

On the thermodynamic consistency of the symmetric Poisson-Boltzmann equation in primitive model electrolytes

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The study of electrolyte solutions poses several interesting features and challenges. Their study is important, not only theoretically but for practical reasons. Transport processes occur within the body as ionic exchanges in solutions. The measurement of chemical and thermodynamic properties of electrolyte solutions is important for the success of many industrial processes. These and other reasons have contributed to make the study of electrolyte solutions an active research area in physics and electrochemistry. Their study is complicated because we must consider several kinds of interactions when we try to describe their properties: solvent-solvent interactions, present in the study of pure liquids, plus the ion-solvent and ion-ion interactions that appear due to the presence of the dissociated ions.

The first attempts to find theories that worked for liquids tried to use existing theories of the gaseous phase, considering the differences in density between the two states. As an example, let us take the equation for the pressure of a gas, which can be written as a power series about the number density,

$$\beta p = \rho + B_2(T) \rho^2 + B_3(T) \rho^3 + \dots \quad (1)$$

where p stands for pressure, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the temperature, and ρ is the number density. $B_i(T)$ are the virial coefficients; integral expressions that depend only on the temperature. The $B_i(T)$ take into consideration the interactions between the gas particles, grouping them as interactions between particle pairs, trios, etc. which, in theory, are more tractable than the original N -body problem of the system as a whole. The first term in the expansion gives us the ideal gas law, which is valid for real gases if conditions of high temperature and/or low densities are available and little or no interactions exist between the gas particles. When we try to use this equation for electrolytes, the integrals of the $B_i(T)$ do not

converge. This is because the interactions between particles do not allow us to divide them into small group interactions as before. In 1950, Mayer¹ was able to end the convergence problems of the virial expansion by rearranging the divergent terms in such a way that allowed convergence of the series. He proved there is a one-to-one correspondence between gas and liquid equations for dilute solutions and the applicability of the formalism of the former into the latter. This work established the basis of modern theories for electrolyte solutions.

The interactions among the various components of a solution are difficult to account for. One of the models used for electrolytes calls for taking the total potential energy $U_N(r)$ of our N-body system as pair-wise additive,

$$U_N(r_1, \dots, r_N) = \sum_{s,t} u_{st}(r) \quad (2)$$

where

$$u_{st}(r) = \frac{e_s e_t}{\epsilon r} + u^{HS}(r) \quad (3)$$

$u^{HS}(r)$ is the hard sphere potential. When we assume that our system is made up of hard spheres with the charges of each ion at their centers and that these spheres are immersed in a continuum dielectric, this model is referred to as the primitive model (PM) of electrolytes. When all the ions have equal sizes the model is known as the restricted primitive model (RPM).

The information on the structure of single electrolytes with ions of species i and j can be given by the radial distribution function (RDF), $g_{st}(r)$, between two ions of species s and t respectively. The RDF is written as a Boltzmann factor, $\exp[-\beta W_N(s;t)]$, where $W_N(s;t)$ is the potential of mean force for an ion of type t due to a set of N ions with a central ion of type s . As we approach conditions of infinite dilution, $W_N \rightarrow U_N$. When this condition is met, all the thermodynamic quantities can be obtained in terms of $g_{st}(r)$, at least theoretically². Experimental $g_{st}(r)$ can be obtained, allowing us to check our theoretical results.

Several theoretical models have been presented to study the physical properties of dilute electrolyte solutions. The oldest approach used in these studies is the Poisson-Boltzmann (PB) theory. Its goal is to find an expression for the mean electrostatic potential ψ_r and, from there, the expressions for the desired thermodynamic quantities. The general expression for the PB equation can be found by using Poisson's equation for a reference ion of type s ,

$$\nabla^2 \psi_s(r) = - \frac{4\pi}{\epsilon} q_s(r), \quad r > a_{st}, \quad s,t = (i,j) \quad (4)$$

ϵ is the dielectric constant of the solution, a_{st} is distance of closest approach for ions of different type, and $q_s(r)$ is the charge density present at a distance r from the central ion s , represented by

$$q_s(r) = \sum_t \rho_t e_t g_{st}(r) \quad (5)$$

e_t and ρ_t are the charge and mean number density of ions of type t , and $g_{st}(r)$ is the RDF of s,t ions. The ion of type s is centered at $r=0$. When we write the general expression for the RDF in Eq.(5), and substitute it in Eq.(4) we get

$$\nabla^2 \psi_s(r) = - \frac{4\pi}{\epsilon} \sum_t \rho_t e_t \exp[-\beta W_N(s,t)], \quad r > a_{st} \quad (6)$$

Taking the potential of mean force $W_N(s;t)$ equal to the mean electrostatic potential energy, $e_t \psi_s(r)$, we get the Poisson-Boltzmann equation,

$$\nabla^2 \psi_s(r) = - \frac{4\pi}{\epsilon} \sum_t \rho_t e_t \exp[-\beta e_t \psi_s(r)], \quad r > a_{st} \quad (7)$$

