

# Nernst expression and Poisson's equation: Are they consistent?

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*A paradox exists between the implications of Poisson's equation and the demands of equilibrium Nernst expression in physical chemistry. Poisson equation relates the second derivative of electric potential profile in an inhomogeneous system, to local charge density. Local charge density is a function of concentrations of various ions, and can be expressed as proportional to concentration of a specified ion or electrolyte in the bulk homogeneous region, the proportionality coefficient being an yet unspecified function of position variable. Therefore, Poisson's equation requires that the electric potential should be a linear function of concentrations. On the other hand, Nernst equilibrium expression states that electric potential should be independent of the absolute values of concentrations and is related to only ratio of concentrations. Since Poisson's equation and Boltzmann distributions are fundamentally valid, it is imperative that this inconsistency existing between these two valid relations of physical chemistry is resolved.*

THIS paper is concerned with a fundamental question existing, in physical chemistry, which requires an answer. Poisson's equation relates the differentials of the electric potential profile at a specified location in an inhomogeneous region, with the charge density at that location. Poisson's equation is exact, and is valid for all states of the system. It is derivable from an equation of continuity<sup>1</sup> and is one relation relating three unknowns, namely (i) the electric potential profile, (ii) the dielectric profile and (iii) the charge density profile. The electric potential at a specified location in the system arises from contributions from all charged ions present in the system. The charge density at a specified location in the system, is the product of protonic charge and the algebraic sum of concentrations of all ionic species present at this location, weighted down by their signed valence charge numbers. The charge density is therefore, proportional to concentration of a specified ionic species in the homogeneous region, where such concentrations are independent of position variable. With the usual convenient assumption that the positional dependence of dielectric coefficient can be neglected, one may integrate the charge density profile, derivable from concentration profiles, to obtain the electric field profile. One can also obtain the electric potential profile by a second integration with respect to position variable, over the extent of the inhomogeneous region,  $d$ . Such resultants will still be proportional to concentration of a

specified ionic species of the electrolyte in the bulk homogeneous region (see note 1).

On the other hand, the Nernst expression relates the difference in electric potential at two locations in the system, with the ratio of concentrations of a specified ionic species at these two locations. Therefore, Nernst or, Boltzmann kind of expression requires that the electric potential is independent of the absolute value of concentration of a specified ion in the bulk homogeneous region and is dependent only on the ratio of concentrations.

Boltzmann equilibrium distribution, from which the Nernst expression is obtained as an approximation, is valid exactly. This is because, concentrations represent probability, and probabilities are related to energies in an exponential manner. This is the basis of the famous Boltzmann law,  $S = k \ln W$ , where  $S$  denotes the entropy,  $W$  is probability and  $k$  is the Boltzmann constant. Therefore, so long as relation of the Nernst kind is valid for concentrated electrolyte solutions, the magnitude of the electric potential should not be proportional to concentration of a specified ion in the homogeneous region. Thus, there exists a paradox which needs to be resolved (see note 2).

The contents of this paper and its conclusions are based on the validity of three fundamental (nearly) exact equations of physical chemistry and the conclusions derived from them:

1. Poisson's equation states that the second derivative of the electric potential,  $\Phi$ , can be expressed as product of a function of position variable and concentration  $C$  of the electrolyte in the homogeneous region. This depend-

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ence on  $C$ , cannot and should not vanish upon integration of the charge density profile of an inhomogeneous region, with respect to position variable  $x$ , over the finite extent of the inhomogeneous region. Integration of the charge density profile will lead to the electric field profile. A second integration over the position variable of the resultant will yield the electric potential profile. The position variable  $x$ , is defined along a coordinate normal to the surface, say, containing a set of fixed charges. Therefore, the validity of the Poisson's equation requires that the electric potential at a specified location in the inhomogeneous region, should be proportional to the concentration  $C$ , of the electrolyte in the bulk homogeneous region. Since the integration is to be performed over the finite extent of the inhomogeneous region, the extent of the inhomogeneous region,  $d$  enters as a parameter. It is assumed that the inhomogeneous region is finite and extends, from  $x = 0$  to  $x = d$ . Therefore, the first derivative of the electric potential profile, namely, the electric field will be proportional to  $d$ . Similarly, a second integration will result in a function proportional to  $d^2$ .

2. At equilibrium the Boltzmann distribution derivable from statistical mechanics is exactly valid. Since entropy is additive and probability is multiplicative, the relation between energy and concentration is logarithmic. The Nernst expression, derivable from exact Boltzmann law, states that the electric potential should not be dependent on the absolute value of concentration but only on the ratio of concentrations.

3. The third equation which is again exact, when positional dependence of dielectric coefficient in the inhomogeneous region, can be ignored, is the Maxwell's Osmotic Balance equation, discussed in this paper later. Maxwell's Osmotic Balance equation relates the electric field profile,  $\Phi'(x)$ , with the profile,  $A(x)$ , which represents the sum of concentrations of all solute molecules in the system. This equation leads to the conclusion that electric field at a specified location should be proportional to square root of concentration,  $C$  of the electrolyte. Maxwell's Osmotic Balance equation also stipulates that the inhomogeneous region should be finite in extent. These three conclusions are satisfied, (i) if the extent of the inhomogeneous region is finite and (ii) its magnitude varies inversely as the square root of electrolyte concentration in the homogeneous region. Knowledge of concentration profiles in the inhomogeneous system enables one to evaluate the electric field at any arbitrarily chosen location in absolute terms. Equating this with the results obtained by integration of the charge density profile, enables one to evaluate the extent of the inhomogeneous region. These enable one to verify the contentions of this paper. These summarize the basic results of this paper.

