

MESCon 2014 [4th -5th September 2014]
National Conference on Material for Energy Storage and Conversion- 2014

Study on dissociation of Amino Benzoic Acid isomers in Dimethyl Formamide and Poly Ethylene Glycol₂₀₀

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Abstract : Dissociation of amino benzoic acid isomers was examined in N, N- dimethyl formamide (DMF) and polyethylene glycol (PEG₂₀₀) that are going to act as a plasticiser in the polymer electrolyte later. Liquid electrolytes were prepared and vibrational behaviour was investigated by FTIR spectroscopy. Conductivity was also measured by conductometry technique, which has shown the increasing trend of conductivity with increase of salt concentration up to 25wt% and 20 wt% and then decreases in m- and p- isomers respectively. In o- isomer the conductivity decreases with the increase of salt concentration in DMF and it is due to the formation of zwitterion. The formation of zwitterion was confirmed by the strong peak that arises at 1387 cm⁻¹ and 1541 cm⁻¹. This indicates the formation of COO⁻ ion and also the symmetric and asymmetric stretching of N-H mode of o-isomer were blend to form a broad peak in solution. And in PEG₂₀₀, the proton in the acid group of o-isomer is not dissociated in to COO⁻ ion, which has been confirmed by strengthening of stretching mode of C-OH bond and thus conduction decreases. The m- isomer has highly dissociated in DMF and as well as in PEG compared to p- isomer. The acid group in the m-isomer retains its carboxylate anion behaviour (1388cm⁻¹) and it donates its proton for conduction. The Conductivity measurement also proved that the m- isomer has shown highest conductivity and its value is 1.466X10⁻³S cm⁻¹ and 1.066X10⁻²S cm⁻¹ in DMF and PEG₂₀₀ respectively.

Keywords: Amino benzoic acid (ABA), N, N- dimethyl formamide (DMF), Polyethylene glycol (PEG₂₀₀), Zwitterion.

1. Introduction:

Ionically conducting polymers have been of considerable interest because of their potential application as solid polymer electrolytes. The main advantages of polymeric electrolytes are their mechanical properties ease of fabrication of thin films of desirable sizes and their ability to form proper electrode / electrolyte contact. One of the feasible methods to enhance the ionic conductivity in these polymer electrolytes is the addition of

Organic / Inorganic salts. In preparing the network polymer electrolyte, two different methods were taken in the incorporation of salt into the network polymer. In the first method, the porous polymer was dipped into the salt solution with or without plasticiser and in the other method the network formation was preceded in the presence of the salt in the reaction medium with or without plasticiser[1].

The amino benzoic acids (aba) belong to the aromatic amino acids, which are biologically active substances. Many amino acids in aqueous solution[2] as well as in the crystalline state exist as zwitter ions, where the proton migrates from $-\text{COOH}$ group to the basic $-\text{NH}_2$ group to form the ionic groups NH_3^+ and COO^- with in the same molecule[3]. Amino benzoic acid isomers are capable to form a conducting polymer[4,5]. Coating of the electrodes with polymer of amino benzoic acid isomers films has been used frequently to improve their properties for a wide variety of applications[5,6] because of its high conductivity and thermal stability. Solid form of poly *o*-amino benzoic acid (anthranilic acid) would be useful as a self-doped polymer for several applications[7]. Amino benzoic acid isomers enhance the conductivity of certain polymer in some extent by donating proton, because it contains both acid and amine group within the same molecule. In order to further increase the conductivity of the amino benzoic acid isomers based polymer electrolytes, plasticiser is needed to be added in to the system. The addition of plasticiser to the polymer electrolytes decreases the glass transition temperature of the polymer and softens the polymer back bone, which results in higher segmental motion, and thus increases the ionic conductivity[8].

DMF makes an effective solvent for salts, gases, and compounds with high molecular weight. It has several characteristics which aid in its versatility as a solvent. DMF act as a polar solvent for few polymer electrolytes to enhance the ionic conductivity[9,10]. Also DMF has an ability to form a complex because of its small size, high dielectric constant, the proton donor property. Because of these properties, the DMF act as a good plasticiser in lithium salt based polymer electrolytes[8,11].

