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Effect of solvent on Meyer-Neldel rule for conducting polyaniline thin film

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The effects of solvent on electrical properties of polyaniline emeraldine base (PANIEB) are investigated as a function of temperatures. It is observed that PANIEB follows Arrhenius type of conductivity, while Arrhenius pre-exponential factor and activation-energy are found interrelated according to the Meyer-Neldel rule (MNR). The effects of solvent on the activation energy and isokinetic temperature (derived from MNR) are further examined according to the generalized adiabatic polaron hopping mechanism. It is observed that the solvent provides higher Isokinetic temperature and lower activation energy due to the enhancement of solvent-induced crystallization, electronic energy transfer rate between molecular chains, and softening of molecular vibration in PANIEB thin film.

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1. Introduction

To fulfill the serious demand for low-cost, light-weight, flexible, and large-area electronic applications, the conducting-polymers show a great potential in the field of electronic and optoelectronic engineering [1-8]. Most conducting-polymers, e,g. PANIEB and other polymer semiconductors, offer low conductivity, but their conductivity can be significantly enhanced by doping as well as by using proper solvent [9-11]. Different theories are available regarding the improvement of conductivity induced by solvent such as screening effect of solvent [12], improvement of hoping transport [13], improvement in π-electron delocalization [14], enhancement in the connectivity among conducting grains inside the polymer [15] and transition from 3D variable range hopping to quasi 1D variable range hopping [16]. However, the explicit mechanisms concerning the improvement of polymer conductivity as a function of solvent is still not clear [17]. The Meyer-Neldel compensation rule (MNR) efficiently explains many thermal-activated charge transport features for many organic/conducting polymers [18-21].

To determine the origin of MNR for conducting-polymer, different attempts were made, where Wide horn et al., proposed that MNR response is arises due to the intrinsic process as well as process involving density of impurity contributions [22]. While Emin suggested that MNR response is observed due to the carrier-induced softening of the atoms' vibrations (adiabatic polaron contribution) and polaron hopping energy of the materials depending on intermolecular distances [23]. Recently, Fischuk and others justified that MNR originates due to the transport in a random system with variable range hopping (Gaussian Disorder Mobility model, GDM) and disregards the full contribution of polaron formation for MNR process [24-27]. Here, despite the complexity, an attempted is made to obtain the fundamental understanding of MNR in PANIEB films as a function of different solvents such as IPA and acetone.

2. Experimental

All chemicals such as PANIEB, IPA, acetone, and poly-acrylic-acid (PAA) were purchased from Aldrich and were found analytical graded; thus, they were used without any further purification. The conductivity of PANIEB (Mwt ~ 50,000 gm/mole) was improved by doping with PAA, (MW 2000 gm/mole, 50% wt in H_2O) and then further improved by secondary doping with solvent such as IPA and acetone. The resulting solutions were prepared without and with the help of IPA or acetone from the 15 wt% of PANIEB doped with 10% PAA and then stirred nearly whole day at room temperature. Before polymer thin film deposition, a thin layer of aluminum as electrode was deposited by vacuum evaporation over glass substrate. Then thin films of PANIEB, PANIEB-IPA and PANIEB-acetone were deposited by spin-coating method (1100 rpm for 30 second) onto aluminum thin film over glass substrates as shown in Fig. 1. The thickness of PANIEB, PANIEB_IPA and PANIEB-acetone films were estimated with the help of scanning electron microscope and were found in the range of 205 ± 15, 180 ± 15 nm and 195 ± 15 nm respectively. After polymer solution deposition a selected area is exposed and silver electrode was deposited on such area with the help of shadow masking over the top surface of PANIEB samples by vacuum evaporation method.