If the distribution of ions in the inhomogeneous region is determined by the presence of excess charges at one

location, and the extent of inhomogeneous region is finite, then mass conservation equations should necessarily be satisfied. Accumulation of a certain kind of ions in some location should lead to depletion of such kind of ions, elsewhere. Therefore, concentration profiles of such ions in the interfacial region should exhibit extrema values. This implies that the charge density profile, which is the resultant of concentration profiles should also exhibit similar extrema values. Classical theory predicts only monotonic concentration profiles, though Kirkwood and Poirier<sup>2</sup> have suggested the existence of such stratification of layers of alternate charge density, in concentrated electrolyte solutions. If concentration profiles of ions in inhomogeneous region near a surface with one kind of fixed charges are monotonic, as classical theories predict, it is difficult to find the answer to the question, viz. What is the sign and magnitude of charge density and electric potential at the surface?

### Considerations of the theory

In an inhomogeneous region, containing  $n$  kinds of ions, under isothermal equilibrium condition, there are  $(n + 2)$  unknowns, namely the concentration profiles of the  $n$  such ionic species, electric potential profile,  $\Phi(x)$ , and the dielectric profile,  $\epsilon(x)$ . Due to lack of better information, one usually adopts the approximation that the positional dependence of dielectric profile may be neglected. To solve these problems, therefore, one needs  $(n + 1)$  simultaneous equations, which are independent, to obtain these  $(n + 1)$  unknowns. Poisson's equation gives the relationship between the potential and the charge density,  $\rho(x)$ . Charge density can be expressed as proportional to concentration of a specified ionic species of the bulk homogeneous region, where concentrations are position independent, when the extent of inhomogeneous region is of finite extent,  $d$ . Therefore, it follows that the electric potential at a specified location in the inhomogeneous region is proportional to concentration of a specified ion in the homogeneous region.

The basic starting point of the theory of strong electrolytes<sup>3</sup> and diffuse double layer theory<sup>4</sup> has been the Poisson-Boltzmann equation, in its simple form. This equation is derived by the combination of the Boltzmann-Nernst expression and Poisson's equation resulting in a single nonlinear differential eq. (5). By utilization of the convenient assumption that one may ignore the positional dependence of the dielectric coefficient, and that the concentrations of charged species in an inhomogeneous region can be expressed adequately by the Nernst distribution, one reduces this equation to one equation involving one unknown, namely the derivatives of the electric potential profile. In this paper, we do not discuss Poisson-Boltzmann equation. Instead,

we concentrate on the implications of Poisson's equation and Nernst expression.

The Poisson's equation is expressed (in one dimension) in the form,

$$(d/dx)\{\epsilon(x)[d\Phi/dx]\} = Y(x) = -4\pi e\sum_{\sigma}Z_{\sigma}C_{\sigma}(x), \quad (1)$$

where  $\Phi(x)$  is the value of electric potential at location  $x$ , in the system.  $\epsilon(x)$  is the value of dielectric coefficient at location  $x$ .  $x$  is a position variable normal to the  $y$ - $z$  plane, along which the variation of various quantities is considered.  $C_{\sigma}(x)$  is concentration of ionic species of kind  $\sigma$ ,  $Z_{\sigma}$  is its signed valence charge number and  $e$  is the protonic charge. The electric potential profile and the charge density profile are the resultant of the concentration profiles of ionic species (see note 3).

The Nernst expression, utilized in the derivation of Poisson-Boltzmann equation, for the distribution of ions in equilibrium state, is,

$$C_{\sigma}(x_2) = C_{\sigma}(x_1) \exp [(Z_{\sigma}e/kT) \{\Phi(x_1) - \Phi(x_2)\}], \quad (2)$$

where  $k$  is the Boltzmann constant and  $T$  is temperature in the Kelvin scale.

The approximation involved in obtaining the Nernst expression, from Boltzmann equation, is that the energetic part of the free energy of ionic species is ascribed as only due to electrostatic part of the energy. Nernst expression is exactly valid, when the limiting expression for the chemical potential  $\mu_{\sigma}$  of an ion of kind  $\sigma$ , at location  $x$ , in solution, viz.,

$$\mu_{\sigma}(x) = \mu_{\sigma}^0(T, p) + kT \ln C_{\sigma}(x) + Z_{\sigma}e\Phi(x) \quad (3)$$

is valid. In eq. (3),  $p$  is pressure and  $\mu_{\sigma}^0(T, p)$  is the chemical potential of ions of kind  $\sigma$ , in its standard state. The logarithmic dependence of chemical potential on concentrations comes from the statistical considerations of entropy of mixing of ideal solutions, in which the mole fraction has been replaced by concentrations when solute concentrations are small. The contribution to free energy of an ion, from an external potential, such as an electric field to a charged species is added to this mixing terms of ideal solutions, in an *ad hoc* phenomenological manner (see note 4).

An expression of considerable interest to the subject in question, is the Maxwell's Osmotic Balance equation namely,

$$\begin{aligned} [8\pi kT/\epsilon]\{A(x_1) - A(x_2)\} &= \Phi'(x_1)^2 - \Phi'(x_2)^2, \\ A(x) &= \sum_{\sigma}C_{\sigma}(x), \\ \Phi'(x) &= \{d\Phi/dx\}. \end{aligned} \quad (4)$$

$A(x)$  denotes the sum of concentrations of all solute ionic species at location  $x$  in the system.  $\Phi'(x)$  denotes

the value of the electric field at location  $x$ .  $A(x)$  is proportional to concentration  $C$  of a specified ion in the homogeneous region. Maxwell's equation is valid exactly, if the limiting expression (3) for the chemical potential of an ion in solution is valid, and if the dielectric coefficient is independent of the position variable  $x$ . An important conclusion of Maxwell's Osmotic Balance equation is that the electric field is proportional to square root of the concentration.

