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# Effect of Temperature and Acid Molarity on the A.C Conductivity and Dielectric Properties of the Conductive Polymer

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## Abstract

The study included preparing pure polyaniline (PANI) and treating it with sulfuric acid at various strengths while keeping the temperature at 27ºC. The morphology of the polymerization products was examined using a scanning electron microscope (SEM). The SEM images revealed a notable effect of how much acid is present on the formation of PANI. The investigation focused on the relationship of alternating electrical conductivity with temperature and frequency. The A.C. electrical conductivity was represented by the variable (s) and varied with frequency, which ranged from 1 kHz to 10 MHz. The value of s was found to be less than 1, and it decreased as the temperature increased. This observation implies a dominant hopping mechanism. The activation energy was measured within the temperature range of 303-423 K at a frequency of 10 kHz; the measured values ranged from 0.249 to 0.12 eV. The relative dielectric for PANI and the constant loss were determined. The data collected indicated that the actual dielectric constant exhibits a decrease with both frequency and temperature.

**Article Info.**

**Keywords:**
*Electrical Conductivity,*
*PANI, Acidic Solution,*
*Dielectric Constant,*
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## 1. Introduction

Conductive polymers have garnered significant interest in diverse academic and industrial domains owing to their distinctive and promising characteristics, particularly in electrical, mechanical, and biological applications [1,2]. Conjugated materials known as polyaniline (PANI) have gathered significant attention in academic research due to their notable characteristics. These include its ability to exhibit high conductivity when doped with acids or nanomaterials, its cost-effectiveness, and its ease of preparation under reproducible conditions through electro-polymerization or chemical oxidation of aniline. Additionally, polyaniline demonstrates notable chemical and electrical stability, as well as favorable environmental stability [3,4].

Conductive polymers possess conjugate double bonds along their backbone as their primary characteristic. Conjugation involves the presence of single and double alternating bonds between carbon atoms. Each link comprises a localized "sigma" bond that establishes a robust chemical binding. Furthermore, it should be noted that each double bond is accompanied by a less localized "pi" (p) bond, which exhibits lower strength [5].

The regulation of the electrical capacity in polyaniline is a crucial property that can be achieved by incorporating inorganic fillers. The electrical conductivity of polyaniline depends on the presence of dopant ions [6,7]. PANI exhibits diverse chemical structures that can undergo transformation through many processes, such as base/acid treatment or oxidation/reduction [8,9]. PANI exists in three distinct oxidation states depending on the preparation conditions: totally reduced (leucoemeraldine), partially reduced (emeraldine), and fully oxidized (pernigraniline) [10,11]. Each of these oxidation states is associated with unique chemical and physical features. PANI is an electrical isolator; it exhibits a band gap ranging from 3.5 to 2.7 eV in its forms [12]. Formally paraphrased, it is possible that these polymers may also be found in suitable salt forms. However, the chemical structure of the polyaniline chain, which has been demonstrated to possess high conductivity, may be described using the generic formula of Emeraldine Salt (ES) [8]. In theory, the imine atoms can be entirely or partly protonated to generate the related salts; the oxidization rate of the polymeric base and the pH of the acid liquid decide the level of protonation of the polymeric base. When different concentration $H_2SO_4$ or HCl completely protonate imine nitrogen atoms in emeraldine base, for example, a delocalized polysemiquinone, radical cation forms along the polymer backbones, which enhances the electrical conductivity from $10^{-10}$ $S.cm^{-1}$ in emeraldine base to the most frequently green protonated emerald with a conductivity of the order of 100 $S.cm^{-1}$. In recent times, there has been a growing attraction to PANI in the field of electronics and electrical devices. This interest encompasses various applications, including transistors, diodes, electromagnetic interference shielding, antistatic materials, sensing devices, and all-polymer rechargeable batteries [13,14]. Additionally, PANI finds application in manufacturing anti-corrosive coatings [15].

The objective of this study is to investigate the impact of temperature and acid molarity on the electrical conductivity and dielectric constant, both real and imaginary, of polyaniline. The measurements were conducted within the frequency range of 100Hz to 10MHz and temperature range of 303 to 423K.

## 2. Experimental Work

### 2.1 Used Materials

The materials used in this work were: aniline hydrochloric salt ($C_6H_5NH.HCl$) purchased from Hopkins and Williams Ltd. (England), ammonium persulfate ($(NH_4)_2S_2O_8$) (APS) obtained from Central Drug House Pvt. Ltd., (India), acetone ($C_3H_6O$) purchased from CHEM-LAB NV (Belgium), and sulfuric acid ($H_2SO_4$) purchased from Hopkins and Williams Ltd. (England).

