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Electric Potential of Dielectric Macroions in an Electrolyte Solution

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Electric Potential of Dielectric Macroions in an Electrolyte Solution

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Dedication

This thesis is dedicated to Prophet Mohammad, peace be upon him...

To all of my two families, especially to my father and mother, for my encouragement for that....

To my supervisor Dr. Khawla Qamhieh....

To all who were step by step with me.

Acknowledgment

All praise to Allah, for enlightening us on the path of science and knowledge and helping us on this performance, and granting us the completion of this thesis. To the utmost knowledge lighthouse, to our greatest and most honored prophet Mohamed -May the peace and grace from Allah be upon him. I extend our thanks and gratitude to all those who helped me close or far away in the work of completing this research, To begin, I'd want to express my gratitude to my supervisor, Dr. Khawla Qamhieh, as well as my parents and friends, who were always by my side and helped me acquire strength. I also want to express my gratitude to my family members. Many thanks to those who taught us gold letters and gem words of the highest and sweetest sentences in all of our knowledge.

Finally, I asked Allah to make my work a benefit for all the students who are waiting to graduate

DECLARATION

I confirm that this thesis, which is being presented for a master's degree, is the result of my research, unless where otherwise stated, and that this thesis or any portion of it has not been submitted to any university or institution for a higher degree.

The research was carried out at Al-Quds University in Palestine, under the leadership of Dr. Khawla Qamhieh.

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Abstract

The electrostatic interaction between macroion and counterions in the different electrolyte solution have been studied by using Monte Carlo simulation methods, the different effect has been studied, changing macroions dielectric constant, changing the radius of counterions, and concentrations of adding salt (monovalent (1:1), trivalent (3:1) and pentavalent (5:1) on the charge inversion and the properties of the electric double layer in spherical cell conditions. The radial distribution functions between macroion and other ions, integrated charge number, and the potential of the electric double layer were plotted. For free salt systems, different types of macroions dielectric constant, and several values of counterions charge were used. For systems without salt, It is found that the negative value of zeta potential of the electric double layer increases when macroions dielectric constant, and macroions increases, it also increases when increasing the valence of the counterions radius, and when increasing macroion's charge and counterion's charge the accumulations increase. For systems with salts, at different macroions dielectric constant, (For (60:1) system with salt.) it is found that the negative value of surface potential increases with increasing salt's concentration. In addition, charge inversion occurs for macroions at high values of multivalent salt concentrations.

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List of Abbreviations

EDL	The electrical double layer.
DLVO	The Derjaguin-Landau-Verwey-Overbeek theory
RDFs	Radial Distribution Functions
MC	Monte Carlo simulation.
VDW	Van der Waals attraction.
ε ₀	The permittivity of vacuum =8.854 * 10-12 c/v.m.
ε _s	The relative permittivity= 78.4 at room temperature $25C^{\circ}$ (Dielectric constant of surrounding), (water solvent).
ε _m	macroion dielectric constant
Е	The elementary charge $=1.9*10^{-19}$ C.
obare	Surface-charge density.
В	The concentration of ions in the electrolyte solutions.
Z_C	The charge of the counterions.
Z_M	The charge of the macroion.
R _C	The radius of the counterions.
R_M	The radius of the macroion.
R _{sph}	The radius of the spherical cell.
Å	Angstrom (is a metric unit of length equal to 10^{-10} m).

List of Definitions

Colloids	Defined very small particles, (that do not dissolve) that remain dispersed in a
	liquid for a long time due to their small size and electrical charge.
Monte Carlo	It is a stochastic technique used to predict the probability of different outcomes when
simulations	the intervention of random variables is present and helps to explain the impact of risk
	and uncertainty in prediction models.
EDL	A double layer around a charged particle is formed by the particle surface
	charge(macroions) and its counterions, forming an ionic cloud surrounding
	the particle.
Charge inversion	Is a phenomenon in which the net charge around the macroion surface
	changes as a result of an excess of counterions.
Zeta potential	Is the potential difference between the dispersion medium and the stationary
	fluid layer linked to the dispersed particle.
Macroions	Are they larger in radius and charge than other ions in the solution.
Counterions	Are small ions that have an opposite charge of the macroions (positive).
Co-ions (anions <u>)</u>	Are small ions that have the same charge of macroions (negative).
Cations	Are small ions that have a positive charge.
Molsim	Is the running program that was used, it works under unix.

Chapter One

Introduction

Chapter One

1.1 Introduction:

Electrostatic interaction is the most fundamental contact in the molecular area, resulting in shortrange intramolecular bonding as long as other interactions between molecule aggregates are present (French, Roger H., et al. 2010). The study of the electrostatics of charged ions originated in the second part of the eighteenth century (Whitaker, 1990).

Electrostatic interactions abound in soft matter and biological systems. Soft materials are easily deformed as a result of thermal stresses or thermal fluctuations at room temperature and external stimuli, as well as a poor response with extended relaxation periods, resulting in non-trivial flow activity and stoppage under non-equilibrium circumstances. These materials include polymers, gels, colloids, emulsions, foams, surfactant assemblies, liquid crystals, granular materials, and numerous biological materials and colloids (such as dust, rain, smoke, cloud, gelatin, milk, blood, and butter) (Holm, Kekicheff and Podgeomik, 2001).

The (DLVO) hypothesis, named after the scientists Derjaguin, Landau, Vervey, and Overbeek, is used to characterize colloidal phase stability. The interactions between lyophobic colloids are described by DLVO theory in terms of two separate interactions: a repulsive electrostatic force generated by charges on the particle surface and an attractive van der Waals forces caused by solid parity (Bostrom, Williams and Ninham, 2001).

1.2 Colloid:

The word "colloid" comes from the Greek word "kolla," which means "glue." It was originally employed for gelatinous polymer colloids, and Thomas Graham (a British scientist) was the first to scientifically use it (1860). Colloid science is interested in structures with at least one component with a dimension ranging from nanometer (10^{-9} m) to micrometer (10^{-6} m) . This phrase is older than the term "nano." A 'colloidal system' is produced when one of these states is finely dispersed throughout another. These materials possess unique characteristics that make them highly helpful in practice.

Colloidal systems include aerosols, emulsions, colloidal suspensions, and association colloids. The most fundamental colloidal materials, known as suspensions or dispersions, are composed of two mixed phases. It can exist as a gas, liquid, or solid in both the continuous and dispersed phases (or

even plasma, the fourth phase of matter). The dispersed or suspended phase is formed by the colloid particles. The dispersed materials are more complicated than suspensions and may also be a gas, liquid, or solid, or some mix of the three. Even though they might be heterogeneous at or below the microscale, colloidal dispersions are homogenous mixtures (Hunter 2001).

Because of the structure of the colloid, it possesses a wide range of physical and chemical characteristics. The colloids vary from other molecular or simple electrolyte solutions (such as sugar or salt solution) because they have a large imbalance in size and mass between the colloidal particles and the other solvent molecules (Naji, Kandue, Netz, and Podgomik, 2010)

Colloidal Solution Physical Properties: (a) Stability: Colloids may be found in nature and are relatively stable. The particles of the dispersed phase are constantly moving and stay suspended in the solution. (b) Filterability: For filtration, colloids require specialized filters called ultrafilters. They easily pass through ordinary filter papers without leaving any residue, (c) Heterogeneous nature: Colloids are heterogeneous in nature because they consist of two phases, the dispersed phase, and the dispersion medium, and (d) Homogenous appearance: Even though colloids have suspended particles and are heterogeneous in nature, they appear to have a homogeneous solution. This is because the suspended particles are so small that they cannot be seen with the naked eye.

Because of its relationship with phase stability of colloidal suspensions have a significant presence in medical and technical sectors. It is well known that the presence of oppositely charged counterions severely degrades the stability of colloidal dispersions (Lobaskin and Qamhieh, 2003).

1.3 DLVO:

The (DLVO) hypothesis, named after the scientists Derjaguin, Landau, Vervey, and Overbeek, is used to explain the phase stability of colloidal (Bhattacharjee, Elimelech, and Borkovecb 1998). They presented their theory for understanding the stability of lyophobic colloids in 1943 and 1948. The DLVO theory defines interactions between lyophobic colloids as two distinct interactions (Molina et al, 2006). Figure (1.1) depicts a repulsive electrostatic force (EDL) generated by charges on the particle surface and an attractive interaction van der Waals force (VDW) because of the solid particle cores (Evan, 1994).



Figure 1.1: The two DLVO interactions, (continuous line) obtained as the sum of the electrostatic repulsion and van der Waals attraction.

The theory is based on the assumption of a constant surface charge density $\sigma 0$ about the electrolyte concentration and counterion valency (Evans,1999). Only the Debye length is affected by the electrolyte in the DLVO interaction. According to DVLO theory, a particle's stability in solution is governed by its total potential energy function V_T, which may be calculated using the following equation Eq.1.1

$$v_T = v_S + v_R + v_A \qquad \qquad Eq.1.1$$

Where V_T denotes total potential energy and V_S denotes solvent potential energy.

V_R: stands for repulsive potential energy, whereas V_A: is for attractive potential energy.

Two isolated like-charged plates, (Guldbrand, 1984), cylinders, (Gronbech, 1997), or spheres (Wu, 1998) can be attractive at short separations in an electrolyte solution containing multivalent counterions in the absence of van der Waals interactions. It has recently been demonstrated via molecular simulations. Because it ignores charge density variations in electrostatic double layers, the DLVO theory fails to account for such attraction.

1.4 EDL:

In the 1850s, Helmholtz suggested the EDL via the electrode polarization concept. This is a common phenomenon that is finding increasing use in batteries, superconductors, solar or fuel cells, and ionizing membrane electrodes (Birla and Kant, 2011). In his model, he assumed that no electron transfer processes occur at the electrode and that the solution is solely composed of electrolytes. The interactions between the ions in solution and the electrode surface were thought to be electrostatic in nature and came from the fact that the electrode had a charge density (σ) that originates from either an excess or shortage of electrons at the electrode surface (Birla and Kant, 2013).

