Chapter IV. New Electrostatic Potential Approach

4.1 Introduction and Motivation

In many instances modelers sacrifice the accurate representation of a system, introducing approximation or simplifications, for the sake of the "perfect solution." This recurrent constraint limits the validity of results and research. Therefore, empowering model developers with more alternative tools is of crucial importance since it may encourage the study of more complex phenomena via mathematical models. Furthermore, research can continue and be extended on those areas where restrictions on computational cost, speed, numerical algorithms, explicit mathematical expressions, and precision played an unfavorable terminal role.

Continuing with the previous argument, it has been found that in basic and engineering science, it is of fundamental importance to master differential equations and their solutions. The fact that commonly studied phenomena (physical, chemical and/or biological in nature) are represented by differential equations leads to such a background knowledge requirement. The literature covers fairly well the area of linear ordinary differential equations, first or higher order, solved analytically or numerically, while nonlinear ordinary differential equations are mostly solved by numerical methods. In particular, only first order differential equations that can be written in the Bernoulli equation form, and therefore can be subsequently reduced algebraically to a linear form, are possible to solve analytically. The Bernoulli equation is as follows

$$\frac{dy}{dx} + p(x) \cdot y = g(x) \cdot y^a \qquad (4.1)$$

Equation 4.1 is nonlinear if “a” is distinct than zero or one. Now if an auxiliary variable u(x) is set:

$$u(x) = [y(x)]^{1-a} \tag{4.2}$$

and later substituted in equation4.1, the result is

$$\frac{du}{dx} + (1-a) \cdot p(x) \cdot u = (1-a) \cdot g(x) \tag{4.3}$$

which is indeed a linear ordinary differential equation that can be solved for u(x) using conventional methods and after, by means of equation 4.2, y(x) can be obtained.

In equation 4.1, if the right hand side expression is replaced by a polynomial, exponential or trigonometric form, the equation becomes unsolvable using this method. The same situation takes place if the left hand side of equation 4.1 increases in order. Therefore, although very effective, the Bernoulli form is a very exceptional case of nonlinear ordinary differential equation. Unfortunately, important scientific laws such as Fick for molecular diffusion, Fourier for heat transfer, Darcy for fluid dynamic, Newton for viscosity and others lead to at least second order differential equations. This fact leaves important physical-chemical phenomena out of the analytical solution domain. When this is the case, numerical solutions and/or simplification restrictions come into play.

No specific example can be truer than the solution of the Poisson Boltzmann equation introduced in the previous chapter, equation 3.3, to support the argument presented in the previous paragraphs. As a remainder, the following expressions describe the electrostatic field near a wall region for two geometries of interest (Probstein, 3).

$$\frac{\partial}{\partial \xi}\left(\frac{\partial \psi}{\partial \xi}\right) = \lambda^2 \cdot \sinh \psi \qquad \text{(Rectangular Geometry)} \tag{4.4a}$$

$$\frac{1}{\xi}\cdot\frac{\partial}{\partial\xi}(\xi\cdot\frac{\partial\psi}{\partial\xi})=\lambda^2\cdot\sinh\psi \qquad \text{(Cylindrical geometry)} \qquad (4.4b)$$

On the right side of the equations 4.4 a&b, the hyperbolic sine function makes impossible an analytical solution of this particular case of differential equations. Although the Debye Hückel approximation, $\sinh\psi \approx \psi$, induces an analytical solution, such solution cannot be used for practical purposes as discussed in the previous chapter. This issue justifies the effort of finding an alternative solution for nonlinear ordinary differential equations.

