

## Effect of pH on Formation of Polyaniline Monolayer

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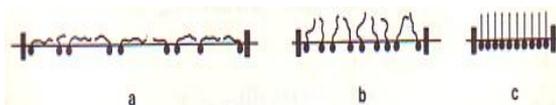
**Abstract :** Recently Langmuir Blodgett (LB) monolayer has been considered by various researchers, as a potential technique for the production of ultra thin films with control molecular orientations. LB films based on conducting polymer are attractive candidates for a variety of applications such as biosensors, ion sensors, integrated optics and molecular electronics devices. Decrease in the pH of the sub-phase increases the level of doping (protonation) of polyaniline emeraldine base (PANI-EB). This research intends to study the effect of pH on formation of PANI-EB monolayer to determine the stability of PANI-EB monolayer that formed in acidic subphase that can be seen through pressure ( $\pi$ ) – trough area ( $\text{cm}^2$ ) by using Langmuir Blodgett (LB) trough. Methods to prepare monolayer are powder method, liquid homogeneous method, sub-phase preparation method and monolayer formation method. For PANI's effect in different pHs (1, 3, 5, 7), U.V.- visible spectrum can be seen above 300nm which showed there were  $\pi$ - $\pi^*$  transfer in the benzenoid chain of polyaniline which indicated that polyaniline has been protonated when an acidic sub-phase was employed for spreading the monolayer, in contrast to the LB monolayer spread on neutral sub-phase. From the  $\pi$  –  $\text{cm}^2$  graph study, stability of monolayer formation could be achieved in injection of 750 $\mu\text{l}$  with surface pressure 12 mN / m and barrier speed 10 $\text{cm}^2$  / min. Liquid phase could be seen at trough area 170-72  $\text{cm}^2$ , where polyaniline molecules are still in the random state. Whereas, solid phase (70-60  $\text{cm}^2$ ) were found to have linear relationship between  $\pi$  and  $\text{cm}^2$ . Eventually the collapse pressure,  $\pi_c$  is reached because of the force exerted upon it became too strong. FTIR spectra proved there was a distinct decrease in intensity with an increase in pH. As a conclusion, pH value plays a vital role in formation of uniform, thin and good control of PANI- EB monolayer.

**Key words:** PANI-EB, Monolayer, Langmuir Blodgett, pH, Pressure

### Introduction

Conjugated organic polymers become highly conducting upon doping and are thus called conducting polymers. They have been used in undoped and doped forms and one of the most promising conducting polymers is polyaniline (PANI). The conducting polymers having the conjugate  $\pi$  bonds are as good as inorganic materials for the application of sensors because of their unique redox reversibility accompanied by variation of conductivity as well as color change, ease of synthesis, high charge capacity, good environmental and electrochemical stability and sensitive at room temperature. LB films based on conducting polymers are attractive candidates for a variety of applications such as biosensors, ion sensors, integrated optics and molecular electronic devices. For any device application, the material should be in the solid state and preferably with a definite molecular packing (Figure 1). During the past decades the Langmuir Blodgett (LB) film deposition process has been considered by various researchers, as a potential technique for the production of ultra- thin organic films with well-defined molecular structures. But the requirement of amphiphilicity (polar head and non- polar tail) and processibility of the material in preparation of LB film limited fabrication of PANI LB film.

There have been only a few reports on LB films of semi- amphiphilic conducting polymers, due to their poor LB processibility.



