Int. J. Electrochem. Sci., 6 **(2011)** 2955 - 2964

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Fabrication of an Y^{3+}-PVC Membrane Sensor Based on Dicyclohexyl-18-Crown-6 for Determination Fluoride Ion

Malihe Samadi. Kazemi[1,*], *Narges Ashraf*[2]

[1] Department of Chemistry, Faculty of Sciences, Bojnourd Branch, Islamic Azad University, Bojnourd, Iran.
[2] Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran.
[*]E-mail: samadi24243@yahoo.com

Received: 5 May 2011 / *Accepted:* 10 June 2011 / *Published:* 1 July 2011

In this research, construction and performance characteristics of a PVC membrane electrode based on dicylohexyl-18-crown-6 (DCH18C6) as a neutral ionophore have been described. The influence of the membrane composition on the potentiometric response of the electrode has been investigated and optimized to improve the performance characteristics. The best performance was obtained with the membrane composition (w/w %) of DCH18C6 (7%): PVC (60%): DOP (23%): C (10%). The proposed electrode exhibits a Nernstian slope of 19.78 mv /decade within the wide concentration range of 1×10^{-2} to 1×10^{-6} M. The limit of detection for Y^{3+} ion was found to be 7.33×10^{-7} M and the potentiometric response was independent from the pH of the test solution in the pH range of 2.0 - 5.0. Also, it has a response time of 20 s for yttrium (III) concentrations ranging from 1×10^{-2} to 1×10^{-6} M. The sensor could be used for a period of 45 days. The analytical usefulness of the proposed electrode has been evaluated by its application in the determination of fluoride ion in mouthwash and toothpaste real samples.

Keywords: Yttrium (III) selective electrode, dicylohexyl-18-crown-6, poly (vinylchloride) membrane, potentiometry.

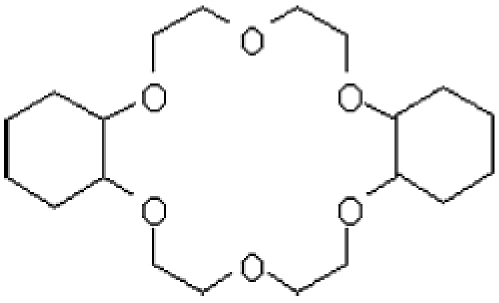
1. INTRODUCTION

The rare earth elements (REEs) are widely distributed in the low concentrations throughout the earth's crust and are considered slightly toxic [1]. Yttrium is a rare earth element which has wide applications in the radiotherapy [2], catalysis [3], synthesis of nanosized materials [4], hydroyttration reagents [5], fluorescence probe [6], nuclear energy and metallurgical industries [7]. Thus, its determination in a wide range of real samples is of great importance.

Ion-selective electrodes (ISEs) are a typical example of chemical sensors that use the principle of molecular recognition chemistry. They are readily prepared by immobilizing host molecules cable of recognizing a specific class of guest ionic species in an appropriate polymeric matrix [8]. Analytical methods based on potentiometric detection with ion-selective electrodes (ISEs) are eco-friendly and non-destructive techniques; provide easy construction and manipulation, present good selectivity; have relatively low detection limits and show a fast response time. Unfortunately, there are only few reports on selective chemical sensors for Y^{3+} ion [9-12].

Macrocyclic compounds containing oxygen, sulfur and nitrogen as donor atoms have gained attention for their ability to form stable complexes with ions within their central cavity [13-15]. Crown ethers are important class of macrocyclic ligands described by Pedersen in 1967 [16]. The selective complexing properties exhibited by crown ethers towards metal ions [17–19] have led to their incorporation into polymeric matrices [20-22].

In the present work, dicylohexyl-18-crown-6 (scheme I) was used as ionophore in a PVC based membrane sensors for determination of yttrium (III) ions.



Scheme I.

Sensor with optimized membrane composition displayed enhanced selectivity, stability, fast and linear response in a wide concentration range of yttrium (III) ion. Also the proposed electrode has been evaluated by its application in the determination of fluoride in mouthwash solution and toothpaste.

