

Journal of the Nevada Water Resources Association

Fall 2006

A publication of the Nevada Water Resources Association, providing hydrologic information to the people of Nevada and adjacent States



Volume 3, Number 2

Technical Note

New method for calculating activity coefficients of surface ions in concentrated electrolytes

ANPALAKI J RAGAVAN, Department of Civil and Environmental Engineering
University of Nevada, Reno, NV 89557

This technical note was intended to introduce a new method for calculating activity coefficients of surface ions in concentrated 1:1 electrolytes that would benefit geochemical modeling of environmental and industrial processes, which is currently severely hindered due to the unavailability of an equation to calculate the activity coefficients of ions adsorbed onto solid surfaces and/or located near solid surfaces in solution-solid interfaces also known as surface ions. In an electrolyte solution Coulomb forces between ions affect the thermodynamic and physical properties of the system. Hence law of mass action is strictly valid only when activities are used instead of concentrations. The only currently available Debye-Huckel (Onsager, 1933; Onsager and Fuoss, 1932; Wingrave, 2001) equation and its extended forms for calculating activity coefficients in real electrolyte solutions are limited to low electrolyte concentrations less than 0.01 moles (M) due to the use of linearized Poisson-Boltzmann equation in their derivation (Onsager, 1933; Onsager and Fuoss, 1932; Wingrave, 2001). Debye-Huckel equation also assumes that the dielectric constant of solvent molecules is unaffected by the concentration of solute ions in solution which limits its use to homogeneous solutions of concentrations less than 0.001 moles (Onsager, 1933; Onsager and Fuoss, 1932; Wingrave, 2001). It is frequently necessary to work with high concentrations of inert electrolytes present. A theoretically based activity coefficient equation for surface ions was derived in this paper based on rigorous electrostatic and thermodynamic laws and non-linear Poisson-Boltzmann equation, and used to simulate the activity coefficients of ions located at or near solid surfaces in solution-solid interfaces of 1:1 aqueous electrolyte solutions. The dielectric constant (DC) of the solvent molecules near the solid surface was calculated as a continuous function of the solute ion concentration. The mathematical incompleteness of Debye-Huckel equation was corrected in the derived equation with the use of non-linearized Poisson-Boltzmann equation. The derived equation gave reasonable results for ions of all types and valences at all concentrations of 1:1 electrolytes. The derived equation can also be easily extended to other type (1:2 and 2:2) of electrolytes.

INTRODUCTION

First of all I would like to give a brief introduction to the purpose for such an equation and the theory behind its derivation. Solids (e.g: metal oxides and hydroxides) are frequently used to remove toxic ions like lead, cadmium, arsenic, and selenium, from drinking and waste-water systems (Standard Handbook of Hazardous Waste Treatment and Disposal, 1989) through the technique called adsorption. Adsorption, also called surface complexation, onto metal oxide surfaces is the best currently available water treatment technology recommended by the U.S. Environmental Protection Agency (USEPA, 2001) to remove toxic ions from water and waste-water systems. Due to the unavailability of an equation to calculate the activity coefficient of surface ions, activity coefficients of surface complexed ions especially at moderate to high concentrations of the electrolyte solutions are incorrectly ignored or set equal to unity when calculating thermodynamic equilibrium constants for surface complexation reactions. Mass action is strictly valid only when activities are used instead of concentrations in real solutions (Onsager, 1933; Wingrave, 2001). Studying very dilute solutions (total electrolyte concentrations less than 10^{-3} M), in which the combination of activity coefficients, are practically equal to unity, is evidently limited to very stable complexes and high electrolyte concentrations are necessary when working with weak or moderately stable complexes. Therefore, ignoring activities in surface complexation models as done by current researchers and treatment facilities (Wang and others, 1997; Goldberg and Johnston, 2001) can lead to erroneous calculations and reporting of the results of the amount of toxic ions adsorbed onto solid surfaces and removed from drinking and waste water systems.

Ions follow Boltzmann's distribution in solution. Any derivation of the activity coefficient of ions in a real solution should be a solution to the Poisson-Boltzmann equation. Serious discrepancies between the Debye-Huckel predictions and the experimentally calculated activity coefficients even in very dilute solutions necessitate far reaching revision, if not rejection of the Debye-Huckel equation (Onsager, 1933). Several researchers have indicated that the discrepancies are due to the incomplete mathematical derivation of the equation (La Mer and others, 1931). In addition, the Debye-Huckel assumption, that the dielectric constant of the solvent in electrolyte solutions is the same as that of pure solvent makes it unusable for ions near solid surfaces in solution-solid (S-S) interfaces. As a result of counter-ion concentration near charged solid surfaces, an electrostatic diffusion double layer of surface ions, and counter-ions are formed in real S-S interfaces, which can result in electric field strength (EFS) of large magnitudes near solid surfaces (James and Healy, 1972), that can electrically saturate the nearby solvent molecules, reducing the dielectric constant (DC) of the solvent medium near solid surfaces, from the pure solvent value to a fully electrically saturated solvent value especially at high ionic strength of the medium. Interfacial EFS and the DC of solvent molecules are continuous functions of the ionic strength of the medium, electrostatic potential, and the distance from the solid surface. Due to the complex nature of the distribution of ions and the electrostatic potentials in an S-S interface, very few studies have been conducted in this area. No attempt has been made so far to develop an equation to estimate the activity coefficients of surface ions in real S-S interfaces with moderate to high concentrations of inert electrolytes present.