**Figure 1:** Formation of monolayer on a water surface (a) expanded (b) partly compressed (c) closely packed

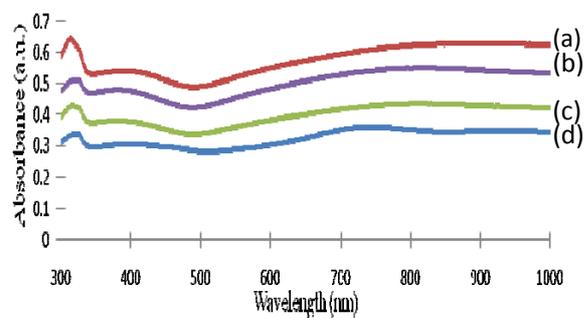
The earlier studies of LB deposition of conducting polymer by several researches showed various use of processing aid such as stearic acid [1-2], use of functionalized acid as dopant [3], use of mixed solvent[4-6], use of processing solvent [7] to help in monolayer formation and transfer PANI successfully to the substrate. The monolayer stability and surface potential isotherms are considerably improved when low subphase pHs are employed. Doping of PANI by protonation with functionalized protonic acids such as *p*-toluene sulfonic acid (PTSA), camphorsulfonic acid (HCSA) or dodecylbenzenesulfonic acid leads to solubility in common organic solvents. However, as shown recently by Riul et al. [3], to obtain conducting LB films the subphase has to be acidic. The attachment of long alkyl substituents to the polymer backbone (either covalently or

electrostatically through the polar substituents already present) generally enhances the monolayer stability and transferability. Here in this paper, we reported detailed studies on the preparation of Langmuir monolayers of PANI emeraldine base and the effect of sub-phase pH on the evolution of monolayer formation. Further, systematic investigation pertaining to the characterization of PANI emeraldine base monolayer have been carried out by U.V.-visible and FTIR spectroscopies.

### Experimental

Polyaniline (PANI) emeraldine base (Sigma Aldrich; MW 10000) was dissolved using methanol (Merck) as a solvent. The resulting solution is kept in ultra sonication bath for 6 hours. The ultra sonicated solution was filtered. A 750  $\mu$ l of solution was spread over Langmuir- Blodgett trough, at air/ water interface and a time of 30 min was allowed for solvent evaporation. Surface pressure against area/ molecule isotherm was recorded using simple filter paper as sensor (Wilhelmy plate). The transfer pressure was maintained at 12mN/m. The pH of the subphase water was maintained at different levels of 1, 3, 5 and 7 by adding *p*- toluene sulfonic acid. Langmuir Blodgett trough (Model LB 312DMC) was used to study the formation of PANI-EB monolayer. Both U.V.-visible and FTIR spectroscopy indicate connection between pH and PANI-EB chains.

### Results and discussion

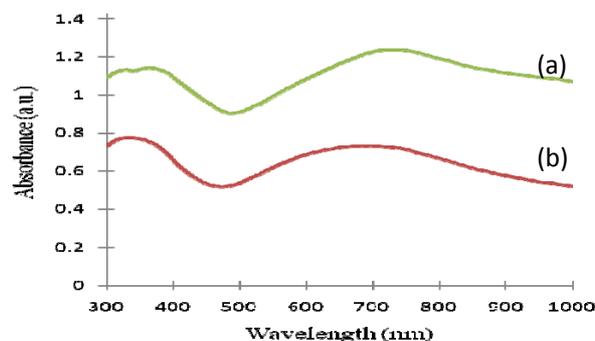


**Figure 2:** Variation of the UV-visible spectrum of PANI-EB in different subphase at (a) pH 1 (b) pH 3 (c) pH 7 (d) pH 5

The UV-visible spectra of PANI-EB in different subphases are shown in figure 2. It indicates that PANI-EB in pH 1 have higher rate absorption than other pH. PANI-EB is an organic polymer that has ability to absorb electromagnetic radiation because of the existence of its electron valency that can be excited to higher level. The result shows, the range of wavelength is around 300nm and above because of limitation by a certain functional groups (chromophore) that have low excitation energy. The PANI-EB shows two absorption peaks at 320nm and 800nm (sharp peak). The peak seen at

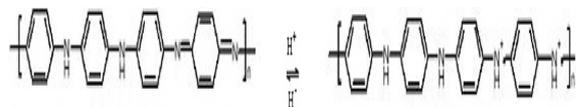
320nm can be attributed to the  $\pi$ - $\pi^*$  transition centred on the benzenoid ring and the peak at  $\sim$ 800nm can be understood to arise from the polaron bands. Acidic sub-phase is maintained by adding functionalized protonic acid like *p*-toluene sulfonic acid that helps in solubility and stability for formation of PANI-EB monolayer. The mixing of protonic acid with emeraldine base results in the shift of the Fermi level where the migration of electrons took place from the valence band into the conduction bands.

