

# Mystery of Missing Co-ions Solved

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Presence of a charged wall distributes like charges (co-ions) and unlike charges (counter-ions) differently within an electrolytic solution. It is reasonable to expect that counter-ions have more population near the wall, while co-ions are abundant away from it; experiments and simulations support this [1, 2]. An analytical formula for the net charge-density distribution  $\rho_e$  has been used widely since almost hundred years, was obtained by solving the Poisson-Boltzmann equation [3–5]. However, the old formula shows excess counter-ions everywhere, cannot account for the missing co-ions satisfactorily, and clearly violates charge conservation principle. Here, I correct the distribution formula from fundamental considerations. The old derivation expresses  $\rho_e$  as a function of electrostatic potential  $\psi$  [6], through Boltzmann distribution, but missed a crucial point that the indefinite nature of  $\psi$  [7–9] makes  $\rho_e$  indefinite as well. We must tune  $\psi$  by adding suitable constant until the integral of  $\rho_e$  becomes consistent with the net charge present in solution; old theory did not do it, that I do here. This result demonstrates how to reconcile a definite quantity to an indefinite one, when they are related. I anticipate, this result is going to have far reaching impacts on many fields like colloid science, electrokinetics, bio-technology etc. that use the old theory [4, 10–12].

The charged wall attracts counter-ions and repels co-ions, hence, the counter-ions appear excess in number near the wall region and that must be accompanied by the absence of same number of them in other regions. In particular, a solution that is electrically neutral as whole, must have regions with excess co-ions to satisfy principle of conservation of charge; any formula for  $\rho_e$  must reflect this. A widely used, simple 1-D, analytical formula shows, how  $\rho_e$  varies with the distance  $x$ , normal to the wall [5, 13]. It turns out that, the  $\rho_e$  vs  $x$  graph never crosses abscissa, see Fig. 1(a), here I plot the graph for a positively charged wall, for definiteness. It shows excess counter-ions everywhere. The area under the graph represents the net charge present in the liquid, so according to the old formula there is always a net amount of counter-ions there. A question naturally comes: “If the liquid is electrically neutral as a whole, why some co-ions are missing?”

Some authors [13–17] tried to find an explanation by considering some ‘particular’ systems, where the wall acquires some net charge from solution by adsorption. They said, an initially neutral wall when acquires some charge from a neutral solution, must have left

