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Polyvinylbenzyl Tris-Aminodicarboxylate Microspheres for the Optical Sensing of Cu^{2+} Ions

Ziad M. Shakhsher¹, Ibrahim Abu Shqair², Hanin R. Qasim², Imad Odeh^{1*}

¹Department of Chemistry and Chemical Technology, Al-Quds University, Jerusalem, Palestine

²Department of Chemistry, An-Najah National University, Nablus, Palestine

Email: *odehim@science.alquds.edu

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ABSTRACT

In this work, a tris(2-aminoethyl)aminodicarboxylate functionality was substituted for the chloride of polyvinylbenzyl chloride (PVBC) which was lightly cross-linked (2%) with divinyl benzene. The resulting derivatized polymer microspheres were embedded in a hydrogel matrix of poly vinyl alcohol cross-linked with glutaraldehyde to produce a sensing membrane. The latter responded selectively to Cu^{2+} solutions of different concentration ranges (1×10^{-4} M to 1×10^{-6} M). The response is based on the interaction between the metal cations and the negatively charged deprotonated dicarboxylate functional group, which led to neutralization of the charges. As a result, an increase in the turbidity of the sensing membrane occurred which is attributed to a change in the refractive index of the derivatized polymer microspheres relative to that of the hydrogel. The change in the turbidity of the sensing membrane was measured as absorbance using a conventional spectrophotometer. It was found that Cu^{2+} ions bind to the aminodicarboxylated-polymer with a formation constant, K_f , of $1 \times 10^5 \text{ M}^{-1}$. SEM, Eds and IR analyses were performed on the aminodicarboxylated microspheres and their Cu^{2+} complex.

KEYWORDS

Tris(2-aminoethyl)aminodicarboxylate-Polymer; Optical Sensing; Refractive Index; SEM; Eds

1. Introduction

Heavy metal ions such as Mercury, Cadmium, Lead, Nickel and Copper discharged into water by natural and anthropogenic sources are causing environmental and biological problems and have become a global concern [1-3]. Although a variety of methods are available for their removal, fast and effective means for their detection are still needed [4-17]. In a recent study, selective determination of copper ions in aqueous solutions utilizing aminodicarboxylic acid for the chelation of copper (II) ions was reported. Lin *et al.* modified the surface of an evanescent wave element by depositing a thin layer of the ligand producing a sensitive and selective infra-red chemical sensor capable of detecting micro molar concentrations of Cu^{2+} ions within a time frame of 20 minutes [4]. We believe that using an optical chemical sensor

would improve significantly the detection limit and produce a faster response time. A variety of analytes were detected using optical sensing elements developed by our group [11-14]. Such a sensor is based on polymer swellings that result from complexation of a specific analyte with a specific functional group located on the polymer microspheres. The latter form a sensing element upon entrapping them in polyvinyl alcohol cross-linked with glutaraldehyde. The resulting sensing element demonstrated excellent resistance to photodegradation and indicator dye leaching as well as to mechanical degradation. In addition, these sensors were effective at very low concentration (down to 1 μM) and responded within a very short time (95% response in 5 minutes) and were insensitive to pH changes [11,14].

In a previous work, we were able to develop an optical chemical sensing element based on polymer swelling, in which polyvinylbenzyl chloride (PVBC) lightly cross-

*Corresponding author.

linked with divinylbenzene as microspheres were derivatized with dicarboxylate and embedded in a hydrogel membrane to form a sensing element [12,13]. This kind of sensing element had some limitations, particularly its lack of selectivity. It responded to varying pH values, and also to Ca^{2+} , Ni^{2+} , Zn^{2+} , and Cd^{2+} ions. To improve the selectivity, we selected a functionality that is chemically similar to that of ethylenediamine tetraacetic acid (EDTA), a common chelating agent for metal ions but known to form highly thermodynamic chelates with Cu^{2+} ions [4]. In this study, polyvinylbenzyl tris(2-aminoethyl)aminodicarboxylate microspheres were synthesized starting from PVBC cross-linked with divinylbenzene (2%). The resulting derivatized microspheres were embedded in a hydrogel matrix of polyvinylalcohol cross-linked with glutaraldehyde to form an optical sensing element. The response to Cu^{2+} ions as change in the turbidity of the sensing membrane was measured as absorbance using a conventional spectrophotometer.