A brief description of what an activity coefficient is and its applicability to surface ions is given below. Thermodynamic properties of ideal solutions are calculable but, of real solutions, in most cases are not calculable, hence must be estimated from ideal solution properties. Activity coefficient (f_Y), describes the relationship between the activity (α_Y) of an ion (Y_Z) of valence Z and its mole fraction (X_Y) in real solutions as: $\alpha_Y = X_Y f_Y$ (Lewis and Randall, 1961). When two phases, where one is a solid and the other is a liquid are allowed to contact, counter-ions (ions of opposite charge) in the solution phase are attracted towards the charges on the solid surface by Coulomb forces, at the same time they tend to move towards the bulk solution because of their thermal motion, establishing an equilibrium distribution of counter-ions near solid surfaces (James and Healy, 1972). As counter-ions accumulate near solid surfaces, ions of the same sign (co-ions) are excluded from near the surface due to electrostatic interaction. Depletion of co-ions and the excess of counter-ions near solid surfaces result in screening of the charge of the surface ions. In real S-S interfaces the role of inert electrolyte concentration on electrostatic free energy of a surface ion is manifest in this screening of the surface charge on the surface ion by the counter-ions that concentrate near solid surfaces (Sen and others, 1975). Due to the counter-ion screening the amount of work required to overcome the electrostatic potential of a surface ion when charging the surface ion, which is the electrostatic contribution of the surface ion to its thermodynamic potential (electrostatic free energy), becomes smaller than the work required in an S-S interface without electrolytes (pure solvent). This can best be understood by a brief explanation of the ion charging process. An increment of work must be expended each time an increment of electrostatic charge is added to the surface of any solute ion. The source of this expenditure of work results from the fact that a surface ion with some amount of electrostatic charge will resist the addition of even more electrostatic charge of like sign. When counter-ions move nearer the surface of a surface ion each time an increment of charge is added to the surface ion addition of charge is favored, and the amount of energy required to make each incremental electrostatic charge addition is lowered (Sen and others, 1975). Absence of screening in ideal S-S interfaces indicates that counter-ions play no role in determining the electrostatic free energy of surface ions in ideal solutions. Therefore, real solution properties can be differentiated from ideal solution properties by deriving an equation for the difference in electrostatic free energy of a surface ion in concentrated real S-S interfaces and in pure S-S interfaces.

METHODS

The electrostatic free energy of any ion, can be computed directly from the work of charging the ion in a given dielectric medium at constant temperature (T) and constant volume (V) of the solution (Sen and others, 1975; Israelachvili, 1992; Wingrave, 2001). During charging an ion (Y_Z) of valence Z , the initial electrostatic charge q of Y_Z is gradually increased from zero by adding an infinitesimal amount of electrostatic charge (dq) to Y_Z , transported from a vacuum at infinite distance from Y_Z , where the electrostatic charge has no interaction energy. Whenever an infinitesimal amount of electrostatic charge (dq) is transferred to Y_Z an infinitesimal amount of work must be done reversibly in T and V to overcome the increasing electrostatic potential on the surface of Y_Z (at

distance r measured radially from the center of Y_Z , where r is the crystallographic radius of Y_Z). The quantity of the reversible work done is equal to the energy created or lost in the work process. Since the system is not thermally isolated but kept at constant temperature (T) the energy created becomes the free energy of the system.

In classical thermodynamics, definition of chemical potential (μ_Y) of a single solute ion (Y_Z) in a real solution phase (gas or liquid) is given as the change in the Gibbs free energy (∂G) of the solution phase with an incremental change in Y_Z (∂n_Y) at T and constant pressure (P). However, the above definition does not describe the dependence of μ_Y on the composition of the solution. The composition dependence of μ_Y requires a different derivation, which was achieved in this technical note by modifying the Gibbs-Duhem equation (Gibbs, 1948; Wingrave, 2001) (eq. 2), which describes the chemical potential of a component gas g (μ_g) in a gaseous system, under the constraints of T , and constant composition of all components except the composition of g (n_g) in the system applicable to liquid solutions.

$$-VdP + SdT + \sum_i^N n_i d\mu_i = 0 \quad . \quad (1)$$

S , and N in eq. 1 are entropy and the total number of all component gases other than g . To make computations easy, eq. 1 can be rearranged into the following integral form between the two hypothetical pressure states p_1 and p_2 :

$$\int_{\mu_g(p_1)}^{\mu_g(p_2)} d\mu_g = \int_{p_1}^{p_2} V_g dp \quad \text{iff, } dT = dn_{i \neq g} = 0 \quad . \quad (2)$$

Eq. 2 when combined with the equation of state for a hypothetical ideal gas (g) yields:

$$\mu_g^{ID}(p_2) - \mu_g^{ID}(p_1) = RT \ln \left[\frac{p_2}{p_1} \right]_{dT=dn_{i \neq g}=0} \quad , \quad (3)$$

where R is the gas constant, and $\mu_g^{ID}(p_2) - \mu_g^{ID}(p_1)$ is the chemical potential change of g between the pressure states p_1 and p_2 . If the pressure variables p_2 and p_1 in eq. 3 are taken to equal the ideal and the reference states of g , the following equation for the chemical potential difference of g between its ideal (μ_g^{ID}) and reference (μ_g^*) states can be derived:

$$\mu_g^{ID} = \mu_g^* + RT \ln X_g^{ID} \quad , \quad (4)$$

where $X_g^{ID} (= p_2/p_1)$ is the partial pressure variable for g in an ideal gas phase, which provides a convenient correspondence to the mole fraction of Y_Z (X_Y^{ID} : the ratio between the ideal molar concentration of Y_Z ($[Y_Z^{ID}]$), and its standard state molar concentration ($[Y_Z^*]$) in an ideal liquid solution. Therefore, an equation of state for an ideal liquid solution can be written in terms of μ_Y^{ID} and X_Y^{ID} as:

$$\mu_Y^{ID} = \mu_Y^* + R_B T \ln X_Y^{ID} \quad . \quad (5)$$

The gas constant ($R=8.3144$ Joule (J) M^{-1} Kelvin (K) $^{-1}$) in eq. 4 needs to be replaced by the Boltzmann's constant ($R_B = 1.381*10^{-23}$ J K^{-1}) for liquid solutions (Lewis and Randall, 1961). Eq. 5 describes the chemical potential of ions in ideal liquid solutions and does not take into account of the non-ideality in real liquid solutions.

The non-ideality in real liquid solutions was taken into account by incorporating the activity of Y_Z (f_Y) in eq. 5 in place of the mole fraction and writing an equivalent expression for the chemical potential (μ_Y) of Y_Z in real liquid solutions (Israelachvili, 1992) as:

$$\mu_Y = \mu_Y^* + R_B T \ln X_Y + R_B T \ln f_Y \quad , \quad (6)$$

where X_Y (ratio between the molar concentration of Y_Z in real liquid solutions [Y_Z] and its standard molar concentration ($[Y_Z^*]$)) is the mole fraction of Y_Z in real liquid solutions. From here onwards the term solutions will be used for liquid solutions. By restricting eq. 5 and eq. 6 to apply to ideal and real equimolar solution phases of Y_Z ($[Y_Z] = [Y_Z^{ID}]$) and subtracting the ideal solution equation (eq. 5) from the real solution equation (eq. 6), the chemical potential difference of Y_Z in real and ideal solutions in terms of f_Y was obtained as:

$$\mu_Y - \mu_Y^{ID} = -R_B T \ln f_Y \quad . \quad (7)$$

Eq. 7 is not an explicit equation for predicting f_Y in real solutions, since μ_Y and μ_Y^{ID} are not directly measurable experimentally. An explicit equation for f_Y requires the estimation of $\mu_Y - \mu_Y^{ID}$ in directly measurable parameters.