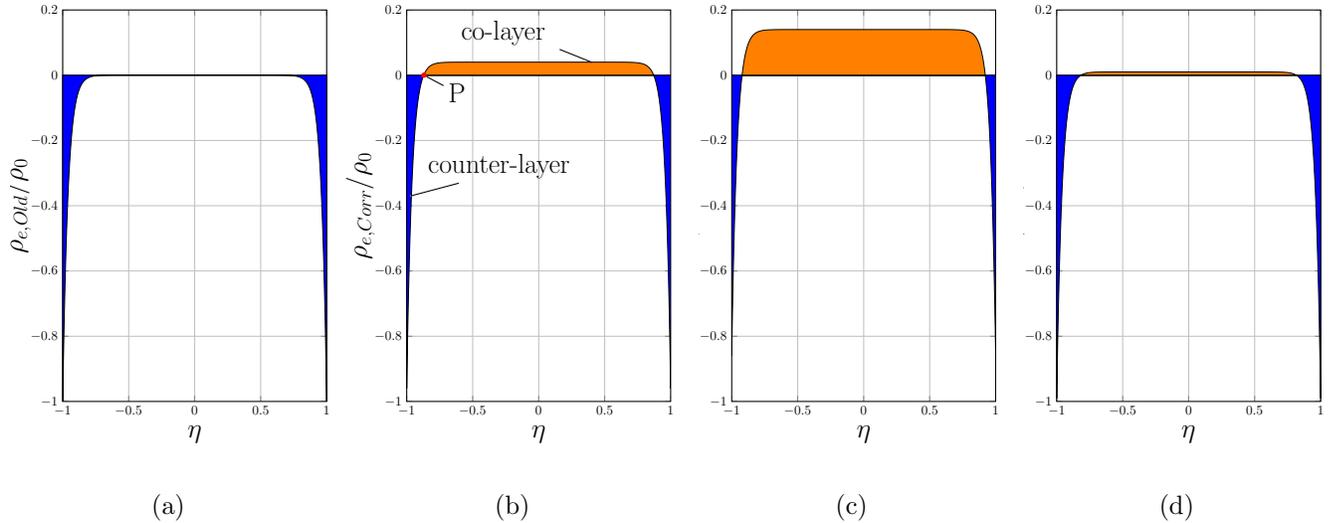


FIG. 1. (Color online) Charge density distribution along the domain cross-section, in an electrolytic solution enclosed by *positively charged* walls. (a) According to the old theory, the graph never crosses abscissa; counter-ions are excess everywhere; it cannot account for missing co-ions that are needed to satisfy principle of charge conservation. (b-d) According to the corrected theory, there are both counter-ion and co-ion abundant regions. The graph can cross the abscissa (at point ‘ $P$ ’) so that it can enclose both positive and negative areas, the algebraic sum of areas gives the net charge  $Q_0$  present in a cross section, which can be of any sign and magnitude. (b):  $Q_0 = 0$  (c):  $Q_0 > 0$  (d):  $Q_0 < 0$ . The old case (a) is a particular case of the general corrected theory, where  $Q_0 \ll 0$  with no layer of co-ions. The corrected graph can be obtained by uniform translation of the old graph, which corresponds to addition of a suitable constant to electrostatic potential  $\psi$ .

equal number of counter-ions in the solution. This apparently explains the old theory, and created a strong mental barrier against thinking about any other explanation. Although, the shortcomings of the classical formula become evident through different experiments [1] and molecular dynamical simulation results [2], no one could find the source of error. I discuss the flaw in the above arguments below.

It must be remembered that the general problem that we were interested to solve is: “ Given a solution, in contact with a charged wall, what is the distribution of ions? ” We never bothered how the wall acquired the charge, the derivation of formula begins when everything settles down to equilibrium; it never considered any adsorption of ions by wall. It does not impose any restriction regarding the net polarity of the solution, it could be of

either type or possibly zero. The derivation never prohibits a wall that does not adsorb any charge from solution, but could be charged by other means, so the net charge present in the liquid remains the same before and after its exposure to the wall. Also, it is possible to add some extra co-ions or counter-ions from outside, to attain a net charge of any polarity. Even if the wall acquires charge from solution, we can remove old solution from the domain and add fresh neutral solution again and again; wall cannot adsorb an indefinite amount of charge, so we are soon left with a charged wall plus a neutral solution. Also, adsorption is a ‘*surface*’ phenomenon, only a thin layer of charge is adsorbed, and it is unlikely that it will leave entire liquid ‘*volume*’ with excess counter-ions; for a concentrated solution it is even more unlikely.

Since, the matter was not understood clearly, it became a topic of debate, whether the solution is electrically neutral or not [18], some authors believe that the near wall regions are dominated by counter-ions and the bulk is neutral [13–15, 19], that means there is a net amount of counter-ions in the liquid. Others [18] say, the issue was settled in favour of total electro-neutrality. So, each of them reached a conclusion with intuitive arguments without theoretical justifications.

It can be noticed from Fig. 1, that, if the graph shown in Fig. 1(a) could be translated uniformly, so that it can change sign, then it encloses both positive and negative areas under it (see Fig. 1(b), Fig. 1(c), Fig. 1(d)); depending upon the amount of translation, the algebraic sum can assume any sign and magnitude (possibly, zero), thus we can get rid of the conservation problem, find a general solution.

But, the translation of the graph must be associated with some physical principle that I describe below. The derivation of the old formula expresses  $\rho_e$  in terms of  $\psi$  [6] in an intermediate step, through Boltzmann distribution. (See the supplementary materials for details.)

$$\rho_{e,Old} = A\psi \tag{1}$$

Where,  $A$  is a constant of known value, that depends upon various parameters. Using it in Poisson’s equation, which arises from one of the Maxwell’s equations applied to electrostatics, one can solve for  $\psi$  and hence get  $\rho_{e,Old}$  as a function of  $x$ .

Now it is well-known that  $\psi$  is defined to within an additive constant, i.e. adding an arbitrary constant should not change the physics [7–9], but here we must fix it to a definite value so that  $\rho_e$  is also consistent with the net charge present in the solution. I add a constant

‘ $C$ ’ to  $\psi$  in Eq. 1 to get the corrected distribution  $\rho_{e,Corr}$ . Hence,  $\rho_{e,Corr} = \rho_{e,Old} + A \cdot C$ . Now, from old theory we know  $\rho_{e,Old}$  as a function of  $x$ , hence ‘ $C$ ’ can be determined in terms of different parameters, using the condition,  $\int_{x=-a}^{x=+a} \rho_{e,Corr} dx = Q_0$ , where  $Q_0$  is the net charge present in a cross-section of the channel and is assumed to be known, we can assign it to any value and sign (in particular, if the solution is electrically neutral as a whole,  $Q_0 = 0$ ).