Although one of the main objectives of the present work is the study of the hydrodynamic effect of electroosmosis via the electrostatic potential, finding an alternative solution for nonlinear ordinary differential equations does not only benefit this thesis work but also other researches involving this type of equations. The next two examples constitute proofs of the extension of this subject matter. The first of the two additional examples can be described in general terms as derived from the diffusion equation of a system with chemical reaction.

$$\frac{\partial}{\partial\xi}(\frac{\partial C_A}{\partial\xi})=\phi^2\cdot {C_A}^2 \qquad \text{(Rectangular Geometry)} \qquad (4.5a)$$

$$\frac{1}{\xi}\cdot\frac{\partial}{\partial\xi}(\xi\cdot\frac{\partial C_A}{\partial\xi})=\phi^2\cdot {C_A}^2 \qquad \text{(Cylindrical geometry)} \qquad (4.5b)$$

where, C_A is the average molar concentration of the species "A" of interest. In particular, when the chemical reaction, represented by the right hand side term in equations 4.5 a&b, is of first order, the differential equation is completely solved by conventional analytical methods. However, when this is not the case, as presented, only a numerical solution can be applied. Several environmental models have restricted their representation of biochemical processes as first order and pseudo-first order type of reaction because of the complexity in solving later the resulting non linear differential model equation.

The last additional example is found in the application of the heat transfer equation when nonlinear boundary conditions are affecting the system. The resulting expression is

$$\frac{\partial}{\partial \xi}\left(\frac{\partial \theta}{\partial \xi}\right) = \phi^2 + \theta^n \qquad \text{(Rectangular Geometry)} \qquad (4.6a)$$

$$\frac{1}{\xi} \cdot \frac{\partial}{\partial \xi}\left(\xi \cdot \frac{\partial \theta}{\partial \xi}\right) = \phi^2 + \theta^n \qquad \text{(Cylindrical geometry)} \qquad (4.6b)$$

where θ is the dimensionless temperature. Equations 4.6 a&b are nonlinear if "n" is other than zero or one. Once again, quite a few heat transfer applications fit the generic model represented by equations 4.6 a&b; however, no intent has been made to solve analytically this model. In particular, the study of the role of ambient radiation follows the behavior of "n=4".

Given the precedent facts, developing an analytical procedure to solve nonlinear ordinary differential equations is needed. The application of such a method could be used to promote understanding of the behavior and effect of important phenomena on its defined dependent variables. In particular, this type of contribution could make mathematical expressions more accurate on predictions but still simple, and used on a wider range of acceptable values as needed for the study of the electroremediation problem.

4.2 Development of a New Algorithm

This section is devoted to the review of models and their analysis for the description of the electrostatic potential. In particular, the representation of the charge density term is analyzed to capture the best ideas. The introduction of the basic mathematical aspect of the new strategy will follow. This includes the use of the charge conservation equation for differential models describing the electrostatic potential as well as the general solution strategy using the new correcting function, f_{AO}, introduced in this study.

4.2.1 Analysis of the Free Charge Density Term

As stated before, the right hand side of the Poisson-Boltzmann equation is the focus of this study. In particular, the free charge density modeled by a hyperbolic sine function must be analyzed prior attempting any solution of the equations 4.4 a&b.

The simplest model of the free charge density is the Debye Hückel approximation, $\sinh\psi \approx \psi$. However, this simplification limits the prediction of the applied electrostatic potential to values smaller than 25 mV which is equivalent to the range of $-1 \le \psi \le +1$ (Masliyah, 1994). Another model that extends the range of valid solutions to $-\infty \le \psi \le +\infty$ proposes splitting electrical potential values in three regions as a way of simplifying the hyperbolic sine function (Philips and Wooding, 1970).

$$\sinh\psi \approx \begin{cases} -\frac{1}{2}\cdot\exp(\psi) & \psi < -1 \\ \psi & -1 \le \psi \le +1 \\ +\frac{1}{2}\cdot\exp(\psi) & \psi > +1 \end{cases} \qquad (4.7)$$

This later proposal has been successfully use for other authors to obtain an interesting strategy to solve the Poisson-Boltzmann equation for these three regions. The drawback is that a considerable number of equations, subordinated equations and restrictions, involving rather complex algebraic procedures, are required. (Kang et. al., 2002). In summary, searching for an explicit mathematical expression of the electrostatic potential, two trends are observed. Simple expressions are not accurate for a large range of potential. On the other hand, more accurate models, reported in the literature (Philips and Wooding, 1970; Kang et. al. 2002), require more than three equations to predict the solution for a single point and this is not efficient from a computational viewpoint. Perhaps these approaches have some benefits depending on the type of application under study; however, they make very difficult the coupling of the Poisson-Boltzmann with other equations, i.e. Navier-Stokes, Laplace for heat transfer, and mass conservation (Bird et. al., 1960; Whitaker, 1984).

