An Electroactive Nickle Complex Modified Sensor for Detection of Alcohol

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Abstract

Herein, a simple Hexamminenickel(II)chloride($[Ni(NH_3)_6]Cl_2$) complex was prepared using a standard procedure. The electroactivity of the complex was examined via electrochemical reaction with a conventional three electrode-based system. A glassy carbon electrode (GCE) modified with ($[Ni(NH_3)_6]Cl_2$), standard Ag/AgCl electrode and Platinum electrode were employed as working, reference and counter respectively. The Ni complex demonstrated that it was electroactive in nature. Further, the prepared GCE/($[Ni(NH_3)_6]Cl_2$) sensor was demonstrated for detection of alcohol in real time rum beverage available commercially. Cyclic voltammetry (CV), flow injection analysis (FIA) were the electrochemical techniques used.The sensor showed a good selectivity towards the real alcohol sample in presence of other biochemicals like nitrite, nitrate, glucose, xanthine, dopamine, uric acid, hypoxanthine, ascorbic acid, sulphide, and hydrogen peroxide. The limit of detection (LoD) was found to be 421 µM and limit of quantification (LoQ) was 620 µM. Thus, proving that a simple Ni complex can be used for selective, non-enzymatic quantification of ethanol in real sample

Keywords: Alcohol detection, Nickle complex, Electrochemical, sensing

1. Introduction

Nickle (Ni) based complexes are simple to synthesize and often regarded as cost effective. Owing to the metallic nature of Ni, it can undergo electrocatalytic oxidation and reduction at specified potential. Similarly, the complexes formed with Ni as centre metal atom has capability to show electroactivity or even redox behaviour based upon the type of ligand they are associated with. The literature

reports several Ni complexes prepared in bulk[1]. In the present work, a well-known, commonly prepared Ni complex, Hexamminenickel(II)chloride ([Ni(NH$_3$)$_6$]Cl$_2$)[2], electro-catalytic activity was explored. A conventional three-electrode system comprising of a glassy carbon electrode (GCE) modified with ([Ni(NH$_3$)$_6$]Cl$_2$), standard Ag/AgCl electrode and Platinum electrode were employed as working, reference and counter respectively. The GCE was chemically modified with as prepared Ni complex and used for detection of alcohol in real time rum samples.

Alcoholic beverage industry constitutes to a great market share globally. Often prepared from various cultivable inputs, around the world, it's abuse and addiction has been growing significantly. As per the International Centre on Alcohol policies (ICAP), only 38% of the alcohol consumption is branded globally[3]. The World Health Organization (WHO) has listed the side effects of heavy alcohol consumption such as liver cirrhosis and failure. About 2.5 million cases of high intoxication of alcohol is estimated to be reported every year especially in teenagers[4]. Generally, the alcohol production in industry is carried out via yeast assisted anaerobic fermentation reaction of sugars followed by distillation. Owing to the increased profits, the adulteration of alcoholic beverages and production of low grade, non-branded alcohols has substantially increased over the years. These can lead to health threatening complications. The products with higher ethanolic content can be eventually fatal and lead to chronic addiction[5]. Hence, quantification of ethanol in alcoholic drinks is of significance especially to ensure safety, quality of the drinks for consumption.

Conventionally, Gas chromatography (GC), Fourier-transform infrared spectroscopy (FTIR), near Infrared (NIR), Raman Spectroscopy, high performance liquid chromatography (HPLC) are the techniques used for determination of ethanolic percentage in the branded alcohols for ensuring consumption limit safety[6][7][8]. Nevertheless, these methods are lab-dependent, requires skill technicians, reagents and expensive equipment like separation columns, pressure pumps, lasers etc. Thus, an alternative approach would be use of electrochemical sensing method wherein enzyme-based biosensors could offer a selective, rapid and point-of-care detection method. For instance, enzymes like alcohol oxidase[9], alcohol dehydrogenase[10] can be immobilized over the electrodes to get selective

biosensors for alcohol detection. In further, voltammetry detection methods could give instant result outputs. However, enzyme being non-robust in nature, their stability becomes major concern in such type of biosensors. In this context, a non-enzymatic electrochemical sensor would be more feasible. The researchers in industry and academia have been exploring nanomaterial based and metallic complex-based mediators as an alternative to enzymatic methods. Consequently, in the present work, a simple Nickle metal complex prepared as a part of the M.Sc. chemistry inorganic practical by students, Hexamminenickel(II)chloride([Ni $(NH_3)_6]Cl_2$) was taken and explored for electro-catalytic activity towards alcohol.