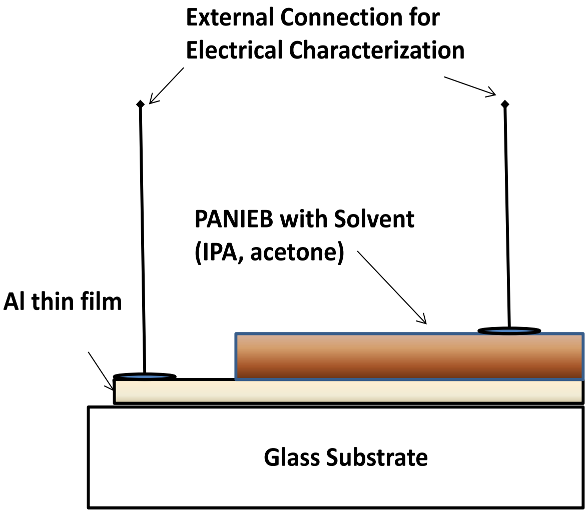

Fig 1. Shows the cros-sectional view of the diode used for electrical characterization.

As the cross-sectional area of top electrode is used to define channel area and here both electrodes were deposited by shadow masking. Therefore the top silver electrode was deposited with cross-sectional area of approximately 25 mm^2. The finished devices, as diodes, were then annealed at 100 ^{o}C for 2 hours in the inert atmosphere of nitrogen and then electrical characterized by HP-4145B parameter-analyzer. Current-voltage characteristics of PANIEB samples were measured by using a dc measurement station in a black-box with temperature adjusting facility at maximum temperature error of ± 0.5 ^{o}C. For conductivity measurement for PANIEB samples, positive voltage was applied at aluminum with respect to silver electrode. It was tried our best to maintain the constant laboratory environmental conditions as much as possible during solution development, fabrication and as well as investigation processes for all freshly prepared devices; therefore, we will discuss only the effect of solvents as a function of temperature to characterize electrical properties of PANIEB based devices.

3. Meyer-Neldel rule (MNR)

The temperature-dependent electrical conductivity (σ) for organic/polymer materials can be defined by Arrhenius equation as [26-28]

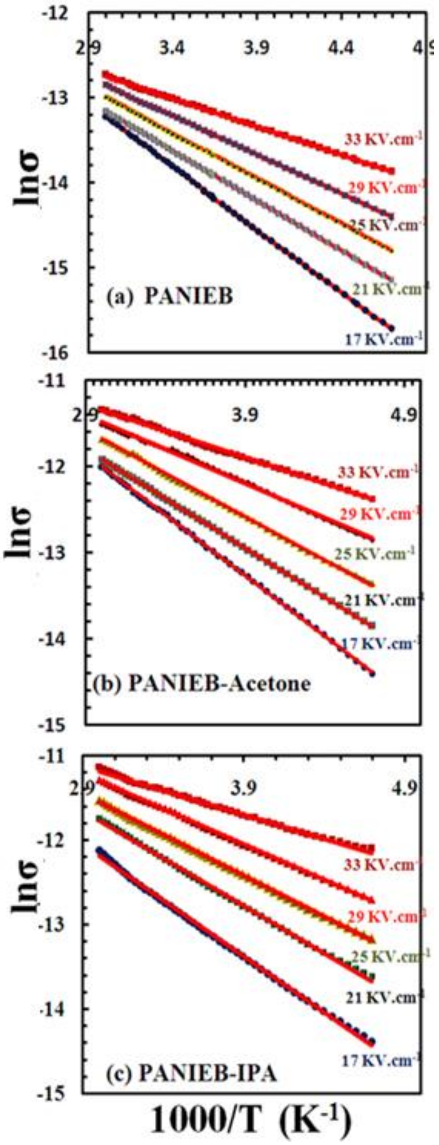

Fig. 2. Shows the graph for ln(σ) vs 1000T^{-1} at different electric fields for (a) PANIEB (b) PANIEB-Acetone and (c) PANIEB-IPA, where conductivity (σ) was measured. Intercept and slope of each straight line give rise the conductivity pre-exponential factor (σ$_o$) and activation energy (E$_a$) for each device as a function of electric field.