Thus, we have three main conclusions: (i) Poisson's equation demands that the second derivative of electric potential profile is proportional to local charge density, and therefore to concentration of a specified ion in the homogeneous region, (ii) that the Maxwell's Osmotic Balance equation, which is exactly valid, if the limiting expression for the chemical potential of an ion is given by eq. (3), states that the electric field is proportional to square root of concentration of a specified ion in the homogeneous region, and (iii) that the Nernst expression requires that the electric potential is independent of absolute value of concentration of a specified ion in the homogeneous region.

When one integrates the charge density profile to obtain the electric field profile, over the finite extent of the inhomogeneous region, as a definite integral, a result proportional to  $(Cd)$  will be obtained, where  $d$  is the extent of the inhomogeneous region, and  $C$  concentration of a specified electrolyte in the homogeneous region. A second integration leading to the electric potential profile will similarly yield a result proportion to  $(Cd^2)$ . Therefore, the basic requirement for the resolution of the inconsistency existing between the Poisson's equation and the Nernst expression is that the extent of the inhomogeneous region is finite and not infinite. The implication of this conclusion with reference to our current concept of the theory of diffuse double layer is very significant. The appropriate boundary conditions that one must therefore utilize, are that the electric potential and its first and second derivatives vanish at finite distance from a surface containing field charges in the adjacent electrolyte. Both in the theory of strong electrolytes and in the Gouy-Chapman theory of diffuse double layer, it is usually assumed that the electric potential and electric field vanish at infinite distance (see note 5).

One must recall that the limiting expression (3), for the chemical potential of an ion in solution, is valid only for extremely dilute solutions. The presence of charges of one kind on a surface in contact with an electrolyte containing both kinds of ions, alters the distribution of ions in the adjacent electrolyte solution, by attraction of oppositely-charged ionic species to be in closer proximity with the surface and repelling similarly-charged ions to be further away from the surface. In this manner, an inhomogeneous region with a charge density profile occurs in the interfacial phase. If the concentration of

localized charges on the surface is larger, one will expect that more ions of unlike kind will be attracted to be in closer proximity to the surface. Such large accumulation of similarly-charged ionic species will, however, be expected to be resisted by the mutual repulsion between similarly-charged species to congregate in close proximity. Therefore, the local charge density will play a role in the distribution of ions in the interfacial region. This can be expressed, at least approximately, by the modification of the simple Nernst expression<sup>7,8</sup>, in the manner

$$\begin{aligned} C_{\sigma}(x_1) &= C_{\sigma}(x_2) \exp[(Z_{\sigma}e/kT)\{F(x_2) - F(x_1)\}], \\ F(x) &= \Phi(x) + [H\varepsilon/4\pi]Y(x), \\ Y(x) &= 4\pi e \sum_{\sigma} Z_{\sigma} C_{\sigma}(x). \end{aligned} \quad (5)$$

The term  $\exp[(Z_{\sigma}eH/4\pi kT)Y(x)]$  denotes the activity coefficient of ions of kind  $\sigma$ , in the inhomogeneous region, where dipole-ion electrostatic energy term contributions have been neglected. When one ignores the presence of the charge density term,  $Y(x)$  in  $F(x)$ , one recovers the familiar Nernst expression. In eq. (5),  $H$  represents a molecular integral term and denotes the integral contribution of all ionic species to the chemical potential of a specified ion arising from intermolecular interionic interactions. The derivation and justification of eq. (5) is presented elsewhere<sup>8</sup>. An important point to be noted is that the concentration distribution of charged species in the interfacial region is determined by the local charge density terms,  $Y(x)$ , in addition to the electric potential terms,  $\Phi(x)$  in the interfacial region, where electrolyte concentrations are not insignificant.

Eq. (5) states that the Boltzmann kind of equation relating the electric potential with the concentrations in a logarithmic manner is still valid for more concentrated solutions. Another important point that one should take into account, in analysing ion distributions in inhomogeneous interfacial region is that accumulation of one kind of species in any specified location in the interfacial region should lead to depletion of such kind of species elsewhere in the region, due to mass conservation conditions. Therefore, extrema points will exist in the concentration profiles of solute ionic species in the interfacial region. The mass balance equation condition can be written as

$$\int_0^d C_{\sigma}(x)dx = C_{\sigma}(d)d, \quad (6)$$

where  $C_{\sigma}(d)$  denotes the concentration of ions of kind  $\sigma$ , in the homogeneous region and  $d$  is the magnitude of the extent of inhomogeneous region (see note 6).

## Results

If what has been stated so far is reasonable and correct, one must conclude that the inconsistency existing be-

tween the implications of the Poisson's equation and the Nernst expression should not exist. The numerical calculations presented in this paper, for the chosen three examples of systems, demonstrate the validity of our conclusions. I choose two examples of a univalent symmetrical ion system (systems 1 and 2), and one example of an unsymmetrical 2-1 ion system, with divalent positive ions (system 3). I assume in the first example (system 1), that a surface containing univalent negative charges with concentration (per unit volume) of five times the concentration of univalent negative charges in the bulk homogeneous region, is in contact with a 1-1 electrolyte. In the second system, the surface is assumed to contain univalent negative charges with ten times the concentration of univalent negative ions,  $C$ , in the bulk homogeneous region. The third example I consider is a 2-1 electrolyte system, with divalent positive ions, which has a surface containing univalent negative charges with five times the surface concentration,  $C$  (per unit volume) of univalent negative ions in the homogeneous region. The stipulation of the concentration (per unit volume) of certain kind of ionic species at the surface and in the homogeneous region yields the values of the gradient of electric potential at the surface, in absolute terms apart from its sign, with the use of universal constants and the Maxwell's Osmotic Balance equation.

