Role of Polyaniline as Chemical Sensor and Acid-Base Titration Indicator

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Abstract: - **Polyaniline (PANI) is a conducting polymer that has been widely studied for electronic and optical applications. Unlike other conjugated polymers, polyaniline has a simple and reversible acid/base doping/ dedoping chemistry enabling control over its various properties like conductivity, optical activity and environmental stability. Conductivity of PANI was measured and it was found that if certain volatile chemicals are exposed to it there is a certain change in its value of conductivity. It was prepared on filter paper, which acts as visual sensor as it changes color when it is dipped in buffer ammonia solution or sodium hydroxide etc. It also acts as endpoint indicator also wherein the small piece of PANI embedded paper was cut and it was used in titration of different acid base solutions comparing it with phenolphthalein and methyl orange as indicators. The same filter paper was used to filter acid and bases. So, authors suggests a polyaniline embedded paper as a lower cost alternative for the sensor and indicator.**

Keywords: Polyaniline, sensor, indicator

I. INTRODUCTION

The emission of gaseous pollutants such as sulphur oxide, nitrogen oxide and toxic gases from related industries has become a serious environmental concern. Sensors are needed to detect and measure the concentration of such gaseous pollutants. A chemical sensor furnishes information about its environment and consists of a physical transducer and a chemically selective layer.

Alan J. Heeger, and Hideki Shirakawa in 1976, carried out intensive investigations on the new generation of "synthetic metals" due to their unique combination of electronic and optical properties and processing advantages [1-2]. The electrical conductivity is achieved in the conjugated polymers by means of delocalised of the π-electrons that allow charge mobility along the backbone of the polymer chain. The synthesis of conducting polymers has been accomplished by oxidising or reducing process either through chemical doping [3] or electrochemical doping [4].

Various applications of conducting polymers have been proposed as transducers of biosensor [5], electrodes of rechargeable batteries [6], artificial nerves and muscles [7], gas sensors [8], solid electrolytic capacitor, diodes and transistors [9], anti-static electromagnetic shielding [10], and biomedical applications [11]. PANI has a erasable optical information storage [12], microwave and radar absorbing materials [13], catalysts [14,15], electronic and bioelectronic components [16] and membranes [17].Polyaniline (PANI) continues to attract considerable attention because its electrical and optical properties can be changed by oxidation and protonation of the amine nitrogen atoms. PANI is known for its excellent thermal and environmental stability but poor processibility due to insolubility and brittleness that limits its commercial applications. PANI could be more processable in the composites form with another water soluble polymers such as PVA, poly (vinyl pyrrolidone), poly (acrylic acid) and poly (styrene sulfonic acid) (PSSA) which are used as stabilisers. A functionalisedprotonic acid can be added into the composites to chemically polymerise PANI. The PANI dispersion can then be casted to form composite film containing PANI nanoparticles [18].

Vibration spectroscopy is extremely sensitive to the changes in electronic structure of PANI. Thus, by using infrared and Raman spectroscopy, one can easily register all interconversions between different oxidation and protonation states of PANI . By using the IR spectroscopy it is possible – in addition to the characterisation of PANI – to study the changes of bonds and the mechanism of doping during the protonation and oxidation process [19].

Conducting polymers showed promising applications for sensing gases having acid–base or oxidizing characteristics. Polyaniline (PANI) is a conducting polymer that has been widely studied for electronic and optical applications. Unlike other conjugated polymers, polyaniline has a simple and reversible acid/base doping/ dedoping chemistry enabling control over properties such as free volume, solubility, unique conduction mechanism, optical activity and environmental stability.PANI exists in three well defined oxidation states: leucoemeraldine, emeraldine and pernigraniline (Fig. 1). Leucoemeraldine and pernigraniline are the fully reduced (all the nitrogen atoms are amine) and the fully oxidized (all the nitrogen atoms are imine) forms, respectively, and in emeraldine the ratio is, 0.5. Starting from the electrically insulating leucoemeraldine, electrically conducting emeraldine can be obtained by standard chemical or electrochemical oxidation, as with other conducting polymers. But, upon further oxidation a second redox process occurs, which yields a new insulating material, pernigraniline.

