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**Some Critical Remarks on the Paper  
Fixed Charge Double Layer Potential Equations — a Derivation  
by M. Mirnik\***

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After a very lengthy correspondence in which I have repeatedly expressed my criticism of the contents of Professor Mirnik's Fixed charge double layer potential equations, Professor Mirnik has sent me a copy of the manuscript as it has been accepted for publication and asked me to express my criticism in the same periodical.

I find the paper *Fixed charge double layer potential equations — a derivation* unclear in many places; it contains arbitrary assumptions about the behavior of ions of different valencies and it contains internal inconsistencies. The main results of the paper are therefore unacceptable.

*a. Lack of Clarity*

Immediately after eq. (5) it is stated that » $a_{M, \text{layer}}$  can be 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 liter of the system instead of the double layer volume).« It is not clear whether this unit for  $a_M$  is (gram eq./gram mole of solid)/liter of system or gram eq./(gram mole of solid/liter of system) but for either choice  $a_M$  would depend on the total amount of the system and thus  $\mu_{M, \text{layer}}^{\circ}$  would depend on the total amount of the system and could not be a standard chemical potential.

After eq. (7) it is stated that »the product  $z \Delta \varphi_M$  would be always negative«. The next sentence says that »the thermodynamic requirement is, that the same product is always positive, in the case of fixed cations or anions«. If »the same product« still applies to  $z \Delta \varphi_M$  where M is a counterion then there is no such »thermodynamic requirement«. If »the same product« applies to fixed cations or anions themselves it is not the same product any more because the index M does not apply to fixed ions.

At the end of this same paragraph it is stated that »absolute values for either  $z$  or  $\Delta \varphi_M$ ,  $\Delta \varphi$ ,  $\Delta^1 \varphi$  are used in the eqs.« and this is done »to satisfy the thermodynamic requirement for the positive product  $0 < z \Delta \varphi_M = \Delta \varphi$ «. »absolute values for either  $z$  or  $\Delta \varphi_M$ « do not prevent  $z \Delta \varphi_M$  from being negative. So what does the author mean?

*b. Arbitrary Assumptions*

In eqs. (4) and (5) the electrochemical potential of the ions is split into an electrical part,  $zF\varphi$ , a concentration dependent part,  $RT \log_e (a/z)$  and a standard chemical potential  $\mu^{\circ}$ , which may have different values in the bulk of the liquid and in the double layer. These standard chemical potentials

\* M. Mirnik, *Croat. Chem. Acta* 42 (1970) 49.

are not directly related to the electrical properties of the ions and therefore eq. (10) in which it is stated that  $\Delta \mu^0$  can be split into a constant  $F \Delta^0 \varphi$  («equal for ions of all valencies») and a part  $z F \Delta^1 \varphi$ , that is proportional to the ionic charge is a purely arbitrary assumption. Since this assumption is the basis for Fig. 1 the way in which the different lines are arranged with respect to each other is purely arbitrary.

Another arbitrary assumption is made shortly after eq. (5) when it is stated that «the double layer volume» is «constant». This may be a reasonable assumption for an ion exchanger at «constant swelling» but there is no justification for such an assumption when applied to an «exchanger having a constant specific surface  $A$ ».

In the beginning of the section «*Interrelation between  $a_A^{z-}$ ,  $a_{M, \text{layer}}$  and  $a_{M', \text{layer}}$* » and  $\Delta^1 \varphi$ , it is stated that « $z \Delta \varphi_M$  equals  $z' \Delta \varphi_M$ , because the energy per ion must be equal for both ions». There is no physical reason why this should be the case. On the contrary any reasonable assumption about a mixture of different counterions in one and the same double layer would come closer to  $\Delta \varphi_M = \Delta \varphi_{M'}$  than to  $z \Delta \varphi_M = z' \Delta \varphi_{M'}$ . Therefore the assumption  $z \Delta \varphi_M = z' \Delta \varphi_{M'}$  is arbitrary.

### c. Inconsistencies

Just before eq. (3) it is stated that «the counter ions . . . are, . . . in the outer layer exposed to an electrostatic potential  $\varphi_{\text{outer}}$  due to the presence of the fixed ions of the opposite sign». Also «The surface area  $A$  . . . and the charge density  $\gamma/A$  are also assumed constant». Since the arrangement of the fixed ions is constant, the potential due to them should also be constant and not depend on concentrations or activities of the counterions. The «zero reference potential  $\varphi_{\text{liquid}}$ » should not depend on concentrations of ions either. Consequently  $\Delta \varphi_M = \varphi_{\text{outer}} - \varphi_{\text{liquid}}$  should be a constant independent of ion concentrations. However, in eq. (8),  $z$ ,  $\Delta \mu_M^0$ ,  $R$ ,  $T$  and  $F$  are constants,  $a_{M, \text{layer}}$  is a constant due to the assumption that  $\gamma$  is a constant (eq. 15) and that only one kind of counter ion is assumed to be present in the derivation of eq. (8). But then  $a_M$ , the concentration of counterions in the bulk liquid should be a constant which is clearly absurd.

It is further stated that in «subtracting eq. (5a) from eq. (4a) one directly obtains eqs. (11a) and 11b». This, however, is not true. If one subtracts eq. (5a) from eq. (4a) one finds\*:

$$0 = \Delta \mu_M^0 + RT \log_e (a_M/a_{M, \text{layer}}) - z F \Delta \varphi_M + z F \Delta^1 \varphi$$

$$\text{or} \quad z \Delta \varphi_M = \Delta \mu_M^0 / F + z \Delta^1 \varphi + RT/F \log_e (a_M/a_{M, \text{layer}})$$

According to eq. (10)  $\Delta \mu_M^0 / F = \Delta^0 \varphi + z \Delta^1 \varphi$  and consequently

$z \Delta \varphi_M = \Delta^0 \varphi + 2z \Delta^1 \varphi + RT/F \log_e (a_M/a_{M, \text{layer}})$  which differs from eq (11a) by the factor 2 before  $z \Delta^1 \varphi$  instead of the factor 1 in eq (11a).

In order to avoid any uncertainties with respect to my criticism I want to state explicitly that the above remarks are not my only points of criticism but I feel they are sufficient to draw the conclusion that the paper does not hold against reasonable criticism and that therefore the theory it is proposing is probably incorrect and is certainly not supported by the paper.

\* Note added in proof: based upon  $\varphi_{\text{outer}}^0 - \varphi_{\text{liquid}}^0 = \Delta' \varphi$ , as mentioned in Professor Mirnik's manuscript, rather than on  $\varphi_{\text{outer}} - \varphi_{\text{liquid}} = \Delta' \varphi$  as it occurs in the printed article.