For illustrative purposes, it is assumed in the following calculations that the dielectric coefficient  $\varepsilon$  equals 80 and that the temperature equals 293.15 K. The values of universal constants utilized are:  $e = 4.80286 \times 10^{-10}$  esu, and  $N = 6.02486 \times 10^{23}$  per mole, and  $k = 1.38044 \times 10^{-16}$  ergs mole<sup>-1</sup>. The knowledge that  $C^-(o)$  equals  $5C$ , and utilization of Nernst kind of equations (3) or (5) yields the result that  $C^+(0) = 0.2C$ . Therefore, for system (1), we have  $\Delta A$  equals  $3.2C$ , where  $C$  is concentration of the 1-1 electrolyte in the homogeneous region. Thus, one obtains

$$\Phi'(o) = \pm 495.082 \text{ (esu/cm}^2\text{)}, \text{ when } C = 0.01 \text{ (m/l)},$$

$$\Phi'(o) = \pm 1565.59 \text{ (esu/cm}^2\text{)}, \text{ when } C = 0.10 \text{ (m/l)}.$$

For system 2, when  $C^-(o) = 10C$ , one obtains

$$\Phi'(o) = \pm 787.6706 \text{ (esu/cm}^2\text{)}, \text{ when } C = 0.01 \text{ (m/l)},$$

$$\Phi'(o) = \pm 2490.833 \text{ (esu/cm}^2\text{)}, \text{ when } C = 0.10 \text{ (m/l)}.$$

Similarly, for the unsymmetrical ion system (3), one obtains

$$\Phi'(o) = \pm 519.2463 \text{ (esu/cm}^2\text{)}, \text{ when } C = 0.01 \text{ (m/l)},$$

$$\Phi'(o) = \pm 1642.0012 \text{ (esu/cm}^2\text{)}, \text{ when } C = 0.10 \text{ (m/l)}. \quad (8)$$

In obtaining the results of eq. (8), I have utilized the identity that erg.cm equals (esu)<sup>2</sup>. The results of eq. (8) indicate that as concentration of charges on the surface is increased, the electric field at the surface increases, as one should expect. When concentration of electrolyte  $C$  in the bulk is increased ten fold, the electric field at the surface increases by a factor of square root of ten. Maxwell's Osmotic Balance equation yields the value of electric field at the surface, without specifying its sign uniquely. However, the sign of electric field can be specified uniquely, from the integral of charge density profile, by stipulating that the concentrations of ions and the extent of inhomogeneous region, which are physical quantities, have positive definite values.

Evidently, if one has the knowledge of concentration profiles of ionic species in the interfacial region, then one can compute the charge density profile, and an integration of the charge density profile will yield the electric field profile. The computed field profile will however, contain the unknown,  $d$ , namely the magnitude of the extent of the inhomogeneous region. Knowledge of the concentration of solute ionic species at the surface as well as in the bulk homogeneous region, will enable one to compute the value of sum of solute ion concentrations, viz.  $A(x)$ , both at these two locations. Since the value of electric field at location  $d$ ,  $\Phi'(d)$ , can be assumed to equal zero, one knows the magnitude of the electric field at the surface, apart from its sign in absolute terms, from the knowledge of universal constants. Equating the two values of electric field obtained from the integration of charge density profile with the result of the Maxwell's Osmotic Balance equation, yields the value of  $d$ . A second similar integration will lead to the evaluation of both the magnitude and the sign of the electric potential at the surface, assuming that the electric potential has null value in the bulk homogeneous region. Thus, verification of what has been stated in the foregoing is possible, if one has knowledge of concentration profiles of ions in the interfacial region.

Assume that concentration profiles of positive ions, when a surface with excess of negative charges is in contact with the simple electrolyte, can be expressed in a Taylor series. Assume in addition that the concentration profile of positive ions can be adequately represented by retainment of the leading five terms of such a Taylor series and that one can neglect of higher order terms with negligible error. The use of the three boundary conditions, viz. that the first and second derivatives of concentration profile vanish at  $x = d$ , and that such ions obey the mass balance eq. (6), yields the ratio of any two of the leading five Taylor expansion coefficients of the concentration profiles of ions in the inhomogeneous region.

The boundary conditions, to be utilized, for the evaluation of concentration profiles of positive ions of the system are:

$$\{dC^+(x)dx\}_d = 0 = \{d^2C + (x)dx\}_d$$

$$\int_0^d C^+(x)dx = C^+d, \tag{9}$$

where  $C$  is concentration of univalent negative ions of the electrolyte in the bulk homogeneous region. Eq. (9) follows from the fact that in the homogeneous region, over a distance  $d$ ,  $C^+d$  represents the integral amount of ions of kind + present in this layer. This amount of ion is redistributed in the inhomogeneous region of extent  $d$ .