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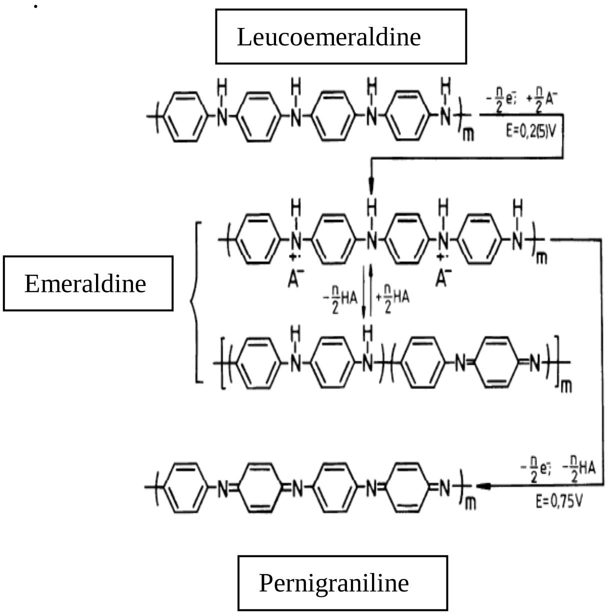

Figure 1: Generalized scheme of the oxidative and non-oxidative (protonic acid) doping of polyaniline: *n*, number of aniline units, *m* =4*n*.[20]

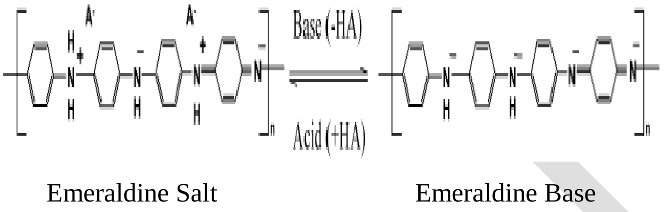

Figure 2: The basic chemical skeletons of emeraldine salt (green form) and emeraldine base (blue form) PANI and their reversible conversion by treatment with base and acid.

II. REAGENT AND MATERIALS:

All the chemicals were bought from high purity chemical ltd. (HPCL). Aniline was purified by distillation and distilled water was used and commercially available Whatmanfilter paper No. 42 were used. Acetone, toluene and 0.1 N NaOH was also used for checking it whether PANI comes out or not when it was pass through it.

III. INSTRUMENT USED:

pH of the solutions were measured with digital Hanna 2215 pH/ORP meter, Absorption spectra were obtained using Shimadzu UV spectrometer.

IV. EXPERIMENTAL SECTION:

A. Preparation of Polyaniline powder

Aniline Hydrochloride was added to 100 ml of water to make 0.4M solution. Ammonium Persulphate was added to 100 ml of water to make solution.Both solution were kept at room temperature for 1 hour, then mixed in a beaker, stirred and left at rest for 24 hours.Next Day, the solution was passed through filter papers,The precipitate was then washed with 100 ml HCl solutionand 100ml Acetone thrice.One of the samples collected were dried on a filter paper using hairdryer and the other samples were kept for drying for a day. But the powder seems to be insoluble in many solvents. So a dispersion is made to further check its sensing ability. Even then it was not properly soluble. So we made it using another method.

B. Preparation of the filter paper containing Polyaniline

A solution of aniline chloride was prepared by addition of aniline in a 2 M HCl solution in distilled water with the use of micropipette. It was stirred for around 3 minutes. Total amount of 100 µl of the anilinium chloride solution was poured drop wise on a pair of Whatmanfilterpaper No 42 (12.5 cm diameter) in four proportions using a pipette in order to get it absorbed on the paper for 5 minutes. Now, on the same filterpaper oxidant solution was added drop by drop in same fashion on both of the filter paper drop by drop and the paper was allowed to dry. Initially there was no changes on the filter but after half an hour green dots started to form on the paper and after a while the paper started to change its colour from white to light green (emeraldine base) from outer side of the paper on which solutions were poured. So the the filter paper deposited with the hydrochloride doped PANI in emerald green color was formed.The filter paper was washed with water and left to dry. PANI didn't come out in acetone and toluene when it was passed through it.

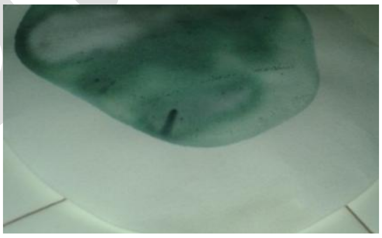

Figure 3: Formation of polyaniline on filterpaper

C. Polyaniline as solution sensor

When the small pieces of filter paper were cut off when it was dip in the solution of ammonia buffer solution. its changes it colour from green to blue but when it is again kept in the atmosphere it changes it colour back to green which can be observed from an naked eye.

Figure 4. Colour change from green to blue of filter paper when it is dipped in buffer ammonia solution.

