

Sonochemical, Thermal and Spectroscopic Analysis on Doped Polyaniline Nano Fluids

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Abstract: Sonochemical investigation in polyaniline non aqueous solutions provides useful information in understanding the behavior of liquid systems, since inter molecular and intramolecular association, complex formation and related structural changes affects the compressibility of the system which in turn produces variation in ultrasonic velocity. Nowadays the conducting polymers have become the center of gravity of polymers and materials science for the researchers due to their novel electronic and electrical properties. Among the conducting polymers, polyaniline has been extensively studied not alone for its conducting property which can be varied by the degree of doping, but also due to its environmental stability and economic feasibility. The present study seeks to ascertain the nature of the molecular interactions in the frame work of the thermodynamic and related parameters by using sonication. Doped polyaniline materials have been prepared through the oxidative polymerization of aniline in the presence of sonicator. The molecular interaction, thermodynamic property, compressibility nature and solvation effect are analyzed through acoustical parameters at different temperatures for various concentrations. The spectral analysis reveals the binding nature of the solute and solvent, hydrogen bond formation and the presence of dopant. The residue extracted from the solution is found to be a nano material which is confirmed through the HR-SEM characterization. The obtained results have been interpreted in the light of intermolecular interactions in terms of structure making or breaking tendency of the solute and solvent in the solution.

Keywords: Sonication, Polyaniline, Solvation, Thermodynamic, Nanomaterials, SEM.

1. Introduction

During the last decade there has been wide spread interest in conducting polymers. Polyaniline (PANI) is one of the most useful conducting polymers due to its ease of synthesis and environmental stability. It also has a wide range of electrical properties which can be easily controlled by changing its oxidation and protonation states [1, 2]. However there are still many unresolved problems concerning the structure and properties of PANI because of the complexities in molecular structure due to synthesis conditions [3, 4]. Improvement of polyaniline properties can be achieved by forming nanocomposites of aniline and blends with commercially available polymers or inorganic materials.

PANI has attracted considerable attention because of its unique electrical, optical and electro optical properties [5]. Various approaches have been tried to improve the processability, including addition of side groups to the polymer backbone [6] such as direct polymerization of intractable polymers into the final desired shape, making a composite of blend of conducting polymers [7,8] and copolymerization.

Extensive research has been directed towards the improvement of the processability of polyaniline by copolymerization with substituted aniline [9,10] or doping polyaniline with stable functionalized protonic acid. Conducting polymers have various applications such as rechargeable batteries [11], electromagnetic interference (EMI) shielding [12], antistatic coatings [13], gas sensors, optical devices, removal of heavy metal from water and waste water etc. Nowadays nanostructured (nanoparticles/-rods/-wires/flakes) conducting polyaniline with unusual physical and chemical properties have attracted great research interest. Recently various strategies have been developed for the preparation of polyaniline nanostructures.

Sonochemistry is one of the simplest techniques used to prepare nanosized materials. 10-20nm size amorphous iron nanoparticles are formed by sonicating Fe (CO) 5 [14]. Single-Walled Carbon Nanotubes (SWCNTs) of high purity is produced in sonochemical way [15]. The SWCNTs can be formed by dispersing phospholipid-polyethylene glycol (PL-PEG) by sonication [16]. Sonication is one of the interesting and simple methods to prepare nanomaterials reported in literature [17]. Ultrasonication is a proven method for the production of nano emulsions and nano dispersions. When sonicating liquids at high intensities, the sound waves that propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles, with rates depending on the frequency. This improves the mixing of the pre-cursors and increases the mass-transfer at the particle surface. This leads to smaller particle size and higher uniformity. To obtain nanoparticles with specific characteristics and functions, the surface of the particles has to be modified. Various nanosystems like polymeric nanoparticles, nanofluids, liposomes, dendrimers, carbon nanotubes, quantum dots etc. can be successfully functionalized for efficient applications.