EDL is a phenomenon that plays an important part in colloidal electrostatic stability. Colloidal particles acquire a negative electric charge as negatively charged ions from the dispersion media adsorb on the particle surface. The positive counterions that surround a negatively charged particle attract them. As illustrated in Figure (1.2), an electric double layer surrounds a particle of the dispersed phase, containing the ions adsorbed on the particle surface and a film of the countercharged dispersion medium. The EDL is an electrically neutral system (Park and Seo, 2011).



Figure 1.2: Diagram of Electric Double Layer.

The electric double layer is made up of three parts: (a) Surface charge: charged ions (usually negative) adsorbed on the particle surface, (b) Stern layer: counterions (charged opposite to the surface charge), attracted to the particle surface and tightly attached to it by electrostatic force, and (c) Diffuse layer: a film of the dispersion medium (solvent) adjacent to the particle. The diffuse layer is made up of free ions with a larger concentration of counterions. The charged particle's electrostatic force affects the ions of the diffuse layer (Elakneswaran, Nawa, and Kurumisawa, 2009).

On the particle surface, the electrical potential within the electric double layer reaches its greatest value (Stern layer). The potential decreases as one move away from the surface and eventually approaches zero at the border of the electric double layer.

A layer of the surrounding liquid remains attached to a colloidal particle as it travels through the dispersion medium. The layer's boundary denotes the slipping plane (shear plane). The value of the electric potential at the slipping plane is known as the zeta potential, it is a critical parameter in the theory of colloidal particle interaction.

There are no electron transfer processes in the electrode, and the solution solely comprises electrol. Electrostatic interactions occur between the ions in the solution and the electrode surface. However, the electrode carries a charge density that is caused by an excess or a scarcity of electrons at the electrode surface. To keep the interface neutral, the charge retained on the electrode is balanced by reallocating the ions near the electrode's surface (Lobaskin and Qamhieh, 2003).

The charge of the macroion is surrounded by the charges of the counterions from the electrolyte solution (Lee et al., 2017), and when salt is added to the electrolyte solution, the salt ions (positive and negative) begin to organize themselves around the macroion surface. The present salt ion distribution will generate an ion cloud around this macroion, concealing the charge of macroions as a result of being in salt-containing electrolyte solutions. Thus, the clarified phrase was screening time, and one of them is Debye Screening Length.

The traditional Debye-Huckel theory defines the Debye screening length as the distance over which a charge (Q) is screened by the ions in a solution. A low salt concentration solution has a long screening duration, but this connection breaks down in a high concentration solution (Nobbmann U., 2018). It is proportional to the solvent's permittivity (Lee et al., 2017).

1.5 Charge inversion:

Charge inversion (overcharging) is a significant electrical phenomenon observed in colloids and molecular biophysics in biological systems. Screening by movable ions controls electrostatic interactions in an electrolyte solution. In the presence of multivalent ions, an unusual phenomenon occurs, such as repulsion between oppositely charged ions and vice versa, as well as the attraction between ions of the same charge (Besteman, Zevenbergen, Lemay, 2005).

In a water solution, charge inversion occurs when a macroion bonds so many Z-ions that its net charge changes sign. Negative DNA (works as a macroion) which must be inverted by positive Z-ions to enter a negatively charged cell membrane) is especially important (Grosberg, 2002).

1.6 Previous studies:

V. Lobaskin and K. Qamhieh (2003) investigated the Effective Macroion Charge and Stability of Highly Asymmetric Electrolytes under varied salt conditions, explaining the electrostatic processes for highly asymmetric electrolyte instability. A rudimentary model of Monte Carlo simulations of charged macroions immersed in a multivalent salt solution was carried out. They discovered that: (1) at low salt concentrations, the effective charge of the macroion is reduced due to multivalent counter ion adsorption. (2) At high salt concentrations, the macroions get overcharged, resulting in an apparent charge with the opposite sign to the stoichiometric charge. The inverted charge then increases to saturation. The salinity rises. They claimed that the system remained stable at both low and extremely high salt concentrations.

K. Qamhieh and P.lines (2005) used Monte Carlo simulations to investigate the effect of substituting the usual uniform macroion surface charge density with discontinuous macroion charge distributions on the structural characteristics of aqueous solutions of like-charged macroions. They looked at two discrete charge distributions: point charges on the macroion surface and finite-sized charges protruding into the solution. They experimented with both discrete charge distributions and fixed and movable macroion charges. Counterions grow bigger accumulated to the macroion with point charges concentrated on the macroion surface, and the impact rises with counterion valence.

To determine the charge inversion concentration, K. Besteman, M. A. G. Zevenbergen, and S. G. Lemay (2005) investigated charge inversion by multivalent ions and its dependence on the dielectric constant of the solvent (ε_s) and the surface-charge density by an experimental method. This was done by direct measurement of the electrostatic interaction between two oppositely charged surfaces. They utilized a Digital Instrument Nano-Scope and an Atomic Force Microscope to measure and visualize the force between the surfaces against their separation in an asymmetric electrolyte at various concentrations. Their findings agreed with the theoretical hypothesis that spatial links between ions are the primary dominant driving mechanism of a charge inversion.

Lopez-Garcia et al. (2010) improved on their prior model by allowing for a distinct closest approach distance to the particle surface for each ionic species. The most significant aspect is that

it forecasts charge reversal under proper conditions by just taking such ionic excluded volume effects into account.

Per Linse and Leo Lue (2011) investigated models of charged spherical colloids in salt-free solution, including instances where the dielectric constant of the macroion interior is less than that of the surrounding solution. The simulations were performed using a novel, precise, and fast technique for quantitatively assessing the electrostatic polarization interaction. Counterion distributions outside a macroion are predicted by the field theory to accord well with simulation findings over the whole spectrum of electrostatic coupling from weak to solid, and a low-dielectric macroion leads counterions to be pushed away from the macroion.

Levy and D. Andelman (2012) investigated how the dielectric response of a dielectric liquid changes when salt is introduced to the solution. Field-theoretical techniques were used to extend the Gibbs free-energy to first order in a loop expansion and compute the dielectric constant self-consistently. They were able to recreate the linear and non-linear dielectric decrement behavior across a wide range of ionic concentrations, and the resulting values are quantitatively consistent with data for numerous kinds of monovalent salts. Furthermore, a qualitative description of the hydration shell defined by a single length scale, Lh, was discovered, and it was noticed that their model does not contain any major ionic-specific effects. They then included the ionic finite-size and specific non-electrostatic short-range interactions to improve the model, which impacts both the bulk characteristics of ionic solutions, such as dielectric constant and viscosity, as well as their behavior at surfaces, particularly surface tension.

M. Kandu, A. Naji, J. Forsman, and R. Podgornik (2012) investigated the interaction of two neutral plane-parallel dielectric bodies in the presence of a highly asymmetric ionic fluid that contained both multivalent and monovalent (salt) ions. Image charge interactions caused by dielectric discontinuities at the boundaries, as well as effects from ion confinement in the slit region between the surfaces, are fully considered, leading to image generated depletion attraction, ion correlation attraction, and steric-like repulsive interactions. These effects were investigated using a combination of methods including Monte-Carlo simulations, both explicit and implication, as is an effective interaction potential analytical theory. The attractive interaction between the neutral surfaces is demonstrated to be considerable when compared to the normal van der Waals

interactions between semi-infinite dielectrics, and can therefore play a significant role at the nanoscale.

K. Qamhieh and R. Afaneh (2012) investigated the electrostatic potential between the macroion surface and the coincident ions in solution using Monte Carlo simulations. As the salt concentration rises, so will the potential and accumulated charge. The critical surface charge density σ_c was found when zeta potential(ζ) is zero.

The Effect of Discrete Macroion Charge Distributions on the Electric Double Layer of a Spherical Macroion was investigated by K. Qamhieh, M. Amleh, and M. Khaleel (2013). Researchers investigated two discrete models of the core macroion charge: point charges concentrated on the macroion surface and finite-sized charges projecting into the solution. They determined that the charge distribution model has a considerable influence on the EDL structure near to the macroion and that the effect is considerably smaller at further distances. They also stated that when point charges are concentrated on the macroion surface, counterions accumulate stronger to the macroion, lowering the absolute values of surface potential (ψ_s) and zeta potential (ζ).

G. Ivan, G. Garca, and M. Olvera de la Cruz (2014) studied the impact of a dielectric discontinuity on the structural and thermodynamic characteristics of a spherical nanoparticle composed of different dielectric materials while immersed in a charge-asymmetric 1:Z supporting electrolyte. As a function of salt content and nanoparticle valence, the mean electrostatic potential, integrated charge, and ionic profiles were investigated. Using Monte Carlo simulations and the nonlinear Poisson-Boltzmann theory (PB), electrostatic screening and charge neutralization at the surface of a nanoparticle rise as the nanoparticle's dielectric permittivity increases. Furthermore, the nonlinear Poisson-Boltzmann theory (PB) corresponds well with simulation results. It was observed that raising the dielectric permittivity or valence of the nanoparticle, lowers the critical salt concentration at which a sign inversion of the mean electrostatic potential occurs at the Helmholtz plane, which is strongly connected to potential action and electrophoretic mobility. Nonetheless, polarization effects were discovered to facilitate surface charge amplification, or the increase of a nanoparticle's net charge by adsorption of similarly charged ions on its surface, in weakly charged spherical nanoparticles with low dielectric permittivity.

