M'})$$

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where $a_{M,\,\mathrm{layer}} = x\gamma$ and $a_{M',\mathrm{layer}} = (1 - x)\gamma$ are the activities in the layer of the two counter ions. Their total activity in the layer is γ and it equals the activity of the fixed and adsorbed ions A^{z-}_{ads} in the layer, x and 1—x are their equivalent ionic fractions.

The theoretical explanation of **a**, and therefore of $\Delta^1\varphi$, is given by

$$\mathbf{a} = \mu_{A^{z-}_{\mathrm{ads}}} / z^- RT = \mu^{\mathrm{o}}_{A^{z-}_{\mathrm{ads}}} / z^- RT + \log_e \gamma / z = \mathrm{const.}$$

where $\mu_{A^{z-}_{\mathrm{ads}}}$ is the chemical potential of fixed or adsorbed ions A^{z-}_{ads}.

The following two eqs. 1 and 2 defining the variation of the fixed charge double layer potential used as the basis of the ion exchange theory of coagulation and for the derivation of the ion exchange equilibrium constant K and the separation factor S read:

$$\Delta\varphi = \Delta^{\mathrm{o}}\varphi + [z\,\mathbf{a} + \log_e(a_M/x\gamma)]RT/F \qquad (1)$$

$$\Delta\varphi = \Delta^{\mathrm{o}}\varphi + \{z'\,\mathbf{a} + \log_e[a_{M'}/(1 - x)\gamma]\}RT/F \qquad (2)$$

Eqs. 1 and 2 are valid if two counter ions M and M' are present in an ideal system composed of an exchanger and an electrolyte. These two eqs. were claimed by Levine erroneous, and their derivation was misinterpreted in two different ways. His first misinterpretation[1] was already proved incorrect[2] and the second one follows as unjustified from the extensive derivation given here. The present derivation is a simplified modification of that given originally[4]. Also, all terms are redefined and their physical explanations are given.

We assume that our system consists of two phases: the electroneutral electrolyte phase and the double layer phase. In the latter the counter ions are separated from the fixed constituent ions by a mean distance. The fixed constituent ions (*e. g.* I^- ions) are adsorbed on the surface at large distances from each other. This means that they are considered discrete. The surface area A (conveniently in cm^2 per liter of the system) and the charge density γ/A are also assumed constant. The counter ions M of valency z are, therefore, in the outer layer exposed to an electrostatic potential φ_{outer} due to the presence of the fixed ions of the opposite sign. Their electrochemical potential is $\tilde{\mu}_{M,\,\mathrm{layer}}$. In the electroneutral electrolyte phase the counter ions are assumed to be under the zero reference potential $\varphi_{\mathrm{liquid}}$ and have the electrochemical potential $\tilde{\mu}_M$, respectively. In the equilibrium the following equality should be valid

$$\tilde{\mu}_{M,\,\mathrm{layer}} = \tilde{\mu}_M \qquad (3)$$

For the liquid phase the electrochemical potentials are defined conventionally by

$$\tilde{\mu}_M = \mu^{\mathrm{o}}_M + RT \log_e(a_M/z) + z\,\varphi_{\mathrm{liquid}}\,F \qquad (4)$$

and for the layer phase by

$$\tilde{\mu}_{M,\,\mathrm{layer}} = \mu^{\mathrm{o}}_{M,\,\mathrm{layer}} + RT \log_e(a_{M,\,\mathrm{layer}}/z) + z\varphi_{\mathrm{outer}}\,F \qquad (5)$$

The double layer volume is not measurable. The activity $a_{M,\,\mathrm{layer}}$ can be therefore expressed in a conventional unit only which is different from that of

a_M (*e. g.* gram equivalent per gram mole of the solid per litre of the system instead of the double layer volume). For this reason it is necessary to assume in eqs. (4) and (5) that the electrolyte volume and the double layer volume are constant. The latter is justified for ideal exchangers having a constant specific surface A (in unit surface per unit amount of the exchanger) or a constant intermicellar volume (= constant swelling). Here μ^o_M and $\mu^o_{M,\,layer}$ are the corresponding standard chemical potentials. The terms a_M/z and $a_{M.\,layer}/z$ are values proportional to the molar ratio, namely to the quotient between the number of counter ions and the total number of molecules (solvent plus ions) in the liquid and layer phase, respectively. R, T and F have their conventional meaning.

