Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **4(8),** 82-87, August **(2014)** *Res. J. Chem. Sci.*

Poly-dispersive Nature of relaxation times Characteristics of Poly-(diamino-naphthalene) doped Poly-(vinyl-alcohol) films from AC impedance analysis

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Available online at: www.isca.in, www.isca.me
Received 5th August 2014, revised 11th August 2014, accepted 18th August 2014

Abstract

The conducting polymer doped inside a macromolecular doped film through chemically oxidative polymerization process, will be a promising field in the material science. This kind of multifunctional conducting materials will also be interesting in terms of biocompatibility, low cost and environmental stability. The alternating current conductivity measurement is an important experimental technique to probe the microscopic images of a highly disordered system and all the studies provided fundamental and technological applications. Polaron defect occurs due to incorporation of conducting polymer inside the synthetic hydrogel, therefore for quantifying and investigating the disordered composites system, use of alternating current conductivity was required. In this paper less known conducting polymer poly-(diamino naphthalene) (PDAN) is doped with poly-(vinyl alcohol) (PVA), is being investigated. The composite films are obtained by chemical-oxidation polymerization method. The experimental PDAN doped PVA films of different weight concentration are being analyzed by AC impedance spectroscope at different temperature and frequency range. The calculated AC conductivities found are 4.65 X 10^{-6} Scm^{-1} for 0.591gm and 6.28 X 10^{-6} Scm^{-1} for 0.791gm PDAN doped PVA films. The complex impedance plot so obtained was semicircular in nature, shows the single AC current mechanism. Again by Cole-Cole impedance plot, the value of parameter "α" so obtained lies between zero and one (i.e. 0.88 and 0.89 for both weight concentration of PDAN doped PVA films), which shows the poly-dispersive nature of relaxation time.

Keywords: Complex impedance plot, poly-(diamino naphthalene), conductivity, poly-dispersive nature of relaxation time.

Introduction

The complex conductivity i.e. ac conductivity, produces information related to the distribution of intra-molecular and inter-molecular hopping rates, which should be distributed in disordered conducting polymers. The hopping rate can be measured by taking account of ac conductivity (σ_{ac}) and temperature. The dc conductivity can measure only individual hopping rate in the distribution, therefore gives less information about the conduction mechanism of conducting polymers, but by measuring ac conductivity one can expected to lead more information about the conduction properties of the conducting polymer composites[1]. To investigate distributions of the parameter "τ" (relaxation time) for the Debye model in comparison to the Cole-Cole model provides the experimental data to enhance, analysis of the complex conductivity of the experimental material. Poly-dispersive materials are those which show a distribution of relaxation times[2-3]. For a Debye medium, the complex impedance is a function of frequency and the distribution of relaxation times are characterized by the parameter "α".

Mostly the conducting polymers are in the powder form and therefore may not be used as such for the practical purpose, therefore it is necessary to obtain these conducting polymers in the film form and therefore an attempt has been made to inculcate with the nonconducting polymers. Poly-(diamino naphthalene) is a less known conducting polymer and possesses chelating properties and reduction properties owing to the presence of electron donating groups (amine and secondary amine group) on the polymer chain[4-6]. It may be coupled with poly-(vinyl alcohol) (PVA) which is hydrophilic polymer to yield matrix film which possesses conductivity along with mechanical strength. Poly-(diamino naphthalene) (PDAN) was traditionally synthesized by an electrochemical polymerization. The PDAN chain contains imine (-N=C), amine (-NH-C) and amide (-NH2) units as linkages between naphthalene rings.

Lots of papers are published in different journals related to the studying the electrical properties like conductivity, impedance[7], capacitance[8], dielectric studies[9-10] and much more, for the conducting polymers[11]. Among all of the conducting polymers composites, poly-(aniline) and poly-(pyrrole) has obtained much more attention due to its conductivity nearer to the metals and even above from the semiconductor materials[12-13]. At the same time conducting polymer nanocomposites are also the matters of investigation by the many renowned scientists, in which AC conducting properties are, described[14-15]. Poly-dispersive behaviors of the conducting polymers are also described in different journals by different authors[16].

