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**Osmotic coefficients and Activity coefficients of Primitive Model electrolyte solutions in the Symmetric and Modified Poisson-Boltzmann theories; A comparative study with Monte Carlo simulations.**

by

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Master of Science.

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## Dedication

To God, to my family, and extended family...

For keeping me sane through this process. My gratitude to all of them, and to my friends, the people that have prayed for this to become a reality.

## Abstract

Osmotic coefficients, individual and mean activity coefficients of primitive model electrolyte solutions are computed at different molar concentrations using the Symmetric Poisson Boltzmann and Modified Poisson Boltzmann theories. The theoretical results are compared with an extensive series of Monte Carlo simulation data obtained by Zareen Abbas, et al. (*J. Phys. Chem. B*, vol. 113, pp. 5905-5916 (2009)). This was achieved by adjusting the ion size parameters and the ion valences in the theories to match the corresponding Monte Carlo data. The agreement between Modified Poisson-Boltzmann predictions with the exact simulation results is almost quantitative for monovalent salts, while being semi-quantitative or better for higher and multivalent salts. The Symmetric Poisson Boltzmann results, on the other hand, are very good for monovalent systems but tend to deviate for higher valency systems. Some recent experimental values for activity coefficients of HCl solution (individual and mean activities) and NaCl solution (mean activity only) have also been compared with the Symmetric and Modified Poisson-Boltzmann theories, and with the Monte Carlo simulations. For HCl, the theories and the simulations reproduce well the experimental results for the mean activity coefficients but reproduce poorly the individual coefficients. For the NaCl solution, the experimental mean activity coefficient matches well with the theories and the simulations.

*“That Science which investigates the attractions and repulsions,  
the emissions of light, and explosions which are produced,  
not only by the friction of vitreous, resinous, and metallic surfaces,  
but by the heating, cooling, evaporation and  
mutual contact of a vast number of substances”*

Electricity: The London Encyclopedia, 1829.

## **Chapter 1**

### **Introduction**

Designing many of the important industrial chemical processes involving electrolytes, ionic solutions, requires an understanding of the thermodynamics of these systems. The same is true of relevant biological processes (see for example, references [1] [2] [3] [4] [5]). Two of the more important properties of such Coulomb fluids, which describe the thermodynamics are the osmotic coefficient ( $\phi$ ) and the activity coefficient ( $\gamma$ ). These are experimentally measurable quantities [2] and are widely used in physical chemistry to quantify the deviation of experimental measurements from theoretically predicted ideal cases. This is because osmotic pressure and vapor pressure tend to deviate from the ideal behavior predicted by the Ideal Gas law and Raoult's law [6], respectively. Without these coefficients, we would not have a way to quantify the degree of non-ideality of real solutions, and scientifically we would be back in the time when deviations from ideal behavior had no explanation. Now we know that these deviations occur because of the interactions between the solvent and the solute molecules.

Ion-ion or ion-surface charge interactions of electrolyte solutions in water are fundamental in physical chemistry, they are also important through biochemistry and biology [7]. These interactions relate to the activity of water and the individual activities of the ions in solution. Water is used in many industrial applications to produce ions. Water produces ions because of its solvating ability, due to the unique polar structure of water molecules. Electrolyte products including *Gatorade* and *Powerade* drinks greatly rely on the solvation of ions in water.

In what follows, we will describe briefly the principal concepts used in this thesis, viz., osmotic coefficient, activity coefficient, and electrolyte solutions. Since electrolytes are the main subject of our investigation, they deserve to be introduced first.

## **1.1 Electrolyte solutions**

Electrolyte solutions, also known as electrolytes, are *homogeneous mixtures* in the bulk that contain charged particles called ions. A good example is table salt (sodium chloride) dissolved in water. In this example, water and table salt are called the *solvent* and the *solute*, respectively. When the solute contained in a solution divides into *positive and negative ions* (a phenomenon called dissociation) so that the solution has a greater electrical conductivity than that of the pure solvent, then we have an electrolyte solution.

Examples of electrolytes are acids, like sulfuric acid ( $\text{H}_2\text{SO}_4$ ) used in some car batteries, and the hydrochloric acid (HCl) which we have in our stomachs to help us digest food. Glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in water is a solution, but not an electrolyte



solution because glucose molecules do not dissociate, hence the conductivity of the solution does not change appreciably.

Electrolytes have been rigorously studied from a scientific standpoint since the advent of electrical batteries during the 18<sup>th</sup> century. Before that time, “*the technical development of electricity consisted mainly of producing a static charge by friction*” [8]. Luigi Galvani (1737-1798) and Alessandro Volta (1745-1827) gave us a new understanding on how electric forces work and what electrolytes are. These two iconic figures were responsible for setting the stage for later physics of electricity.

Galvani studied the effects of the electromotive force produced in frog leg contractions when dissimilar metals were in contact with them. Volta invented the electrical battery, and he proved empirically that the frog legs were not the cause of the electric force and that the secret lies in the combinations of dissimilar metals like zinc and copper, and a moist conductor or electrolyte which didn't have to be animal tissue as Galvani had first suggested. See figure 1.1 for a summary of the discrepancy of ideas between these two scientists.

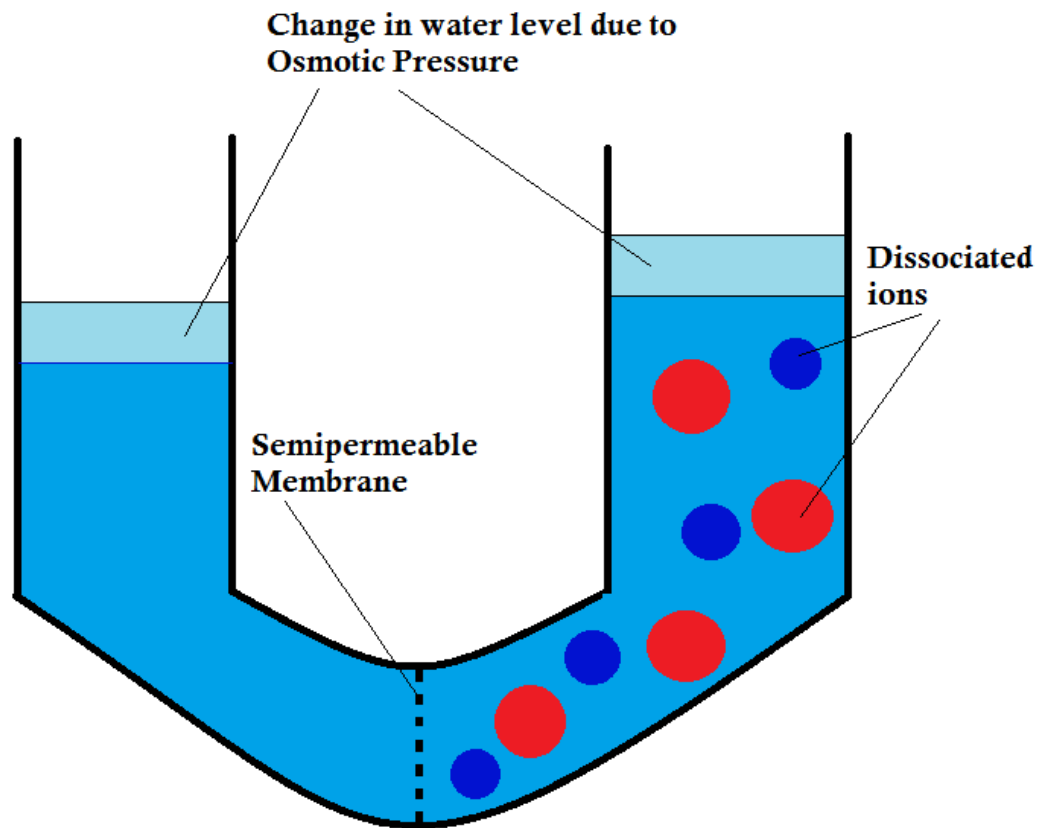


**Figure 1.1**

G. Gage and T. Marzullo, Artists, *Luigi Galvani vs Alessandro Volta*. [Art]. University of Michigan, Copyright © 2009-2017.

## 1.2 Osmotic Pressure and Osmotic Coefficient

Electrolytes in solution can manifest a natural process known as *osmosis*. This process occurs naturally when a *semipermeable membrane* -only solvent molecules can pass through the membrane- separates a solution in two parts, each with different solute *concentrations*. It is experimentally observed that the side with less concentration of solute loses solvent molecules through the membrane. Osmotic pressure is the measurable excess pressure that is needed on the greater concentration side to prevent the natural osmosis process through the membrane. See figure 1.2 for more detail.



**Figure 1.2:** Osmosis through a semipermeable membrane.

In biology, scientists take advantage of osmosis when they isolate the components of a cell since the outer membrane of a cell is semipermeable to water. When a cell is added to an aqueous solution with higher concentration of solute outside of the cell, water leaves the cell and it shrinks due to osmosis. Conversely, when the cell is placed in a solution with less concentration outside of the cell, water is transported into the cell and it expands, the cell may even burst if the concentration difference is large enough.

Osmotic pressure is also very important for the life of trees, which receive their necessary water intake using the membranes in their roots to get water from

the soil when it is wet enough. Indeed, values of osmotic pressure (20-25atm) for sugar molecules can be staggeringly high. The SI unit for pressure measurement is the Pascal [Pa] and it is defined as a force per unit area of 1N/m<sup>2</sup>. Another unit used is the atmosphere (atm.). For example, the osmotic pressure of a one molar (c = 1 mol/dm<sup>3</sup>) solution of sucrose is about 27 atm. at 25°C [2]. Denoting the osmotic pressure by the Greek letter  $\Pi$ , for a nonelectrolyte solution this is written as [9]

$$\Pi = \left(\frac{n}{V}\right) RT = MRT \quad (1.1)$$

In the case mentioned above, sucrose is dissolved in water at 1 mol/dm<sup>3</sup> concentration and at a temperature of 25°C (298.15 K) so that

$$\Pi = \left(1 \frac{\text{mol}}{\text{L}}\right) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (298\text{K}) = 24.5\text{atm}$$

For electrolytes, the concentration  $M$  is multiplied by the Van't Hoff factor  $i$  (number of dissociated ions per electrolyte molecule). Therefore; in electrolytes, the concentration  $M$  is replaced  $iM$ .