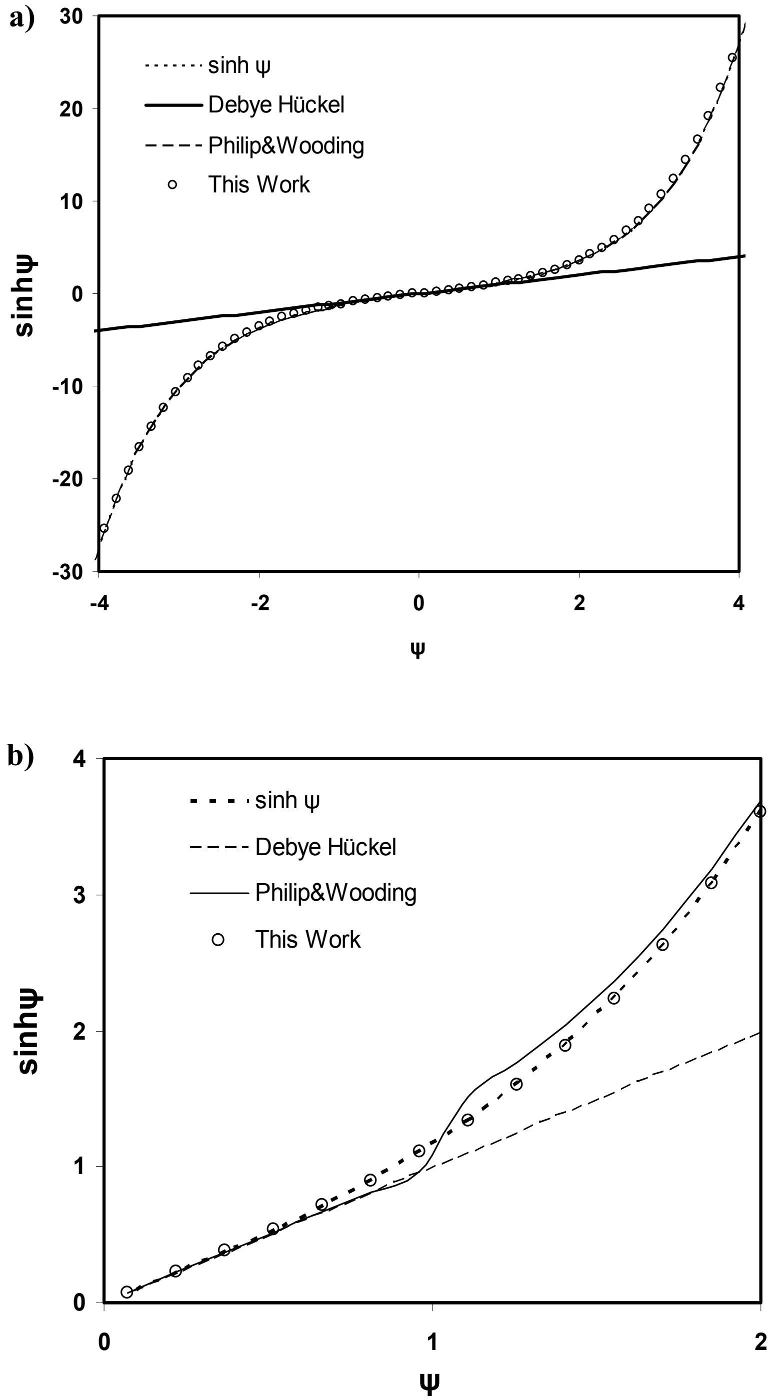

Figure 4.1 Fitness of different analytical approximations for the hyperbolic sine function in the range of $-4 \leq \psi \leq +4$ (a) and amplified version in range of $0 \leq \psi \leq +2$ (b)