Instead of increasing the conductivity, doping by some inorganic dopants, the electrical properties using alternating current impedance spectroscopy of the PDAN doped PVA films have been reported in this paper.

Methodology

PVA (99% hydrolyzed, MW 85,000) was purchased from Hi Media Chemicals, Mumbai, India. The monomer DAN was purchased from Merck Chemicals, Mumbai, India. All other reagents were of high purity grade.

In a typical experiment, 5 g PVA was dissolved in 100 mL of hot distilled water and to this solution pre-calculated amount of glutaraldehyde was added as cross-linking agent. Now, the whole mixture was kept in a Petri dish (Corning glass, 2.5" diameter) at oven at 50°C for 48 hours. After 48 hours, the whole mass was in the form of semi transparent film. The dry film was equilibrated in distilled water for a week to leach out toxic chemicals. The swollen gel was than dried at room temperature, cut into rectangular size piece and stored in air tight plastic bags.

Required quantity of DAN was dissolved in acetonitrile and the PVA gel so prepared was allowed to soak in the DAN solution for 48 hours. The DAN containing swollen gel was dried and than dipped into oxidizing reagent. As the polymerization proceeds, the semi transparent gel turns into black and when seen in white light its color looks darken brown.

All AC impedance measurement was performed at different temperature under ambient conditions using Hioki 3532-50 impedance analyzer. This instrument contain LCR hi-tester impedance meter with a wide test frequency range from 42 Hz to 5 MHz manufactured by Hioki E.E. Corporation, Japan. Impedance measurement was carried out the frequency range from 42 Hz to 1 MHz from Physical Sciences Division, Polymer Unit, Institute of Advanced Study in Science and Technology, Guwahati, INDIA. The thickness of the PDAN doped PVA film is 0.65 mm for 0.591gm weight concentration and 0.61 mm for 0.791gm weight concentration of PDAN. The area of the cross section of the electrode is 1.69 cm^2.

Results and Discussion

The ideal AC impedance responses[17-19] of conducting polymer for different frequency-limited regions are shown in figure 2. At the highest frequency the impedance is measured from the tip of the reference electrode to the surface. In the conducting state of the polymer film in the high frequency region, a charge transfer semicircle is assumed. The vertex of the semicircle gives the characteristics relaxation frequency ($\omega_{max.}$). After the charge transfer semicircle there is a 45° Warburg-type line (diffusion creates impedance which is called Warburg impedance, depends on perturbation frequency i.e. at high frequency a small Warburg impedance and vice-versa) controlled by the diffusion of the counterions into the polymer film. At the low frequency region, polymer film behaves like a simple capacitor and the plot becomes almost vertical.

Figure 3 shows the Cole-Cole plot (complex impedance plot)[20] for the impedance of PDAN doped PVA film at different temperature. All the plots of the impedance shows almost perfect semicircle give the result that the single conduction mechanism is involved in the composite system. It is due to grain site of the material or due to the mobility of polaron or free ions induced by the increases in temperature. The evidence of following the relaxation of Deybe model indicated by obtaining almost perfect semicircle plots. For PDAN doped PVA film of weight concentration 0.791gm, at temperature 35^0C, another impedance region called Warburg impedance found and becomes dimensioned at higher temperature. Due to extra amount of impedance originate at room temperature, the conductivity may be less, and increases, as the temperature increases.