For the next step in the derivation, which involves obtaining an explicit expression for $\mu_Y - \mu_Y^{ID}$ ion charging was used. As discussed earlier, the electrostatic free energy of an ion anywhere in a solution (ideal or real) or in an S-S interface, which is also its chemical potential can be computed directly from the reversible work of charging the ion. The reversible infinitesimal work of charging Y_Z was computed separately in ideal (dW_Y^{ID}) and in real (dW_Y) solutions (Israelachvili, 1992) as:

$$dW_Y = \left\{ \frac{q.dq}{4.\pi.\varepsilon_o.\varepsilon_r.r} \right\} \quad , \quad (8)$$

$$dW_Y^{ID} = \left\{ \frac{q.dq}{4.\pi.\varepsilon_o.\varepsilon_r^{ID}.r} \right\} \quad , \quad (9)$$

where ε_o is the electrical permittivity of the vacuum ($= 8.854*10^{-12}$ coulomb 2 (c 2) $v^{-1}m^{-1}$), r is the crystallographic radius of Y_Z in m, and, ε_r is the DC of the solvent molecules near Y_Z located at or near solid surfaces in a concentrated real S-S interface, which is a

continuous function of the electrostatic field strength $\left(\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r \right)$ of the interfacial

solution near Y_Z in $v m^{-1}$, and ε_r^{ID} is that in a pure solvent medium. The total reversible work done in charging Y_Z , which is the chemical potential of Y_Z in real and in ideal inert electrolyte solutions in T and in V were obtained by integrating eq. 8 and eq. 9 respectively from zero up to the final charge of Y_Z (Q) as:

$$\mu_Y = \int_0^{W_Y} dW_Y = \frac{Q^2}{8.\pi.\varepsilon_o.\varepsilon_r.r} \quad . \quad (10)$$

$$\mu_Y^{ID} = \int_0^{W_Y^{ID}} dW_Y^{ID} = \frac{Q^2}{8.\pi.\varepsilon_o.\varepsilon_r^{ID}.r} \quad . \quad (11)$$

An equation for $\mu_Y - \mu_Y^{ID}$ was made possible in terms of the DC of the solvent molecules near Y_Z by subtracting eq. 11 from eq. 10 as:

$$\mu_Y - \mu_Y^{ID} = \left\{ \frac{Q^2}{8.\pi.\varepsilon_o.r} \right\} \left\{ \left\{ \frac{1}{\varepsilon_r} \right\} - \left\{ \frac{1}{\varepsilon_r^{ID}} \right\} \right\} \quad . \quad (12)$$

Eq. 12 was substituted into eq. 7 for $\mu_Y - \mu_Y^{ID}$ to obtain a simplified expression for f_Y in terms of ε_r as:

$$\ln f_Y = - \left\{ \frac{1.15(10^{-28}).Z^2}{r.R_B.T} \right\} \left\{ \frac{\varepsilon_r^{ID} - \varepsilon_r}{\varepsilon_r.\varepsilon_r^{ID}} \right\} \quad . \quad (13)$$

In eq. 13, ε_r is the only parameter that is unknown. An explicit equation to calculate f_Y of surface ions in real solutions requires an explicit expression for ε_r .

The final step in the derivation involves estimating ε_r at the solution-solid interface. Several equations are available in the literature that allows the calculation of ε_r in terms of $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ in an S-S interface. The equation by Sacher and Laidler (James and Healy, 1972; Sen and others, 1975) was chosen after replacing the high field limits of n_α^2 (where n_α is the optical refractive index) with the DC of the fully electrically saturated solvent molecules (ε_S) for calculating ε_r in real S-S interfaces in this technical note. The modified form of the equation is shown below:

$$\varepsilon_r = \left\{ \frac{(\varepsilon_B - \varepsilon_S)}{\left(1 + B \left\{ \frac{d\psi_Y(r)}{dr} \right\}_r^2 \right)} \right\} + \varepsilon_S \quad , \quad (14)$$

where B is a dimensional constant (James and Healy, 1975) equal to $1.2 * 10^{-17} \text{ m}^2 \text{ v}^{-2}$. The above equation (eq. 14) calculates ε_r as a continuous function of

$\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ between its high (ε_S) and low (ε_B) field limits. Gouy-Chapman equation (Israelachvili, 1992) for 1:1 electrolyte solutions (eq. 15) was chosen to estimate $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ near Y_Z . For surface ions distance from the solid surface was replaced by their ionic radii (r).

$$\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r = - \left\{ \frac{2.k.R_B.T}{e} \right\} . \sinh \left\{ \frac{e.\psi_Y(r)}{2.R_B.T} \right\} \quad , \quad \text{vm}^{-1} \quad . \quad (15)$$

In eq. 15 e is the charge of an electron ($=1.6022 \times 10^{-19}$) in c, and T is the absolute temperature of the medium in K, $\psi_Y(r)$ is the electrostatic potential on the surface of Y_Z in real S-S interfaces, and k is the reciprocal length of the diffusion ion atmosphere in m^{-1} also known as the reciprocal Debye length (Wingrave, 2001). In eq. 15 $\psi_Y(r)$ is the only unknown. If charging of Y_Z was independent of solution composition or ideal $\psi_Y(r)$ would simply be the coulomb electrostatic potential (Sen and others, 1975; Wingrave, 2001) for Y_Z , which would describe the ideal electrostatic potential of Y_Z in pure dielectric medium, which is a function of ϵ_r^{ID} making $\psi_Y(r)$ a constant equal to $\psi_Y(r)^{ID}$. Due to counter-ion concentration near Y_Z the electrostatic charge on the surface of Y_Z (initially ideal) will be partially offset by the proximity of ions of opposite charge. The screened electrostatic charge of the initially ideal surface potential which is the electrostatic potential of Y_Z in real solutions should be a function of ϵ_r . Since there are no other concentration dependent variables in the ideal electrostatic potential equation (Sen and others, 1975) the screening of the diffusion ion atmosphere on $\psi_Y(r)$ due to counter-ion concentration in real S-S interfaces is manifest in ϵ_r where ϵ_r is a continuous function of the solution ion concentration through $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ as shown in eq. 14. The coulomb electrostatic potential in ideal S-S interfaces was modified to compute $\psi_Y(r)$ in real S-S interfaces as follows:

$$\psi_Y(r) = \left\{ \frac{Q}{4\pi\epsilon_o\epsilon_r r} \right\}, \text{ v} \quad (16)$$

