

اندازه‌گیری با گزینش پذیری بالا یون مس (II) بوسیله حسگر شیمیایی نوری فیلم پلیمری بر پایه یک باز شیف با استخلاف پیریدین جدید

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تاریخ دریافت: ۳۰ شهریور ۱۳۹۴ تاریخ پذیرش: ۱۱ اسفند ۱۳۹۴

Highly Selective Sensing of Copper(II) Ion by Polymeric Film Optical Chemosensor Based on a New Pyridine-Substituted Schiff-Base

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Received: 21 September 2015

Accepted: 1 March 2016

چکیده

یک اپتود جدید برای اندازه‌گیری گزینش‌پذیر و حساس یون‌های مس بر پایه طیف جذبی یک فیلم پلیمری نازک در محیط‌های آبی ارائه شد. یک غشای شامل پلی وینیل کلراید، نرم‌کننده‌های مختلف و اولئیک اسید به عنوان افزودنی آنیونی تهیه شد. اثر نرم‌کننده‌های مختلف روی حساسیت، گستره خطی و گزینش‌پذیری فیلم غشا مطالعه شد. به‌طور رضایت‌بخشی ویژگی‌های آنالیز تجزیه‌ای یون‌های مس شامل گزینش‌پذیری، تکرارپذیری و تکثیرپذیری در محدوده‌های بسیار خوبی از تشخیص به دست آمدند. به علاوه فیلم‌نوری به‌طور برگشت‌ناپذیری به یون‌های مس در گستره دینامیکی 3.1×10^{-10} تا 2.3×10^{-4} مولار با زمان پاسخ حدود ۵ دقیقه پاسخ می‌دهد. این اپتود به‌طور موفقیت‌آمیزی جهت اندازه‌گیری یون‌های مس (II) در نمونه‌های افزوده شده، به کار رفت.

واژه‌های کلیدی

حسگر شیمیایی؛ مس (II)؛ باز شیف؛ فیلم پلیمری؛ اپتود.

Abstract

A new optode for the sensitive and selective determination of copper (II) ion based on a change in absorption spectrum of a polymeric thin film in aqueous solution was proposed. A composed membrane of polyvinylchloride, different plasticizers and oleic acid as anionic additive was prepared. The influence of different plasticizers on sensitivity, linear range and selectivity of the membrane film were studied. Satisfactorily, analytical sensing characteristics, to determine of the copper ion in terms of the selectivity, reversibility and reproducibility in a good detecting range were obtained. In addition, the optical film responds to copper (II) ion, irreversibly, over a wide dynamic range 3.1×10^{-10} to 2.3×10^{-4} M with a response time ≈ 5 Min obtained confidently. The optode membrane was successfully, applied to determination of copper (II) ion in spiked samples.

Keywords

Chemosensor; Copper (II) Ion; Schiff Base; Polymeric Film; Optode.

1. INTRODUCTION

Many area of applied analytical chemistry such as process control, clinical, food, beverage and environmental samples require a fast and simple method for the determination of the concentration of ionic species in aqueous system. Ion sensors which function in water are in high demand to be used in medicine, food analysis, environmental monitoring and biotechnology. Numerous efforts have been devoted to the development of optical molecular chemosensors in heavy metal ions, especially, during the last decade [1-2].

Copper is an essential trace element for humans, plants and other animals. This metal occurs naturally in soil, water and air throughout the environment. Copper compounds are generally employed in treating plant diseases, water treatment and as protective for woods and leathers. Daily ingestion of copper is indispensable for good health. However, high amounts of copper can be harmful, causing irritation of nose and throat, nausea, vomiting and diarrhea. Very high doses of copper can cause damage to liver and kidney. Humans are commonly exposed to copper through drinking

water, breathing air, eating food. Having skin contact with copper, or particles attaching to copper, copper-containing compounds can give rise to such diseases. In this manner, the determination of trace amounts of copper in several matrices is fundamental to identify the metal contamination in environment, water or human body [3-4].