2. EXPERIMENTAL

2.1. Chemicals

The following chemicals and solvents have been used in this study. Yttrium(III) nitrate (Aldrich), dicylohexyl-18-crown-6 (DCH18C6) (Aldrich), high molecular weight (polyvinylchloride) (Aldrich), dioctylphthalate (DOP) (Reidel), powder carbon(Merck), tetrahydrofuran (THF) (Merck), Cyclo hexylenedinitrilotetraacetate(Merck), sodium hydroxide (Merck), sodium chloride(Merck) and acetic acid(Merck) were of analytical grade and used without further purification.

2.2. Electrode preparation

The general procedure to prepare the PVC membrane was to mixed thoroughly 150 mg of powdered PVC, 57.5 mg of the plasticizer DOP and 25.0 mg powder carbon in 5 ml of THF. To this mixture was added 17.5 mg of the ionophore DCH18C6 and the solution was mixed well.

To prepare the coated Y (III) selective electrodes, graphite rods (with 10 cm length and 3 mm diameter) were used. A polished graphite electrode was dipped into the membrane solution mentioned above, and then, the solvent was evaporated.

The membrane was formed on the graphite surface, and the electrode was allowed to stabilize overnight. The electrode was finally conditioned for 24 h by soaking in a 1×10^{-2} M solution of yttrium (III) nitrate.

2.3. Emf measurements

All emf measurements were carried out using the following assembly: Graphite surface│PVC membrane│sample solution│KCl (saturated), Ag-AgCl

The potentials were measured with an ATC pH/mv meter GP353 at 25.0±0.1°C. The performance of the electrode was investigated by measuring its potential in yttrium (III) solutions prepared in the concentration ranges of 1×10^{-2} to 1×10^{-6} M by serial dilution at constant pH. The solutions were stirred and potential readings recorded when they reached a steady state value. The pH of the solutions was adjusted with dilute hydrochloric acid or sodium hydroxide solution.

2.4 Real samples preparations

2.4.1. Preparation of toothpaste sample

Accurately, about 0.2 g of toothpaste was transferred into a beaker and 50 ml ionic strength adjustor of TISAB added. The mixture was then boiled gently for 3 minutes. The suspension was cooled and transferred to a volumetric flask and diluted with distilled water to a final volume of 100 ml.

2.4.2. Preparation of mouthwash sample

A 50 ml portion of mouth wash solution was transferred into a volumetric flask and made to volume with the TISAB solution.

3. RESULTS AND DISCUSSION

3.1. Effect of membrane composition

Formation constant of the ion-ionophore complex within the membrane phase is a very important parameter that indicates the practical selectivity of the sensor [16, 23-24]. In previous experiments, we showed that the dicyclohexyl-18-crown-6 (DCH18C6) ligand with Y^{3+} cation formed a stable 1:1 complex [25].

The sensitivity, selectivity and linearity of ion-selective sensors not only depend on the nature of the ionophore but also significantly on the membrane composition. The effects of the membrane composition on the potential response of the Y^{3+} sensor were investigated and the results are summarized in Table 1. As seen from this Table, the use of 23% DOP in the presence of 60% PVC, 7% ionophore and 10% powder carbon results in the best sensitivity with a Nernstian slope of 19.78 mv/decade.

Table 1. Optimization of the membrane composition

No.	Composition(%)				Slope	Linear range(M)
	PVC	Ionophore	Plasticizer	Powder carbon		
1	63	4	23	10	23.50	1.0×10^{-6}-1.1×10^{-2}
2	62	5	23	10	24.87	1.0×10^{-6}-1.1×10^{-2}
3	60	7	23	10	19.78	1.0×10^{-6}-1.1×10^{-2}
4	59	8	23	10	21.46	1.0×10^{-6}-1.1×10^{-2}
5	73	7	10	10	18.02	1.0×10^{-6}-1.1×10^{-2}
6	68	7	15	10	19.69	1.3×10^{-5}-1.1×10^{-2}
7	63	7	20	10	18.36	1.0×10^{-6}-1.1×10^{-2}
8	58	7	25	10	20.45	3.6×10^{-6}-1.1×10^{-2}
9	69	7	23	1	14.28	1.0×10^{-6}-1.1×10^{-2}
10	59.5	7	23	17.5	18.90	4.9×10^{-5}-1.1×10^{-2}
11	50	7	23	20	22.17	8.3×10^{-5}-1.1×10^{-2}