The first thermodynamic property that we present in our work is the osmotic coefficient “ $\varphi$ ”. This is a number, which quantifies the deviation of a solution’s osmotic pressure from *ideal* behavior as predicted by classical laws [10]. There are different ways to compute this number, depending on the system of units in use and the concentration scale. We will first present the formula for the molal osmotic coefficient, which in equilibrium conditions is defined as [2].

$$\varphi = \frac{-1000\Pi V_A}{vmW_{ART}} \quad (1.2)$$

The quantity represented with the Greek letter phi  $\varphi$  is the ‘molal’ osmotic coefficient, the variables in the right side of Eq. 1.2 are the osmotic pressure  $\Pi$ , the

partial molar volume of the solvent ( $\bar{V}_A$ ), the number of moles of ions formed from 1 mol of electrolyte ( $\nu$ ), the molality of the solution ( $m$ ), and the molecular weight of the solvent ( $W_A$ ), the 1000 is to convert  $W_A$  to kg/mole (SI).

According to Robinson and Stokes [2] the rational osmotic coefficient, ‘g’, is defined by the following relation (in terms of the activity  $a_A$ )

$$\begin{aligned} \ln a_A &= -g \ln \left( 1 + \frac{\nu m W_A}{1000} \right) \\ &= -g \left[ \frac{\nu m W_A}{1000} - \frac{1}{2} \left( \frac{\nu m W_A}{1000} \right)^2 + \dots \right] \end{aligned} \quad (1.3)$$

The molal osmotic coefficient in Eq. 1.2, is clearly the first term of the rational osmotic coefficient.

The practical osmotic coefficient or simply the osmotic coefficient, is the ratio of measured osmotic pressure and ideal pressure, analogous with the compressibility of real gases [10]. This means

$$\varphi = P_{measured}/P_{ideal} \quad (1.4)$$

where  $P_{measured}$  is the measured (or calculated) osmotic pressure and  $P_{ideal}$  is the ideal pressure. Essentially, most theoretical calculations give us the Virial Osmotic Coefficient in molar scale, while experimental results are given in molal scale.

### 1.3. Activity and Activity Coefficient

Activity is a mathematical concept related primarily to the vapor pressure lowering of the components of a solution [9]. Vapor pressure is a colligative property. The word colligative means: *Relating to the binding together of molecules*. Freezing point, boiling point, and osmotic pressure are all examples of colligative properties.

To grasp the concept of activity and the related activity coefficient we need to understand the behaviors of ideal and non-ideal solutions regarding experimental vapor pressure measurements.

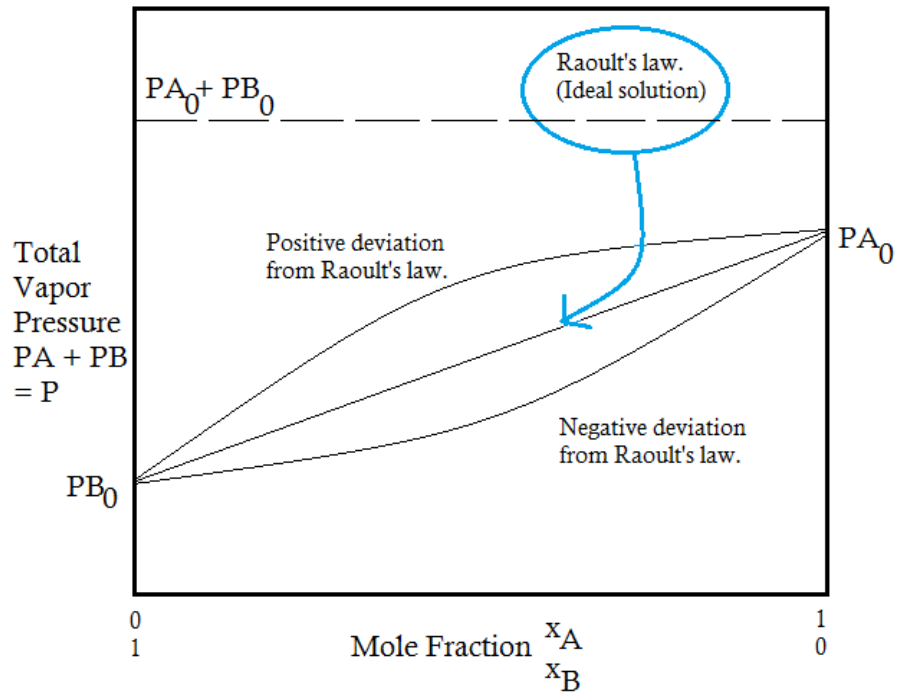
An ideal solution is one in which any of two (2) laws can be observed [6]

**Raoult's Law:** The vapor pressure of a solvent in solution is proportional to its mole fraction. (for liquid solutions)

$$P_i = x_i^l P_i^*, \quad (1.5)$$

where  $P_i$  is the partial vapor pressure of substance  $i$  in solution at temperature  $T$ ,  $x_i^l$  is the mole fraction of substance  $i$  in the ideal solution, and  $P_i^*$  is the vapor pressure of pure liquid  $i$  at the same temperature.

**Henry's Law:** The partial pressure of a gas is proportional to its mole fraction (for gases or gas solutions)



**Figure 1.3:** Vapor pressure vs mole fraction of components A and B.

Deviations from this ideal behavior are due mainly to the intermolecular forces between different types of molecules [6]. In a pure substance all the forces between them (random motion and electric repulsions and attractions) are of the same nature, causing a vapor pressure dependent on these forces. But in solution, the forces between dissimilar molecules can be stronger (negative deviation) or weaker (positive deviation) than the forces between similar molecules [9]. This is what causes the deviation from Raoult's law, we call it non-ideal behavior of real solutions.

There are two important mathematical definitions that will be crucial for understanding of our results, the activity of the solvent A, and the activity of dissociated solute B.

Activity of solvent "A" is defined [2]

$$a_A = \frac{p_A}{p_A^0} \quad (1.6)$$

Mathematically given by the ratio between the partial vapor pressure " $p_A$ " of a given quantity (mass) of solution, in equilibrium with its vapor in solution, and the vapor pressure  $p_A^0$  of the same quantity (mass) of pure solvent in equilibrium with its vapor. Both quantities must be measured at the same temperature and pressure.

The activity of a dissociated electrolyte solute (B) is given by the definition [2]

$$a_B = a_1^{v_1} a_2^{v_2} \quad (1.7)$$

Here,  $a_1$  and  $a_2$  are the individual ionic activities,  $v_1$  is the quantity of moles of ion 1 per 1 mole of dissociated electrolyte, similarly  $v_2$  for ion 2. In this thesis we will be focusing on the latter definition.

In the literature activity can be found in three different units of concentration: molal (m), molar (c) and molar fraction ( $x_i$ ) scales. Again, theoretical results are usually presented in the molar scale – the convention that we will adopt here, whereas it is convenient to present experimental results in the molal scale. However, transforming results from the molal scale to the molar scale is easily accomplished through the following relation where  $\rho_0$  is the density of the solution (see for example, reference [11]).

$$\gamma_{\pm} = \frac{m}{c} \rho_0 \gamma_{\pm}$$

The activity is related to the chemical potential “ $\mu$ ” by the relation

$$\ln(a_i) = \frac{\mu_i - \mu_i^0}{RT}, \quad (1.8)$$

where the subscript denotes species ‘i’ and the superscript refers to the ideal state.

The chemical potential  $\mu_i$  has the thermodynamic definition

$$\mu_i = \frac{\partial G}{\partial n_i}, \quad (1.9)$$

Where G is the Gibbs free energy  $G = H - TS$ , H being the enthalpy, T is the absolute temperature, and S the entropy. The variable  $n_i$  is the number of moles of substance  $i$ . The terms on the exponential in the right-hand side  $\mu_i^{id} - \mu_i^0$  and  $\mu_i - \mu_i^0$  are the ideal and non-ideal chemical potential differences respectively. Eq. 1.11 and 1.12 are not crucial for the purposes of this work, they merely illustrate the relation of chemical *potential* with activity.

Another quantity that we will be referring to in this work is the mean activity coefficient  $\gamma_{\pm}$  in the molar scale, which is obtained from the mole fraction scale  $f_i$  activity coefficient [12].



$$RT\ln(f_i) = \frac{N_A(z_i e_0)^2}{2\epsilon_0 \epsilon_{r,A} \kappa^{-1}}, \quad \kappa^2 = \frac{1}{\epsilon_0 \epsilon_{r,A} k_B T} \sum_i n_i^0 z_i^2 e_0^2, \quad (1.10)$$

where  $n_i^0$  is the mean number density of ion species  $i$  per unit volume, and we get the mole fraction scale coefficient  $f_i$ . The osmotic and activity coefficients are connected through the Gibbs-Duhem (GD) equation of thermodynamics. For a simple, two-component (single) electrolyte the GD equation reads [13]

$$\ln y_{\pm} = \varphi - 1 + \int_0^c (\varphi - 1) \frac{dc'}{c'}, \quad (1.10)$$

where  $c$  is the concentration of the electrolyte. Vlachy and coworkers [13] have recently generalized the GD equation for a multi-component electrolyte.

Theoretically the osmotic and activity coefficients are calculated using statistical mechanical theories of fluids. For electrolytes, liquid structure integral equations such as the hypernetted chain (HNC) and the mean spherical approximation (MSA) [14] [15] [16], and potential based approaches, viz., the symmetric Poisson-Boltzmann (SPB) [17] and modified Poisson-Boltzmann (MPB) [18] theories have been useful. Parallel numerical simulations, for example, Monte Carlo (MC) simulations [19] have been valuable in theoretical development.

A few years ago, Abbas and her group [11] made extensive MC simulations for a series of symmetric (in ion size and valency) and asymmetric electrolytes and reported their osmotic and activity coefficient results. In this thesis we will obtain the corresponding SPB and MPB results for these systems and will compare the theoretical predictions against the MC data.

