

# Study of Electrochemical and Thermodynamical Properties of PANI Acetate Solutions

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**Abstract:** Polyaniline (PANI) is one of the most conducting polymers has attracted more attention because of its low cost superior electrochemical performance and mechanical flexibility. In the present investigation, non-aqueous solutions of PANI acetates have been prepared with various concentrations and the experiments were carried out to measure ultrasonic velocity, density, viscosity from low temperature to high temperature. Using these experimental data the thermodynamic parameters is computed. The electrochemical properties of the solutions are also studied. The electrochemical property is correlated with internal pressure. The variation of these parameters are used to confirm the molecular interaction between the molecules. The results are also corroborated with the spectroscopic study.

**Keywords:** Polyaniline, Acetates, Thermodynamic, Conductance.

## 1. Introduction

Polyaniline (PANI) is a conducting polymer which possesses three distinct oxidation states namely leucoemeraldine base (fully reduced), emeraldine base (half-oxidized), and pernigraniline base (fully oxidized) [1 & 2]. Besides the three states, emeraldine base is the form that when doped with acids like monochloro, dichloro and trichloro acetate changes from insulating to conducting nature. In the present work, PANI is doped with these acids. Monochloro acetate is used to produce wide variety of useful compounds. Dichloro acetate has a history in medicine for helping to treat a group of metabolic diseases in children primarily but also in adults for several decades. Trichloro acetate is widely used in biochemistry for the participation of macromolecules such as proteins, DNA and RNA. The ultrasonic velocity is useful for evaluating different parameters. The electrochemical property (Specific conductivity, Equivalent conductance ( $\Lambda_c$ )) and thermodynamic properties (Internal pressure, free volume) play a vital role in analyzing the physical nature and strength of the intermolecular interactions. The aim of the present work is to study the intermolecular interactions occurring in the solution through thermodynamic property and to correlate these results with the electrochemical property. The results are also conformed from the analysis of UV spectra of the solutions.

## 2. Experimental Procedure

In the present work, the solutions of PANI acetates in formamide are prepared with five different molalities. PANI is synthesized by oxidative polymerization of aniline using ammonium persulphate as an oxidant in the presence of the

chloro acids at room temperature. Formamide is used as a solvent. Basic measurements such as density, viscosity and ultrasonic velocity have been measured at different concentrations.

## CALCULATION

Thermodynamic and electrochemical parameters are analyzed using the following formulae.

### (1) Thermodynamic Properties

#### (i) Internal pressure ( $\pi_i$ )

$$\pi_i = bRT \left( \frac{K\eta}{u} \right)^{\frac{1}{2}} * \left( \frac{p^{\frac{2}{3}}}{M_{eff}^{\frac{2}{3}}} \right) \text{atms} \quad (1)$$

#### (ii) Freevolume ( $V_f$ )

$$V_f = \left( M_{eff} \frac{u}{K\eta} \right) \text{cc} \quad (2)$$

### (2) Electrochemical Property

$$\Lambda_c = \frac{K_c * 1000}{N} \text{ mho cm}^2 \quad (3)$$

## 3. Results and Discussion

### 3.1 Thermodynamic Parameters

The internal pressure values of PANI Mono Chloro Acetate (PANI MCA) & PANI Di Chloro Acetate (PANI DCA) is found to be decreasing with respect to concentrations, which suggests that there is a weak solute- solvent interaction. The decreasing trend reveals the tendency of breaking the structure of the solvent (Fig 1). This behavior emphasizes that the solute behaves as a structure breaker. This effect is also confirmed by increasing values of free volume.