Here, pH 7 refers to a standard to show the probability that happened if no PTSA added in the sub-phase of PANI-EB. In terms of the absorbance, pH1 > pH3 > pH7 > pH5. pH 7 has higher absorbance than pH 5 because the difference in the volume of PTSA. There is no PTSA for pH 7 compared with pH 5. Thus, the absorbance in pH 7 that shows in Figure 2 comes from the PANI-EB molecule. When the sub-phase of PANI-EB was add with PTSA, this situation related to the protonation process occurred between PANI-EB and PTSA. Absorbance is proportional to the thickness of the sample and the concentration of the absorbing species in the sample. The absorbance of PANI-EB is more than one (Figure 3) due to the higher concentration of PANI-EB (absorbing species) and indirectly limitS the protonation process with PTSA. During protonation, the mass and the charge of the species each increase by one unit. Protonating a molecule or ion alters many chemical properties beyond the change in the charge and mass such as hydrophilicity, reduction potential, optical properties and more. Protonation often rapid because of the high mobility of protons in water. Besides that, charge delocalization and the electrical properties in molecular structure will increase. In neutral sub-phase (without PTSA), no protonation occurs because the rate of protonation is related to the acidity of the protonated species (Figure 4). In terms of protonation: pH1 > pH3 > pH5 > pH7. At pH 5, we can see a peak at wavelength 700nm, which is considered to be the electron transition of quinoid unit.



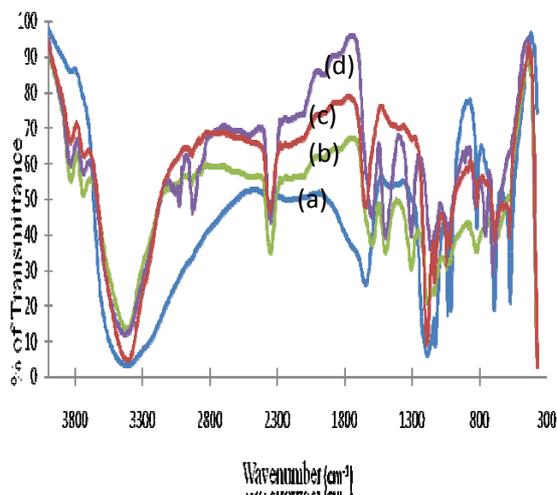
**Figure 3:** Variation of UV-visible spectrum of PANI-EB (a) with PTSA (b) without PTSA

When PTSA was added to PANI-EB solution, the resulting solution became acidic because of the PTSA presence. At lower pH, PANI emeraldine base (dark blue) is protonated to PANI emeraldine salt (dark green) (Figure 6).



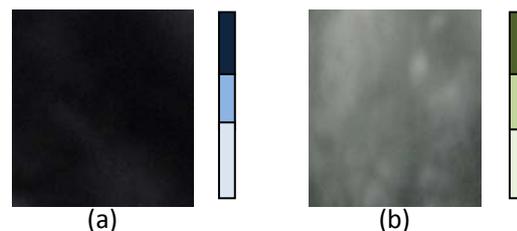
Emeraldine base (blue) → Emeraldine salt (green)