N. Gavish and K. Promislow (2016) proposed a unique micro field method for investigating the effect of the orientational polarization of water in aqueous electrolyte solutions on salt content and

temperature. The model predicts a dielectric functional dependence of the form $\varepsilon(c) = \varepsilon_w - \beta L(3\alpha c/\beta)$, $\beta = \varepsilon_w - \varepsilon_m s$, where L is the Langevin function, c is salt concentration, ε_w is the dielectric of pure water, $\varepsilon_m s$ is the dielectric of the electrolyte solution at the molten salt limit, and α is the total excess polarization of the ions. Furthermore, the model takes into consideration the potential contribution to the static dielectric constant owing to ion-pair orientational polarization via a fitting parameter $\varepsilon_m s$, which corresponds to the limiting dielectric constant of highly concentrated electrolyte solutions.

The electrolyte-induced instability of colloidal dispersions in nonpolar solvents was investigated by G. Smith, S. Finlayson, S. Rogers, P. Bartlett, and J. Eastoe (2017). They developed modern methods to mediate colloidal stability and instability because these would be extremely useful for tracking the properties of nanoparticles, particularly in nonpolar solvents, and they then studied the effect of adding an oil-soluble electrolyte on colloidal interactions in their work. They demonstrated the attractive qualities of this system as well as the macroscopic and microscopic implications, as well as the relationship with concentrations.

The charge regulating macro-ions in salt solutions, as well as the screening characteristics and electrostatic interactions, were investigated by Y. Avni, D. Andelman, T. Markovich, and R. Podgornik (2018). They investigated the impacts of the relationship between distinct adsorption-desorption sites, as well as the associated behavior in terms of solution effective screening characteristics. They also demonstrated that such behavior can be quantified in terms of the macroions' charge asymmetry, which is characterized by their preference for a non-zero effective charge. They discovered that macro-ions that behave as donors exhibit quite typical behavior, but those that function as acceptors have a pounding on-monotonic Debye length, and their findings are particularly relevant for protein solutions.

1.7 Statement of the problem

Most of the Previous studies have studied the electric double layer, zeta potential, and charge inversion phenomena in an electrolyte solution of dielectric constant similar to the dielectric constant of the macroion. In my study the electric double layer, zeta potential, and charge inversion are investigated considering the dielectric constant of the solution to be different than the dielectric constant of the macroion, where different radii of the counterions are used, using Monte Carlo (MC) simulations.

In addition, the effect of the dielectric constant of macroion on the charge inversion and EDL properties of the colloidal particles has been studied in the presence of multivalent salts (monovalent, trivalent, and pentavalent).

This simulated work when the dielectric constant of the macroion interior is different from the surrounding solution has an intriguing practical significance in that it opens the door to more research on charge inversion in the colloidal environment.

Chapter Two

Model and Method

Chapter Two

2.1 Introduction

To satisfy the aim of this study, Monte Carlo (MC) simulation has been used. Mainly to investigate the effect of macroion dielectric constant on the colloidal particle, the radius of counterions, and the concentration of salt was changed while the effect on the properties of the electric double layer was observed.

The solvent is treated as a dielectric medium with a relative permittivity ε_s equal to that of bulk water at 298K in this primitive model of electrolyte solutions established within the context of Mc-Millan–Mayer theory. Once charged hard spheres represent colloids, counterions, cations, and anions, and once charged soft spheres represent colloids, counterions, cations, and anions (Curtis 2001).

2.2 Model

In this model, we have different systems of solutions in asymmetric electrolytes, consisting of two types of charged spherical particles labeled as:

1-Macroion: are represented as hard spheres with radius ($R_M = 20$ Å), and has a different total charge ($Z_M e = -10 e$, -60 e, and -80 e), where e is the elementary charge.

2- Counterions: are represented by charged hard small spheres with radius ($R_C = 2$ Å, and zero Å) with a charge of $Z_C e = +1, +2, +3, +4$, and +5.

Treated within the framework of the fundamental model in which the solvent (water) enters our models via its dielectric constant (ε s = 78.4).

The macroion's total charges are concentrated in the center of the large hard spherical. Assume that the origin point is the center of a spherical cell with a radius of ($R_{sph} = 100$, and 93).

First, we study the effect of the dielectric constant of macroion on EDL characteristics.

Moreover, the effect of changing the valence of counterions is investigated. Table 2.1 represents the investigated systems.

System	Z_M	Z_C	Φ_M	R_M	R_C	R _{sph}
60:1	-60	+1	0.008	20	2	100
60:2	-60	+2	0.008	20	2	100
60:3	-60	+3	0.008	20	2	100
60:4	-60	+4	0.008	20	2	100
60:5	-60	+5	0.008	20	2	100

Table 2.1: specification of the five systems.

Where:

Z_M: charge of macroion,

Z_C: charge of counterions,

 Φ_M : macroion volume fraction,

R_M: radius of macroion,

R_C: radius of counterions,

R_{sph}: radius of the spherical cell.

The macroion total charges are located at the center of the hard sphere (sph).

The second stage was to study the effect of surface charge density of macroion, the size effect of counterions, and valence as shown in table 2.2.

Table 2.2: sł	hows the	specification	of the three	systems.
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System	Z_M	Z_C	$\mathbf{\Phi}_{M}$	R_M	R_C	R _{sph}
10:1	-10	+1	0.01	20	2 and zero	93
80:1	-80	+1	0.01	20	2 and zero	93
80:2	-80	+2	0.01	20	2 and zero	93

Usually, the dielectric constant of the macroion is taken to be equal to that of the solvent, (homogeneous dielectric solution), $\varepsilon_m = \varepsilon_s = 78.4$

The total potential energy of interaction of the U_T system in our model is the sum of three potenti al energies.

$$U_T = U_{hs} + U_{elec} + U_{ext}, \qquad \text{Eq. 2.1}$$

Where U_{hs} is Hard-sphere repulsion, which is given by:

$$U_{hs} = \sum_{i < j} u_{ij}^{hs}(r_{ij}), \qquad \text{Eq. 2.2}$$

With,

$$u_{ij}^{hs}(r_{ij}) = \begin{cases} \infty, \ r_{ij} < (R_i + R_j) \\ 0, \ r_{ij} \ge (R_i + R_j) \end{cases}, \quad \text{Eq. 2.3}$$

Where;

i and j denote either a macroion, a m, or a counterion,

 R_i and R_j represents the radius of the hard spheres i and j respectively,

 r_{ij} is the distance between the centers of particles i and j,

The U_{elec} is the coulomb interaction, which is given by:

$$U_{elec} = \sum_{i < j} u_{ij}^{elec}(r_{ij}), \qquad \text{Eq. 2.4}$$

With, the following formula of Coulomb's Law:

$$u_{ij}^{elec}(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 \varepsilon_s r_{ij}},$$
 Eq. 2.5

Where;

 Z_i and Z_j are the valances of ions i and j respectively.

 r_{ij} is the center-to-center separation between ions i and j.

e is the elementary charge $(1.9 * 10^{-19} \text{ C})$.

 ε_0 is the dielectric constant of the vacuum (8.854*10⁻¹²C/V.m).

 ε_s or (ε_r) is the dielectric constant of each solvent.

The confinement potential energy U_{ext} in Eq. 2.6, is given by:

$$U_{ext} = \sum_{i} u_i^{ext}(i), \qquad \text{Eq. 2.6}$$

With,

$$u^{ext}(r_i) = \begin{cases} 0, \ r_i \le R_{sph} \\ \infty, \ r_i > R_{sph} \end{cases}, \qquad \text{Eq. 2.7}$$

Where R_{sph} is the radius of the spherical cell in case of the boundary conditions is spherical.

The particle interaction is pairwise additive and is given by:

$$U_{ij}(r) = \begin{cases} \infty, \ r_{ij} < (R_i + R_j) \\ \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 \varepsilon_s} \frac{1}{r_{ij}}, \ r_{ij} \ge (R_i + R_j) \end{cases}, \qquad \text{Eq. 2.8}$$

Finally, the case where the macroion has a dielectric constant lower, and higher than that of the solvent, heterogeneous dielectric solution $\varepsilon_m \neq \varepsilon_s$ was considered and which is a more realistic description for colloids in aqueous

In this case, the interaction energy U_T of the system can be given as Eq.2.9

$$U_T = U_{hs} + U_{elec} + U_{ext}, + \frac{1}{2} U_{pol}$$
 Eq.2.9

U_{pol} is the polarization energy is determined by Eq.2.10

$$U_{pol}(r_j, r_i) = \frac{q_j q_i}{\varepsilon_s} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \left[\frac{\varepsilon_s - \varepsilon_m}{\varepsilon_{s(1+1/l)+\varepsilon_m}} \right] \left(\frac{R_d^{2l+1}}{r_j^{l+1} r_i^{l+1}} \right) Y_{lm}(\theta_j, \phi_j) Y_{lm}^*(\theta_i, \phi_j)$$
Eq.2.10

In the case that $\varepsilon_m = \varepsilon_s$ (homogeneous dielectric solution), the polarization energy u_{pol} is zero. And, if $\varepsilon_m \neq \varepsilon_s$ (heterogeneous dielectric solution), a polarization surface charge density will appear at the dielectric discontinuity and U_{pol} becomes nonzero.

To simplify, let the dielectric discontinuity be spherical with radius R_d . Then, the potential energy involving the polarization surface charge density and the counterions can be cast as an ionic selfterm $U_{pol}(r_i, r_i)$ and an ion-ion term $U_{pol}(r_j, r_i)$ with applicable to both j = i and $j \neq i$, where $r = (r, \theta, \Phi)$, Y_{lm} is the spherical harmonics, and $Y^*_{lm}(\theta_i, \Phi_j)$ is the complex conjugate. In the following, the dielectric discontinuity will be placed at the hard-sphere surface of the macroion, i.e., $R_d = R_M$. This maximizes the effect of the polarization surface charge density. (Leo Lue and Per Linse, 2014), and (Qamhieha and Lines, 2005).