Commercial standard ethanol was used initially for determination of electrocatalytic oxidation and ensuring that the modified electrode gave a good limit of detection. Furthermore, areal market based Rum beverage was purchased and used as a sample. Distillation was carried out for removing the additives and acquiring the pure alcohol. The GCE chemically modified with ([Ni $(NH_3)_6]Cl_2$) was exposed to this distilled sample.Cyclic voltammetry (CV), flow injection analysis (FIA) were the electrochemical techniques used. The sensor exhibited a good selectivity towards ethanol in the real

alcohol sample in presence of other biochemicals like nitrite, nitrate, glucose, xanthine, dopamine, uric acid, hypoxanthine, ascorbic acid, sulphide, and hydrogen peroxide. The limit of detection (LoD) was found to be 421 µM. Henceforth, a non-enzymatic, chemically modified electrochemical sensor was fabricated here using ([Ni $(NH_3)_6]Cl_2$) as a mediator for electro-catalytic oxidation of ethanol.

2. Experimental Section

2.1 Chemicals and Apparatus

All the chemicals used here are of analytical grade. Sodium phosphate monobasic anhydrous (NaH_2PO_4), sodium phosphate dibasic dihydrate ($Na_2HPO_4.2H_2O$) was purchased from SRL Chemicals (Mumbai, India). Commercial absolute ethanol was purchased from local vendor. All the electrochemical experiments were performed using phosphate buffer solution (PBS) of pH =7, prepared using ($Na_2HPO_4.2H_2O$) and (NaH_2PO_4), as a supporting electrolyte. Nickle chloride, Conc. NH_3, acetone, nitrite, nitrate, glucose, xanthine, dopamine, uric acid, hypoxanthine, ascorbic acid, sulphide, and hydrogen peroxide were acquired from Sigma Aldrich. Experiments were carried out in CHI 660 potentiostat.

2.2 Preparation of pH 7 PBS

2.17 gm of $(Na_2HPO_4.2H_2O)$ and 1.17 gm of (NaH_2PO_4) were dissolved in 500 mL of double distilled (de-ionised) (DD) water. The pH was checked using a pH meter (PC 700)obtained from Oakton Instruments, USA. The pH was adjusted to 7 using 0.01 N phosphoric acid. This was used as a supporting electrolyte.

2.3 Preparation of ($[Ni (NH_3)_6]Cl_2$)

4 gm of Nickle chloride was dissolved in 10 mL warm water. Using a filter paper, the solution was filtered to remove undissolved particles. 18 mL of conc. NH_3 was added slowly with constant and rapid stirring. This lead the $Ni(OH)_2$ green precipitate to dissolve. The mixture was left undisturbed for 30 mins at room temperature followed by filtering using a Buckner funnel. The obtained violet colour precipitate is washed with Conc. NH_3 and acetone and dried at room temperature.

2.4 Preparation of GCE/($[Ni (NH_3)_6]Cl_2$)

A glassy carbon electrode (GCE) with surface diameter 0.0707 cm^{2}was cleaned with alumina powder. Electrochemical pre-treatment[11] was carried out using CV from +1 to -1 V, for n=20 cycles at 50 mV/s to ensure there is no characteristic peak and the surface is clean. 2 mg of ($[Ni (NH_3)_6]Cl_2$) was taken in 500 μL of acetone and dispersed in ultrasonication bath for 10 mins. 5μL of this solution was drop casted[12] using a pipette over the clean GCE surface and left for air-drying at room temperature for 45-50 mins. This was used as a working electrode.

2.5 Preparation of Standard Ethanolic Solutions

A stock solution of Ethanol with 99% purity was taken. A serial dilution method was adapted and standard solutions of 600 μM, 700 μM, 800 μM, 900 μM, 1 mM, 2 mM, 3 mM, 4 mM, 5mM were prepared diluting with a pH 7 PBS. These standard solutions were used for sensing.

2.6 Experimental set-up

GCE/($[Ni (NH_3)_6]Cl_2$) was used as a working electrode, Ag/AgCl as a reference electrode and Platinum as a counter electrode. 5 mL working volume of electrolyte was used. A potential window of -0.8 to +0.8 V was used for carrying out the experiments.

2.7 Preparation of Rum sample

A commercially available rum bottle was purchased and subjected to distillation to remove additives. Scheme I show the distillation set-up. 500 mL of rum was used as crude sample to obtain a yield of 100 mL ethanol. TLC was used to check the distilled sample.

Scheme I: Distillation set-up used for distillation of Rum sample.