For a positively charged wall, I plot  $\rho_{e,Corr}$  in Fig. 1 for different cases: Fig. 1(b):  $Q_0 = 0$ , Fig. 1(c):  $Q_0 > 0$ , Fig. 1(d):  $Q_0 < 0$ . The point ‘P’, where the graph crosses the abscissa, is electrically neutral and can be called ‘neutral point’. In a 3-D domain, the collection of neutral points forms a neutral surface. We have three distinct kinds of electric layers, layer-1: a layer of wall surface charge, layer-2: adjacent to wall, layer of excess counter-ions (counter-layer) and layer-3: after counter-layer, a layer of excess co-ions (co-layer). The aggregate can be called Electric Triple Layer or ETL. Unlike this, the old Electric Double Layer (EDL) theory contains two electric layers: layer of wall charge and layer of counter-ions. However,  $\rho_{e,Old}$  can be thought of as a special case of  $\rho_{e,Corr}$ , when  $Q_0 \ll 0$ ; co-layer is absent here.

Another very important thing can be done with the corrected theory that is not possible with the old one. It turns out that the integral of  $\rho_{e,Old}$  i.e. the net charge in liquid varies if we increase the solution concentration (Debye length changes with concentration) and cannot explain the fact that if we add some more extra neutral salt to solution, that increases its concentration but keeps the net charge unchanged (assume there is no further adsorption by wall). In the corrected theory the net charge  $Q_0$  can be specified explicitly to a constant value and that nicely accounts for the variation in concentration by the addition of salt.

In the old theory, charged layer was thought to occupy only a fraction of the fluid domain and its extent was estimated using Debye length scale. In new ETL theory, the spatial extents of different electrical layers in the fluid domain can be calculated accurately (although numerically) by solving for the neutral point ‘P’, i.e. solving the equation  $\rho_{e,Corr} = 0$ , for  $x$ .

Thus we detect a serious error in a very important formula by observing a graph; the graph itself suggested how to rectify the error and it has been achieved invoking a deep physical principle.

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## I. SUPPLEMENTARY MATERIALS:

### A. derivation of charge distribution $\rho_e$

#### 1. Old charge distribution $\rho_{e,Old}$

Consider a rectangular domain of width  $2a \ll \text{length}$ ;  $y$ -axis is aligned with long, vertical domain-axis;  $x$ -axis is normal to the long, charged walls that are placed at  $x = \pm a$ . Define,  $\eta \equiv x/a$ . The suffix ‘Corr’ means ‘Corrected’. The initial steps for the derivation of  $\rho_{e,Corr}$  are similar to that of  $\rho_{e,Old}$ . For electrostatics, the electric field  $\mathbf{E}$  is related to electrostatic potential as,  $\mathbf{E} = -\nabla\psi$ , hence, one of the Maxwell’s equation reduces to Poisson’s equation,  $\nabla^2\psi = -\rho_e/\epsilon$ , where,  $\epsilon$  is the permittivity of the solution (assuming polarization is proportional to  $\mathbf{E}$ ). Since  $2a \ll \text{length}$ ,  $\rho_e$  essentially varies in  $x$  direction, and we get a 1-D equation.

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\epsilon} \quad (2)$$

We can derive a relationship between  $\rho_e$  and  $\psi$  that can be used to solve the above equation. The number density distributions of  $\pm ve$  ions separately follow Boltzmann distribution; for small values of arguments in the exponential that can be linearized (an equation containing  $\psi$  is physically meaningful only if it is linear in  $\psi$ ; superposition principle is strictly valid).

$$\begin{aligned} n_{Old}^{\pm} &= n_0 \exp[\mp(ez\psi)/(k_B T)] \\ &\approx n_0 [1 \mp (ez\psi)/(k_B T)] \end{aligned} \quad (3)$$

Where,  $n_0$  is mean of number densities of  $\pm ve$  ions; for a symmetric electrolyte  $z = |z_{\pm}|$ , where  $z_{\pm}$  are valences of  $\pm ve$  ions;  $e$ ,  $k_B$  and  $T$  are elementary charge, Boltzmann constant and absolute temperature respectively.

$$\begin{aligned} \rho_{e,Old} &= ez^+ n_{Old}^+ + ez^- n_{Old}^- \\ &= ez(n_{Old}^+ - n_{Old}^-) \\ &= -\left[\frac{2e^2 z^2}{k_B T}\right] \psi = -\epsilon \left[\frac{2e^2 z^2}{\epsilon k_B T}\right] \psi = -\left[\frac{\epsilon}{\lambda_D^2}\right] \psi \\ \rho_{e,Old} &= -\left[\frac{\epsilon \kappa^2}{a^2}\right] \psi \end{aligned} \quad (4)$$

