

An-Najah National University

Faculty of Graduate Studies

**SYNTHESIS OF SWELLABLE FUNCTIONALIZED
POLYMER MICROSPHERES AND STUDY OF
THEIR SELECTIVE OPTICAL SENSING
PROPERTIES**

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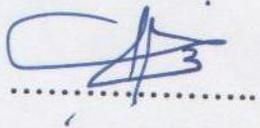
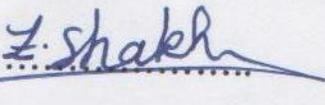
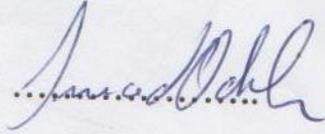
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DEDICATION

To my parents

To my brothers

To my sisters

And

my husband , my daughter

And

my frinds

Acknowledgment

Praise and thanks to Allah, the most merciful for assisting and directing me to the right path, without his help my effort would have gone astray. Special thanks are due to my research supervisors, Dr. Ibrahim Abu Shqair, Dr. Ziad Shakhsher for the opportunity to work with them in their research group. I am deeply grateful to them for their constant presence, their willingness to help at any time and their encouragement throughout this research project.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحت عنوان

Synthesis of swellable functionalized polymer microspheres and study of their selective optical sensing properties

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي من نتاج جهدي الخاص باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل أية درجة علمية أو بحث علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's name:

اسم الطالب:

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Date:

التاريخ:

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Synthesis of swellable functionalized polymer microspheres and study of their selective optical sensing properties

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Abstract

An optical chemical sensor based on polymer swelling and shrinking has been studied by way of optical transmission. Tris(2-aminoethyl)amine-polymer is synthesized. The sensing Polymer has been formed from poly(vinylbenzylchloride), Tris(2-aminoethyl)amine by a nucleophilic substitution reaction then, acidified with Chloroacetic acid.

The sensing element has been produced by dispersing the acidified Tris(2-aminoethyl)amine-polymer beads and entrapping them as microspheres in a hydrogel membrane formed by cross linking of poly(vinylalcohol) with glutaraldehyde .

The response is based on the interaction between the metal cations and the deprotonated acidified Tris(2-aminoethyl)amine functional group, whereby the swellable polymer undergoes shrinking as a result of neutralization of the negative charges of this functional group. This complex formation of a metal cation with acidified Tris(2-aminoethyl)amine functionality causes significant changes in the optical properties of the sensing element. Shrinking of the polymer microspheres resulted in a decrease in the optical transmission through the sensing

membrane. This is due to the increasing difference in the refractive indices between the microspheres and the dispersing hydrogel membrane.

This sensor showed good response particularly to copper ions. Also, there was insignificant response to pH 5 up to pH 8. In addition, there was no detectable response towards alkali, alkaline earth metals and other metal ions such as Ni^{2+} , Co^{2+} , Hg^{2+} , and Al^{3+} .

CHAPTER I

INTRODUCTION

The chemical sensor market has been projected to grow worldwide. Some of the primary motivations to develop chemical sensors are monitoring and control of environmental pollution; improved diagnostics for point of care medical applications; reductions in measurement time, sensor size, and power consumption; improvement in measurement precision and accuracy; and improved detection limits for homeland security, battlefield environments, and process and quality control of industrial applications.¹

1.1 Chemical sensors:

Chemical sensors can be defined as miniaturized devices that can deliver real-time and on-line information on the presence of specific compounds or ions even in complex samples.^{2, 3} And they provide continuous information about their physical, chemical, and biological environment.^{4, 5}

Chemical sensors transform chemical property generated from a chemical reaction of the analyte or physical property generated from physical property of the system studied into measurable signals, whose magnitude is normally proportional to the concentration of the analyte.⁶

Chemical sensors are made up of two basic units: a receptor part and a transducer.⁷

The transducer part is a device that converts energy which is carrying the chemical information about the sample into useful analytical signals. The receptor is the part of a sensor in which the chemical information is

converted into a form of energy which is then measured by the transducer.^{7,8}

An ideal sensor requires many characteristics:

fast response time, high sensitivity and selectivity, long life time, excellent reproducibility, provides a certain type of response directly related to the amount of the analyte present in the sample, no hysteresis, good signal to noise ratio, inexpensive, simple to operate, easily calibrated, reversible, small and can analyze nondestructively.^{5,9}

1.2 Classification of chemical sensors:

Chemical sensor can be classified according to the property to be determined as:

1.2.1 Mass sensors :

Changes of mass can be viewed as a general feature of the interaction of the chemical species with the sensor, so the mass sensor is defined as a device that relies on changes and disturbances of the mass of the surface of the sensor during interaction with chemicals. The signal will be obtained only if the interaction between the sensor and the basic species results in a net change of the mass of the chemically selective layer which is attached to the piezoelectric crystals which are used due to their small size, high sensitivity and stability. They are also inexpensive and available.⁷

The major advantages of mass sensors are their simplicity of construction and operation, light weight, and high sensitivity. They require low power and can be used for a broad range of compounds.¹⁰

The advantage of surface acoustic wave devices is its greatly designed flexibility and the fact that the sensing part of the device, the waveguide, is separate from the piezoelectric transducer/receiver. On the other hand, the physics is complex, which makes it difficult to obtain a general explicit relationship between the added mass and the change in the output.¹¹

1.2.2 Thermal sensors:

Thermal sensors are a class of chemical sensors that use the heat generated by a specific chemical reaction or adsorption as a source of analytical information. The general strategy of designing a thermal sensor is to place the chemically selective layer on the top of a thermal probe and measure the heat evolved in the specific chemical reaction which takes place in that layer, as the temperature of the sensing element or as the heat flux through the sensing element. Since the heat is evolved continuously, the thermal sensors are in a non equilibrium state and their signal is obtained from a steady-state situation.⁷

There are some requirements built into the operation of these sensors: in order for the sensor to interact with the chemical species it must exchange matter, this means that it should be a thermodynamically open system. Also in order to obtain a maximum response it should be as adiabatic (thermally insulated) as possible.

There are two thermal probes used for monitoring thermal process: thermistors and pyroelectric devices. Although thermopiles (thermocouples) sometimes are proposed as thermal transducers but their sensitivity is much lower. Thermistors are the most widely used because they are stable, inexpensive, small, chemically inert and sensitive.¹¹

1.2.3 Catalytic gas sensors:

These devices are conceptually similar to enzymatic transistors. Heat is liberated as a result of catalytic reaction taking place at the surface of the sensor and the related temperature change inside the device is measured.

On the other hand, the chemistry involved is very similar to that of high-temperature conductimetric oxide sensors. Catalytic gas sensors have been designed specifically for the detection of sub threshold concentrations of flammable gases in ambient air with the safety of mining operations in mind.¹¹

1.2.4 Electrochemical sensors:

Electrochemical sensors are the largest and the oldest group of chemical sensors. They are defined as devices which transform the effect of the electrochemical interaction analyte-electrode into a useful signal. Such effect may be stimulated electrically or may result in spontaneous interaction at zero-current condition.⁷

Compared to optical, mass, and thermal sensors, electrochemical sensors are especially attractive because of their remarkable detectability, experimental simplicity and low cost.⁵

They are divided by their mode of measurement into *potentiometric* (measurement of voltage), *amperometric* (measurement of current), and *conductimetric* (measurement of conductivity) sensors.

Electrochemistry implies the transfer of charge from an electrode to another phase which can be a solid or a liquid sample. During this process chemical changes takes place at the electrodes and the charge is conducted through the bulk of the sample phase. Both the electrode reaction and/ or the charge transport can be modulated chemically and serve as the basis of

the sensing process. There are some common rules which apply to all electrochemical sensors, the cardinal one being the requirement of *a closed electrical circuit*. This means that at least two electrodes constitute an *electrochemical cell*. From a purely electrical point of view there is a sensor electrode and *a signal return*.¹¹

1.2.4.1 Potentiometric sensors:

Potentiometric measurements are conducted under conditions of zero current.¹¹ Potentiometric sensors are the most widely spread since the early 1930s. These systems tend to be low in cost, simple to use, easily automated for rapid sampling, with low interference from matrix and can be applied to small volumes. These advantages make them an ideal choice for both clinical and industrial measurements where speed, simplicity and accuracy are essential. These sensors monitor circuit potential at zero current, There are three types of these devices: ion-selective electrodes (IES), coated wire electrodes (CWES), and field effect transistors (FETS).^{5, 7}

The most widely used potentiometric device is the pH electrode, it has been used for several decades to its advantages, such as simplicity, rapidity, nondestructive, low cost, applicability to a wide concentration range and has high selectivity for hydrogen ions.⁵

1.2.4.2 Amperometric sensors:

Amperometric sensors are devices monitoring the change in the current while the potential is kept constant, where as voltammetric sensors monitor the change in current while varying the applied potential. In this group of electrochemical sensors the information is obtained from current-concentration relationship.^{5, 6}

A common application for potentiometric and amperometric sensors is in water analysis. However, the sensitivity of amperometric sensors is better than potentiometric sensors.¹⁰

1.2.4.3 Conductimetric sensors:

A conductimetric sensor can be defined as a device that monitors conductivity changes.⁶ This sensor relies on the changes of electric conductivity of a film or a bulk material, whose conductivity is affected by the presence of the analyte, but it is non-selective. There are some characteristics that make conductimetric methods attractive, such as low cost, simplicity, no reference electrodes are needed and they give a rapid and easy determination of analyte.⁵

There are different types of conductimetric sensors, such as the polymer-absorption sensor which indicates the change in resistance in the conductive polymer electrodes when exposed to chemicals. The catalytic bead sensor which requires elevated temperatures to burn the chemical vapors (as hydrocarbon vapors) and change the resistance of an active element and metal-oxide semiconductor sensors which response to change in partial pressure of oxygen and requires elevated temperatures to induce the combustion of the chemical vapors that change the resistance of the semiconductor.¹⁰

1.2.5 Gas sensors:

In potentiometric gas sensors the change in potential is obtained from the interaction of electrically neutral gas molecules with the sensor. The sample can be in the gaseous or liquid phase. Potential difference implies charge separation, so there must be a mechanism which link the

primary inter-action of the electrically neutral gas to partitioning of ions or electrons at an interface within the sensor.¹¹

1.2.6 Ionic sensors:

Optical sensors for ions employ indicators, which exist in two different color forms depending on whether or not the ligand is bound to them. The use of colored indicators is one of the oldest principles of analytical chemistry and is used extensively in both direct spectroscopy and visual titrations. The indicator is usually confined to the surface of the optical sensor or immobilized in an adjacent layer. In that sense the oldest and most widespread optical sensor is a pH indicator paper (litmus paper), which is commonly used for rapid and convenient semiquantitative estimate of the pH of solutions.¹¹

1.2.7 Optical sensors:

Optical sensors and classical spectroscopic measurements employ the same equipment, but the arrangement of experiment itself is different. In spectroscopic measurements, the sample is generally placed in well-defined path of beam and the emerging radiation is captured by the detector. On the other hand, in optical sensors the beam is guided out of the spectrophotometer, allowed to interact with the sample, and then reintroduced into the spectrophotometer in either its primary or secondary form for further processing.¹¹

Optical sensors can be defined as devices that transform the change of optical phenomena, which are the result of an interaction of the analyte with the receptor part. The type of optical properties that should be available in chemical sensors include:⁷

1. Absorbance which is measured in a transparent and caused by absorptivity of the analyte itself or the reaction with suitable indicator.
2. Luminescence which is based on the measurement of the intensity of light emitted by chemical reaction in the receptor system.
3. Reflectance which is measured in non-transparent medium and usually using an immobilized indicator.
4. Fluorescence which is measured as the positive emission effect caused by irradiation.
5. Refractive index which is measured as result of change in solution composition.
6. Light scattering which is based on effects caused by particles of definite size present in the sample.
7. Optothermal effect which is based on a measurement of the thermal effect caused by light absorption.