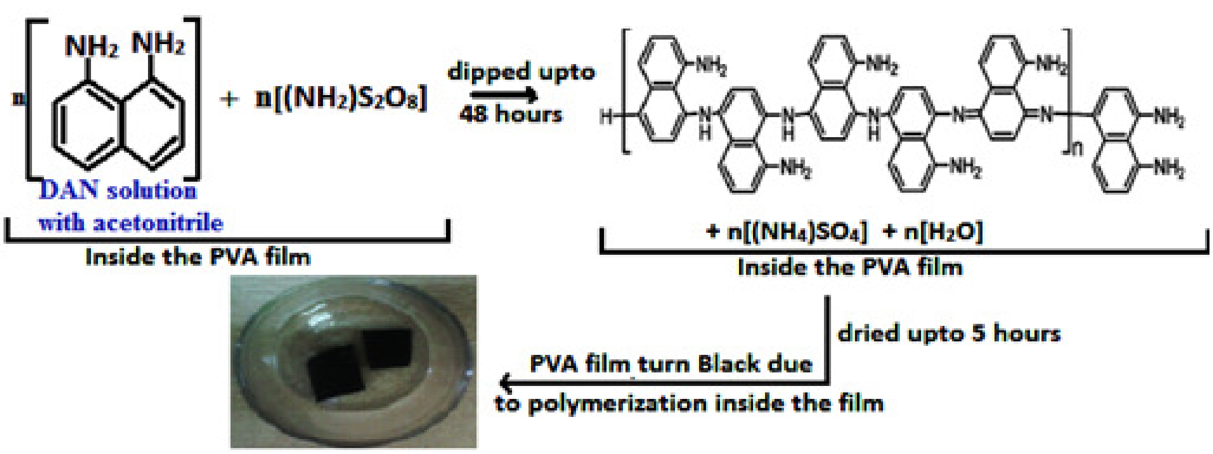


Figure-1
Proposed mechanistic pathway for synthesis of the PDAN-based PVA film

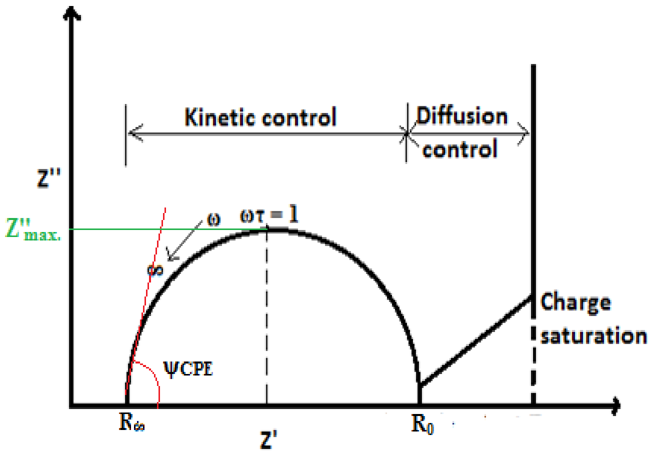
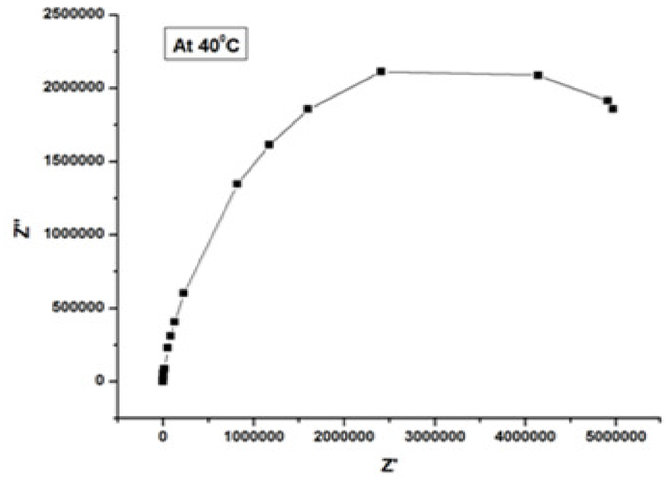
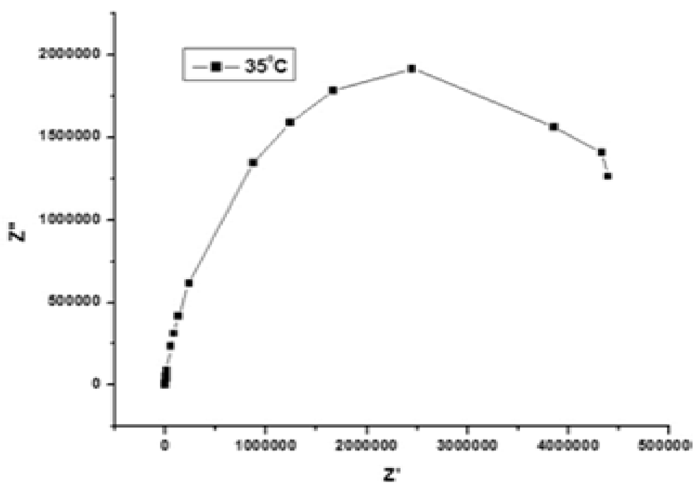