Where,  $\lambda_D \equiv [(2n_0 z^2 e^2)/(\epsilon k_B T)]^{-1/2}$ , the Debye length scale. An important non-dimensional parameter is  $\kappa \equiv a/\lambda_D$ . Using this relationship in the Poisson’s equation, remembering

$\eta \equiv x/a$ , we arrive at linearized Poisson-Boltzmann equation.

$$\frac{d^2\psi}{d\eta^2} = \kappa^2\psi \quad (5)$$

It can be solved using boundary conditions, at  $\eta = \pm 1, \psi = \zeta$ ,

$$\psi = \zeta \frac{\cosh(\kappa\eta)}{\cosh(\kappa)} \quad (6)$$

Using it in Eq. 4 we get,

$$\rho_{e,Old} = - \left[ \frac{\epsilon\kappa^2\zeta}{a^2} \right] \frac{\cosh(\kappa\eta)}{\cosh(\kappa)} \quad (7)$$

Define  $\rho_0 \equiv (\epsilon\kappa^2\zeta/a^2)$ , which takes  $\pm ve$  values for  $\pm ve$  values of  $\zeta$  i.e. when wall charge is  $\pm ve$ . Hyperbolic cosine function is strictly positive, so,  $\rho_{e,Old}$  does not change sign, in particular, for positively charged wall it takes negative values only, implies counter-ions everywhere in liquid.

## 2. Corrected charge distribution $\rho_{e,Corr}$

Now, I correct the old formula by adding a final step to it. Add a constant ‘ $C$ ’ to  $\psi$  in Eq. 4, call  $\rho_e$  as  $\rho_{e,Corr}$ , use Eq. 7 at the end.

$$\begin{aligned} \rho_{e,Corr} &= - \left[ \frac{\epsilon\kappa^2}{a^2} \right] (\psi + C) \\ &= - \left[ \frac{\epsilon\kappa^2}{a^2} \right] \psi - \left[ \frac{\epsilon\kappa^2}{a^2} \right] \cdot C \\ &= \rho_{e,Old} - \left[ \frac{\epsilon\kappa^2}{a^2} \right] \cdot C \\ &= - \left[ \frac{\epsilon\kappa^2\zeta}{a^2} \right] \frac{\cosh(\kappa\eta)}{\cosh(\kappa)} - \left[ \frac{\epsilon\kappa^2}{a^2} \right] \cdot C \end{aligned} \quad (8)$$

Now, use the condition  $\int_{-1}^{+1} \rho_{e,Corr} d\eta = Q_0$ , where  $Q_0$  is the net charge present in a cross-section and assumed to be known; in particular, if the liquid is electrically neutral as a whole,  $Q_0 = 0$ . Hence, we get ‘ $C$ ’ in terms of various parameters and  $Q_0$ ,

$$C = - \left[ \frac{\tanh(\kappa)}{\kappa} \zeta + \left( \frac{a^2}{\epsilon\kappa^2} \right) \left( \frac{Q_0}{2} \right) \right] \quad (9)$$

Using this, finally we arrive at the corrected charge distribution,

$$\rho_{e,Corr} = \left[ \frac{\epsilon\kappa^2\zeta}{a^2} \right] \left( \frac{\tanh(\kappa)}{\kappa} - \frac{\cosh(\kappa\eta)}{\cosh(\kappa)} \right) + \frac{Q_0}{2} \quad (10)$$

$$= \left[ \frac{\epsilon\kappa^2\zeta}{a^2} \right] \left[ \left( \frac{\tanh(\kappa)}{\kappa} - \frac{\cosh(\kappa\eta)}{\cosh(\kappa)} \right) + \frac{Q_0 a^2}{2\epsilon\kappa^2\zeta} \right] \quad (11)$$

## B. Corrected ion density distributions

Adding ‘ $C$ ’ to  $\psi$  in Eq. 3 from Eq. 9, we obtain corrected distribution for co-ions and counter-ions,

$$n_{Corr}^{\pm} = n_0 \left[ 1 \mp \frac{ez}{k_B T} \psi \right] \pm \frac{n_0 ez}{k_B T} \left[ \frac{\tanh(\kappa)}{\kappa} \zeta + \left( \frac{a^2}{\epsilon \kappa^2} \right) \frac{Q_0}{2} \right] \quad (12)$$