In the present work PANI Nano fluids are prepared by the sonication method through double step process. The nano size and morphology of the samples are characterized through HR-SEM. Solute - solvent interaction, band gap energy and binding nature are characterized through spectral as well as acoustical analysis. Acoustical investigation of these PANI samples with a polar protic solvent like formamide provides useful information in understanding the behaviour at liquid state level.

2. Materials And Methods

Polyaniline perchlorate (PAPC), polyaniline formate (PAF) and polyaniline trichloro acetate (PATCA) are prepared by oxidative polymerization of aniline (emeraldine base),

perchloric, formic and trichloro acetic acids are used as dopants and ammonium per sulfate is used as oxidant. During the polymerization of aniline with acids in deionised water, ammonium per sulfate was added drop wise under constant stirring for 4 hrs. The temperature of the mixture is slowly raised, followed by cooling. Continuous stirring of the solution makes it darker and then it is changed to emerald colour which indicates the polymerization reaction. The precipitate was filtered and washed thoroughly with distilled water, alcohol, acetone and ether.

The prepared doped PANI is hard and brittle and insoluble in common organic solvents. Since the insolubility/infusibility of PANI is related to its π - π^* conjugation system. So the prepared PANI is dispersed in a non-aqueous medium in the presence of sonicator at different temperatures. The solution thus prepared was kept in a constant temperature bath at 5°C. The sonicator is set for 15 minutes, making sure that the temperature doesn't rise above 10°C. This can be done by sonicating in 5 minutes intervals, then pausing and letting the solution cool to 5°C before the next sonication period. The clear resulting solution is indicating that the particles are evenly dispersed. The same procedure is repeated for the room temperature preparation also. The final product was found to be nanofluid which is taken for further analysis. For HR-SEM characterization a small amount of the nano fluid is taken and deposited on a glass plate of area 1cm².

Ultrasonic investigation of PAPC, PAF and PATCA solutions have been carried out in formamide at different concentrations. Variable path ultrasonic interferometer with a crystal frequency of 2MHz is used to measure the ultrasonic velocity of the solutions with an accuracy of $\pm 0.05\%$ error and the densities of the solutions are also measured with 25 mL specific gravity bottle. All the above measurements are carried out at different temperatures (5°C - 55°C) using a thermostatically controlled water bath with $\pm 0.1^\circ\text{C}$ accuracy. From the obtained data the thermodynamic parameters like internal pressure (π_i) and free volume (V_f), adiabatic compressibility (β) and solvation number (η_h) are calculated. The formulae used are given below.

$$\pi_i = bRT \left(\frac{K\eta}{u} \right)^{\frac{1}{2}} * \left(\frac{P^{\frac{2}{3}}}{M_{\text{eff}}^{\frac{7}{6}}} \right) \text{atms} \quad (1)$$

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

$$\beta = \frac{1}{u_2 \rho} \text{ cm}^2/\text{dyne} \quad (3)$$

$$\eta_h = \left(\frac{n_s}{n_i} \right) \left[1 - \left(\frac{\beta}{\beta_0} \right) \right] \quad (4)$$

3. Results and Discussion

(i) HR-SEM ANALYSIS

The SEM results of PAPC, PAF and PATCA indicate that after 10 mins of intermittent sonication and subsequent filtration, the sample consists of almost nanoparticles. Formation of very large particles is prevented possibly through a milling type of process or due to small-scale turbulence in the solution. The appreciable reduction in the size of nanoparticles is obtained due to the two major facts