2. Experimental

2.1. Reagents

All chemical reagents used were of analytical grade. N,N-dimethylformamide (DMF), tris(2-aminoethyl)amine (TAA), polyvinyl alcohol (PVA), glutaraldehyde 8% by weight, were purchased from Sigma-Aldrich. Bromoacetic acid was obtained from Riedel. All solutions were prepared in deionized distilled water. Polyvinylbenzyl chloride (PVBC) lightly cross-linked with divinylbenzene (2% mole) microspheres of 1 - 3 μm diameter were supplied by the Chemistry Department at the University of New Hampshire (USA).

2.2. Instruments

Absorption measurements were performed on Shimadzu UV-VIS-NIR Scanning spectrophotometer (Shimadzu UV-3101PC). A Fourier transform infrared spectrophotometer (Testscan Shimadzu FT-IR 8000 series) was used to obtain IR-Spectra. The pH measurements were recorded on a Jenway pH meter (3510). SEM and EDS analyses of the adsorbent before and after complexation with copper (II) ions were performed by mounting the samples on metal stubs and coating them with gold (Polaron Sputter coater). The microphotographs were recorded using a scanning electron microscope JEOL model, JSM-5410 LV (available at the microscopy lab at the faculty of agriculture, food and environmental quality Sciences, The Hebrew University). The images were taken with an accelerating voltage of 25 kV, at high vacuum (HV mode) and secondary electron image (SEI). The analysis was done using Oxford systems—Liquid Nitrogen cooled solid state Energy Dispersive Spectrometer detector and link ISIS software.

2.3. Synthesis of the Tris(2-aminoethyl)amino (TAA) Polymer

One gram (0.0066 mole) of PVBC was stirred in 12 ml DMF for two hours then 4 ml of the tris-amine (TAA, 4 equivalents) were added and the reaction was stirred for one week. The DMF and excess tris-amine were then removed by a series of centrifugations, and decantations. Then the polymer was washed several times (3 times) with distilled water. The water was also removed by a series of centrifugations, and decantations. The polymer was allowed to dry in air. The mass of tris-amine polymer obtained was 1.384 g.

2.4. Synthesis of the Tris(2-aminoethyl)aminodicarboxylate (TAAD) Polymer

One gram of the tris-amino polymer was added to a solution of 2 g of Bromoacetic acid in 25 ml 3 M NaOH and the reaction was allowed to stir at room temperature for one week. The reaction was then stopped and the polymer collected by suction filtration. The mass of the polymer obtained was 1.160 g.

2.5. Preparation of the Optical Sensing System

The TAAD derivatized polymer microspheres (10 mg) were soaked in a few drops of DMF for a few minutes, then 1 ml of 5% aqueous PVA solution was added and the mixture was placed in a sonicator until the polymer microspheres were dispersed and the mixture became uniform. Then, the PVA/TAAD mixture was cross-linked by mixing with 80 μl of 8% aqueous glutaraldehyde, followed by 80 μl of 3 M HCl (aq). A few drops of the resulting mixture were immediately transferred and spread on the inner clear side wall of a plastic cuvette. The sensing membrane was allowed to formulate and stick in position. The resulting sensing element was washed with and stored in distilled water. The cuvette with the sensing element stuck on its inner sidewall was secured in the cell holder of a conventional spectrophotometer, so that the membrane was positioned in the path of the light beam (Figure 1).

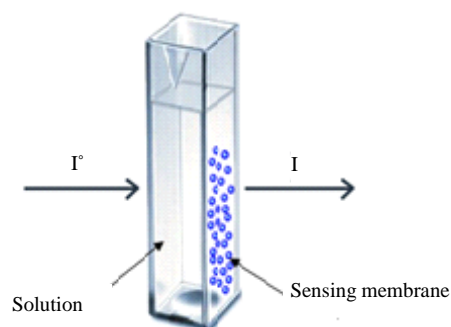


Figure 1. Diagram of optical sensing system.