The concentration profile of positive ions is expressed in a truncated Taylor series,

$$C_+(x) = \sum_{i=0}^4 C_{+i}x^i.$$

The ratios of the leading five Taylor coefficients are obtained as

$$\begin{aligned} C_{+1} &= -(8/5)C_{+4}d^3, \\ C_{+2} &= (18/5)C_{+4}d^2, \\ C_{+3} &= -(16/5)C_{+4}d, \\ 5C_{+4} &= C^+(d) - C^+(0). \end{aligned} \tag{10}$$

Similarly, for a 2-1 ion system, when  $C^-(0) = 5C^-(d)$ ,  $C^{2+}(0)$  equals  $0.04 C^-(d) = 0.02 C^{2+}(d)$ ). The concentration profiles of the positive ions in the interfacial region are known. From the knowledge of the concentration profile of specified kind of positive ions, the concentration profiles of all other ions present in the system can be computed, with the utilization of the equations,

$$\begin{aligned} C^+(x)C^-(x) &= C^+(d)C^-(d), \\ [C^{2+}(x)/C^{2+}(d)] &= \{C^-(d)/C^-(0)\}^2. \end{aligned} \tag{11}$$

These are the simplest concentration profiles of ions that one can assume to be valid in the interfacial region. Such resultant profiles are subject to the validity of the assumptions invoked about the boundary conditions and neglect of higher order terms. If better knowledge about the concentration profiles is available in future, then the calculations may be improved. However, Nature is simple. The demonstration that the values of electric potentials obtained with these concentration profiles are indeed independent of absolute values of concentrations, as required by the Boltzmann-Nernst kind of equations suggests that the concentration profiles presented in this paper may have more general validity than one may initially suspect.

An extremum in the concentration profiles occurs at location  $x = 0.4 d$  for all the three systems considered. At this location, the maximum accumulation of positive ions is about 1.17 times their concentrations in the homogeneous region. In all three cases considered, the charge density equals zero at  $x = 0.2 d$ . Also the value of  $A(0.2 d)$  equals  $A(d)$ , implying that an extremum in electric potential profile occurs at this location in the interfacial region. However, since the charge density also equals zero at this location, an inflection point of electric potential profile also occurs at the same location. (Since, inflection and extrema points occur at the same location, the existence of an extremum in electric potential profile in the interfacial region is no longer assured.) From the computed concentration profiles of cations and anions, one can calculate the charge density profile. The resulting charge density profile is fitted numerically into a finite polynomial of sixth order. These represent the leading seven Taylor coefficients of the charge density profiles. The results obtained for the three systems are presented in Table 1. The assumed values of boundary concentrations for system 1, that  $Y_0 = 4.8 C$ , imply that  $Y_0$  equals  $21.81756 \times 10^8$  (esu/cm<sup>3</sup>), when  $C = 0.01$  (m/l). The utilization of the values listed in Table 1, and integration, yields the result that  $\Phi'(o) = +7.5349 (C/\epsilon_0) d$ , where  $\epsilon_0$  is the value of dielectric coefficient at  $x = 0$ , namely the surface. Assuming that  $\epsilon_0$  equals 80, one obtains  $\Phi'(o) = 13.5445 \times 10^8 d$  (esu/cm<sup>2</sup>) for system 1. Since both  $C$  and  $d$  are positive definite, the electric field at the surface is positive definite. Thus, for system (1), one obtains the results that  $d$  equals  $36.551 \times 10^{-8}$  cm when  $C$  equals  $1 \times 10^{-5}$  (moles/cm<sup>3</sup>), [ $C = 0.01$  (m/l)] and that  $d$  equals  $11.585 \times 10^{-8}$  cm, when  $C$  equals ten times larger, i.e. [ $C = 0.10$  (m/l)]. The computed values of  $d$  for the three systems are listed in Table 2.

### Conclusions

The value of the electric potential at the surface containing an excess of negative charges can be obtained by twice integrating the resulting charge density profiles, over the extent of the inhomogeneous interfacial region

$$\left[ \int_0^d \left\{ \int_0^d Y(x) dx \right\} dx \right] = \Phi(d) - \Phi(o). \quad (12)$$

For system 1, the values of Table 1, utilized yield that the electric potential at the surface should equal

$$\begin{aligned} \Phi(o) &= -8.999146 \times 10^8 C d^2, \\ \Phi(d) &= 0. \end{aligned} \quad (13)$$

**Table 1.** Computed values of the leading seven Taylor coefficients of charge density profiles for the three systems

	System 1	System 2	System 3
$Y_0/C$	4.8	9.9	4.98
$Y_1 d/C$	-82.062	-195.808	-91.051
$Y_2 d^2/C$	603.063	1,554.072	694.298
$Y_3 d^3/C$	-2,370.409	-6,204.841	-2,739.029
$Y_4 d^4/C$	4,991.961	12,861.689	5,663.593
$Y_5 d^5/C$	-5,205.397	-12,998.777	-5,723.434
$Y_6 d^6/C$	2,058.044	4,973.764	2,190.643

**Table 2.** Computed values of various quantities for the three systems

Quantity	System 1	System 2	System 3
$d (C = 0.01)$	36.551 Å	18.987 Å	53.6775 Å
$d (C = 0.10)$	11.559 Å	6.004 Å	16.974 Å
$\Phi(o) [C = 0.01]$	-39.3194148 mV	-48.544647 mV	-37.993833 mV
$\Phi(o) [C = 0.10]$	-39.319415 mV	-48.547814 mV	-37.993844 mV
$F(o)$	+40.9227 mV	+58.54714 mV	+40.9227 mV

1 Å =  $1 \times 10^{-8}$  cm. The values of electric potentials are exhibited with larger than required number of decimal places to emphasize the excellent agreement.

Since both  $C$  and  $d$  are positive definite, eq. (13) implies that the electric potential at the surface should be negative definite as it should be, when one recognizes that the concentration of charges at the surface is predominantly negative.