i.e. increased duration of sonication and another one is the low temperature (5°C) effect. This effect is achieved by setting duty cycle of the sonicator with 5 min intermittent sonication and the solution is kept in an ice bath so that the temperature of the solution does not rise above 5°C. The sample is found to be a finer one than at room temperature. The existence of PANI nanoparticles is confirmed from the SEM analysis. The duration of sonication plays a dominant role in the size reduction of the particles. The SEM morphology indicates the presence of polymer overgrowth leading to agglomeration. As given in literature that is the application of sonication with a definite duration resulted in smaller particles than without the sonication treatment [18]. The sample PAF is kept in sonicator for 10 minutes which results in nanoparticles of size around 60nm (Fig.1). The PAF sample's SEM image before sonication is also shown in the Fig.2. But in the case of PAF appreciable reduction in particle size from 60 nm to 30 nm is observed when the sonication time is increased to 30 mins (Fig.3). Thus sonication time is also an important factor to be considered and optimized in order to obtain the well suited characteristics. Among these samples the PATCA is found to be entirely different in its morphology which reveals the formation of nanoflakes (Fig.4). The flakes are found to be effective as a catalyst in the preparation of fuel cells. The success of this method will likely depend on the nature of the samples used.

(ii) FT-IR Analysis

The FT-IR spectrum of formamide exhibits a broad absorption at 3600 -3000cm⁻¹ (Fig.5). This indicates the presence of stretching vibration due to O-H, N-H groups. The frequency at 3404 cm⁻¹ arises due to intra molecular associations between formamide molecules. Frequencies at 2770 and 2687 cm⁻¹ may be due to the enolic form (Fig.6a) of formamide which may contribute a smaller extent compare to the dimer form (Fig.6b). The frequency at 2196 cm⁻¹ is due to the NH⁺ frequency of the enolic form. The stretching frequency at 1684 cm⁻¹ confirms the existence of intra molecularly bound carbonyl group [19].

When PAF is dispersed in formamide, the NH stretching absorption is shifted to 3417 cm⁻¹ i.e. towards higher frequency side by 1 cm⁻¹. C=O stretching is shifted to 1688 cm⁻¹ i.e. towards higher frequency side by 1.99 cm⁻¹. These slight deviations in the absorption peaks are due to the tightening of H-bonds in the caged structure. It is already confirmed that, when PANI is dissolved in polar non aqueous solvent, it promotes thermodynamically a more stable chain [20]. The Cl⁻ doping of the synthesized polyaniline is confirmed by the C-Cl stretching peak arises at 601 cm⁻¹ [21]. The C=C stretching absorption of aromatic compounds generally occurs in the range of 1475 -1625 cm⁻¹. In the present study this peak was obtained at 1605 cm⁻¹ (Fig.7). The peaks at 1040 and 505 cm⁻¹ correspond to the stretching and bending vibrations [22]. The occurrence of these peaks in the PAF spectrum indicates that polyaniline is successfully doped and also confirmed the strong solute-solvent interaction.

The FT-IR spectrum of PAF solution resembles peaks similar to formamide. The peaks at 3407 cm⁻¹ is due to NH

of formamide has undergone a blue shift (9 cm^{-1}) indicating weakening of C=O-NH bonds in the dimeric formamide. The well defined peaks observed at 2440, 2397, 2300 and 2197 cm^{-1} are assigned to C=N group of enolic form of formamide (Fig.8). Among these vibrations the band at 2300 cm^{-1} has undergone a red shift (12 cm^{-1}) in the solution. This shows that the solute molecules have bound to the C=NH of formamide [23]. The amide I band at 1697 cm^{-1} has blue shifted by 12 cm^{-1} . This suggests the loosening of C=O-NH dimer and solvation of the polymer salt at this site by the solvent (Fig.9). These observations reveal that solute-solvent interaction is not appreciable as observed in PAPC.