2.6. Optical Measurements

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 at 800 nm. The response of the sensing element to pH was obtained starting with lower pH and proceeding to the higher ones with an interval of 10 minutes between each spectrum run. The reproducibility of the sensor response was evaluated by cycling between blank and 0.001 M Cu^{2+} ions solution several times. Between measurements, the sensing element was eluted by a saturated solution of EDTA and then washed extensively with distilled water until obtaining the blank reading. The response time of the sensing element towards 0.001 M of Cu^{2+} ions was obtained by measuring the change in absorbance with time, until steady state is reached.

3. Results and Discussion

3.1. Characterization of the Ligand- Cu^{2+} Complex

The variation in the appearance of the IR spectra of the tris(2-aminoethyl)aminodicarboxylate polymer- Cu^{2+} complex from that of the tris(2-aminoethyl)aminodicarboxylate polymer is indicative of the complex formation. Thus, the carboxylate characteristic bands for the asymmetric and symmetric stretching frequencies appearing at ca. 1594 and 1438 became less intense [4]. Also two new bands are observed at ca. 1063 and 532 cm^{-1} which are attributed to the C-O and N-Cu stretching frequencies [18] (Figure 2). SEM analysis showed an increase in the average size of the polymer microspheres possibly due to adsorption of copper ions on the polymer surface in addition to chelation with the aminodicarboxylate functionality (Figure 3). Elemental analysis of the surface of the polymer at three different points using Energy Dispersive Spectrometry (EDS) showed beyond doubt the presence of nitrogen, oxygen and copper, the three-element component of the aminodicarboxylate functionality (Table 1).

3.2. Sensing Element Evaluation

As the sensing element was examined with different buffer solutions (pH 5 - 12), insignificant changes in absorbance were observed. This is probably related to the fact that the tris-aminodicarboxylate polymer contains both basic amino groups and acidic carboxyl groups. The nitrogen and the oxygen are both protonated at low pH. Thus, the positive charges on nitrogen repel each other causing the polymer to be in a swollen state. As the pH is raised, the oxygen on the carboxylic group becomes de-

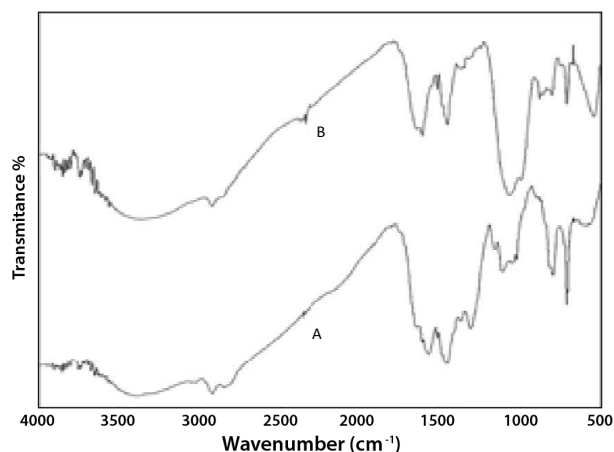


Figure 2. FTIR spectra: (A) Tris amino dicarboxylate (TAAD) polymer; (B) Tris amino carboxylate- Cu^{2+} complex.