One obtains for the system 1, the values

$$\begin{aligned} \Phi(o) &= -1.202264 \times 10^{-4} \text{ (esu/cm)} \\ &= -39.3194 \text{ millivolts,} \end{aligned} \quad (14)$$

when concentration of univalent symmetrical electrolyte  $C$  equals either 0.01 moles per l or ten times larger, viz.  $C = 0.1$  moles per l. In these calculations, I have utilized the conversion relation that 10 millivolts equal  $0.3313733 \times 10^{-4}$  (esu/cm). I have demonstrated by these kind of calculations that the calculated values of electric potential at the surface are independent of the absolute values of concentrations of a specified ion in the homogeneous region, as required by the Boltzmann-Nernst kind of relations, while retaining at the same time, the validity of the Poisson's equation that the second derivative of electric potential profile be proportional to concentration of a specified ion in the homogeneous region.

The existing paradox has been solved in this paper, by the use of the three fundamental equations. In order to convince ourselves that this is not an accidental result, the calculations are repeated for all three systems and the results are presented in Table 2. In that table, the resultant values of electric potentials obtained are pre-

sented in larger number of digits than usually required to exhibit the excellent agreement obtained for all the three systems. The computed values of electric potentials are very sensitive to determined values of  $d$ .

An interesting point that one may notice from the values listed in Table 2, is that the value of  $d$ , the extent of inhomogeneous region for the 1-1 electrolyte system 1, when concentration of electrolyte is 0.01 moles/liter, equals 36.551 Å. This value approximates very closely the value of ion atmosphere radius ( $1/\kappa$ ) of the classical Debye-Huckel theory, which yields a value of 30.942 Å, under similar conditions (see note 7).

One of the basic requirements for the evaluation of  $d$ , the extent of the inhomogeneous interfacial region, as well as the resolution of the paradox mentioned, is that the extent of inhomogeneous region is finite and that both  $\Phi(d)$  and the electric field,  $\Phi'(d)$  vanish at  $x = d$ . Recall that the boundary conditions utilized in strong electrolyte theory and in Gouy-Chapman theory of double layer are that the electric potential and the electric field vanish at infinite distance rather than at finite distance from a specified ion or surface in question. Though these are reasonable and valid boundary conditions, it should be remembered that no effect remains finite in magnitude up to infinite distance in the real world<sup>9</sup>.

In summary, the main conclusions derived in this paper may be listed as follows: Both Poisson's and Boltzmann expressions are rigorously valid. These lead to what appears to be mutually contradictory conclusions regarding the dependence of electric potentials on concentrations of ions in solution. This apparent inconsistency is resolved by resorting to considerations of the validity of Maxwell's Osmotic Balance equation, which implies that the electric field is proportional to square root of ion concentrations. Both Nernst equation and Maxwell's Osmotic Balance equation are valid exactly, if the limiting expression for chemical potential of ions in solution is valid, and positional dependence of dielectric coefficient is ignored. This approximation also enables one to evaluate the extent of the inhomogeneous interfacial region. Assumed validity of Maxwell's Osmotic Balance equation enables one to evaluate the electric field in absolute terms using universal constants. The analysis presented in this paper reinforces the basic belief, that if a plane in the system contains an excess of negative charges, then the potential on this surface should be negative. An evaluation of contributions from ion-ion interaction energy to chemical potential is also presented.

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## Notes

1. The statement that Poisson's equation stipulates that the second derivative of electric potential,  $\Phi''$ , the electric field and the electric potential are all proportional to concentration  $C$  of the electrolyte, or, concentration  $C_\sigma$ , of a specified ion  $\sigma$ , in the homogeneous solution requires clarification. Poisson's equation gives the relationship between the electric potential and charge density. This is exhibited in eq. (1) of this paper. The validity of the statement is best seen for a system with a simple symmetrical univalent ion system, in the inhomogeneous interfacial region. For a system with a 1-1 electrolyte system, eq. (1) can be written with the assumption of constant dielectric coefficient,  $\epsilon$ , for one dimensional case as,

$$\epsilon \{d^2\Phi/dx^2\} = -4\pi eC \{ \exp(-y) - \exp(+y) \},$$

since  $C^+(x) = C^+(\infty) \exp(-y)$ .

In this equation,  $y(x) = [e\Phi(x)/kT]$  and  $x$  is a position variable normal to plane of an interface. Since  $C^+(\infty) = C^-(\infty) = C$ , the concentration of electrolyte in homogeneous region, it follows that the second derivative of electric potential at a specified location in the inhomogeneous region is indeed proportional to concentration of either a specified ion or an electrolyte in the homogeneous region. This dependency of  $\Phi(x)$  on  $C$ , cannot and does not vanish upon integration, and hence the statement that Poisson's equation implies proportionality between the electric potential  $\Phi(x)$  and concentration  $C$ , of the electrolyte in the homogeneous region. Though very approximate, the solution for the electric potential obtained by simple Debye-Huckel theory, where  $\Phi(x)$  is dependent on  $\kappa^2$ , where  $\kappa$  is the ion atmosphere parameter, also supports our contention. When the inhomogeneous region contains an unsymmetrical electrolyte mixture, the concentration of a specified ion, say  $\sigma$ , denoted by  $C_\sigma(x)$  at location  $x$ , in the inhomogeneous interfacial region can always be stated as some fraction or multiple of concentration of same ion  $C_\sigma(d)$ , in the bulk homogeneous solution.  $C_\sigma(d)$  again can be stated as some fraction of  $C$ , where  $C$  is the concentration of electrolyte in the bulk homogeneous system. In the same manner, one may consider the situation at an electrode/electrolyte interface. At equilibrium, the charge on the electrode is proportional to the number of electrons, or ions, present on the (metal) electrode per unit area or per unit volume. The net charge residing on the electrode, and resultant electric field resultant in the inhomogeneous region, is a function of concentration of electrons in this case. Concentrations are particles per unit volume and have the same dimensions as concentration of charges, which can be expressed as the number of electrons per unit volume. Therefore, the net charge on the electrode can also be expressed as product of bulk electrolyte concentration times a proportionality constant. Therefore, it follows that the charge density at any arbitrary location in the interfacial region can always be expressed as a product