1.2.7.1 Classification of optical sensors :

1.2.7.1.1 Optical sensors based on immobilized indicator:

Recent years have seen an increasing interest in the development of fiber optic chemical sensors (FOCS) for ions or molecules in industry, environment, food processing...etc, as they have a number of advantages over conventional system. The development of FOCS during recent years is related to two of the most important scientific advances of the 1960s, the laser technology (1960) and modern low-cost optical fiber (1960). So, during the late 1960s and early 1970s some of these optical fibers were used in the development of the first chemical sensors, then their applications have continued to spread to very different areas, particularly, environmental and industrial applications.^{12, 13}

These are optical sensors that employ indicator dye, which exist in two different color forms depending on whether or not the measured is bound to them. The interaction with the analyte is accompanied by a change in the absorbance or fluorescence, this mean that the indicator acts as a transducer for the chemical species that cannot be determined directly by optical means.¹³

These sensors involve the following steps. First is the use of optical fiber light from a spectrophotometer to a sample and back. The second is the use of immobilization as means of allowing a chemical reagent to be used on a continuous rather than on a one-time basis and allow to do chemistry on the sample in situ.¹⁴

Many indicators cannot be used in optical sensors because of unfavorable analytical wavelengths, poor photostability, low molar absorptivity or the need for additional reagent. In addition, most of them bind with the metal ion irreversibly or only at low or high pH so they cannot be used for continuous sensing at near neutral pH.¹⁵

A variety of methods for immobilizing indicators and attaching them to optical fibers have been employed including: coupling indicator to a polymer powder that is confined at the end of a fiber by a membrane, attaching porous glass to a fiber and using it as substrate for covalent indicator immobilization, covalently bonding polymer-bound indicator directly to the end of an optical fiber, embedding the indicator in a membrane that is attached to the end of fiber bundle and confining a thin layer of dissolved indicator behind a hydrophobic, gas permeable membrane.

After immobilization process, the group which is responsible for the chemical interaction is inaccessible to the analyte, so the immobilized

indicator prohibits the reversible response because of very strong binding of the analyte. There is much interest in the immobilization technique that prevents leaching of indicators and imparts a rapid response, reversibility and long lifetime to the sensor.^{16, 17}

Cross-linked poly(vinyl alcohol) (PVOH) is used as a substrate for immobilizing indicators used in fiber optic chemical sensor. Since PVOH has hydrophilic properties which are suitable for ion sensing and due to its ability to form very homogeneous film of high quality. It should be cross-linked in order to be useful for a wide range of applications.¹⁷

Some of the common cross-linking agents used for PVOH hydrogel preparation include glutaraldehyde, acetaldehyde and formaldehyde in the presence of acid like HCl which act as a catalyst.¹⁷

1.2.7.1.2 Optical sensor based on polymer swelling:

There is an interest in developing fiber-optic chemical sensors based on optical changes accompanying polymer swelling because they offer the improved robustness and calibration stability with low cost. In this sensing element a cross-linked polymer swells or shrinks as a function of analyte concentration, since changes in analyte concentration cause changes in the polymer size which affect the affinity of the polymer for external solvent, the intensity of light reflected into the optic fiber changes accordingly.¹⁸

Cross-linking prevents the polymer from dissolving in solvents. Instead, it absorbs solvent and swells to reach an equilibrium volume where the swelling forces due to the polymer solvation are balanced by the refractive force due to stretching of the chemical bounds in the polymer. The degree of swelling is dependent on the affinity of the polymer for the solvent and the extent of cross-linking. If the polymer is ionic, the electrostatic forces can contribute to swelling. The driving force for

swelling is the difference between the number of charges per unit volume in the polymer and the ionic strength of the external aqueous solution, so the solvent enters the polymer to equalize the change in densities inside the polymer.

As the ionic strength of the solution increase, the difference in charge density inside and outside the polymer decrease, so the driving force for the swelling will decrease.¹⁹

Polystyrene is chosen as a polymer substrate because it is thermally stable, mechanically strong and amenable to a wide variety of derivatization chemistries. One common approach is to chloromethylate styrene, then the chloromethyl group can undergo a variety of reactions with primary and secondary amines, but poly(vinylbenzyl chloride) is directly prepared to avoid a separate chloromethylation step which might cause extra cross-linking that reduces dramatically the swelling process. Also pores may be introduced by polymerizing styrene in the presence of an inert solvent which is called a porogen; this improves analyte access to the interior of the polymer. But the problem with polystyrene is that it has a glass transition temperature above the room temperature, so material based on polystyrene will develop cracks and eventually fall apart when subjected to the stress of repetitive swelling and shrinking. The toughness is improved by adding an elastomer or a plasticizer.^{20, 21}

Kraton G1652, a styrene-ethylene, butylene-styrene triblock copolymer is added as a toughness agent to prepare beads that can undergo multiple swelling and shrinking cycles without any observable mechanical deterioration.^{19, 20, 21}

Chemical sensing process involving bulk polymer swelling leads to mechanical problems:¹⁹

1. Swelling process introduces stress that can cause the polymer to crack or tear.
2. To incorporate the swellable material into a sensor it has been necessary to bind the polymer to a surface so it is held in a fixed position, so that it can only swell in the direction perpendicular to the surface.
3. Delamination it can result from the stresses that result from shear forces at polymer-substrate interface when the polymer swells.

These serious problems inhibit the development of a practical sensor based on polymer swelling. So a new approach is developed to minimize these problems in which the polymer microspheres are entrapped in a hydrogel membrane.¹⁹

Recently, Seitz et.al. and Shakhsher et.al developed an optical sensing element in which lightly cross-linked chemically derivatized polymer microspheres with dimensions of a few micrometers that are designed to swell and shrink as a function of analyte concentration (such as metal ions), then these microspheres are suspended in a hydrogel membrane which change its volume reversibly in response to change in environment conditions.²²

This chemical sensing is based on the changes in the optical properties of the membrane that accompany swelling and shrinking. In swelling, the refractive index of the microspheres become closer to that of the hydrogel resulting in a decrease in the membrane turbidity.²³

The most important advantages of this chemical sensing are:

1. It can be used at any wavelength including near-infrared used in fiber optic telecommunication.^{22, 23}
2. Since photoexcitation of an indicator is not required, they are resistant to photodegradation and leaching of indicator dye.^{22, 23}
3. They are not subject to electrical interference as are electrical sensors.²²
4. The polymer is free to swell uniformly in all direction rather than being confined on a surface, this enhances sensitivity and reduce mechanical stress within the polymer. So these materials undergo large number of swelling and shrinking cycles without degrading mechanically.²³
5. They are simple and inexpensive.²²
6. By formulating a swellable polymer as a microsphere the diffusion distance are reduced to get faster response time in the order of μ m.²³
7. Swelling and shrinking has minimal effects on the size of the hydrogel and doesn't generate enough force to affect adhesion on the substrate.²³

In these days a great deal of interest is directed towards developing chemical sensors particularly ion selective sensors based on polymer swelling.^{24, 25} A certain work has been done on the development of chemically selective sensors for analytical purposes.

In a previous work,²⁰ an optical chemical sensor based on polymer swelling was developed, in which the sensing polymer membrane was immobilized on a solid substrate at the end of an optical fiber. This type of sensor had some limitations. It swelled only in the direction perpendicular to the surface of the membrane. Also, shear forces at the polymer/substrate interface caused the sensing membrane to delaminate. Furthermore,

mechanical problems associated with swelling and shrinking forces were observed.

Recently,²⁵ these limitations were overcome by using swellable functionalized polymer microspheres with dimensions of the order of a few micrometers that were suspended and entrapped in a hydrogel membrane, such as polyvinyl alcohol cross linked with glutaraldehyde. These new types of sensing elements were used successfully at different wavelengths in the UV-Visible and near IR regions. The properly functionalized, lightly cross linked polymer microspheres underwent swelling as a result of repulsion between adjacent similar charges on the polymer backbone. This led to a higher percentage of water in the polymer, resulting in the decrease of the refractive index and hence a change in the optical properties of the polymer, as shown in figure 1.1. This change was monitored by measuring light transmission or reflection.

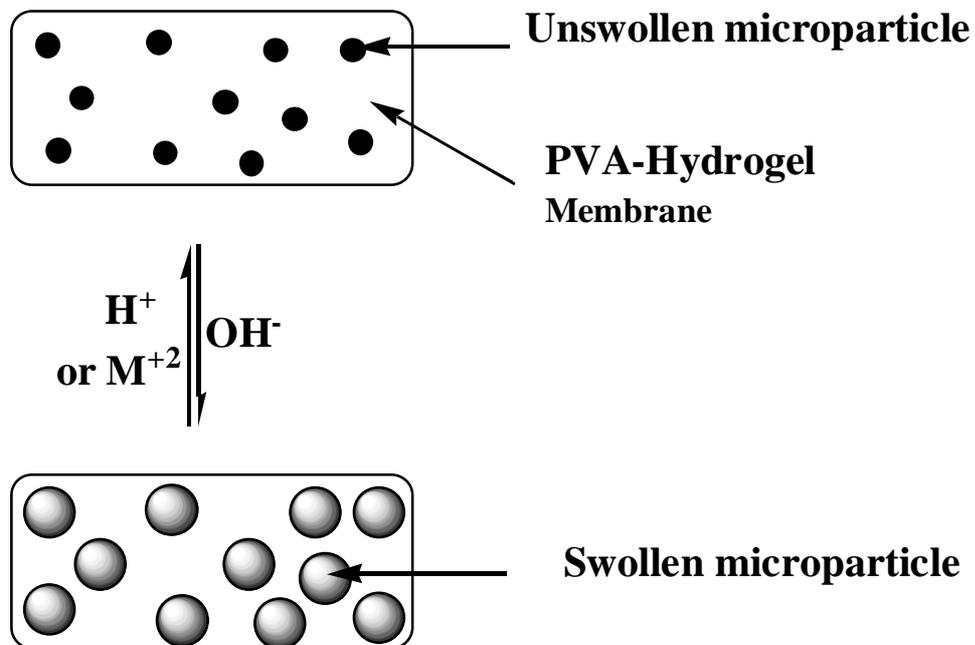


Figure 1.1: Schematic diagram of sensing response to pH and metal ions.