Polyethylene glycol (PEG) is one of the additives used to promote pore formation in the polymeric membranes. PEG is water-soluble. It is also soluble in many organic solvents including aromatic hydrocarbons. Thus PEG has been reported as a pore former to enhance the permeation in hydrophilic membranes¹². In PEG, the low molecular weight and low viscosity facilitates ion diffusion and their hydroxyl group reduces the ion association in the polymer salt complex[13]. It extends the lifetime of flexible articles, improve weathering resistance, and usually blend with lower viscosity plasticizers[14]. PEG reduces the glass transition temperature of PVP based polymer electrolyte and hence induces the ionic conductivity[15].

In the present study, shows the effect of plasticisers DMF and PEG₂₀₀ in the amino benzoic acid isomer based polymer electrolytes in their conductivity measurements. Preliminary study was made by preparing the liquid electrolytes of amino benzoic acid isomers in dimethyl formamide and poly ethylene glycol, their conductivity and salt interaction were analysed by conductivity measurement and vibrational analysis.

2. Experimental Details:

2- amino benzoic acid (Aldrich) - 98% pure, 3- amino benzoic acid (Himedia) - 97% pure, 4-amino benzoic acid (Avra) – 98% pure, DMF (Merck) – 99.8% pure, Poly Ethylene Glycol₂₀₀ (Merck, Mean MW=190-210) were used as the materials. Liquid electrolytes were prepared by dissolving amino benzoic acid isomers in DMF and PEG at different concentration (Expressed as Weight Percentage). The conductivity of liquid electrolyte was measured by using Deep Vision- Digital conductivity meter – 611. The FT-IR spectra of the samples were recorded by using JASCO FT/IR-4100 Spectrometer within the region of 4000 cm^{-1} - 400 cm^{-1} with the resolution of 4 cm^{-1} .

3. Result and Discussion:

a. Conductivity Measurements:

Liquid electrolytes were prepared by dissolving 5-25 wt% of amino benzoic acid isomers in DMF and 2-12 wt% of amino benzoic acid isomers in PEG₂₀₀. The conductivity was measured by using conductometry. The conductivity of electrolyte generally depends upon the concentration of salt containing the mobile species as well as on the extent up to which the salt is dissociated. If the salt is completely dissociated, then nearly all ions shall be available for conduction, but if the salt is not completely dissociated, then it will result in a decrease in carrier concentration which shall lower the conductivity. Similarly, the presence of more number of charge carriers may also lead to ion association resulting in the formation of ion aggregates which do not take

part in the conduction process and as a result, reduction in the number of carrier concentration and, hence the decrease of conductivity.

Figures 1&2 show the variation of the conductivity of amino benzoic acid isomers in DMF and PEG₂₀₀ respectively. The conductivity measurement has shown that the m-isomer in DMF as well as in PEG₂₀₀ and p-isomer in DMF, the conductivity increases with an increase in concentration and then decreases at higher concentration. The initial increase in conductivity is due to the availability of free mobile ions whereas decrease in conductivity at higher concentration is due to the formation of ion aggregates, which do not take part in conduction. In the case of p-isomer in PEG₂₀₀, the conductivity increase with an increase in concentration, it reaches the maximum and then reaches the saturation point. But in the case of o-isomer in both DMF and PEG₂₀₀, the conductivity decreases with increase in concentration and this may be due to the formation of zwitter ion. In both DMF and PEG₂₀₀ solutions, the conductivity value of the amino benzoic acid isomers are in the order of m-isomer > p-isomer > o-isomer. 25 wt% m-isomer in DMF and 11wt % of m- isomer in PEG₂₀₀ shows the highest conductivity i.e. $1.466 \times 10^{-3} \text{ S cm}^{-1}$ and $1.066 \times 10^{-2} \text{ S cm}^{-1}$ respectively

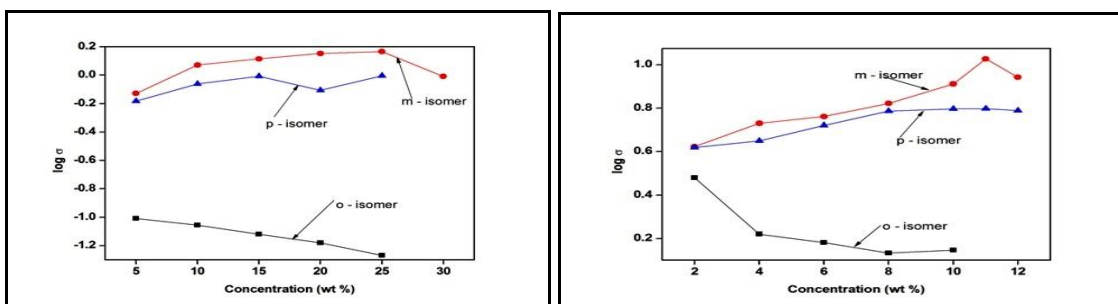


Fig.1 & 2. Variation of $\log \sigma$ with concentration of amino benzoic acid isomers in DMF and in PEG₂₀₀

b. FT-IR spectral studies:

FT- IR Spectroscopy is used to analyse the interactions among atoms or ions in electrolyte systems. The assignment has been done on the basis of literature data^{3, 16-20}.

i. 2- Amino benzoic acid (o-isomer) in DMF:

The δ (O=C-N) and ν (C=O) of DMF at 658 cm^{-1} and 1673 cm^{-1} respectively, which are shifted to higher and lower wave number respectively in the solution. This is due to the interaction of the salt and DMF. In pure o-isomer shows the peaks at $759, 839, 1372 \text{ cm}^{-1}$ are responsible for $\gamma, \beta, \nu_{\text{sym}}$ vibration of COO^- ion. The characteristic peaks of γ and ν (OH) of o-isomer (2583 cm^{-1}) are absent in the liquid electrolytes and a new peak arises at 1541 cm^{-1} indicates that the formation of COO^- ion. The Characteristic strong band appears at 1230 cm^{-1} and 1458 cm^{-1} are assigned to ν (C-OH) and β (OH), which are slightly shifted to a higher (1254 cm^{-1}) and lower (1455 cm^{-1}) wave number respectively. The Characteristic two peaks of primary amine that are $\nu_{\text{sym}} \& \nu_{\text{asym}}$ (N-H) at 3238 cm^{-1} and 3323 cm^{-1} are shifted to higher wave number and broadened, which indicates that there is a salt and solvent interaction. The formation of COO^- ion and blending of N-H peaks imply that the o-isomer forms a zwitterion in DMF solution.

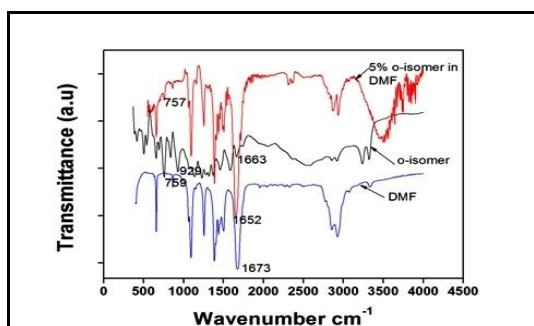


Fig.3a. IR spectra of o-isomer in DMF

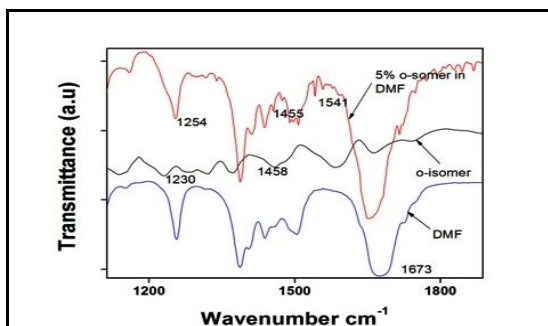


Fig.3b. In the region of $1200 \text{ cm}^{-1} - 1800 \text{ cm}^{-1}$

ii. 3- amino benzoic acid (m-isomer) in DMF:

In general, the pure 3-amino benzoic acid (m-isomer) salt exists as a zwitterion³. The peaks at 761 cm^{-1} (strong) ($\gamma_{\text{sym}}\text{ COO}^-$), 1390 cm^{-1} ($\nu_{\text{sym}}\text{ COO}^-$), 1500 cm^{-1} ($\nu_{\text{asym}}\text{ COO}^-$) are attributed to the formation of zwitterion in the pure m-isomer. The new broad peak arises around 3400 cm^{-1} in the low concentration (not shown) of the salt and then it will become two peaks (range of 3200 cm^{-1} - 3400 cm^{-1}) in the 25% and 30% concentration salt solution, which are responsible for the $\nu_{\text{sym}}\&\nu_{\text{asym}}$ (N-H). The above results reveal that the zwitterion character was absent in the salt solution. Also the ν (OH) (791 cm^{-1}) is absent in the salt solution. The carboxylic acid donates its proton to some extent in the salt solution, which has been confirmed by the higher concentration the salt solution which shows the strong peaks at 761 cm^{-1} and 1558 cm^{-1} , that are attributed to the $\gamma_{\text{sym}}\&\nu_{\text{asym}}\text{ COO}^-$. This proton contributes the ionic conduction thus the m-isomer possesses highest conductivity in DMF solution.