of a yet unspecified function of position variable times  $C$  or  $C_\sigma(d)$  both of which are independent of position variable  $x$ . Therefore, the second derivative of electric potential can always be expressed as some function of position variable times  $C$ . Hence the statement, that Poisson's equation states that the electric potential at any specified location  $x$ , in the interfacial region is proportional to  $C$  or  $C_\sigma(d)$ , where  $C_\sigma(d)$  denotes the concentration of specified kind of ion in the homogeneous region, is always valid.

- Concentrations denote probability of observing a particle in a small element of space. One obtains the ideal entropy of mixing, as well as the expression for the dependence of the chemical potential of a substance  $j$ ,  $\mu_j$ , on composition of a mixture containing noninteracting species as,

$$\mu_j(T, p, X_j) = \mu_j^0(T, p) + kT \ln X_j,$$

where  $X_j$  is the mole fraction of species  $j$  in the mixture.  $T$  is temperature and  $p$  is pressure.  $k$  is Boltzmann constant. For solutes such as electrolytes, where solvent is present in excess, mole fractions can be replaced by concentrations. For charged species such as ions, the contribution from external field to partial molal free energy (chemical potential) of an ions of kind,  $\sigma$ , is phenomenologically added in an *ad hoc* manner. One obtains in this manner, the limiting expression for the chemical potential of an ion in solution as

$$\mu_\sigma(T, p, x) = \mu_\sigma^0(T, p) + kT \ln C_\sigma(x) + Z_\sigma e \Phi(x),$$

where  $Z_\sigma e$  is the charge present on an ion of kind  $\sigma$ .  $\Phi(x)$  is the electric potential at location  $x$ , in the inhomogeneous region, and  $C_\sigma(x)$  is its concentration at location  $x$ . Since at equilibrium, the chemical potential of a species should be the same everywhere, equating the values of chemical potential at two distinct locations, one obtains the basic Nernst expression (3), relating the difference in electric potential at these two locations with the ratio of concentrations of a specified ion at these two locations.

- This statement is best explained by the following argument. If  $C_\eta(x)$  represents concentration of ions of kind  $\eta$  at location  $x$ , while  $C_\eta$  denotes concentration of ions of kind  $\eta$  the inhomogeneous region, one may express  $C_\eta(x) = C_\eta F_\eta(x)$ . If  $r_\eta$  represents the ratio of concentrations of ions of kind  $\sigma$  and ions of kind  $\eta$  in the bulk homogeneous region, ( $r_\eta = \{C_\sigma/C_\eta\}$ ), the right hand side of eq. (1) may be written, for example, for a three ion system, as

$$-4 \pi e C_1 \{F_1(x) + r_2 F_2(x) + r_3 F_3(x)\}.$$

Therefore, the charge density at location  $x$ , in the inhomogeneous region can always be expressed as proportional to concentration of a specified ion 1,  $C_1$  in the homogeneous region. An integration of the second derivative of the electric potential profile, leading to electric field profile, will also be proportional to concentration. An additional integration over the extent of inhomogeneous region, resulting in the electric potential profile, will again lead to a result proportional to concentration of specified kind ions,  $C$ , in the homogeneous region.

- For concentrated electrolyte solutions, in order that equation of the kind (3) is valid, one replaces the concentration terms  $C_\sigma$  of eq. (3) by a term called the activity,  $a_\sigma$ , of ions of kind  $\sigma$ , in solution. Activity is related to concentration by definition by the relation,

$$a_\sigma = \gamma_\sigma C_\sigma,$$

where  $\gamma_\sigma$  is called the activity coefficient. Both the definition of activity and activity coefficients are only phenomenological and are only fudge factors, expressing our ignorance about the variation of chemical potential of a specified species with composition

of a solution. The dependence of chemical potential on concentration is one of the unsolved problems of physical chemistry, though it is claimed in the literature, that both Mayer-McMillan theory and Kirkwood-Buff theory of solutions have solutions to this problem. One should disagree with this claim, since both these theories are symmetrical in their dummy indices, denoting components of a mixture, while experimental observations of free energy of mixing of various solutions are invariably unsymmetrical. In concentrated electrolyte solutions also, when activities are utilized in place of concentrations, one still obtains Nernst kind of expressions, where the electric potential term is modified by a local charge density term, which is discussed later in this paper. Activity coefficient is the resultant due to interparticle interactions and is a correction term to the equilibrium expression for chemical potential.

- Eq. (4) may be derived as follows: The differential of eq. (3) yields

$$\{dC_\sigma/dx\} = - \{[Z_\sigma e/kT]C_\sigma(x)\} \{d\Phi/dx\}$$

valid for all ions of the system. Summing over all ionic species present in the system, with the utilization of the Poisson's equation results in the expression,

$$\{dA(x)/dx\} = [\epsilon/4\pi kT] \{d\Phi/dx\} \{d^2\Phi/dx^2\},$$

in which the assumption that the dielectric coefficient is independent of  $x$  has been inserted. Use of the identity,

$$\{d/dx\} \{[(d\Phi/dx)^2]\} = 2 \{d^2\Phi/dx^2\} \{d\Phi/dx\}$$

and integration yields eq. (4).

