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Studies on transport properties of polyaniline transition metal salt composites

T.D. Kose

Abstract

Polyaniline-containing transition metal salts were synthesized by oxidizing the complex of aniline with corresponding metal salts in solution. The effect of transition metal salts on the electrical conductivity of polyaniline (Pani) was discussed in details. The as-prepared products were characterized by FT-IR spectroscopy. The transition metal has been successfully incorporated into the polymer, which affects transport properties of the composites; the fact is supported by the ample of experimental results and characterization evidences.

Keywords

composites, transport properties, transition metal salt

Introduction

In recent years, there has been a growing interest in conducting polymer–metal systems.[1] Polyaniline (Pani) is a highly promising material for electronics applications due to its combination of electrical conductivity and environmental stability.[2–4] The incorporation of inorganic semiconducting nanoparticles in Pani matrices results in materials with modified properties which are again of interest for their electronic properties.[5–7] Transition metal salts influence the polymer conformations which play an important role in the electrical conductivity of the polymer. Understanding of mechanism of Pani and metal ions or a metal atoms is an important problem in view of potential applications of the polymer/metal pair in various fields such as organic electronics, where Pani/metal hetero-junctions are employed for electrical transport and rectification, as protective coatings against the corrosion of metal surfaces, as a redox active catalyst for inducing chemical reactions in coordination chemistry, as membranes for separation and recovery of noble metals.[8]

The conductive polymers with facile interconversion of redox states could have different conductive attributes varying from metallic, semiconductive to insulating, which strongly depends on the doping. Different doping methods such as Solvato-controlled doping,[9] self-acid doping,[10] and corolla discharge[11] have been introduced to change the redox states in the conductive polymers. The doped conductive polymers have unique properties including polymer conformation, doping level, conductivity, and color, which make them good potential candidates for applications such as displays, energy storage devices, actuators, and sensors.[12–23] Conductivity switching phenomenon has been studied after doping with HCl and H_2SO_4 acidic solutions at different concentration levels. It becomes more obvious with an increase in acid concentration.[24] The effect of addition of iron oxide nanoparticle on the physicochemical properties of the polypyrrole (PPy) was investigated.[25] Also, PPy/silicon carbide nanocomposites with tunable electrical conductivity were studied by researchers.[26]

Physical aspects of the Pani complex formation, namely how an inorganic salt influences the polymer conformations which plays an important role in the electrical conductivity of the polymer film are still beyond the understanding.[27,28]

Department of Chemistry, A.C.S. College, Tukum, Chandrapur 442 401, Maharashtra, India.

Corresponding author:
T.D. Kose, Department of Chemistry, A.C.S. College, Tukum, Chandrapur 442 401, Maharashtra, India
Email: tikukose@gmail.com; t.kose@rediffmail.com

This study revealed a successful synthesis of incorporation of transition metal into Pani by simplest method and reported conductivities and dielectric property of Pani transition metal salt composites.

Experimental procedure

Reagents and materials

All chemicals used were of AR grade; aniline was distilled twice prior to use. Nickel sulfate (dihydrated), copper sulfate (dihydrated), cadmium sulfate ($8H_2O$), cobalt chloride (dihydrated), $(NH_4)_2S_2O_8{\cdot}2H_2O$ ammoniumperoxidisulfate, hydrochloric acid, and ethanol were analytical reagents and were used as received.

Sample preparation

Pani emeraldine base and its hydrochloric salt (Pani–HCl) were prepared according to the procedure reported in literature.[29] Pani-containing transition metal salts were synthesized as follows: quantitative amount of transition metal salt was added into the 100 mL 0.5 M aniline solution. The solution was stirred continuously for 2 h. $(NH_4)_2S_2O_8{\cdot}2H_2O$ solution (0.5 M) was added dropwise with bubbling of H_2S gas. The reaction was carried out with constant stirring for 24 h in nitrogen atmosphere. The products were washed thoroughly plenty of times with 95% ethanol and acetone. The resulting product was dried in oven at 60°C for 24 h. The products were named as CuS–Pani, CdS–Pani, NiS–Pani, $NiSO_4$–Pani, $CoCl_2$–Pani, and CoS–Pani.