3. Results and Discussion

3.1 Electrocatalytic oxidation

The modified electrode GCE/([Ni $(NH_3)_6$]Cl$_2$) , along with Ag/AgCl and platinum were subjected to CV. Figure 1A is the CV response of modified electrode in 5 mL pH 7 PBS at 50 mV/s for n=20 cycles. As can be seen, the complex showed and irreversible peak at approximately -0.2 V plausibly due to the presence of Ni. Figure 1B is the comparative CV response of GCE/([Ni $(NH_3)_6$]Cl$_2$) in pH 7 PBS and pH7+1mM ethanol. A sharp increase in the oxidation current starting from E^0 +0.4 V was observed in the presence of standard ethanol. Therefore, the rise in current showed that the modified electrode could increase the electron transfer behaviour and hence can detect the ethanol in the electrolyte.
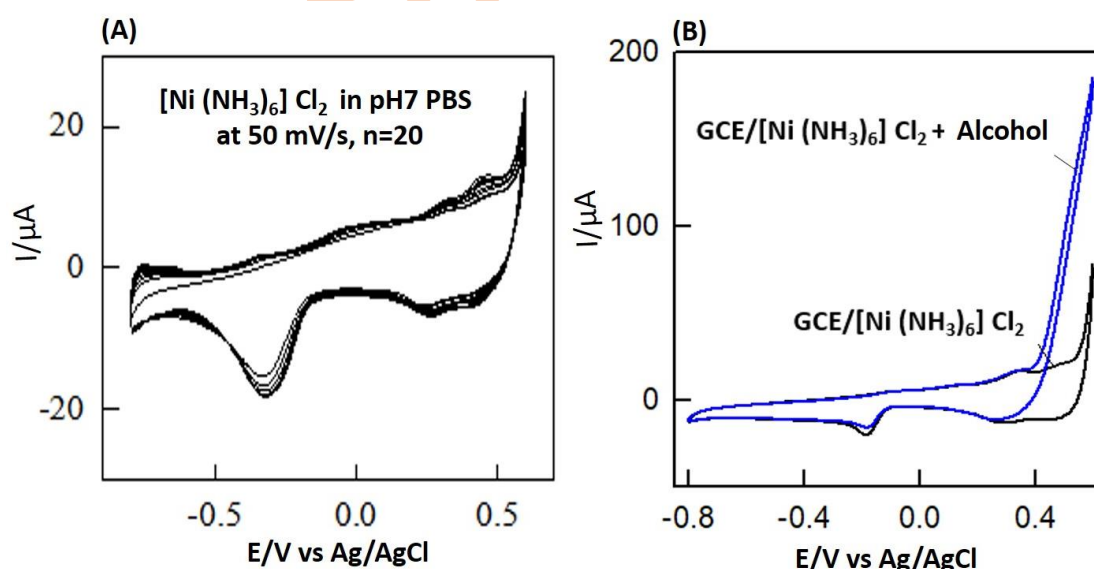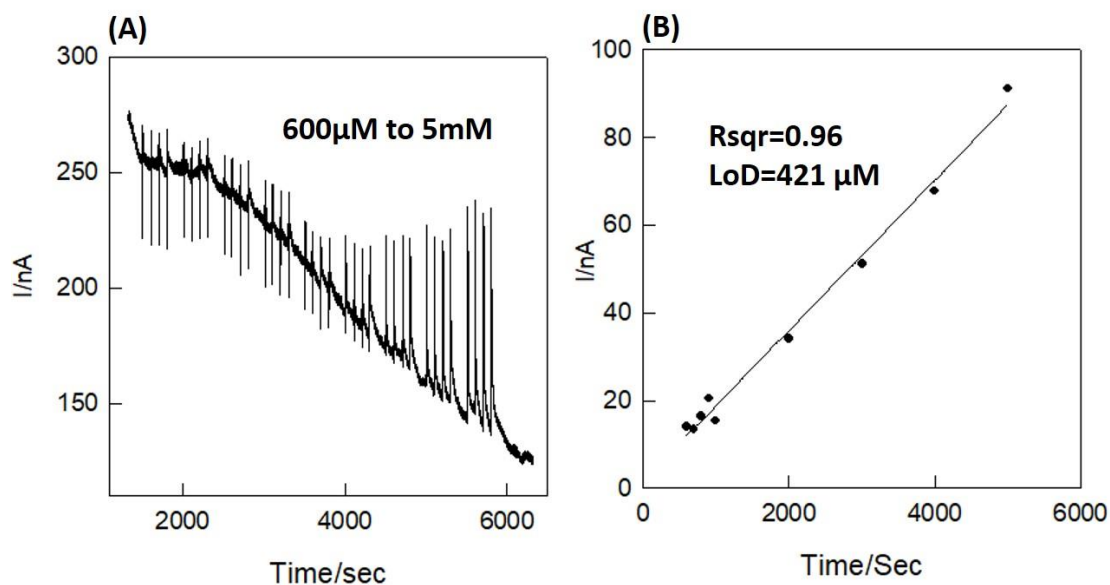

Figure 1: (A) CV response of GCE/[Ni $(NH_3)_6$]Cl$_2$] in pH 7 PBS at 50 mV/s for n=20

cycles. (B) CV response of GCE/[Ni $(NH_3)_6$]Cl_2] in pH 7 PBS+ ethanol with control at 20 mV/s for n=4 cycles.