When added the salt, we study the effect of different concentrations of salt was adding on the systems 60:1, 60:3, and 60:5 at three dielectric constants of macroion. The salt concentration is expressed as the ratio of the multivalent charges to the charge of the

macroin, which may be calculated using the following equation:

$$\beta = \frac{Z_c \rho_c}{Z_M \rho_M},$$
 Eq. 2.10

Where;

 Z_c are the valence of the corresponding salt species

 ρ_c the number density of the corresponding salt species,

 Z_M are the valence of the macroion

 ρ_M are the number density of the macroion.

For both systems that are represented in table 2.1 and table 2.2 we calculated the macroion number density by :

$$\rho_M = 2.5 * 10^{-7} \text{ Å}^{-3}$$
, and $2.97 * 10^{-9} \text{ Å}^{-3}$

respectively to the volume fraction of the macroion $Ø_M$ =0.008, and 0.001 respectively, keeping the temperature constant at, T=298 K. (Vladimir and Qamhieh 2003).

2.3 Method and Simulation setting

The Monte Carlo simulation is named after the town of Monte Carlo in Monaco, famous for gambling. Monte Carlo simulations are used to model the likelihood of various outcomes in a mechanism that cannot be easily predicted due to the intervention of random variables. It is a methodology used to consider the effect of risk and uncertainty on prediction models.

This simulation can be used to solve problems in almost any field, including economics, engineering, supply chain management, and research. It is a commonly utilizes mathematical analytical methodology in most scientific research subjects, including both non-engineering and engineering fields. It has been used to solve a wide range of problems, starting with the simulation of complex physical events like atom collisions and traffic flow simulation.

Monte Carlo is very well suited to solving complicated physical issues since it can handle a large number of random variables, numerous distribution forms, and extremely non-linear engineering models (Siddall, 2003).

This method will be taken for the isothermal-isobaric (NPT) ensemble (constant number of particles, pressure and temperature), depending on the standard Metropolis algorithm (Per Lines et al, 2004).

3.4 Metropolis Algorithm:

In 1953, Metropolis made the first paper on a technique that was central to the method now known as simulated annealing, which was fundamental to the process currently known as simulated annealing. This study revealed the first numerical simulations of a liquid, for producing samples from the Boltzmann distribution. Monte Carlo methods are a type of computing procedure that computes results through repeated random sampling. Before the development of the Metropolis algorithm, Monte Carlo methods were used in statistical mechanics applications in a variety of ways, but they all followed the same pattern:

Defining the possible range of input values generating a large number of random configurations of the system (input value), applying the required arithmetic operations to those values computing the properties of interest (such as energy or density) for each configuration, repeating the process for a specified number of times (the accuracy of the results increases with the number of iterations),

a compilation of current results with previous results and then producing a weighted average where the weight of each configuration is its Boltzmann factor.

It is implemented using the following algorithm:

- 1. Chose the particles to move at random and move them by a random distance.
- 2. Calculate the energy difference $\Delta U_{trial} = U_{new} U_{old}$ between the old and new configuration.

If $\Delta U_{trial} \leq 0$ accept the new configuration, else if random number generating $0 \leq x \leq 1$ is smaller than exp($-\Delta U_{trial}/K_BT$), accept the move, else reject the move and count the old configuration as the new configuration. After every step, data for averages is accumulated before a new trial move is attempted (Schneider, 2003).



Figure .2.1: Scheme of accepting and rejecting trial moves in Metropolis algorithm.
Chapter Three

Results and Discussion

Chapter Three

Results and discussions:

3.1 Introduction:

In this section, the results and outcomes of the investigation are presented, discussed, and built on. To start with, let's clarify that calculations have been achieved by advanced computational software, the Molsim package (Per Lines et al, 2004). The present work has been divided into two systems:

- 1-Systems without adding salts.
- 2- System with multivalent salts at different concentrations:
 - (a) monovalent salt,
 - (b) trivalent salt,
 - (c) pentavalent salt.

3.2 Systems without salt:

Monty Carlo simulations were used to study the effect of the dielectric constant of macroion, and valency of counterions on EDL characteristics through five systems that have been previously represented in table 2.1. For all systems we have run 10^7 (steps/ passes) for equilibration (production), 10^7 (steps/ passes) for running.

Central charge distribution:

Effect of macroion dielectric constant and counterion charge:

The RDF provides the relative density of small ions at a distance r from the macroion. Its value is unity in the absence of any spatial correlation.

Figure 3.1 shows Macroion–counterions radial distribution functions (RDFS) for the central charge distributions with different (counterion valences) in systems without salt. The graphs are plotted concerning counterions distance (r) from the center of the macroion in Angstroms, for different macroion dielectric constant ε_m .



Figure 3.1: Macroion-counterion radial distribution function (RDFs), without salt, for different macroion dielectric constant. The valence of macroion is Z_M = -60. and at different counterion valences Z_C : a) +1, b)

+2, c) +3, d) +4, and e) +5, red, black, and blue curves correspond to dielectric constants of macroion 2,78.4, and 500 respectively. the dielectric constant of the solvent $\varepsilon_s = 78.4$.

Figure 3.1 shows that the distribution of counters around the macroion, which has the largest value at the highest value of the total dielectric constant ($\varepsilon_m = 500$). While the smallest electrostatic correlation is found for the lowest value of the macroion dielectric constant ($\varepsilon_m = 2$), the low macroion dielectric constant shifts the variances away from the macroion. See the reference (lue, and linse, 2014) for further information.

When the macroion dielectric constant is smaller than that of the surrounding solvent, this results in an additional repulsive force acting on the counterions caused by the surface charges of the dielectric break. This repulsion is often attributed to the photo charges (or image charge densities) on the other side of the dielectric discontinuity as viewed from the counterions.

It is clear that when the macroion dielectric constant is smaller than the solution dielectric constant, the counter accumulation around the macroion decreases, and when the macroion dielectric constant is higher than the solution dielectric constant, the counter accumulation around the macroion increases.

Table 3.1: Values of the maximum accumulation of counterions RDF in the vicinity of macroion for macroion counterion radial distribution functions at system valence 60:1,60:2, 60:3,60:4, and 60:5, at different dielectric constants of macroion.

System valence _{Em}	60:1	60:2	60:3	60:4	60:5
2	137	279	330	332	345
78.4	166	465	772	1051	1282
500	193	667	1330	1974	2488

Based on data from table 3.1it can be concluded that the maximum value of accumulation is the highest in counterion valence Zi = 5 in system 60:5. Moreover, it can be said that the increase in the dielectric constant of macroion causes an increase in the accumulation of counterions, which means at macroion dielectric constants =500 higher accumulation.

In addition, the electrostatic correlation between macroion and counterions has the highest value at the valence of a system that equals 5, followed by valence 4. As for the lowest electrostatic correlation it was found in the monovalent system.

Also, it is clear that when the counterion valence increased the accumulation of counterions around the macroion also increased at different counterion valences (Zi = 1,2,3,4, and 5) for each macroion dielectric constant.



Figure 3.2: The distribution of counterions (green, small balls) around macroion (red large balls) inside the 100 Å spherical cell, without salt, at a)60:1, b) 60:2, c) 60:3, d) 60:4, and e) 60:5. At macroion dielectric constant =78.4

Figure 3.2 shows the snapshots for the distribution of counterions around the surface of macroion inside the spherical cell at different valance of counterions Z_c , at macroion dielectric constant =78.4, without salts, it is clear that the accumulation of counterions near macroion surface increases rapidly when valence of counterions gets greater, because of decrease the number of counterions. The results agree with the findings of (Per, and Khawla, 2005), also aligns with (Reem, and Khawla, 2012) results.

The radial functions of the local charge density of the counterions $\rho i(r)$ are calculated according to equation 3.1 and plotted as a function of the distance (r) from the center of the macroion as shown in figure 3.3.

Local charge density $(\rho_i(r))$ was obtained by:

$$\rho_i(r) = Z_i \varrho_i RDF \qquad \text{Eq. 3.1}$$

Where

Zi is the valence of counterions,

Qi is the uniform density of counterions

RDF is the radial distribution function of counterions around macroion.

The functions of charge density can classify the structure of the ionic space of macroion. The functions display the local charge density of counterions at that distance r from the center of the macroion.



Figure 3.3: Radial Function of local charge density of counterions $\rho_i(r)$, without salt. The valence of macroion is Z_M = -60. and at different counterion valences Z_C : a) +1, b) +2, c) +3, d) +4, and e) +5, red,

black, and blue correspond to dielectric constants of macroion 2,78.4, and 500 respectively .the dielectric constant of the solvent $\varepsilon_s = 78.4$.

System valence Em	60:1	60:2	60:3	60:4	60:5
2	314	640	759	767	773
78.4	381	1067	1754	2405	2962
500	443	1530	3049	4553	5715

Table 3.2: Values of the local charge density of counterions at different counterion valences when: a) 60:1, b) 60:2, c) 60:3, d) 60:4, and e) 60:5, at different dielectric constants of macroion.

Figure 3.2 illustrates that by decreasing the dielectric constant of macroion, the value of macroioncounterion electrostatic attraction is decreased, and decreasing macroion's dielectric constant leads to a displacement of the counterions away from the macroion, and macroion-counterion electrostatic attraction decreases.

The uniform counterion distribution around the macroion is a compromise between the macroioncounterion electrostatic attraction force showing the need for complete counterion adsorption on the macroion surface and counterion entropy improvement a homogeneous counterion density distribution.

From table 3.2: demonstrates the fact that the accumulation of the counterions near the macroion surface with all counterion valences. Generally, this accumulation is increased by increasing the valence, where the highest charge density of the counterions is established for systems with pentavalent at the highest macroions dielectric constant. For the same reason when decreasing the dielectric constant of macroion, the value at the dielectric constant of macroion 78.4 agrees with (Mirfit, Mai, and Khawla, 2013) results.

The integrated charge number P(r) is the net charge of macroion within a distance r from the center of the macroion, which is calculated using equation 3.2.

$$P(r) = -Z_M + \int_r^{\infty} \sum [Z_i \rho_i(r)] 4\pi r^{2} dr$$
 Eq. 3.2

Where

 Z_M is the charge of macroion (-60),

Z_i is the valence of counterions,

 ρ_i the local charge density of the countries,

r is the distance between the center of macroion and counterion.