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right), \qquad (1)$$

where, σ_0 is the pre-exponential factor for conductivity, E_a is the activation energy and k is the Boltzmann constant. Many conducting polymers follow MNR in term of either conductivity or mobility as a function of temperature. [23,29]. Therefore, MNR in terms of σ_0 and E_a can be written as [30]

$$\sigma_0 = \sigma_{00} \exp\left(-\frac{E_a}{E_{MN}}\right), \qquad (2)$$

By incorporating of MNR from above equation 2 into the equation 1, then

$$\sigma = \sigma_{00}\ \exp\left(\frac{E_a}{kT_{MN}}\right)\exp\left(-\frac{E_a}{kT}\right). \qquad (3)$$

where, σ_{00} is the Meyer-Neldel constant and E_{MN} is the Meyer-Neldel energy and can be correlated with isokinetic temperature (Meyer-Neldel temperature, T_{MN}) as $E_{MN} = kT_{MN}$. So T_{MN} is such temperature where E_a does not depend on the biasing conditions [31]. The origin of MNR for the conducting polymer can be described by generalized adiabatic polaron hopping transport mechanism [23].

The polaron interaction can be classified into two types, as long-range polaron and short-range polaron, depending on the electron-molecular chain interaction in polymer.

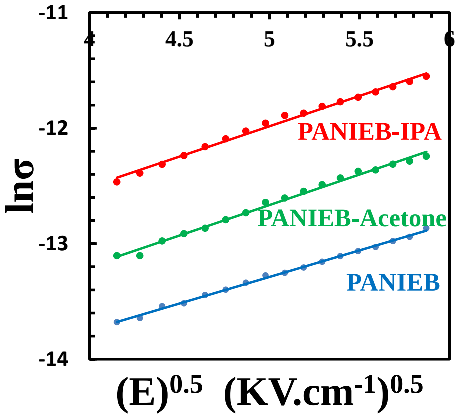

Fig. 3. Illustrates the linear relationship between conductivity pre-exponential factor $ln\sigma_0$ and activation energy (E_a) for PANIEB, PANIEB-Acetone and PANIEB-IPA. Figure clearly justifies that PANIEB with or without solvent follow Meyer-Neldel rule (MNR) for conductivity.

If such interaction consists of many localized sites and offers a larger delocalization path for the movement of carriers inside polymer then such interaction is described as large-range polaron interaction. Similarly, if this interaction shrinks to a single localized site then such interaction is referred as small-range polaron interaction [32]. Emin justified that the Meyer-Neldel compensation effect originates from the carrier-induced softening of atomic vibration for molecules in polymers chain. The jump rate ($R_{adiabatic}$) for such adiabatic-polaron hopping can be written as [33]

$$R_{adiabatic} = \upsilon\ \exp\left(\frac{E_a}{kT_0}\right)\exp\left(-\frac{E_a}{kT}\right), \qquad (4)$$

where, υ is the characteristics phonon frequency, T_0 is the characteristic temperature (isokinetic temperature T_{MN}) and defined as $T_o = t/k$, where t is the electronic transfer energy. Both conductivity and mobility of carriers have direct relation with $R_{adiabatic}$. Where E_a is the adiabatic hopping activation energy and can be defined for three dimensional medium as [23]

$$E_a \approx \frac{V_S}{2R^3} + \frac{V_L}{2}\left(\frac{1}{R} - \frac{1}{\sqrt{R^2 + S^2}}\right). \qquad (5)$$

Here V_s and V_L are the parameter depends on materials constants to control the intensity of the both short-range and long-range electron-phonon interaction respectively, R is the radius of localized state and S is the distance between the centroid of these localized states.