Eq. 16 was substituted for $\psi_Y(r)$ into eq. 15 along with values for the constants (R_B, T , and e) to obtain the following simplified equation for $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ in real solutions at 25°C:

$$\left\{ \frac{d\psi(r)}{dr} \right\}_r = \{-0.0514 k\} \sinh \left\{ \frac{280.2(10^{-10})Z}{\epsilon_r \cdot r} \right\}, \text{ vm}^{-1} \quad (17)$$

In eq. 17 k and ϵ_r are the concentration dependent variables. At 25°C values of k in m^{-1} for 1:1 electrolyte solutions (Israelachvili, 1992) can be calculated as:

$$k = \frac{[I]^{0.5}}{0.304 \times 10^{-9}}, \quad (18)$$

where I is the ionic strength of the medium in M. As k increases with increasing electrolyte concentration in real solution interfaces $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ will increase in agreement with eq. 17. This increase in $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ is due to the decrease in $\psi_Y(r)$ of the nearby solute ions due to screening by the diffusion ion atmosphere of counter-ions around and near the solute ions. In real solution interfaces ϵ_r is inversely related to $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ as

shown in eq. 14. Increase in $\left\{\frac{d\psi_Y(r)}{dr}\right\}_r$ due to increase in k is very much larger (Wingrave, 2001) compared to that due to decrease in ε_r . For example in 1:1 aqueous electrolyte solutions of 1 M, k (from eq. 18) is equal to $3.29 * 10^9 \text{ m}^{-1}$, $\left\{\frac{d\psi_Y(r)}{dr}\right\}_r$ (from eq. 17) is equal to $1.22 * 10^{8.5} \text{ vm}^{-1}$, and ε_r (from eq. 14) is equal to 35.45. The influence of ε_r on the value of $\left\{\frac{d\psi_Y(r)}{dr}\right\}_r$ is much less than $2.7 * 10^{0.5}$, which is almost negligible compared to the influence of k on the value of $\left\{\frac{d\psi_Y(r)}{dr}\right\}_r$, which is in the order of $1.22 * 10^{8.5}$. The influence of k on the value of $\left\{\frac{d\psi_Y(r)}{dr}\right\}_r$ further increases as values of I increase. In aqueous S-S interfaces at very high I values equal to infinity k becomes equal to infinity (according to eq. 18) leading $\left\{\frac{d\psi_Y(r)}{dr}\right\}_r$ to approach infinity, but the value of ε_r approaches 6. In aqueous S-S interfaces at very low values of I close to zero, k as well as $\left\{\frac{d\psi_Y(r)}{dr}\right\}_r$ approaches zero, but values of ε_r remains close to 78.46. Therefore, k can be considered as the only significant concentration dependent (screening) variable in eq. 17. Therefore, the argument inside the sinh() in eq. 17 can be considered independent of I and the variations in ε_r with I especially in aqueous electrolyte solutions can be ignored. For the same reason and since the argument inside the sinh() term is in the order of 10^{-10} , the sinh() term in eq. 17 was replaced by the argument itself according to the following hyperbolic identity:

$$\sinh(x) = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \frac{x^7}{7!} + \dots + \dots, \quad (19)$$

where ! stands for factorial notation. When the argument inside the sinh() term is small enough the higher order terms after x in eq. 19 were ignored and the following

simplified equation was obtained for $\left\{\frac{d\psi_Y(r)}{dr}\right\}_r^2$ after substituting x for sinh(x) in eq. 17:

17:

$$\left\{\frac{d\psi(r)}{dr}\right\}_r^2 = \left\{\frac{14.4(10^{-10})k.Z}{\varepsilon_r.r}\right\}^2, \text{ v}^2\text{m}^{-2}. \quad (20)$$

The maximum and the average percent error associated with the above substitution of x for sinh(x) in eq. 17 in aqueous electrolyte solutions at I values between 10^{-10} M and 250 M were calculated and found to be equal to 0.02 percent and 0.005 percent

respectively which are negligible. Eq. 20 was substituted for $\left\{\frac{d\psi(r)}{dr}\right\}_r^2$ into eq. 14 and

the resulting cubic equation was solved for ε_r in 1:1 electrolyte solutions in MATLAB

(version 7.0). Ignoring the negative roots (since ε_r cannot be negative) the following solution for ε_r in 1:1 electrolytes was obtained:

$$\varepsilon_r = \left\{ \frac{(\varepsilon_B \cdot A \cdot r^2) + (\varepsilon_S \cdot C \cdot k^2 \cdot Z^2)}{(A \cdot r^2) + (C \cdot k^2 \cdot Z^2)} \right\} , \quad (21)$$

Using eq. 21 ε_r of water molecules near solid surfaces in 1:1 aqueous electrolyte solutions at 25°C at a wide range of k values were calculated varying Z and r . In addition interfacial $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ using eq. 20 and eq. 21 as a function of I and the distance from the solid surface in 1:1 aqueous electrolyte solutions at 25°C was calculated.

Eq. 13 along with eq. 21 provides an explicit solution to calculate f_Y of surface ions in S-S interfaces of 1:1 electrolyte solutions. Eq. 13 was simplified to obtain an explicit expression for f_Y of surface ions in 1:1 electrolyte solutions at 25°C (eq. 23). Eq. 23 was used to calculate f_Y of surface ions in 1:1 aqueous electrolyte solutions (i.e., NaCl) at 25°C at a wide range of I values (10^{-20} M to 250 M). Surface ions of two different valences (± 1 , ± 3) and two different radii (0.5, and 5.0 nm (nanometers)) were used in the calculations.