Integrate number P(r) are plotted as a function of distance (r) from the center of macroion in Angstroms, for different systems and several values of macroion dielectric constant, as in figure 3.3.





Figure 3.4: The integrated charge number P(r) within a distance r from the center of the macroion, without salt. The valence of macroion is Z_M = -60. and at different counterion valences Z_C : a) +1, b) +2, c) +3, d) +4, and e) +5, red, black, and blue correspond to dielectric constants of macroion 2,78.4, and 500 respectively the dielectric constant of the solvent ε_s =78.4.

In figure 3.4 at r = 24 Å, shows that there is a positive correlation between the dielectric constant of macroions and accumulated charge.

Table 3.3: The values of P(r), without salt, at system valence 60:1,60:2, 60:3,60:4, and 60:5, at different dielectric constants of macroion.

System valence Em	60:1	60:2	60:3	60:4	60:5
2	-42	-24	-13	-12.8	-12
78.4	-40	-19	-6	-1.7	-0.6
500	-39	-16	-2.3	-0.13	0.01

From table 3.3 it is established that values of P(r) at r = 24 Å, reach the maximum value for each system at the highest macroion dielectric constant, and the value of accumulated charge increases when the counter ion valences increase due to increase electrostatic attractions.

The value of integrating number at the dielectric constant of macroion 78.4 results is in agreement with (Reem, and Khawla, 2012) results.

By using equation 3.3 and from the curves of P(r), the electrostatic potential $\varphi(r)$ of the EDL concerning distance r at each valence of counter ion has been plotted, as shown in figure 3.5. The mean electrostatic potential, EDL $\varphi(r)$, obtained by:

$$\varphi(\mathbf{r}) = \frac{e}{4\pi\varepsilon} \int_{r}^{\infty} dr' \frac{P(r)}{r^{2}}$$
 Eq. 3.3

Where,

e is the elementary charge,

- P(r) is the integrated charge number,
- *r*` the distance from the center of the colloids (macroion),
- ε ` is the ratio permittivity of the solution ($\varepsilon_0^* \varepsilon_r$),
- ε_0 the permittivity of vacuum (8.854*10⁻¹² C/v.m),
- ε_r : the permittivity of water (78.4).

The potential is determined at any point on the double layer, in my study the point is at 60 Å, as shown in figure 3.5.



Figure 3.5: Electrostatic potential of EDL $\varphi(r)$, for different systems, without salt. The valence of macroion is Z_M = -60. and at different counterion valences Z_C : a) +1, b) +2, c) +3, d) +4, and e) +5, red, black, and blue correspond to dielectric constants of macroion 2,78.4, and 500 respectively .the dielectric constant of the solvent ε_s =78.4.

Figure 3.5 shows that the magnitude of the negative electrostatic potential decreases gradually near the surface of the macroion by increasing the dielectric constant of the macroion. Also, it decreases with the increase of the counterions valence, with pentavalent counterions the decrease is the largest, because of the increase of electrostatic attraction.

when the concentration of counterions increases near the surface, a double electric layer (EDL) is formed around each particle e. The distribution of ions in the surrounding interlayer affects the development of net charge. The importance of zeta potential is that its value can be related to the stability of colloidal dispersion.

Zeta potential refers to the degree of repulsion between adjacent particles of a similar charge in the dispersion, zeta potential is the potential of the slipping plane (R_S) in EDL difference between the dispersion medium and the fixed layer of the liquid associated with the scattered particle, The total charge of the double layer is zero, and because the charges are spatially oriented and not randomly organized, they give rise to an electrical potential.

The slipping plane (R_s) is calculated by the relation: $R_s = R_M + 2R_C$.

where:

R_C is the radius of the counterion.

R_M is the radius of macroion.

In my case, $R_s = 20+2*2=24$ Å. At r = 24 Å, zeta potential can be found from figure 3.6 (b), page (36).

		Electrostatic potential	Zeta potential (ζ),
Counterions valence	Macroion dielectric	(Surface potential) φ_s	(mV) at $r=24$ Å
	constant	(mV) at r=20 Å	
	2	-211	-123
+1	78.4	-201	-118
	500	-192	-109
+2	2	-125	-47
	78.4	-119	-45
	500	-109	-39
+3	2	-81	-7.89
	78.4	-67	-2.73
	500	-62	-1.99
+4	2	-80	-5
	78.4	-64	-3.2
	500	-56	-1.7
+5	2	-80	-3.47
	78.4	-59	-1.67
	500	-53	-1.05

Table 3.4: Electrostatic potential and zeta potential for all systems (counterions valence), with a different dielectric constant of macroion.

The potential at the surface of macroion (ϕ) has been taken at (20 Å), while at (24 Å) for Zeta potential(ζ).

As shown in table 3.4 the absolute values of surface electrostatic potentials (ϕ), and zeta potential (ζ), decrease linearly with increasing the dielectric constant of macroions ϵ_m , and counterions

valence increase. It is noticed that the surface electrostatic potential (ϕ) values that are larger than zeta potentials were found on the surface at 20 Å, the effect of surface charge of macroion (-60 e).



Figure 3.6: EDL potential as a function of macroion dielectric constant (2, 78.4, and 500), figure (a) are Surface potential at r = 20 A, and (b) are Zeta potential of EDL at r = 24 A, without salt, at different system.

In figure 3.6 the electrostatic potential increases when the valence of counterion increases at the potential of surface and zeta potential, its value close to zero at the high value of counterion valences system 60:5. When the values of counterions are small the change of potential is large then it becomes fixed at a high value of concentration. (Reem, and Khawla 2012).

Figure 3.6. (a) shows the values of surface potentials increase linearly with increasing ε_m , and counterions valance increase.

Figure 3.6. (b) shows that the value of zeta potentials increases in linear relation as the dielectric constant of macroions increases. Also, the maximum value of the potential is reached at the highest values of ε_m , as the decreasing of dielectric constant caused a reduction of the electrostatic attractions between macroion and counterions.

Also, we study the effect of the dielectric constant of macroion, the surface charge density of macroion and counterions, and the size of counterions on EDL characteristics, the three systems are used in this study were shown in Table 2.2, by applying Monty Carlo simulations. For all those systems we have run 10^7 (steps/ passes) before equilibration (production), and also after equilibration, runs 10^7 (steps/ passes), to reach the stability of energy.

The effect of macroion charge:



Figure. 3.7. counterion number density $\rho(r)/\rho_{avg}$ as a function of the scaled radial distance r/RM from the center of the macroion for System I (red) (10:1), System II (black) (80:1), System III (green) (80:2), fig (a) when the radius of counterion =zero and fig (b) when the radius of counterion =2, where the dielectric constant of the macroions and the surrounding solvent are equal $\varepsilon_m = \varepsilon_s = 78.4$

Generally, in figure 3.7 shows that the accumulation of the counterions near the macroion increases, when increasing surface charge density for the macroion and the counterions, because of the increase in the electrostatic attractive between macroion and counterion interaction, and the maximal density appears at contact $r = R_M$. but a shift in the maxima to the left as figure 3.6 and a decrease in the size of the counterion (radius of counterions) was increasing the electrostatic interaction between macroion and counterions at a closer approach between them.

The electrostatic coupling parameter (depends on the valance of macroion Q), where the counterion distributions deviate only moderately from a uniform distribution, which originates from the electrostatic coupling parameter is comparably small as in System I. The distribution of the counterions becomes much more nonuniform in Systems II and III, respectively. this result is in agreement with what was obtained by (Leo Lue and Per Linse, 2014).



Figure 3.8: Normalized counterion number density $\rho(r)/\rho avg$ as a function of the scaled radial distance $(r/R_M - 1)$ from the center of the macroion for (a) System I ,(b) system II ,(c) system III , with $\varepsilon_m = \varepsilon_s$ (black)=78.4 and $\varepsilon_m = 1$ (red), at counterion radius=2.



Figure 3.9: Normalized counterion number density $\rho(r)/\rho avg$ as a function of the scaled radial distance (r/R_M -1) from the center of the macroion for (a) System I, (b) system II, (c) system III, with $\varepsilon_m = \varepsilon_s$ (black)=78.4 and $\varepsilon_m = 1$ (red), at counterion radius=zero.

According to figure 3.8 and 3.9 show that the accumulation of the counterions near the macroion at the different radius and dielectric constant of the macroion.

The accumulations increase when the increasing macroion of a dielectric constant because the low dielectric constant leads to displacement of the counterions away from the macroion.

Table 3.5: (a) The values of maximum number density, at ε_m (78.4, and 1), when the radius of counter ions (2, and zero).

System	ZM: ZC	ε _m =7	8.4	ε _m =1	
		R _C =zero	Rc=2	Rc=zero	Rc=2
System I	10:1	7	5.69	4	4.6
System II	80:1	224	157	144	171
System III	80:2	868	646	483	689

Table 3.5 shows that the value of maximum number density When the macroion surface charge density increases then the accumulations around macroions also at the valence of the counterions increase, the accumulations increase because of increase of the electrostatic attractive between macroion and counterion interaction, this result is in agreement with what obtained by (Leo Lue and Per Linse, 2014)

Also, show a shift in the maxima to the left (the distance between macroion and counterions (r) decreases) at decreasing the size of the counterion (radius of counterions) where increasing the electrostatic interaction between macroion and counterions at closer approach between them. The agreement of this results with what was obtained by (Mirfit, Mai, and Khawla, 2013).



Figure. 3.10. The integrate number P (r) as a function of r, for System I (red) (10:1), System II (black) (80:1), System III (green) (80:2), when radius of counterion =zero (dotted curves) and radius of counterion =2 (solid curves), where, (a) $\varepsilon_m = 1$, and $\varepsilon_s = 78.4$, and (b) $\varepsilon_m = \varepsilon_s = 78.4$.