Figure 4.1 presents the plot of different approximation expression for *sinh* Ψ, the free charge density, in the range of $-4 \leq \psi \leq +4$, (a), and in the range of $0 \leq \psi \leq +2$, (b). In addition, in figure 4.1 (a&b) the *exact* plot of *sinh* Ψ has been included for comparison and reference. The Debye-Hückel approximation presents increasing deviations beyond its range of applicability of Ψ values. For the Philip and Wooding's approach (Philip and Wooding, 1970), the three region equations, apparently makes a very good fit of the exact plot in the entire range of Ψ (see figure 4.1a). However, by using a larger scale and focus only in the positive domain of the electrostatic potential, Ψ (see figure 4.1b), stronger deviations are clearly seen in the range of $0.5 \leq \psi \leq +2$. This has been also observed in the negative range of the $-2 \leq \psi \leq -0.5$. These trends are in agreement with Kang's reports (Kang et. al., 2002). Now, by observing the figure 4.1b, the best fit is obtained with the use of polynomial functions. Indeed, this excellent behavior has been the basis for the introduction of the correction function approach that will be detailed in a section below. Furthermore, the expression that would be the foundation of this work proposal has a polynomial form given by:

$$\sinh \psi \approx \quad a \cdot \psi + b \cdot \psi^3 + c \cdot \psi^5 \tag{4.8}$$

where "a", "b" and "c" are polynomials coefficients with values of 1.000, 0.147 and 0.01367 respectively (for the case of figure 4.1) that can be adjusted or the number of term increased to obtain an even better fit or curve representation. If the approximation given by equation 4.8 is introduced in the Poisson-Boltzmann equation the result is a nonlinear second order differential equation which precisely has been avoided. Consequently, another path needs to be followed; however, the main idea that should remain is that a polynomial function is the best approximation of a hyperbolic sine function.

4.2.2 Introduction of the f_{AO} Correction Function

As described in the previous section, a better approximation or better fit can be achieved with a polynomial expression. This approach has the additional advantage that the polynomial's coefficients can be adjusted to more accurately represent the electrostatic potential if it is needed. However, further development is required to induce an explicit solution of the Poisson-Boltzmann equation. On the other hand, it is very well known that the Debye-Hückel approximation conveniently produces the analytical solution of the Poisson-Boltzmann equation in both the geometries most frequently used, i.e., planar and cylindrical. Therefore, it forms an excellent basis to try a different solution approach. In order to take advantage of these two mutually complementary approximations the following conditions must be true.

$$\lambda^2 \cdot \sinh\psi \approx \psi \cdot \lambda^2 \cdot [f_{AO}]^2 \equiv \psi \cdot \lambda^{*2} \tag{4.9}$$

and, therefore, that

$$[f_{AO}(\psi)]^2 \equiv 1 + b \cdot \psi^2 + c \cdot \psi^3 + d \cdot \psi^4 + \ldots \tag{4.10}$$

where $\boldsymbol{f_{AO}}(\Psi)$ is the correction function developed in this thesis. The role of the introduced correction function, $\boldsymbol{f_{AO}}(\Psi)$, is to modify the inverse Debye length, λ, when the electrostatic potential is calculated by using the equations 4.4 (a&b), analytically solved by mean of the Debye-Hückel approximation. This proposed modification can be written as follows

$$\lambda^* \equiv \lambda \cdot f_{AO} \tag{4.11}$$

where λ^* is the modified inverse Debye length. For simplicity the argument of the correction function, f_{AO}, has been dropped.

The use of the f_{AO} correction function is very simple and it can be described in the following set of steps:

I. An initial predictor value of Ψ is obtained from the analytical solution of equation 4.4 (a&b) for the Debye-Hückel approximation with a target inverse Debye length, λ, and a coordinate location, ξ.