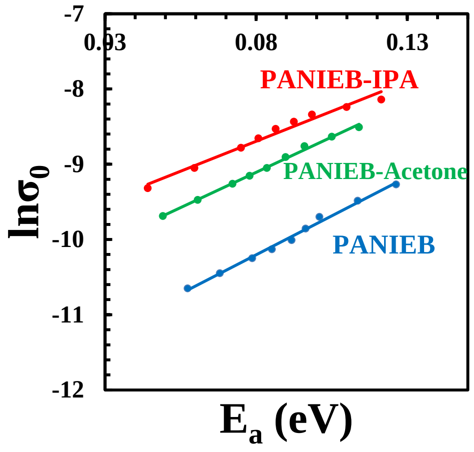

Fig. 4. Shows the relation between ln σ vs $E^{0.5}$ for PANIEB, PANIEB-Acetone and PANIEB-IPA. It is clearly observed that conductivity of each device increases with applied electric field in a Poole-Frenkel manner.

4. Result and discussions

4.1 Thermal-activated conductivity

Fig. 2 shows that the graph between $ln(\sigma)$ vs $1000T^{-1}$ at different applied electric fields for a) PANIEB b) PANIEB-acetone and c) PANIE-IPA. From the figure, it is clear that all devices follow nearly linear response for thermal-activated conductivity at various electric fields, demonstrates that the thermally activated high field conduction through the PANIEB with or without solvents is fully consistent with Arrhenius equation and PANIEB-IPA offers relatively higher conductivity for given temperature range comparing with PANIEB and PANIEB-acetone devices.

Table 1. Calculated activation energy (E_a) and Isokinetic temperature (T_{MN}) for PANIEB, PANIEB-Acetone and PANIEB-IPA at 33 KV/cm of applied electric field.

E = 33 KV/cm		
Polymer	**T_{MN} (K)**	**E_a (eV)**
PANIEB	568	0.057
PANIEB-Acetone	625	0.049
PANIEB-IPA	693	0.044

From Fig. 2, σ_0 and E_a were calculated at different applied electric field for PANIEB, PANIEB-acetone and PANIEB-IPA devices. In order to justify the MNR for PANIEB with or without solvent, a graph was plotted between $ln(\sigma_o)$ and E_a as shown in Fig. 3 and similar quasi linear response are observed for each device, which proves that PANIEB with or without solvent follows MNR for given temperature range. The slope of each straight line gives the value of E_{MN} (or T_{MN}) for PANIEB, PANIEB-IPA and PANIEB-acetone. The T_{MN} value is increases in the presence of solvents IPA and acetone and relatively maximum values or T_{MN} is achieved for PANIEB-IPA matrix as shown in Table 1. Similarly, the activation energy is decreases in the presence of solvent for PANIEB matrix.

4.2 Effect of electric field on conductivity

To investigate the effect of electric field on PANIEB with or without solvent, a plot between $ln(\sigma)$ vs $E^{0.5}$ were drawn for PANIEB, PANIEB-IPA and PANIEB-acetone as shown in Fig. 3 and obtained a strong linear relation between electric field and conductivity of PANIEB, PANEIB-acetone and PANIEB-IPA. Figure justifies that devices ensure Poole-Frenkel behavior within the given range of electric field at room temperature at increasing trend of conductivity with solvents as discuss above. Here, electric field may increases the influence of intermolecular electrostatic interactions, which in turn decreases the inter-molecular chain separation for efficient hopping for polymer. Such inter-molecular chain separation is further decreases with solvent (especially IPA compared to acetone) in the presence of applied electric field and hence further improves the overall carriers hopping inside the PANIEB matrix [33-35].