In figure.3.10, P(r) at r = 24 Å, it shows that the integrated charge number increases by decreasing radius of counterion (decrease in the size), due to increasing the electrostatic interaction between

macroion and counterions at closer approach between them, also shows the increasing when counterions valence increase, because increase electrostatic interactions between macroion and counterions.

Table 3.6 The values of P(r) at r=24 Å, when the radius of counterion changes from zero to 2, at two macroion dielectric constant (78.4, and 1).

		(a) $\varepsilon_m = \varepsilon_s =$	=78.4	(b) $\varepsilon_m = 1$ and $\varepsilon_s = 78.4$		
System	Z _M : Z _C	P(r) at	P(r) at	P(r) at	P(r) at	
		R _C =zero	Rc=2	Rc=zero	R c=2	
System I	10:1	-9	-9.5	-9.67	-9.77	
System II	80:1	-30	-46	-36	-47	
System III	80:2	-8	-19	-16	-23	

From table 3.6 (a) and (b) clearly show that when deto creasing dielectric constant of macroion The integrated charge number increases by increasing the dielectric constant of macroion the value of P(r) decrease, due to low- macroion dielectric constant that leads to a displacement of the counterions away from the macroion. the integrated number also increases by increasing the charge of counterions, but increases by decreasing macroion charge because decrease the surface charge density of macroion.

at 78.4 dielectric constants of macroion, we can compare for 10:1, 80:1, and 60:1 systems when $R_C = 2$, at the same conditions the greatest integrated charge number of counterions establishes for this systems it that have the lowest macroion charge Z_M (surface charge density of macroions), means that at $Z_M = 10$ it shows the highest integrate number, then 60 and 80 respectively, as shown in figure 3.10



Figure. 3.11. The integrate number P (r) as a function of r, for different valance of macroion (10:1) (red), (60:1) (blue) and (80:2) (black), when radius of counterion =2 and $\varepsilon_m = \varepsilon_s = 78.4$.

And we can compare between 80:1, and 80:2, according to table 3.6 when increasing the charge of counterions Z_C (small number of counterions), the integrated number increases, it also shows the increases of the integrate number with the highest dielectric constant at 78.4. The result is in agreement with (Leo Lue and Per Linse, 2014) simulations results.



Figure 3.12: Electrostatic potential of EDL $\varphi(r)$ as a function of r, for System I (red) (10:1), System II (black) (80:1), System III (green) (80:2), when radius of counterion =zero (dotted curves) and radius of counterion =2 (solid curves), where, (a) $\varepsilon_m = 1$, and $\varepsilon_s = 78.4$, and (b) $\varepsilon_m = \varepsilon_s = 78.4$.

According to figure 3.12 when the radius of counterions equals zero, the electrostatic potential is increased, due to increasing the electrostatic interaction between macroion and counterions at closer approach between them, also the increasing it shows when counterions valence increase, also because increase electrostatic interactions between macroion and counterions.

In figure 3.12 the magnitude of the negatively electrostatic potential is diminished gradually near the surface of the macroion by decreasing the radius of counterions.

Surface potential (φ _s), at r=20 Å		(a) $\varepsilon_m = \varepsilon_s = 78.4$		(b) $\varepsilon_m = 1$ and $\varepsilon_s = 78.4$	
System	Q: q	R _C =zero	R _C =2	R _C =zero	R _C =2
System I	10:1	-53	-54	-54	-55
System II	80:1	-169	-221	-184	-239
System III	80:2	-67	-129	-115	-156

Table 3.7: The values of surface electrostatic potential (ϕ), at r=20 Å.

Table 3.8: The values of zeta potential (ζ), at r=24 Å.

Zeta potential (ζ), at 24 Å		(a) $\varepsilon_m = \overline{\varepsilon_s} = 78.4$		(b) $\varepsilon_m = 1$ and $\varepsilon_s = 78.4$	
System	Q: q	R _C =zero	R _C =2	R _C =zero	R _C =2
System I	10:1	-38	-39	-39	-40
System II	80:1	-94	-116	-95	-132
System III	80:2	-27	-36	-36	-59



Figure 3.13: The surface potential of the macroion as a function of the radius of counterions, (a) at macroions dielectric constant =78.1, and (b) at macroions dielectric constant =1.



Figure 3.14: Zeta potential of EDL of macroion as a function of the radius of counterions, (a) at macroions dielectric constant =78.1, and (b) at macroions dielectric constant =1.

Figure 3.13. (a), and (b) show the surface potential of macroion as a function of the radius of counterions, from figure 3.12. (a), and (b) the absolute values of surface potentials decrease linearly with increasing radius of counterions (increase size of counterions), also from table 3.7 show that increase the surface potential, when macroion dielectric constant increases.

From figure 3.14. (a), and (b) it is clear that the value of zeta potentials decreases in linear relation as the radius of counterions increases. Mean that the maximum value of the potential is reached at the small size of counterions (R_C =zero), but table 3.8 shows that when increasing macroions dielectric constant increases the value of zeta potential.

Also, we can compare at 78.4 dielectric constant of macroion, at $Z_M = -10,-60$, and -80 the values of the surface potential (φ_s), are about -54 mv, -210 mv, and -221 mv, respectively, while the values of zeta potential (ζ) are -39 mv, -118 mv, and -116 mv. That means at $Z_M = -10$ show the highest value of zeta and surface potential, 60 and 80 respectively, because decreasing the surface charge density of macroion.

3.2 Systems with salt:

The concentration of salt is determined by the ratio of the counterion charge to the charge of the macroion, which may be determined using equation 2.10:

The solution will be ionized and changed into two oppositely charged ions, counterions positive charge and coions (anions) negative charge, after adding salt to it.

The effect of adding salt to the electrolyte solution on the EDL characteristics created after adding multivalent salt at different concentrations ($\beta = 0.3, 1, 3, \text{ and } 4$) has been studied for the 60:1 system for the central charge distribution spherical cell.



Figure 4.1: RDFs between macroion and the counterions as a function of r, monovalent salt, at indicated β values (0.3, 1, 3, 4), when (a) $\epsilon_m = 500$, (b) $\epsilon_m = 78.4$, and (c) $\epsilon_m = 2$.

According to figure 4.1 shows the radial distribution of monovalent counterions (1:1) around the macroion, these results show that the accumulation of monovalent counterions decreases with the increase of salt concentration.



Figure 4.2 RDFs between macroion and the counterions as a function of r, trivalent salt, at indicated β values, when (a) $\varepsilon_m = 500$, (b) $\varepsilon_m = 78.4$, and (c) $\varepsilon_m = 2$.

Figure 4.2 shows the distribution of trivalent counterions (3:1) around the macroion, these results showed that as the salt concentration increased, the accumulation of trivalent counterions around the macroion decreased. However, when $\varepsilon_m = 78.4$, the macroion becomes overcharged and their apparent charge has the opposite sign, the counterions expel the multivalent counterions and take their place



Figure 4.3: RDFs between macroion and the counterions as a function of r, pentavalent salt, at indicated β values, when (a) $\varepsilon_m = 500$, (b) $\varepsilon_m = 78.4$, and (c) $\varepsilon_m = 2$.

The distribution of pentavalent counterions (5:1) around the macroion is shown in figure 4.3. These results show that as the salt concentration increases, the accumulation of pentavalent counterions around the macroion decreases. However, at high concentrations with $\beta = 3$ and 4, the macroion becomes overcharged and their apparent charge has the opposite sign, resulting in the ion's correlation with macroion being reversed.



Figure 4.4: RDFs between macroion and cations as a function of r, monovalent salt, at indicated β values, when (a) $\epsilon_m = 500$, (b) $\epsilon_m = 78.4$, and (c) $\epsilon_m = 2$.



Figure 4.5 RDFs between macroion and cations as a function of r, trivalent salt, at indicated β values, when (a) $\epsilon_m = 500$, (b) $\epsilon_m = 78.4$, and (c) $\epsilon_m = 2$.



Figure 4.6: RDFs between macroion and cations as a function of r, pentavalent salt, at indicated β values (0.3, 1, 3, and 4), when (a) $\epsilon_m = 500$, (b) $\epsilon_m = 78.4$, and (c) $\epsilon_m = 2$.

In figures 4.4, 4.5, and 4.6, monovalent, trivalent, and pentavalent salts respectively, show the radial distribution of multivalent salt cation near the macroion, and it is clear that when the salt concentration increases the cation number decreases. Also, we observe that for the lowest dielectric constant the monovalent, trivalent, and pentavalent counterions show a strong repulsive interaction with the macroions, where the dielectric properties of the macroion and water are kept the same (absence of polarization effects), the contact value of both ionic species increases in comparison to that of the previous case. As cations are the counterions of the negative macroion, they are preferentially adsorbed because of electrostatic interactions. For the material with the highest dielectric constant, the adsorption of both ionic species is further enhanced.



Figure 4.7 RDFs between macroion and anions as a function of r, monovalent salt, at indicated β values (0.3, 1, 3, and 4), when (a) $\varepsilon_m = 500$, (b) $\varepsilon_m = 78.4$, and (c) $\varepsilon_m = 2$.

Figure 4.7 shows that as salt concentration decreases, the radial distribution between macroion and anion decreases due to multivalent counterions adsorption on the stern layer. However, at high concentrations, such as $\beta = 3$ and 4, the macroion becomes overcharged and their apparent charge has the opposite sign, causing the ion's correlation with macroion to change, and the coions expel the multivalent counterions.



Figure 4.8: RDFs between macroion and anions as a function of r, trivalent salt, at indicated β values, when (a) $\epsilon_m = 500$, (b) $\epsilon_m = 78.4$, and (c) $\epsilon_m = 2$.