In the following, for the differences of the different potentials in the layer and liquid the symbol Δ is used. For the difference of the standard terms we introduce the symbol $\Delta\mu^o_M$

$$\mu^o_M - \mu^o_{M,\,layer} = \Delta\mu^o_M \tag{6}$$

The difference between the actual average potential φ_{outer} under which the counter ions M of valency z are exposed in the double layer and the potential φ_{liquid} in the liquid phase, defines the actual potential difference $\Delta\varphi_M$ of counter ions by

$$\varphi_{outer} - \varphi_{liquid} = \Delta\varphi_M \tag{7}$$

The electrostatic potential difference $\Delta\varphi_M = \varphi_{outer} - \varphi_{liquid}$ is the work necessary to bring unit positive charge from the liquid to the double layer phase. It is positive in the case of fixed cations, and negative in the case of fixed anions. Consequently, the signs of φ_{outer} or $\Delta\varphi_M$ and the valency of the counter ion z are always opposite, and the product $z\Delta\varphi_M$ would be always negative. On the other hand, the thermodynamic requirement is, that the same product is always positive, in the case of fixed cations or anions. It is namely necessary to spend energy on the system in order to transport ions of any sign against the dissociating forces from the liquid to the layer phase. The product $z\Delta\varphi_M F$ is therefore the work necessary to bring, when $z < 0$, $|z|$ faradays of positive charges (+ F) into the positive field of cations ($0 < \Delta\varphi_M$). When $0 < z$, it is necessary to bring $|z|$ faradays of negative (—F) charges into the negative field ($\Delta\varphi_M < 0$) of fixed anions. In the following, therefore, to satisfy the thermodynamic requirement for the positive product $0 < z\Delta\varphi_M = \Delta\varphi$, absolute values for the negative either z or $\Delta\varphi_M$, $\Delta\varphi$, $\Delta^1\varphi$ are used in the eqs.

Because of the equality (3), eq. (5) should be subtracted from (4) and in this way the electrochemical potentials $\tilde{\mu}_{M,\,layer}$ and $\tilde{\mu}_M$ are eliminated. The resulting eq. reads

$$O = (\mu^o_M - \mu^o_{M,\,layer}) + RT\log_e(a_M/a_{M,\,layer}) - zF(\varphi_{outer} - \varphi_{liquid}) \tag{8a}$$

Introducing for the differences in the brackets the symbols as defined by eqs. (6) and (7) one obtains