D. Polyaniline as acid-base indicator

Filter paper were cut into small pieces and one piece was kept in a solution of 1 M HCl solution and solution was titrated by 1 M NaOH solution. While on same time, another solution of 1 M HCl solution was titrated by 1 M NaOH solution using phenolphathalein as indicator. It was observed that it was same time in which the colour of the paper change from green to blue and the solution containing phenolphthalein which get titrated. In other words, both titration have same results of endpoint.

Moreover, it is checked for the alkalinity mixture of 0.1M Na_2CO_3 and 0.1M $NaHCO_3$ titrated against 0.1M HCl solution and the result came same as that of the end point result when indicators like phenolphathalein and methyl orange were used. Filter paper can be used for several times as its colour can be changed when it is doped again. So for determination of different mixtures of compounds responsible for alkalinity of water, this proved to be a better method, as there is no need of adding two indicators.

RESULT AND DISCUSSION

The UV-visible absorption spectrum of the green filter paper which was dipped in a solution NaOH and titrated with HCl, it was operated in between 300 nm to 600 nm.the solution consist of it when observed found with a absorption maxima at 280 nm similarly for a solution containing phenolphthalein was sound have absorption maxima at 230 nm.

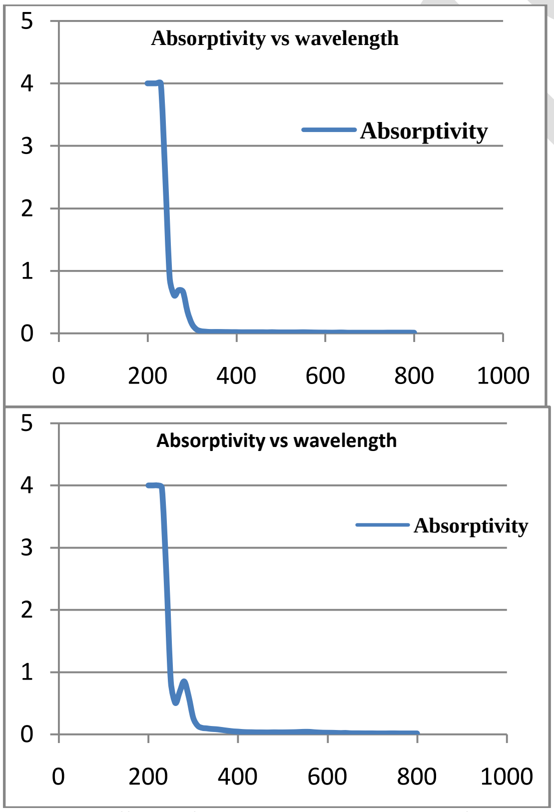

Figure5.a) Diffuse reflective UV-visible spectra of titrated solution against 0.1 NaOH containing emeraldine salt embedded filter paper.**b)**Diffuse reflective UV-visible spectra of titrated solution against 0.1 NaOH containing phenolphthalein.

We have further studied that PANI embedded filter paper which acts as sensor for acid and base, when a green PANI paper was treated with buffer ammonia solution,the paper turned blue,similarly occurs with NaOH solution. Fig shows the 2 photographs of 2 filter papers,one with water where no change of colour is observed whereas one in 0.1 M NaOH solution,the colour changes from green to blue.From this we can clearly state that the filter paper has an ability to act as a sensor for buffer ammonia solution as well as NaOH solution.

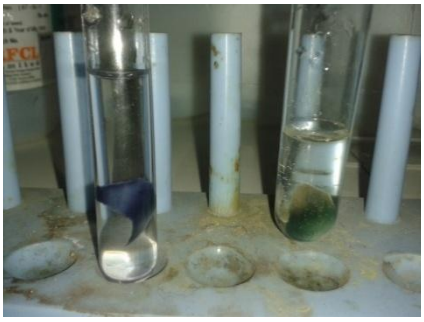

Figure7. Test tube placed in left, consist of filter paper dipped in ammonia buffer solution and in right showing filter paper dipped in water

CONCLUSION

PANI synthesized by different methods in powder form and absorbed on filter paper form has sensing ability. In this paper, we have reported a comparatively cheaper method for synthesis of PANI in a filter paper. The PANI in the paper could be reversibly converted between 2 forms. We have demonstrated the ability of PANI which acts as a sensor for buffer ammonia solution, it can be further used to see for sensing for minimum ppm of ammonia solution exposed to it. It is used as acid/base sensor and also acts an endpoint indicator of different acid base titrations.In this project, we have tested PANI to be used as sensing material for different solution like sulphuric acid, hydrochloric acid, propanol, phenol, benzene, nitrobenzene, ammonia etc.Better selectivity and rapid measurements can also be achieved by replacing it further by polymer involving nano technology and exploiting either the intrinsic or extrinsic functions of polymers.

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