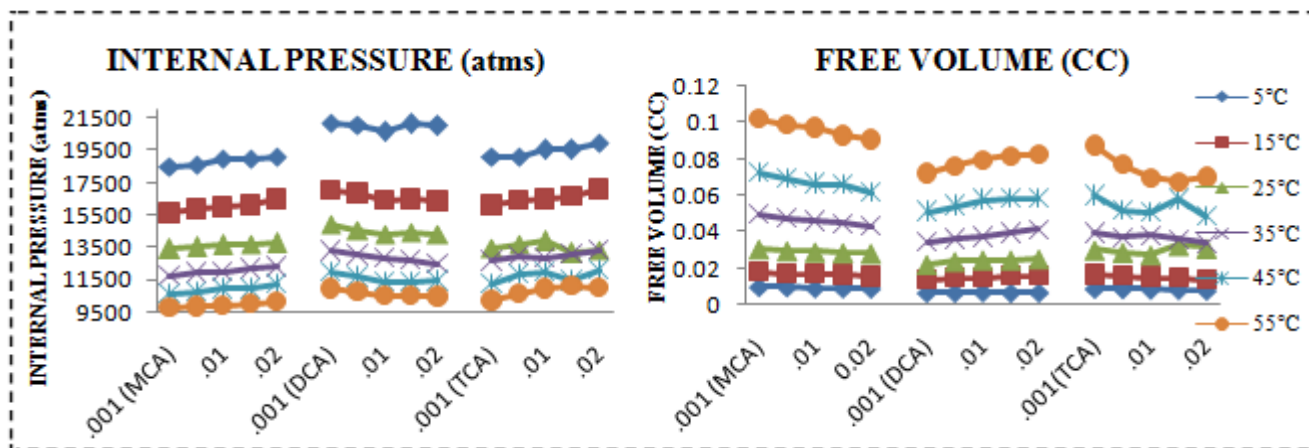


Figure 1: Variations of internal pressure and free volume with molality-PANI ACETATES

But in Polyaniline trichloro acetate (PANI TCA) the internal pressure value increases with increase in concentration, but decreases while temperature increases. This behaviour emphasizes that there is a strong solute – solvent interaction occurring in the solution through hydrogen bonding. The structure making nature is also confirmed by the decreasing values of free volume as expected (Fig 1) [4&5].

### 3.2 Electrochemical Property

The equivalent conductance is defined as the conducting power of all ions produced by one gram equivalent of an electrolyte in a given solution. The variations of equivalent conductance with concentration of the solutions are shown in

(Fig.2), of all the solutions, the equivalent conductance is found to be high at low concentrations and low in higher concentrations. It is also found to be decreasing exponentially with concentration and increases as temperature increases. Variation of equivalent conductance is found to be very small at higher concentrations.

In concentrated solutions of the ionic atmosphere appreciably reduces the velocity of the ions and hence the equivalent conductance. In the present study high conducting nature of the solutions are observed at low molalities at all temperatures [6].