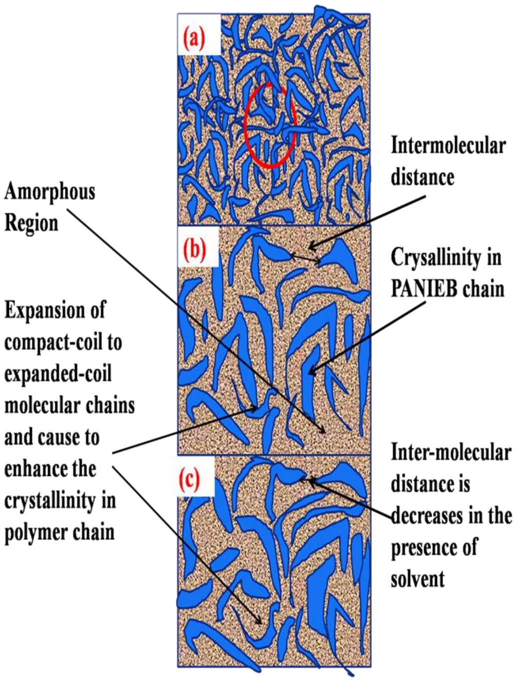

Fig.5. Presents the overall picture of solvent-induced charge transport mechanism of PANIEB matrix. The Figure 5a) shows that randomly oriented molecular chains are dispersed inside the conducting polymer matrix. Figure 5b) shows the zoomed picture of figure 4a, where molecular chain provides somehow crystallinity for the intra-molecular carrier transport mechanism. But this transport mechanism will be disturbed by the twisting, folding, vibration and irregular rotation of molecular chains. Figure 5c) demonstrates that by the incorporation of solvent cause to straighten the compact coil to the expanded form of the coil and hence decreases the intermolecular distances to improve the conductivity by improving hopping transport inside polymer. Therefore, the solvent overall improves the conductivity of the PANIEB matrix.

4.3 Effect of solvent on E_a and T_{MN}

Table-1 shows that the solvent enhances the activation energy (calculated at electric field 33 KV cm^{-1}) for PANIEB, where activation energy of PANIEB-IPA is found higher than PANIEB-acetone matrix. From equation 5, it is obvious that activation energy is inversely proportional to the average radius of localized state and average distances between localized states. For one-dimension conducting polymer, we can simply associate S and R by the average intermolecular chain distance and the localization length for PANIEB matrix.

The resulting conformational state of the molecular chains with solvent inside the conducting polymer in the solution is remain same even after thin film deposition by spin coating method, because the interaction of solvent is approximately remain unchanged at the early stage of evaporation. Polymer chains follow very slow conformation changes due to the small period during thin film deposition process [10]. When PANIEB is solvated with IPA or acetone, the solvent allows the PANIEB chains to extend from compact-coil to extended-coil conformational adjustment, which establish topologically less distorted structure of PANIEB matrix [2]. As soon as the polymer chains turn into expanded state, the polaron band becomes more delocalized and causes to raise the polymer conductivity. At the same time, solvent also significantly affect the molecular vibration [36]; because, solvent also induce the softening of molecular vibration and causes further to delocalize the carriers movement. It is both theoretically proved and experimentally observed that less distorted polymer molecular chains reduce π-conjugation defects and improved the delocalization of carriers, which in turn offers higher electronic energy transfer from one molecular chain to the other molecular chain [37]. So, it can be infer from the above discussion that in the presence of solvent, PANIEB offers higher energy transfer rate comparing to PANIEB without solvent. Meyer-Neldel characteristic temperature (isokinetic temperature) is directly proportional to the electron transfer energy; therefore, T_o of PANIEB-IPA, PANIEB-acetone is higher than PANIEB. Now question arises, how PANIEB-IPA offer higher electronic transfer energy as compared to PANIEB-acetone. The relatively higher expanded conformation of PANIEB molecular chains in the presence of IPA solvent is due to the higher boiling point of IPA as compared to the acetone solvent. Low evaporation rate (due to higher boiling point of solvent IPA during thin film deposition by spin-coating) shrinks the amorphous domain and improve the crystallinity of the PANIEB matrix [38]. Enhancement of crystallinity in PANIEB matrix by IPA further softens the molecular vibration inside the polymer chain and hence improves the overall the flow of charge carriers. Therefore, a PANIEB-IPA interaction provides higher electronic energy transfer from one chain to the other molecular chain as compared to PANIEB-acetone and gives rise relatively high value of T_{MN}. Similarly, the activation energy is also decreases with the solvent. Therefore, the activation energy of PANIEB is decreases in the presence of solvent (Table-1) and the activation energy of PANIEB-IPA is found lowered as compared to PANIEB-acetone due to the high degree of crystalline offered by IPA for PANIEB matrix.

