

An Optical Chemical Sensor Based on Polymer Swelling and Shrinking using Dithiocarbamate-Polymer Microspheres

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Abstract

In this work, an optical chemical sensor based on a swelling and shrinking polymer has been developed. A dithiocarbamate functional group was attached chemically to the backbone of poly vinyl benzyl chloride which was lightly crosslinked with divinyl benzene. The derivatized polymer microspheres were dispersed in a hydrogel membrane to produce a sensing element. This modified membrane was used for sensing specific heavy metal ions, such as Hg^{2+} .

The response is based on the interaction between the metal cations with the negative charges of the deprotonated dithiocarbamate 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 a dithiocarbamate 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 refractive indices between the microspheres and the dispersing hydrogel membrane. This sensor showed a good response particularly to mercury ion.

There was insignificant response to H^+ in the pH range 2 -13. In addition, there was no detectable response towards alkali, alkaline earth metals and other heavy metal ions such as Pb^{2+} , Zn^{2+} , and Cd^{2+} .

Keywords: Optical sensor; Dithiocarbamate- polymer; Polymer swelling.

Introduction

Recently, a great deal of interest is directed towards developing chemical sensors particularly ion selective sensors^[1-12]. Chemical sensors based on polymer swelling exhibited superior properties over other optical and electrical sensors due to their excellent resistance to photodegradation and electrical interference. In addition, these sensors are particularly stable for a long period of time due to their mechanical stability, they are simple and inexpensive. In addition, they can be used successfully at different wavelengths in the UV-visible and near IR regions.

We have demonstrated^[6] that dicarboxylate functionalized polymer microspheres underwent swelling and shrinking upon being subjected to solutions of varying pH values ranging from 6 to 8, and also to calcium and some heavy metal ions of different concentrations.

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In this work, dithiocarbamate-polyvinyl benzyl chloride microspheres were synthesized and entrapped in a polyvinyl alcohol membrane to form an optical sensing element. The dithiocarbamate functionality was selected due to its well known stable chelates with heavy metal ions of environmental concern, and to its negligible affinity towards alkali and alkaline earth metal ions present in real samples ^[13].

Experimental

Reagents

Analytical grade N,N-dimethylformamide (DMF), ethylenediamine, 2-propanol, carbon disulfide (CS₂), polyvinyl alcohol, glutaraldehyde 8 % by weight, mercuric chloride, lead nitrate, cadmium chloride, zinc chloride, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, were purchased from Sigma-Aldrich Co. (USA). All solutions were prepared in deionized distilled water. Also different aqueous solutions of Hg²⁺ of different concentrations (1.0 x 10⁻⁶ up to 0.1M) were prepared using local tap water, directly without any pretreatment. Polyvinylbenzyl chloride lightly crosslinked with divinylbenzene (2 % mole) microspheres of 1-3 micrometers diameter was supplied by the Chemistry Department at University of New Hampshire (USA).

Instruments

Absorption measurements were performed on a Perkin-Elmer Lambda 5 UV-visible spectrophotometer. The pH measurements were recorded on a Jenway pH meter (3310) with a combination glass electrode and a tolerance of ± 0.01 pH units. A Fourier transform infrared spectrophotometer (Testscan Shimadzu FT-IR 8000 series), was used to obtain IR-Spectra.

Synthesis of the dithiocarbamate polymer

Two grams of poly vinyl benzyl chloride microspheres (**1**) were soaked in few milliliters of dimethylformamide for several days. The soaked polymer was filtered and washed several times with distilled water and then immersed in 15 milliliters of ethylenediamine (**2**) at room temperature and stirred for one week. The aminated polymer was washed several times with distilled water then traces of ethylenediamine were removed under reduced pressure.