In the presence of the solute PATCA, the FT-IR spectrum of formamide (Fig.10) exhibits the following peaks. A broad and well defined absorption at 3418 cm^{-1} is due to the N-H vibrations of formamide. A very close absorption at 3425 cm^{-1} , 3430 cm^{-1} has also been found. These may be due to the presence of solute molecules which also contain N-H group. Thus solvent and solute particle exhibits N-H stretching vibrations in this region. The C-H stretching frequencies are observed at 2886, 2771 and 2689 cm^{-1} , these peaks have merged with the broad N-H vibrations. The C-H groups in solvent and solute molecules may be responsible for this. The NH^+ frequencies found at 2396 and 2287 cm^{-1} are due to the solute particles while the frequency at 2194 cm^{-1} may be due to the solvent NH^+ groups. This peak has grown up in intensity compare to the pure solvent. This indicates the presence of more enolic form in solution. At 1680 cm^{-1} C=O stretching vibration is found. Lengthening of C-O bond causes decrease in frequency. Thus hydrogen bonding between the solute particle and C-O group is envisaged. The bifurcated absorption founding formamide have broadened. This is the region where C=N and C-N amide vibrations are found. The remarkable change in this region indicates the strong solute - solvent interaction. The C-O absorption has also broadened. Thus the finger print region from $1700 - 1000\text{ cm}^{-1}$ is remarkably affected by the entry of solute. At 658 cm^{-1} broadening is noted. This also may be due to solute - solvent interaction [23].

(iii) UV-Visible Analysis

The presence of two close peaks at 213 nm and 210 nm in the UV-Visible spectrum of the solvent (Fig.11) are attributed to the enolic and dimer form. The absorption band of PAPC at 385 nm corresponds to $n-\pi^*$ transition in the benzenoid units (Fig.12). The broad band at 300-500 nm is due to $n-\pi^*$ transitions of quinone-imine groups [24]. This broad band is ascribed to the exciton like transition in quinoid imino units. The PAF also exhibits the same absorbance at 385 nm but the absorption is slightly broadened at 500-600 nm region (Fig.13). The band gap energy of both samples is found to be 3.07eV. In the visible spectra of PATCA (Fig.14) before sonication, 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 while peaks at 262 nm and 271 nm have shifted bathochromically by $\sim 50\text{ nm}$ from the solvent. This indicates the strong solute- solvent interaction. A broad peak is obtained at 539 nm after sonication (Fig.15). The band gap energy is 2.1eV. This reveals that sonication induces the ionic conductivity.

In all the above three PANI solution the presence of quinoid and benzenoid 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 a reduction in the energy level of the excited state accompanying the dipole-dipole interaction which in turn results in intermolecular hydrogen bonding [23]. When a transition ($n \rightarrow \pi^*$) appears in the spectrum of an aromatic compound that contains ($\pi \rightarrow \pi^*$) transitions the shift occur at longer wavelengths. From this analysis, it is inferred that solutions of PANI are enhancing the structure of the solvent. The spectroscopic studies obtained are found to be in good agreement with the acoustic study.

(iv) Acoustical Analysis

a) Thermodynamic Parameter

Internal pressure (π_i) is the single factor which varies due to all the internal interactions. In the present study, internal pressure increases with concentration in PATCA. It is due to increase in cohesive energy (Fig.16). This increase in π_i suggests that there is a strong solute - solvent interaction taking place in the solution. But, when at higher temperatures, the temperature is increased there is a tendency for the ions to move away from each other. Hence there is a reduction in π_i with increase in temperature [25]. π_i and V_f are easily measurable parameters which are fundamentally responsible for the structure of a liquid or solution. The structure making effect is also confirmed by the decreasing values of free volume (Fig.17). In PAF π_i is found to be decreasing with respect to increasing molality up to 0.01 m. There is a rise in π_i values for 0.015 m and 0.02 m at all temperatures. Decrease in internal pressure suggests that there is a weak solute - solvent interaction. Among these PANI solutions, PATCA has strong solute-solvent interaction.

b) Solvation number

The effect of solvation is appropriate only at lower concentrations for all solutions. Below room temperature positive solvation number is found and at all other temperatures both positive and negative values are observed (Fig.18). The solutions are found to be more compressible above the room temperature due to the passage of ultrasonic /pressure waves through the solution. Negative values of solvation number indicate that the solutions are more compressible than the solvent. Many authors in literature report negative solvation number [26-28]. The positive values are an indication of strong interaction between the molecules [29]. Comparing to the three PANI solutions the solvation effect is found to be high in PATCA. This implies that PATCA solution is more compressible than the other two solutions. These results indicate that strong solute-solvent interaction takes place in the solution.

c) Adiabatic compressibility

The irregular behavior of adiabatic compressibility with increasing concentration (Fig.19) emphasizes the strong association between the molecules of the PANI solutions [30].

