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Research Article

Electrochemical Self Assembled Monolayer based sensor for Sodium ion using 4-aminobenzo-15-crown-5 as ionophore

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Abstract: A novel sodium ion (Na^+) selective sensor based on gold surface functionalized by immobilization of ionophore, 4-aminobenzo-15-crown-5 (4-AB-15-C-5) through a self-assembled monolayer has been developed. Host-guest complexation of lithium ions and ionophore was confirmed by conductance studies, UV-Vis and FTIR Spectroscopic measurements. The binding of sodium ion to the ionophore at sensor surface was monitored using a redox probe $\text{Ru}(\text{NH}_3)_6^{3+}$ / $\text{Ru}(\text{NH}_3)_6^{4+}$ as 'reporter ion' employing cyclic voltammetry and differential pulse voltammetry. The sensor was found to be responsive 1mM Na^+ .

Keywords: Sodium ion, electrochemical sensor, crown-ether, self-assembled monolayer, cyclic voltammetry

INTRODUCTION

Sodium is most essential ion in human physiology. It is used in opposition of potassium ions, to allow the organism to build up an electrostatic charge on cell membranes, and thus allow transmission of nerve impulses when the charge is allowed to dissipate by a moving wave of voltage change¹. Sodium ions are important in neuron (brain and nerve) function, and in influencing osmotic balance between cells and the interstitial fluid, with their distribution mediated in all animals (but not in all plants) by the so-called Na^+/K^+ -ATPase pump. Our body requires a fixed concentration of sodium ion [135 to 145 mM/L], the increase in Na^+ concentration above 145mM/L causes Hypernatremia and concentration below 135mM/L causes hyponatremia²⁻⁴. If Na^+ ion concentration is deficient or in excess, cell permeability is affected and the health of the cells suffers. Hence it is important to monitor its concentration accurately.

Several techniques have been reported for determination of Sodium ion viz. atomic absorption spectrophotometry, flame photometry, UV-vis spectrophotometry⁵⁻⁸, potentiometry⁹⁻¹⁸ and by amperometry¹⁹.

In this paper we reported development of a simple, sensitive and accurate method for micro level estimation of sodium ion in aqueous samples. Herein, we demonstrate a novel sodium ion sensor based on gold surface functionalized by immobilization of ionophore, 4-aminobenzo-15-crown-5 through self-assembled monolayer. The sensor is simple to fabricate and showed promising characteristics for sensitive and specific detection of sodium ions.

2. MATERIALS AND METHODS

2.1. Chemicals: 11-mercaptoundecanoic acid (11-MUA), N-hydroxysuccinimide (NHS), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), 4-aminobenzo-15-Crown-5 (4-AB-15-C-5), potassium ferricyanide (K_3FeCN_6), hexaammineruthenium(III) chloride $[Ru(NH_6)Cl_3]$ and tetra butyl ammonium bromide (TBAB) (Sigma–Aldrich, USA) and AR grade potassium thiocyanate, sodium thiocyanate, potassium chloride, sodium chloride (E. Merck, India) were used without further purification. De-ionized water and HPLC grade solvents were used to prepare the solutions.

2.2. Instrumentation: UV spectra were recorded on Perkin-Elmer UV-VIS Spectrophotometer and IR spectra were recorded with FTIR Spectrometer, Model 8101 A, Shimadzu, Japan, with KBr pellet samples. Agilent 4284-A precision LCR meter and Agilent 16542 A liquid dielectric test fixture wire was used for conductance measurement. Cyclic voltammetric studies were carried out with μ -Autolab potentiostat/galvanostat with GPES 4.9 software (Eco-Chemie, Utrecht, The Netherlands) in a 10mL one compartment electrochemical cell, with BASi gold electrode (1.6 mm dia.) as the working electrode, Ag/AgCl electrode (sat. KCl) as reference and platinum wire as counter electrode. Differential pulse voltammetric studies were carried out with disposable screen printed electrode (DRP-220AT, DropSens, Spain) with gold as the working (4 mm dia.) and gold and silver as counter and reference electrode respectively.

2.3. Preparation of Cation-crown ether complex: To obtain 1:1 complex²⁰, Equimolar quantities of crown ether derivative, 2×10^{-4} M 4-AB-15-C-5 and 2×10^{-4} M metal thiocyanate in methanol were mixed with gentle stirring under a soft stream of nitrogen for 5-7 min, the resultant brown mass was stored in dark colored vials and reserved for conductometric and spectral characterization.

