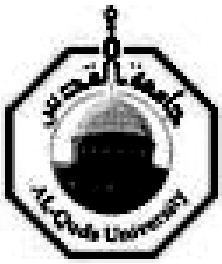

Deanship of Graduate Studies

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Interaction Between Charged Macroions In Electrolyte Solution

Mowafaq Khaled I. Hoshieh

M.Sc Thesis

Jerusalem – Palestine

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By

Mowafaq Khaled I. Hoshieh

B.Sc in Physics from Al-Quds University

Palestine

Supervisor

Dr. Khawla Qamhieh

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College of Science and Technology

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Thesis Approval

Interaction Between Charged Macroions In Electrolyte Solution

By:

Student Name: Mowafaq Khaled I. Hoshieh

Registration No: 20211610

Supervisor: Dr. Khawla Qamhieh

Master thesis submitted and accepted, Date: / / 2009

The names and signatures of the examining committee members are as follows:

1. Dr.Khawla Qamhieh (Head of committee) signature
2. Dr.Imad A.Barghouthi (Internal examiner) signature
3. Dr.Wael karain (External examiner) signature

Jerusalem – Palestine

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Dedication

To Prophet Mohammad Peace Be upon him.....

To my father who is engraved in my memory .....

To my mother.....

DECLARATION

I certify that this thesis, which is submitted for the degree of master, is the result of my own research, except where otherwise acknowledged, and that this thesis or any part of the same has not been submitted for a higher degree to any university or institution.

signed:

Mowafaq Khaled I. Hoshieh

Date: / / 2009

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Abstract

Interactions between two like-charged and unlike-charged Macroions in the presence of their counterions with various amount of simple 1:3 salt confined into a cylindrical cell have been investigated by Monte Carlo simulations. The mean force as a function of Macroion separation has been determined. Without additional salt, a strongly repulsive force was obtained for the 60:1 system, consistent with a stable solution of Macroions. At a trivalent counterion-to–Macroion charge ratio $\beta \approx 0.4$, the mean force became attractive at short separation, but stayed a substantialy repulsion at longer separations. For all systems the attractive However, at stoichiometric amount of trivalent counterions, no long-range repulsion remained and the attraction became substantial. In excess of salt, the magnitude of the attractive force was reduced. For systems with unlike-charged macroions, the attractive force is less than that with like-charged macroions. The attractive component of the mean force originates from spatial correlations between counterions residing near different Macroions and is not captured by mean-field theories such as Poisson-Boltzmann equation or any of its simplifications. The observed sequence of mean-forces are consistent with recent experimental observations on aqueous solution on SDS micelles as $Al\left(NO_3\right)_3$ is added, demonstrating evidence of attractive forces appearing between like-charged colloids induced by multivalent counterions in aqueous solutions.

In this study we were use Monte Carlo simulations, it is easiest to work in the canonical ensemble, just moving particles, not bothering whether the internal energy is changing. We could still just randomly sample the phase space, and calculate the weight of each sampled point. This is not very efficient, since there are usually only few configurations that significantly contributed to the average. It is possible to visit the configurations corresponding to their weight. This method is called the Metropolis MC method and the algorithm was first introduced in 1953 by Metropolis, Resenbluth, Teller, and Teller (6).

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List of Definitions

Colloids :any particles which has dimension between 10Å and 10^-6 m (1µ m) .

Surfactant: material that can reduce the surface tension of water when used in very low concentrations .

Micro emulsion :a mixture of water , water insoluble and water transparent liquid.

Physio-chemical :The physical characteristics and chemical composition of a particle in water like particle size , surface charge , hydrophobicity and solvent effects ….etc .

Primitive model : model which both ions and solvent molecules are soft core spheres and the polar nature of the solvent is represented implicitly as a background with a given dielectric constant .

Pmf u(r) : the potential of mean force .

Markov chain : is a sequence of random values whose probabilities at a time interval depends upon the value of the number at the previous time
.

Coion: any of the small ions entering a solid ion exchanger and having the same charge as that of the fixed ions .

Stochastic method : A method that system's subsequent state is determined both by process's prediclable actions and by a random element .

Molsim : is the running program that used, work under unix .

List of Abbreviations

DLVO theory: Derjaguin, Landau, Verwey, and Overbeek theory

rdf"s: radial distribution function

$Z_j = 1$:monovalent counterions

$Z_j = 2$ divalent counterions.

$Z_j = 3$ trivalent counterions

β : Trivalent counterion to Macroion charge ratio.

$F_{ideal}(r)$: Ideal component of the mean force.

$F_{elec}(r)$: Electrostatic component of the mean force.

$F_{hs}(r)$: Hard-Sphere component of the mean force .

SDS micelle: sodium Dodecyl Sulfate micelle

MC: Monte Carlo

NVT: Canonical Ensemble, constant number of particles (N), temperature (T), and volume (V) .

التفاعل بين الايونات في المحاليل الكهرلية

إعداد:موفق خالد إبراهيم الحوشية

إشراف:الدكتورة خولة قمحية

الملخص:

ان طبيعة قوى الترابط بين الايونات ذات الحجم الكبير(Macroions)والتي يمكن ان تكون متشابهة او مختلفة في نوع الشحنة وذلك بوجود الايونات الاصغر حجماً ، والمختلفة عن شحنة الايونات كبيرة الحجم والتي تسمى(Counterion) ، بالاضافة الى تأثير وجود الملح الثلاثي الذرية، يمكن التعرف عليها بواسطة طريقة محاكات الـ Monte-Carlo.

فقد تم معرفة مقدار القوة بين هذه الايونات الكبيرة نسبياً ، وكيفية تغيرها بتغير المسافة بين الايونات. فعند عدم وجود الملح الثلاثي الذرية فان هذه القوة تكون قوة تنافر بين هذه الايونات المتشابهة . ولكن مع بدء اضافة هذا الملح الثلاثي الذرية وبالذات عندما تكون نسبة شحنة الملح الثلاثي المضاف الى شحنة الايونات كبيرة الحجم (Macroions)والتي تعرف بـ β تساوي 0.4 ، فان طبيعة القوة بين الايونات الكبيرة تبدأ بالتحول من قوة تنافر الى تجاذب لكنها تبقى تتأثر بتغير المسافة بين الايونات. ولكن عند زيادة النسبة لتصبح $\beta = 0.8,1,6$ فان قوة التجاذب تصبح اكثر وضوحاً.

ان السبب في ظهور قوة التجاذب تلك هو التجمع المكاني للايونات الصغيرة الحجم(counterions)حول الايونات الكبيرة مما يعمل على عكس شحنة تلك الايونات وبالتالي تتحول القوة من تنافر الى تجاذب ، فقد ظهر هذا النوع من القوى في تجارب على محاليل ملحية تحتوي على مايسلات (SDS)عند اضافة ملح $AL(NO3)3$. مع العلم أنه لم يرد ذكره في Poisson-Boltzmann .

في هذا البحث تم دراسة والتعرف على هذه القوى بين تلك الايونات (Macroions)في انظمة تحوي ملح احادي الذرية (Zj=1)وثنائي الذرية (Zj=2)وثلاثي الذرية (Zj=3) وكذلك التعرف على تاثير اضافة ملح ثلاثي الذرية الى تلك الانظمة على مقدار قوة التجاذب هذه وذلك كعلاقة مع المسافة بين هذه الايونات الكبيرة ، وكان من نتائج البحث ان مقدار قوة التجاذب تلك تزداد مع زيادة تركيز الملح الثلاثي المضاف.