3.2. Effect of pH on the sensor response

The pH dependence of the potentials of the constructed ion selective electrodes was investigated by measuring their potential over a pH range of 1–8, where pH was adjusted with dilute HNO_3 and NaOH solutions. The potentials were found to stay constant from the pH 2.0 to 5.0 (Fig. 1). Variation of the potentials at the pH >5 can be related to formation or precipitation of hydroxyl complexes of Y^{3+} ion which reduces the free cation concentration in the solution. On the other hand, at the pH <2, the protonation of the ligand may results in a loss of its ability to complex with Y^{3+} ion.

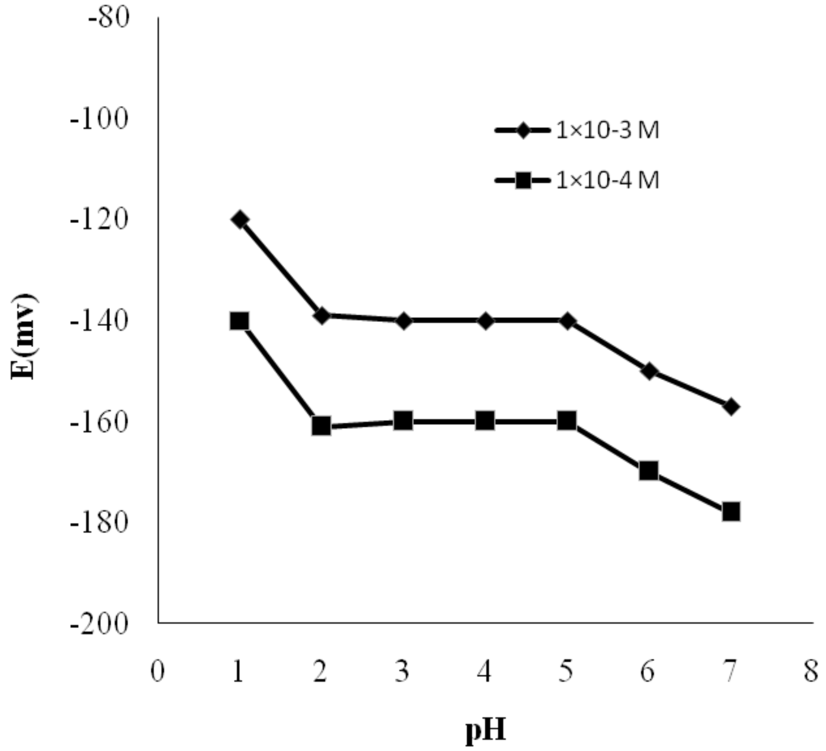


Figure 1. Effect of pH of the test solutions on the potential response of the Y^{3+} -ISE.

3.3. Potentiometric selectivity

The selectivity coefficients $K_{Y,M}^{MSM}$ values which were evaluated graphically by the mixed solution method [26] from the potential measurements on the solutions containing a fixed concentration of Y(III) ion(1×10^{-4} M) and varying amount of the interfering ions (M^{n+}) according to the following equation:

$$a_M^{3/n} K_{Y,M}^{MSM} = a_Y \{\exp(E_2 - E_1)2F/RT\} - a_Y$$

where a_Y is the activity of the Y^{3+}cation, a_M the activity of the interfering ion, M, with a charge of n, and E_1 is the potential measured when only Y^{3+} is present in solution, E_2 is the potential measured in the presence of both the Y^{3+} cation and the interfering ion, M^{n+}. The $K_{Y,M}^{MSM}$ values for ions can evaluated from the slop of graph of $a_Y^{3+}\{\exp(E_2 - E_1)2F/RT\} - a_Y^{3+}$ versus a_Y^{3+}.