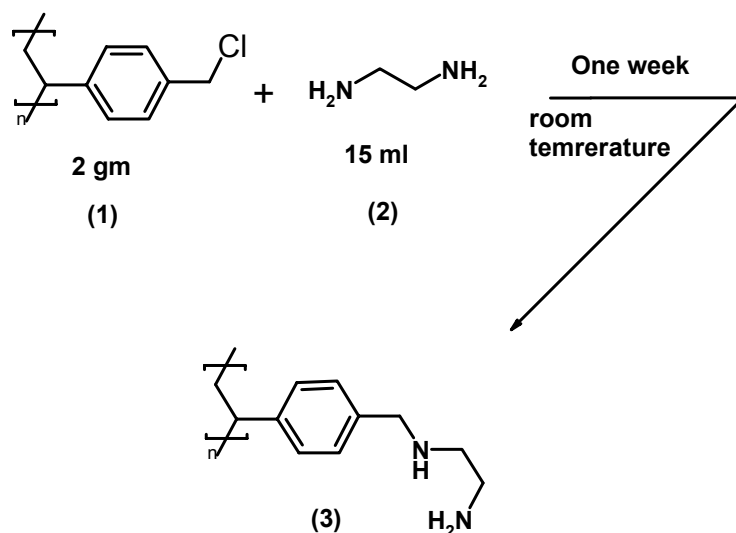


Figure 1: Synthesis of aminated polymer (3)

One gram of the aminated polymer microspheres (3) was stirred with a mixture of 15 ml of 2-propanol, 5ml CS₂, and 20 ml DMF for one hour. This was followed by the addition of 5ml of 10% aqueous NaOH and the resulting solution was stirred for five days. The dithiocarbamate polymer microspheres were then filtered and washed several times with distilled water and dried under reduced pressure.

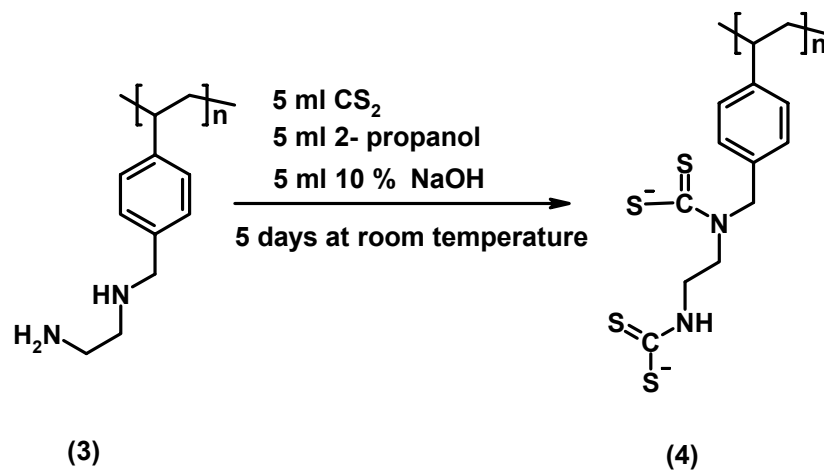


Figure 2: Synthesis of dithiocarbamate polymer (4)

Polymer capacity

The capacity of dithiocarbamate polymer microspheres (4) towards metal ions was determined by initially soaking a 0.1 gram of the derivatized polymer in 20 ml of aqueous 0.1M HgCl₂ and stirring over night. Then, filtering and washing extensively with distilled water. Finally, the loaded metal ions on the polymer were eluted by an aqueous solution of 3.0M HCl. And then, determined by titration with standard EDTA solution, after adjusting the pH to 10.0 with ammonia buffer.

Optical measurements

The sensing element prepared as described previously^[6] was stuck on the inner sidewall of a cuvette which was then secured in the cell holder of a Perkin Elmer conventional spectrophotometer, so that the membrane was positioned in the path of the light beam. The solution in the cuvette was changed using a disposable pipette, starting with the lower concentrations of analyte and proceeding to the higher ones, with an interval of 10 minutes between each spectrum run. The response of the sensor to pH was performed starting with the lower pH and proceeding to the higher ones (3.0-13).

The reproducibility of the sensor response was evaluated by cycling between blank and $5 \times 10^{-3} \text{M}$ Hg^{2+} ions several times. Readings as turbidity absorbance at wavelength (700nm) were taken after 10 minutes of introducing the solution in the cuvette. Between each reading, Hg^{2+} ions were eluted by a saturated solution of EDTA and then washed extensively with distilled water until obtaining the blank reading.