3.2 Effect of concentration

To obtain more accurate response, amperometry i-t curve technique was used couple with flow injection analysis. Herein, a flow injection analysis set-up was used wherein, a flow rate of 1mL/ min was set using the pressure pumps. A continuous flow of pH PBS was regulated. The set-up was coupled with amperometry to obtain time vs current read out. 20 µL of standard ethanol sample was spiked in a linear concentration range of 600 µM-5 mM.The potential E^0chosen was +0.4 V. Time for completion of concentration effect experiment was 8000 secs. Syringe needle was used to spike the ethanol in the set-up where it comes in contact with the modified electrode and instantly gives sharp rise in current. As can be seen in Figure 2A, with increasing the concentration of the standard ethanol, sharp rise in current was observed. Figure 2B is the corresponding base-line corrected calibration plot of this. A linear square fit of R^2= 0.96 was obtained with a LoD of 421 µM. Thus, the practical sensing limit of the electrode for pure ethanol was 600 µM whereas, the theoretical LoD was 421 µM. Limit of quantification (LoQ) was 620 µM.

Figure 2: (A) Flow injection analysis response of GCE/[Ni $(NH_3)_6$]Cl_2] in pH 7 PBS+ alcohol increasing concentration. (B) Corresponding calibration, base line corrected linear plot.

3.3 Real sample

In addition, to further validate the use of sensor in real time, a commercial Rum sample subjected to distillation was used. Post distillation, the boiling point and chromatography was done to find out the ethanol presence. This sample was subjected to flow injection analysis along with 1mM of various other biochemicals like nitrite, nitrate, glucose, xanthine, dopamine, uric acid, hypoxanthine, ascorbic acid, sulphide, and hydrogen peroxide. As can be seen in Figure 3, the modified electrode was highly selective to the sample whereas the other biochemicals gave negligible peak currents. Hence, the electrode demonstrated an interference mitigated, selective detection of the crude ethanol in real sample even presence of various interferents.
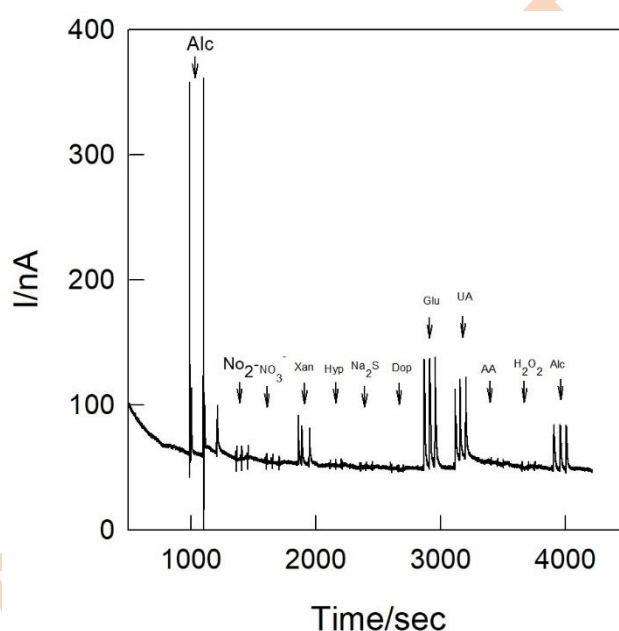
Figure 3: Flow injection analysis showing the selectivity alcohol with other biochemicals.

4. Conclusion

In the present work, a simple Hexamminenickel(II)chloride ($[Ni(NH_3)_6]Cl_2$) complex was prepared and modified over a glassy carbon electrode. The electroactivity of the complex was examined via electrochemical reaction with a conventional three electrode-based system using Ag/AgCl electrode and Platinum electrode as reference and counter electrodes respectively. The Ni complex confirmed electroactive nature. Further, the prepared GCE/($[Ni(NH_3)_6]Cl_2$) sensor was verified for detection of alcohol in real time rum beverage. Cyclic voltammetry (CV), flow injection analysis (FIA) were the electrochemical techniques used.

The sensor showed a good selectivity towards the real alcohol sample in presence of other biochemicals with a limit of detection (LoD) for crude ethanol as 421 µM and limit of quantification (LoQ) was 620 µM. Hence, a simple Ni complex was used for selective oxidation of ethanol.

Acknowledgement

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