Various analytical techniques have been proposed for determination of copper including spectrophotometric methods [5-8], atomic absorption spectrometry (AAS) [9-10], inductively coupled plasma emission spectrometry (ICP-ES) [11] and potentiometric methods [12]. These methods usually have a sufficiently low detection limit and specificity. They have also drawbacks such as high costs for equipment and assays, time-consuming and complicated operation. Optical chemical sensors (optodes) for heavy metal ions and the other types of sensors may easily be incorporated into low-cost, easy to use kits and can offer, selectivity and sensitivity for copper(II) ion monitoring in different real samples [13-16].

To extend our studies in the field of sensors and study in the coordination chemistry of the new Schiff base ligands, in this work, we present the synthesis and application of, 2-((*E*)-(2-amino-pyridin-3-ylimino) methyl)-4-bromophenol (DAP-Br) Fig.1, in polymeric optical sensor construction [16-20].

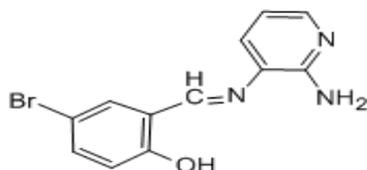


Fig. 1. Chemical structure of tested chromoionophore.

The aim of the present work was to develop a new polymeric membrane optical sensor for the selective determination of copper(II) ion based on its complexation reaction with DAP-Br. For this propose, the solution studies about the stoichiometry and structure of the complex is carefully studied with different cations in acetonitrile solution. The best of our knowledge, there is no report to synthesis and application of this new Schiff base ligand for the construction optical sensor.

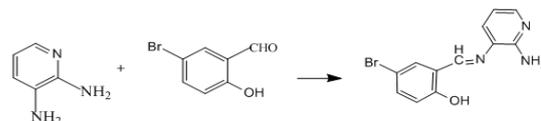
2. EXPERIMENTAL

2.1. Reagents

Reagents grade dioctyl phthalate (DOP), acetophenone (AP), oleic acid (OA), nitrophenyl octyl ether (NPOE), high relative molecular weight PVC and tetrahydrofuran (THF), were

purchased from Merck and used as received. The sodium salts of the anions used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. Doubly distilled deionized water was used throughout.

The (DAP-Br) was synthesized by condensation of 5-bromo-salicylaldehyde and 2, 3-diamino pyridine (Scheme 1) and used after recrystallization.



Scheme 1. Synthesis procedure for DAP-Br

The spectroscopic results for $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis are: $^1\text{H-NMR}$: 4.8221 ppm/s; 6.73048ppm /t; 6.93342ppm/d; 7.24441 ppm/d; 7.47458 ppm/d; 7.51886 ppm/s; 8.03766 ppm/s; 8.52788 ppm/s.

$^{13}\text{C-NMR}$: 161.154/ 158.716/ 152.157/ 146.315/ 135.181/ 133.326/ 128.857/ 124.092/ 119.573/ 118.251/ 113.492/ 109.941 ppm.

The stock Cu(II) solution, by dissolving appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in deionized water was prepared. Working standard solutions of Cu(II) were prepared by appropriate volume dilution of the stock solution. According to methods by using Metrohm combined pH glass electrode, Buffer solutions were prepared.

2.2. Instrumentation

All Absorbance measurements were carried out with a Perkin-Elmer double beam spectrophotometer with quartz cells. A Metrohm combined pH glass electrode was used for pH measurement at 25.0 ± 0.1 °C.

2.3. Preparation of optode films

The general polymeric membrane films, by dissolving different amounts of PVC and three types of plasticizers solvent mediator in the minimum amount of THF, were prepared. Appropriate amount of chromoionophore (DAP-Br) was added to the mixture. The solution mixed well. The resulting mixture was poured on the previously prepared 0.8×1.8 cm glass slides, then was subsequently mounted in the UV-visible quartz cell. Blank reference membranes were prepared in a similar way, except without using DAP-Br. Then the glass plate covered with the membrane was placed vertically inside the sample quartz cell that contained 2mL aqueous solution. The blank membrane (without chromoionophore) that was covered on glass plate put in the

reference cell. The sample cell was finally titrated with standardized cation ion solutions.