### 2.2 PANI Preparations

PANI preparations were based on aniline hydrochloride salt oxidation with ammonium persulfate in an aqueous medium. The samples were made in three $H_2SO_4$ aqueous solution molarities (0.5, 1 and 2 M). 1.5 g of aniline salt was placed in a container and diluted with 50 mL of acid solution. This mixture was poured into a 500mL glass beaker, kept under stable stirring, and remained under an ice bath at $0^oC$ for 20 minutes. Meanwhile, to produce the other solution, which included 1 M of ammonium persulfate, 50 mL of $H_2SO_4$ was added to 4.85 g of ammonium persulfate. This solution was kept at $0^oC$ with steady stirring. The aniline liquid was then gradually mixed with the ammonium per sulfate liquid. It was noticed that the color of the liquid changed to dark green after being transparent with the appearance of granules. This liquid was left for around 1-2 hrs under stable stirring at $0^oC$, allowing the polymerization process to be completed. Then, the liquid was left to settle for 24 hrs, i.e. until the next day. A filter paper was used to capture the precipitate PANI and was purified with 200 mL of 0.1M HCl and 50 mL of acetone. Fig. 1 shows the preparation setups of PANI.
The powder of PANI (emeraldine) was dried in the air for an hour, then in an oven at 80 $^oC$ for 6 hours. The yield of the prepared PANI was 2.05 g. PANI powder was extensively crushed with a mortar to produce tiny particles and then compressed as a pellet under a pressure of 10 tons. The resultant pellet is 1 cm in diameter and 1.88-1.79 mm thick. Fig. 2 shows the finale shape of sample.

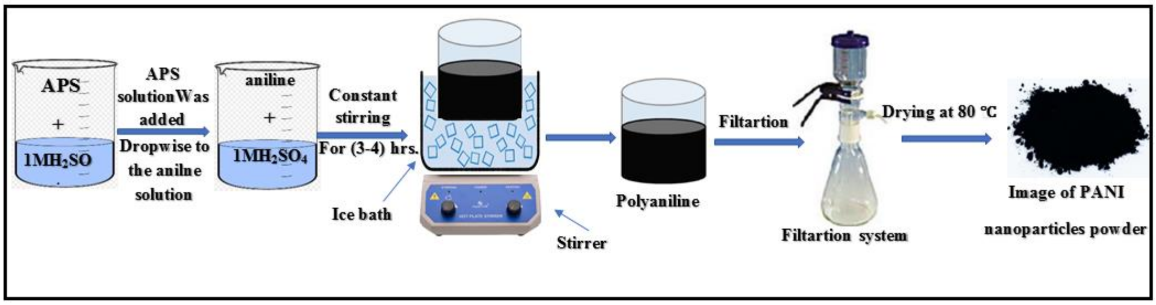

*Figure 1: The preparation process of PAN.*

*Figure 2: The final shape of the sample.*

### 2.3 Theoretical Part and Calculation

An LCR meter (type HP-4274A and HP-4275A) was used to measure capacitance (Cp), dissipation factor (D), and resistance (R) of the sample under examination. This was done at a frequency range between 100Hz and 10MHz. The total conductivity $\sigma_t(\omega)$ was estimated, using the formula

$$\sigma_t(\omega) = d/RA \tag{1}$$

where d is the thickness of the sample, and A represents the effective area of the sample. The a.c conductivity $\sigma_{ac}(\omega)$ was obtained by applying the relation [16]

$$\sigma_t(\omega) = \sigma_{ac}(\omega) + \sigma_{dc} \tag{2}$$

where $\sigma_{dc}$ is the direct conductivity. The real part of the dielectric constant ($\varepsilon_1$) was measured from the formula

$$\varepsilon_1 = \frac{dc_p}{A\varepsilon_\circ} \tag{3}$$

where $\varepsilon_o$ is the permittivity of free space. The dielectric loss (imaginary part) ($\varepsilon_2$) was estimated from the equation

$$\varepsilon_2 = \varepsilon_1 \tan\delta \tag{4}$$

The ac conductivity for the amorphous material changes with frequency depending on the following equation [16]

$$\sigma_{ac}(\omega) = \sigma_t - \sigma_{d.c} = B\omega^s \tag{5}$$

where B is a constant independent of temperature, ω is the angular frequency, and s is a frequency exponent. The temperature dependence of $\sigma_{a.c}(\omega)$ is represented by the Arrhenius equation [16], where $\sigma_\circ$ is a constant and $E_{ac}$ is the activation energy