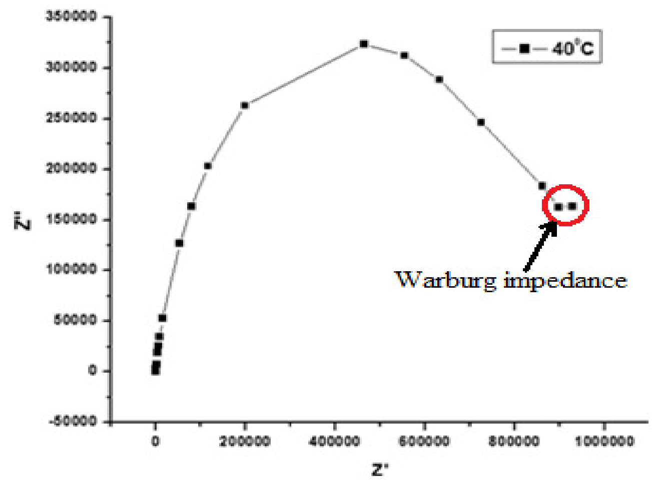
Figure-2
Argand diagram or complex locus diagram



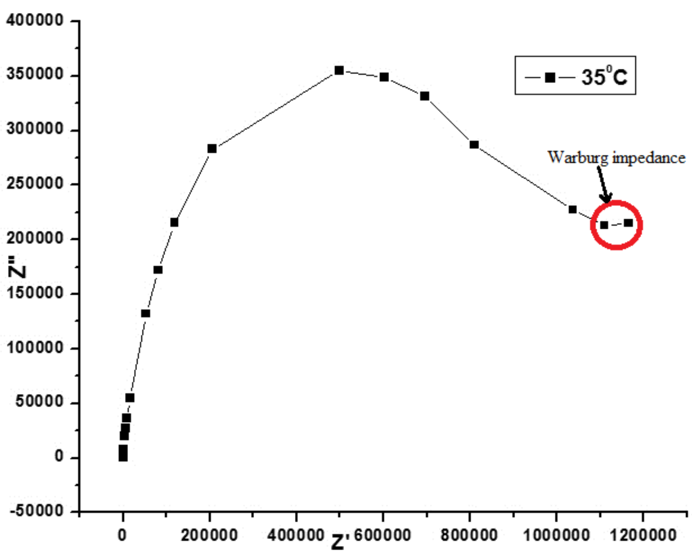
(c)



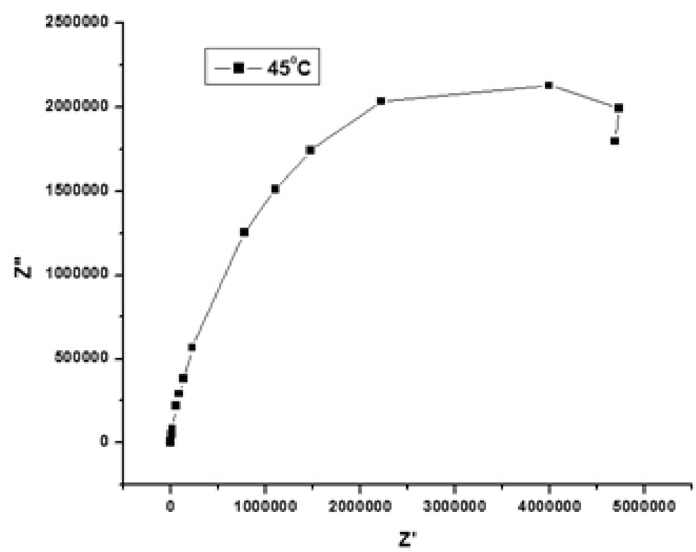
(a)