**Figure 4:** Mechanism of protonation of PANI-EB to PANI-S

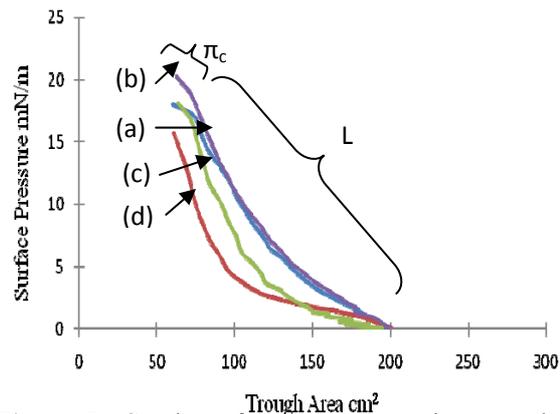


**Figure 5:** FTIR spectral analysis for PANI-EB in different subphase (a) pH 1 (b) pH 3 (c) pH 7 (d) pH 5

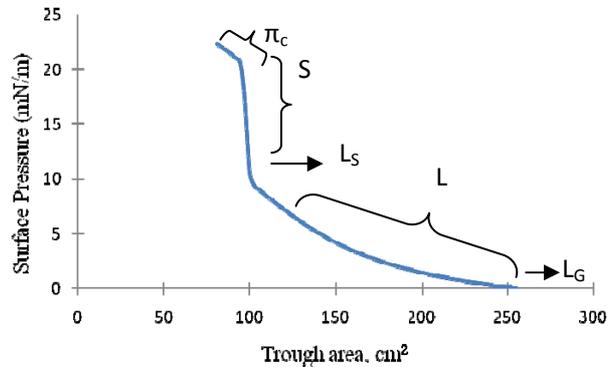
Figure 5 shows the FTIR spectra LB films of PANI-EB obtained in different sub-phase. FTIR analysis proves the protonation process of PANI-EB. The wave number  $1597\text{cm}^{-1}$  (neutral) shifts to  $1595\text{cm}^{-1}$  (pH 1), which denotes PANI emeraldine base is protonated to PANI emeraldine salt. The peaks seen at  $3430$ ,  $3035$ ,  $2929$ ,  $1597$ ,  $1595$  and  $1302\text{cm}^{-1}$  are characteristics of PANI-EB (neutral pH). The strong band seen at  $1302\text{cm}^{-1}$  can be assigned to the combination of several stretching and bending vibrations emanating from the C=N bonds (quinoid). The newly formed peak corresponding to the wave number  $393\text{cm}^{-1}$  confirms the presence of anions. The intensities of the various peaks in the respective FTIR spectra show a distinct decrease with an increase of pH.



**Figure 6:** Comparison colour of PANI-EB during protonation process (a) Before (dark blue) (b) After (dark green)



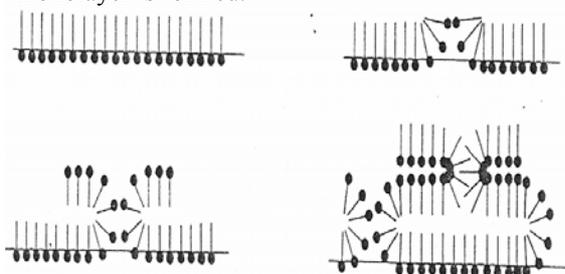
**Figure 7:** Graph surface pressure against trough area for Langmuir monolayer of PANI-EB (a) pH 1 (b) pH 3 (c) pH 7 (d) pH 5



**Figure 8:** Graph surface pressure against trough area of Langmuir monolayer PANI-EB when more PTSA are added

Figure 7 shows graph  $\pi$ - $\text{\AA}^2$  isotherm for Langmuir monolayer of PANI-EB in different pHs. There are different for each pH in area/ molecule  $\text{\AA}^2$  but indicate no significant phase (solid, liquid and gas). This indirectly showed that the stability of the monolayer not achieved with this condition. Collapse pressure,  $\pi_c$  is still reached after liquid phase formed at trough area  $200\text{-}90\text{cm}^2$ . This is due to the low concentration of PTSA that used in each pH. PTSA plays an important role in protonation process of PANI-EB but it can also helps in stability and formation of PANI-EB monolayer. Figure 8 shows PANI-EB monolayer