4. Conclusion

The present study shows that sonication provides an efficient way to synthesize polymeric nano materials. Both the size distribution and crystallinity of the particles can be controlled by controlling the duration of sonication and the temperature effects. The temperature influences the size of the nano particles, improved the synthesis condition and reduced the single particle size. The spectral results show that solute solvent interaction is higher and polymer is successfully doped. The morphology obtained from the SEM characterization results in the existence of doped PANI nanoparticles around 60 nm in PAPC and 30 nm in PAF and the formation of flakes in PATCA. The sonication time was observed to be an effective factor on the average size and size distribution of the resulting nanoparticles. The interacting nature of the molecules, binding nature and the band gap energy of them are also explored through the spectral results. Among the three PANI solutions, PATCA is found to be more conductive.

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FIGURES INDEXED

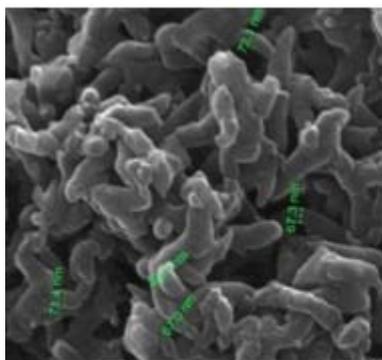


Figure 1: SEM - PAPC

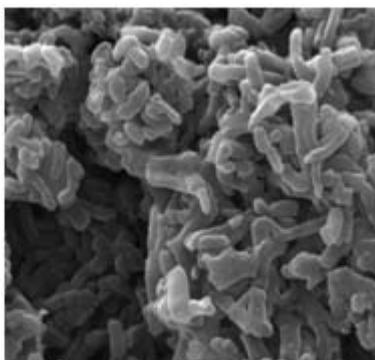


Figure 2: SEM - PAPC

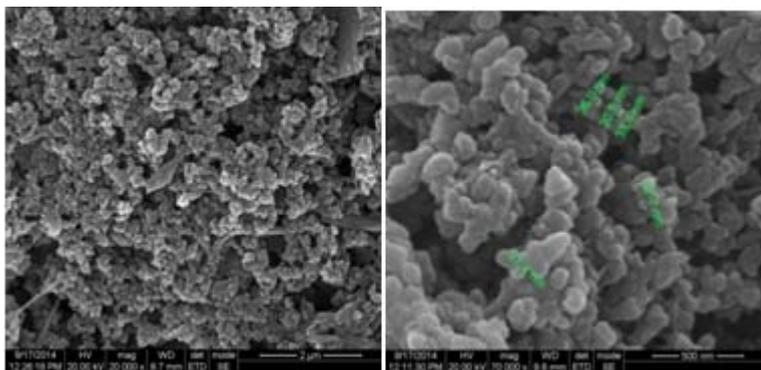


Figure 3: SEM – PAF

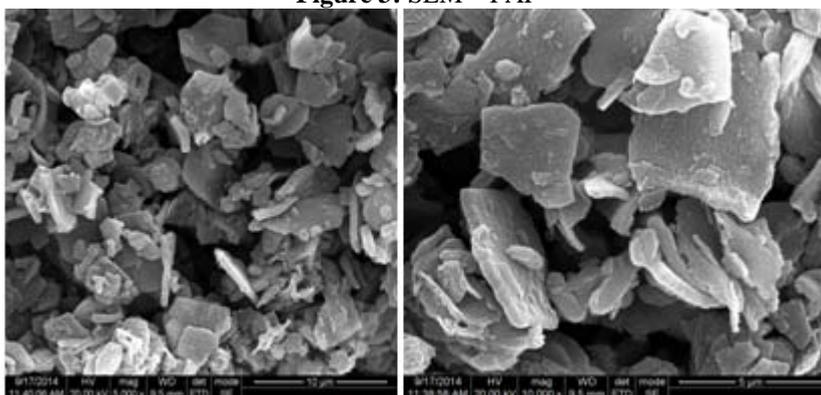


Figure 4: SEM - PATCA

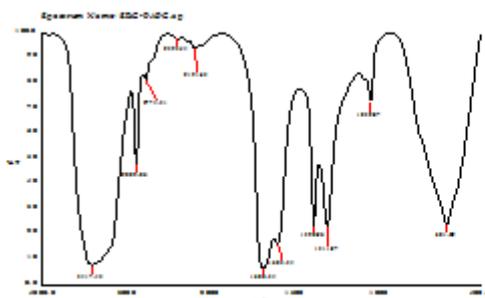
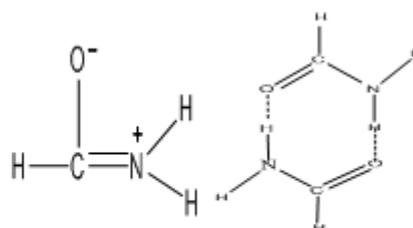