$$z\Delta\varphi_M = \Delta\mu^o_M/F + (RT/F)\log_e(a_M/a_{M,\,layer}) \tag{8}$$

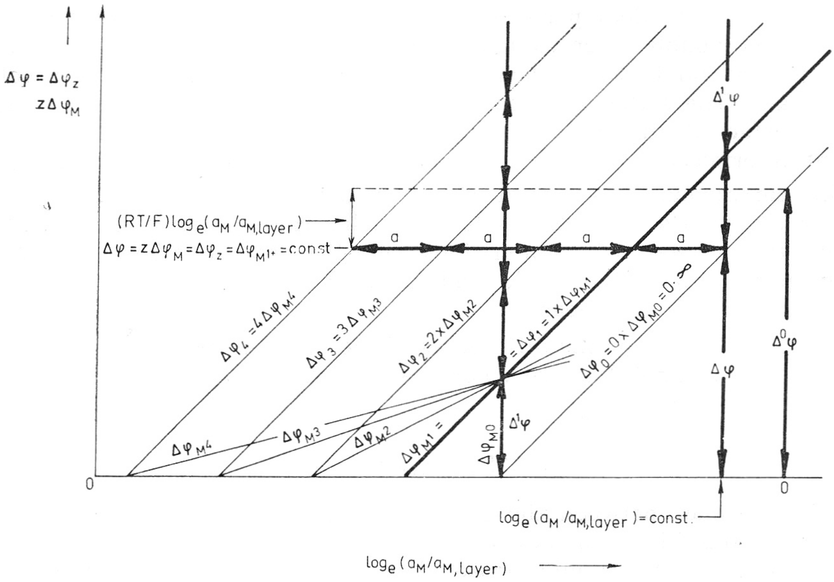

Fig. 1. The $z\Delta\varphi_M$ and $\Delta\varphi$ against $\log_e(a_M/a_{M,\,layer})$ plots for ions of different valencies z.

For different z the plots $z\Delta\varphi_M$ against $\log_e(a_M/a_{M.\,layer})$ can be parallel lines only (Fig. 1). The terms z and $\Delta\varphi_M$ are interdependent variables. Also for each different z there is a different value for $\Delta\mu^o_M$. We can define a constant standard term $\Delta^o\varphi$ assuming $z = O$ and $a_M/a_{M,\,layer} = 1$. Then

$$(\Delta\mu^o_M\ /F)_{z=0} = \Delta\mu^o_{M^o}\ /F = \Delta^o\varphi = \text{const.} \tag{9}$$

The latter term is constant and equal for ions of all valencies because these are assumed to be charged particles equal in all properties except in charge. All possible specific effects like nonelectrostatic adsorption, ion size, ion polarization and others are neglected.

Derivation of $\Delta^1\varphi$

We consider now two fictive systems: in the first the counter ions M of valency z, and in the second M' of valency z', have the same value $a_M/a_{M,\,layer}$ and $a_{M'}/a_{M'.\,layer}$, *i. e.* their chemical free energies are constant. Because of Coulomb's formula the variation of the electrostatic energy should be proportional to z, z'. If we designate the proportionality constant by $\Delta^1\varphi$ we obtain

$$\Delta\mu^o_M\,/F = \Delta^o\varphi + z\,\Delta^1\varphi \tag{10}$$

and in the general case

$$z\,\Delta\varphi_M = \Delta\varphi = \Delta^o\varphi + z\,\Delta^1\varphi + (RT/F)\,\log_e\,(a_M/a_{M,\,layer}) \tag{11a}$$

or for the ion M'

$$z'\,\Delta\varphi_{M'} = \Delta\varphi' = \Delta^o\varphi + z'\,\Delta^1\varphi + (RT/F)\,\log_e(a_{M'}/_{M',\,layer}) \tag{11b}$$

Eqs. 11a and 11b are equal to eqs. 1 and 2.*

At the same time we replaced the product $z\,\Delta\varphi_M$, $z'\,\Delta\varphi_M$, by the variable potential $\Delta\varphi$, $\Delta\varphi'$ which we call the »fixed charge double layer potential«. Its physical meaning is given below.

By subtraction of (11a) from (11b) one obtains

$$(z'\,\Delta\varphi_{M'} - z\,\Delta\varphi_M) = \Delta\varphi' - \Delta\varphi = (z' - z)\ \Delta^1\varphi \tag{12}$$

For $z' - z = \Delta z = 1$ one obtains

$$(\Delta\varphi' - \Delta\varphi)_{\Delta z = 1,\ a_M/a_{M,\ \mathrm{layer}} = a_{M^{z+1}}/a_{M^{z+1},\ \mathrm{layer}}} = \Delta^1\varphi = \mathrm{const.} \tag{13}$$

The constant potential $\Delta^1\varphi$ is the difference between the fixed charge double layer potentials in two systems of two counter ions having their chemical potentials in both phases constant when the valencies of the ions differ by unity (superfix^1!).