While the response time of the sensing element towards 0.1M of Hg^{2+} ions was obtained by measuring the change in absorbance with time, until steady state is reached.

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

Results & Discussion

Identification of the dithiocarbamate polymer

The formation of the dithiocarbamate functional group on the polymer microspheres was determined from IR-spectra, by comparing the IR-spectrum of Polyvinylbenzylchloride with the IR-spectrum of the dithiocarbamate polymer; The C-Cl peak at about 710 cm^{-1} has become less intense after substitution with the amine groups.

Capacity studies indicated that the dithiocarbamate binds significantly with Hg^{2+} ions. Titration with EDTA showed that the capacity of the dithiocarbamate polymer to Hg^{2+} is equal to 1.1 mmol per gram polymer.

Sensor evaluation

When the sensing element was examined with different pH buffer solutions (pH 3-13), we observed very small (insignificant) changes in absorbance. This is probably related to the fact that the dithiocarbamate polymer (**4**) contains both basic (amine groups) and acidic groups (CS_2H). The nitrogen (hard base) and the sulfur (soft base) 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 sulfur on the dithiocarbamate 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 are recorded.

Contrary to expectations, the deprotonated dithiocarbamate-polymer showed no optical response towards most tested metal cations (Pb^{2+} , Zn^{2+} , Cd^{2+}) as shown in figure 3. On the other hand, it showed very high affinity towards the soft metal cation Hg^{2+} [14].

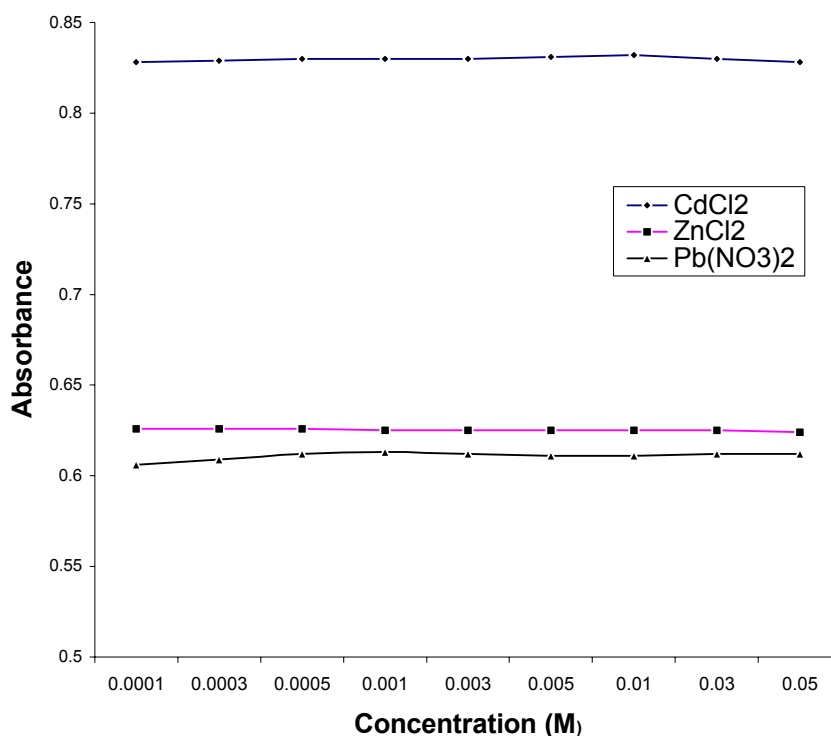


Figure 3: Turbidity absorbance vs. concentration of Pb^{2+} , Zn^{2+} , Cd^{2+}

This is an indication that the dithiocarbamate functional group did not bind with these tested heavy metal cations, even at high concentrations. But did so significantly with mercury ion (II). The complex formation between Hg^{2+} and the deprotonated polymer microspheres caused them to shrink as a result of neutralization of the deprotonated sulfur. Shrinking of the polymer microspheres resulted in an increase in turbidity absorbance.

