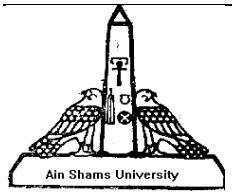



**Faculty of Education**
**Chemistry Department**

# Thermodynamics, Theoretical Studies and Biological Effect of Some Nano Metal Salts in Absence and Presence of Some Crown Ethers in Various Solvents

**Thesis Submitted**

**By**

**Sameh Gamal Sanad Bekhit**
**B.Sc., Ed. 2009-M.Sc. 2015**

**For**

## The Degree of
## Ph.D. of Teacher's Preparation in Science
## (Physical Chemistry)

**To**

**Chemistry Department**
**Faculty of Education**
**Ain Shams University**
**Cairo, Egypt**
**2018**

Ain Shams University
**Faculty of Education**
**Chemistry Department**

# Thermodynamics, Theoretical Studies and Biological Effect of Some Nano Metal Salts in Absence and Presence of Some Crown Ethers in Various Solvents

**By**

## Sameh Gamal Sanad Bekhit

**B.Sc., Ed. 2009-M.Sc. 2015**

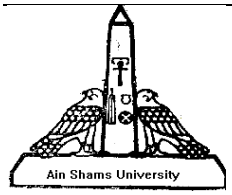
## Under the Supervision of:

**Prof. Dr. : Esam Arafa Hassan Gomaa**
Professor of Physical Chemistry, Department of Chemistry, Faculty of science, Mansoura University

**Dr. Laila Ibrahim Ali**
Assistant Professor of Physical Chemistry, Department of Chemistry, Faculty of Education, Ain Shams University

**Dr. Nevien Ahmed Salah**
Lecturer of Bio Chemistry, Department of Chemistry, Faculty of science, Mansoura University

**Dr. Shimaa Abd El Halim Hussein**
Lecturer of Physical Chemistry, Department of Chemistry, Faculty of Education, Ain Shams University




**Faculty of Education**
**Chemistry Department**

# Approval Sheet

Name of candidate: **Sameh Gamal Sanad Bekhit**

Degree: **Ph.D. of Teacher's Preparation in Science (Physical Chemistry)**

## Thermodynamics, Theoretical Studies and Biological Effect of Some Nano Metal Salts in Absence and Presence of Some Crown Ethers in Various Solvents

This Thesis has been approved by:

**Approval**

**Prof. Dr. : Esam Arafa Hassan Gomaa**
Professor of Physical Chemistry, Department of Chemistry, Faculty of science, Mansoura University

**Dr. Laila Ibrahim Ali**
Assistant Professor of Physical Chemistry, Department of Chemistry, Faculty of Education, Ain Shams University

**Dr. Nevien Ahmed Salah**
Lecturer of Bio Chemistry, Department of Chemistry, Faculty of science, Mansoura University

**Dr. Shimaa Abd El Halim Hussein**
Lecturer of Physical Chemistry, Department of Chemistry, Faculty of Education, Ain Shams University

**Prof. Dr. Mahmoud Mohamed Mashaly**
Head of the Chemistry Department
Faculty of Education
Ain Shams University

Ain Shams University
**Faculty of Education**
**Chemistry Department**

# Title Sheet

Name of candidate: Sameh Gamal Sanad Bekhit

Date of Birth: 22/3/1988

Place of Birth: Cairo

First University Degree: B.Sc.& Ed., May 2009 - M.Sc. 2015.

Name of University: Ain Shams

## ACNOWLEDGEMENT

I would like to express my sincere gratitude and indebtedness to **Prof. Dr. Esam Arafa Hassan Gomaa,** Professor of Physical Chemistry, Department of Chemistry, Faculty of science, Mansoura University, for all things, for his suggestions, continuous encouragement, valuable helping in interpretation of the results and to follow the progress of the work with keen interest and guidance. I would like to express my thanks to him for his efforts in this thesis.

Also, I would like to express deep thanks and gratitude to **Dr. Laila Ibrahim Ali,** Assistant Professor of Physical Chemistry, Department of Chemistry, Faculty of Education, Ain Shams University, for her continuous and valuable discussions during supervision, her suggestions, valuable helping in interpretation of the results and to follow the progress of the work.

Also, I would like to express deep thanks and gratitude to **Dr. Nevien Ahmed Salah,** Lecturer of Bio Chemistry, Department of Chemistry, Faculty of Science, Mansoura University, for her suggestions, valuable helping in interpretation of the results and to follow the progress of the work.

Also, I would like to express deep thanks and gratitude to **Dr. Shimaa Abd El Halim Hussein,** Lecturer of Physical Chemistry, Department of Chemistry, Faculty of Education, Ain Shams University, for her continuous and valuable discussions during supervision, her suggestions, valuable helping in interpretation of the results and to follow the progress of the work.