A good example of this technology is the membrane which is prepared by suspending aminated polystyrene microspheres in a hydrogel. Thus, lightly cross-linked poly (vinylbenzyl chloride)microspheres with one micrometer in diameter was aminated with diethanolamine, then the microspheres were suspended in a poly (hydroxyethylmethacrylate) (poly HEMA) hydrogel membrane. The resulting membrane is turbid because the refractive index of the microspheres is greater than that of the hydrogel. In acidic media the protonation of the amino groups led to swelling by introducing a positive charge onto the polystyrene backbone. This increased the affinity of the polymer for aqueous media, and thus the turbidity decreased.^{28, 29}

Swelling affects turbidity in two ways: by increasing microspheres diameters and reducing the refractive index of the microspheres so that it is closer to the refractive index of the hydrogel. Since hydrated poly HEMA is not affected by pH, so the observed changes in membrane turbidity are associated with the swelling and shrinking of the microspheres.

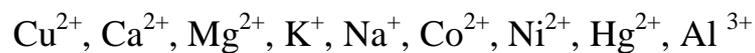
In another previous study,²² dicarboxylate functionalized polymer microspheres were prepared and their sensing properties were tested. The polymer exhibited good response to varying pH solutions and to solution of copper and calcium ions of different concentrations.

Another example of previous study,³⁰ the detection system based on two modified electrodes, each of them containing a chelating agent, as the chelator is able to capture the metal ion at very low concentrations. The system is able to differentiate eight metal ions(Al^{+3} , Fe^{+3} , Pb^{+2} , Hg^{+2} , Cu^{+2} , Ca^{+2} and Ag^{+})

1.3 Objectives:

In this we plane to construct a new sensing membrane made up of an acidified tris(2-aminoethyl)amine polymer microspheres entrapped in a cross-linked PVA hydrogel. The microspheres will be first synthesized, and then the sensing membranes optical properties studied, according to the following methodology:

1. Testing its response to different cations particularly:



2. Studing the response of different pH,s.
3. Studing the reproducibility of the membrane.
4. Test the response to different concentrations of the above cations.
5. Studing the response time.

Chapter II

EXPERIMENTAL

2.1 Reagents:

N,N-Dimethylformamide (DMF), Tris(2-aminoethyl)amine (TAA), Poly vinyl alcohol, and glutaraldehyde 5% by weight from Sigma-aldrich. Polyvinylbenzylchloride (PVBC) polymer was supplied by professor W.R.Seitz's group at University of New Hampshire, USA.

NaOH, KCl, NaCl, MgCl₂, and AlCl₃ from Frutarom. Chloroacetic acid, CaCl₂, and CoCl₂ from Riedel. CuSO₄ from Carlo Erba. EDTA, and HgCl₂ from Avacado. NiCl₂ from Alfa Aesar.

All solutions were prepared in deionized distilled water.

2.2 Apparatus:

Shimadzu UV-VIS-NIR SCANNING (UV-3101DC) spectrophotometer was used for absorption measurements. JENWAY (3510) pH Meter was used to measure pH. A Fourier transform infrared spectrophotometer (Testscan Shimadzu FT-IR 8000 series) was used to obtain IR-Spectra. TCC-CONTROLLER was used to control temperature. A transsonic 310 Sonicator was used to make the mixture uniform. Plastic cuvettes.

2.3 Procedure:

2.3.1 Preparation of the tested solutions:

The following solutions were prepared using deionized distilled water:

- a- ammonia buffer of different pH's (5-12).
- b- Different aqueous solutions of Cu^{2+} concentrations (1.0×10^{-6} up to 0.001M).
- c- Different solutions of 0.001M Cu^{2+} in different pHs (5-12).
- d- Aqueous solutions of different metal ions Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Co^{2+} , Ni^{2+} , Hg^{2+} , Al^{3+} of various concentrations (5.0×10^{-6} up to 0.008 M).

2.3.2 Synthesis of the acidified Tris(2-aminoethyl)amine polymer:

0.5g of dried PVBC polymer was soaked in a 3 drops of DMF for one week, then the mixture was filtered and suspended in Tris(2-aminoethyl)amine [TAA] for one week at room temperature with stirring. The produced mixture was filtered, and placed in an aqueous solution containing 1 M NaOH and 3 M chloroacetic acid and left for one week at room temperature. Finally, the mixture was washed with distilled water, and dried at room temperature for one week.

2.3.3 Preparation of the sensing element:

In order to prepare the sensing element, the polymer microspheres were dispersed in the hydrogel as follows: 10 mg of the derivatized polymer microspheres were soaked in a 3 drops of DMF for few minutes, then 1 ml of (5%) aqueous poly(vinylalcohol) solution in water was added

and the mixture put in asonicator until the polymer microspheres are dispersed and the mixture became uniform. Then, 80 microliters of a glutaraldehyde solution in water were added to the mixture and stirred for few seconds, followed by 80 microliters of 3M $\text{HCl}_{(\text{aq})}$ as a catalyst. The resulting mixture was mixed for 5 minutes.

(3-5) drops of the mixture were transferred and spread on the inner clear side of a cuvette and the sensing membrane is allowed to formulate and stick in position. The resulting sensing membrane was washed with and stored in distilled water.

2.3.4 Optical measurements:

The cuvette with the sensing element stuck on its inner sidewall was secured in the cell holder of a spectrophotometer, so that the membrane was positioned in the path of the light beam. Figure 2.1.

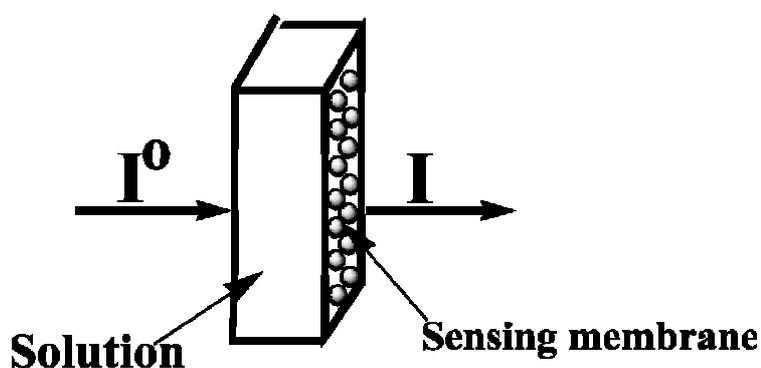


Figure 2.1: Diagram of optical sensing system.

The solution in the cuvette was changed using a disposable pipette, starting with the lower concentrations of analyte and proceeding to the higher ones. The change in turbidity of the sensing element as a function of analyte concentration was measured as absorbance.

All reading was taken at 25° C.

2.3.5 Testing the sensor response to pH:

Solutions of different pHs (5-12) were prepared, using ammonia buffer solutions. The solution in the cuvette was changed by using a disposable pipette, starting with the lower pH and proceeding towards higher ones, with an interval of 10 minutes between each spectrum run. The response of the sensor towards these buffer solutions was examined by recording the UV-Vis spectrum in the range (600-800) nm.

2.3.6 Testing the sensor response to metals :

The response to heavy metal cations of various concentrations was tested as follow. Different concentrations of aqueous metal cation solutions,

$5.0 \times 10^{-6} - 0.008$ M, of Co^{2+} , Ni^{2+} , Hg^{2+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and Al^{3+} were prepared.

The solutions of different concentrations were placed in the cuvette, one at a time starting with the lower concentration. Metal with an interval of 5 minutes, between each run. The response of the sensing element was obtained by monitoring the change in the absorbance spectrum in the range (600-800) nm.

2.3.7 Testing the reproducibility of the sensor response :

The reproducibility of the sensor response was evaluated by cycling between blank and 0.001M Cu^{2+} ions solution several times. Readings as turbidity absorbance at wavelength (800 nm) were taken after 5 minutes of introducing the solution in the cuvette. After each reading, Cu^{2+} ions were eluted by a saturated solution of EDTA and then washed extensively with distilled water until obtaining the blank reading.

2.3.8 Determination of the response time of the sensor:

The response time of the sensing element towards 0.001M of Cu²⁺ ions was obtained by measuring the change in absorbance with time, until steady state is reached.

2.3.9 Regeneration of the sensor:

After the sensor responded to a divalent metal cation, a saturated solution of EDTA was added, then followed by a basic buffer solution and finally washed successively with distilled water to regenerate the sensing element.

Chapter III

Results and Discussion

3.1 Identification of the acidified Tris-amine polymer:

The sensing polymer was formed from poly(vinylbenzylchloride), and Tris(2-aminoethyl)amine by a nucleophilic substitution reaction followed by acidification with Chloroacetic acid. Figure 3.1

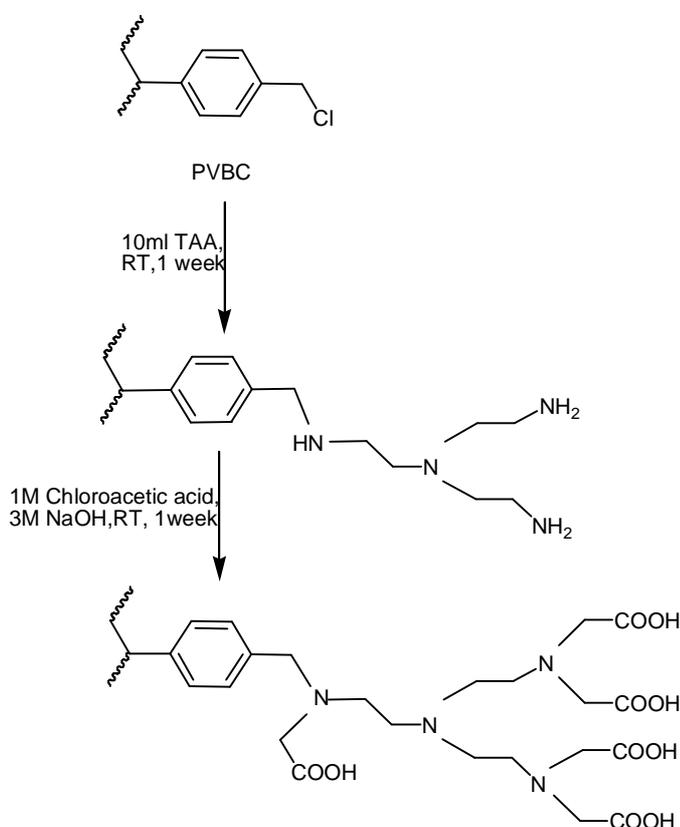


Figure 3.1: Synthesis of acidified Tris-amine polymer[ATAA] .