- One may conclude with much haste, that eq. (6) is not tenable for the following reasons. Since charge density profile consists of the algebraic sum of concentration profiles of ions, weighted by their signed valence charge numbers, and the sum of such integrals over the extent of the inhomogeneous region, over all the ionic species present in the system, will be zero, since the integral operator is a linear operator and therefore, will result in constant zero charge density profile and hence lead to constant zero electric potential profile. The influence of an external electric field arising from the presence of a surface with charges is to separate charges of opposite signs, while electroneutrality conditions facilitate charge unification. The balance between these two conflicting tendencies results in the existence of the charge density profile of the inhomogeneous region.

The validity of the Nernst-Boltzmann equation requires that when ions of certain kinds satisfy the mass balance conditions presented by eq. (6), there exists at least one kind of ionic species in a many-ion system, whose profile does not satisfy the mass conservation conditions. One should expect that the kind of charges that do not satisfy eq. (6) is the same kind of ions present in the surface. This is identical to the classic statement that integral of the charge density profile over the extent of the inhomogeneous interfacial region, equals the negative of the surface charge density (macroscopic electroneutrality condition). One may verify that if in a symmetrical univalent ion system, if concentrations of positive ions and negative ions are respectively given by relations of the kind

$$C^+(x) = C \exp [-f(x)],$$

$$C^-(x) = C \exp [+f(x)],$$

then the integral

$$\int_0^d \{C^+(x) - C^-(x)\} dx, \text{ will not equal zero,}$$

$$\text{for any reasonable function, } f(x). \tag{7}$$



Therefore, eq. (6) does not suggest constant, zero electric field or electric potential profile, as one may suspect due to the linear nature of the integral operator. The right hand side of eq. (7) will equal  $-\sigma$  (surface charge density). If the net charge density on the surface is negative in sign, eq. (6) will not be satisfied by the negative ions of a 1-1 electrolyte of the homogeneous region.

7. Though our conclusion that the extent of the inhomogeneous region,  $d$ , varies inversely as square root of electrolyte concentrations,  $C$ , is similar to the conclusion of Debye-Huckel theory that the ion atmosphere parameter,  $\kappa$ , also varies as square root of electrolyte concentration,  $C$ , these two are not the same. Poisson-Boltzmann equation is a nonlinear differential equation, obtained by insertion of the Boltzmann distribution of concentrations in the Poisson's equation, replacing in this manner, the charge density term, by the electric potential term, resulting in a single

differential equation involving a single unknown, namely the electric potential  $\Phi$  and its derivatives. Expansion of the exponential and retention of only the first nonvanishing terms, and neglect of all higher order terms, results in a simple linear differential equation of the kind,

$$\{d^2\Phi/dx^2\} = \kappa^2\Phi(x),$$

where  $\kappa^2$  is proportional to concentration  $C$ . Thus, the conclusion that one obtains from the Debye-Huckel theory is an approximation and bears no relevance to the conclusions obtained in this paper regarding  $d$ . Although Debye-Huckel theory of strong electrolytes furnishes a strikingly satisfactory account of many of the properties of electrolyte solutions, it is based upon physical assumptions which, though plausible, are not in exact accord with the formal theory of statistical mechanics.

Received 23 June 1997; Revised accepted 11 November 1997

## Wait and see strategy for leaf miner control in rainfed groundnut

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*We propose a methodology for analysis of rainfall data to develop a management strategy for a rainfed crop. As an illustration we discuss control of leaf miner in groundnut. The strategy derived from rainfall analysis saves about 10% and 6.5% of gross yield more than other simple strategies namely (i) never spray or (ii) always spray respectively. The recommended strategy is to wait for rains up to six days after onset of leaf miner attack and then spray if rains fail.*

IMPROVEMENT in the productivity of rainfed agriculture is a major challenge for India today. Apart from the possibility of developing crop varieties better suited to rainfed conditions, it is also important to fine-tune management strategies including choice of sowing date, pest control measures, disease prevention, etc. Our contention is that detailed analysis of rainfall data can throw more light on relative profitability of alternative strategies. Daily rainfall data available for about a century can be used to gauge the conditions most likely to occur. They usually determine the consequence of a specific action. This evaluation is necessarily based on a series of assumptions about crop growth, occurrence and development of pests, etc. The assumptions used herein are tentative and can readily be modified. That of course may change the conclusions reached. The attempt, however, is to propose a heuristic methodology which can be applied no matter how the assumptions change.

As an illustration of our methodology, we consider the problem of controlling leaf miner in groundnut. Leaf miner (*Aproaerama modicella* Dev.) is a major pest of

groundnut in southern and central India. It is capable of almost totally wiping out the crop which has a potential yield of about 4 quintals per acre. The common measure to control this pest is to spray chloropyrephas at 2 ml/l using 250 l/acre. For the purpose of illustration we use market prices of 1995 given by Gadgil *et al.*<sup>3</sup>. At these rates the gross income per acre is Rs 4000 and cost of pesticide spray is Rs 750 per acre. The pesticide is sprayed on observing the occurrence of attack. If a wet spell occurs, the attack is controlled naturally.

Two simple strategies that can be practised are (i) ignore the occurrence or otherwise of the pest attack and never spray the pesticide and (ii) spray the pesticide as soon as attack is noticed. We introduce a third 'wait and see' strategy according to which a farmer waits for six days after noticing the attack and sprays the pesticide only if rains adequate for controlling the pest fail to occur till then.

### Assumptions

Farmers sow groundnut during July to August as soon as the fields receive adequate presowing rains (0.5 cm in 7 days). Starting from sowing date, leaf miner occurs during plant age 35 to 75 days (peg formation phase) if

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