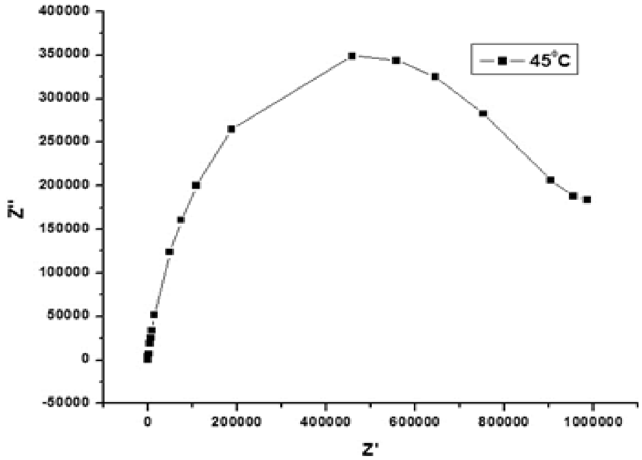
(d)



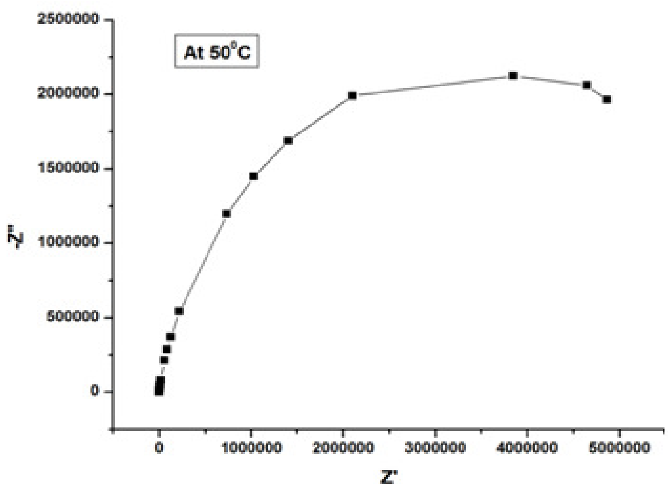
(b)



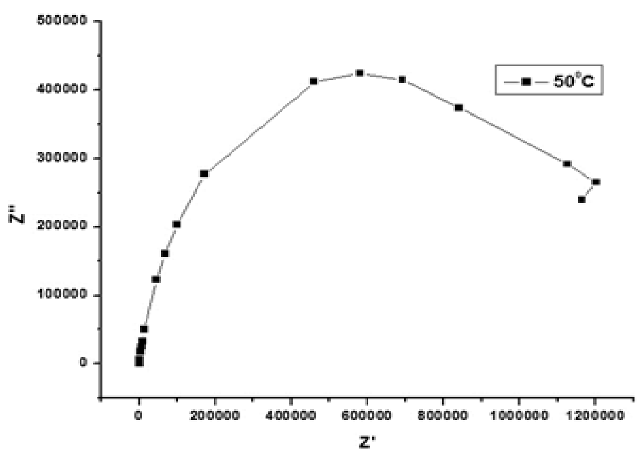
(e)



(f)



(g)



(h)

Figure-3

Cole-Cole plot at temperature (a) 35^0C, (c) 40^0C, (e) 45^0C and (g) 50^0C for 0.591gm PDAN doped PVA films, and at temperature (b) 35^0C, (d) 40^0C, (f) 45^0C, (h) 50^0C for 0.791gm PDAN doped PVA films

Figure 4 indicate the temperature dependence of total impedance of 0.791gm PDAN doped PVA film at frequency range from 10^2Hz to 10^6Hz.

It shows that, at higher frequency range i.e. from 10^4Hz to 10^6Hz, the total impedance remains unchanged even the temperature increases from 35^0C to 87^0C. But for lower frequencies, at higher temperature the total impedance increases frequently, clearly indicated that multiple relaxation process generated during measurement.

The AC conductivity of the PDAN doped PVA film can be measure with the help of Cole-Cole impedance plot. In this method, by plotting the graph between Z'' Vs Z' and seeing the intersection point the semi circle cuts with Z', we can find the AC conductivity using the formula

$$\sigma_{ac} = \frac{0.033}{intersection\ point\ Z'\ X\ 0.57921} \quad (1)$$

By bulk AC calculating, the AC conductivity from eq.(1), for 0.591gm PDAN doped PVA film, becomes 4.65 X 10^{-6} Scm^{-1} and for 0.791gm PDAN doped PVA film, the value becomes 6.28 X 10^{-6} Scm^{-1}.