II. By using this first value of Ψ the corresponding correction Function, f_{AO}, is obtained from equation 4.10.

III. Next, a modified inverse Debye length, λ^*, for the target inverse Debye length, λ, must be calculated using equation 4.11, where the Correction Function, f_{AO}, plays its role.

IV. Finally, a new and corrected value of Ψ is obtained as in step I, this time however, the modified inverse Debye length, λ^*, is used instead.

As can be realized, this process can go further as many times as required from step IV to step II since subsequent iterations yield better and corrected Ψ values. It has been found, however, that in practice a second or third iteration does not substantially enhance the results obtained in a first calculation. In fact, the first iteration produces considerably improved results. This fast convergence characteristic is perhaps the most important feature of the iteration process.

4.3 Test Examples and Illustrative Results

To illustrate the methodology, this section includes three examples that have been already discussed and documented in the previous chapter. These examples develop the methodology presented herein in perhaps the worst case scenario of nonlinearity. That is the case of the complete Poisson Boltzmann equation, presented as equations 4.4 a&b, where the nonlinearity source term is a hyperbolic sine function. Testing the methodology under this condition, including the geometry complexity (planar, cylindrical or annular), is very important to establish the universality of the solution herein proposed. Therefore, a comparison between the numerical solution of the complete Poisson Boltzmann equation and the analytical results found in the previous section of this work is presented and graphically illustrated. Once again this section concentrates in the methodology to solve a given ODE with its boundary conditions and not necessarily in the modeling behind the ODE. More specific information with regard to the physical system that leads to the EDOs herein exemplify the description and development can be found in the previous chapter, section 3.2.

4.3.1 Planar Capillary System

The system being suggested, in general terms, consists of two parallel walls each one subjected to an electrical potential equal to Ψ_w. If the coordinates have been placed in the vertical center of the capillary then the right hand side wall is at location ξ=1 while the left hand side wall is at ξ=-1 (see figure 3.1). In term of the electrostatic forces the system is completely defined by equation 4.4a; however, applying the methodology herein introduced and rewriting this equation in its linear form, equation 4.12a is obtained with the following boundary conditions for the system

$$\frac{\partial^2 \psi}{\partial \xi^2} = \lambda^2 \cdot \psi \cdot f^2_{AO} \tag{4.12a}$$

$$\psi = \psi_W \qquad @ \qquad \xi = -1 \tag{4.12b}$$

$$\frac{\partial \psi}{\partial \xi} = 0 \qquad @ \qquad \xi = 0 \tag{4.12c}$$

$$\psi = \psi_W \qquad @ \qquad \xi = +1 \tag{4.12d}$$

In order to write the nonlinear ODE equation 4.4a in its linear form, equation 4.12a, the algebraic transformation $\sinh\psi = f_{AO}{}^2 \cdot \psi$ had to be applied. In this case, the hyperbolic sine function must be expressed in its polynomial series form and later factorized in Ψ to isolate the term $f_{AO}{}^2$. This practice yields the following expression

$$[f_{AO}(\psi)]^2 = 1 + a_1 \cdot \psi^1 + a_2 \cdot \psi^2 + a_3 \cdot \psi^3 + a_4 \cdot \psi^4 + a_5 \cdot \psi^5 \ldots \tag{4.13}$$

In addition, notice that the correction function, f_{AO}, has been conveniently set to the square power to match the algebraic form of constant λ in equation 4.12a. This is a rather elegant algebraic move that will pay off in the form of the final analytical expression, but that has nothing to do with the successful application of the methodology.

Continuing with the methodology, the analytical solution of the linear ODE, equation 4.12a, is obtained using a conventional analytical method, or by analogy with equation 3.6, to yield

$$\psi(\xi) = 2 \cdot \psi_w \cdot \frac{\mathrm{Cosh}(\lambda \cdot f_{AO} \cdot \xi)}{\mathrm{Cosh}(\lambda \cdot f_{AO})} \tag{4.14}$$

As expected, equation 4.14 has an implicit type form since the correction function, f_{AO}, depends of the variable $\Psi(\xi)$. Traditionally, implicit equations are solved numerically and the form of the equation 4.14 suggests that the "Fixed-Point Iteration" method may yield the solution when conditions of convergence apply (Kreyszig, 1999). Precisely, this is the type of algorithm described in the previous section that will be tested next.