(Alternative: The constant $\Delta^1\varphi$ is the variation in the fixed charges double layer potential of two counter ions present at the same constant ratio $a_M/a_{M,\ \mathrm{layer}} = a_M^{\ z+1}/a_{M\ \mathrm{layer}}^{\ z+1}$ = const. if their valencies differ by unity.) (Eq. 13).

At the same time $\Delta^1\varphi$ is a standard electrostatic potential, which can be defined by $\Delta\varphi_M = \Delta^1\varphi$ for $\Delta^0\varphi + (RT/F)\log(a_M/a_{M,\ \mathrm{layer}}) = 0$.

For ions of other valency differences this potential difference is proportional to $\Delta^1\varphi$ and to the valency difference. It follows that the valencies z, z' were not omitted in the eqs. 1,2 and 8 in the derivation as purported by Levine.

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* In fact the definition of the electrochemical potential (eqs. 4 and 5) is insufficient. There is no indication that in a most general case the electrostatic and electrochemical potentials should equal zero when the chemical potential equals zero. Namely, it is not necessary that $\tilde{\mu}_i = 0$ and $\varphi_i = 0$ when $\mu_i^o + RT\log_e a_i = 0$, or that $\varphi_i = 0$ when $\tilde{\mu}_i = \mu_i^o + RT\log_e a_i$. Standard electrostatic term φ_i^o should be inserted and the general definition of the electrochemical potential should read

$$\tilde{\mu}_i = \mu_i^o + RT\log_e a_i + z(\varphi_i - \varphi_i^o)\,F$$

In the case of the counter ion in the liquid and layer the same definition reads

$$\tilde{\mu}_M = \mu_M^o + RT\log_e (a_M/z) + z\,(\varphi_{\mathrm{liquid}} - \varphi_{\mathrm{liquid}}^o)\,F \tag{4a}$$

and

$$\tilde{\mu}_{M,\ \mathrm{layer}} = \mu_{M,\ \mathrm{layer}}^o + RT\log_e (a_{M,\ \mathrm{layer}}/z) + z\,(\varphi_{\mathrm{outer}} - \varphi_{\mathrm{outer}}^o)\,F \tag{5a}$$

By designating the difference as $\varphi_{\mathrm{outer}} - \varphi_{\mathrm{liquid}} = \Delta^1\varphi$ and by subtracting (5a) from (4a) one directly obtains eqs. (11a) and 11b) instead of eq. (8). Then the difference $\tilde{\mu}_i^o = \mu_i^o - z\,\varphi_i^o\,F$ for $a_i = 1$ and $\varphi_i = 0$ can be considered the standard electrochemical potential. For $a_M/a_{M,\ \mathrm{layer}} = 1$ and $\Delta\varphi = 0$ the sums

$$\Delta\tilde{\mu}_M^o = \Delta\mu_{M0}^o + z\,\Delta^1\varphi\,F = \tilde{\mu}_M^o - \tilde{\mu}_{M,\ \mathrm{layer}}^o = (\Delta^0\varphi + z\,\Delta^1\varphi)\,F$$

can be considered the standard electrochemical potential difference. It defines the equilibrium constant, *i. e.* the distribution coefficient for the transition of the counter ion from the liquid in the layer.

The derivation of $\Delta\varphi$

The slope of the $\Delta\varphi_M$ plots determines the valency of the ions constituting the outer layer. The $\Delta\varphi$ plots for any valency have the same slope RT/F as the $\Delta\varphi_M$ plot for $z = 1$. For $z = 1$ we have, namely

$$(z\,\Delta\varphi_M)_{z=1} = \Delta\varphi_{M^{1+}} = \Delta\varphi \qquad (14)$$

We can, therefore, conclude that: the fixed charge double layer potential $\Delta\varphi$ of ions of different valencies is equal to the potential to which the elementary counter ion charge would be exposed if replaced in the layer by ions of valency one and if their electrostatic free energy per ion in the layer would be equal. Alternatively, the product $\Delta\varphi F$ is the electrostatic energy for the transport of one gram ion of counter ions of any valency from the liquid to the layer phase expressed as the electrostatic energy for the transport of one faraday of charges.