$$\sigma_{ac}(\omega) = \sigma_{\circ} e^{-\frac{E_{ac}}{K_B T}} \qquad (6)$$

## 3. Results and Discussion

The purpose of scanning electron microscope (SEM) is to examine the surface morphology and size distribution of the PANI particles. The morphology of PANI was examined to investigate the impact of $H_2SO_4$ molarity. Fig. 3 demonstrates the presence of PANI in all $H_2SO_4$ molarities. The average diameters of PANI for 0, 1 and 2 M $H_2SO_4$ were 60nm as determined from Fig.3A, 90nm from Fig.3B, and 150 nm from Fig.3C. The SEM images demonstrated that the acid molarity significantly influenced the process of PANI polymerization. Increasing the acidity of the solvent, larger diameters and better yields of PANI were obtained [15]. As the acid molarity is further increased, the polymer showed aggregation. As depicted in Fig. 3C, there was an observed rise in the precipitation of PANI nanoparticles as the molarity of $H_2SO_4$ increased. This can be attributed to the occurrence of heterogeneous nucleation during the polymerization process. The growth of PANI molecules resulted in the development of thicker and more agglomerated particles. The SEM image shown in Fig.3C demonstrated the enhancement of connecting routes, improving charge transport and resulting in high electrical conductivity and great optical quality. This finding is consistent with the results of other reported works [17, 18].

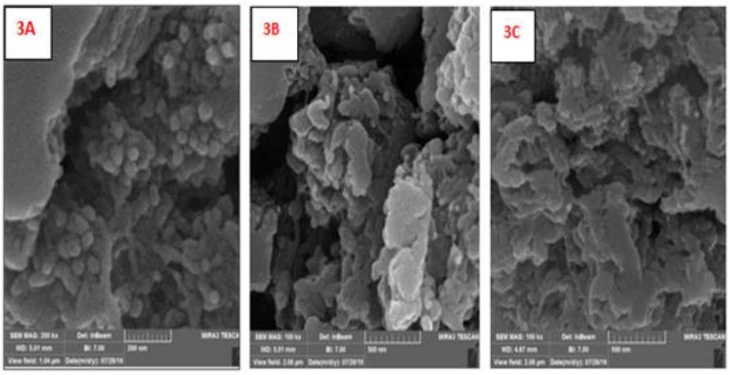

***Figure 3: SEM images of the prepared PANI in (A) water, (B) 1M $H_2SO_4$, and (C) 2 M $H_2SO_4$.***

Fig. 4(a, b, c, and d) show the total conductivity as a function of angular frequency for pure PANI, and doped with different molarities of $H_2SO_4$ (0.5, 1, and 2) M for different temperatures in the range 303-423K. An increase in total conductivity was observed with increasing the angular frequency and temperature. It was noted from Fig. 4(c) that the rate of increase in conductivity was noticeable. From this result, it can be concluded that the result obtained at (1M) $H_2SO_4$ was excellent.

$\sigma_{ac}$ was calculated after extracting the continuous (D.C.) conductivity from the total conductivity according to Eq. (1). Fig.5 illustrates the alternating (A.C.) conductivity as a function of frequency at different temperatures. It is clear that the relationship between ln $\sigma_{a.c}$ and ln ω was linear; the A.C. conductivity increased with frequency. Fig. 5(a and b) shows that the change was irregular, but increasing the acid concentration led to a noticeable increase in the conductivity value, as in Fig. 5(c and d).

The frequency exponent (s) was computed from the slope of the straight lines of Fig.5; it was less than 1 and decreased with increasing temperature, as shown in Fig. 6. This change in the (s) value was reported by Morocho et al. [10] for amorphous material. The general values of (s) and this behavior resulted from the charge carrier (polaron) hopping activity between polymer chains.