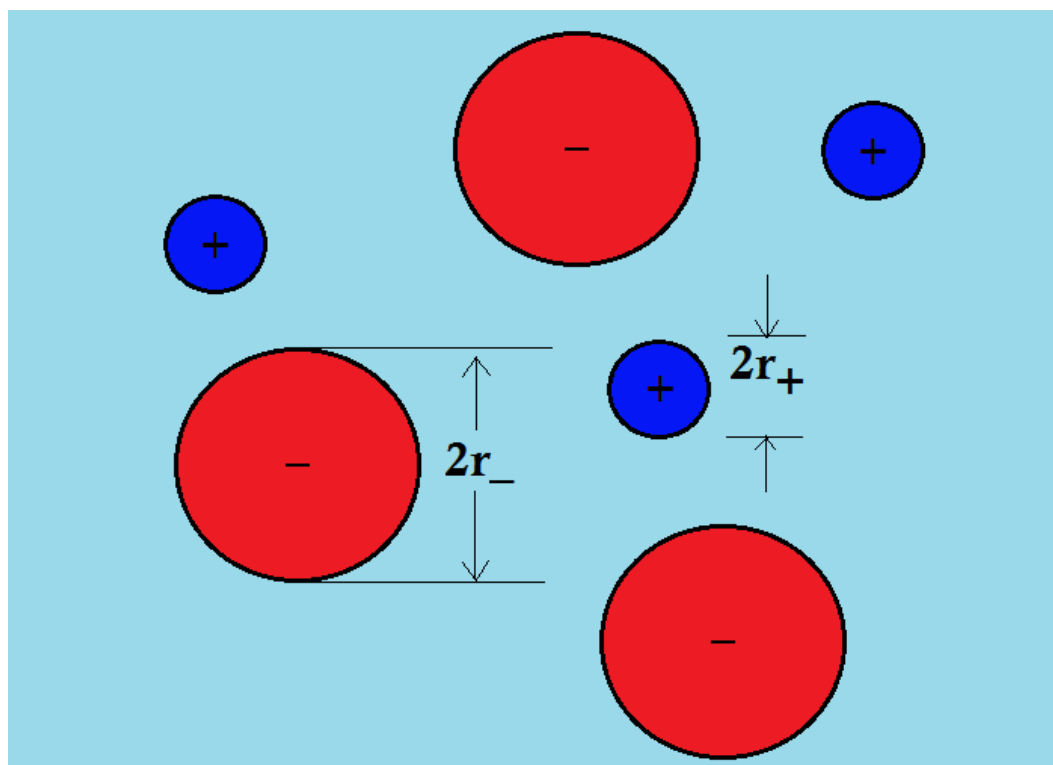
## Chapter 2

### Model and Methods

In this Chapter we will describe the model Hamiltonian used in all the calculations in this thesis. One of the widely used physical models in statistical mechanical theories and numerical simulations of charged fluids is the primitive model of electrolytes. This is a simple yet non-trivial model that retains physics of electrostatic interactions among ions and a hard-core like repulsion between two ion cores that precludes overlap of ions.

#### 2.1 The Primitive Model

Simplified models treating water as a continuum are often used to solve the industrially important problems where the number of ions is large [7]. One such model is the **primitive model** (PM).



**FIGURE 2.1: PRIMITIVE MODEL OF ELECTROLYTE SOLUTION.** THE CHARGE OF THE IONS AND THE RADII ARE THE MAIN ADJUSTABLE PARAMETERS, THE MOLECULAR STRUCTURE OF WATER IS NOT TAKEN INTO ACCOUNT, WATER IS TREATED AS A DIELECTRIC CONTINUUM (SIMILAR TO VACUUM, WITH A DIFFERENT DIELECTRIC CONSTANT).

The model electrolyte used in this work is a single electrolyte, which in general, is composed of arbitrarily sized positive and negative ions with arbitrary valences. The interaction potential energy between an ion pair can be written as

$$U_{ij}(r) = \begin{cases} \infty & r < a_i + a_j \\ \frac{z_i z_j e^2}{4\pi\epsilon_0\epsilon_r r} & r > a_i + a_j \end{cases}, \quad (2.1)$$

where:  $a_s$  and  $Z_s$  are the radius and valency of ion species  $s$ ,  $e$  is the proton charge,  $r$  is the separation between the centers of ions  $i$  and  $j$ , and  $\epsilon_0$  the vacuum permittivity. The solvent is taken to be a dielectric continuum characterized by the relative permittivity or dielectric constant  $\epsilon_r$ . If the ions are of the same size, that is,  $a_i = a_j$ , then we have the **restricted primitive model** (RPM). A schematic diagram of the PM is given in Figure 2.1.

When positively and negatively charged species approach in solution, they can form ion pairs or hold water in between. The *effective* radii ( $r_i$  and  $r_j$ ) of the interacting shells are used in MC simulations. One such set of simulations was carried out by a team headed by Abbas [11]. They fixed the anion radius to the experimental crystallographic value and adjusted the cation radius in their algorithm so that the results for the properties are consistent with experimental values. [11].

**Note** that “effective” radii are not necessarily the crystallographic ionic radii of the salt. In solution, the ion radii are those which give with greatest consistency with the thermodynamic properties (activity and osmotic coefficients calculated with MC simulations) when compared with experimental values for that salt in the context of the primitive model.

## 2.2 Classical theory: Debye – Hückel

The most extensively used theory of electrolytes is the classical Debye – Hückel (DH) theory, which was proposed in 1923 principally to derive mathematical expressions for the ionic activity coefficients of electrolyte solutions, concepts that had been previously introduced by Lewis [20], viz., the natural logarithms of the individual activities  $\gamma^+$ ,  $\gamma^-$ , and the mean activity  $\gamma_{\pm}$ . In this section, we will discuss the physical assumptions and some results of the theory, including the DH limiting law, which is the reason osmotic coefficients and natural logarithm of activity coefficients are plotted against the square root of concentration.

In the DH theory an electrolyte solution is a collection of point ions. The solvent is interpreted as a structure-less medium with relative dielectric constant  $\epsilon_r = 78.30$  for water. Thus, in a medium like water, where the value of the dielectric constant is around 80 times greater than in vacuum or in air, the cation – anion interaction force is weaker and hence counterions are less strongly attracted, while co-ions are less strongly repelled. This significant decrease in force due to the dielectric constant of water is the classical explanation for the separation of ions in solution.

From these assumptions, and after a careful mathematical treatment of the Nonlinear Poisson-Boltzmann equation [12], Debye and Hückel imagined the electrolyte as a continuous charge distribution around a central ion, linearized the Poisson-Boltzmann equation (cf. the following sub-section) and obtained analytical

expressions for the activity coefficients at the limit where the concentration approaches zero (ideally dilute solution) [6]

Natural logarithms of cation and anion activity coefficients are given by

$$\ln(\gamma_+) = -\frac{z_+^2 C I_m^{1/2}}{1 + D a I_m^{1/2}} \quad (2.2a)$$

$$\ln(\gamma_-) = -\frac{z_-^2 C I_m^{1/2}}{1 + D a I_m^{1/2}} \quad (2.2b)$$

In the above equations C, D and  $I_m$  are defined as:

$$C \equiv (2\pi N_A \rho_A)^{\frac{1}{2}} \left( \frac{e^2}{4\pi \epsilon_0 \epsilon_r} \right), \quad D \equiv e \left( \frac{2N_A \rho_A}{\epsilon_0 \epsilon_r k_B T} \right)^{\frac{1}{2}}, \quad I_m = \frac{1}{2} \sum_i Z_i^2 m_i$$

where  $N_A = 6.022142 \times 10^{23}$  is the Avogadro's number,  $e = 1.6021765 \times 10^{-19}$  C is the magnitude of the charge of an electron,  $\rho_A$  is the density of the pure solvent (997.05 kg/m<sup>3</sup> for pure water at 25° (298K) and 1 atm [6]),  $k_B = 1.38065 \times 10^{-23}$  J/K is the Boltzmann constant, and T the temperature of the solvent in absolute scale. The term  $I_m = \frac{1}{2} \sum_i Z_i^2 m_i$  is known as the ionic strength in molal-scale. 'C' and 'D' are constants which depend on the physical properties of the solvent. For pure water at 25° (298K) the values of C and D are listed below.

$$C \equiv 1.1744 \left( \frac{\text{kg}}{\text{mol}} \right)^{\frac{1}{2}}$$

$$D = 3.285 \times 10^9 \left( \frac{\text{kg}}{\text{mol}} \right)^{\frac{1}{2}} \text{m}^{-1} = 0.3285 \left( \frac{\text{kg}}{\text{mol}} \right)^{\frac{1}{2}} \text{\AA}^{-1}$$

Using  $a$  in angstrom units ( $1 \text{\AA} = 10^{-10}$  m) we have the natural logarithm of the mean molal activity coefficient

$$\ln(\gamma_{\pm}) = -1.1744 Z_+ |Z_-| \frac{I_m^{1/2}}{1+0.329a[\text{\AA}]I_m^{1/2}} \quad (2.3)$$

To get Eq. 2.5 and 2.6 for molar activity coefficients we need to replace the molal ionic strength with the analog molar ionic strength:

$$I_c = \frac{1}{2} \sum_i Z_i^2 c_i \quad (2.4)$$

When concentration  $c_i$  approaches zero, we get the DH limiting law at very low molar concentrations.

$$\ln(\gamma_{\pm}) = -1.1744 Z_+ |Z_-| I_c^{1/2} \quad (2.5)$$

## 2.3 The Poisson Boltzmann and Symmetric Poisson-Boltzmann theories

The starting point in the development of potential based theories such as the DH, the Poisson-Boltzmann (PB), the symmetric Poisson-Boltzmann (SPB), and the modified Poisson-Boltzmann (MPB) is the basic Poisson equation, viz.,

$$\begin{aligned} \nabla^2 \Phi_i(r) &= -\frac{1}{\epsilon_0 \epsilon_r} Q_t \\ &= -\frac{e}{\epsilon_0 \epsilon_r} \sum_j Z_j n_j^0 g_{ij}(r), \end{aligned} \quad (2.6)$$

where  $\Phi_i$  is the mean electrostatic potential at a distance  $r$  from the central ion and  $Q_t = e \sum_j Z_j n_j^0 g_{ij}(r)$  is the total charge density at  $r$ ,  $g_{ij}$  is the pair-correlation or the radial distribution function.

The Boltzmann statistical distribution function is now used for the  $g_{ij}$

$$g_{ij}(r) = e^{-Z_j e \Phi_i / k_B T} \quad (2.7)$$

Essentially the equation tells us that the curvature of the potential is a decreasing exponential of the potential itself. After linearization of the exponent we can get the DH equation, whose solution is of the form

$$\Phi(r) = \text{constant} \frac{e^{-\kappa r}}{r}, \quad (2.8)$$

where

$$\kappa^2 = \frac{e^2}{\epsilon_0 \epsilon_r k_B T} \sum_i n_i^0 Z_i^2 \quad (2.9)$$

defines the Debye-Hückel constant.