As ions move from the bulk solution towards the solid surfaces due to Coulomb attraction they loose all or part of their hydration sphere before they reach the solid surface for adsorption. The ions that loose part of their hydration sphere form hydrated complexes (outer-sphere complexes) with the solid surfaces while the ions that loose their hydration sphere completely form non-hydrated complexes (inner-sphere complexes) with the solid surfaces. Thus ions that form outer-sphere complexes are considered to be at distance r_e from the solid surface and the ions that form inner-sphere complexes are at distance r from the solid surface where r_e is the radius (effective radius) of the partially hydrated ion and r is the radius (crystallographic radius) of non-hydrated ion. The effective radii of partially hydrated surface ions (Sverjensky and Molling, 1992) at the S-S interface were obtained as:

$$r_e = r + Z * (0.94) , \quad (22)$$

where Z is the valence of the ion. The final form of the derived AC equation is shown below.

$$f_Y = \exp \left\{ - \frac{2.8 * 10^{-8} (\varepsilon_B - \varepsilon_r) Z^2}{\varepsilon_B \cdot \varepsilon_r \cdot r} \right\} , \quad (23)$$

$$\text{where } \varepsilon_r = \left\{ \frac{(\varepsilon_B \cdot A \cdot r^2) + (\varepsilon_S \cdot C \cdot k^2 \cdot Z^2)}{(A \cdot r^2) + (C \cdot k^2 \cdot Z^2)} \right\} ,$$

where A ($= 6.16 * 10^3$) and C ($= 2.5 * 10^{-35}$) are constants without units.

Eq. 23 is explicit since all the terms in the equation can be either calculated or measured in the laboratory and also does not restrict its application to any concentration of the inert electrolyte present, since its derivation involves rigorous electrostatic and thermodynamic laws that are applicable at all concentrations of real solutions. The

Gouy-Chapman equation used to obtain interfacial $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ is based on non-linear

Poisson-Boltzmann equation (La Mer and others, 1931) and leads to reasonable values for the variables at a wide range of inert electrolyte concentrations. Extensions of eq. 23 to other electrolyte types (1:2, 2:2) are possible with careful reconstruction of the Gouy-Chapman equation (Israelachvili, 1992). The magnitude of all parameters including k depends solely on the properties of the solution and not on any property of the solid.

The above derived equation was applied to a simulated 1:1 electrolyte S-S interfacial system (i.e., NaCl) with selected system parameters to a) calculate activity coefficients of cations (i.e., M^+ , M^{2+} , M^{3+}) and anions (i.e., A^- , A^{2-} , A^{3-}) as a function of ionic radii (5 to 50 Angstroms) and valences, b) to validate the existence of values of $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ greater than 10^8 vm^{-1} near (0.9 nm from solid) solid surfaces in 1:1 aqueous electrolyte solutions at I values greater than 0.01M (Figure 1) which can electrically saturate the solvent molecules near solid surfaces and, c) to study the relationships among $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$, I and ϵ_r . The I values were varied between 250 M and 10^{-20} M, and the distance from the solid surface was varied between 0.1 Angstroms and 1000 Angstroms. ϵ_r was calculated using eq. 21, $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ using eq. 20 and f_Y using eq. 23. The calculations were performed in Microsoft EXCEL 2003.

RESULTS

According to the results, interfacial $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ were strongly and positively correlated with I at all I values as I was increased from 10^{-20} to 250 M ($R^2=0.99$) (Figure 1), and decayed exponentially away from the solid surface (Figure 2). $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ values above 10^8 vm^{-1} were found to exist near solid surfaces (0.9 nm from solid) which can cause significant electric saturation of solvent molecules (Figure 1). As $\left\{ \frac{d\psi_Y(r)}{dr} \right\}_r$ increased ϵ_r of the solvent (water) molecules decreased continuously from the pure solvent value ($=78.46$ at 25°C), towards the fully electrically saturated solvent value ($=6$ at 25°C) (Figure 3). Solvent ϵ_r increased continuously from the fully electrically saturated value ($=6$ at 25°C) towards the pure solvent value ($=78.46$ at 25°C) as the distance from the solid surface was increased (Figure 4) indicating a decay in electric saturation of the solvent molecules away from solid surfaces.

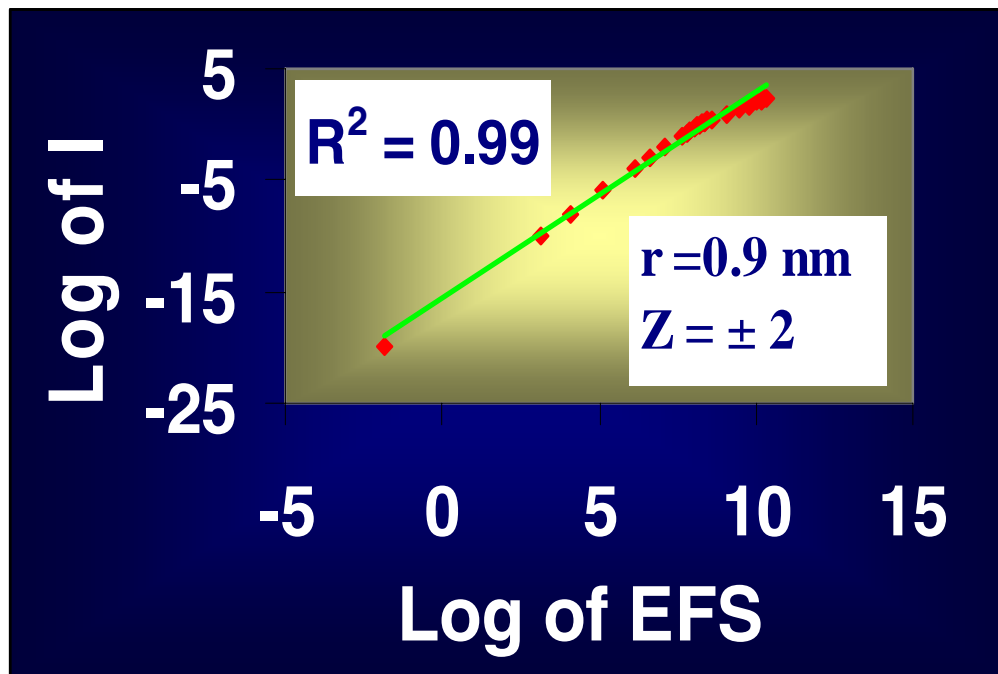


Figure 1. Log of interfacial electric field strength (EFS) as a function of the log of medium ionic strength (I) near divalent ions at 0.9 nanometers (nm) from the solid surface. Unit of EFS is volts per meter and that of I is moles.