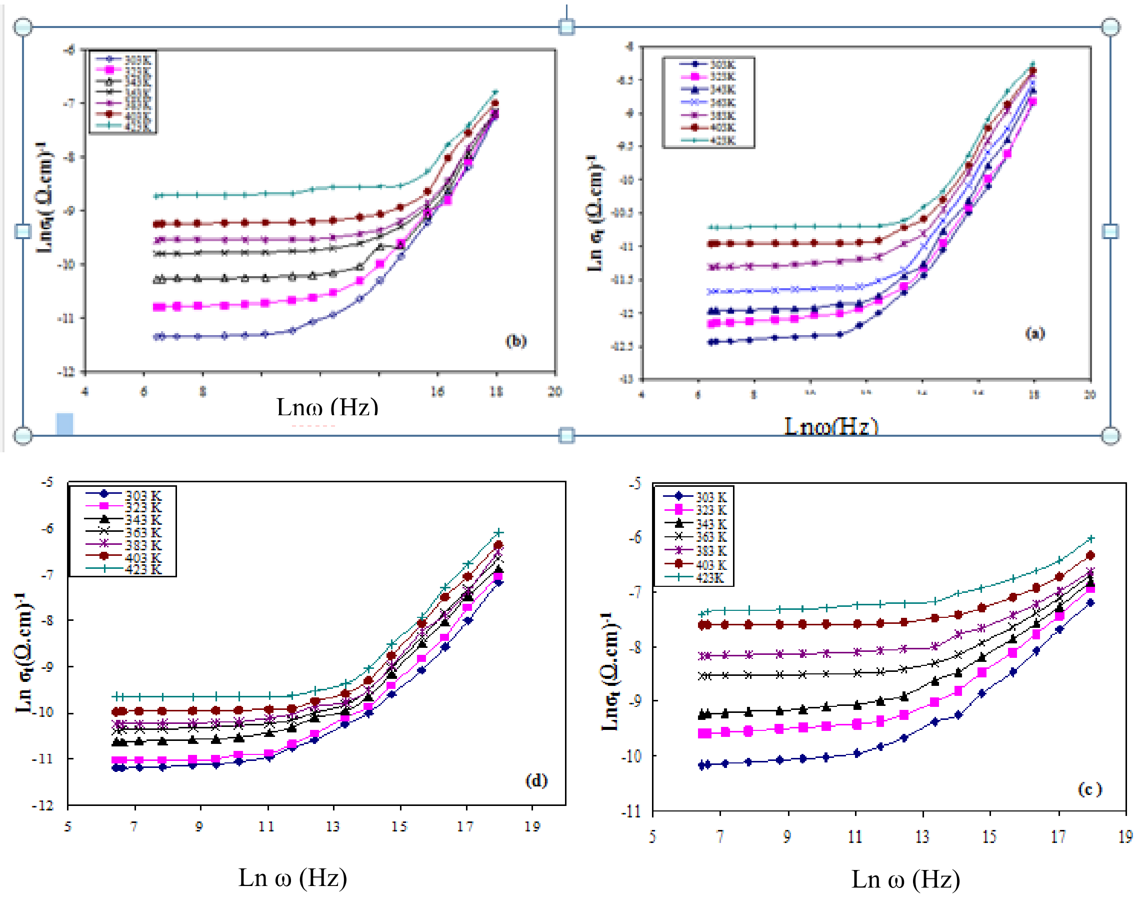

*Figure 4: ln $\sigma_t$ as a function of ln ω for (a) pure PANI, (b) 0.5 M, (c )1M, and (d) 2M $H_2SO_4$ at different temperatures.*