As the Eq. (2.10) implies, both the DH and the PB are mean field approximations, that is, inter-ionic correlations are not considered [21]. Two other difficulties with the PB equation are: (1) the radial distribution function is not symmetric for ions of different size and/or valency. The Onsager condition for a bulk fluid, viz.,  $g_{ij}(r) = g_{ji}(r)$  is not satisfied. (2) the important hard-sphere effect is inadequately treated. To address the latter two points, Outhwaite and co-workers symmetrized the  $g_{ij}(r)$ , included an exclusion volume term and called it the symmetric Poisson-Boltzmann theory [22].

In the SPB the radial distribution function  $g_{ij}(\mathbf{r})$  between two ions  $i$  and  $j$  a distance  $r$  apart is given by:

$$g_{ij}(r) = g_{ij}^0(r) \exp\left\{-\frac{\beta}{2} [e_j(\Phi_i + \Phi_i^0) + e_i(\Phi_j + \Phi_j^0)]\right\} \quad (2.10)$$

where  $\Phi_i$  is the mean electrostatic potential around an ion  $i$  as before, and  $\Phi_i^0$  is the discharged potential when the charge on ion  $i$  is zero, and similarly for ion  $j$ . The quantity  $g_{ij}^0(r)$  is the exclusion volume term. The essential objective is to compute the  $g_{ij}$ 's. from these  $g_{ij}$ 's, all the other thermodynamic properties are obtained.

The *virial osmotic coefficient* -represented in our work by the Greek letter phi  $\varphi$ , is one of the thermodynamic quantities that we calculate, and is mathematically given by [23].

$$\varphi = 1 + \text{contact} + \beta E/3n \quad (2.11)$$

In the afore mentioned formula, “contact” involves the contact values of the  $g_{st}$ 's

$$\text{contact} = 2\pi/3n \sum_t \sum_s n_t^0 n_s^t g_{st}(a_{st}) a_{st} , \quad (2.12)$$

For our discussion, it will be sufficient to know that “contact” depends primarily on total solute concentration,  $n = \sum n_s^0$ , and on the sum of the contact values of all the radial distribution functions  $g_{st}(a_{st})$ .

The internal energy term is similarly given by [18]

$$E = \frac{1}{2} \sum_s Z_s e n_s [\Phi_s(a_{is}) - \frac{e_s}{4\pi\epsilon_0\epsilon_r a_{is}}] \quad (2.13)$$

Similarly, the mean and individual activity coefficients, are given by the following mathematical formulas [24]:

$$\ln\gamma_{\pm} = \frac{|Z_-|\ln(\gamma_+) + |Z_+|\ln(\gamma_-)}{|Z_+| + |Z_-|} \quad (2.14)$$

The individual activity coefficient calculation involves two quantities, namely: The hard sphere part, and the electronic part.

$$\ln\gamma_s = \ln\gamma_s^{HS} + \ln\gamma_s^{el} \quad (2.15)$$

where these two quantities are given by [22]



$$\ln\gamma_s^{HS} = \beta \sum_t n_t^0 \int_0^1 \int u_{st}^{HS}(r_{12}) g_{st}(r_{12}|\lambda) dr_2 d\lambda$$

$$\ln\gamma_s^{el} = \beta Z_s e \sum_t n_t^0 \int_0^1 \int \left( \frac{Z_t e}{4\pi\epsilon_0\epsilon_r r_{12}} \right) g_{st}(r_{12}|\lambda) dr_2 d\lambda$$

The integration variable  $\lambda$  is a charging parameter used in the Kirkwood charging process [18].

## 2.4 Modified Poisson Boltzmann theory

The modified Poisson Boltzmann theory is different from its SPB predecessor in that the pair radial distribution functions  $g_{ij}$  are adjusted to better approximate the ionic correlation, numerically speaking a term called the fluctuation potential is added to the mean electrostatic potential presented before. Thus the main difference between SPB and MPB comes from a new term called the fluctuation potential due to ionic correlation.

In the modified Poisson-Boltzmann theory, a new operator ‘L’ related to the fluctuation potential or ionic correlation, is introduced:

$$g_{ij}(r) = g_{ij}^0(r) \exp\left\{ \left( -\frac{\beta}{2} \right) (e_i [L_j(u_j) + L_j(u_j|e_j = 0)] + e_j [L_i(u_i) + L_i(u_i|e_i = 0)]) \right\} \quad (2.16)$$

Where  $u_i = r\Phi_i$  ;  $u_j = r\Phi_j$  and for  $a_i \leq a_j$

$$L_s(u) = \frac{u(r + A_s) + u(r - A_s) + k_B \int_{r-A_s}^{r+A_s} u(R) dR}{[2r(1 + k_B A_s)]} \quad (A_s = a_i + a_s) \quad (2.17)$$

## Chapter 3

### Results

The SPB and the MPB equations of the previous Chapter were solved numerically using a quasi-linearization iterative scheme [25]. This algorithm has been successfully utilized earlier by Outhwaite and co-workers in the implementation of these theories in bulk electrolytes and electric double layers (see for example, references [26] [27] for electrolyte in the bulk and reference [28] for electrolyte near a charged interface). The physical parameters of the electrolytes used in the numerical solutions are from experiments [2] and the MC simulations of Abbas et. al. [11]. Both the experiments and the simulations were carried out at room temperature 25<sup>0</sup> C. The relative permittivity of the solvent, that is water, in the simulations was taken to be  $\epsilon_r = 78.30$ .

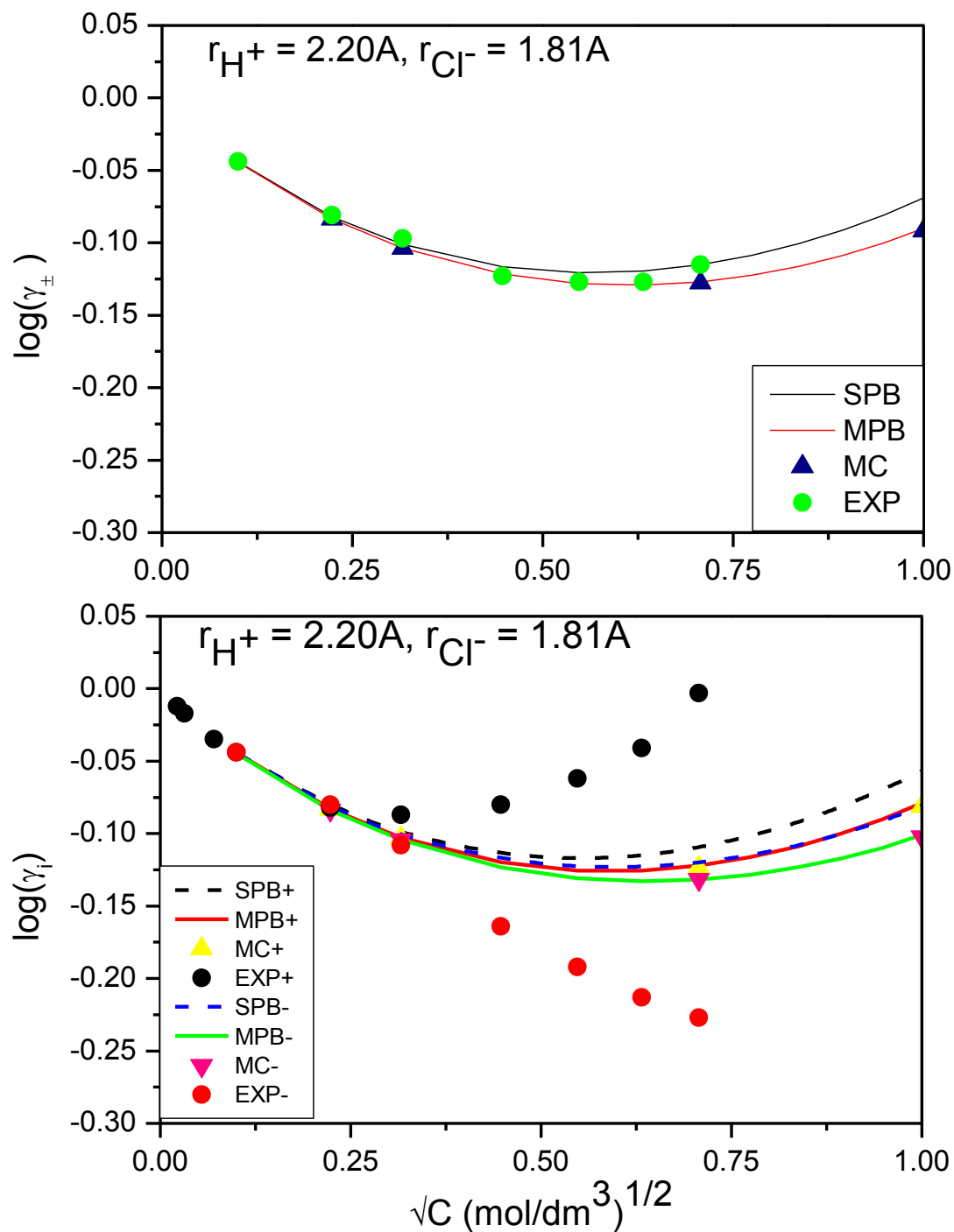
#### 3.1 Experimental

The experimental systems studied during our work were solutions of HCl and NaCl monovalent salts dissociated in water at several concentrations. Individual and mean activity coefficients have been previously measured for HCl by Sakaida and Kakiuchi [28]. Mean activity coefficients have been recorded for NaCl [2] [29] although we didn't find standard individual activity measurements in the literature for this solution system. In this Section, we will compare these experimental thermodynamic properties of HCl and NaCl solutions with the corresponding results from the SPB and MPB theories and the MC simulations.

### 3.1.1 HCl

Sakaida and Kakiuchi have measured the individual activity coefficients of HCl (and hence the mean activity coefficient) using a physical apparatus called an ionic liquid salt bridge (ILSB) [28]. The authors determined with good accuracy (95% confidence level), the activity coefficients of single ions  $H^+$  and  $Cl^-$  (25 °C). We used our SPB and MPB programs with fixed ion radii taken from the Abbas et. al. [11] simulation data and from Fraenkel's [29] theory and obtained results for the activity coefficients for HCl at different concentrations. The experimental and theoretical results for the individual and mean activity coefficients for this system at various concentrations are given below.