Figure 5: FT-IR spectrum- solvent



a. Enol form b. Dimer form

Figure 6: structure of formamide

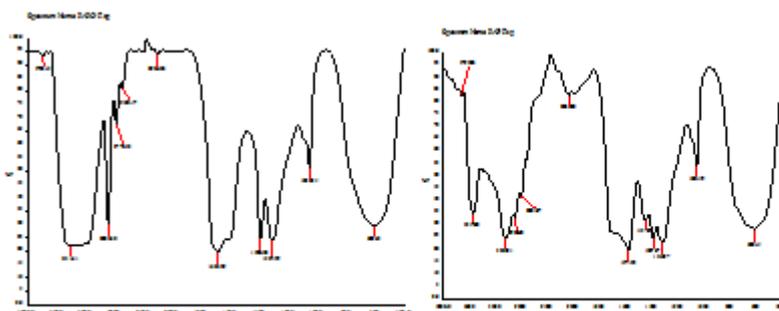


Figure 7: FT-IR - PAF

Figure 8: FT-IR – PATCA

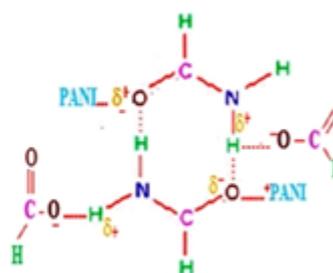


Figure 9: Solvated form – PAF

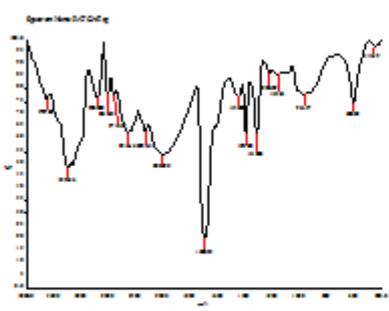


Figure 10: FT-IR – PATCA