The resulting values of the selectivity coefficients are summarized in Table 2. As is obvious from this Table for polyvalent cations the selectivity coefficients are in the order 10^{-2} or smaller, while the selectivity coefficient seems to be larger in the case of univalent cations. However, it should be noted that such deceptively larger coefficients arise from the term $a^{3/n}$ in related equation, the smaller the charge of interfering ion, *n*, the larger the selectivity coefficient, $K_{Y,M}^{MSM}$. Thus, despite their larger selectivity coefficients, the univalent cations used would not disturb the function of the sensor significantly.

Table 2. Selectivity coefficients of various the interfering ions M^{n+}

^{a} $\mathbf{M^{n+}}$	^{b} $K_{Y,M}^{MSM}$
Zn^{2+}	2.12×10^{-2}
Tl^{+}	1.10×10^{-1}
Pb^{2+}	8.96×10^{-2}
Na^{+}	4.20×10^{-1}
Ag^{+}	$4.8\ 0\times10^{-1}$
Co^{2+}	7.64×10^{-2}
K^{+}	0.80×10^{-1}
Ca^{2+}	1.34×10^{-3}
Mg^{2}	2.12×10^{-4}
Cu^{2+}	3.00×10^{-2}

[a] Interfering ion [b] The selectivity coefficient

3.4. Calibration curve and statistical data

The *emf* response of the membrane at varying concentrations of Y^{3+} ion indicates a rectilinear range from 1×10^{-2} to 1×10^{-6} M. The slope of the calibration curve was 19.78mV/decade of Y^{3+} concentration (Fig. 2).

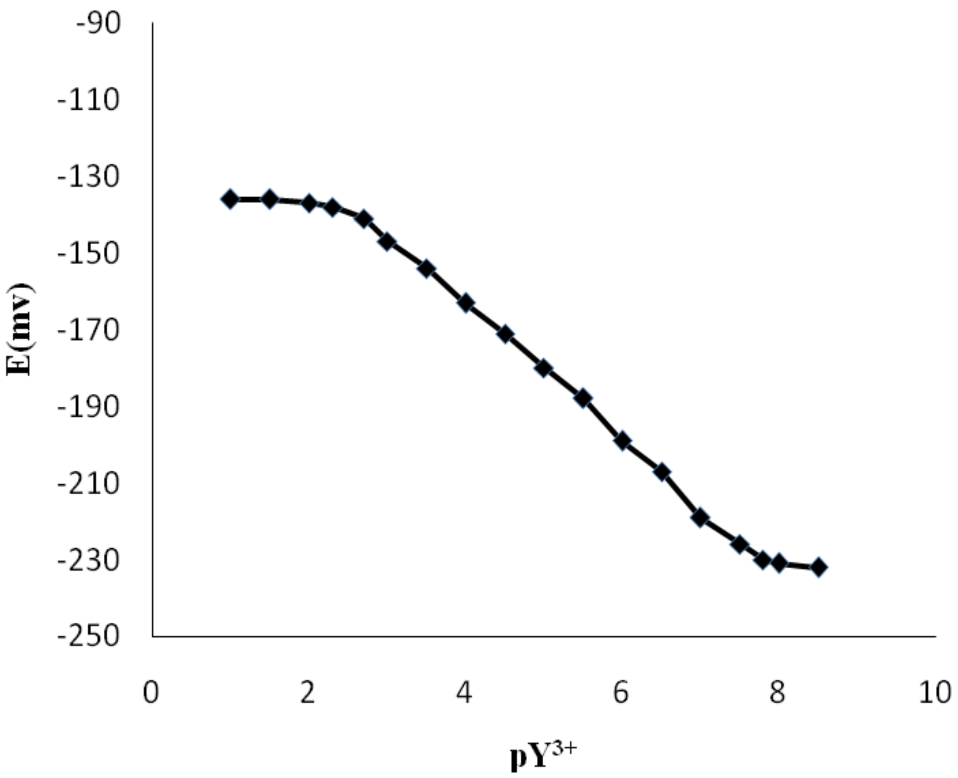


Figure 2. Calibration graph for the Y^{3+} -ISE.