3.2 Formation of the sensing element:

The formation of the Tris-amine functional group on the polymer microspheres was determined by IR-spectra, by comparing the IR-spectrum of Poly vinylbenzylchloride with the IR-spectrum of the tris-amine polymer, the C-Cl peak at about 710 cm^{-1} has become less intense after

substitution with the amine, and carboxyl groups peak and -C=O peak appeared at about 1580 & 1380 cm^{-1} respectively. Figure (3.2 , 3.3).

The sensing element was formed by dispersing the acidified Tris(2-aminoethyl)amine-polymer beads and entrapping them as microspheres in a hydrogel membrane formed by cross linking of poly (vinylalcohol) with glutaraldehyde.

Acidified Tris-amine (ATAA) was chosen as a ligand because of it's;

1. Similarity to EDTA (common chelating agent for metal ion).
2. High stability in water.
3. Stable complex formation with metal ion. Since this functional group is similar to EDTA, which has formation constant(K_f) with $\text{Cu}^{2+} = 6.3 \times 10^{18}$.
4. Insensitivity to changes in pH particularly above 4.
5. Consideration as a highly selective ligand.

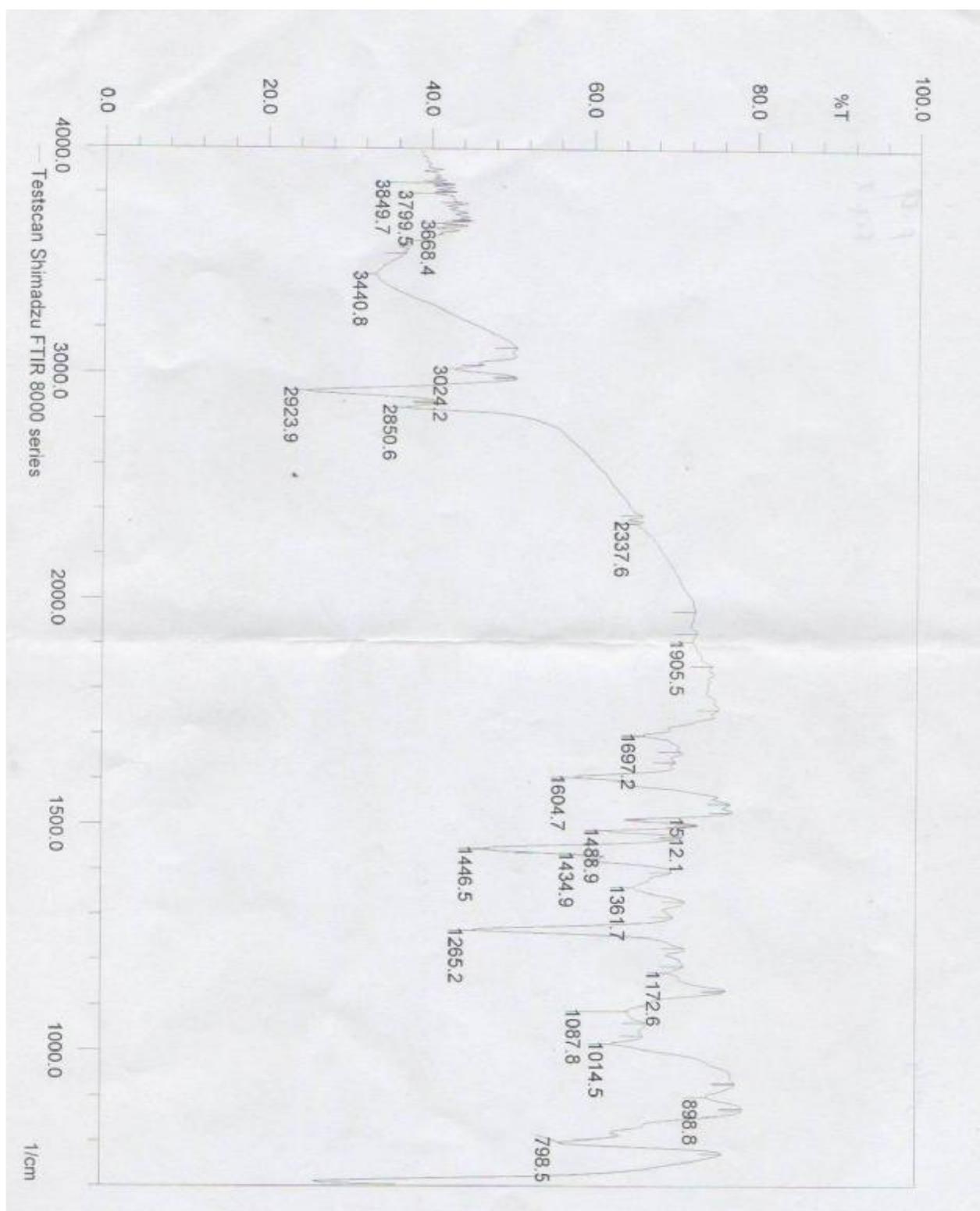


Figure 3.2: IR spectrum of Poly vinylbenzylchloride [PVBC] polymer

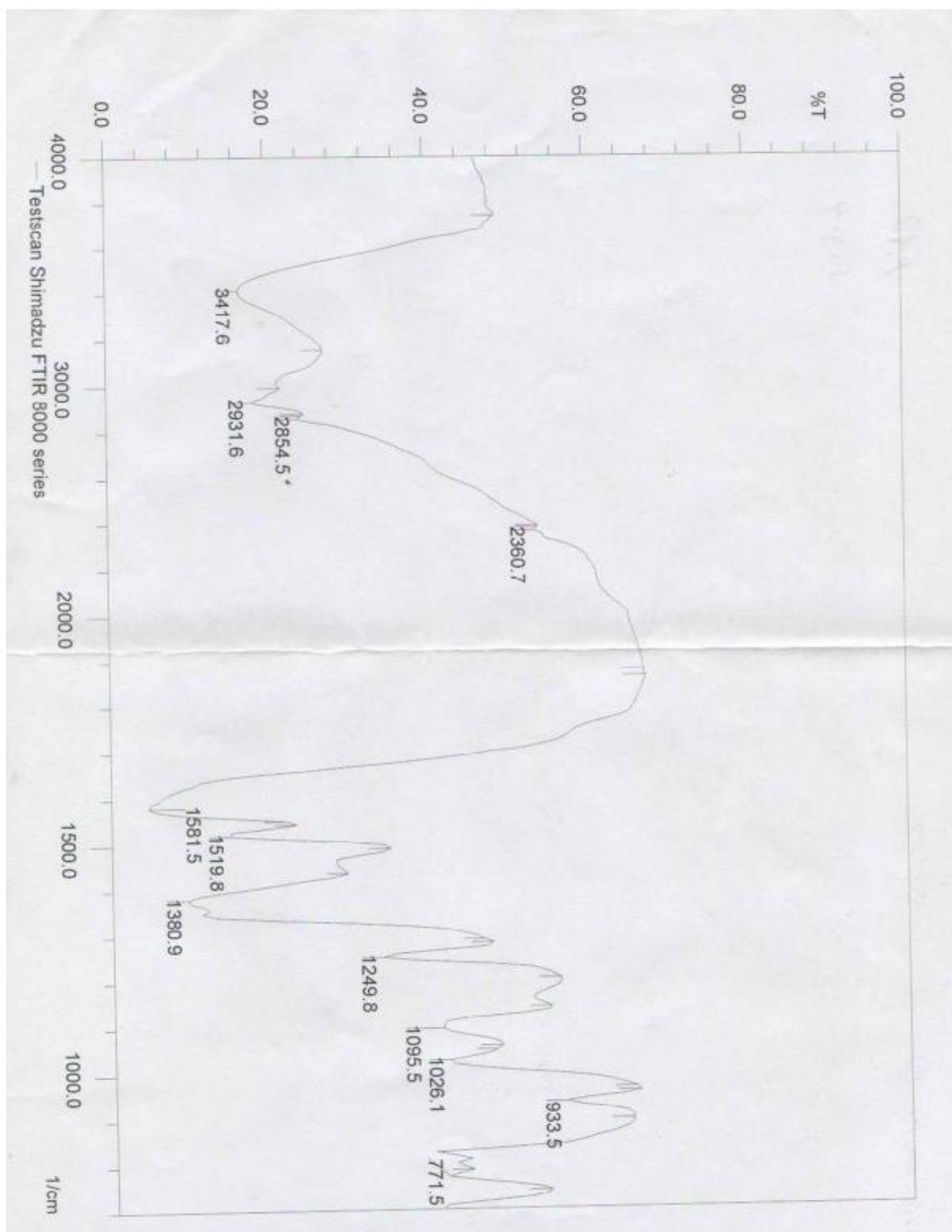


Figure 3.3: IR spectrum of acidified Tris-amine [TAA] polymer .

3.3 The response of the sensor to pH:

When the sensing element was examined with different buffer solutions (pH 5-12), it showed very small changes in absorbance. This is probably related to the fact that the acidified tris-amine polymer contains both basic (amine groups) and acidic groups (COOH). The nitrogen and the oxygen are both protonated, where positive charges of nitrogen repel each other causing the polymer to be in a swollen state. As the pH is raised, the oxygen on the acidified tris-amine group becomes deprotonated, the negative charges repel each other causing the polymer to stay in a swollen state. This behavior does not lead to any significant and observable shrinking process, and thus no detectable changes in absorbance. Figure 3.4.