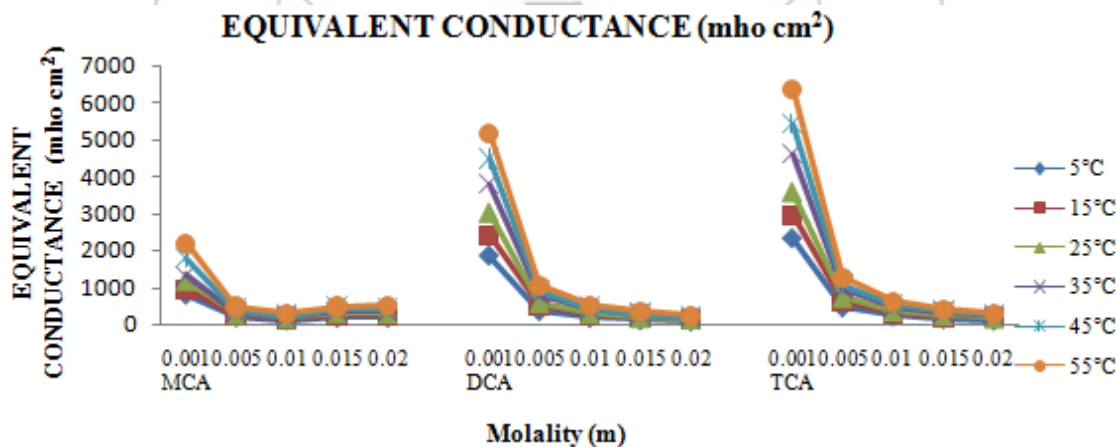


Figure 2: Variation of equivalent conductance with molality - PANI ACETATES

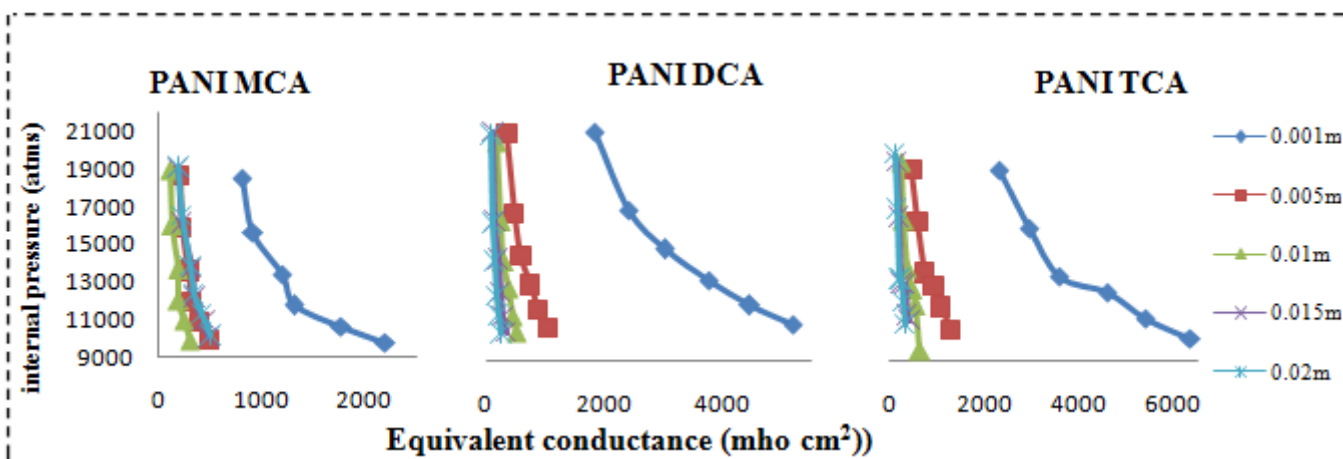
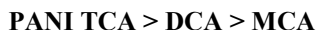


Figure 3: Variation of equivalent conductance with internal pressure-PANI ACETATES

When equivalent conductance ( $\Lambda_c$ ) increases, internal pressure ( $\pi_i$ ) is found to be decreases (Fig 3). The conducting natures of the PANI acetates are found to be high with low  $\pi_i$ . Equivalent conductance is found to be high at very low concentration and also  $\pi_i$  is found to be high. The conducting nature is found to be in the order as shown below.



### III. OPTICAL ANALYSIS

The presence of two very close peaks at 210 nm and 213 nm in the visible spectrum of the solvent (Fig.5) are attributed to the dimer and the enolic form (Fig.4)

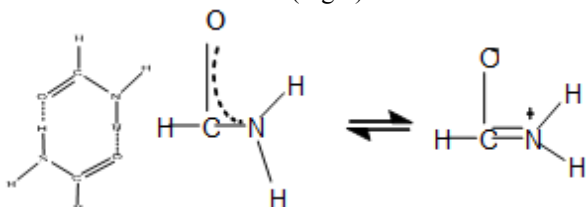


Figure 4: Dimer and Enolic form of formamide

#### (i) TRI CHLORO ACETATE

In the UV-visible spectrum of PANI TCA solution (Fig 5) peaks are observed at 262 nm, 271 nm and 380 nm. These absorptions are due to formamide and solute. The peak at 380 nm is due to the solute particle. The peaks at 262 nm and 271 nm have shifted bathochromically by  $\sim 50$  nm from the solvent. This indicates the strong solute- solvent interaction.

#### (ii) DI CHLORO ACETATE

In the UV-visible spectrum of PANI DCA solution (Fig 5) peaks are observed at 262 nm, 270 nm, 375 nm and 571 nm. The solvent peaks are bathochromically shifted by  $\sim 50$  nm. These shifts are indicative of solute- solvent interaction.