At very low I ($\leq 10^{-10}$ M), ϵ_r near solid surfaces remained equal to that of pure solvent value indicating very low or no electric saturation of the solvent molecules at these low I values. Higher the I values higher were the deviations of ϵ_r near solid surfaces (0.9 nm from solid) from that of the pure solvent value ($=78.46$ at 25°C) (Figure 5). The difference in ϵ_r near monovalent and trivalent ions at 0.9 nm from the solid surface were not statistically significant at the 5% level (Figure 5).

According to the activity coefficient (f_γ) of the surface cations and anions calculated from eq. 23, f_γ of surface ions vary inversely with I at I values greater than 0.01 M indicating significantly decreased activities of surface ions at electrolyte concentrations greater than 0.01 M, and approached unity at lower I values leading activities to approach concentrations at these lower I values (Figure 6 and Figure 7). In addition higher the valence of the ion higher were the deviations of f_γ from unity at I values greater than 0.01M and vice versa. The differences in f_γ of the surface ions of the two valences (± 1 , ± 3) were significant at the 5% level ($P > |t| = 0.004$). Differences in f_γ of the surface ions of two radii (5.0 and 0.5 nm) were not statistically significant at the 5% level.

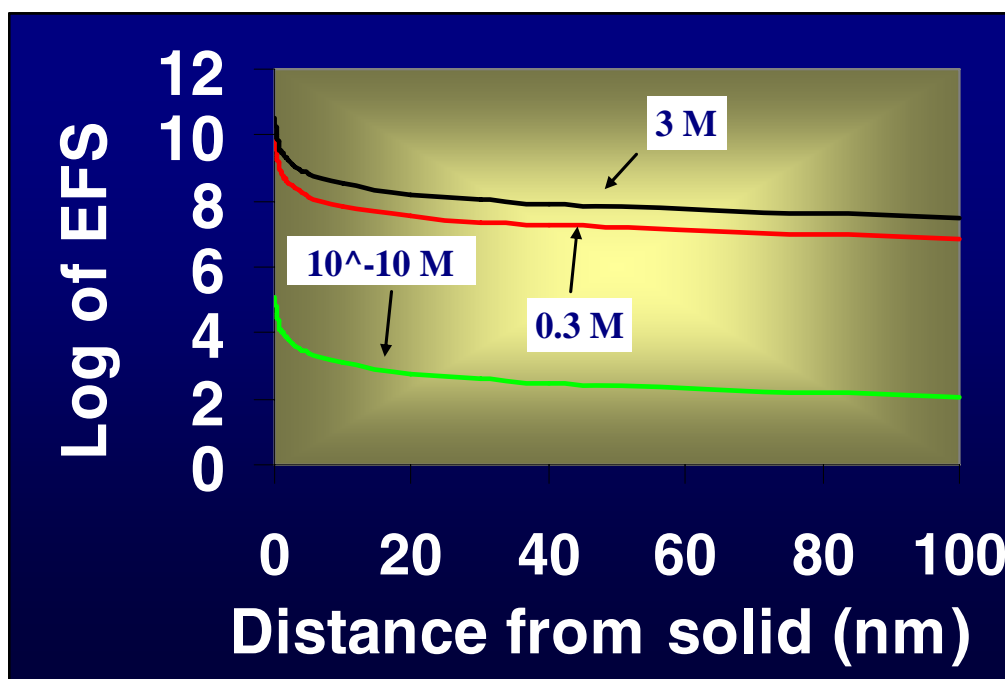


Figure 2. Log of interfacial electric field strength (EFS) as a function of the distance from the solid surface at three selected medium ionic strength (I) values. Unit of EFS is volts per meter, and that of I is moles (M).

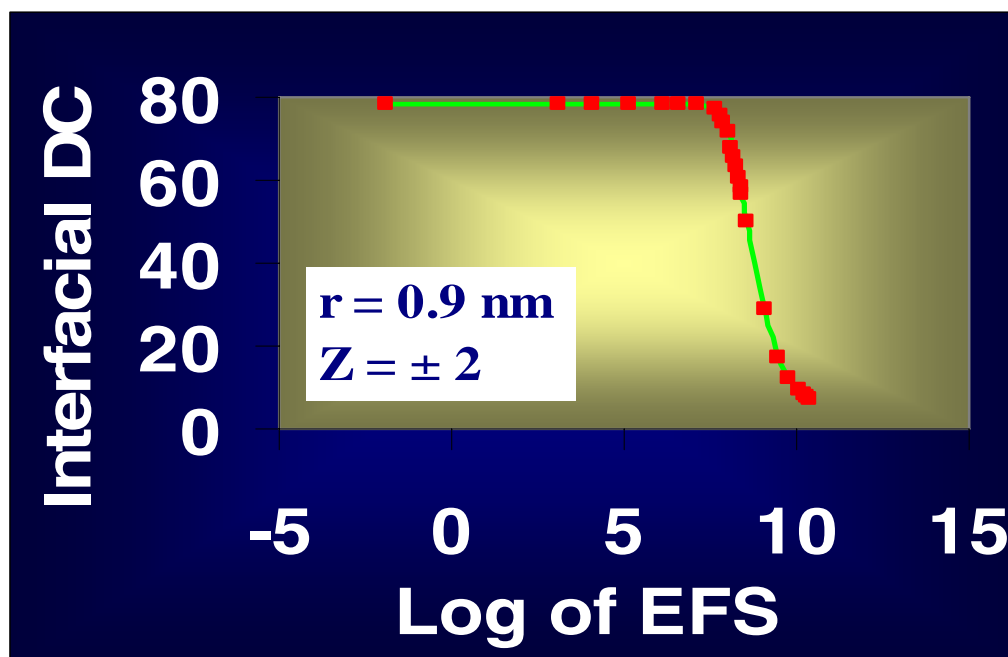


Figure 3. Interfacial solvent dielectric constant (DC) as a function of log of electric field strength (EFS) near divalent ions at 0.9 nm from the solid surface. Unit of EFS is volts per meter.