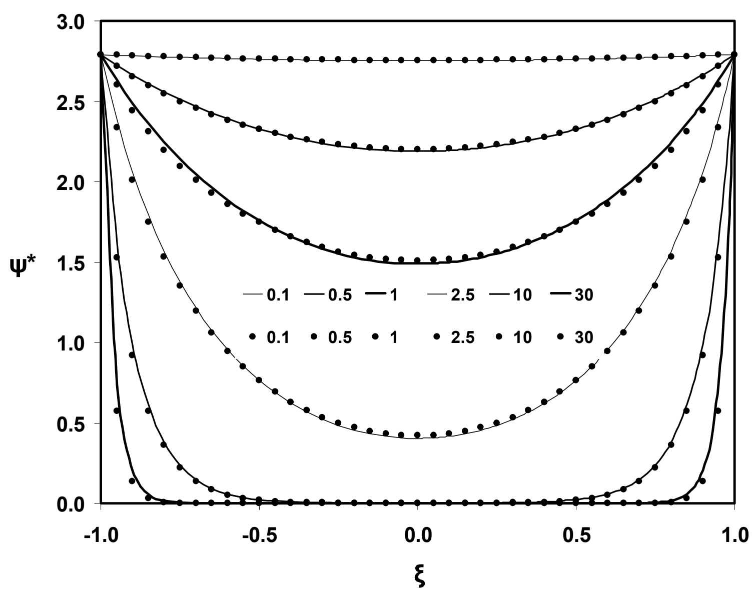

Figure 4.2 Dimensionless electrical potential profiles, in a planar geometry, for various values of the dimensionless inverse Debye length using the f_{AO}, Correction Function

Based on the characteristic fast convergence, observed in all the cases studied, three equations are required to solve the planar capillary system according to the analytical algorithm being presented. A Comparison of the results obtained from the numerical solution of the complete Poisson Boltzmann equation (4.4a) and the Debye Hückel linear approximation modified by the f_{AO}, Correction Function is presented in figure 4.2. This figure demonstrates that the use of the Correction Function, f_{AO}, method gives values in excellent agreement with those of the numerical solution of the complete original equation.

4.3.2 Cylindrical Capillary System

The other interesting geometry used to test the methodology herein presented is the cylindrical. The example system under analysis consists of a cylindrical capillary subjected to an electrical potential equal to Ψ_w at the wall. By reason of symmetry the coordinates have been set in the center of the capillary (see figure 3.2). In dimensionless coordinate the center of the system is at location ξ=0 and the wall is at ξ=+1 using only the positive coordinate. For this cylindrical case the system is completely defined by equation 4.4b with the following linear form and boundary conditions

$$\frac{1}{\xi}\cdot\frac{\partial}{\partial\xi}(\xi\cdot\frac{\partial\psi}{\partial\xi}) = \lambda^2\cdot\psi\cdot f^2{}_{AO} \qquad (4.15a)$$

$$\left.\frac{\partial\psi}{\partial\xi}\right|_{\xi=0} = 0 \qquad @ \qquad \xi = 0 \qquad (4.15b)$$

$$\left.\psi\right|_{\xi=+1} = \psi_W \qquad @ \qquad \xi = +1 \qquad (4.15c)$$

Following closely the same steps as in the previous test example, the correction function (f_{AO}) for the nonlinear source has to be defined first. In this particular case, the hyperbolic sine function continues to be the nonlinear source and therefore, equation 4.13 is still valid. Second, the linear ODE, equation 4.15a, is solved using conventional analytical methods, in which case the solution is

$$\psi(\xi) = \psi_w \cdot \frac{I_0(\lambda \cdot f_{AO} \cdot \xi)}{I_0(\lambda \cdot f_{AO})} \tag{4.16}$$

where I_0 is the modified Bessel function of first kind.