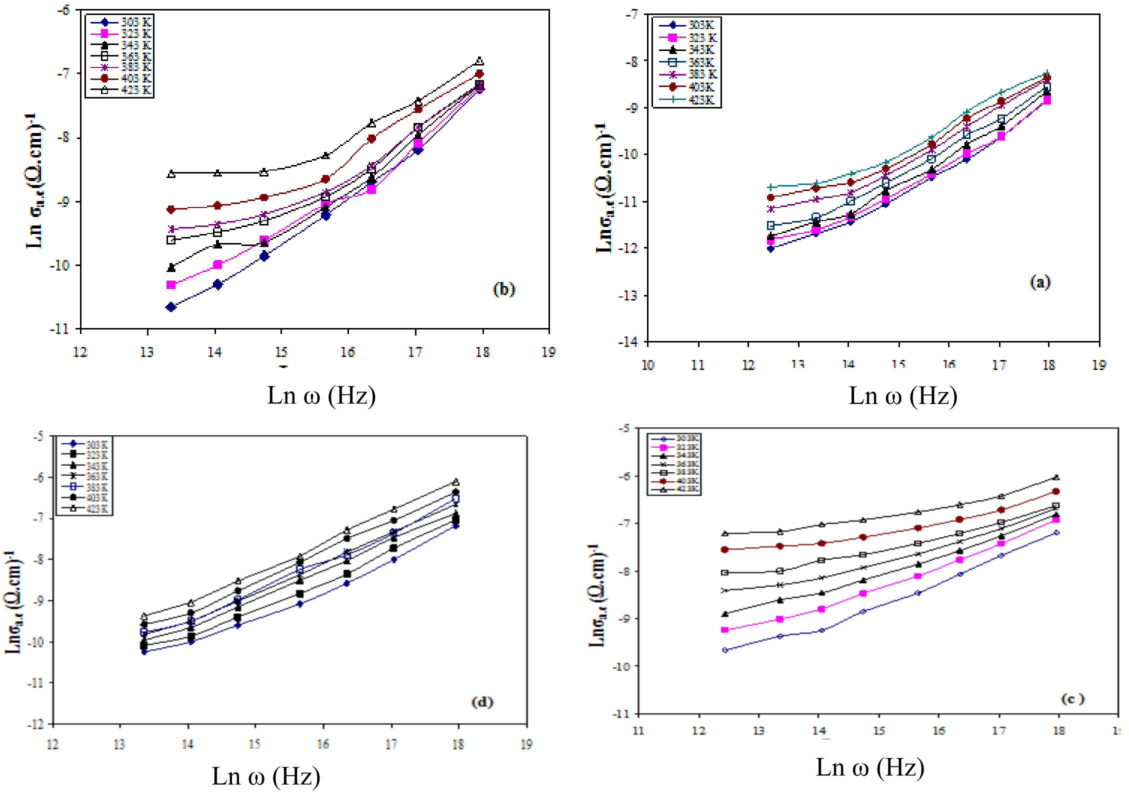

*Figure 5: ln $\sigma_{a.c}$ as a function of ln ω for (a)pure PANI, (b) 0.5 M, (c) 1M, and (d) 2M $H_2SO_4$ doping at different temperatures*

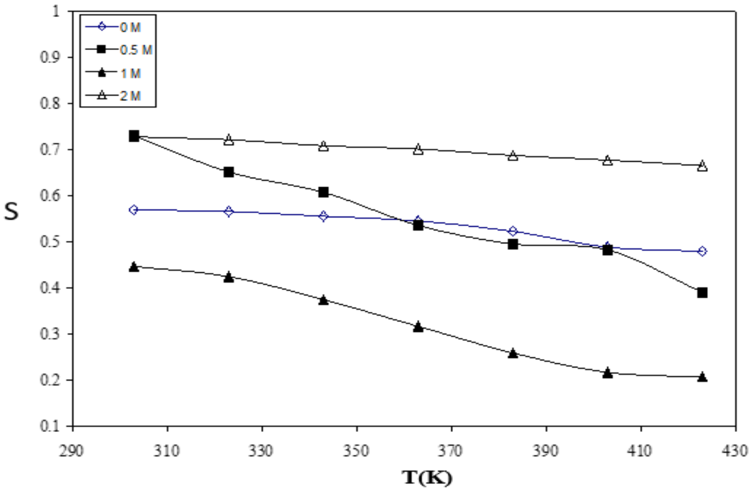

***Figure 6: Exponential factor (s) as a function of temperature.***

The relation of the activation energy of $\sigma_{a.c}(\omega)$ for the samples of polyaniline doped with (0, 0.5, 1, and 2 M) $H_2SO_4$ with the reciprocal of temperature is shown in Fig. 7 at 10 kHz. According to the graph, $\sigma_{a.c}(\omega)$ increased linearly with the temperature rise. This might reflect that the A.C. conductivity is a thermally activated process arising from various localized states in the energy gap.

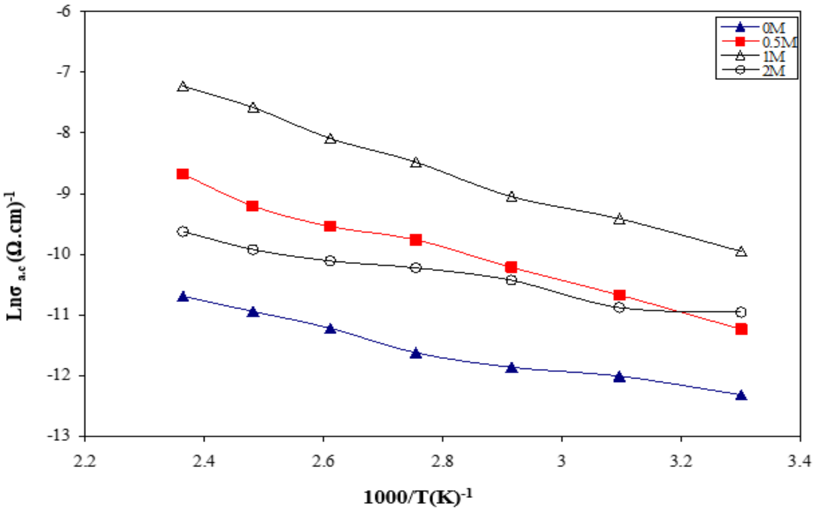

***Figure 7: Temperature dependence of ln($\sigma_{a.c}$)for pure PANI and doped with $H_2SO_4$ at 10 KHz.***

The alternating activation energy was obtained using Eq.(6) at 10 KHz, as in Table 1. From the table, it was noticed that the value of the activation energy for the pure polyaniline was 0.249 eV; it decreased to 0.122 eV when the acid concentration was increased to 2M. The electrical conduction occurred with one electronic transmission mechanism; the conduction was done by hopping and tunneling between local energy levels within the forbidden energy gap [19].