The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph was 7.33×10^{-7} M. The standard deviation of 10 replicate measurements is ±0.3 mV.

3.5. Response and lifetime of the proposed sensor

Dynamic response time is an important factor for any ion selective electrode. To measure the dynamic response time of the proposed electrode the concentration of the test solution was successively changed from 1×10^{-2} to 1×10^{-6} M. The average time required for the electrode to reach a potential response within ±1mv of the final equilibrium value after successive immersion in a series of Y^{3+} ion solutions, each having a 10-fold difference in concentration is 20 s (Fig.3). Potentials generated by the developed sensor remained stable for more than ~5 min after which a slow divergence was recorded. Also the sensor could be used a period of 45 days without observing any significant change in response time, slope and working concentration range.

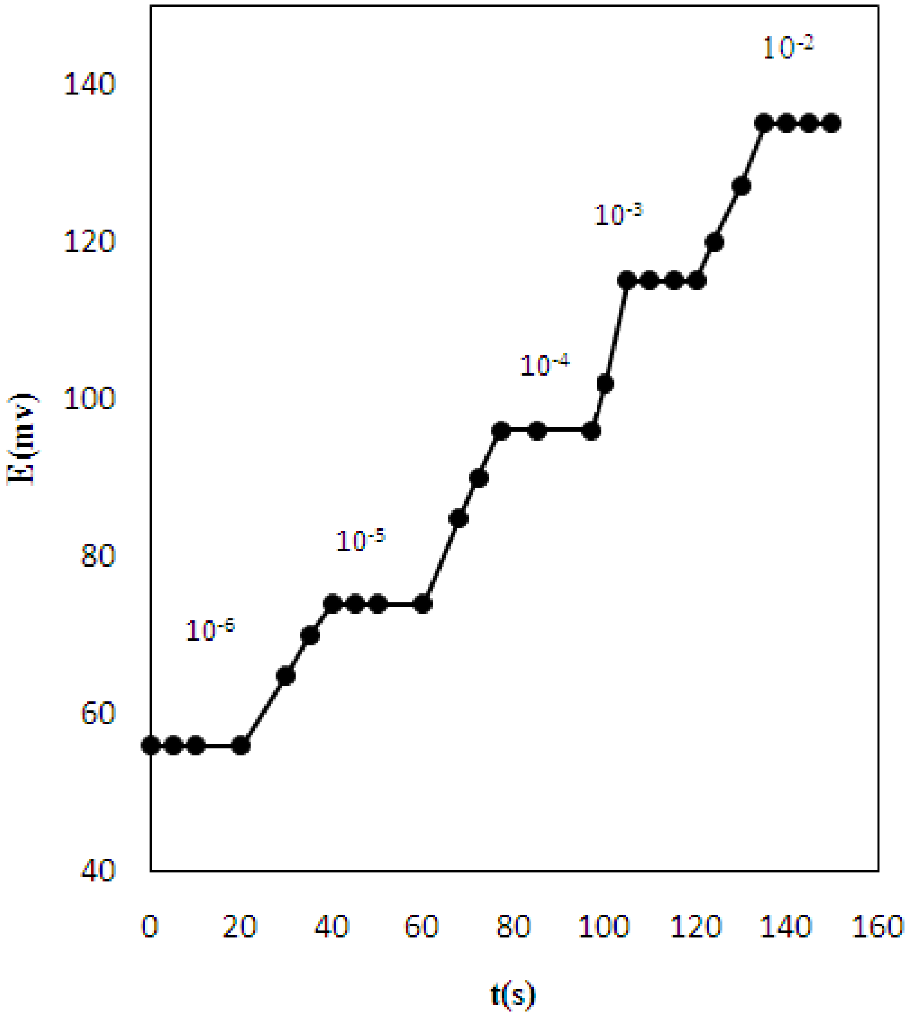


Figure 3. Response time of the Y^{3+}-ISE with change of concentration from 1.0×10^{-6} to 1.0×10^{-2} M.