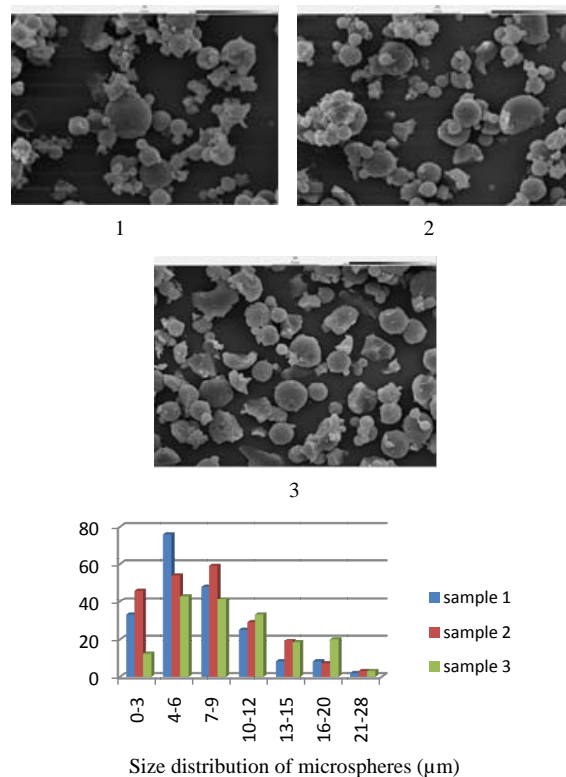


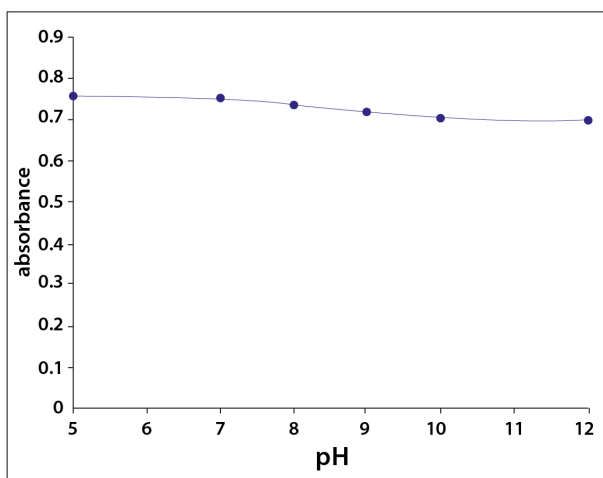
Figure 3. SEM images of (1) Tris(2-aminoethyl)amino (TAA) polymer; (2) Tris(2-aminoethyl)aminodicarboxylate (TAAD) polymer; (3) Tris(2-aminoethyl)aminocarboxylate polymer- Cu^{2+} complex and the size distribution of the polymer microspheres.

protonated. The negative charges repel each other causing the polymer to stay in a swollen state. This behavior does not lead to any significant change in refractive index, and thus no detectable change in absorbance was recorded (Figure 4).

The tris-aminodicarboxylate polymer showed no response towards tested heavy metal cations (Co^{2+} , Ni^{2+} ,

Table 1. Elemental analysis of tris(2-aminoethyl)aminodicarboxylate polymer-Cu²⁺ complex.

Element	Weight %		
	pt1	pt2	pt3
C-K	27.57	51.01	50.01
N-K	10.53	16.66	17.59
O-K	46.71	21.14	23.72
F-K			1.30
Na-K	1.02		
Al-K	0.45	0.35	0.33
Si-K	12.04	2.27	2.60
Cl-K	0.16	1.13	0.40
K-K	0.13		
Cu-K	0.89	4.20	2.94
Ag-L	0.50	3.24	1.11