3. RESULTS AND DISCUSSIONS

3.1 Solution studies

In order to find a clue about the stability and selectivity of new complex, in the preliminary studies, the UV-visible spectra of DAP-Br with different important cations in acetonitrile solution was investigated. When a 5.0×10^{-5} M solution of DAP-Br in acetonitrile was titrated with standard solutions of different cations, a rapid color change occurred after the addition of copper(II) ion (yellow to orange). As seen in Figure. 2, the absorption UV-band of DAP-Br at 375 nm was decreased and a new band of complex in range of 450-500 nm was appeared. While adding other cations, including Ni^{2+} , Cd^{2+} , Zn^{2+} , Co^{2+} , Fe^{2+} and Hg^{2+} small spectral changes was observed in the sensing solution. This high selectivity was attributed to the formation of new adduct between the center of DAP-Br and the Cu(II) ion.

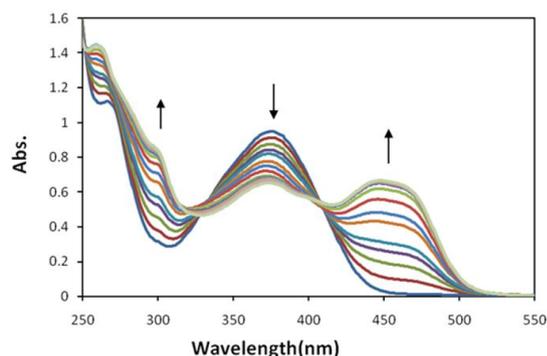


Fig. 2. Electronic absorption spectra solution of 2.0×10^{-6} M DAP-Br in AN after equilibration with increasing concentration of Cu^{2+} ion.

The stoichiometry of the resulting complexes can be distinguished by mole-ratio plot. Electronic absorption spectra and typical absorbance vs. $[\text{Cu}^{2+}]/[\text{DAP-Br}]$ mole-ratio plots for titration of copper(II) ion in acetonitrile solution was shown in Fig.3.

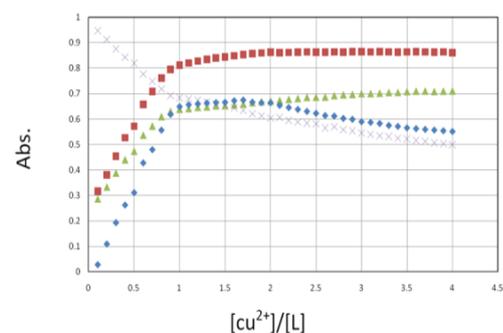


Fig. 3. Absorption vs. mole ratio plots at different wavelengths.

The formation constants of the resulting complexes were evaluated by computer fitting of the absorbance-mole ratio data to an appropriate equation as described [21-22] and the results summarized in Table 1. As it is obvious from the data in Table 1, the stability of the 1:1 complexes decreases in the order $\text{Cu}^{2+} > \text{Hg}^{2+} > \text{Fe}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$.

Table.1. K_f values for different cation 1:1 complex with DAP-Br in acetonitrile solution.

Temp= 25°C	Cu^{2+}	Hg^{2+}	Cd^{2+}	Ni^{2+}	Fe^{2+}	Co^{2+}	Zn^{2+}
Log K_f	5.3 ± 0.001	5.2 ± 0.0005	2.9 ± 0.011	3.05 ± 0.0008	5.08 ± 0.01	4.5 ± 0.01	4.8 ± 0.0008

Thus, the based on this selectivity DAP-Br compound was expected to act as a selective chromoionophore in the preparation of a PVC-based ion-selective optode for Cu^{2+} . The electronic absorption spectra for polymeric film in titration with Cu^{2+} was shown in Fig. 4.