3.6. Analytical application

The analytical utility of the electrode was evaluated by carrying out potentiometric titration of 40 ml of 1×10^{-4} M fluoride ion solution against the 1×10^{-3} M of Y^{3+} ion at pH 5.0. The titration plot is shown in Fig. 4. It is interesting to note that the resulting titration curve is unsymmetrical, as was noticed before [26]. The membrane sensor was also applied to the direct determination of fluoride ion concentration in mouthwash solution and toothpaste. The results of triplicate measurements for these samples were presented in Table 3. As can be seen from Table 3, there is a good agreement between the declared content and the determined values.

Table 3. Determination of fluoride in various samples by the Y^{3+} - ISE.

Sample no	Sample	Labelled(%)	Found(%)[a]
1	Mouthwash (Aquafresh, Brentford, U.K.)	1.35(mg/ml)	1.34±0.02(mg/ml)
2	Toothpaste	0.020	0.018±0.01

[a] Mean value ± standard deviation(three measurements).

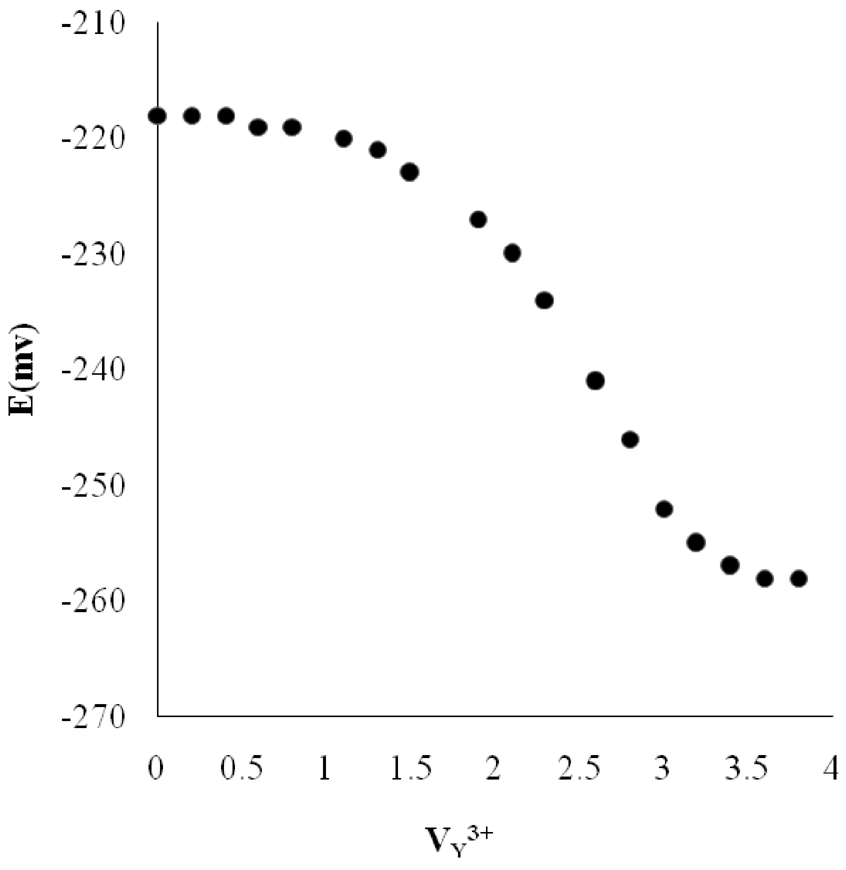


Figure 4. Potentiometric titration curve of 40 ml of 1×10^{-4} M F^- solution with 1×10^{-3} M Y^{3+} using the proposed sensor as an indicator electrode.

4. CONCLUSIONS

This work demonstrated that the dicyclohexyl-18-crown-6 can be used as a good ionophore in the development of a PVC-based yttrium ion-selective electrode. The electrode responded to Y^{3+} ion in a Nernstian fashion and displayed a low limit of detection and adequate selectivity for Y^{3+} ion. The electrode characteristics such as linear range, response time and specially selectivity were comparable to the previously reported yttrium ion-selective electrodes. The electrode can be successfully has been evaluated by its application in the determination of fluoride ion in mouthwash and toothpaste real samples.