If we examine carefully Figure 1, we can see that the numerical difference between the values for the activity coefficients, obtained with SPB and MPB is practically zero for small concentrations up to about  $c \sim 0.07$  M. But there is a slight difference even at these small concentrations with respect to the experimental values of cation activity that can be attributed to approximation errors in the theory. SPB and MPB give the same results in the limit of low concentration and this is consistent with DH limiting law as previously discussed in chapter 2. However, as concentration increases, ionic correlation effects start to deviate MPB results from SPB. However, both the SPB and MPB results for the individual activity coefficients show significant deviation from the experimental results beyond  $c \sim 0.07$  M. Interestingly, the MC data for the individual activities also start deviating from the experiments starting around this concentration.



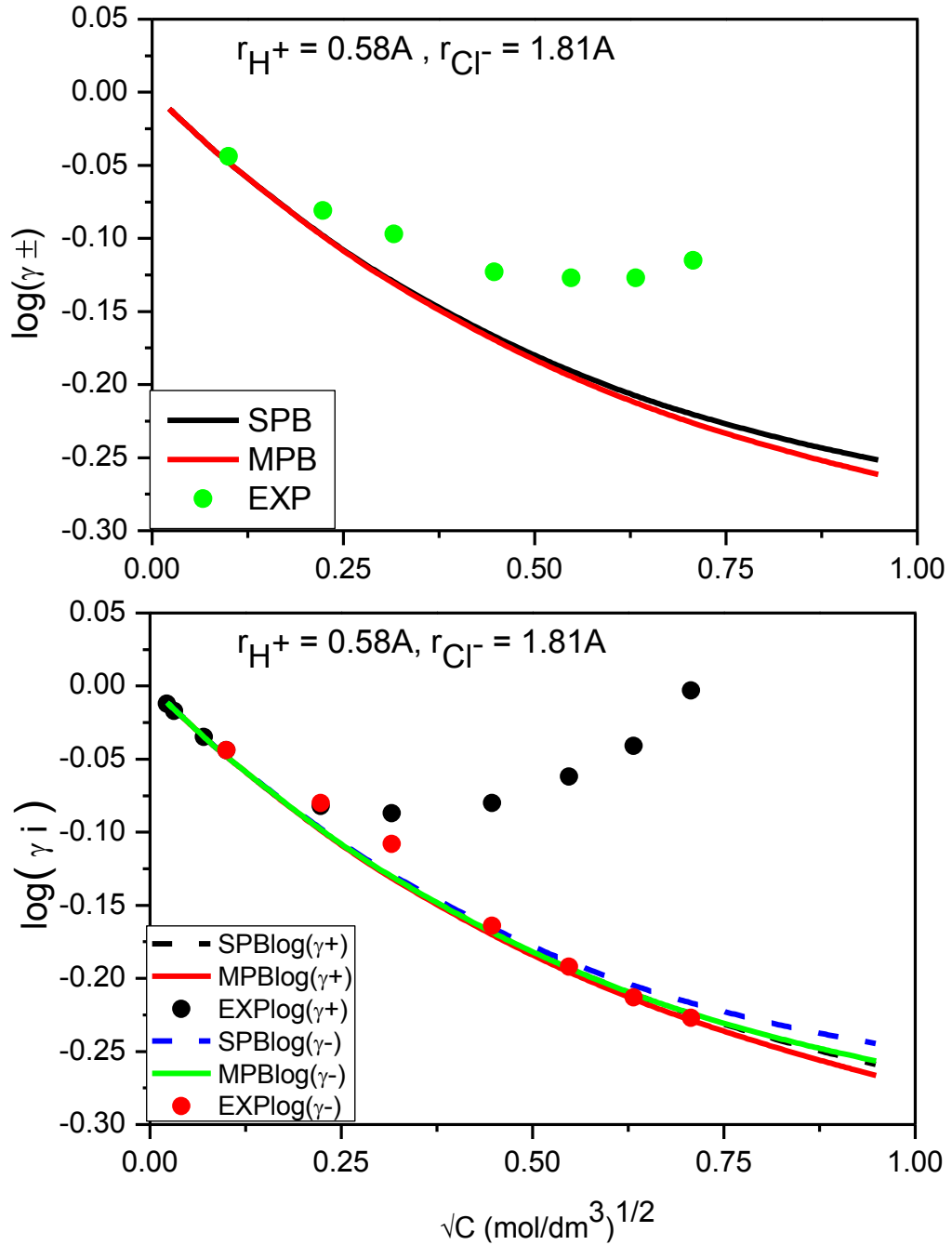
**Figure 3.1** Experimental, theoretical, and MC decadic logarithm of individual and mean activity coefficients of HCl solution at various concentrations. In the MC, SPB, and MPB calculations the ionic radii are  $r_{\text{H}^+} = 2.2 \text{ \AA}$ ,  $r_{\text{Cl}^-} = 1.81 \text{ \AA}$  and are taken from the MC simulation data of Abbas et. al. [11].

However, the experimental and MC mean activity coefficients are quite consistent throughout, which suggests some error cancellations for the MC! It is noted that for this range of concentration, the SPB and MPB results follow the simulations rather well. While the MPB difference is almost quantitative with the MC, the SPB shows deviations at higher concentrations, which can be attributed to the neglect of ionic correlations in the SPB. Such correlations become more significant for dense solutions.

The MC data are conventionally taken to be ‘*exact*’ for a given model. Thus these results suggest that the PM is probably not an adequate physical description of HCl at high concentrations. Fraenkel [30] took this idea further and developed the Smaller ion Shell (SiS) theory, which is not based on the PM but

conc. (mol/dm <sup>3</sup> )	Activity + log <sub>10</sub> (γ <sub>+</sub> )			Activity - log <sub>10</sub> (γ <sub>-</sub> )			Activity ± log <sub>10</sub> (γ <sub>±</sub> )		
	SPB	MPB	EXP	SPB	MPB	EXP	SPB	MPB	EXP
0.0005	-0.011	-0.011	-0.012	-0.011	-0.011		-0.011	-0.011	
0.0010	-0.016	-0.016	-0.017	-0.016	-0.016		-0.016	-0.016	
0.0050	-0.035	-0.035	-0.035	-0.035	-0.035		-0.035	-0.035	
0.0100	-0.049	-0.049	-0.044	-0.048	-0.049	-0.044	-0.049	-0.049	-0.044
0.0500	-0.100	-0.100	-0.082	-0.099	-0.099	-0.08	-0.099	-0.100	-0.081
0.1000	-0.132	-0.132	-0.087	-0.130	-0.131	-0.108	-0.131	-0.132	-0.097
0.2000	-0.169	-0.171	-0.08	-0.167	-0.169	-0.164	-0.168	-0.170	-0.123
0.3000	-0.193	-0.196	-0.062	-0.189	-0.193	-0.192	-0.191	-0.195	-0.127
0.4000	-0.211	-0.215	-0.041	-0.205	-0.211	-0.213	-0.208	-0.213	-0.127
0.5000	-0.225	-0.229	-0.003	-0.217	-0.224	-0.227	-0.221	-0.227	-0.115
0.7000	-0.245	-0.251		-0.234	-0.244		-0.239	-0.247	
0.9000	-0.259	-0.266		-0.244	-0.256		-0.252	-0.261	

**Table 3.1** Experimental and theoretical individual and mean activity coefficients of HCl solution at various concentrations. In the SPB and MPB calculations the ionic radii are  $r_{\text{Cl}^-} = 1.81 \text{ \AA}$  and  $r_{\text{H}^+} = 2.2 \text{ \AA}$ , values taken from the MC simulation data of Abbas et al. [11].



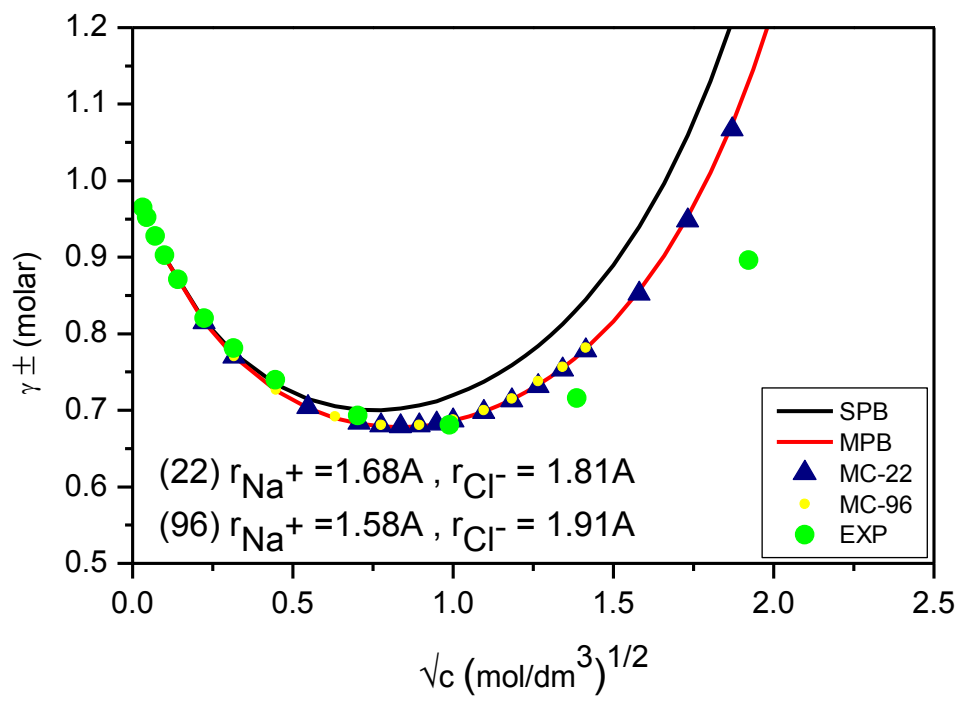
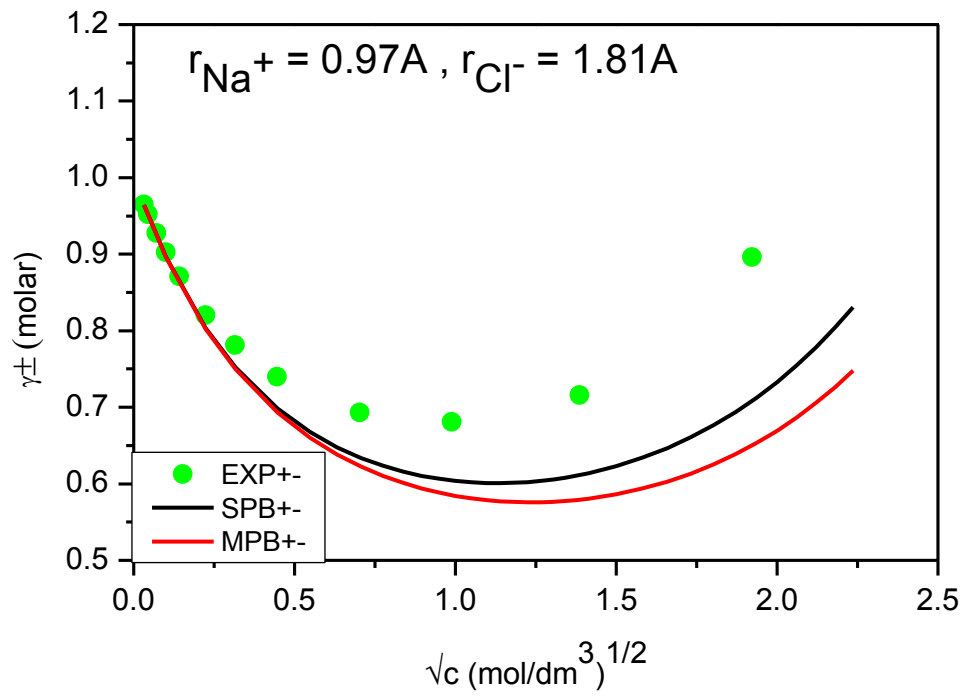
**Figure 3.2** Experimental and theoretical decadic logarithm of individual and mean activity coefficients of HCl solution at various concentrations. In the SPB and MPB calculations the ionic radii are  $r_{Cl^-} = 1.81 A$  and  $r_{H^+} = 0.58 A$ , values taken from the SiS theory of Fraenkel [30].