A similar trend was observed with dithiocarbamate functionalized microspheres.²⁷

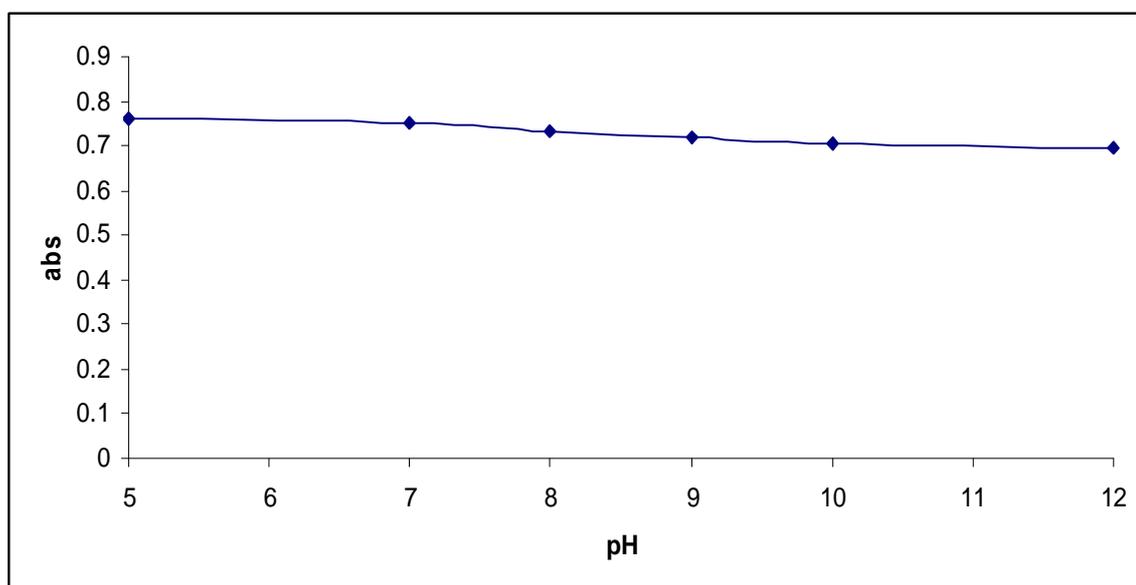


Figure 3.4: Absorbance of the sensing element without metal at different pHs.

3.4 The response of the sensor to heavy metal ions:

The deprotonated acidified Tris-amine polymer showed no optical response towards most tested metal cations (Co^{2+} , Ni^{2+} , Hg^{2+}). On the other hand, the acidified Tris-amine ligand showed high affinity towards the cation Cu^{2+} . Figure(3.5, 3.6, 3.7, 3.8).

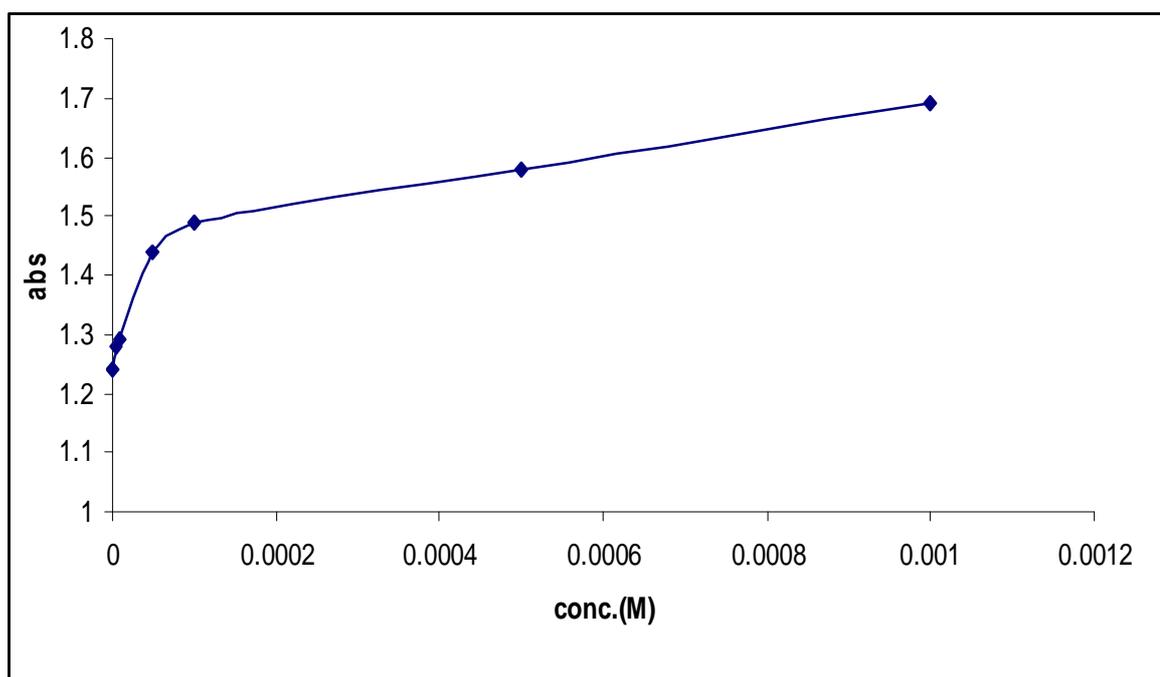


Figure 3.5: Absorbance vs. concentration of Cu^{2+} in distilled water at 800 nm, 25°C.

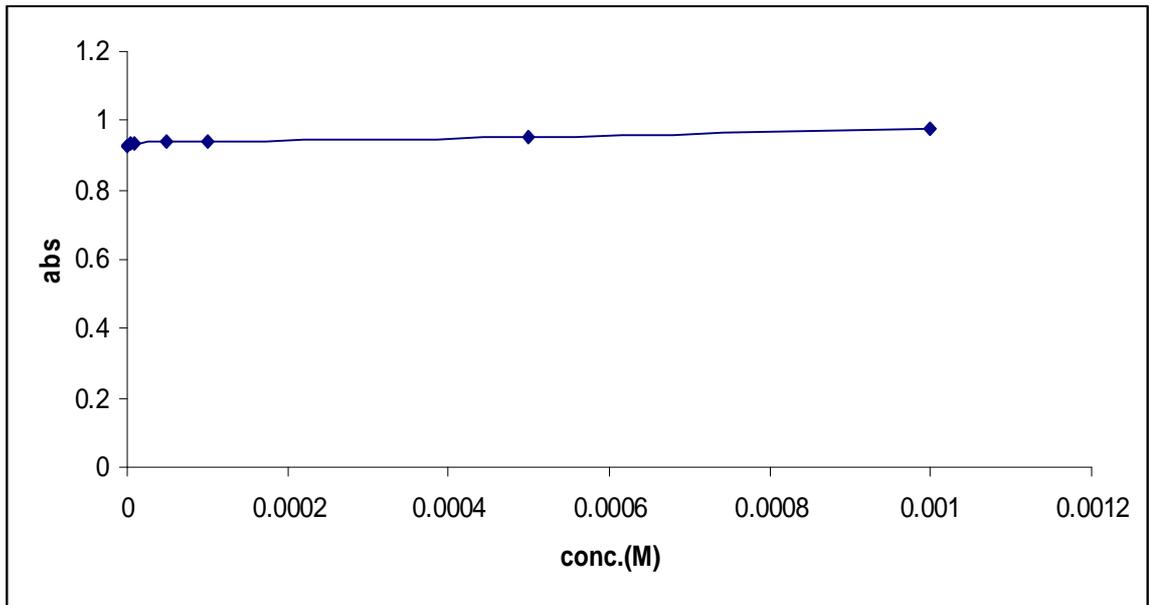


Figure 3.6: Absorbance vs. concentration of Co^{2+} .

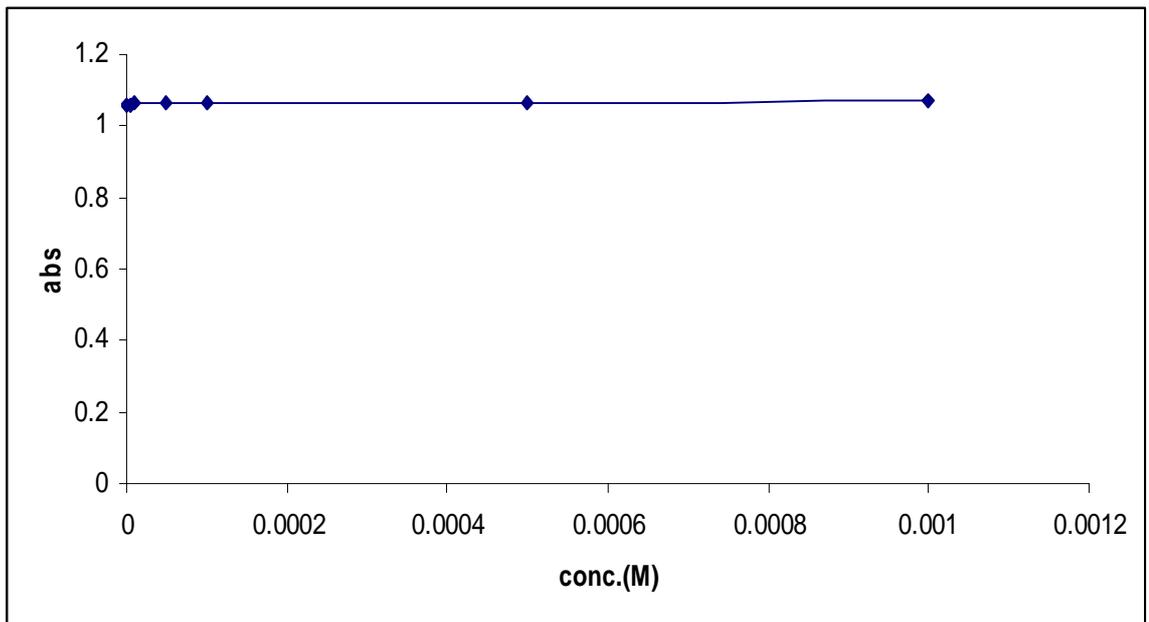


Figure 3.7: Absorbance vs. concentration of Ni^{2+} .