As the molar concentration of Hg^{2+} was increased the corresponding turbidity absorbance along the visible region (300-800nm) increased as shown in figure 4. The reading of absorbance for each solution was taken after 10 minutes of introducing the solution in the cuvette. This was the period needed to reach almost 90% response as shown in Figure 6. The absorbance registered at 700nm increased sharply up to a concentration of 0.01M. Beyond that a slower increase in turbidity absorbance was obtained as shown in figure 5. This is probably due to the high ratio of the complexation between Hg^{2+} ions and the functional groups on the polymer. The lowest concentration of Hg^{2+} measured at low noise to signal ratio was 1.0×10^{-4} M.

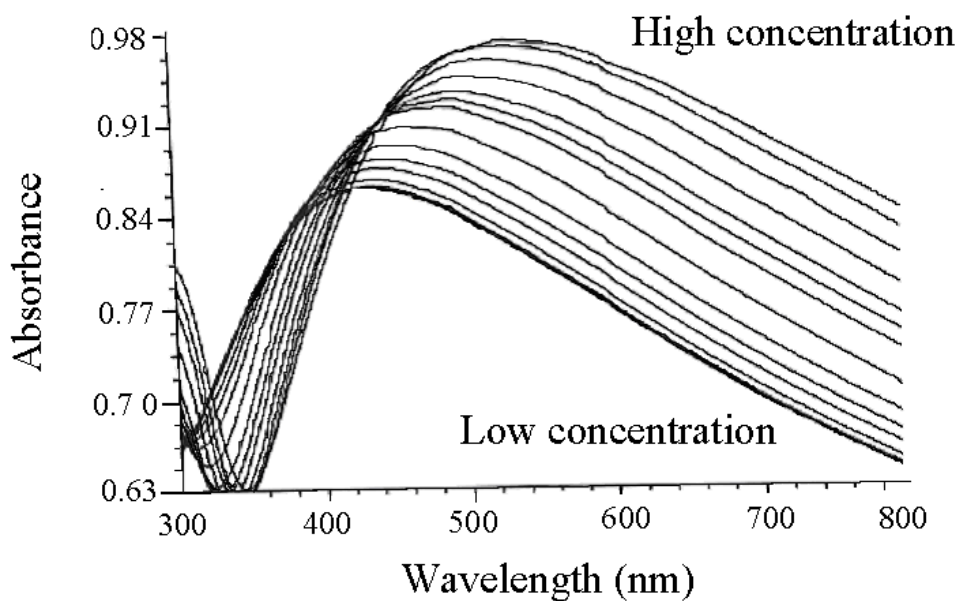


Figure 4: Absorbance spectra of different concentrations of Hg^{2+}

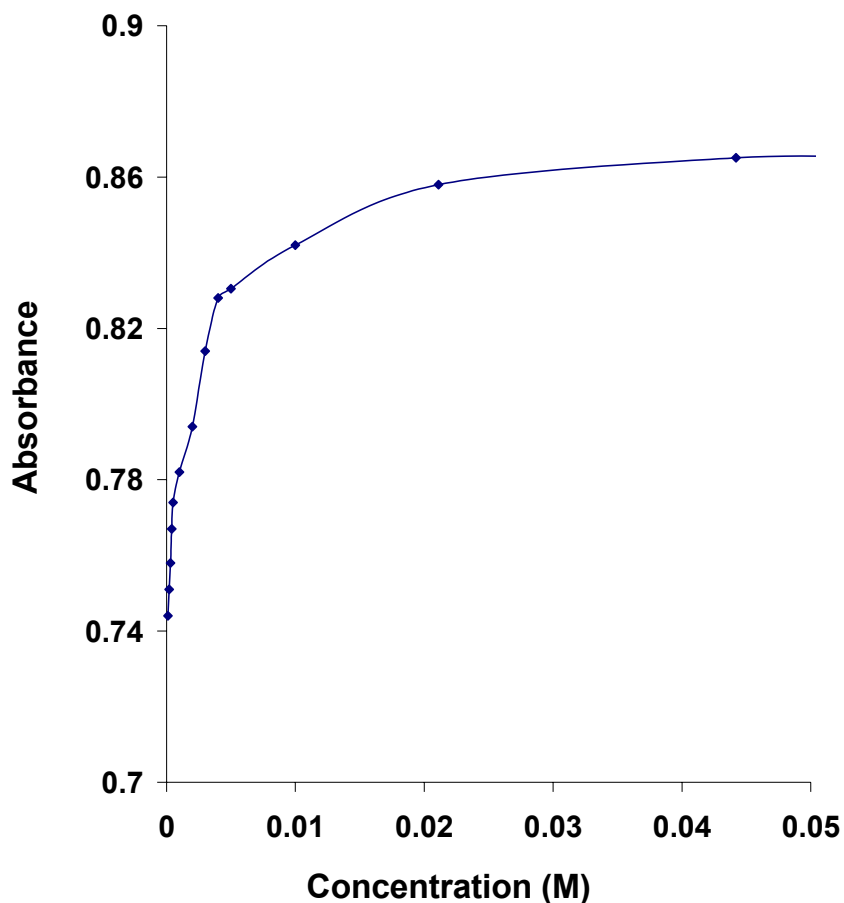


Figure 5: Turbidity absorbance vs. concentration of Hg^{2+}

The response time of the sensing element toward Hg^{2+} ions was obtained by measuring the change in absorbance of a $0.1 \text{ Hg}^{2+} \text{ M}$ solution at 700 nm with time. As the time increased the absorbance increased sharply up to about 10 minutes; at that time the response is about 90%. After that the absorbance continued to increase