3. RESULTS AND DISCUSSION

Conductometry: The recognition properties of chosen ionophore, 4-aminobenzo-15-crown-5 (4-AB-15-C-5) in solution were first tested by measuring conductance and spectral properties in absence and presence of alkali metal salt. The specific conductivity of methanolic solution of 2×10^{-4} M NaSCN, 2×10^{-4} M 4-aminobenzo-15-crown-5 and 2×10^{-4} M metal ion-ionophore complex at 27 °C was recorded to be 7×10^{-3} , 0.92×10^{-3} and $2.82 \times 10^{-3} \text{ SM}^{-1}$ respectively **Fig 1**. Quenching of high mobility of sodium thiocyanate salt in presence of equimolar ionophore shows successful host-guest complexation.

UV-Study: **Fig2** shows that all the three (a,b and c) compounds shows spectra in the region < 240 nm and 260-340 nm, confirms the presence of a benzocrown ether fragment and an auxochromic group. Only Na+: 4-AB-15-C-5 complex i.e. (b) shows the absorption maxima at 248 nm. The presence of this peak confirms the complexation²⁰ of sodium ion with 4-AB-15-C-5.

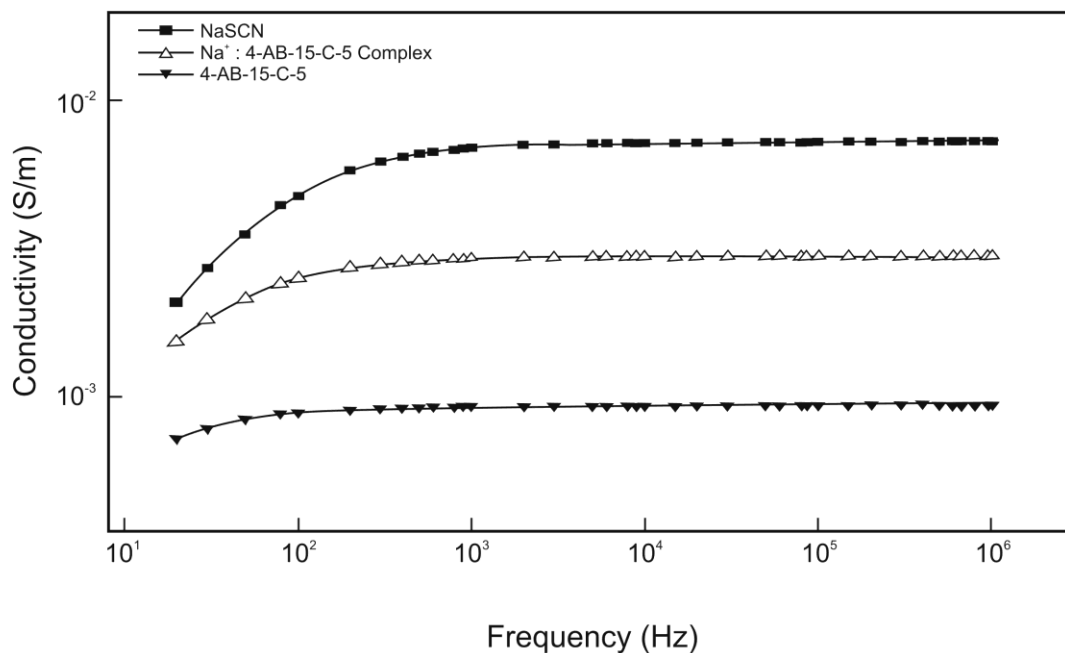


Figure 1: Conductivity of 2×10^{-4} M NaSCN, 2×10^{-4} M 4-AB-15-C-5 and 2×10^{-4} M NaSCN:4-AB-15-C-5 complex in MeOH.