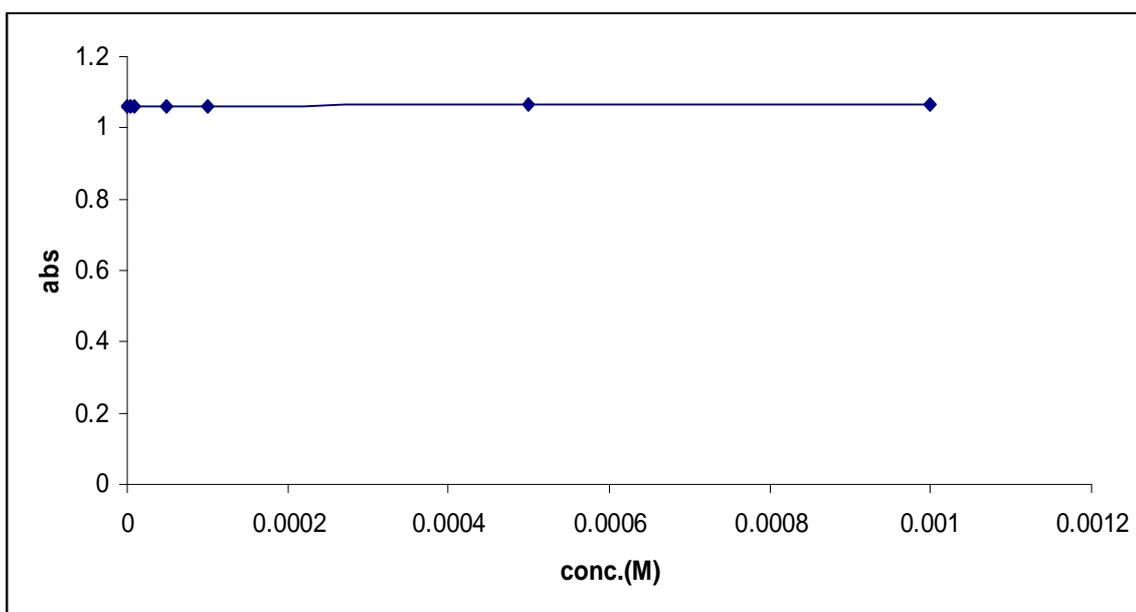


Figure 3.8: Absorbance vs. concentration of Hg^{2+} .

This is an indication that the acidified tris-amine functional group did not bind with these tested transition metal cations, even at high concentrations. A significant response to Cu^{2+} was observed. The complex formation between Cu^{2+} and the acidified tris-amine functional group caused the polymer microspheres to shrink. Shrinking of the polymer microspheres resulted in an increase in turbidity and absorbance.

Since the sensor showed a significant response to Cu^{2+} , The chelate reached its optimum level at about pH 8. This is probably due to at pH about 8, the acidified tris-amine functional group are completely deprotonated and are free to chelate with Cu^{2+} ions, the response to various concentrations of Cu^{2+} aqueous solutions (1×10^{-6} up to 0.001 M) was tested.

As the molar concentration of Cu^{2+} was increased the corresponding turbidity absorbance along the visible region (600-800 nm) increased. Figure(3.9a, 3.9b, 3.9c)

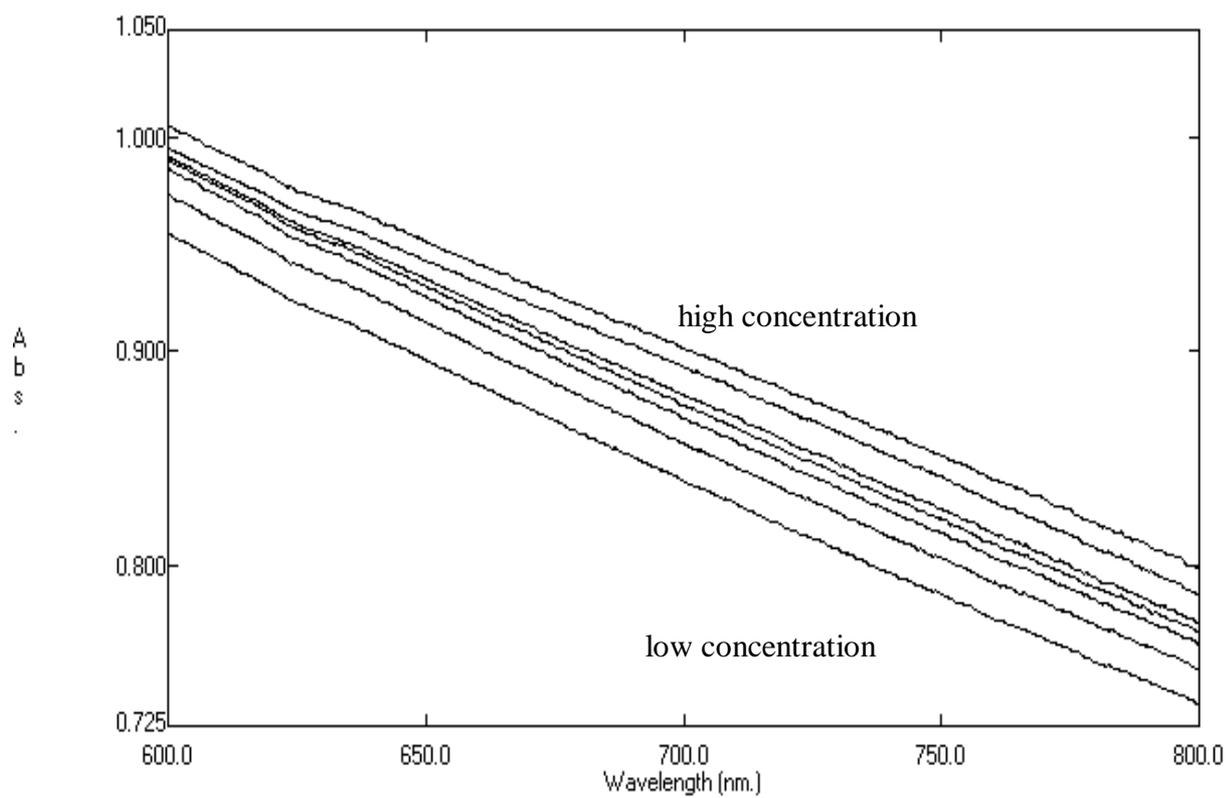


Figure 3.9(a): Absorbance spectra of different concentration of Cu^{2+} in distilled water, 25°C .

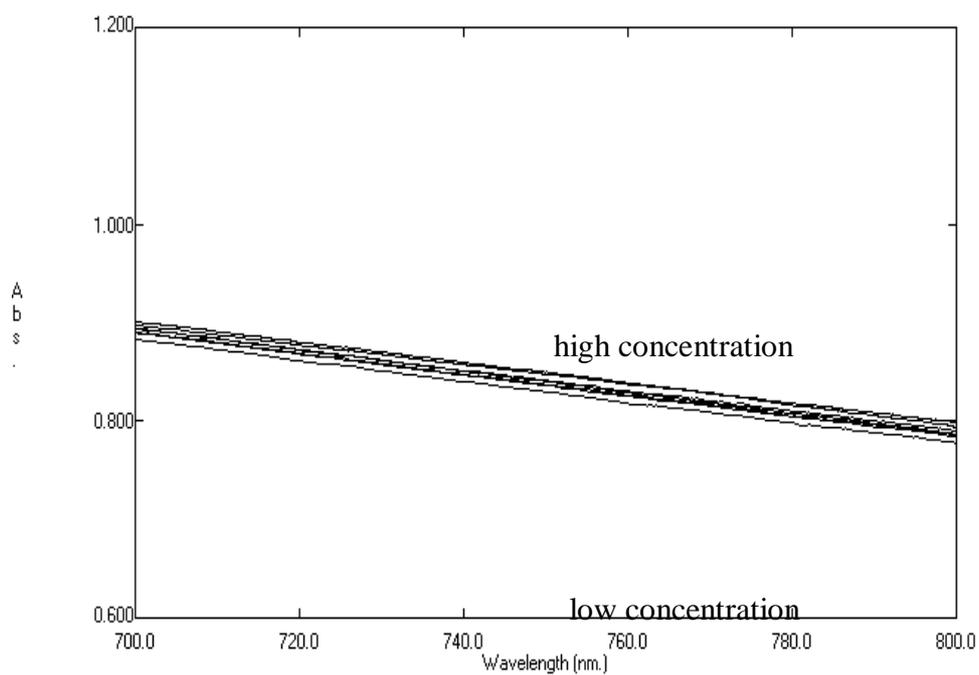


Figure 3.9(b): Absorbance spectra of different concentration of Cu^{2+} at pH=2, 25°C.

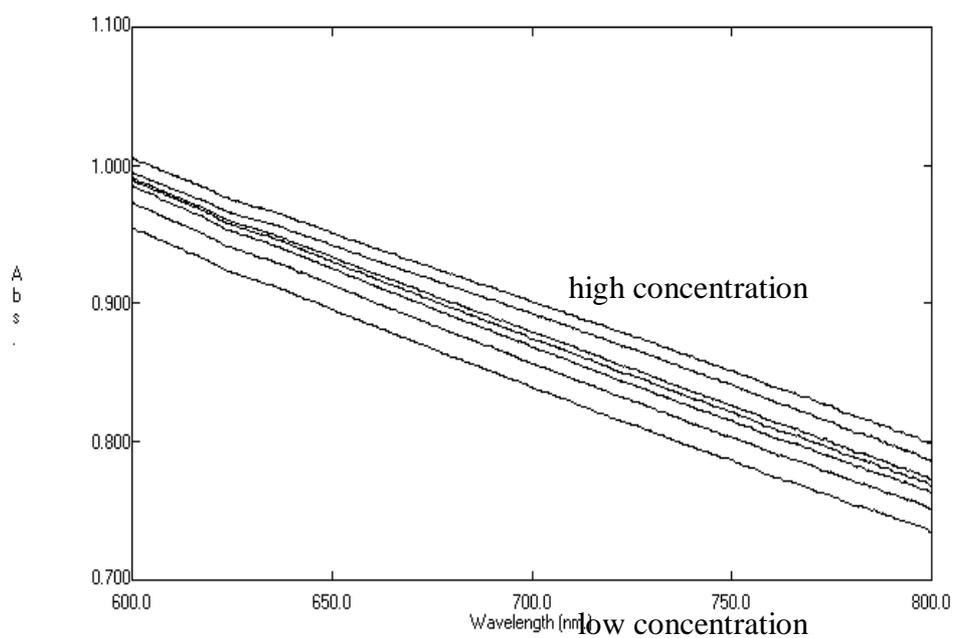


Figure 3.9(c): Absorbance spectra of different concentration of Cu^{2+} at pH=8, 25°C.

3.5 The response time of the sensor:

The response time of the sensing element toward Cu^{2+} ions was obtained by measuring the change in absorbance of 0.001 M Cu^{2+} at 800 nm with time.

As the time increased the absorbance increased sharply up to about 5 minutes; with a response of about 90%. After that the absorbance continued to increase slightly up to about 10 minutes then it leveled off as shown in Figure 3.10.