slowly up to about 30 minutes as shown in figure 6. The slow response after 10 minutes may be due to the increase in the thickness of the shrinking outer layer of the microsphere surface due the binding between the metal cation and deprotonated functional groups on the polymer microspheres. This resulted in a significant reduction in the rate of diffusion of ions through the sensing membrane.

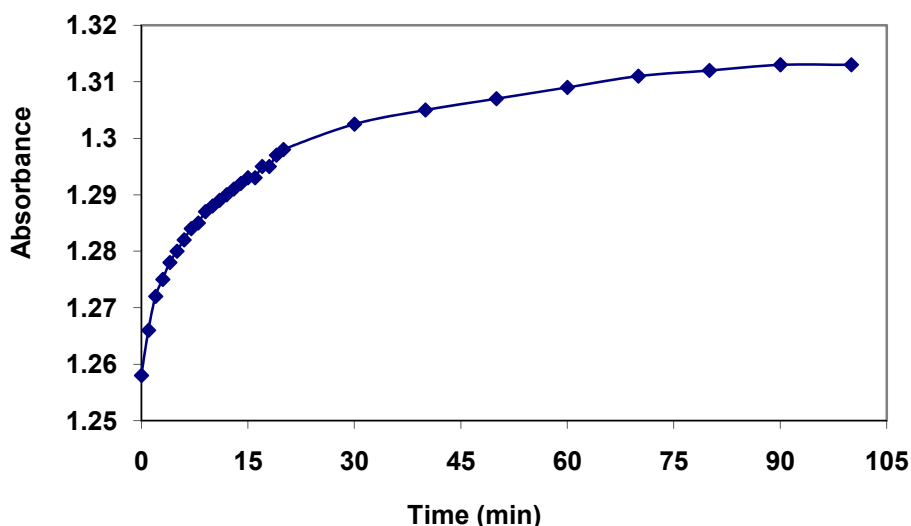


Figure 6: Turbidity absorbance vs. time

The reproducibility of the sensing element was examined by observing the turbidity absorbance of 0.005 M Hg^{2+} aqueous solution at 700 nm, as shown in table 1. When the sensing membrane was in distilled water, the absorbance was 0.682. When the sensing membrane was exposed to an Hg^{2+} solution of 0.005M, the absorbance was almost constant. Between each run the sensor was eluted with saturated aqueous solution of EDTA which eluted instantly and was washed successively with distilled water.