Figure 5(a) and (b) shows the relation of relaxation time with temperature for weight concentration 0.591gm and 0.791gm PDAN doped PVA films. The relaxation time on both the cases follows Arrhenius low.

The relaxation time increases with the increases in temperature is indicated in the plots. It means that with the increase in cross-linking between the polymer-polymer with increase in temperature, the polymer chains are bounded to each other much tighter hence inducing a longer time to return to their original equilibrium configuration.

Mono-dispersive or poly-dispersive nature of relaxation time characteristics can be analyzed with the help of complex Argand plane plot between Z' and Z''. For a mono-dispersive Debye process the value of "α" which is a measure of the distribution of relaxation time is always equal to zero i.e. centre of the semicircular plot located on the Z'-axis, whereas for poly-dispersive Debye process the value of α lies between zero and one i.e. complex impedance plot are similar to circular arc with end points on the axis of Z' and centre below this axis[21-22].

The parameter "α" is determined from the angle subtended by the radius of the circle with the Z'-axis passing through the origin of the Z''-axis. The constant phase element angle φ_{CPE} (in radian) and the parameter α are related as[23]

$$\alpha = \frac{2\varphi_{CPE}}{\pi} \quad (2)$$

and the values found for 0.591gm and 0.791gm PDAN doped PVA film, are 0.88 and 0.86 respectively. The value α lies between 0 and 1, describes the poly-dispersive Debye process.