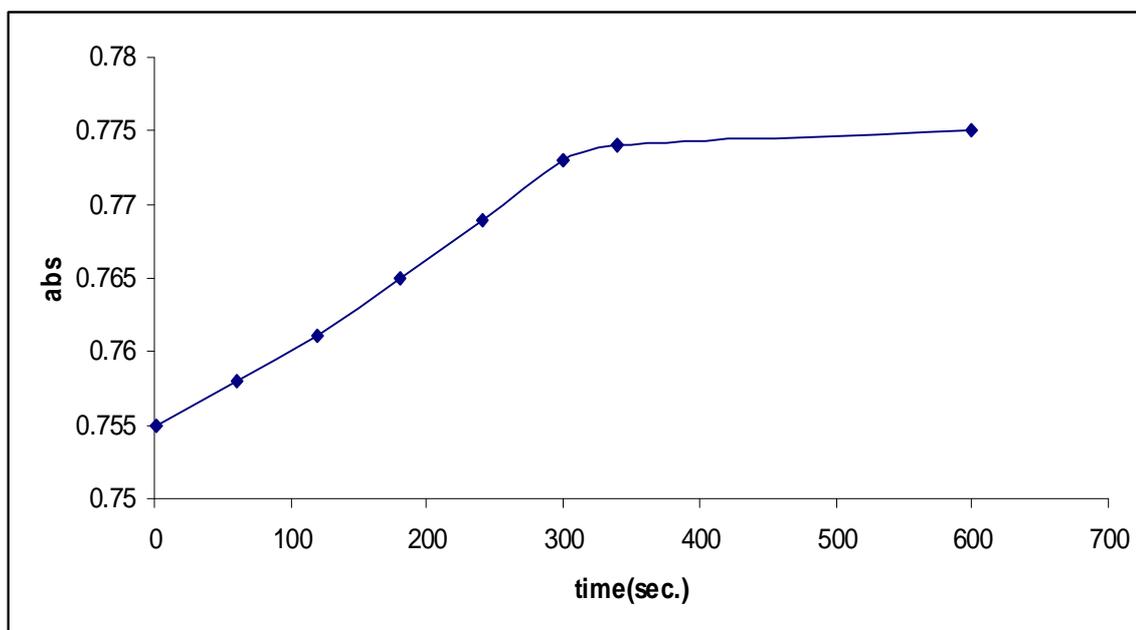


Figure 3.10: Absorbance vs. time to Cu^{2+} in distilled water.

The slow response after 5 minutes may be due to the increase in the thickness of the shrinking outer layer of the microsphere surface, resulting in a significant reduction in the rate of diffusion of ions through it. As it becomes less hydrophilic due the binding between the metal cation and deprotonated functional groups on the polymer microspheres.

3.6 Reproducibility of the sensor response:

The reproducibility of the sensing element was examined by observing the turbidity absorbance of 0.001 M Cu^{2+} aqueous solution at 800 (nm), as shown in Table(1). When the sensing membrane was in distilled water, the absorbance was 0.977. When the sensing membrane was exposed to Cu^{2+} solution of 0.001M, the absorbance was almost constant =1.023. After each run the sensor was eluted with saturated aqueous solution of EDTA and washed successively with distilled water. So this sensor response is reproducible.

Table(1): The tested reproducibility of sensing element:

Conc.(Cu^{2+})	1 st run	2 nd run	3 rd run	4 th run
0M	0.977	0.977	0.977	0.977
0.001M	1.023	1.023	1.024	1.024

3.7 Effect of pH on the sensor response :

The dependence of Cu^{2+} chelating with the acidified tris-amine polymer on pH was examined by preparing 0.001M Cu^{2+} in buffer solutions (pH 2 -8). Figure 3.11. shows the effect of pH on the complex formation between Cu^{2+} ions and the acidified tris-amine polymer. The buffer solution were adjusted using dilute NaOH and HCl.¹¹

Because the values of pKa of amino and carboxyl groups are about 10 and 3, respectively, it was anticipated that spectral variations of the sensing phase at high and low pH values would be observed.²⁶

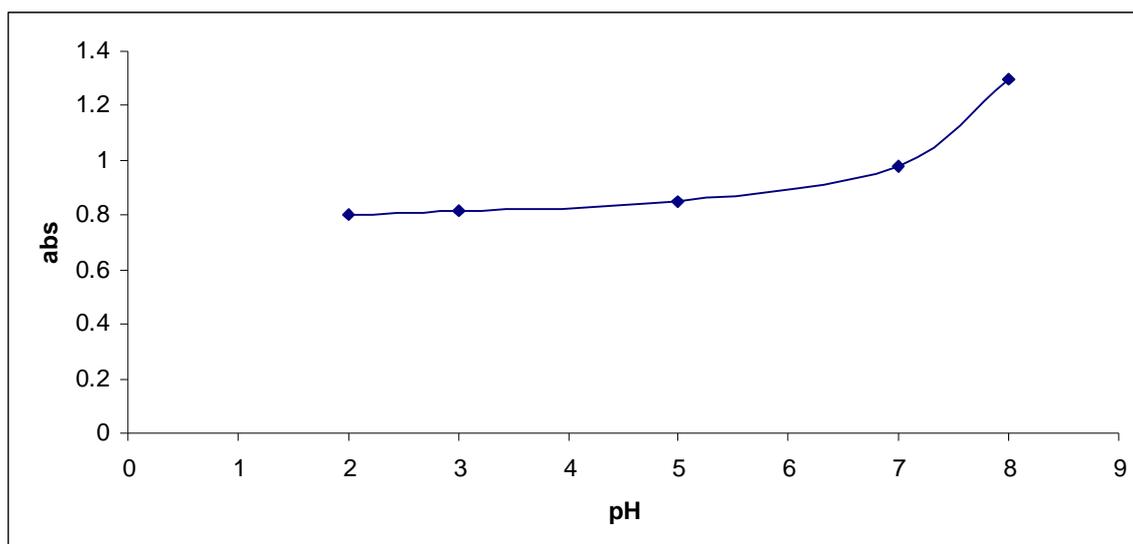


Figure 3.11 : Absorbance of the sensing element containing (0.001M) Cu^{2+} at different pHs.

3.8 Sensor response towards other alkali and alkaline earth metal cations:

As expected the tris-amine group polymer has no response toward alkali and alkaline earth metal cations, this is because the oxygen atoms of the tris-amine group are soft ligands and do not interact with hard metal cations (alkali and alkaline earth metals).⁷ The presence of these metal cations will not affect the optical properties of the sensor. The insignificant response toward the alkali and alkaline earth metals ions will allow us to apply this sensor on a real sample even at high concentration of these ions Ca^{2+} , Mg^{2+} , K^+ , and Na^+ , and Al^{3+} . Figure(3.12, 3.13, 3.14, 3.15, 3.16)

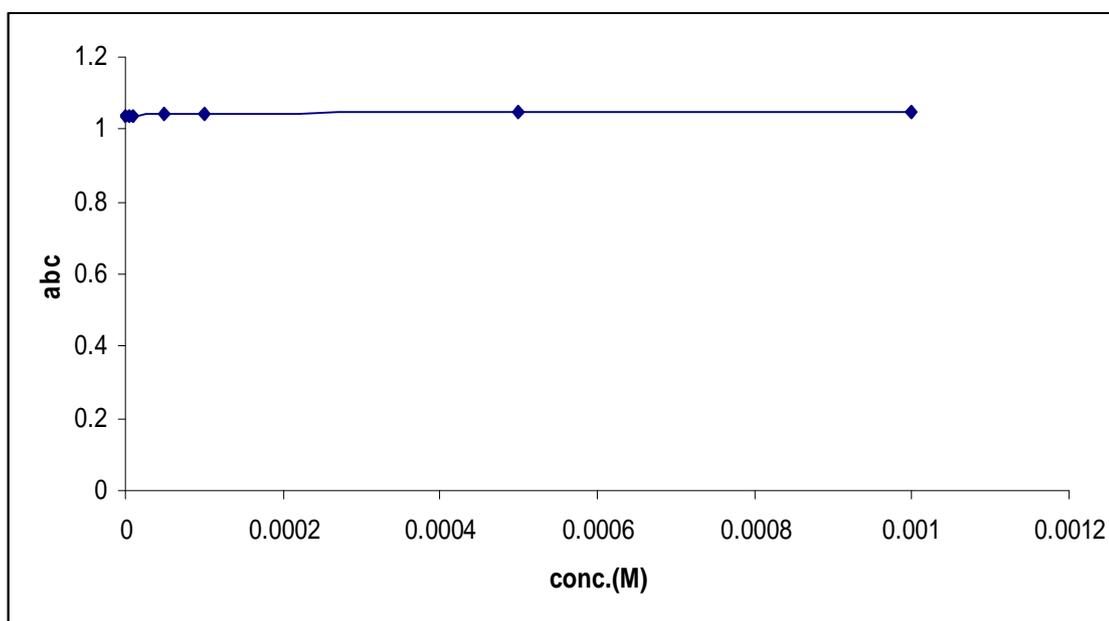


Figure 3.12: Absorbance vs. concentration of Ca^{2+} .

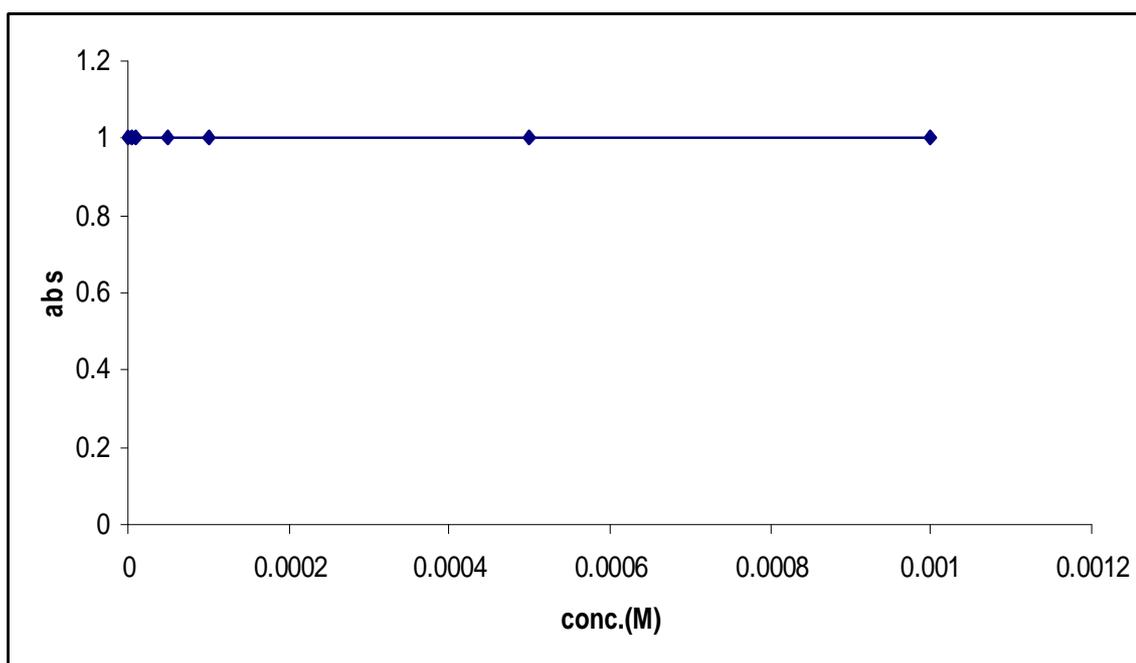


Figure 3.13: Absorbance vs. concentration of Mg^{2+} .