Characterization of samples

The Fourier transform infrared (FT-IR) spectroscopy (Perkin-Elmer 100 FT-IR spectrophotometer) was used to record a spectrum using KBr pellets for all the samples. The NMR spectra were carried out using Bruker Avance II 400 spectrometer. The electrical conductivity of the samples was measured at a temperature ranging from 30°C to 100°C with dry-pressed pallets using DFP-02 four-probe set-up. The capacitance and *D*-factor of thin pallet of a polymer sample were measured as a function of temperature using Direct Reading, LCR bridge, 8 C (Pacific), at frequency 1 kHz.

Result and discussion

Optimization of synthetic conditions

The molar ratio of aniline to transition metal ion was fixed. The yield and conductivity of the product increased rapidly with an increase in the quantity of oxidant; whereas when the molar ratio of aniline to oxidant was fixed, the polymer yield increases gradually with an increase in the quantity of transition metal ion; but the conductivity was maximum when the ratio of aniline:transition metal ion:oxidant = 1 : 1 : 1. Temperature was found to have the least impact on the polymer yield but most impact on the conductivity of resulting Pani transition metal salt composites. Especially, conductivity of the Pani decreases acutely when the reaction temperature exceeded 30°C. The reaction time seemed to have little influence on the yield after 2 h; however, the conductivity increased with the reaction time. In the concentration range of 0.5–1.5 M HCl, the change of temperature from 2°C to 30°C practically did not change the conductivity of polymer. Experimental conductivity at room temperature of CuS–Pani, CdS–Pani, NiS–Pani, $NiSO_4$–Pani, $CoCl_2$–Pani, and CoS–Pani has been reported in Table 1. It has been observed that conductivity of transition metal salt composites was greater than Ge (10^{-2} S cm^{-1}) and Si (10^{-4} S cm^{-1}) semiconductors. Also, $CoCl_2$–Pani composite exhibited low conductivity at room temperature than other transition metal composites.

FT-IR of the resulting samples at different conditions

Figure 1 shows the FT-IR spectra of Pani-containing transition metal salt were prepared under the optimal synthetic conditions. The presence of sharp peaks near 1510 and 1605 cm^{-1} is attributed to C = C stretching of the benzenoid and quinoid rings, respectively. The peak at 1298 cm^{-1} corresponds to C–N stretching of secondary amine in polymer main chain and can be clearly seen in all samples. The existence of absorption band at 1120 cm^{-1} has been interpreted as originating from plane bending vibration of C–H, which was formed in the structure of B–N^+–M, Q–N^+–M, and N = Q = N during protonation of transition metal salt to Pani. The broad absorption band ranges from 3600 to

Table 1. Observed conductivities of Pani transition metal salt composites

Polymers	Conductivity (S cm^{-1})
CuS–Pani	5.98×10^{-2}
CdS–Pani	6.50×10^{-2}
NiS–Pani	2.43×10^{-2}
$NiSO_4$–Pani	3.2×10^{-2}
$CoCl_2$–Pani	2.21×10^{-2}
CoS–Pani	3.2×10^{-2}

3500 cm^{-1} as shown in Figure 1(a)–(f). It was attributed to the protonation of amines functional group at polymer backbone and was observed for the highly attached Pani with transition metal salts.

Absorption band near 2900 cm^{-1} is assigned to aliphatic C–H stretching of the polymer. A weak vibration absorption peak at 405 cm^{-1} for Cd–S bond was observed in FT-IR spectrum for CdS–Pani composite; it showed that the concentrations of CdS in the composites were very low. Also, weak vibration absorption at 410–550 cm^{-1} indicated low concentrations of CuS, NiS, $NiSO_4$, $CoCl_2$, and CoS in respective composite.

Dielectric properties of composites

The capacitance and *D*-factor of thin pallet of a composite–polymer samples were measured as a function of temperature using Direct Reading, LCR bridge, 8 C (Pacific), at 1 kHz frequency.[30]

The dielectric constant and dielectric losses were calculated from the capacitance measurement, dimension of the sample, and the *D*-loss factor. The dielectric constant (ε') and dielectric loss (ε'') were plotted as a function of temperature as shown in Figures 2 and 3. Study revealed that dielectric constant (ε') was increased with temperature.