Figure 4.8 shows that as salt concentration decreases, the radial distribution between macroion and anion decreases due to multivalent counterions adsorption on the stern layer, but in figure (c), when $\varepsilon_m = 2$, macroions become overcharged and their apparent charge has the opposite sign, causing the ions correlation with macroion to change, and the coions to expel.



Figure 4.9: RDFs between macroion and anions as a function of r, pentavalent salt, at indicated β values, when (a) $\epsilon_m = 500$, (b) $\epsilon_m = 78.4$, and (c) $\epsilon_m = 2$.

In figure 4.9 shows that when decrease salt concentration the radial distribution between macroion and anion decreases because of multivalent counterions adsorption on the stern layer, but at high concentration at $\beta = 3$ and 4 the macroion become overcharged and their apparent charge has the opposite sign, so the ions correlation with macroion change, the coions expel the multivalent counterions and take their place. This can be explained qualitatively by this behavior in terms of the self-energy of one point charge immersed in a medium that has a different dielectric constant than the surrounding. The self-energy of a charged point particle in these conditions is given by

$$u_{self} = -\frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + \varepsilon_s} \frac{e_0^2}{4\pi\varepsilon_0\varepsilon_s} \frac{Z^2}{x}$$

where x is the perpendicular distance from the dielectric discontinuity to the position of a point charge of valence Z (or charge Ze₀), ε_s the dielectric constant of the medium in which the charged particle is located, and ε_m the macroion dielectric constant.

As a result, the ionic self-energy is positive if $\varepsilon_m < \varepsilon_s$. This can be associated with a repulsive interaction between the charged particle and the dielectric interface. On the contrary, if $\varepsilon_m > \varepsilon_s$, then the ionic self-energy is negative and the interaction between the charged particle and the dielectric interface becomes attractive.

Quantitatively, enhanced these are effects when the interactions with the images of other charges due to the spherical dielectric. However also observe that the magnitude of the self-energy of a charged point particle grows as the square of its valence of counterions. Thus, the behavior observed in the case of monovalent ions then trivalent should be exacerbated for the pentavalent cations.


Figure 4.10: Examples of distribution of counterions and the ions that come from the salt around macroion surface for ($\beta = 1$, 60 cations and 60 anions), inside the spherical cell, monovalent salt, when: a) $\epsilon_m = 2$, b) $\epsilon_m = 78.4$, and c) $\epsilon = 500$.

Figures 4.10 displays the distribution of counterions around macroion in presence of monovalent salt ions (cations and anions) around surface of macroion inside spherical cell, at indicated values of ϵ m and β , it is pure that the accumulation of counterions near macroion surface increases rapidly when ϵ m increases at the same β . The number of cations and anions increases when β increases.



Figure 4.11: Examples of distribution of counterions and the ions come from the salt around macroion surface for ($\beta = 1$, 20 cations and 60 anions), inside the spherical cell, trivalent salt, when: a) $\epsilon_m = 2$, b) $\epsilon_m = 78.4$, and c) $\epsilon = 500$.

Figures 4.11 displays the distribution of counterions around macroion in presence of trivalent salt ions (cations and anions) around surface of macroion inside spherical cell, at indicated values of ϵm and β , it is pure that the accumulation of counterions near macroion surface increases rapidly when ϵm increases at the same β . The number of cations and anions increases when β increases.



Figure 4.12: Examples of distribution of counterions and the ions come from the salt around macroion surface for ($\beta = 1$, 12 cations and 60 anions), inside the spherical cell, pentavalent salt, when: a) $\varepsilon_m = 2$, b) $\varepsilon_m = 78.4$, and c) $\varepsilon = 500$.

Figures 4.12 displays the distribution of counterions around macroion in presence of pentavalent salt ions (cations and anions) around surface of macroion inside spherical cell, at indicated values of ε_m and β , it is pure that the accumulation of counterions near macroion surface increases rapidly when ε_m increases at the same β . The number of cations and anions increases when β increases.



Figure 4.13: Integrated charge number at r from the center of the macroion, with monovalent salt at indicated values of macroions dielectric constant, when: a) $\beta = 0.3$, b) $\beta = 1$, c) $\beta = 3$, and d) $\beta = 4$.

Figure 4.13. Shows that when we add salt concentration at monovalent salt, when increase macroion dielectric constant increase the integrated number, and the charge inversion do not occur at all β concentrations, also it clear show integrate number P(r) increase when increase β , because an increasing number of cation and anions.

At the last two values of β , the total charge increases and reaches zero only at the cell boundary, in all the macroions dielectric constant the charge shows a sharp drop to zero within an extended

area almost between 80 Å < r <100 Å, and 70 Å < r < 100Å, when β =3, and 4 respectively. That means it is close to zero between these values of r.



Figure 4.14: Integrated charge number at r from the center of the macroion, with trivalent salt at indicated values of macroions dielectric constant, when: a) $\beta = 0.3$, b) $\beta = 1$, c) $\beta = 3$, and d) $\beta = 4$.

Figure 4.14 shows the integrated charge number, in presence of trivalent salt at different macroions dielectric constant values, From figure 4.14 the integrated charge number in case of adding trivalent salt increase by increasing the dielectric constant of macroions,

Charge inversion does not happen at 24Å, in all β values but, occurs when r is higher than 24.5, and the first two values of $\beta = 0.3$ and 1 in all macroions dielectric constant, the charge inversion does not happen. But in the case of $\beta = 3$, and 4 the charge inversion occurs at all macroions dielectric constant.

Figure 4.14. it clear shows Integrate number P(r) increases when the increase β , because of the increasing number of ions around the macroion, so the increasing ions quantity do the sign inversion of charge change from negative to positive which means the macroion is overcharged that accumulate around macroion surface.

At the last two values of β , the total charge decays monotonically and reaches zero only at the cell boundary, in all the macroions dielectric constant the charge shows a sharp drop to zero within an extended area almost between 50 Å < r <80 Å. That means it is close to zero between these values of r, then the accumulated charge number starts to increase gradually when 80 Å < r < 98Å.

At r = 98.5 Å it back to zero up to the spherical cell boundary, close to the cell boundary, the cation charge (+3) which originates from repulsion between the charge inverted macroions (from negative to positive) and cations. As the results in the article of (Lobaskin and Qamhieh, 2003).



Figure 4.15: Integrated charge number at r from the center of the macroion, with pentavalent salt at indicated values of macroions dielectric constant, when: a) $\beta = 0.3$, b) $\beta = 1$, c) $\beta = 3$, and d) $\beta = 4$.

Figure 4.15. it clear shows integrate number P(r) increase when increase β , and shows increase P(r) when increasing the ε_m value of macroions, and shows the effect of adding pentavalent salt on the integrated charge of the macroion within a distance of r inside the spherical cell and the happening of charge inversion.

Charge inversion does not occur at the first two values of $\beta = 0.3$ and 1 at all values of macroions dielectric constant. As in monovalent, and trivalent salt. But when β increased to 3, the sign of the

charge is changing from negative to positive that means the macroion is overcharged and charge inversion occurred in this case, charge inversion occurs at all macroions dielectric constant, at r = 24Å, when $\beta=3$, P(r) = 16, 16.2, and 16.8. when $\epsilon m = 2$, 78.4, and 500, respectively (From table 4.1).

At the last two values of β , the total charge decays monotonically and reaches zero only at the cell boundary, in all the macroions dielectric constant the charge shows a sharp drop to zero within an extended area almost between 60 Å < r <80 Å. That means it is close to zero between these values of r, then the accumulated charge number starts to increase gradually when 80 Å < r < 98Å.

At r = 98.5 Å it back to zero up to the spherical cell boundary, close to the cell boundary, the cation charge (+5) which originates from repulsion between the charge inverted macroions (from negative to positive) and cations. As the results in the article of (Lobaskin and Qamhieh, 2003) at macroion dielectric constant =78.4.



Figure 4.16: Electrostatic potential of EDL $\varphi(r)$, with monovalent salt at indicated values of macroions dielectric constant, when: a) $\beta = 0.3$, b) $\beta = 1$, c) $\beta = 3$, and d) $\beta = 4$.

Figure 4.16 represents the electrostatic potential of the macroion EDL for the systems at different concentrations of monovalent salt. From Figure 4.16 we can see that the absolute values of electrostatic potentials of the systems decrease by increasing the value of β , the value of electrostatic potential $\phi(\mathbf{r})$ keeping as a negative value at all β values, and the charge inversion of the macroion charge does not occur at all cases, and increase when increase macroions dielectric constant.



Figure 4.17: Electrostatic potential of EDL $\varphi(\mathbf{r})$, with trivalent salt at indicated values of macroions dielectric constant, when: a) $\beta = 0.3$, b) $\beta = 1$, c) $\beta = 3$, and d) $\beta = 4$.

Figure 4.17 shows that the electrostatic potential of the macroion EDL for the systems at different concentrations of trivalent salt. From Figure 4.17 we can see that the absolute values of electrostatic potentials of the systems decrease by increasing the value of β , keeping the value of electrostatic potential $\varphi(\mathbf{r})$ as a negative one, while the value becomes positive for $\beta > 1$, which reflect the charge inversion of the macroion charge, and increase when increase macroions dielectric constant.



Figure 4.18: Electrostatic potential of EDL $\varphi(\mathbf{r})$, with pentavalent salt at indicated values of macroions dielectric constant, when: a) $\beta = 0.3$, b) $\beta = 1$, c) $\beta = 3$, and d) $\beta = 4$.

Figure 4.18 represents the electrostatic potential of the macroion EDL for the systems at different concentrations of pentavalent salt. From Figure 4.18 we can see that the absolute values of electrostatic potentials of the systems decrease by increasing the value of β , keeping the value of electrostatic potential $\varphi(\mathbf{r})$ as a negative one, while the value becomes positive for $\beta > 1$, which reflect the charge inversion of the macroion charge, and increase when increase macroions dielectric constant.