ACKNOWLEDGEMENTS
The author gratefully acknowledgement the support of this research by Islamic Azad University Bojnourd Branch, Bojnourd-Iran.

References

1. A.K. Sing, P. Singh, S. Banerjee and S. Mehtab, *Anal. Chim. Act*, 633 (2009) 109.
2. W. A. Volkert and T. J. Hoffman, *J. Chem. Rev*, 99 (1999) 2269.
3. C. J. Anderson, M. J. Welch and M. Welch, *J. Chem. Rev*, 99 (1999) 2219.
4. M. Shibasaki, H. Sasai and T. Arai, *Angew. Chem, Int. Ed*. 33 (1994) 773.
5. X. Wang and Y. D. Li, *Chem. Eur. J*, 9 (2003) 2627.
6. L. Zhang, Y. Luo and Z. Hou, *J. Am. Chem. Soc*, 127 (2005)14562.
7. J. H. Shim, I. S. Joeng, M. H. Lee, H. P. Hong, J. H. On, K. S. Kim, H-S, Kim, B. H. Kim, G.S. Cha and H. Na, *Talanta*, 63 (2004) 61.
8. X. Zhu, A. Gong and S. Yu, *Spectrochim, Acta part. A*, 69 (2008) 4782.
9. M. H. Chhatre and V. M. Shinde, *Talanta*, 47 (1998) 413.
10. Z. L. Liu, L. Jiang, Z. Liang and Y. H. Gao, *Tetrahedron*, 62 (2006) 3214.
11. T. Gunnlaugsson, *Tetrahedron Lett*, 42 (2001) 8901.
12. S. D. Alexandratos and C. L. Stine, *Reactive & Functional Polymers*, 60 (2004) 3.
13. A.K. Singh, S. Mehtab and P. Saxena, *Anal. Chim. Acta*, 551(2005) 45.
14. V. K. Gupta, A. K. Jain, P. Kumar, S. Agarwal and G. Meheshwari, *Sens. Actuatirs B*, 113 (2006) 182.
15. C.J. Pedersen, *J. Am. Chem. Soc*, 89 (1967) 7017.
16. H. Tsukube, T. Hamada, T. Tanaka and J. Uenishi, *Inorg. Chim. Acta*, 214 (1993) 1.
17. R.A. Sachleben, M.C. Davis, J.J. Bruce, E.S. Ripple, J.L. Driver and B.A. Moyer, *Tetrahedron Lett*, 34 (1993) 5373.
18. J.A. Rusanova, K.V. Domasevitch, O.Y. Vassilyeva, V.N. Kokozay, E.B. Rusanov, S.G. Nedelko, O.V. Chukova, B. Ahrens and P.R. Raithby, *J. Chem. Soc., Dalton Trans*, (2000) 2175.
19. E. Eder, P. Preishuber-Pflugl and F. Stelzer, *J. Mol. Catal. A: Chem*, 160 (2000) 63.
20. H. Watanabe, T. Iijima, W. Fukuda and M. Tomoi, *React. Funct. Polym*, 37 (1998) 101.
21. L.M. Dulyea, T.M. Fyles and G.D. Robertson, *J. Membrane Sci*, 34 (1987) 87.
22. A.J. Hamdan, *Int. J. Electrochem. Sci*, 5 (2010) 215.
23. F. Faridbod, M. R. Ganjali, R. Dinarvand, P. Norouzi and S. Riahi**,** *Sensors*, 8 (2008) 1645.
24. S. Sadeghi and S. Doosti, *Sensors and Actuators B*, 135 (2008) 139.

25. M. S. Kazemi, *J Incl Phenom Macrocycl Chem,* 68 (2010) 331.
26. A.R. Fakhari, M. R. Ganjali and M. Shamsipur, *Anal. Chem*, 69 (1997) 3693.