gives a better representation of the HCl experimental individual activity coefficients. Fraenkel's theory gives ionic radii to be  $r_{Cl^-} = 1.81A$  and  $r_{H^+} = 0.58A$ .

With these values of the ion sizes for the PM we have calculated the SPB and MPB activities and these are given in tabular form in Table 3.1 and in graphical form in Figure 3.2. Although MC data are not available at these ionic radii, from the consistency of the simulation data with the theories for all the 104 cases for which the MC data are available, it is a fair conjecture that the SPB and MPB curves in this figure will be very close to the ‘exact’ results for the model. Again, in general the theories show deviations from experiment. At these radii too, the shortcomings of the PM are clearly seen. The closeness of the theoretical and experimental activities for  $\text{Cl}^-$  seems fortuitous.

### 3.1.2 NaCl

We have plotted the SPB and MPB results for three sets of ionic parameters:  $r_{\text{Na}^+} = 0.97 \text{ \AA}$ ,  $r_{\text{Cl}^-} = 1.81 \text{ \AA}$  [29],  $r_{\text{Na}^+} = 1.68 \text{ \AA}$ ,  $r_{\text{Cl}^-} = 1.81 \text{ \AA}$ , and  $r_{\text{Na}^+} = 1.58 \text{ \AA}$ ,  $r_{\text{Cl}^-} = 1.91 \text{ \AA}$ , [11]. We do not consider individual activities of NaCl as we have found no individual activity coefficient data for NaCl. The experimental values of the mean activity coefficients are from the standard text by Robinson and Stokes [2], where they are given directly as  $\gamma_{\pm}$  in molar units. We have followed the same convention here. The results are shown in the two figures below. At the Fraenkel ion-size parameters the theoretical activities are qualitative with the experiment. However, in the bottom panel of Figure 3.3, the SPB and MPB theories are in good agreement with the MC data.



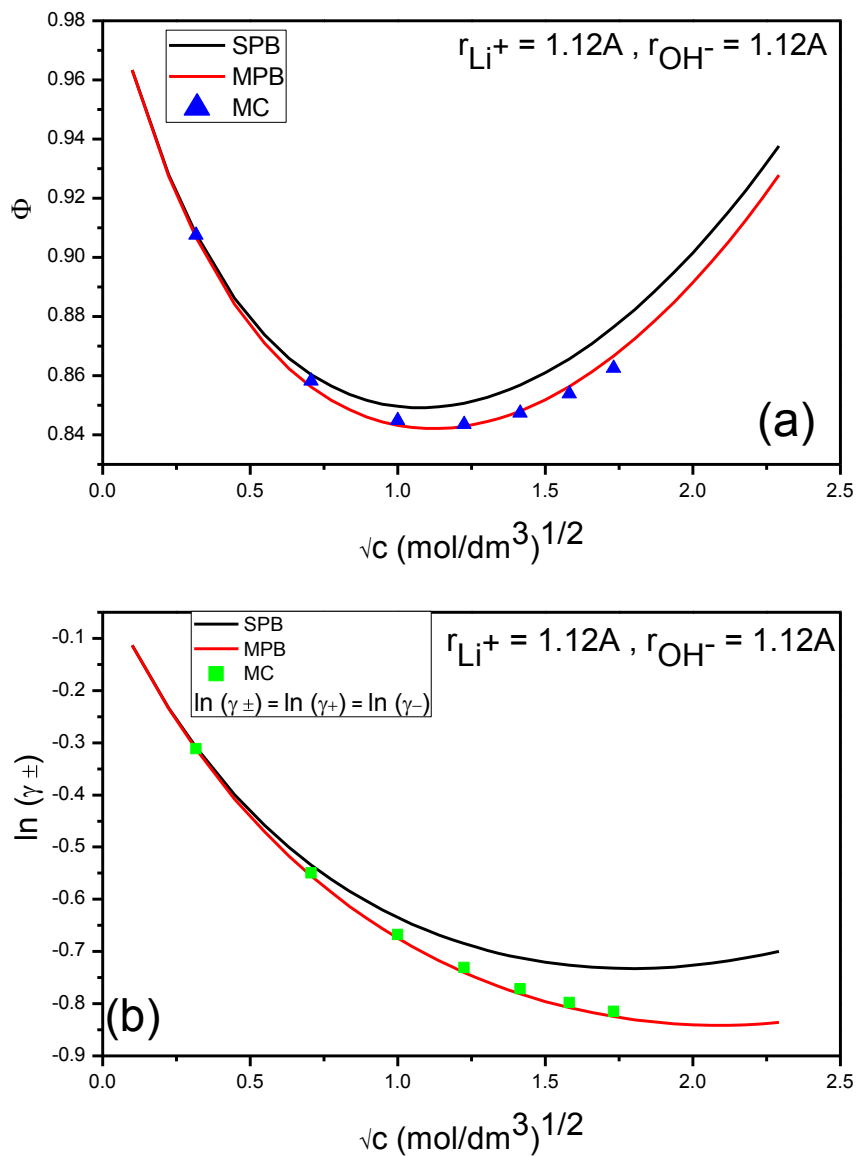
**Figure 3.3** Experimental and theoretical mean activity coefficients of NaCl solution at various concentrations and different sets of ionic radii. The ionic radii are given in the two sub-figures.



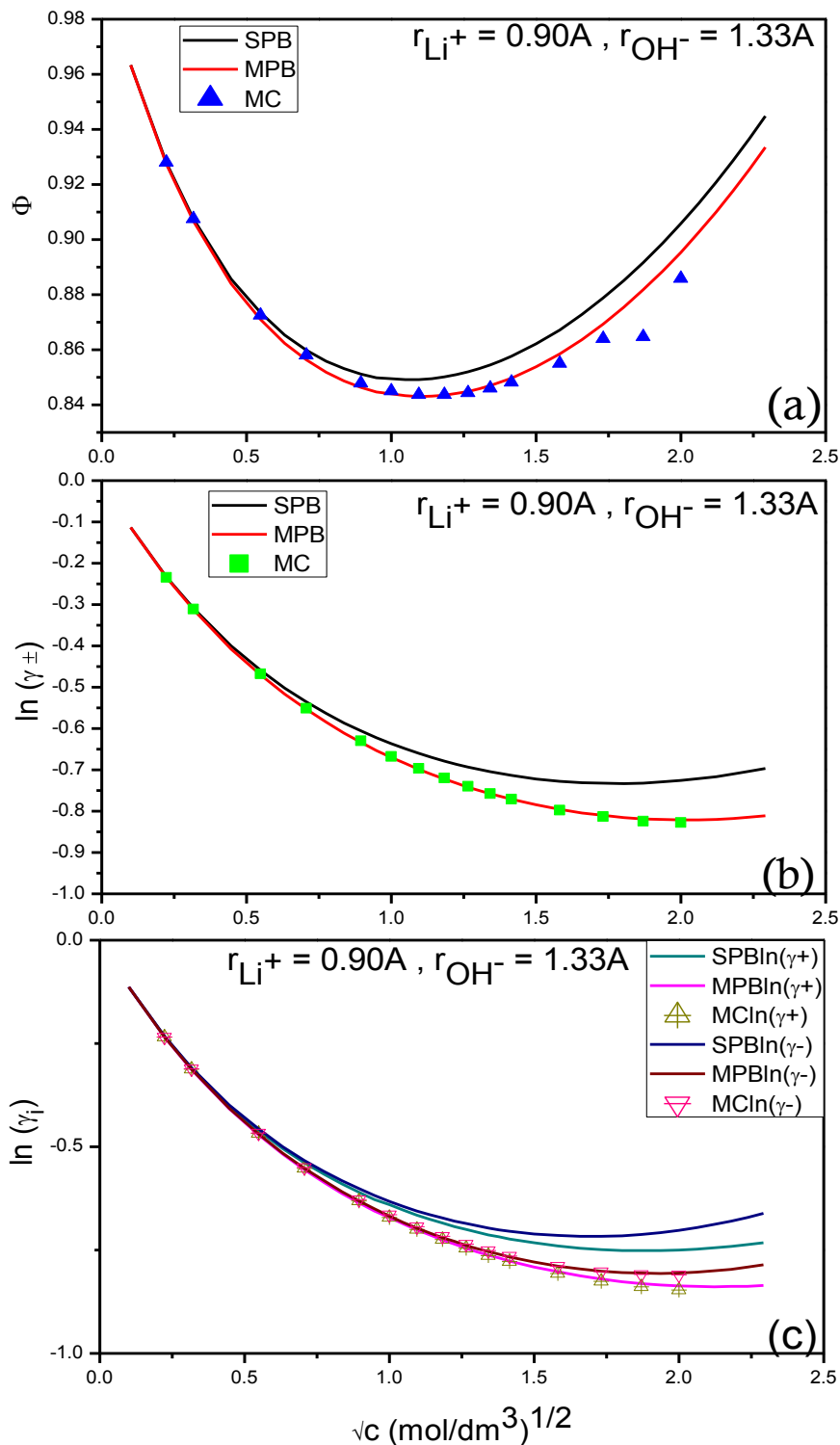
### 3.2 MC Simulation vs SPB and MPB theories

The scope of the present section is to compare thermodynamics of electrolyte solutions obtained through the SPB and MPB theories with the MC simulation data of Abbas et al. [11] for the same systems in the PM framework. These authors computed osmotic coefficients, individual and mean activity coefficients of a total of 104 salt solutions and found optimized values for the cation and anion radii using their MC programs. We took the optimized radii from their work and used them in the SPB and MPB programs. The simulated systems cover a wide range of concentrations, ionic sizes, and valency combinations of 1:1, 2:1, and 3:1. These results, all 104 of them, are presented in the Appendix.