*Table 1: Activation energy.*

| **Samples** | **$E_{a.v}$(eV)** |
|---|---|
| PANI pure | 0.249 |
| 0.5 M $H_2SO_4$ | 0.222 |
| 1 M $H_2SO_4$ | 0.251 |
| 2 M $H_2SO_4$ | 0.122 |

### 3.1 Concentration Dependence of A.C Conductivity

Protonation is the addition of hydrogen ions (to increase proton concentration); this happens in the presence of an acid. The protonation rate depends on the acid solution's acidity (pH) [2, 12, 20]. Fig. 8 shows the change of the alternating conductivity with frequency for different values of $H_2SO_4$ molarity at R.T. The low-frequency behavior is observed in this graph. All samples showed an almost constant value (D.C conductivity dominated) for frequencies less than or equal to $10^3$ Hz; the conductivity rises after that with ω. With the increase in $H_2SO_4$ molarity (0.5 and 1 M); the A.C. conductivity increases, except for 2 M $H_2SO_4$ molarity sample. This increase is due to the charge being displaced inside the polymer chains (stronger localization) because the increased proton concentration and polymer cross-linking make hopping of electrical charges in polymer chains more difficult. The $H_2SO_4$ treatment caused anion exchange [21] and also prevented the undulating movement of polymer chains due to the reduction in conductivity. Therefore, it is not preferable to prepare polyaniline with a molarity higher than 1.5 M.

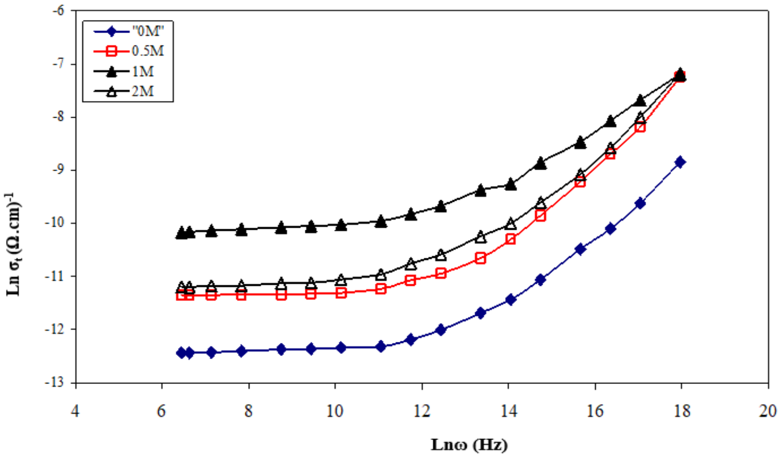

*Figure: 8 Frequency dependence of conductivity for different $H_2SO_4$ molarity.*

### 3.2 The Dielectric Constant

The real part of the dielectric constant ($\varepsilon_1$) was determined using Eq. (1) by measuring $C_p$ in the frequency range (100-10 M) Hz. Fig. 9 shows its variation with frequency. $\varepsilon_1$ decreased as the frequency increased. The reduction in $\varepsilon_1$ (for polar materials at low frequencies) with frequency is owing to the accumulation of many forms of polarization (orientation, electronic, ionic, and interfacial). When the frequency is raised, the dipole cannot rotate fast enough. As a result, their oscillation is too far behind the field, and the dipole cannot follow the field, and the orientation is lost. And so $\varepsilon_1$ decreases, reaching a stable value owing to interfacial polarization [22-23].