As before, equation 4.16 is defined as implicit since f_{AO}, the correction function, depends of the variable $\Psi(\xi)$. To solve this equation, the analytical algorithm proposed in the present work is applied to the cylindrical capillary system.

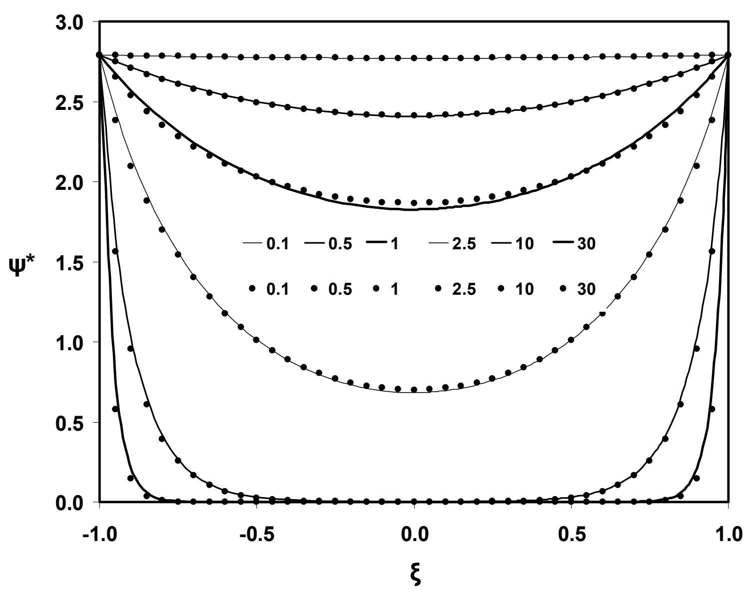

Figure 4.3 Dimensionless electrical potential profiles, in a cylindrical geometry, for various values of the dimensionless inverse Debye length using the f_{AO}, Correction Function

Figure 4.3 displays the comparison of solutions obtained from the numerical solution of the complete Poisson Boltzmann equation (4.4b) and the analytical algorithm approach, using the Debye Hückel linear approximation modified by the f_{AO} Correction Function. By the results observed in this figure, it is demonstrated that the use of the Correction Function, f_{AO}, method gives values in excellent agreement with those of the numerical solution of the complete original equation.

4.3.3 Annular Capillary System

The last system to be tested is a variation of the cylindrical capillary system. In particular, the system can be considered as a double cylindrical capillary system where the inner circular wall is subjected to an electrical potential equal to Ψ_1 and the outer circular wall is subjected to an electrical potential equal to Ψ_2. The coordinates have been set in the center of the capillary because of the symmetry (see figure 3.3). In dimensionless coordinate the center of the system is at location ξ=0, the inner wall is at ξ= b, and the outer wall is at ξ= +1, in both cases using only the positive coordinate. As in the previous case, the electrostatic forces acting in the system are completely defined by equation 4.4b with the same linear form; however, the boundary conditions change.

$$\frac{1}{\xi}\cdot\frac{\partial}{\partial\xi}(\xi\cdot\frac{\partial\psi}{\partial\xi}) = \lambda^2\cdot\psi\cdot f^2{}_{AO} \qquad (4.17a)$$

$$\psi\Big|_{\xi = b} = \psi_1 \qquad @ \qquad \xi = b \qquad (4.17b)$$

$$\psi\Big|_{\xi = +1} = \psi_2 \qquad @ \qquad \xi = +1 \qquad (4.17c)$$

The nonlinear source has not changed and therefore f_{AO}, the correction function, is well defined by equation 4.13. In terms of the solution of a linear system as the one describe by equations 4.17 a,b&c, the analytical solution for this system can be obtained by simple analogy with equation 3.10 and presented as equation 4.18.