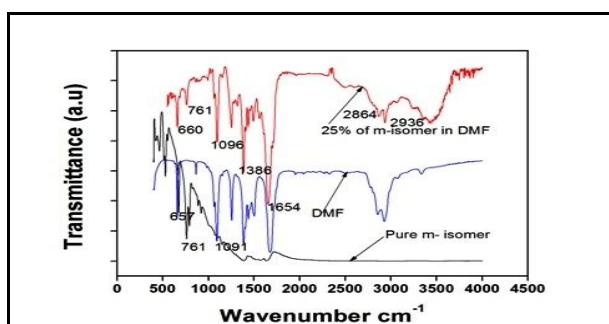


Fig.4a. IR spectra of m-isomer in DMF

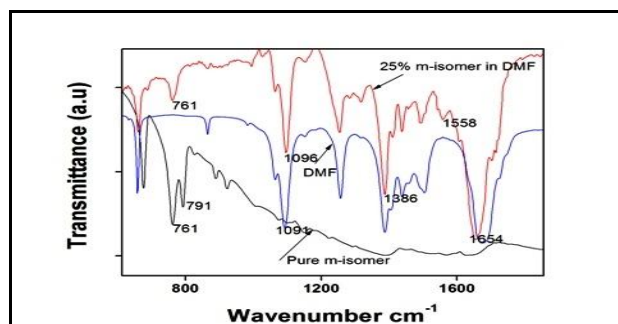


Fig.4b. In the region of 800 cm^{-1} - 1600 cm^{-1}

iii. 4- amino benzoic acid (p-isomer) in DMF:

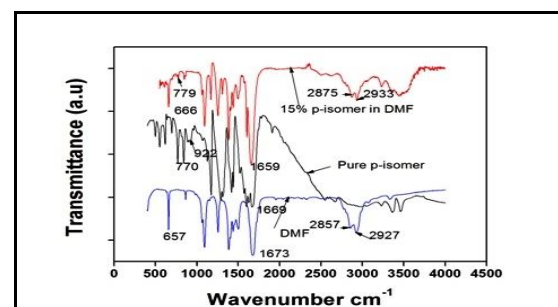


Fig.5a. IR spectra of p-isomer in DMF

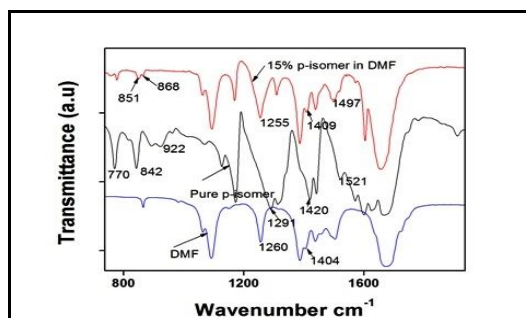


Fig.5b. In the region of 800 cm^{-1} - 1600 cm^{-1}

From the IR spectra of p-isomer and its salt solution, the peaks in pure p-isomer at 770 cm^{-1} and 842 cm^{-1} responsible for $\gamma_{\text{sym}}\&\beta_{\text{asym}}\text{ COO}^-$ are shifted to higher wave number and weakened. The characteristic peaks of γ (OH) & ν (OH) at 922 cm^{-1} and 2676 cm^{-1} (broad) are absent in the salt solution. The peaks responsible for ν (C-OH) (1291 cm^{-1}), β (OH) (1420 cm^{-1}), $\nu_{\text{asym}}\text{ COO}^-$ (1521 cm^{-1}) are shifted to lower wave number in solution. The new sharp peak arises at 1386 cm^{-1} in salt solution, which is responsible for the symmetric stretching mode of COO^- . The peaks of $\nu_{\text{sym}}\&\nu_{\text{asym}}$ (N-H) (3362 cm^{-1} , 3460 cm^{-1}) are blend together and form a broad peak in the region of 3200 cm^{-1} - 3600 cm^{-1} . This analysis reveals that there is an interaction between the salt and solvent take place effectively and the behaviour of OH group in salt produce the proton for conduction.

iv. 2- Amino benzoic acid (o-isomer) in PEG₂₀₀:

The peaks at 759 cm^{-1} , 839 cm^{-1} , 1372 cm^{-1} are responsible for γ_{sym} , β_{asym} , and ν_{sym} of COO^- ion. These peaks are weakened in salt solution. γ (OH) (929 cm^{-1}) & $\nu\text{ C=O}$ (1663 cm^{-1}) are shifted to higher wave number around 935 cm^{-1} and 1715 cm^{-1} (very strong) respectively. ν (C-OH) peak (weak) at 1231 cm^{-1} is shifted to higher wave number and strengthened (1241 cm^{-1}). The peaks at 2583 cm^{-1} , 3238 cm^{-1} , 3323 cm^{-1} and 3389 cm^{-1} are responsible for ν (OH), $\nu_{\text{sym}}\&\nu_{\text{asym}}$ (N-H) and ν (OH) in PEG₂₀₀ respectively are blend and form a broad and multiple peak in the region of 3200 cm^{-1} - 3500 cm^{-1} . From the IR spectra the proton in the o- isomer has not been involved in conduction. Thus the conduction decreases as the salt concentration increases.

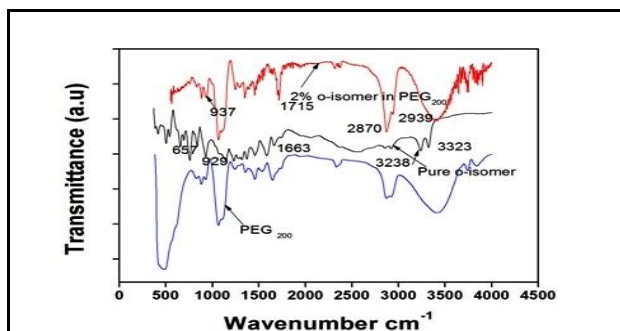
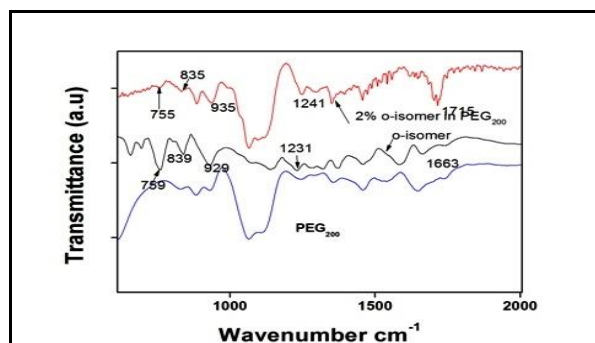


Fig.6a. IR spectra of o-isomer in PEG200

Fig.6b. In the region of 700 cm⁻¹ - 2000 cm⁻¹

v. 3- Amino benzoic acid (m-isomer) in PEG₂₀₀:

The peaks at 787 cm⁻¹, 822 cm⁻¹, 1147cm⁻¹ are characteristic peaks of ν (OH), $\beta_{\text{asym}} \text{COO}^-$ and $\beta_{\text{asym}} \text{NH}_2$, which are absent in salt solution. The zwitterion characteristic peaks at 762 cm⁻¹, 1390 cm⁻¹ and 1507 cm⁻¹ responsible for γ_{sym} and $\nu_{\text{sym}} \& \nu_{\text{asym}} \text{COO}^-$ are weakened in salt solution. In salt solution the $\nu \text{C=O}$ appeared as strong and is shifted to higher wave number side. The γ (OH) is shifted to higher wave number (916 cm⁻¹ to 937 cm⁻¹) and strengthened. Stretching mode of C-OH is shifted to lower wave number and weakened. The above results reveal that the m-isomer is completely dissociated in PEG₂₀₀ and produces proton for conduction and hence possess higher conductivity. The characteristic peaks of PEG₂₀₀ are shifted to lower or higher wave number indicates that there is an interaction between the salt and solvent.