Table 1: The tested reproducibility of the sensing element:

Concentration (Hg^{2+})	1 st run	2 nd run	3 rd run	4 th run
0 M	0.682	0.682	0.682	0.682
$5 \times 10^{-3} M$	0.699	0.699	0.700	0.700

The dependence of Hg^{2+} ion chelation with the dithiocarbamate group on pH was examined by preparing 0.1M Hg^{2+} in buffer solutions (pH 2 -7). We avoided the study below pH 2 because of possible decomposition of the dithiocarbamate functional group^[13], and above pH 7, due to the possible precipitation of Hg^{2+} ions as hydroxide. Figure 7 shows the effect of pH on the complex formation between Hg^{2+} ions and the dithiocarbamate polymer. The chelate reached its optimum level at about pH 5.5. This is in agreement with previous studies^[15, 16]. At pH about 5.5, the sulfur atoms of the dithiocarbamate functional group are completely deprotonated and are free to chelate with Hg^{2+} ions

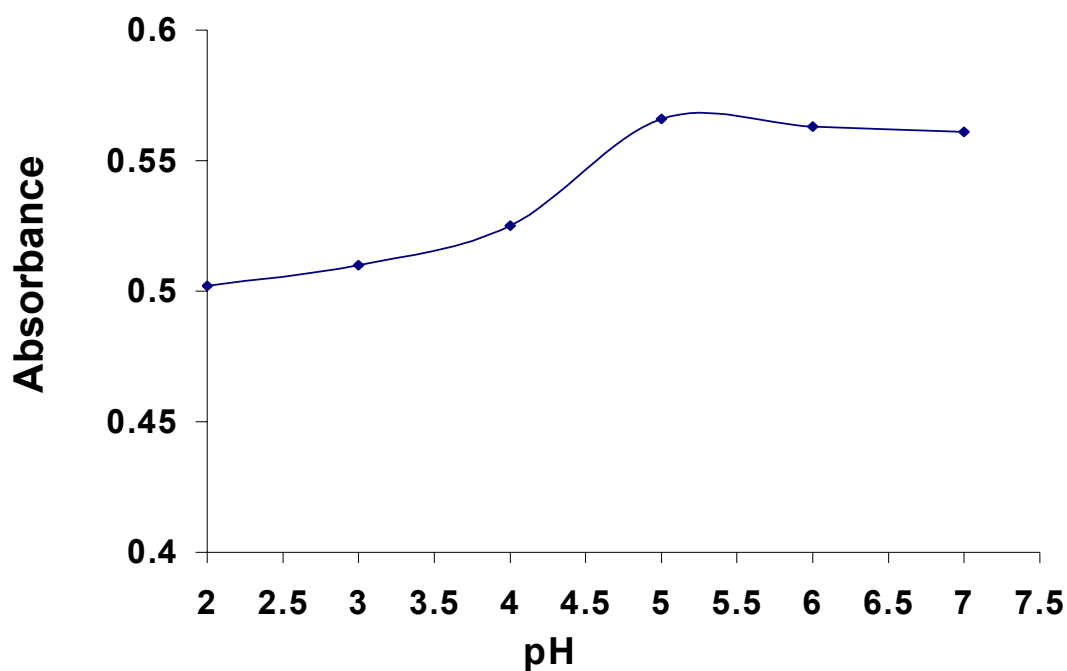


Figure 7: Turbidity absorbance of the sensing element containing 0.1M Hg^{2+} at different pH's.

As expected the dithiocarbamate polymer had no response towards alkali and alkaline earth metal cations as shown in figure 8. This is because the sulfur atoms of the dithiocarbamate group are soft ligands and do not interact with hard metal cations (alkali and alkaline earth metals) ^[13]. Thus, the presence of these metal cations will not affect the optical properties of the sensor; this will allow us to apply this sensor on real samples even at high concentration of these ions (Ca^{2+} , Mg^{2+} , K^+ , and Na^+).

Further studies showed that the response was the same whether Hg^{2+} ions were dissolved in real tap water or in deionized distilled water as shown in figure 9. This demonstrates the applicability of this sensor to actual samples.