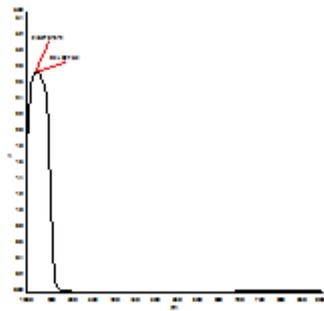


Figure 11: UV-Vis – solvent

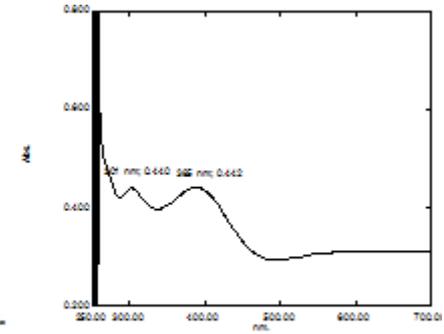


Figure 12: UV-Vis – PAF

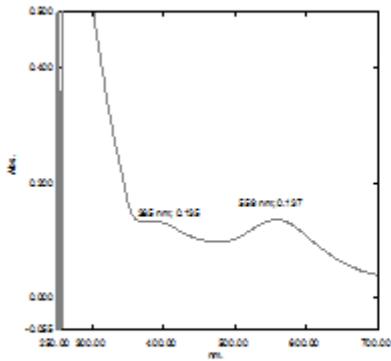


Figure 13: UV-Vis – PATCA

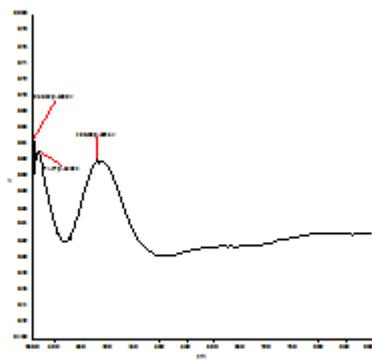


Figure 14: UV-Vis – PATCA

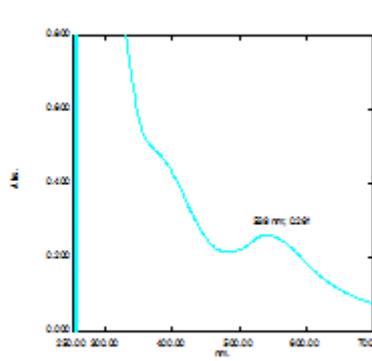


Figure 15: UV-Vis – PATCA