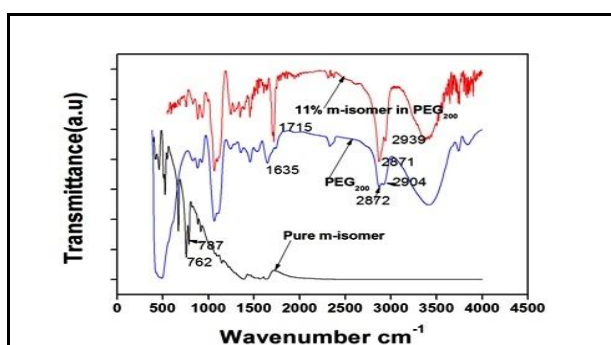
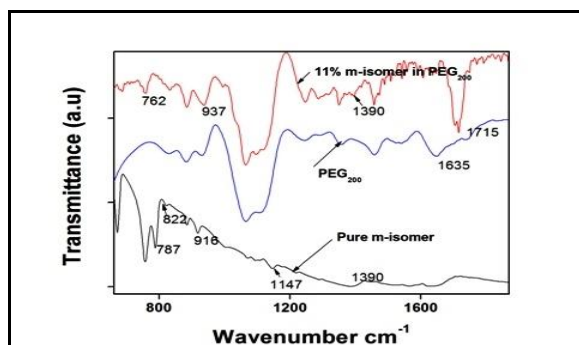


Fig.7a. IR spectra of m-isomer in PEG200

Fig.7b. In the region of 800 cm⁻¹ - 1600 cm⁻¹

vi. 4- amino benzoic acid (P- isomer) in PEG₂₀₀:

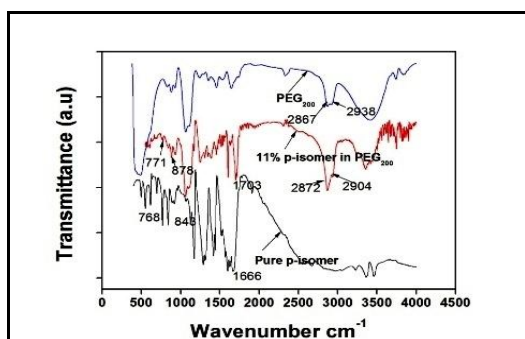
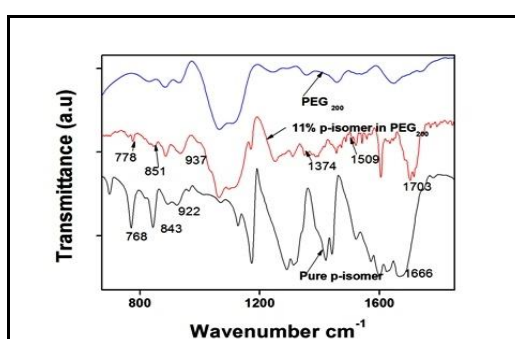


Fig.8a. IR spectra of p-isomer in PEG200

Fig.8b. In the region of 800 cm⁻¹ - 1600 cm⁻¹

The characteristic peak of ν_{sym} of C=O at 1666 cm⁻¹ in pure p-isomer is shifted to higher wave number (1703 cm⁻¹) in salt solution and very sharp peak was observed. The peaks at 3362 cm⁻¹, 3460 cm⁻¹ and 3389 cm⁻¹ are responsible for $\nu_{\text{sym}} \& \nu_{\text{asym}} \text{NH}$ and νOH in PEG₂₀₀ are blend and form a broad and multiple peak in the region of 3200 cm⁻¹ - 3500 cm⁻¹. The peaks at 768 cm⁻¹ and 843 cm⁻¹ are ascribed to γ_{sym} & β_{asym} of COO⁻ respectively which are shifted to higher wave number side and get weakened. The γOH (922 cm⁻¹) are weakened and νOH (2682 cm⁻¹) are absent in salt solution. The new peak responsible for $\nu_{\text{sym}} \& \nu_{\text{asym}} \text{COO}^-$ appears

at 1374 cm^{-1} (very weak) and 1509 cm^{-1} , which reveal that the p-isomer salt has dissociated into ions in PEG₂₀₀ and it produces proton for conduction.

Conclusion:

The liquid electrolytes of amino benzoic acid isomers in DMF and PEG at different concentrations were prepared. The conductivity measurement has shown that the m- isomer possessed highest conductivity in both DMF ($1.466 \times 10^{-3}\text{ S cm}^{-1}$) and PEG₂₀₀ ($1.066 \times 10^{-2}\text{ S cm}^{-1}$). IR analysis reveals that the m-isomer is completely dissociated into ions and produces the proton for conduction in PEG₂₀₀ effectively and hence possesses higher conductivity. And also the zwitterion character of o-isomer in DMF has also been observed in IR analysis and hence the conductivity decreases. The conductivity and interaction of the salt and solvent are in the order of m-isomer > p-isomer > o-isomer.

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