was formed when more PTSA were added (higher concentration) and indicated three distinct regions (solid, liquid and gas). After initial spreading of PANI-EB onto the sub-phase, no external pressure is applied to the monolayer and the molecules behave as a two-dimensional gas. On compression of the monolayer, some ordering of the molecules PANI-EB takes place and it behaves as would be expected of a two-dimensional liquid. The liquid phases, L is clearly visible. It may be seen that these liquid phases ( $L_G$ - $L_S$ ) are pronounced for trough area of 170- 72  $\text{cm}^2$ . With continued closing of the barrier, the increase of pressure causes additional ordering, the monolayer behaving as a quasi- solid. The solid phase transition can be clearly seen to occur at the trough area of 70-60  $\text{cm}^2$ . Solid state is characterized by a steep and usually linear relationship between surface pressure and trough area. As a result, there is rising in pressure, mN/m. At this point, the PANI-EB monolayer is formed.



**Figure 9:** Collapse of a monolayer

Eventually the collapse pressure,  $\pi_c$  is reached at which the film irretrievably loses its monomolecular form (Figure 9). The forces exerted upon it become too strong for confinement in two dimensions and molecules are ejected out of the monolayer plane into either the sub-phase (more hydrophilic molecules) or the super-phase (more hydrophobic molecules). However the collapse is not uniform across the monolayer but it is usually initiated near the leading edge of the barrier. The collapse pressure can be defined as the maximum to which a monolayer can be compressed without the detectable expulsion of molecules from the Langmuir monolayer. It depends upon the details of the experimental procedure used, the chemical substances used, the temperature, the rate at which the film is compressed and procedures to which the monolayer has been subjected.

## Conclusions

We conclude that the stability of formation Langmuir monolayer PANI-EB can be achieved by using the acidic sub-phase (more PTSA) in a Langmuir- Blodgett trough. pH plays a vital role in formation of PANI-EB monolayer. In terms of stability of PANI-EB monolayer for each pH;  $\text{pH1} > \text{pH3} > \text{pH5} > \text{pH7}$ . Both UV-visible and FTIR spectroscopies prove there are different absorption and bonding of PANI-EB in different pHs.

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## References

1. Troitsky V.I., Berzina T.S. and Fontana M.P. (2002) *Deposition of uniform conductive polyaniline films and approach for their patterning*. Journal Synthetic Metal, **129**: 34-96.
2. Cheung J.H., Punkka E., Rikukawa M., Rosner R.B., Royappa A.T. and Rubner M.F. (1992) *New developments in the Langmuir- Blodgett manipulation of electroactive polymers*. Journal Thin Solid Films, **210-211**: 246-249.
3. Riul Jr. A., Mattoso L.H.C., Mello S.V., Telles G.D. and Oliveira Jr. O.N. (1995) *Langmuir and Langmuir- Blodgett films of parent polyaniline doped with functionalized acids*. Journal Synthetic Metals, **71**:2067-2068.
4. Huo L.H., Cao L.X., Wang D.M., Cui H.N., Zeng G.F. and Xi S.Q. (1999) *Preparation and characterization of doped polyaniline films*. Journal Thin solids films, **350**: 5-9.
5. Granholm P. Paloheimo J. and Stubb H. (1997) *Conducting Langmuir- Blodgett films of polyaniline: Fabrication and charge transport properties*. Journal Synthetic Metals, **84**:783-784.
6. Riul Jr.,A. Mattoso L.H.C., Telles GD, Hermann PSP and Colnago L.A.(1996) *Characterization of Langmuir- Blodgett films of parent polyaniline*. Journal Thin Solids Films, **285-285**: 177-180.
7. Dabke R.B., Dhanabalan A., Major S., Talwar S.S., Lal R. and Contractor A.Q. (1998) *Electrochemistry of polyaniline Langmuir-Blodgett films*. Journal Thin Solid Films, **335**: 203-208.