Interrelation between $a_{A^{z-}_{ads}}$, $a_{M,\,\mathrm{layer}}$ and $a_{M',\,\mathrm{layer'}}$

If the two ions M and M' are present in the same system, $\Delta\varphi$ equals $\Delta\varphi'$ the same as $z\,\Delta\varphi_M$ equals $z'\,\Delta\varphi_M$, because the energy per ion must be equal for both ions, whereas $\Delta\varphi_M$ is different from $\Delta\varphi_{M'}$. Also the sum of the activities (in equivalents per litre) of both ions in the layer must be constant because the ion exchange capacity γ in equivalents is constant:

$$a_{M,\,\mathrm{layer}} + a_{M',\,\mathrm{layer}} = \gamma = \mathrm{const.} \qquad (15)$$

If we assume $a_{M,\,\mathrm{layer}} = x\gamma$, where x is a proper fraction, we must have $a_{M',\,\mathrm{layer}} = (1 - x)\,\gamma$. γ/z^- is proportional to the amount of fixed ion charges and to the ratio: number of fixed ions/number of solvent molecules in the double layer phase. It equals the relative activity in gramequivalents of the ionogenic group A^{z-}_{ads} of valency z^- in the double layer

$$a_{A^{z-}_{ads}} = \gamma \qquad (16)$$

Interrelation between **a** *and* $\Delta^1\varphi$

The difference between eqs. (11a) and (11b) when eq. (15) is also considered for $\Delta\varphi = \Delta\varphi'$, gives the well known separation factor S equation of ion exchange which reads:

$$\log_e S = (z' - z)\,\Delta^1\varphi\, F/RT = \log_e[a_M(1 - x)/a_{M'}x] \qquad (17)$$

in which γ, $\Delta^0\varphi$, and $\Delta\varphi$, $\Delta\varphi'$ cancelled out.

Earlier[5], the same separation factor equation was derived empirically from counter ion exchange measurements on silver iodide. S or **a** were derived from experimental data using the equation

$$\log_e S = (z' - z)\,\mathbf{a} = \log_e(a_M/a_{M'})_{x=1-x=0.5} \qquad (18)$$

An application of chemical thermodynamics to the ion exchange process[6] resulted in an analogous separation factor equation in which **a** was explained by

$$\mathbf{a} = \mu_{A^{z-}_{ads}}/RTz^- \qquad (19)$$

i. e. **a** was found to be proportional to, or determined by the chemical potential of the ionogenic group A^{z-}_{ads} in the layer. This latter potential is determined using eq. (16), by the relationship

$$\mu_{A^{z-}_{ads}} = \mu^{o}_{A^{z-}_{ads}} + RT \log_e(\gamma/z^-) \tag{20}$$

From eqs. (17), (18), and (19) it follows that

$$\mathbf{a} = \Delta^1\varphi\, F/RT = \mu_{A^{z-}_{ads}} / z^- RT \tag{21}$$

The constants **a** and $\Delta^1\varphi$, are proportional to, or determined by the chemical potential of the ionogenic group in the double layer of ion exchangers.

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IZVOD

Izvod jednadžbi potencijala dvostrukog sloja fiksnih naboja

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Na temelju pretpostavke jednakosti elektrokemijskih potencijala

$$\tilde{\mu}_M = \tilde{\mu}_{M,\,\mathrm{sloj}}$$

dvaju protuiona M i M′ u dvosloju i u otopini sistema »kruto-tekuće«, te na temelju pretpostavki:

$$\tilde{\mu}_M = \mu^o_M + RT \log_e (a_M /z) + z\,(\varphi_{\mathrm{tekuće}} - \varphi^o_{\mathrm{tekuće}})\,F$$

$$\tilde{\mu}_{M,\,\mathrm{sloj}} = \mu^o_{M,\,\mathrm{sloj}} + RT \log_e (a_{M,\,\mathrm{sloj}} /z) + z\,(\varphi_{\mathrm{vanjsko}} - \varphi^o_{\mathrm{vanjsko}})\,F$$