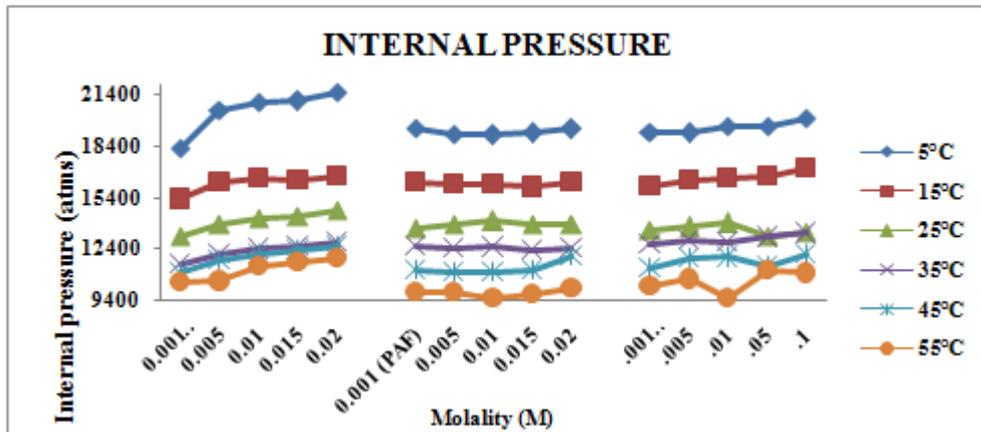


Figure 16: Internal Pressure - PANI solutions

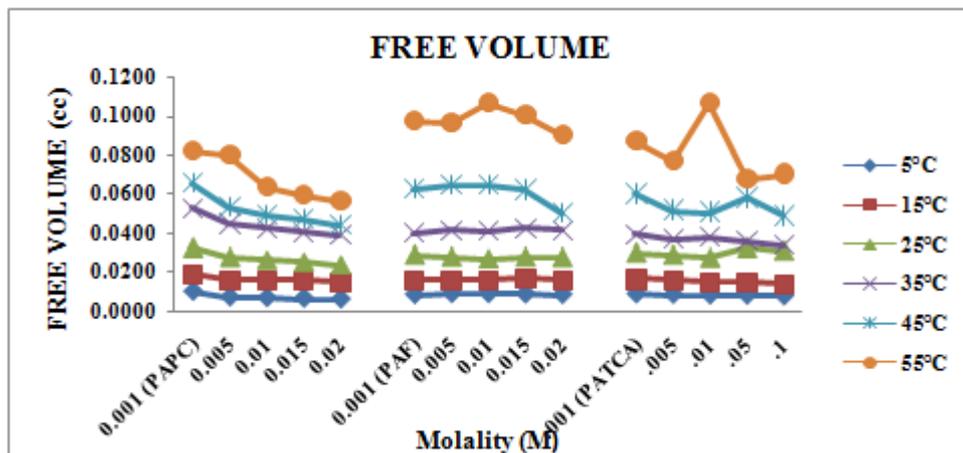


Figure 17: Free volume - PANI solutions

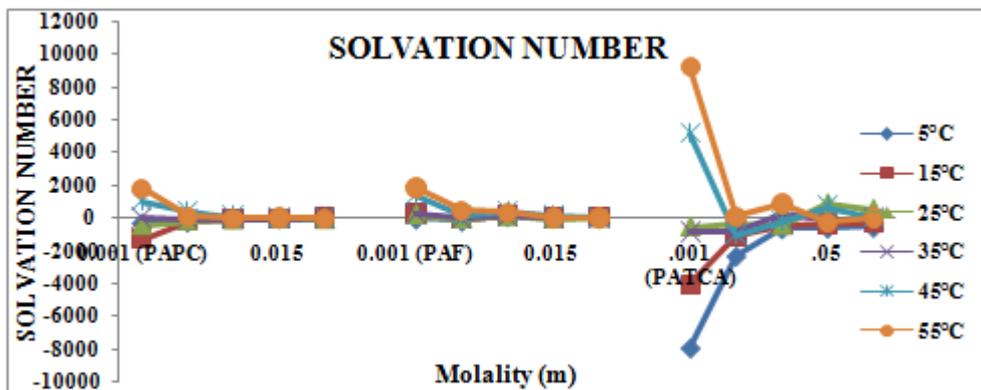


Figure 18: Solvation Number – PANI solutions

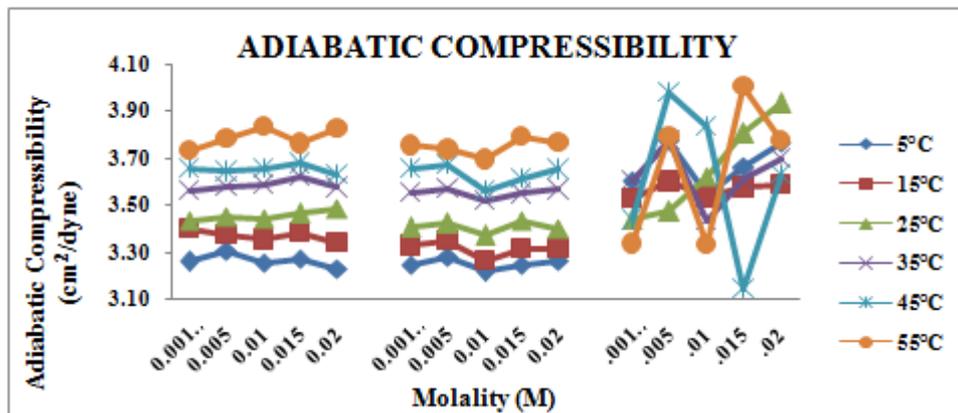


Figure 19: Adiabatic Compressibility - PANI solutions