Also, I would like to express deep thanks and gratitude to **Dr. Asmaa Ismail Nabil,** Lecturer of Bio Chemistry, Department of Chemistry, Faculty of Education, Ain Shams University, for her valuable helping in chapter of biological activity.

I am truly thankful to **Prof. Dr. Mahmoud Mohamed Mashaly**, Head of the Chemistry Department, who introduced great kind facilities and encouragement.

Last but not the least, I remember with gratitude my friends and family members who were always a source of strength, support and inspiration.

*ABSTRACT*

# Thermodynamics, theoretical studies and biological effect of some nano metal salts in absence and presence of some crown ethers in various solvents

*Department of chemistry, Faculty of Education, Ain Shams University*

In this thesis, the solvation parameters, molar solubilities, free energies of solvation, solubility products, enthalpies and entropies of solvation were calculated for nano-copper sulphate, bulk copper sulphate, nano-cadmium chloride and bulk cadmium chloride at different temperatures (298.15, 303.15, 308.15 and 313.15K). in different concentrations of mixed solvents(ethanol–water).

The molar volume ($V_M$), Van der Waals volume ($V_W$) and electrostriction volume ($V_e$) for nano-copper sulphate, bulk copper sulphate, nano-cadmium chloride and bulk cadmium chloride at different temperatures were calculated.

From conductivity measurements, the association parameters (association constants, $\Delta G_A$, $\Delta H_A$ and $\Delta S_A$) in absence and in presence of ligands (12-crown-4, 18-crown-6 and 1,4-dioxane) were estimated at different concentrations of mixed solvents (ethanol– water) at different temperatures (298.15, 303.15, 308.15 and 313.15K).

Also, from conductivity measurements, the formation parameters (formation constants, $\Delta G_f$, $\Delta H_f$, and $\Delta S_f$) for nano-copper sulphate, bulk copper sulphate, nano-cadmium chloride and bulk cadmium chloride were estimated at different concentrations of mixed solvents (ethanol– water) at different temperatures (298.15, 303.15, 308.15 and 313.15K). The calculations show the ratios of metal : ligand will be 1:1 and 1:2.

From cyclic voltammetry measurements, diffusion coefficients of anode and cathode in absence and presence of ligands were calculated at different scan rate at 287.15 and 292.15K. The stability constants, $\Delta G$, $\Delta H$, and $\Delta S$ in presence of ligands (12-crown-4, 18-crown-6 and 1,4-dioxane) were estimated at 287.15 and 292.15K by using cyclic voltammetry.

Theoretical study of the electronic structure, nonlinear optical properties (NLO), and natural bonding orbital (NBO) analysis of 12-crown-4, 18-crown-6 and 1,4-dioxane were investigated using DFT- B3LYP method with 6-311G (d,p) basis set. The optimized structures of the ligands (12-crown-4, 18-crown-6 and 1,4-dioxane) are nonplanar as indicated from the dihedral angles. Natural bonding orbital (NBO) analysis have been analyzed

in terms of the hybridization of each atom, natural charges (Core, Valence and Rydberg), bonding and antibonding orbital's second order perturbation energy ($E^{(2)}$), exact configurations and Lewis and non-Lewis electrons. The calculated $E_{HOMO}$ and $E_{LUMO}$ energies of the title molecules (12-crown-4, 18-crown-6 and 1,4-dioxane) can be used to explain the charge transfer in the molecule and to calculate the global properties; the chemical hardness ($\eta$), softness ($S$) and electronegativity ($\chi$). The NLO parameters: static dipole moment ($\mu$), polarizability ($\alpha$), anisotropy polarizability ($\Delta\alpha$) and first order hyperpolarizability ($\beta_{tot}$) of the studied molecules have been calculated at the same level of theory promising electrical properties of the molecules (12-crown-4, 18-crown-6 and 1,4-dioxane) compared with the prototype para-nitro-aniline (PNA). The 3D plots of the molecular electrostatic potential (MEP) and electrostatic potential (ESP) for the title molecule were investigated and analyzed. Also the electronic absorption spectra were measured in ethanol and water solvents and the assignment of the observed bands has been discussed by TD-DFT calculations. The correspondences between calculated and experimental transitions energies are satisfactory.

The biological activity of dibenzo 18-crown-6 as an example of cyclic ether and the biological activity of dibenzo 18-crown-6 with nano and bulk copper sulphate complexes were studied.