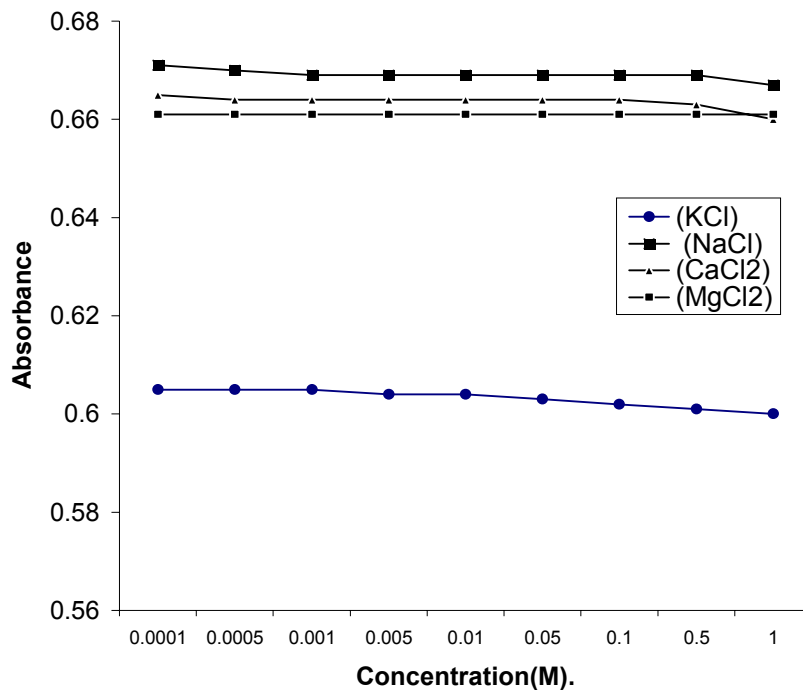


Figure 8: Turbidity absorbance vs. concentration of alkali and alkaline metal ions

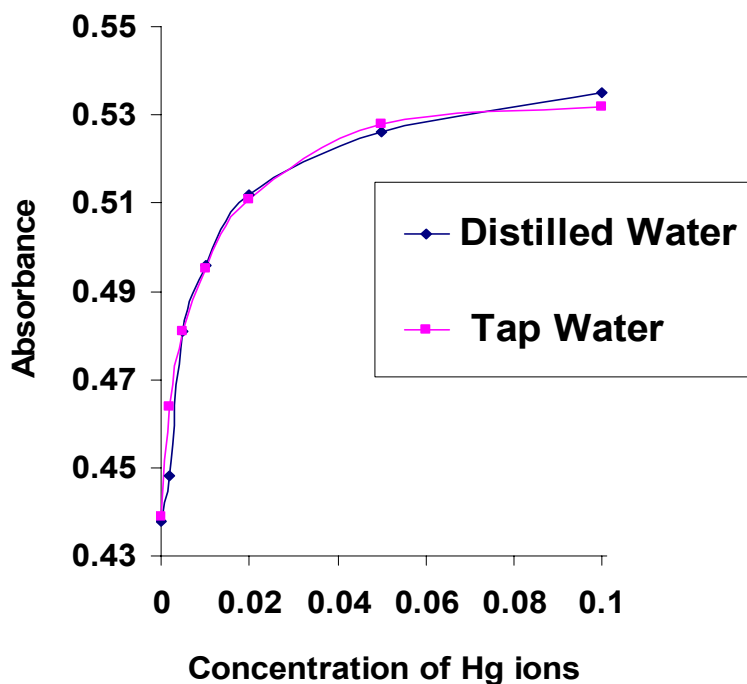


Figure 9: Turbidity absorbance vs. concentration of Hg²⁺ in distilled and in tap water

Conclusion

In this work a new modified optical sensor based on swellable polymer microspheres is developed using a dithiocarbamate functional group covalently bonded to a polyvinyl benzyl polymer back-bone. The dithiocarbamate group shrank in contact with mercury ions. It did not show any response to tested metal ions, especially alkali and alkaline earth metal and Pb²⁺, Zn²⁺, Cd²⁺ ions, regardless of their

concentrations. An optimum response to Hg^{2+} was obtained at pH 5.5. This new generation of optical chemical sensors showed good chemical and mechanical stability.

Chemical sensors based on polymer swelling and shrinking possess many advantages. They are simple and cheap, 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 dithiocarbamate making them capable of targeting different and specific metal ions. Overall; these dithiocarbamate polymers can be used in remote sensing of mercury (II) ions which are among the major environmental pollutants of natural water.

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