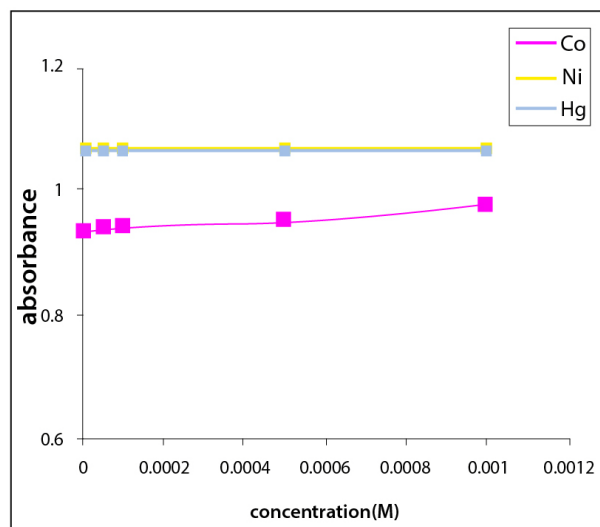
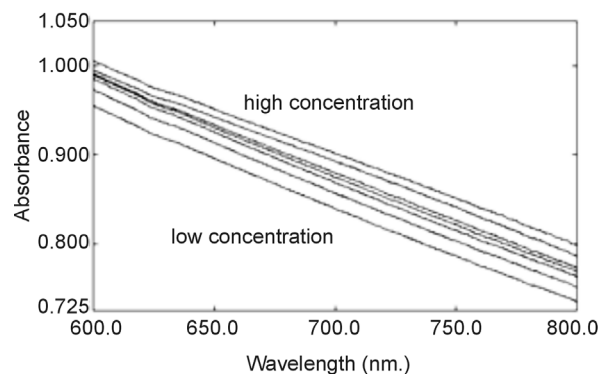
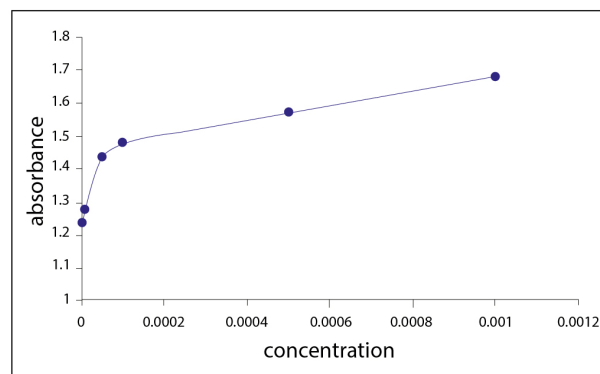
**Figure 4.** Turbidity absorbance of the sensing element at different pHs.

Hg²⁺) at all concentrations (Figure 5). On the other hand, it demonstrated a significant affinity towards Cu²⁺ ions in agreement with previous reports [4] (Figures 6 and 7).

The response of the sensing membrane to Cu²⁺ ions is based on the interaction between these ions and the aminodicarboxylate functional group situated on the polymer microspheres.

As a result, an increase in the turbidity of the sensing element occurred due to a change in the refractive index of the derivatized polymer microspheres relative to that of the hydrogel. Thus, as the concentration of the Cu²⁺ solution was varied between 1×10^{-6} M and 1×10^{-4} M an increase in absorbance was observed. The sensing element demonstrated good reproducibility in response towards Cu²⁺ ions.

The formation constant (K_f) of binding of Cu²⁺ ions with the tris-aminodicarboxylate-polymer was obtained

**Figure 5.** Turbidity absorbance of sensing element vs concentration of Co²⁺, Ni²⁺ and Hg²⁺ ions.**Figure 6.** Variation of absorbance of sensing element vs wavelength of different Cu²⁺ concentration (1×10^{-6} to 1×10^{-4}).**Figure 7.** Turbidity absorbance of sensing element vs concentration of Cu²⁺ ions.

from the plot of Figure 7. As the amounts of the free and the bonded ligand will be equal at the point half-way to the maximum response, K_f is equal to $1/[Cu^{2+}]$, where the concentration of Cu²⁺ ion is 1×10^{-5} M. Thus, the forma-

tion constant (K_f) is calculated to be $1 \times 10^5 \text{ M}^{-1}$. This result ensures the high selectivity of the prepared sensing element toward Cu^{2+} ion.

The response of the sensing element was examined towards Cu^{2+} (0.001 M), at different pH buffered solutions (pH 2 - 9). We detected a small change in absorbance up to about pH 7. But, above that, significant increases in absorbance were observed. This is probably due to an increase in the fraction of the deprotonated functional groups that resulted in an enhancement of the complex formation between ligand and Cu^{2+} ions (Figure 8).

The response time of the sensing membrane toward Cu^{2+} ions was obtained by measuring the change in absorbance of a solution of $1 \times 10^{-3} \text{ M}$ Cu^{2+} ions at 800 nm versus time. The absorbance increased sharply up to about 5 minutes and then leveled off (Figure 9). This pattern in the response time may be attributed to the increase in the thickness of the shrinking outer layer of the microsphere surface, which resulted in a significant reduction in the rate of diffusion of Cu^{2+} ions and water through it.