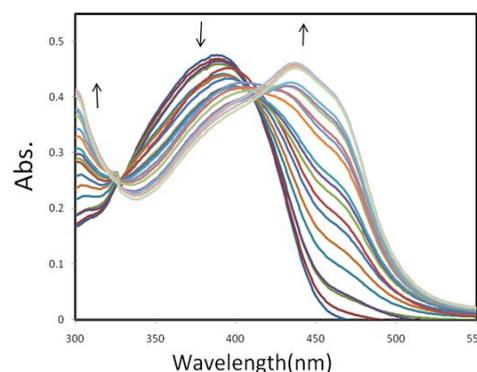
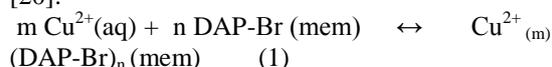


Fig. 4. Absorption spectra of the optode film in the presence of different concentration of Cu^{2+} .

3.2. Operation principle

The response mechanism of the optical sensor membrane based on the change in absorption spectrum can be explained as follows. When the sensing membrane film contacts with various concentrations of Cu^{2+} ions in aqueous solution phase (aq) and DAP-Br in membrane phase (mem) the following equilibrium along with the formation of a m: n complex, being established [20]:



Here, K is the equilibrium constant. The difference between the activities and concentrations is neglected. According to the law of mass action, K can be expressed as:

$$K = \frac{[\text{Cu}^{2+}_{(m)}] (\text{DAP-Br})_n (\text{mem})}{([\text{Cu}^{2+}_{(aq)}]^{m} [\text{DAP-Br}]^n)} \quad (2)$$

3.3 Response behavior of different membrane formulation

It is well known that the membrane film composition may largely influence the response characteristics and working concentration range of the optical sensors [23-25]. Thus, in this work, nine PVC-membranes along with the same plasticizer/PVC ratios, but varying nature and amount of other ingredients were prepared.

It should be noted that the plasticized PVC-membranes used in sensors will usually result in the response membrane characteristics at a plasticizer / PVC ratio of about 2 [26].

Since in bulk membrane optodes, the membrane must be in thermodynamic equilibrium with the sample, a mass transfer of analyte into the membrane is required [27-28].

Thus, in the proposed Cu^{2+} selective optosensor containing DAP-Br as a neutral chromoionophore, the presence of a lipophilic additive like OA is necessary to facilitate the ion-exchange equilibrium. The absence of OA was found not only in the working concentration range of the sensor, but also caused the response time be prolonged and selectivity be reduced [29-30].

The presence of 66-69% plasticizer in the PVC-membranes resulted in optimum physical properties, as well relatively high mobilities of their constituents. The nature of plasticizer is well known to influence considerably the measuring range of the solvent polymeric membrane sensors and their selectivity coefficients. The use of DOP as plasticizer resulted in a large widening of measuring range 2.3×10^{-4} to 3.1×10^{-10} M with LOD 1.5×10^{-10} M of the proposed optical sensor over the membrane based on DOP and AP. The novelty of this work is plasticizer free composition with a large widening range 1.1×10^{-4} to 9.8×10^{-8} M with LOD 1.02×10^{-8} M. It seems that OA play role of plasticizer.

3.4. Effect of pH, calibration curve and response time

The influence of pH of the test solution on the response of the optode membrane film was tested for a 1.0×10^{-6} M Cu^{2+} solution in the pH range 3.0 -11.0 (adjusted with HNO_3 or NaOH). As it is seen response of the sensor is remain constant from pH 3.0-8.0 beyond which the α -value changes considerably. The observed drift at lower and higher pH values could be due to the protonation of the ion carrier and formation of some hydroxyl complexes of Cu^{2+} ion in solution, respectively.

The optical response of the proposed copper(II)

selective optosensor at different copper(II) concentrations was tested under optimal experimental conditions. The resulting calibration graph for Cu^{2+} ions were obtained at wavelength 466 nm in Fig. 5.