Debye and Huckel² proposed this approximation as a first step taken to solve Eq.(4). They would then linearize the exponent of Eq.(7), keeping terms up to first order in $\psi_s(r)$. The resulting equation can be regrouped,

$$\begin{aligned} \nabla^2 \psi_s(r) &= - \frac{4\pi}{\epsilon} \sum_t \rho_t e_t [1 - \beta e_t \psi_s(r)] \\ &= + \frac{4\pi}{\epsilon} \sum_t \rho_t e_t^2 \psi_s(r) \end{aligned} \quad (7a)$$

because the term $-\frac{4\pi}{\epsilon} \sum_t \rho_t e_t$ cancels due to the condition of electroneutrality. Defining $K^2 = \frac{4\pi}{\epsilon} \sum_t \rho_t e_t^2$ which is now known as the Debye-Huckel screening length, we get an equation that can be easily solved using traditional techniques for second order differential equations,

$$\nabla^2 \psi_s(r) = K^2 \psi_s(r) \quad (8)$$

The linearization of Eq.(7) is performed to correct an inconsistency of the PB $g_{st}(r)$: when the ions have different valences and/or ionic radii, $g_{st}(r) \neq g_{ts}(r)$. This restricts the usefulness of the model to study unequal ion sized systems.

With the introduction of integral equation methods to study electrolyte solutions, the PB equation was set aside. These methods gave a more detailed view of the ionic distribution around reference ions. There are still

good reasons to work with the PB theory: it is relatively simple to solve numerically, and it gives a useful first description of the structure and thermodynamics of RPM systems of univalent ions. Christopher Outhwaite^{3,4} has proposed a solution method which drops the need of the linearization process by using a symmetric $g_{st}(r)$

$$g_{st}(r) = \theta(r-a_{st}) \exp\left[\left(\frac{-\beta}{2}\right) (\epsilon_s \psi_t(r) + \epsilon_t \psi_s(r))\right] \quad (9)$$

where $\theta(r-a_{st})$ is the Heaviside (unit step) function. Substituting Eq.(9) in Poisson's equation (Eq.(4)), we obtain an expression that will depend on the central ion and the region where we are testing it. This corrects the inconsistency of the $g_{st}(r)$ and allows us to work in the bulk solution of dilute electrolytes.

In my master's thesis, I worked with my advisor, Dr. Lutful B. Bhuiyan, in a study of the PB equation using a symmetric expression of the RDF. We calculated the values of the osmotic coefficients and mean activity coefficients for dilute electrolyte solutions. The ions studied had different radii and electric valences. The thermodynamic properties already mentioned were calculated through three different methods: virial, compressibility, and energy. The virial approach uses the virial expansion available for dilute solutions. The "compressibility" route takes its name from the use of the compressibility equation of state² to calculate the pressure of the system; and the "energy" route's name comes from the use of the internal energy of the system to calculate the Helmholtz free energy and, through it, the pressure. The results obtained from these three routes would be consistent only if the RDF is exact; any inconsistencies found will be a measure of the inaccuracy in the predicted $g_{st}(r)$'s of the PB equation. Studies on thermodynamic consistency had been performed on several other theories, but Outhwaite had recently mentioned that it had not been done for the PB equation .

The thesis research had two main parts. First, we worked on the solution of the PB equation for a single electrolyte using Outhwaite's expression for a symmetric RDF. During the second part of the research we worked with the linearization of the PB equation using Outhwaite's expression for the RDF and comparing it with the known results of Debye and Huckel, and the nonlinear results. The resulting analytical expressions were evaluated using the method⁵ described for the first section. For the main work of the thesis, we found the expressions that described our ionic solution with the modified version of the PB equation. These were solved using a quasilinearization method after writing them in non-dimensional form. When we got the expressions for the $g_{st}(r)$ of the system, the equations for the virial, compressibility, and energy equations of the thermodynamic properties were

checked and compared for consistency. The ionic systems studied were of equal ionic sizes with electric valences of 1:1, 1:2, 1:3, and 2:2. For unequal ion sizes 2:1 and 3:1 systems were studied too. We found that, for RPM systems, the full thermodynamic consistency (virial, compressibility, and energy) is limited to 1:1 electrolytes at very dilute concentrations. The consistency between only the virial and compressibility routes can be traced for 1:1 systems to higher concentrations. Consistency between those two routes decreases for the other systems considered in the following order: 1:2, 1:3, and 2:2, where 2:2 had the worst consistency results. For PM systems, the consistency between virial and compressibility routes again is best for 1:1 systems, and decreases in the following order: 1:2/2:1, 1:3/3:1, and 2:2. The virial route shows the best agreement with integral equation results, the energy route was not consistent with the other two routes nor with other methods of calculation.

During the two years of our numerical research we received both encouragement and advice from Dr. C. Outhwaite through private communications. A paper was published by the three of us (Martinez, Bhuiyan, and Outhwaite) in the *Journal of the Chemical Society, Faraday Transactions II*⁶; (a publication of the Royal Society of Chemistry).

References

1. J. E. Mayer, *Journal of Chemical Physics*, 1950, 18, 1426.
2. D. A. McQuarrie, 1976. *Statistical Mechanics*, Harper & Row Publishers, New York.
3. C. W. Outhwaite, *Journal of Chemical Society, Faraday Transactions II*, 1987, 83, 949.
4. C. W. Outhwaite, *Chemical Physics Letters*, 1978, 53, 599.
5. M. M. Martinez, 1990. Master in Science Thesis, University of Puerto Rico, Rio Piedras Campus.
6. M. M. Martinez, L. B. Bhuiyan, and C. W. Outhwaite, *Journal of Chemical Society, Faraday Transactions II*, 1990, 20, 3383.