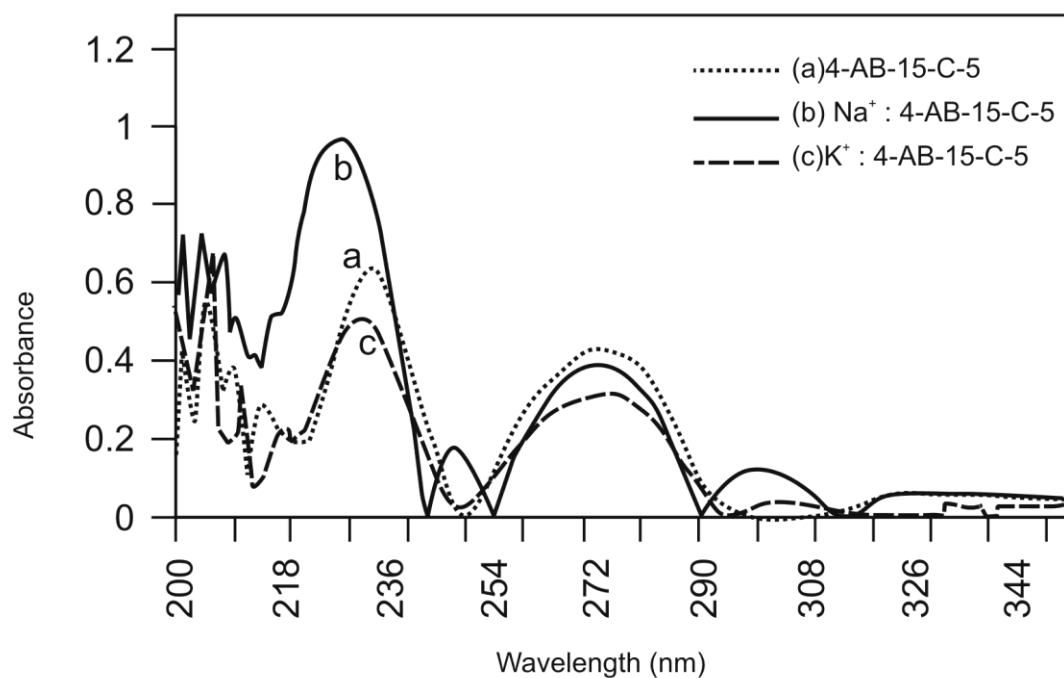


Figure 2: UV spectrum of (a) 2×10^{-4} M 4-aminobenzo-15-crown-5 in methanol, λ_{\max} 235(ξ 3120), 276(ξ 2050) (b) 2×10^{-4} M Na^+ :4-AB-15-C5 complex, λ_{\max} 228(ξ 6835), 248(ξ 842), 276(ξ 2115) and 297 (ξ 5465) (c) 2×10^{-4} M K^+ :4-AB-15-C5 complex in methanol, cell path 1cm, λ_{\max} 229(ξ 2785), 271 (ξ 1770)

IR Study: The synthesized complex is used for IR detection, a small amount of complex is mixed with KBr, and a pellet is formed for analysis. We studied IR of 4-AB-15-C-5 **Fig 3(a)** and its complex with sodium ion **Fig 3 (b)** we found that complex shows thiocyanate band at 2064.67 cm^{-1} . Aside from thiocyanate band the spectra of 4-aminobenzo-15-crown-5 and its Na^+ complex differ most strikingly in the region 1400 to 700 cm^{-1} which contain bands attributable to the wag, twist and rock modes of vibration of methylene groups. These modes are opposed by adjoining groups, and changes in the bonding character of these groups will affect the wag, twist and rock modes of vibration. The significant variation in the aromatic bands between 1300 to 800 cm^{-1} is the shift to shorter wavelengths with complex formation. Since these bands are attributable to the carbon-hydrogen out-of-plane bending mode of vibration, it is apparent that the Sodium ion is bounded in such a way as to cause this carbon-hydrogen vibration to be more restricted in the complex [20].