In agreement with previously reported results, the tris-aminodicarboxylate polymer microspheres showed no response toward alkali and alkaline earth metal cations, such as Ca^{2+} , Mg^{2+} , K^+ , and Na^+ .

Thus, the presence of these metal cations will not be expected to affect the optical properties of the sensing membrane (Figure 10).

4. Conclusion

In this work, a tris-aminodicarboxylate functional group was substituted for the chloride of PVBC which was cross-linked with divinyl benzene (2%). The resulting derivatized microspheres were entrapped in a hydrogel membrane (PVA) to produce a sensing element. The resulting sensor responded selectively to Cu^{2+} ions at concentrations ranging between $1 \times 10^{-6} \text{ M}$ and $1 \times 10^{-4} \text{ M}$,

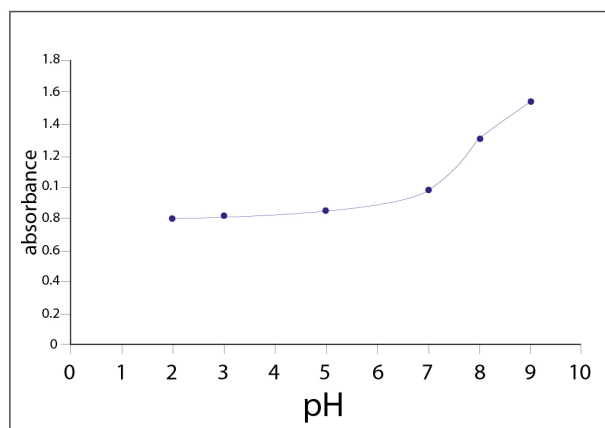


Figure 8. Turbidity absorbance of the sensing element for 0.001 M Cu^{2+} at different pHs.

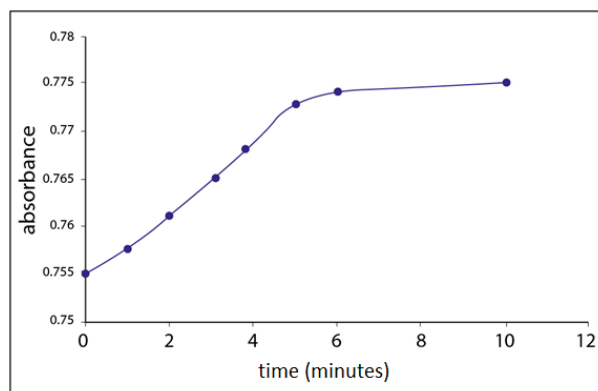


Figure 9. Response time of the sensing element towards Cu^{2+} ions.

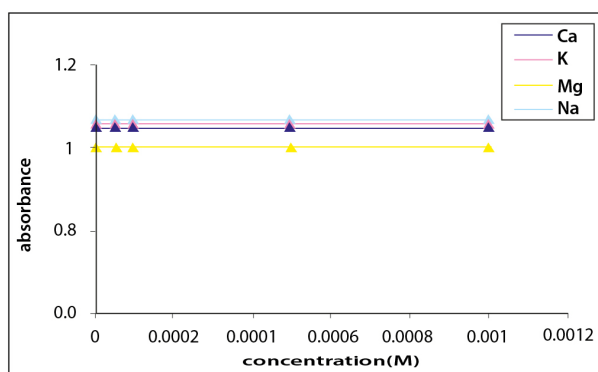


Figure 10. Turbidity absorbance of sensing element vs concentration of alkali and alkaline earth metal ions.

with a formation constant (K_f) of $1 \times 10^5 \text{ M}^{-1}$. In addition, no significant response to other metal ions, especially alkali and alkaline earth metal and some heavy metal ions (Co^{2+} , Ni^{2+} , Hg^{2+}) was detected, regardless of their concentrations.

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