Electrolyte valence	В	δ(mv) at r= 24 Å		
		$\varepsilon_m=2$	$\varepsilon_m = 78.4$	ε _m =500
1:1	0	-123	-118	-109
	0.3	-103	-102	-99
	1	-88	-87	-86
	3	-68	-67	-66
	4	-61	-65	-59
3:1	0	-123	-118	-109
	0.3	-85	-84	-82
	1	-11	-9	-10
	3	11	11	10
	4	12	14	14
5:1	0	-123	-118	-109
	0.3	-87	-88	-88
	1	2	1.4	-0.2
	3	43	45	43
	4	41	41	43

Table 4.2 Zeta potential $\delta(mv)$ at r=24 Å for system 60:1, with different electrolyte at $\beta = 0, 0.3, 1, 3, and 4, at different macroion dielectric constant.$



Figure 4.19: The electrostatic potential (zeta potential) $\delta(mv)$ at indicated values of β as a function of macroion's dielectric constant for the 60:1 system., at different salt concentrations, a) 1:1, b) 3:1 and c) 5:1 electrolyte.

The charge inversion of the macroion is clear also in Figure 4.19, which represents the electrostatic potential of the macroion EDL for the 60:1systems with different concentrations of 1:1,3:1, and 5:1 salt. From Figure 4.19 we can see that the absolute values of zeta potentials of the systems decrease by increasing the value of salt concentrations, keeping the value of electrostatic potential

as a negative for monovalent salt (as figure 4.19 a), while the value of electrostatic potential becomes positive for trivalent and pentavalent salt the valence of cations (counterions) increases (as figure 4.19 b, and c), when the salt concentration increase (β increase), a sign inversion of the electrostatic occurs at high concentrations for the macroions with the highest dielectric constant.



Figure 4.20: The ratio of effective macroion charge Z_{eff} to Z_M as a function of β at indicated values of the salt valance, with a) 2, b) 78.4, and c) 500 macroion dielectric constant.

Figure 4.20 shows the ratio of effective macroion charge Z_{eff} to Z_M as a function of β in presence of monovalent, trivalent, and pentavalent salt, at different values of macroion dielectric constant. It is clear that the effective charge of macroion decreases by values from positive to negative gradually until reaches zero at $\beta = (0 \text{ to } 1)$, and decreases values when increasing salt valance.

At pentavalent salt for all macroions dielectric constant, when β is greater than 1, the effective macroion charge Z_{eff} starts to increase in the negative region at all ε_m , which means that charge inversion occurs strongly in this case.

 Z_{eff}/Z_M starts from about 0.35 for all the systems and all dielectric constant of macroions, at low added salt, and then decreases orderly. The effective charge changes its sign for pentavalent salts, at all macroion dielectric constant. While Vladimir's results at dielectric constant 78.4 Z_{eff}/Z_M starts from about 0.3 for all the systems at low added salt, and also decrease orderly, these results when compare with Vladimir's results have been close to each other at the same conditions, but the slight difference is due to change in the input file.

The effective charge slow dependence on salt content is due to a logarithmical increase in counterion entropy with counterion number density. For dilute and deionized systems, where the effective charge is far from its saturated value, the drop in effective charge with salt concentration, for $\beta < 1$, is typical. The ionic double layer saturates at increasing monovalent salt concentrations, $\beta > 1$, and Z_{eff}/Z_M begins to rise with salt concentration toward unity. Due to the failure of the inflection point criterion in this location, we were unable to notice this upturn. See the reference (Vladimir and Khawla, 2003) for further information.

Also due to figure 4.8 we can see at low macroion dielectric constant, the Z_{eff}/Z_M is that higher value than high macroion dielectric constant, because the absolute value of Z_{eff} increase at low macroion dielectric constant while Z_M is constant -60



Figure 4.21: Reduced electrostatic energy as a function of β , at different salts monovalent salt, trivalent salt, and pentavalent salt at macroions dielectric constant (a) 2, (b) 78.4, and (c) 500, respectively.

Figure 4.21 shows the numerical results from the thermodynamic properties of the multivalent electrolytes as a function of the salt concentration. we plotted the reduced electrostatic energy of the solution U/NK_BT , where N is the total number of the ionic species, K_B is the Boltzmann constant.

Because of the strong attraction between the macroions and counterions, the total potential energy is negative for monovalent, trivalent, and pentavalent salts and at all concentrations, but its values fall as the salt content increases due to the increased number of particles. The inflection point was found to be at $\beta = 0.3$. All of the curves have similar forms with variable curvatures, with a practically constant motion from $\beta = 0$ to 0.3 on each curve, then gradually increasing in the negative area for all values of β .

Chapter Four

Conclusion and Future Work

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Conclusions and Future Work

The study focuses on the effect of macroions dielectric constant on macroions charge inversion and electric double layer properties, specifically changing macroions dielectric constant, by changing the radius of counterions (size of counterions), changing models of systems (macroion charges), and the concentration of multivalent salt, monovalent (1:1), trivalent (3:1), and pentavalent (5:1).

When the dielectric constant of a macroion grows, and the size of counterions decreases, the concentration of counterions around the macroion surface increases in non-salt fluids. In the case of increased macroion concentrations, the electrostatic contact between the macroion and the counterions becomes stronger. Because a low macroion dielectric constant causes counterions to move away from the macroion, the attraction between macroions and counterions is reduced. Furthermore, reducing the size of counterions leads to the accumulation maxima moving to the left (the distance between macroion and counterions (r) decreases), increasing the values of these maxima. This is explained by the increased electrostatic contact between macroions and counterions and counterions as they got closer together.

When the macroion dielectric constant is increased in solutions with monovalent, trivalent, and pentavalent salts, the concentration of counterions around the macroion surface increases, also at the same macroion dielectric constant accumulation increases when the salt valence increases generally.

Accumulation of salt cations around the macroion surface grows at the same rate as the macroion dielectric constant increases, and increases when the macroion dielectric constant increases. Furthermore, as ε_m grows, RDFs between macroion and salt anions become higher, and the maximal concentration of anions around the macroion becomes closer to the surface.

When the dielectric constant of macroions increases, the zeta potential and surface potential of the system without salt increase linearly (in negative values), When the radius of the counterion decreases and the dielectric constant of macroions is increased.

Finally for systems with salt, when increasing the concentration of ions β , zeta potential starts to be positive at $\beta = 1$ with trivalent and pentavalent salts which means that charge inversion occurs in these cases. Whereas the surface potential remains negative at all values of β and salt valence.

Future works:

We predict that additional results could be acquired in the future to study different properties of EDL structure as we can change the dielectric constant of macroions and dielectric constant of surrounding (solutions) by using other conditions such as change temperature, and by adding different types of salt at different concentrations. Also, we can change the size of the counterion, the radius of macroion, and the radius of the spherical cell.

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العنوان: الجهد الكهربائي لثابت السماحية للأيون الكبير في المحلول

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الملخص

تمت دراسة أثر تغيير الأيون الكبير (macroion) من خلال قيمة ثابت العازلية الكهربائية (ε_m) في المحلول الذي له ثابت سماحية ثابتة (dielectric constant of solution ε_s) على ظاهرة الإنقلاب الشحني (charge inversion) وكذلك على خصائص(EDL) باستخدام طريقة محاكاة

(Monte Carlo simulation). بحيث تم تمثيل النظام الكروي (spherical cell condition) لكل من الأيون الكبير (macroion) والأيونات الصغيرة متعاكسة الشحنة (counterions) على شكل كرات (60:1) ، (60:2) ، (60:3) ، (60:4) ، (60:5) أيضًا (1: 10) ، (80:1) ، و (80:2) ، وتغيير نصف قطر الأيونات الصغيرة (R_c) ، وإضافة الملح (ملح احادي (1:1)، ملح ثلاثي (3:1)، وملح خماسي(5:1) بتراكيز مختلفة على إنعكاس الشحنة (EDL) في ظروف (2011) وخصائص الطبقة الكهربائية المزدوجة (EDL) في ظروف الخلية الكروية.

surface) في المحاليل التي لا تحتوي على الملح، لقد وجد أن القيم السالبة لجهد زيتا وكذلك قيمة جهد السطح (surface) تزداد عندما يزداد ثابت السماحية للأيون الكبير (ϵ_m) ، ويزيد أيضًا عند زيادة شحنة الأيون الصغير (z_c). بالإضافة إلى ذلك، عند تقليل نصف قطر الأيون الصغير (z_c) ، يزيد تراكم الأيونات الصغير (z_c). بالإضافة إلى ذلك، عند تقليل نصف قطر الأيون الصغير (z_c) ، يزيد تراكم الأيونات الصغيرة (z_m) ، ويزد النظام (شحنة الأيون الكبير (z_m) ، ويزو تراكم الأيونات الصغير (z_m) ، يزيد تراكم الأيونات الصغيرة (z_m) ، يزيد المحادي المحادي الأيونات الصغيرة (z_m) ، يزيد تراكم الأيون الكبير (z_m) ، وعند زيادة النظام (شحنة الأيون الكبير (z_m)) والأيون الصغيرة (z_m) ، يزيد التراكمات.

بالإضافة إلى ذلك فقد تمت دراسة المتغيرات في حالة إضافة ملح إلى المحلول، عند استخدام عدة قيم لتركيز الملح (ملح أحادي وثلاثي وخماسي التكافؤ) في النظام (60:1) ، وجد أن القيم السالبة لجهد السطح

(surface potential) تزداد مع زيادة (β).

بالإضافة إلى ذلك، يحدث إنعكاس الشحنة (charge inversion) بوضوح عند القيم العالية لتركيز ات الملح. بحيث يز داد عدد الأيونات الملحية بشكل كبير مع زيادة (β) ، وكذلك تز داد قيمة جهد زيتا (zeta potential) ويحدث انعكاس للشحنة (charge inversion) على سطح الأيون الكبير (macroion) عند زيادة شحنة الملح عند نفس التركيز (β).