**Key words:** Nano-copper sulphate, bulk copper sulphate, nano-cadmium chloride and bulk cadmium chloride carbonate, solvation, solubility, association constants, formation constants, free energy, emthalpy, entropy, volumes, cyclic voltametry, TD-DFT, theoretical investigation**,** NLO and NBO analysis, UV-spectra, MO-calculation, 12-crown-4, 18-crown-6 and 1,4-dioxane, biological activity, dibenzo 18-crown-6.

**Supervisors:**

**Prof.Dr. : Esam Arafa Hassan Gomaa**
Professor of Physical Chemistry, Department of Chemistry, Faculty of Science, Mansoura University.
**Dr. Laila Ibrahim Ali**
Assistant Professor of Physical Chemistry, Department of Chemistry, Faculty of Education, Ain Shams University
**Dr. Nivin Ahmed Salah**
Lecturer of Bio Chemistry, Department of Chemistry, Faculty of Science, Mansoura University.
**Dr. Shimaa Abd El-Halim Hussein**
Lecturer of Physical Chemistry, Department of Chemistry, Faculty of Education, Ain Shams University

# *CONTENTS*

## CHAPTER I
## INTRODUCTION and LITERATURE SURVEY

***CONTENTS***

***CONTENTS***

***CONTENTS***

| **LIST of ABBREVIATIONS** | |
|---|---|
| Gibbs free energy , (kJ $mol^{-1}$). | G |
| Entropy,(kJ $mol^{-1}$ $K^{-1}$). | S |
| Enthalpy, (kJ $mol^{-1}$). | H |
| Gas constant, ($J.K^{-1}mol^{-1}$). | R |
| Molar volume, ($cm^3.mol^{-1}$). | $V_m$ |
| Van der Waals volume,($cm^3.mol^{-1}$). | $V_w$ |
| Electrostriction volume, ($cm^3.mol^{-1}$). | $V_e$ |
| Activity coefficient. | $\gamma$ |
| Degree of dissociation. | $\alpha$ |
| Solubility product. | $K_{sp}$ |
| Molar solubility (g.mol/L.solvent). | $S_M$ |
| Mole fraction. | $X_s$ |
| Difference. | $\Delta$ |
| Free energy change of solvation (kJ $mol^{-1}$). | $\Delta G_s$ |
| Enthalpy change of solvation (kJ $mol^{-1}$). | $\Delta H_s$ |
| Entropy change of solvation (kJ $mol^{-1}$). | $\Delta S_s$ |
| Free energy change of association (kJ $mol^{-1}$). | $\Delta G_A$ |
| Enthalpy change of association (kJ $mol^{-1}$). | $\Delta H_A$ |
| Entropy change of association (kJ $mol^{-1}$). | $\Delta S_A$ |
| Free energy change of formation (kJ $mol^{-1}$). | $\Delta G_f$ |
| Enthalpy change of formation (kJ $mol^{-1}$). | $\Delta H_f$ |
| Entropy change of formation (kJ $mol^{-1}$). | $\Delta S_f$ |
| Observed molar conductance (S $cm^2.mol^{-1}$). | $\Lambda_{obs..}$ |
| Molar conductance (S $cm^2.mol^{-1}$). | $\Lambda_m$ |
| Limiting molar conductance (S $cm^2.mol^{-1}$). | $\Lambda_o$ |
| Molar conductance of the complex (S $cm^2.mol^{-1}$). | $\Lambda_{ML}$ |
| Fuoss-Shedlovsky factor. | S(Z) |
| Absolute Temperature. | T |
| Natural bonding orbital | NBO |
| Nonlinear optical properties | NLO |
| Chemical hardness | $\eta$ |
| Softness | S |
| Electronegativity | X |
| Dipole moment | $\mu$ |
| Polarizability | $\alpha$ |
| Anisotropy polarizability | $\Delta\alpha$ |
| First order hyperpolarizability | $\beta_{tot}$ |
| Para-nitro-aniline | PNA |
| Molecular electrostatic potential | (MEP) |
| Electrostatic potential | ESP |
| The total energy | $E_T$ |
| Energy of highest occupied molecular orbital | $E_{HOMO}$ |
| Energy of lowest unoccupied molecular orbital | $E_{LUMO}$ |
| Energy gap | $E_g$ |

| | |
|---|---|
| Stabilization energy | $E^{(2)}$ |
| Fock matrix element between i and j NBO orbital | $F_{(i, j)}$ |
| Valence lone pair orbital (n) on atom. | $LP_{(n)}$ |
| The ionisation potential | (**I** /eV), |
| Electron affinity | (**A** /eV) |
| Mean polarizability | $<\alpha>$ |
| Hyperpolarizability | $<\beta>$ |
| Wave length | $\lambda$ |