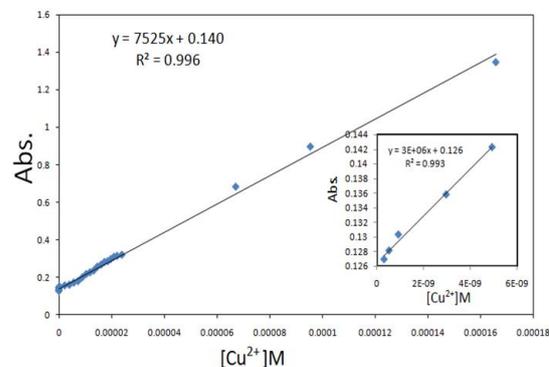


Fig. 5. Calibration curve for the optical thin film at 466nm for sensor.

The dynamic concentration range of the proposed sensor for Cu^{2+} ion was 2.3×10^{-4} to 3.1×10^{-10} M. The limit of detection, as determined based on the 3σ of the blank membrane film was 1.5×10^{-10} M. The static response time obtained for the sensor is only about 300 s, over entire concentration range. The typical response curve of optode membrane film at 466 nm as a function of time for Cu^{2+} ion addition was shown in Fig. 6.

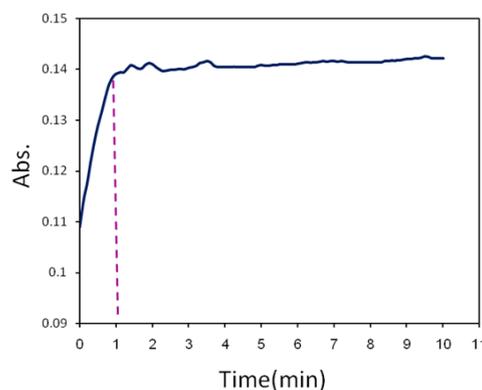


Fig. 6. Response curve of the sensor at 466nm as a function of time for different concentration of Cu^{2+} .

3.5. Interference tests

The selectivity of the proposed optosensor toward Cu^{2+} with respect to various interfering ions was determined by the error percent method [31]. The resulting error percent values are summarized in Fig. 7.

As seen, the selectivity pattern is $\text{Ag}^+ > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$. From the data given in Fig. 7, it is obvious that the proposed copper (II) sensor is highly selective with respect to other cations.

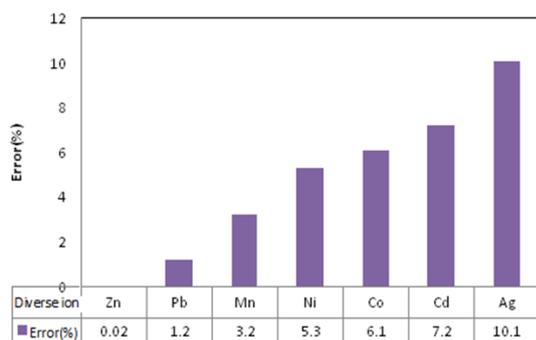


Fig. 7. Diagram of selectivity for proposed optical sensor based on percent error.

3.6. Application for real samples

The proposed optical sensor was also successfully applied to the direct determination of copper ion in real samples by add found method. The results were compared with each other and they were in agreement. The results for three replicate are presented in Table 2.

CONCLUSIONS

In this work, a composed membrane of PVC/ plasticizer/ oleic acid was used and a new optode was prepared for determination of copper(II) in aqueous samples. In optimum conditions a wide linear range 3.1×10^{-10} to 2.3×10^{-4} M of Cu(II) was obtained.

ACKNOWLEDGEMENT

We gratefully acknowledge financial support from the research council of the Payame Noor University (PNU).