4.4 Solvent effect on charge transport

The Fig. 5 furnishes the overall picture of solvent-induced charge transport mechanism of PANIEB matrix. Fig. 5a illustrates the randomly distributed molecular chains fill the amorphous regions inside the conducting polymer and the molecular π-conjugation structure provides the delocalization to the flow of charge carriers inside the conducting polymer. Fig. 5b shows the zoomed portion of Fig. 5a, where the flow of charge carriers inside the conducting polymer depends on both intra-molecular delocalization and inter-molecular hopping mechanism. Conducting polymers are different from amorphous materials as the molecular chains in the conducting polymer provide somehow crystalline domain for intra-molecular flow of charge carriers as compared to the amorphous materials. But this movement is disturbed by twisting, folding, vibration and irregular rotation of the molecular chains inside conducting polymer. Each molecular chain is separated with other molecular chain by some amorphous region and inter-molecular charge transport takes place by variable range hopping mechanism. Charges are injected from electrode into the polymer chain under the influence of applied electric field and facing the energy barrier both by amorphous and deformed molecular chain region (carrier-lattice interaction as polaron). At higher thermal energy the lattice vibration or phonons assists the carriers to hop easily through the amorphous region and enhance the conductivity and in this way, the conductivity depends on temperature in an Arrhenius manner. At the same time the interaction of carriers with the movement of atoms in molecule of a chain with polar surrounding (adiabatic polaron hopping) induced the softening of molecular vibration, which is responsible for the improvement of conductivity by Meyer-Neldel compensation phenomena observed in PANIEB matrix. As solvent significantly affect the molecular vibration [31]; therefore, solvent induces further softening of molecular vibration and enhance the conductivity. Simultaneously, the interaction of solvent results in a compact-coil to expanded-coil molecular chains and causes to enhance the crystallinity inside the molecular chains and reduce the effective 1D inter-molecular chain distance as shown in Fig 5c. In the presence of solvent, the electronic energy transfer and hopping rates are improved due to the reduction of inter-molecular chain distances, softening of molecular vibration and crystallinity. As isokinetic temperature is directly proportional to the electronic energy transfer and activation energy is inversely proportional to average intermolecular distances, therefore T_{MN} is increases and E_a is decreases in the presence of solvent. Similarly, IPA solvent offers higher crystallinity and softening of molecular vibration for PANIEB as compared to acetone, therefore, high value of T_{MN} and lower value of E_a is observed for PANIEB-IPA device.

5. Conclusion

The temperature dependent conductivity of PANIEB matrix was determined with or without solvent. It was observed that all samples followed Arrhenius equation for temperature dependent conductivity and such response for PANIEB-IPA device was superior comparing with PANIEB-acetone device. It was also observed that the pre-exponential factor of conductivity and activation energy follows Meyer-Neldel rule for all devices. Both activation energy and isokinetic temperature, derived from Arrhenius and MNR was interpreted by generalized adiabatic polaron hopping mechanism as reported by Emin. The higher value of T_{MN} and lower value of activation energy in the presence of solvent was achieved due to enhancement of solvent-induced crystallization, softening of molecular vibration and improvement of electronic energy transfer rate between molecular chains. It was also observed that IPA offers superior solvent response as compared to acetone for PANIEB matrix and these findings will facilitate to improve our understanding for both the origin of MNR for conducting polymer and the temperature-activated charge transport mechanism for conducting polymer in the presence of solvent.

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