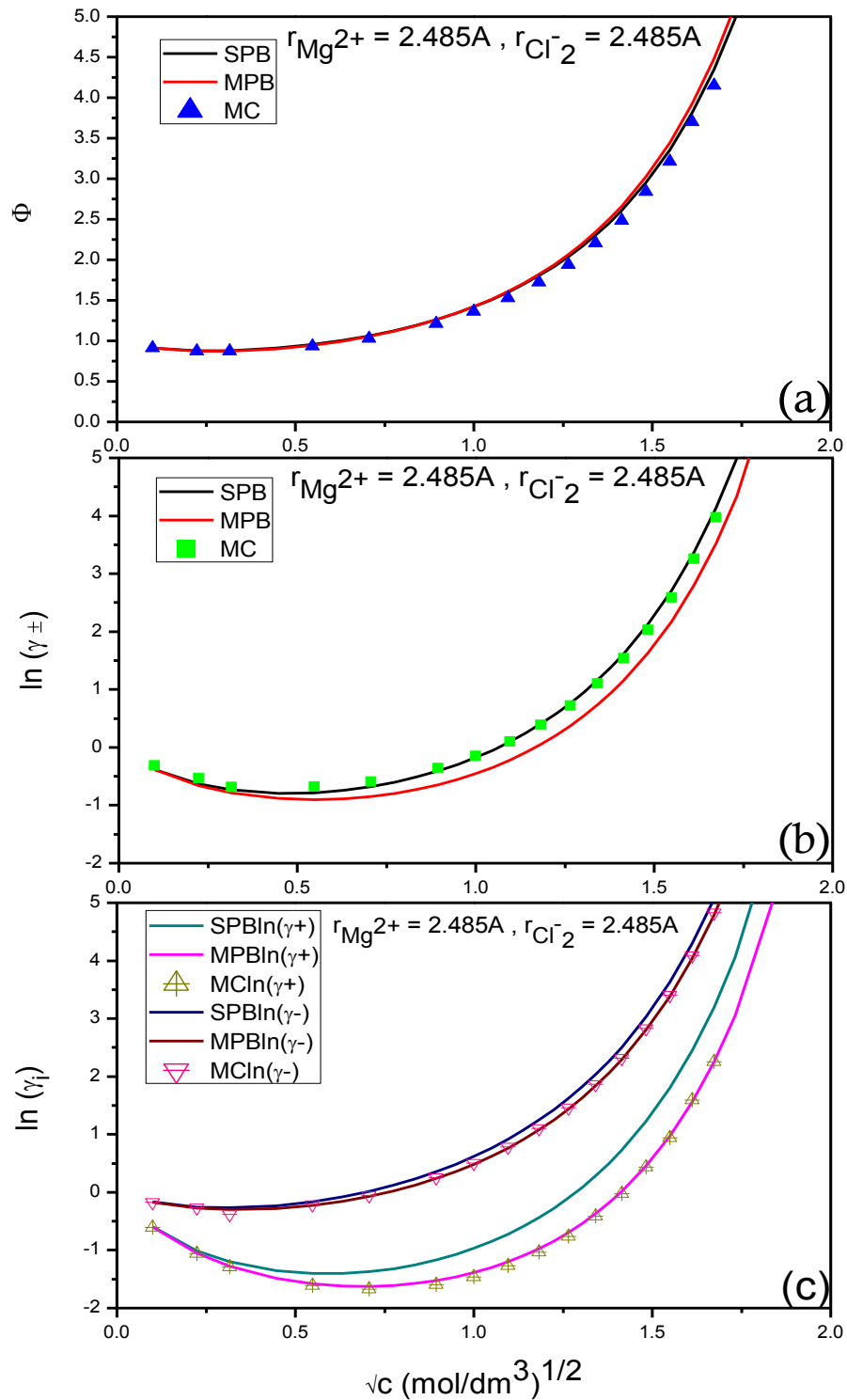
We will present here, a sampling of the results for 1:1, 2:1, and 3:1 valence systems, which will involve both the RPM and PM. For the 1:1 case we have chosen the LiOH for which MC results are available for both RPM (Figure 3.4) and PM (Figure 3.5). LiOH is a widely used salt in rechargeable batteries and hence the importance of its thermodynamic properties. Another factor behind this choice is the fact that a comparison of the RPM and PM results is possible. For the 2:1 case we have chosen MgCl<sub>2</sub>, (RPM Figure 3.6 and PM Figure 3.7), and AlCl<sub>3</sub> system was chosen for the 3:1 case (RPM Figure 3.8) and PM Figure 3.9). In the graphs, the most conspicuous general feature is the consistent overall agreement between the theories and the MC results for almost all concentrations. This is one of the main findings in our investigation. All the other  $104 - 6 = 98$  cases not shown here, reveal the same patterns as the ones presented here.



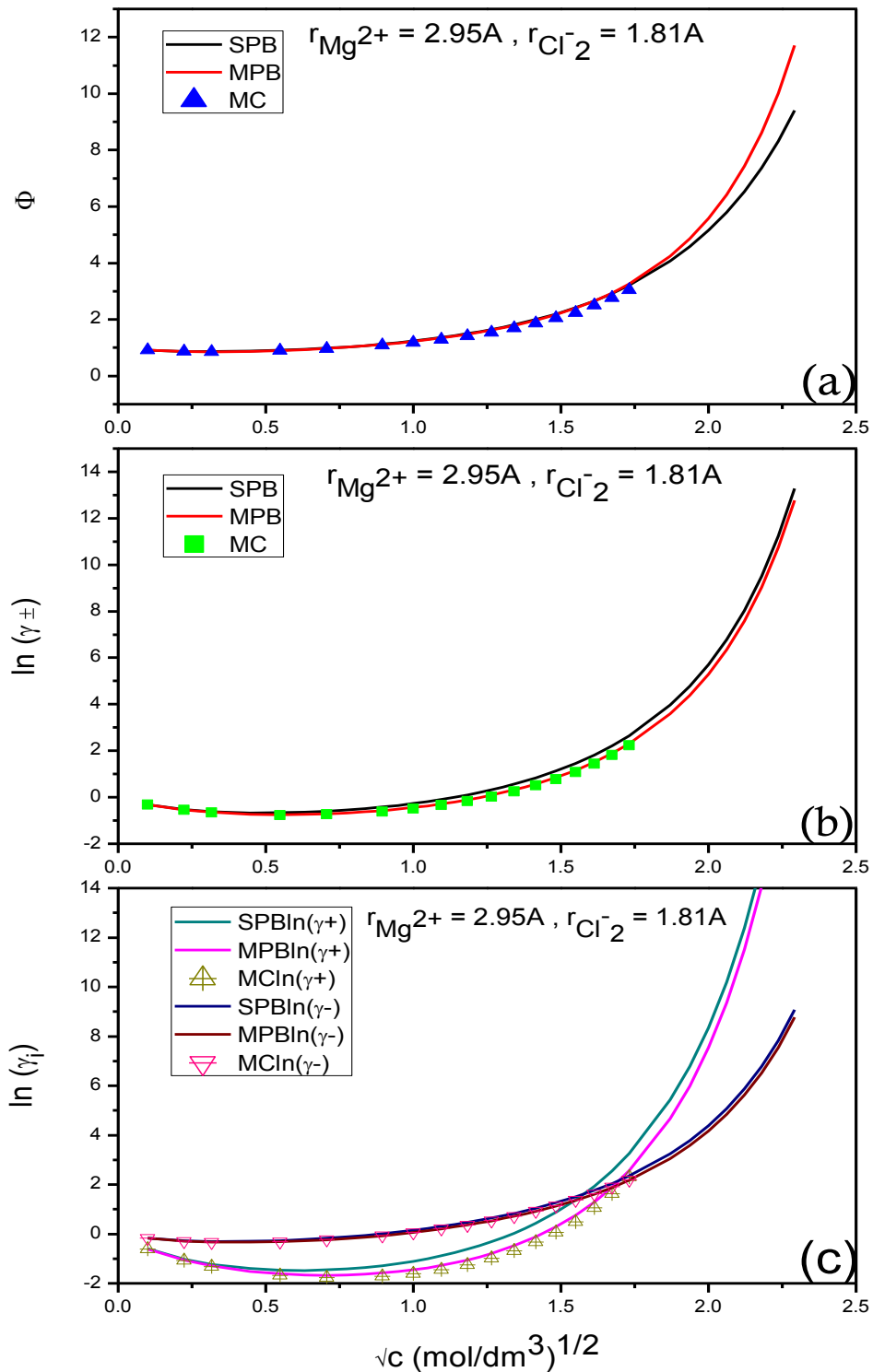
**Figure 3.4** Monte Carlo, symmetric Poisson-Boltzmann, and modified Poisson-Boltzmann osmotic coefficient (sub-figure (a)), and natural logarithm of the activity coefficients (sub-figure (b)) for LiOH using RPM.