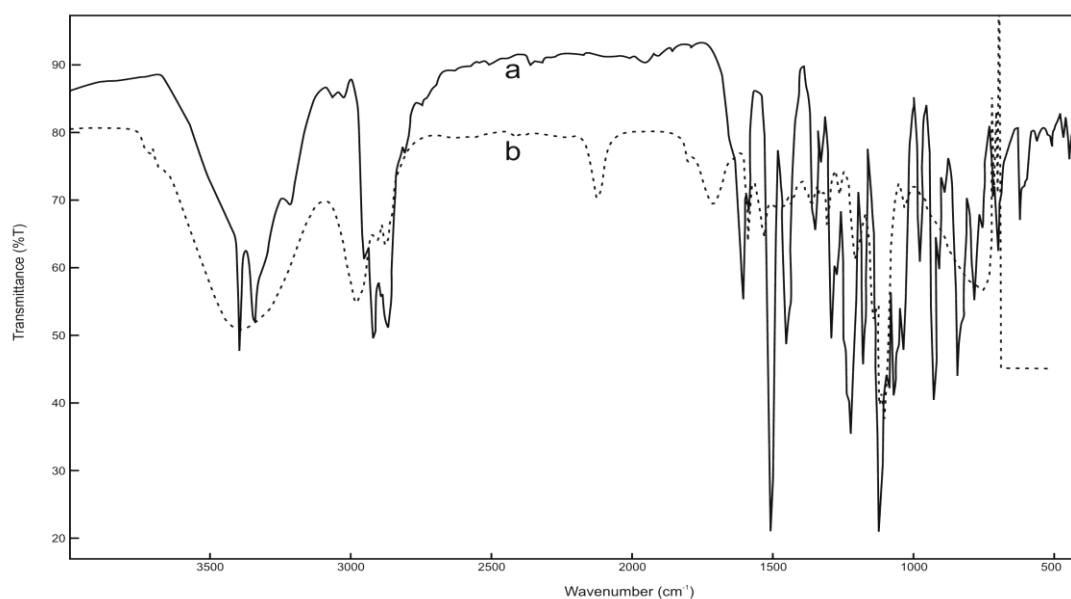


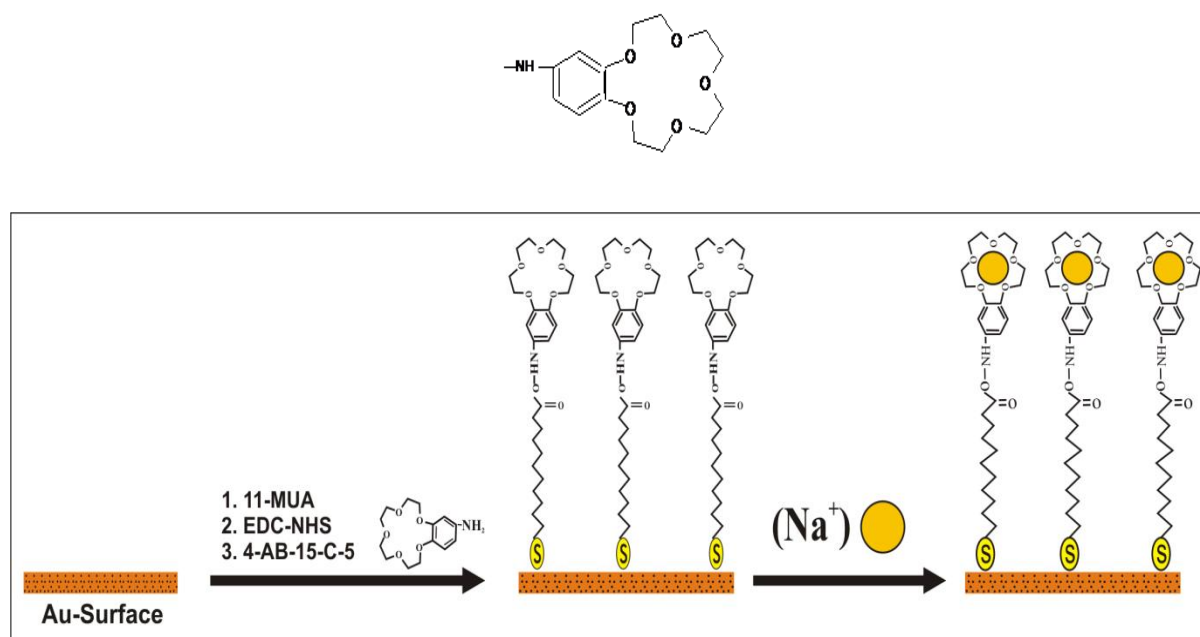
Figure 3: Infrared spectrum of (a) 4-aminobenzo-15-crown-5, (b) Na^+ :4-aminobenzo-15-crown-5 complex, KBr pellet

Electrochemical Study:

Preparation of modified gold electrode: Gold electrode has high affinity for sulphur. We have used 11-mercaptoundecanoic acid (11-MUA) to get a monolayer on to the gold working electrode. The objective for chemical modification by monolayer of thioic acid is to block the working electrode with a charged species and observe its effect on electrochemical redox signal of a typical electroactive species such as potassium ferricyanide and or rutheniumhexammine trichloride at gold electrode. The gold sensor chip was cleaned by ultrasonication with ethanol followed by deionised water. The cleaned gold chip was then immersed in 11-mercaptoundecanoic acid for 24 hours. Characterization of self assembled monolayer (SAM) on Au surface was achieved by cyclic voltammetry (CV) using gold as the working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode. CVs were measured using a solution containing $1\text{ mM K}_3[\text{Fe}(\text{CN})_6]$ and $1\text{ mM } [\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$. CV of $\text{K}_3[\text{Fe}(\text{CN})_6]$ on SAM of 11-MUA modified gold electrode wherein no redox peak current is observed in comparison to that of bare gold electrode in the potential range of -0.7 to $+0.5$ in 0.1 M KNO_3 . The significant drop in back ground current may be due to the stable modified 11-mercaptoundecanethiol that reduces the electron transfer rate between the surface of the electrode and