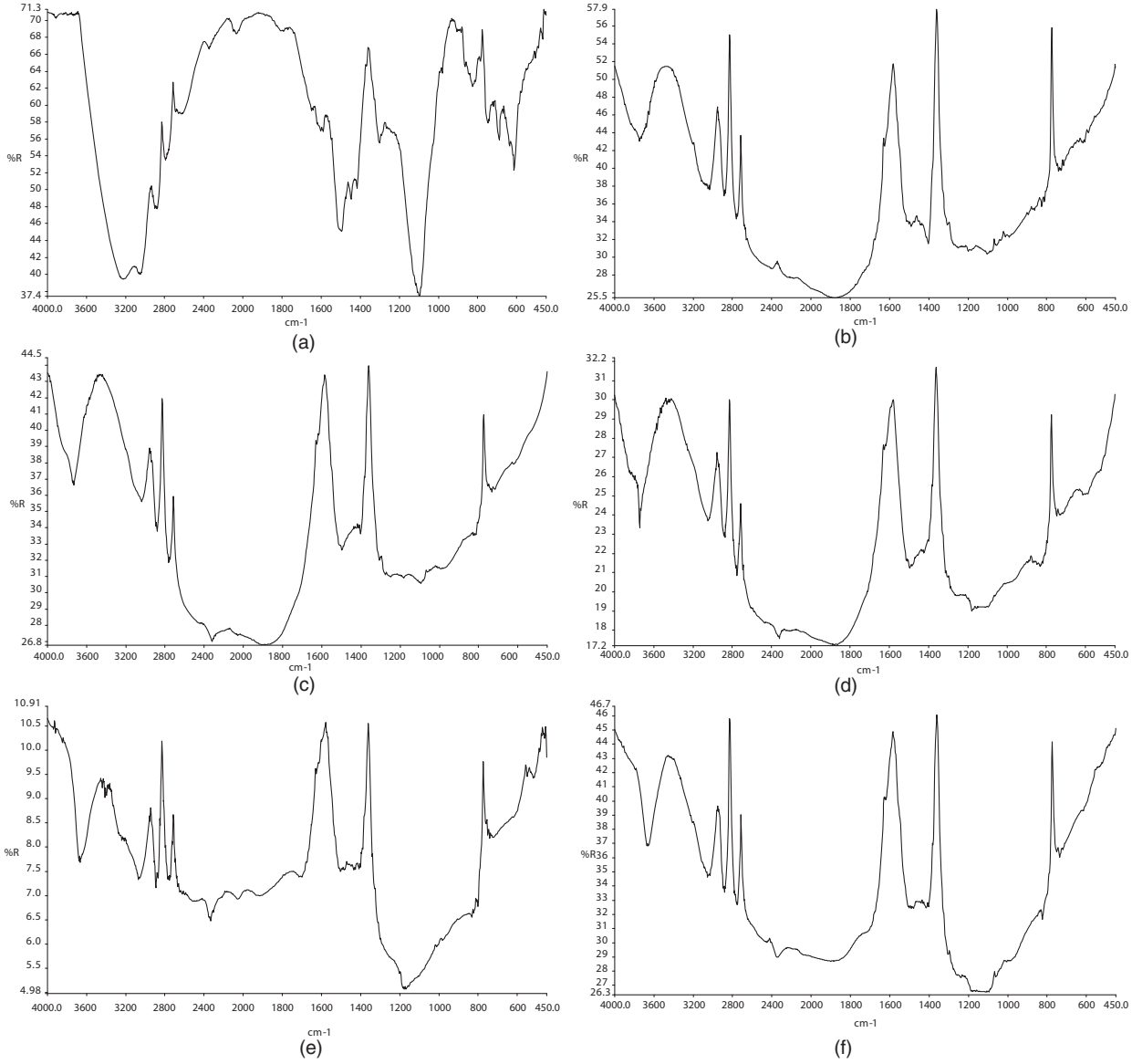

Figure 1. FT-IR spectra of (a) CoS–Pani, (b) $CuCl_2$–Pani, (c) $NiSO_4$–Pani, (d) NiS–Pani, (e) CdS–Pani, and (f) CuS–Pani.