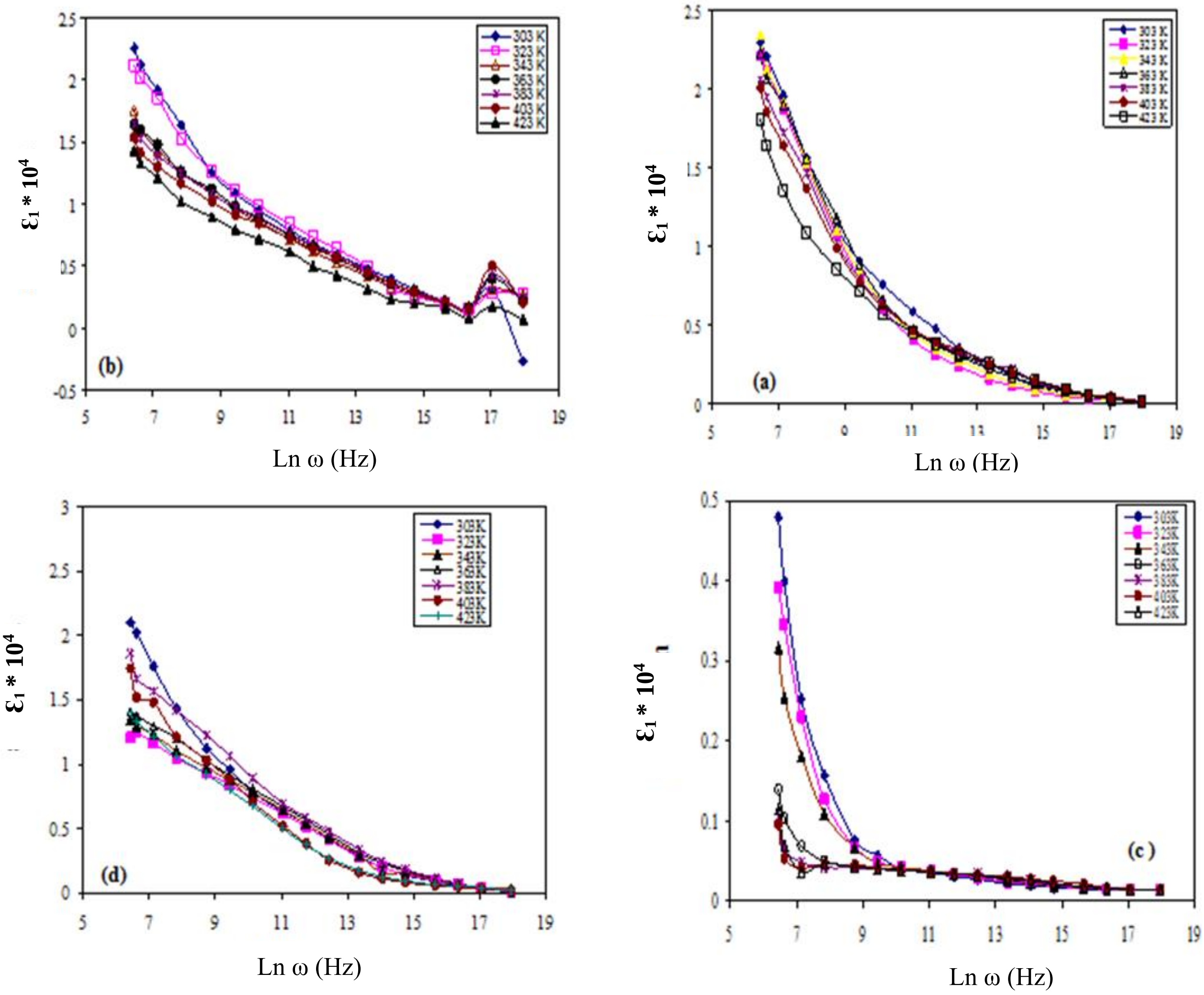

***Figure 9: The real part of the dielectric constant dependence on ln ω for: (a) pure PANI, (b) 0.5 M, (c) 1M, and (d) 2M $H_2SO_4$ doping at different temperatures.***

The $\varepsilon_1$ decreased with the temperature increase, as seen from the figure; this behavior is not systematic. This decrease is because the dipoles cannot rotate freely when the temperature rises; the increase in temperature prevents the polymeric chains from moving as a result of the increase in the cross-linking between them [24].

### 3.3 The Dielectric Loss

The imaginary part of the dielectric constant (dielectric loss), $\varepsilon_2$, was evaluated as a function of frequency and temperature. Fig. 10 demonstrates the dependence of $\varepsilon_2$ on the frequency at different temperatures. It is noticed from the figure that $\varepsilon_2$ decreased with ω and T. The reason of the dielectric losses is the losses of conduction current [25,26]. So, when conductivity increases with temperature, the loss increases, this result is shown in Fig. 10.