the electrolyte solution²¹. The electron transfer behaviour of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ in 0.1M TBAB clearly indicate that no drop in back ground current of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ at SAM surface is due to the electrostatic attraction between the negatively charged SAM and positively charged $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in the electrolyte solution²².

Immobilization of 4-aminobenzo-15-crown-5 onto the 11-MUA coated gold electrode (Sensor surface): After immobilization of 11-MUA onto Au electrode the carboxylic groups of 11-MUA was activated by EDC-NHS mixture. After activation of SAM 50 μl solution of 0.1M 4-aminobenzo-15-crown-5 was placed onto the activated surface for 20 minutes. The amine group of 4-AB-15-C-5 and carboxylic group of activated surface forms a stable amide bond $\{-\text{S}(\text{CH}_2)_{10}\text{COONHR}$, where $\text{R} =$ }



Scheme 1 shows the immobilization process.

Sodium ion sensor using Au/11-MUA/4-AB-15-crown-5 as sensor surface and hexammineruthenium(III) chloride (1mM) as receptor ion : A three electrode set up was used with Au/11-MUA-4-aminobenzo-15-crown-5 as the working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode. CVs were measured using a solution containing 1mM $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ with 0.1M tetra butylammonium bromide (TBAB) as supporting electrolyte at potential range of 0.2 to -0.5V. **Fig.4 (b)** shows the cyclic voltammogram (CV) of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ in the presence of 1mM sodium ion on SAM of 4-AB-15-C-5 modified gold electrode wherein no redox peak current is observed in comparison to that of **Fig 4(a)** i.e. in the absence of sodium ion in the potential range of 0.2 to -0.5V in 0.1M TBAB + 1mM $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ as supporting electrolyte. The significant drop in back ground current may be due to the electrostatic repulsion between the positively charged SAM, that is, one with complexed sodium ion on the SAM surface and positively charged species in electrolyte solution i.e. $[\text{Ru}(\text{NH}_3)_6]^{3+}$. This sensor surface is selective for sodium ion and there is no interference with lithium, potassium and ammonium ions. The lower detection limit for this sensor was found to be 1mM.