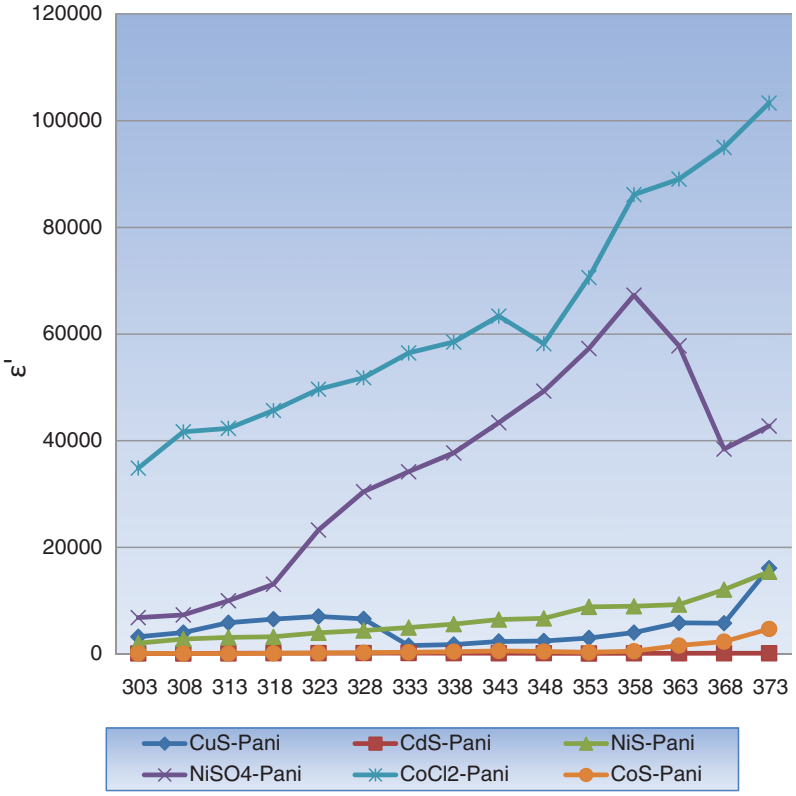

Figure 2. Temperature dependence of dielectric property for different transition metal Pani composites.

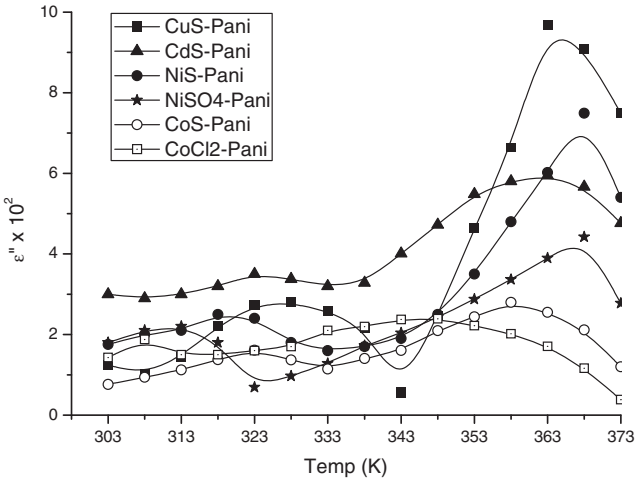

Figure 3. Dielectric loss as a function of temperature for different transition metal Pani composites.

Electrical conductivity

The temperature dependence of the electrical conductivity data (in the middle range of temperature) fits the Arrhenius type of equation (1) in the temperature range investigated,

$$\sigma(T) = \sigma_0 \exp(-E_0/2KT) \tag{1}$$

Slight variation of electrical conductivity for different composites was observed as shown in Figure 4. It was observed that CuS–Pani, CdS–Pani, NiS–Pani, $NiSO_4$–Pani, $CoCl_2$–Pani, and CoS–Pani exhibited high conductivity than pure Pani. The activation energy σ_0 (T) was calculated, and shown in Table 2. Thus, the conduction in these composites may be predominant by tunneling of electron mechanism. The presence of electron withdrawing group in the chain decreases the probability of tunneling of electron.