$$\psi(\xi) = \frac{I_0(\lambda \cdot f_{AO} \cdot \xi) \cdot \{\psi_1 \cdot K_0(\lambda \cdot f_{AO}) - \psi_2 \cdot K_0(\lambda \cdot f_{AO} \cdot b)\}}{I_0(\lambda \cdot f_{AO} \cdot b) \cdot K_0(\lambda \cdot f_{AO}) - I_0(\lambda \cdot f_{AO}) \cdot K_0(\lambda \cdot f_{AO} \cdot b)} + \frac{K_0(\lambda \cdot f_{AO} \cdot \xi) \cdot \{\psi_2 \cdot I_0(\lambda \cdot f_{AO} \cdot b) - \psi_1 \cdot I_0(\lambda \cdot f_{AO})\}}{I_0(\lambda \cdot f_{AO} \cdot b) \cdot K_0(\lambda \cdot f_{AO}) - I_0(\lambda \cdot f_{AO}) \cdot K_0(\lambda \cdot f_{AO} \cdot b)} \quad (4.18)$$

where I_0 and K_0 are the modified Bessel functions of first and second kind respectively and as expected equation 4.18 has an implicit form.

Using the analytical algorithm proposed in section 4.2, the four step solution of the annular capillary system is obtained.

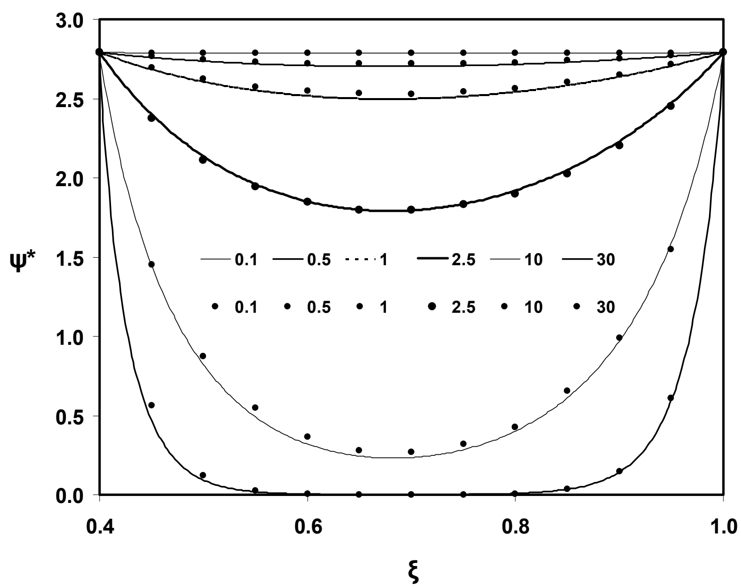

Figure 4.4 Dimensionless electrical potential profiles, in an annular geometry, for various values of the dimensionless inverse Debye length using the f_{AO} Correction Function

For comparison purposes, Figure 4.4 shows the numerical solution of the complete Poisson Boltzmann equation for the annular capillary system and the analytical algorithm presented above. Figure 4.4 demonstrates that the use of the Correction Function, f_{AO}, generates values close to the numerical solution of the complete original equation.

4.4 Summary of the Chapter

The need for more accurate predictions of the electrostatic potential has been addressed because of its importance in the study of electroosmosis. In the effort, a new alternative solution to the complete Poisson-Boltzmann equation has been developed. Although the new algorithm is meant to solve the electrokinetic problem, other environmental discipline, may benefit from it. In the achievement of these contributions, different aspects are analyzed and discussed through the chapter.

First, the lack of analytical methods for solving nonlinear differential equation is discussed. A description of cases of environmental interest is made. In addition, the modeling complexity of the electroremediation problem is enunciated in terms of the coupling of equations.

Second, this chapter introduces the most typical trend of representation of the free charge density equation. Three approaches are presented; these are the Debye-Hückel approximation, the three region approach and the polynomial representation. This last approach is presented as the basis of the proposed new algorithm.

Finally, this chapter presents the four step algorithm for the solution of nonlinear differential equations. The new approach introduces the Correction Function, f_{AO}, as the main mathematical tool to improve electrostatic potential predictions in a more realistic range of values.