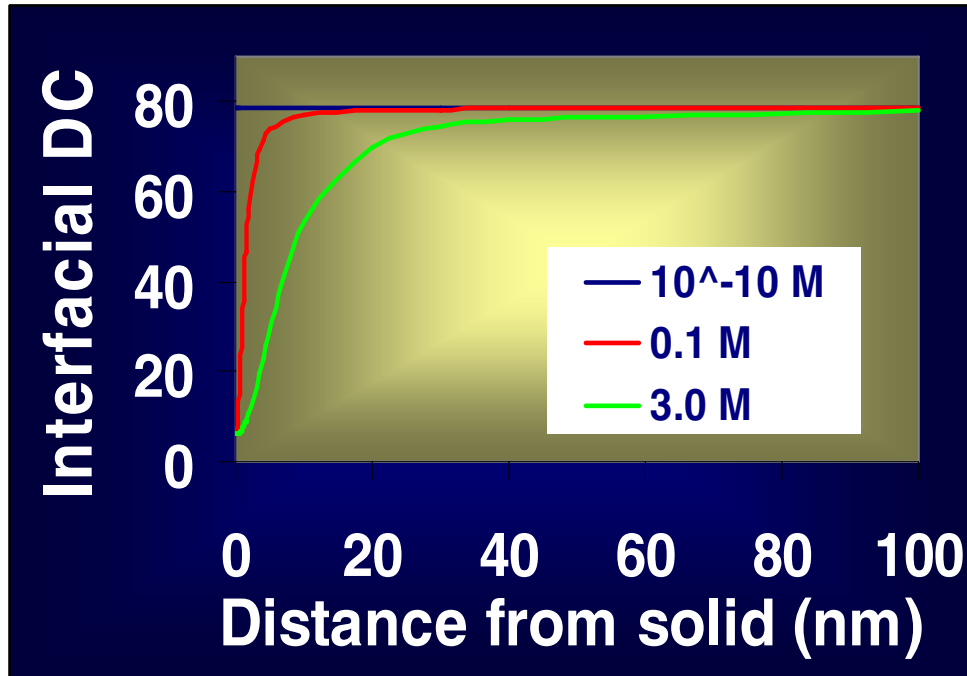


Figure 4. Interfacial solvent dielectric constant (DC) as a function of the distance from the solid surface at three selected medium ionic strength (I) values. Unit of I is moles (M).

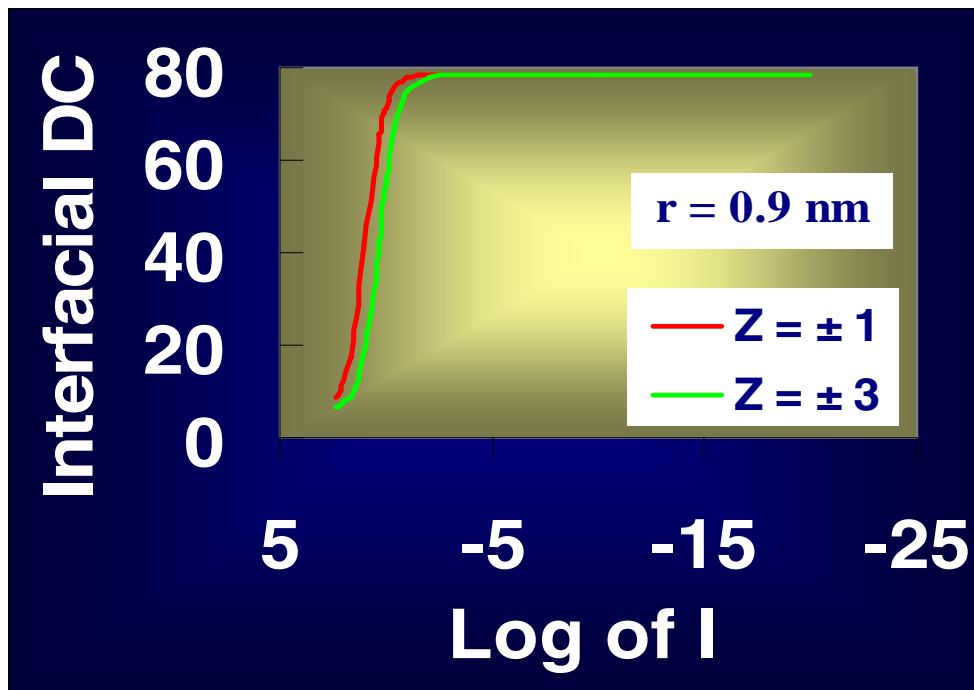


Figure 5. Interfacial solvent dielectric constant (DC) as a function of the log of medium ionic strength (I) near monovalent, and trivalent cations and anions at 0.9 nm from the solid surface. Unit of I is moles.

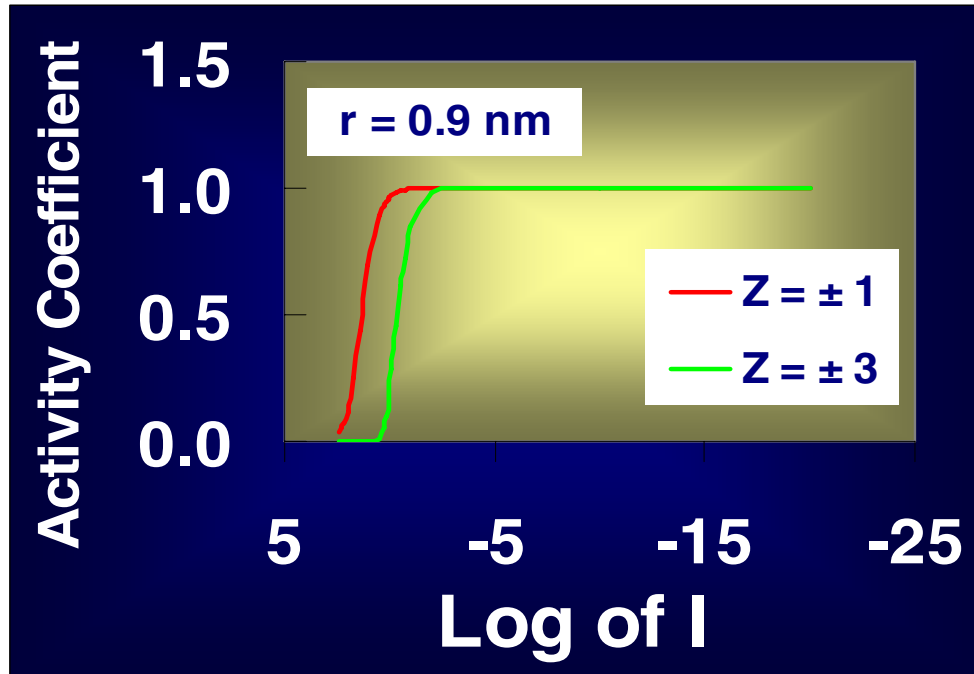


Figure 6. Activity coefficients as a function of the log of medium ionic strength (I) for monovalent and trivalent ions at 0.9 nm from the solid surface. Unit of I is moles.