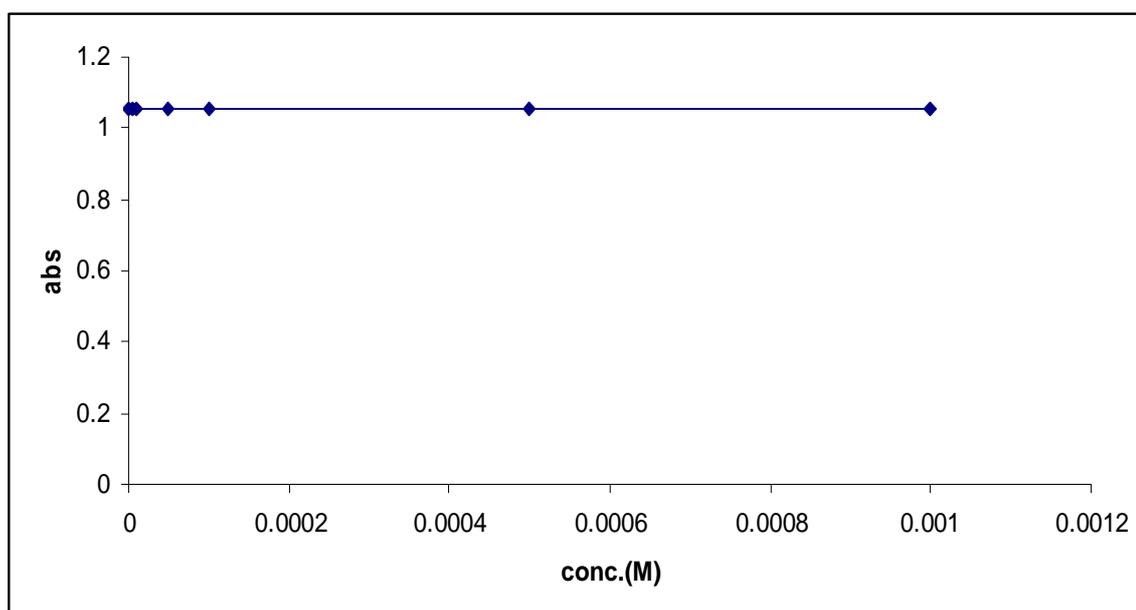


Figure 3.14: Absorbance vs. concentration of K^{+} .

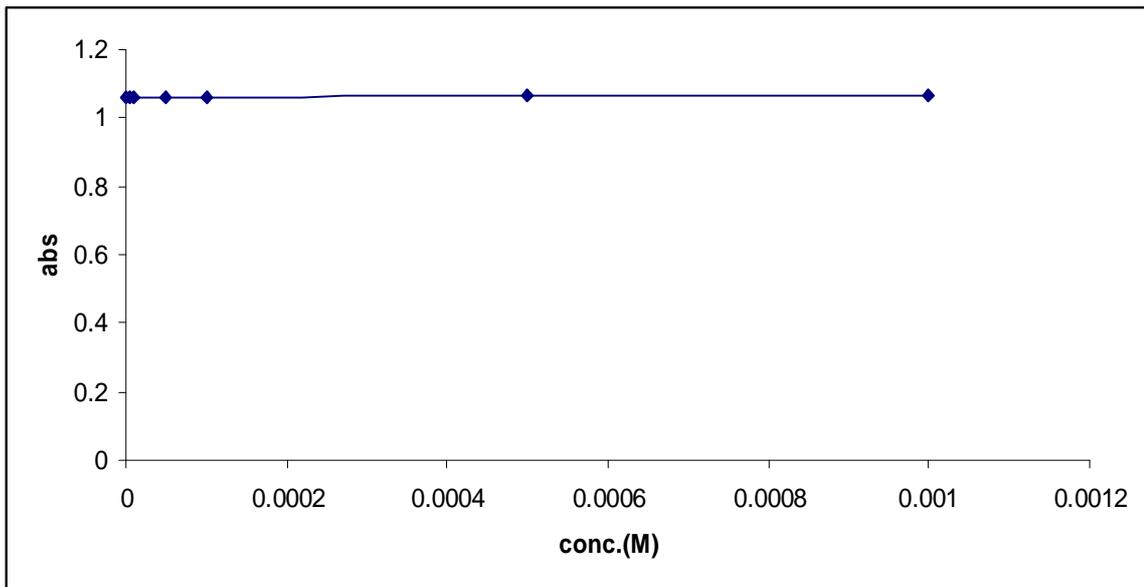


Figure 3.15: Absorbance vs. concentration of Na⁺.

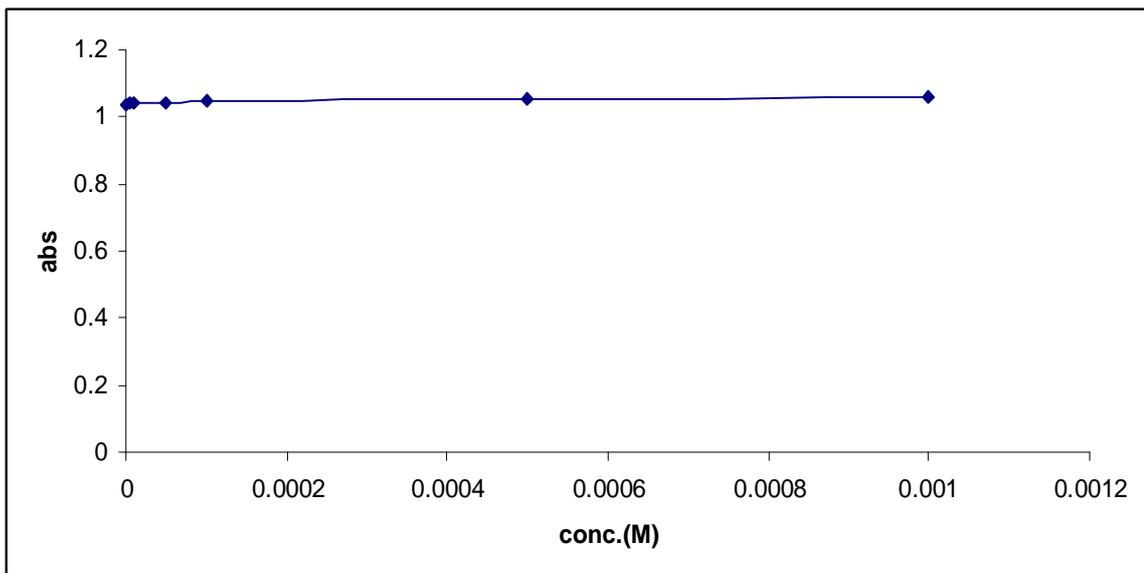


Figure 3.16: Absorbance vs. concentration of Al³⁺.

Conclusion

In this work a modified sensing element with a selective functional group as optical sensor based on swellable polymer microspheres is developed. Acidified tris-amine functional group covalently bonded to a polyvinyl benzyl polymer back-bone was prepared. These derivatized microspheres are entrapped in a hydrogel membrane. The acidified tris-amine group showed a selective response to Cu^{2+} ion. It did not show response to other metal ions, especially alkali and alkaline earth metal and other heavy metal ions regardless of their concentrations. This generation of optical chemical sensors showed good chemical and mechanical stability.

Chemical sensors based on polymer swelling and shrinking have many advantages: They are very simple to make and they are of low cost which makes them good candidates for remote sensing upon using a LED light source and a photodiode detector. In addition to the possibility of introducing a variety of functionality in place of the acidified tris-amine making them capable of targeting other different metal ions.

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جامعة النجاح الوطنية

كلية الدراسات العليا

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خصائصها الإنتقائية البصرية

إعداد

حنين رفيق خالد قاسم

إشراف

د. إبراهيم أبو شقير

د. زياد الشخشير

قدمت هذه الرسالة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية
الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2010م

ب

تحضير حبيبات بوليمر منتفخة مرتبطة بمجموعة وظيفية ودراسة خصائصها الإنتقائية

البصرية

إعداد الطالبة

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إشراف

د. إبراهيم أبو شقير

د. زياد الشخشير

الملخص

في هذا البحث تم دراسة مجس كيميائي بصري مستند على انتفاخ وانكماش البوليمر عن طريق الامتصاص البصري.

تم تحضير بوليمر مرتبط بمجموعة ترس-2-أمينو إيثيل أمين، البوليمر الناتج تكون من بوليمر بولي فينيل بنزويل كلورايد و ترس-2-أمينو إيثيل أمين عن طريق تفاعل استبدال. مادة المجس انتجت عن طريق غمر حبيبات البوليمر المحمضة المرتبطة بمجموعة ترس-2-أمينو إيثيل أمين داخل غشاء هلامي مكون من بولي فينيل الكحول مشبوك بواسطة غلوتيرالدهيد.

استجابة المجس تعتمد على التجاذب بين أيونات العناصر الموجبة مع مجموعة ترس-2-أمينو إيثيل أمين فتتكشف حبيبات البوليمر المنتفخة نتيجة معادلة الشحنة السالبة على المجموعة الوظيفية.

هذا المركب المعقد بين أيونات العناصر الموجبة و مجموعة ترس-2-أمينو إيثيل أمين المحمضة يسبب تغيرات في الخصائص البصرية لمادة المجس. الإنكماش في حبيبات البوليمر يسبب نقصان الخصائص الإمتصاصية لغشاء المجس. هذا نتيجة زيادة الفرق بين معامل الإنكسار بين حبيبات البوليمر والغشاء الهلامي المغمورة فيه. هذا المجس أعطى تحسس جيد لأيون النحاس. أيضا وأعطى تحسس مهمل لدرجة الحموضة من (5-8). بالمقابل لم يعط هذا المجس تحسس إلى أيونات القلويات وأيونات القلويات الترابية وبعض أيونات العناصر الإنتقالية مثل: أيونات النيكل(2+)، الكوبالت(2+)، الزئبق(2+)، الألمنيوم(3+).