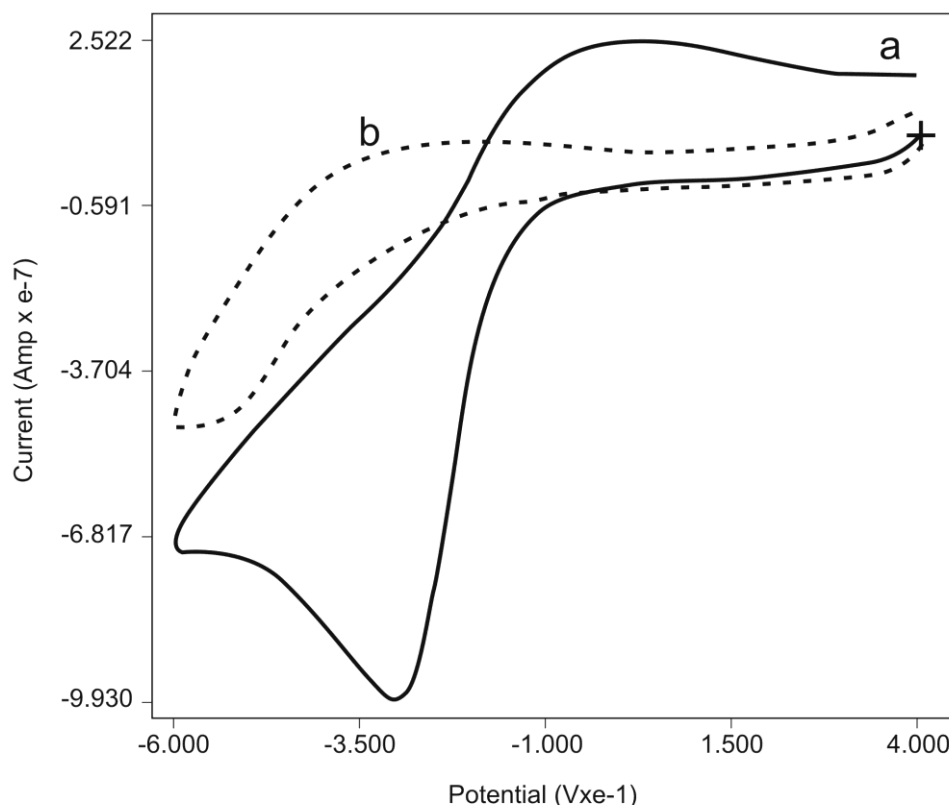


Figure 4. Cyclic voltammogram (CV) of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ on Au/11-MUA-4-AB-15-C-5 modified gold sensor surface

(a) In absence of Na^+ ion (b) In presence of Na^+ ion

Concentration: supporting electrolyte 0.1 M TBAB and 1mM $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$, initial potential= 0.2V, final potential = -0.5V, scan rate = 100mV. S^{-1}

4. CONCLUSION

We have constructed a simple chemical sensor electrode surface based on self-assembled, covalently bonded 4-aminobenzo-15-Crown-5 ether as the selective ionophore, onto a gold electrode surface for recognition of Na^+ ion in solution employing a redox probe, hexammineruthenium(III)chloride as a reporter ion. The sensor interface is highly stable, reproducible and showed good sensitivity for detection of Na^+ ion. The selective recognition of the crown ether system enables selective detection of Na^+ making the system highly promising for real-time applications. The charged monolayer of ionophore at sensor surface acts as an 'ion gate' for the diffusion of reporter ion.

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REFERENCE

1. J.P. Granger, Adv Physiol Edu. 1998, 20, S157-S68
2. P. Robert, M.D. Heaney, J. Am. College Nutr., 2006, 25, 271-276
3. R.E. Fuisz, Medicine. 1963, 1963, 149-170.
4. W.H. Waugh, Metabolis, 1969, 18, 706-712.
5. V.A. Murphy, Anal. Biochem. 161(1) (1987) 144-151.
6. D.E. Uddin, T.M. Hickey, S.A. Fisher, Clin. Chem. 1977, 23, 1125.
7. R.L. Coleman, Clin Chem. 1979, 25(10), 1865-6.
8. P.H. Schaffar, O.S. Wolfbeis, Bernhard, Microchim. Acta. 1989, 99(1), 109-116.
9. M.S. Mohan, R.G. Bates, J.M. Hiller, J. Brand, Clin. Chem. 1978, 24, 580-584.
10. G.B. Levy, Clin. Chem. 1979, 25, 1516.
11. G.B. Levy, Clin. Chem. 1981, 27(8), 1437-1438.
12. M.E. Tohamy, S. Razeq, M.E. Maamly, A. Shalaby, Cent. European J. Chem. 2010, 4, 937-945.
13. J.H. Ladenson, J. Clin. Invest. 1963, 42, 293.
14. K. Kimura, Y. Tsujimura, M. Yokoyama, Pure & Appl. Chem. 1995, 67(7), 1085-1089.
15. X. Zhou, Y. Luo, C. Wu, Z. Zou, Q. Hu, Anal. Chim. Acta. 1988, 212, 325-329.
16. N.G. Lukyanenko, N.Y. Titova, O.S. Karpinchik, O.T. Melnik, Anal. Chim. Acta. 1992, 259(1), 145-148.
17. J.G. Schindler, M.M. Schindler, K. Herna, Fresenius J. Anal. Chem. **1991**, 340(11), 696.
18. T. Takami, J.W. Son, J.K. Lee, B.H. Park, T. Kawai, Japanese J. Appl. Phys. 2011, 50(8), 08LB13-1-4.
19. S. Flink, B.A. Boukamp, A. van den Berg, F.C.J.M. van Veggel, D.N. Reinhoudt, J. Am. Chem. Soc. 1998, 120, 4652-4657.
20. C.J. Pedersen, J. Am. Chem. Soc. 1967, 89, 7017-7036.
21. R. Gehlot, K. Sharma, M. Mathew, S. Kumbhat, Indian Journal of Chemistry, 2008, 47A, 1804-1808
22. Sheela Berchmans, R. G. Nirmal, G. Prabakaran, A. K. Mishra, V. Yegnaraman, J Solid State Electrochem 2006, 10, 439-446

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