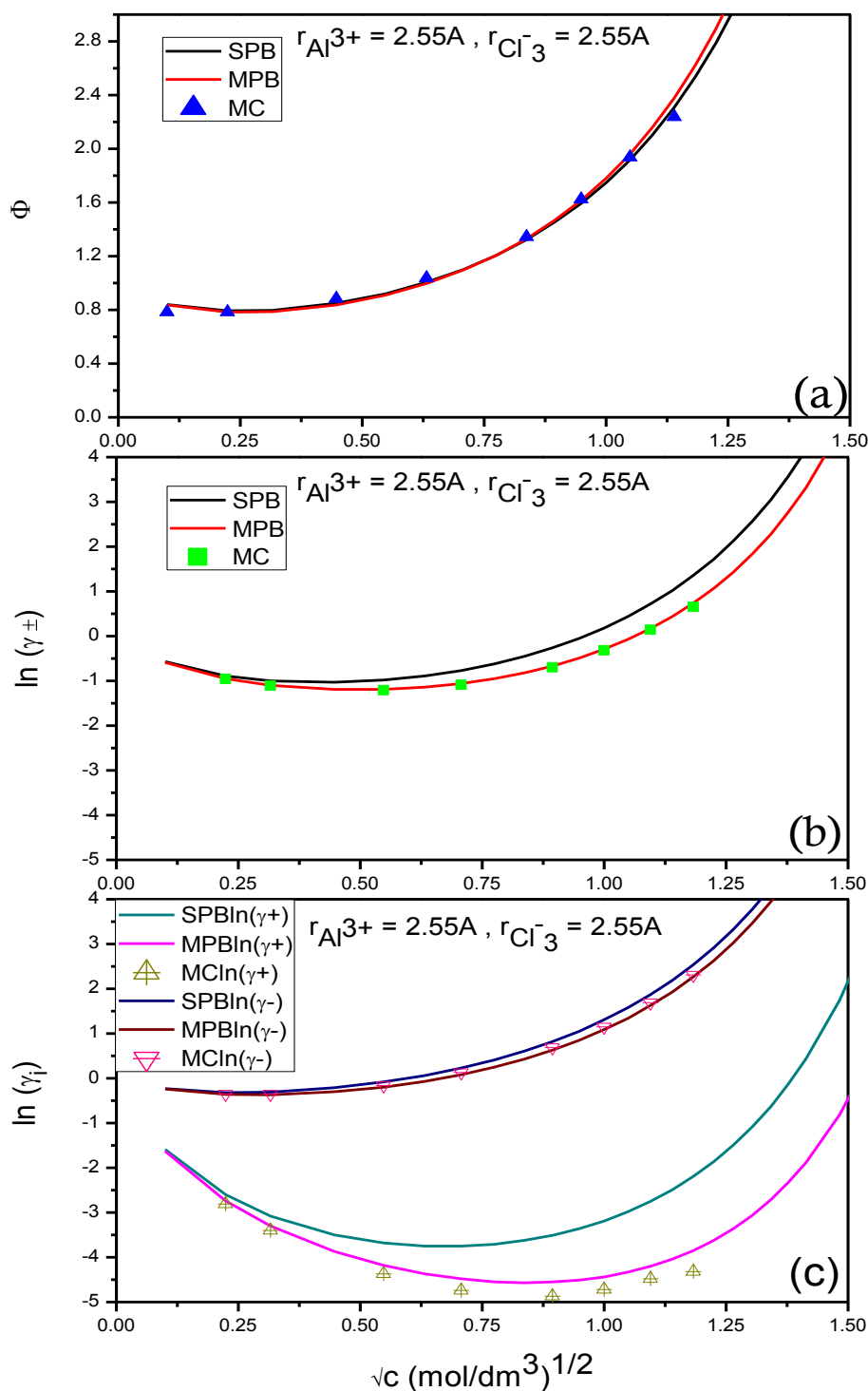
**Figure 3.5** Monte Carlo, symmetric Poisson-Boltzmann, and modified Poisson-Boltzmann osmotic coefficient (sub-figure (a)), natural logarithm of the mean activity coefficient (sub-figure (b)), and natural logarithm of the individual activity coefficients for LiOH using PM (sub-figure (c)).



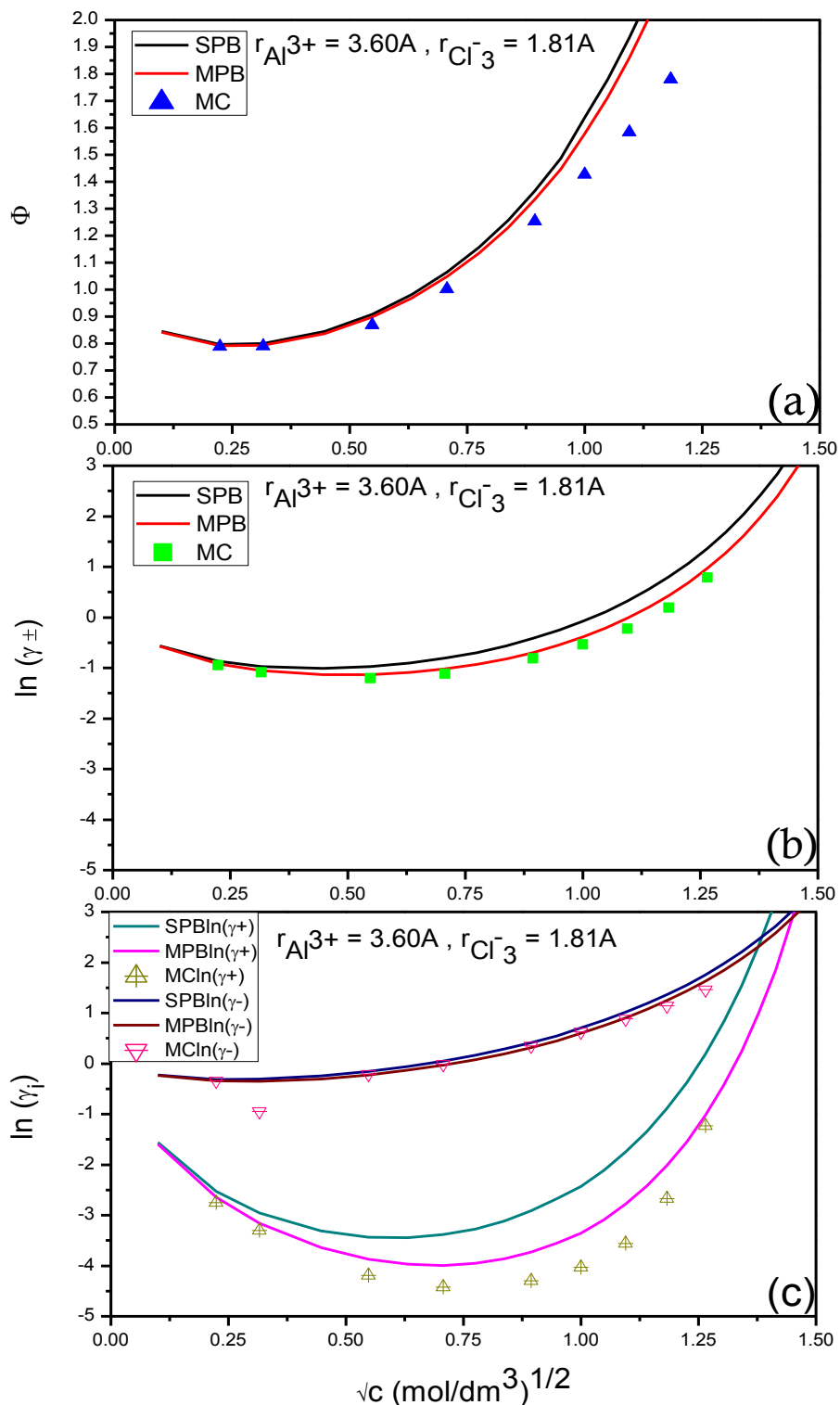
**Figure 3.6** Monte Carlo, symmetric Poisson-Boltzmann, and modified Poisson-Boltzmann osmotic coefficient (sub-figure (a)), natural logarithm of the mean activity coefficient (sub-figure (b)), and natural logarithm of the individual activity coefficients for  $\text{MgCl}_2$  using RPM (sub-figure (c)).



**Figure 3.7** Monte Carlo, symmetric Poisson-Boltzmann, and modified Poisson-Boltzmann osmotic coefficient (sub-figure (a)), natural logarithm of the mean activity coefficient (sub-figure (b)), and natural logarithm of the individual activity coefficients for  $\text{MgCl}_2$  using PM (sub-figure (c)).



**Figure 3.8** Monte Carlo, symmetric Poisson-Boltzmann, and modified Poisson-Boltzmann osmotic coefficient (sub-figure (a)), natural logarithm of the mean activity coefficient (sub-figure (b)), and natural logarithm of the individual activity coefficients for  $\text{AlCl}_3$  using RPM (sub-figure (c)).



**Figure 3.9** Monte Carlo, symmetric Poisson-Boltzmann, and modified Poisson-Boltzmann osmotic coefficient (sub-figure (a)), natural logarithm of the mean activity coefficient (sub-figure (b)), and natural logarithm of the individual activity coefficients for  $\text{AlCl}_3$  using PM (sub-figure (c)).

## Chapter 4

### Conclusion

In this thesis, we have employed the Symmetric Poisson-Boltzmann and the Modified Poisson-Boltzmann theories of statistical mechanics to characterize the thermodynamics of electrolyte solutions. Electrolytes are highly relevant in many technological processes. For example, HCl is often used to study activity through the measurement of pH [31]. The osmotic coefficient, the individual activity coefficients and hence the mean activity coefficients of 104 primitive model electrolyte systems with arbitrary ionic sizes and ionic valences were calculated and the results compared with the corresponding Monte Carlo simulations. In addition, the theoretical predictions were also contrasted with the experimentally measured activity coefficients of HCl and NaCl solutions.

We have found that overall the SPB and MPB theories reproduce the MC simulation results to a remarkable accuracy for 1:1 electrolytes, and to a slightly lesser extent for the asymmetric 1:2 and 1:3 systems. At concentrations higher than approximately  $2\text{mol/dm}^3$ , discrepancies between SPB and MPB tend to become relatively more prominent even for 1:1 valency cases. This can be appreciated clearly in every graph of MC vs MPB and SPB and is rooted in the negligence of interionic correlations in the classical mean field approximation [16]. Although at dilute solution concentrations the influence of correlations is minimal, they can be substantial at higher concentrations. These findings lead to a principal take-away of this work: The agreement of the MC results and the SPB, MPB results is



excellent at small concentrations, whereas the SPB and MPB theories tend to deviate from each other at higher concentrations. In general, the MPB does a better job of reproducing the MC results overall.

The comparison of the experimental individual activity coefficients of HCl solutions with the corresponding simulations and the theoretical results reveals some shortcomings of the primitive model itself. Indeed, the discrepancy between the MC and the experiments must be due to the inadequacy of the model. However, the consistency of the mean activity coefficients implies cancellation of errors.

The 104 electrolyte solutions for which MC data are available [11] cover a wide range of concentration, ion sizes and valences. The agreement of the MPB predictions and to a lesser extent the agreement of the SPB predictions with the relevant simulation data suggest the viability of these theoretical approaches in describing the thermodynamics of charged fluids in the electrolyte solution regime within the framework of the primitive model.

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## Appendix