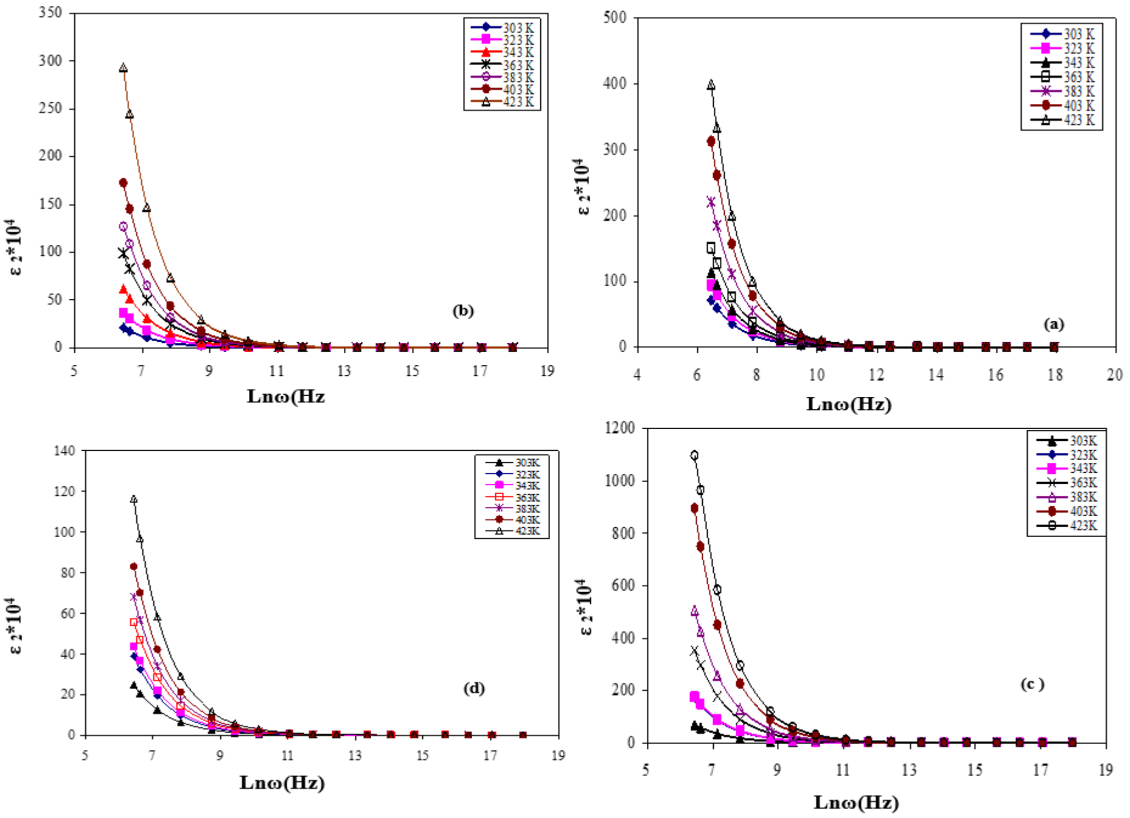

***Figure.10: Frequency dependence of dielectric losses for (a) polyaniline pure, (b) 0.5 M, (c) 1M, and (d) 2M $H_2SO_4$ doping at different temperatures.***

## 4. Conclusions

The morphology was studied; it showed a rise in the precipitation of PANI nanoparticles as the molarity of $H_2SO_4$ increased. The alternating conductivity of pure and protonated PANI with different $H_2SO_4$ molarities was measured as a function of ω and T. The s value was less than 1 and decreased with the temperature increase, suggesting a dominating barrier-hopping mechanism. The A.C. conductivity at 100 Hz- 10 MHz frequency fluctuated. A linear increase in conductivity was seen with temperature dependency and activation energy calculation. It was found that the real part of the dielectric constant, $\varepsilon_1$, decreased with an increase in frequency and temperature; these increases were irregular. The imaginary part, $\varepsilon_2$, was also found to decrease with increasing frequency and temperature. The best results were obtained with the sample PANI protonated with 1M $H_2SO_4$. These results can be used with electrical switching applications and smart capacitors.

## Acknowledgements

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## Conflict of interest

Authors declare that they have no conflict of interest.

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# تأثير درجة الحرارة ومولارية الحامض على موصلية التيار المتناوب وخواص العزل الكهربائي للبوليمر الموصل

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## الخلاصة

تضمن البحث تحضير البولي انيلين النقي (PANI) وبروتنته مع حامض الكبريتيك في مولاريات مختلفة من محلول يحتوي على حامض عند درجة حرارة التحضير 27 درجة مئوية. تم فحص مورفولوجية منتج البلمرة باستخدام المجهر الإلكتروني الماسح (SEM). تكشف صور SEM عن تأثير ملحوظ لكمية الحمض الموجودة في تكوين البولي انيلين (PANI). ركز البحث على العلاقة بين التوصيل الكهربائي المتناوب ودرجة الحرارة والتردد. لوحظ أن التوصيل الكهربائي للتيار المتردد يختلف بمقدار s ضمن نطاق التردد من 1 كيلو هرتز إلى 10 ميجا هرتز. وقد وجد أن قيمة s أقل من 1، وتنخفض مع ارتفاع درجة الحرارة. تشير هذه الملاحظة إلى وجود آلية التنقل السائدة. تم قياس طاقة التنشيط ضمن نطاق درجة الحرارة 303-423 كلفن بتردد 10 كيلو هرتز. تراوحت القيم المقاسة من 0.249 إلى 0.12 فولت. تم تحديد العازل النسبي,وثابت الفقد. تشير البيانات التي تم جمعها إلى أن المادة العازلة الفعلية تظهر انخفاضًا في كل من التردد ودرجة الحرارة.

**الكلمات المفتاحية:** التوصلية الكهربائية، البوليمرات الموصلة (بولي انلين)، محلول حامضي، ثابت العزل الكهربائي، البلمرة الكيميائية.