#### (iii) MONO CHLORO ACETATE

In the UV-visible spectrum of PANI MCA solution (Fig 5) broad absorptions are observed at 328 nm and 644 nm. These peaks are due to strong absorption of solute particles. Strong solute – solvent interaction may be inferred from the intense absorption found at 328 nm.

In all the above three PANI acetate solutions, the presence of quinoid and benzenoid forms are identified. By comparing the solvent spectrum with the solutions it is observed that the absorption peaks are shifted towards the longer wavelength region. This may be due to the solvent effect. It has been found that there is a bathochromic shift which results from the reduction in the energy level of the excited state accompanying the dipole-dipole interaction which in turn results in intermolecular hydrogen bonding [7].

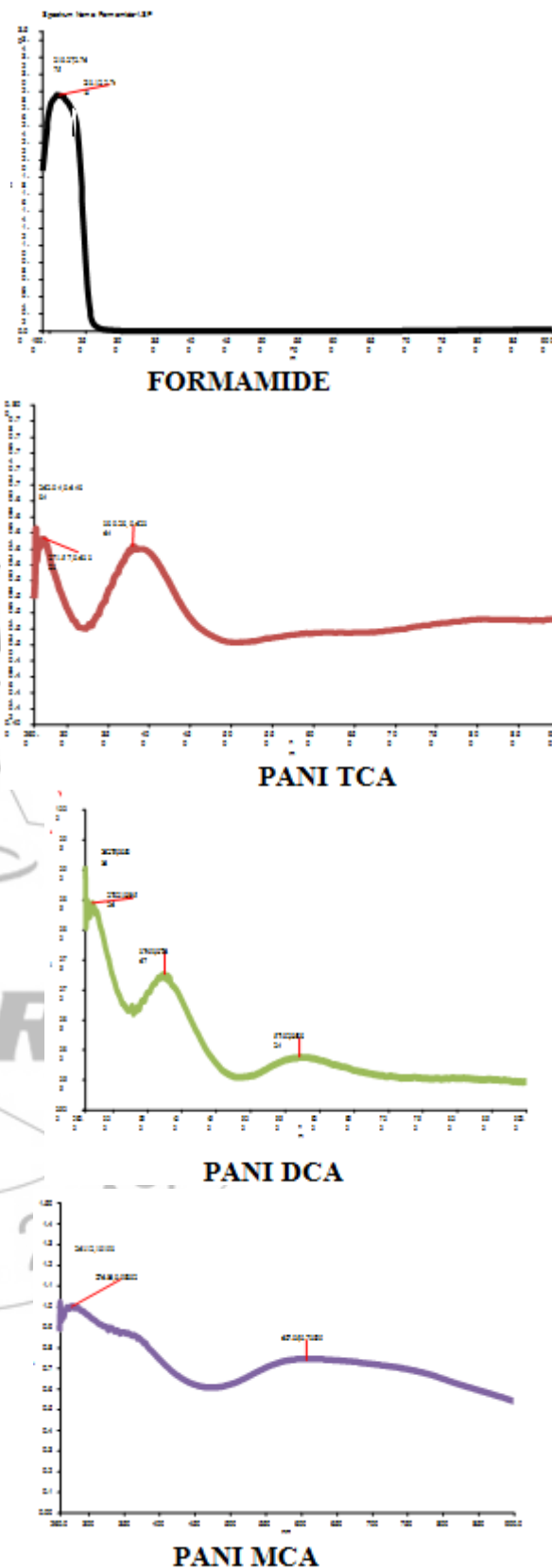


Figure 5: UV-Visible Spectra For PANI Acetates

### 4. Conclusion

From the analysis of PANI acetate solutions, the structure making and breaking tendency are elucidated and also the conducting natures of the PANI solutions are predicted. The spectroscopic results obtained from the UV-Visible analysis

are found to be in good agreement with the thermodynamic and electrochemical results

## 5. Acknowledgement

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