$$\varphi_{\mathrm{vanjsko}} - \varphi_{\mathrm{tekuće}} = \Delta\varphi_M = \Delta\varphi/z$$

$$\varphi^o_{\mathrm{vanjsko}} - \varphi^o_{\mathrm{tekuće}} = \Delta^1\varphi = \mathbf{a}\,RT/F$$

$$\mu^o_M - \mu^o_{M,\,\mathrm{sloj}} = \mu^o_{M^0} - \mu^o_{M^0,\,\mathrm{sloj}} = \Delta\mu^o_{M^0} = \Delta^0\varphi F$$

izvedene su dvije jednadžbe potencijala dvosloja fiksnih naboja

$$\Delta\varphi = \Delta^0\varphi + [z\,\mathbf{a} + \log_e (a_M/x\,\gamma)]\,RT/F$$

i

$$\Delta\varphi = \Delta^0\varphi + \{z'\,\mathbf{a} + \log_e [a_M'/(1 - x)\gamma]\}\,RT/F$$

Simboli znače: μ^o_M i $\mu^o_{M,\,\mathrm{sloj}}$ standardni kemijski potencijal u otopini i u sloju, a aktivitete u otopini, $\Delta\varphi_M$ činjenični elektrostatski potencijal kome su izloženi protuioni u vanjskom dijelu dvosloja relativan prema potencijalu neutralne tekuće faze, $\Delta^0\varphi$ standardni elektrostatski potencijal, $\Delta\varphi$ je potencijal dvosloja fiksnih naboja iona raznih valencija izražen potencijalom jednovalentnih iona iste elektrostatske slobodne energije, $\Delta^1\varphi$ je razlika standardnih elektrostatskih potencijala $\varphi^{o}_{\mathrm{vanjsko}} - \varphi^{o}_{\mathrm{tekuće}}$ u vanjskom sloju i u tekućoj fazi. $\mathbf{a} = \Delta^1\varphi F/RT$ je konstanta proporcionalnosti linearnog Schulze-Hardy-jeva pravila. Tom je konstantom određena jednadžba faktora separacije S ionske izmjene, te glasi:

$$\log_e S = (z' - z)\,\mathbf{a} = \log_e (a_M\, a_{M',\,\mathrm{sloj}} / a_{M,\,\mathrm{sloj}}\; a_{M'})$$

Ovdje su $a_{M,\,\mathrm{sloj}} = x\gamma$ i $a_{M',\,\mathrm{sloj}} = (1 - x)\,\gamma$ aktiviteti oba iona u sloju. Njihov ukupni aktivitet jednak je teoretskom kapacitetu izmjene $\gamma = a_{M,\,\mathrm{sloj}} + a_{M',\,\mathrm{sloj}}$ i ujedno i aktivitetu fiksnog adsorbiranog iona u nutarnjem dijelu dvosloja A^{z-}_{ads}, x i 1—x njihove su ekvivalentne ionske frakcije u dvosloju.

Teoretsko objašnjenje **a**, a time i $\Delta^1\varphi$ određeno je izrazom

$$\mathbf{a} = \mu_{A,\,{}^{z-}_{\mathrm{ads}}} / z^{-}RT = \mu^{o}_{A,\,{}^{z-}_{\mathrm{ads}}} / RT + \log_e (\gamma/z^{-})^{1/z^{-}} = \mathrm{const.}$$

u kojem je $\mu_{A,\,{}^{z-}_{\mathrm{ads}}}$ kemijski potencijal fiksnog odnosno adsorbiranog iona A^{z-}_{ads}.

Navedene dvije jednadžbe koriste se za izvod teorije ionske zamjene koagulacije i za izvod termodinamske konstante ravnoteže uz upotrebu aktiviteta K_a, iste konstante uz upotrebu ekvivalentnih ionskih frakcija K_α i faktora separacije S ionske zamjene.

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