REFERENCES

- [1] P. Buhlmann, E. Pretsch and E. Bakker, Chem. Rev. Carrier-Based Ion-Selective Electrodes and Bulk Optodes, *J. Gen. Characterist.* 98 (1997) 3083- 3132.
- [2] W. Qin, P. Parzuchowski, W. Zhang and M. E. Meyerhoff, Optical and Electrochemical Anion Sensors Based on Metalloporphyrins and dimer-monomer equilibrium of indium (III) octaethylporphyrin in polymeric film, *Anal. Chem.* 75 (2003) 332-340.
- [3] C. Baird, *Environmental Chemistry*, 2nd ed., Freeman and Longman, UK, 1999.
- [4] H.A. McKenzie and L.E. Smythe, *Quantitative Trace Analysis of Biological Materials*, Elsevier, Amsterdam, (1988).
- [5] I. Oehme and O.S. Wolfbeis, Optical Sensors: Industrial, Environmental and Diagnostic Applications, *Mikrochim. Acta*, 126 (1997) 177–192.
- [6] H. Tavallali, H. Shafiekhani, M. K. Rofouei and M. Payehghadr, A new triazene ligand immobilized on triacetylcellulose membrane

- for selective determination of mercury ion, *J. Braz. Chem. Soc.* 25 (2014) 799-821.
- [7] E. Pourbasheer, S. Morsali, A. Banaei, S. Aghabalazadeh, M. R. Ganjali and P. Norouzi, Design of a novel optical sensor for determination of trace amounts of copper by UV/VIS spectrophotometry in the real samples, *Ind. Eng. Chem.* 26 (2015) 370-374.
- [8] N. Chimpalee, D. Chimpalee, S. Lohwithee, L. Nakwatchara and D.T. Burns, Spectrophotometric determination of copper after extraction of its chelate with bis(acetylaceton)ethylenediimine, *Anal. Chim. Acta* 329 (1996) 315–318.
- [9] S. Karabocek, S. Nohut, O. Dalman and S. Guner, A new spectrophotometric reagent for copper: 3,3'-(1,3-propanediyl diimine)bis-[3-methyl-2-butanone]dioxime, *Anal. Chim. Acta* 408 (2000) 163–168.
- [10] M.H. Mashhadizadeh, M. Pesteh, M. Talakesh, I. Sheikhshoae, M.M. Ardakani and M.A. Karimi, Solid phase extraction of copper (II) by sorption on octadecyl silica membrane disk modified with a new Schiff base and determination with atomic absorption spectrometry, *Spectrochim. Acta B* 63 (2008) 885–888.
- [11] R.J. Cassella, O.I.B. Magalhaes, M.T. Couto, E.L.S. Lima, M.A.F.S. Neves and F.M.B. Coutinho, Synthesis and application of a functionalized resin for flow injection/F AAS copper determination in waters, *Talanta* 67 (2005) 121–128.
- [12] M.H. Mashhadizadeh, S. Ramezani and S. Ebrahimi, Potentiometric determination of nanomolar concentration of Cu (II) using a carbon paste electrode modified by a self-assembled mercapto compound on gold nanoparticles, *Sens. Actuators, B: Chem.* 169 (2012) 305-311.
- [13] A. Mohadesi and M.A. Taher, Voltammetric determination of Cu(II) in natural waters and human hair at a meso-2,3-dimercaptosuccinic acid self-assembled gold electrode, *Talanta* 72 (2007) 95–100.
- [14] M. Shamsipur, T. Poursaberi, A. Avanes and H. Sharghi, Copper(II)-selective fluorimetric bulk optode membrane based on a 1-hydroxy-9,10-anthraquinone derivative having two propenyl arms as a neutral fluorogenic ionophore, *Spectrochim. Acta B* 63 (2006) 43-48.
- [15] A. Yari and F. Papi, Ultra trace mercury(II) detection by a highly selective new optical sensor, *Sens. Actuator* 138 (2009) 467- 473.
- [16] M. Shamsipur, S. Ershad, N. Samadi, A. Rezvani and H. Haddadzadeh, The first use