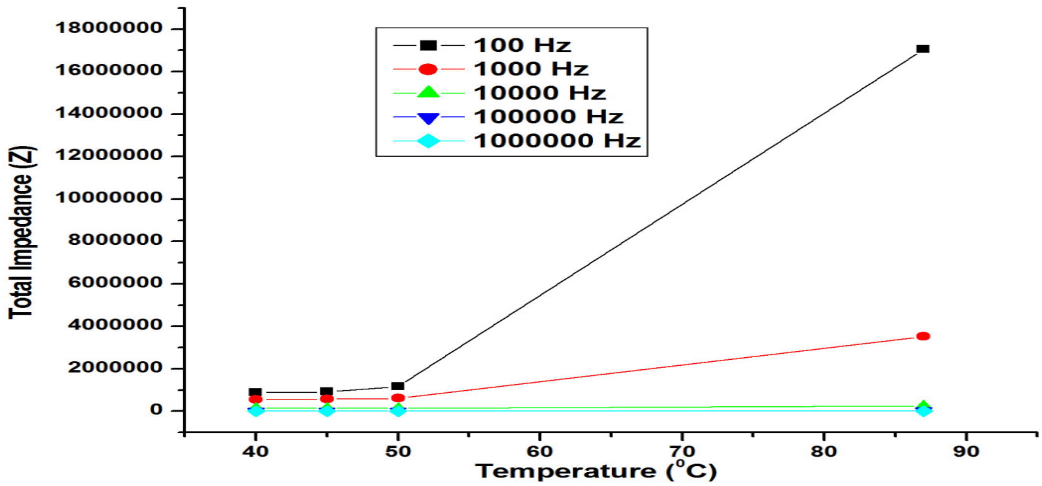
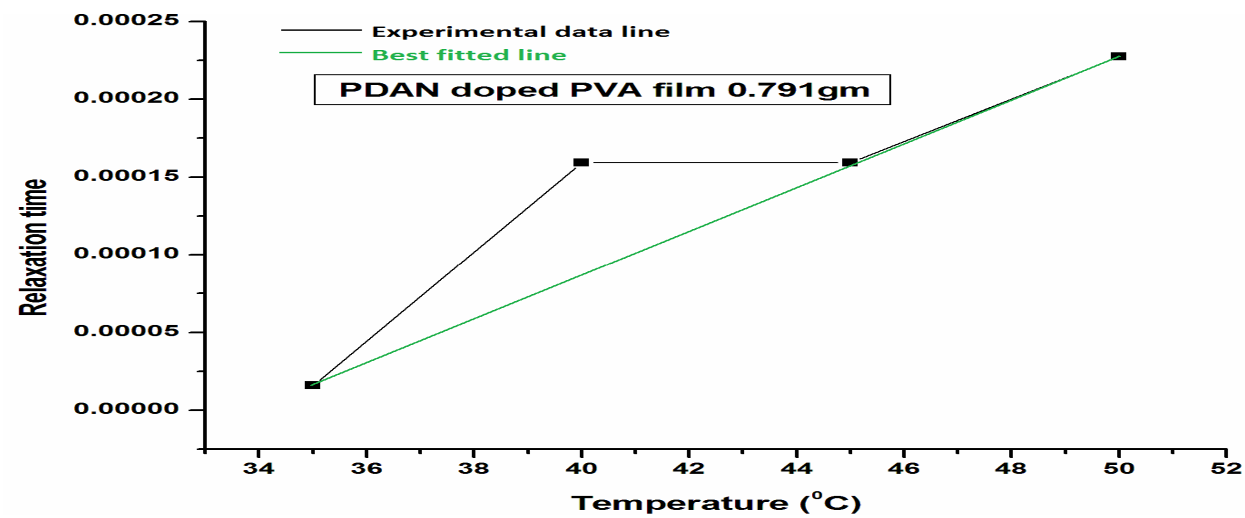
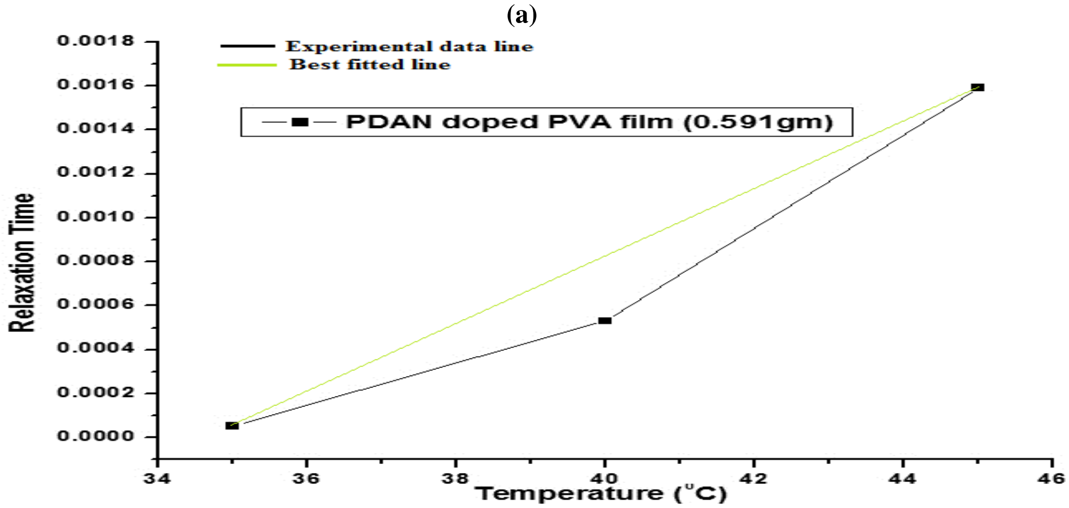


Figure-4
Graph shows the temperature dependence of total impedance



(a)



(b)
Figure-5
Arrhenius plots

Conclusion

In the impedance plot, it is confirm that the single mechanism mode follows in current mechanism. Although the small Warburg line was obtained at higher weight concentration of conducting polymer poly-(diamino-naphthalene) inside the film, but it was disappear when temperature increases. The AC conductivity found from the measurement is 3 X 10^{-6} Scm^{-1}, which is better for the film as no inorganic dopent is use. It is also observed that the relaxation time follows Arrhenius low. The PDAN doped PVA film follows poly-dispersive relaxation Debye process. The result obtains from the Argand plot and the value of α lies, in between zero and one. It's concluded that for best use of PDAN doped PVA film in AC electric applications, the selective low temperature and high frequency will be required.

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