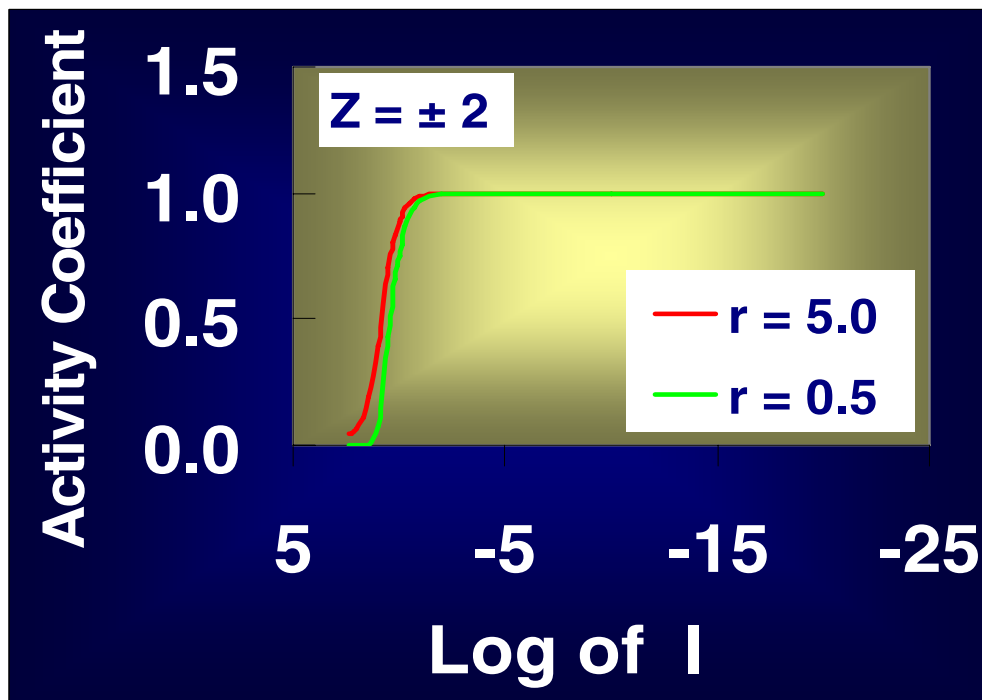


Figure 7. Activity coefficients as a function of the log of medium ionic strength (I) for two divalent ions of 0.5 nm, and 5 nm radii. Unit of I is moles.

CONCLUSIONS

According to the results, electrostatic field strength of large magnitudes ($>10^8$) exist near charged solid surfaces in real solution solid interfaces especially at high concentrations of inert electrolytes, and vary positively and linearly with the concentration of electrolytes. The screening of the electrostatic potential of a surface ion located at or near charged solid surfaces is manifest on the dielectric constant of nearby solvent molecules as well on the reciprocal length of the diffuse ion layer through this electric field strength. The dielectric constant of the solvent molecules near charged solid surface and the reciprocal length of the diffuse ion layer can be used to describe real solution properties almost completely in solid solution interfaces. The electrostatic free energy of an ion located at or near charged solid surfaces, which is a function of the dielectric constant of the solvent molecules near the ion can be used explicitly to calculate the activity coefficients of surface ions in real solution solid interfaces. Equation 23 computes f_γ reasonably accurately for surface ions at all valences and sizes, at all concentrations of 1:1 inert electrolyte solid-water interfaces at 25°C. In addition setting f_γ of the surface ions equal to unity or ignoring f_γ of surface ions in surface complexation models can lead to significant errors in the calculation of equilibrium constants of surface complexation reactions especially at electrolyte concentrations greater than 0.01 M. The results are general hence can be applied to other types of solvents and temperatures with very little modification.

REFERENCES

- Gibbs, J.W., 1948, The Collected Works of J. Willard Gibbs: Yale University Press, New Haven, CT.
- Goldberg, S., and Johnston, C.T., 2001, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling: *Journal of Colloid and Interface Science*, v. 234, p. 204-216.
- Israelachvili, J.N., 1992, *Intermolecular and Surface Forces*, (2nd ed.): Academic Press, London.
- James, R.O., and Healy, T., 1972, Adsorption of hydrolysable metal ions at the oxide-water interface III, A thermodynamic model of adsorption: *Journal of Colloid and Interface Science*, v. 40, no. 1, p. 65-81.
- La Mer, V.K., Gronwall, T.H., and Greiff, L.J., 1931, The influence of higher terms of Debye-Huckel theory in the case of unsymmetric valence type electrolytes: *Journal of Physical Chemistry*, v. 35, p. 2245-2288.
- Lewis, G.N., and Randall, M., 1961, *Thermodynamics*, (3rd ed.): McGraw-Hill Higher Education, New York.
- Onsager, L., 1933, Theory of concentrated electrolytes: *Chemical Reviews*, v. 13, p. 73-89.
- Onsager, L., and Fuoss, R.M., 1932, Irreversible processes in electrolyte, diffusion, conductance, and viscous flow in arbitrary mixtures of strong electrolytes: *Journal of Physical Chemistry*, v. 36, p. 2689-2778.

- Sen, R.K., Yeager, E., and O'Grady, W.E., 1975, Theory of charge transfer at electrochemical interfaces: *Annual Review of Physical Chemistry*, v. 26, p. 287-314.
- Standard Handbook of Hazardous Waste Treatment and Disposal, 1989: McGraw-Hill Higher Education, New York.
- Sverjensky, D.A., and Molling, P.A., 1992, A linear free energy relationship for crystalline solids and aqueous ions: *Nature*, v. 356, p. 231-234.
- U.S. Environmental Protection Agency, 2001, EPA to implement 10 ppb standard for arsenic in drinking water-EPA 815-F-01-010: U.S. Government Printing Office, Washington DC.
- Wang, F., Chin, J., and Forsling, W., 1997, Modeling sorption of trace metals on natural sediments by surface complexation model: *Environmental Science and Technology*, v. 31, p. 448-453.
- Wingrave, J.A., 2001, Activity coefficient and electrostatics at S-MO interface: *Surfactant Science Series*, v. 103, p. 201-254.