- of a Rh(III) complex as a novel ionophore for thiocyanate selective polymeric membrane electrodes, *Talanta* 65 (2005) 991-997.
- [17] M. Shamsipur, S. Ershad, N. Samadi, A. Moghimi and H. Aghabozorg, A novel chemically modified carbon paste electrode based on a new mercury(II) complex for selective potentiometric determination of bromide ion, *J. Solid State. Electrochem.* 9 (2005) 788-793.
- [18] M. Shamsipur, S. Ershad and F. Jalali, preparation of a diclofenac potentiometric sensor and its application to pharmaceutical analysis and to drug recovery from biological fluids, *J. Pharm. Biomed. Anal.* 37 (2005) 943-947.
- [19] N. Daneshvar, A.A. Entezami, A.A. Khandar and L. A. Saghatforoush, Synthesis and characterization of copper(II) complexes with dissymmetric tetradentate Schiff base ligands derived from aminothioether pyridine. Crystal structures of [Cu(pytlal)]ClO₄•0.5CH₃OH and [Cu(pytlal)]ClO₄, *Polyhedron* 22 (2003) 1437.
- [20] S. Ershad, L. Saghatforoush and G. Karimnezhad, A Selective Optical Chemosensor Based on a Thia-Containing Schiff Base iron (III) Complex for Thiocyanate Ion, *Anal. Sci.* 25 (2009) 665-670.
- [21] M. Shamsipur, S. Ershad, A. Yari, H. Sharghi and A.R. Salimi, hydroxythioxanones as a suitable neutral ionophores for the preparation of PVC membrane potentiometric sensors for Al(III) Ion, *Anal. Sci.* 20 (2004) 301-306.
- [22] M. Shamsipur, S. Ershad, N. Samadi, A. R. Esmailbeig, R. Kia and A. Abdolmaleki, polymeric membrane lanthanum(III) selective electrode based on n,n-adipybis (5-phenyl azo salicylaldehyde hydrazine, *Electroanal.* 17 (2005) 1828-1834.
- [23] M. Shamsipur, G. Khayatian and S. Tangestanijad, Thiocyanate-Selective Membrane Electrode Based on (Octabromotetraphenylporphyrinato) manganese(III) Chloride, *Electroanal.* 11 (1999) 1340-1344.
- [24] M. Shamsipur, T. Poursaberi, A. R. Karami, M. Hosseini, A. Momeni, N. Alizadeh, M. Yousefi and M. R. Ganjali, Development of a new fluorimetric bulk optode membrane based on 2,5-thiophenylbis(5-tert-butyl-1,3-benzoxazole) for nickel(II) ions, *Anal. Chim. Acta* 501 (2004) 55-60.
- [25] W.E. Morf, K. Seiler, B. Lehmann, C. Behringer, K. Hartman and W. Simon, Carriers for chemical sensors: Design features of optical sensors (optodes) based on selective chromoionophores, *Pure Appl. Chem.* 61 (1989) 1613-1618.
- [26] A.A. Ensafi and A. Kazemzadeh, Monitoring Nitrite With Optical Sensing Film, *Microchem. J.* 72 (2002) 193-199.
- [27] T. Rostazin, E. Bakker, K. Suzuki and W. Simon, Lipophilic and immobilized anionic additives in solvent polymeric membranes of cation-selective chemical sensors, *Anal. Chim. Acta* 280 (1993) 197-208.
- [28] G.J. Moody, R.B. Oke and J.D.R. Thomas, A calcium-sensitive electrode based on a liquid ion exchanger in a poly(vinyl chloride) matrix, *Analyst* 95 (1970) 910-918.
- [29] M.A. Simon and R.P. Kusy, The molecular, physical and mechanical properties of highly plasticized poly(vinyl chloride) membranes, *Polym.* 34 (1993) 5106.
- [30] E. Bakker, A. Xu and E. Pretsch, Optimum composition of neutral carrier based pH electrodes, *Anal. Chim. Acta.* 295 (1994) 253-262.
- [31] N. Alizadeh, A. Momeni and M. Shamsipur, Poly(vinyl chloride)-membrane ion-selective bulk optode based on 1,10-dibenzyl-1,10-diaza-18-crown-6 and 1-(2-pyridylazo)-2-naphthol for Cu²⁺ and Pb²⁺ ion, *Anal. Chim. Acta* 464 (2002) 187-196.