It was observed that when electron withdrawing group was chloro, the conductivity and activation energy of conduction was less. Hence, for $CoCl_2$–Pani composite, conductivity and activation energy found to be less than CoS–Pani composite.

Conduction mechanism of Pani transition metal salt composites through grain barrier conduction, hopping conduction, and tunneling conduction was considered accordingly:[31–35]

$$\ln(\sigma/T^{1/2}) \text{vs. } 1000/T \tag{2}$$

$$\ln(\sigma/T^{1/2}) \text{vs. } T^{-1/4} \tag{3}$$

and

$$\log \sigma \text{ vs. } 100/T^{1/2} \tag{4}$$

were plotted and linear plots are obtained as shown in Figures 5–7.

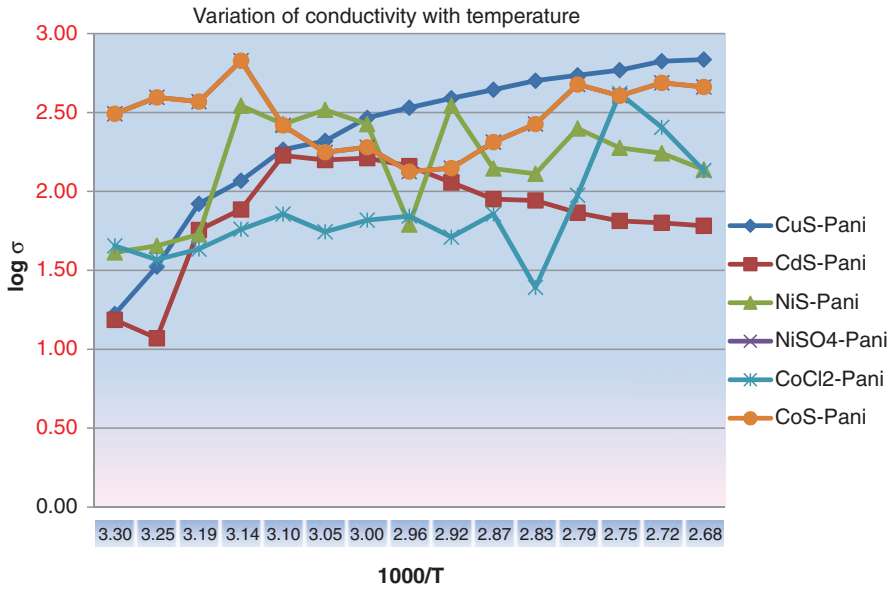

Figure 4. The temperature dependence of conductivity (σ) for different transition metal Pani composites.

Table 2. Conductivity, activation energy, and dielectric constant of Pani transition metal salt composites

Name of polymer	σ (T) (cm^{-1} ohm^{-1})	Activation energy (eV)	Dielectric constant (ε')
CuS–Pani	5.98×10^{-2}	0.84	3.24×10^{3}
CdS–Pani	6.50×10^{-2}	0.30	1.15×10^{2}
NiS–Pani	2.43×10^{-2}	1.16	2.05×10^{3}
$NiSO_4$–Pani	3.2×10^{-2}	0.34	8.84×10^{3}
$CoCl_2$–Pani	2.21×10^{-2}	0.24	3.49×10^{4}
CoS–Pani	3.2×10^{-2}	0.34	1.14×10^{2}

From results, it is believed that conduction in these polymers may be predominant by a tunneling mechanism. Presence of electron withdrawing tendency of transition metal salt in the chain decreases the probability of tunneling of electron, but intercalation of transition metal salts in Pani helps to increase the conductivity due to enhancement of crystallinity of the transition metal salt composites.

Conclusion

Pani-containing transition metal salts were synthesized by oxidizing the complex of aniline with metal salt solution. FT-IR spectra demonstrated that the transition metal salt had been successfully incorporated into polymer chain. Electrical conductivity of Pani–metal

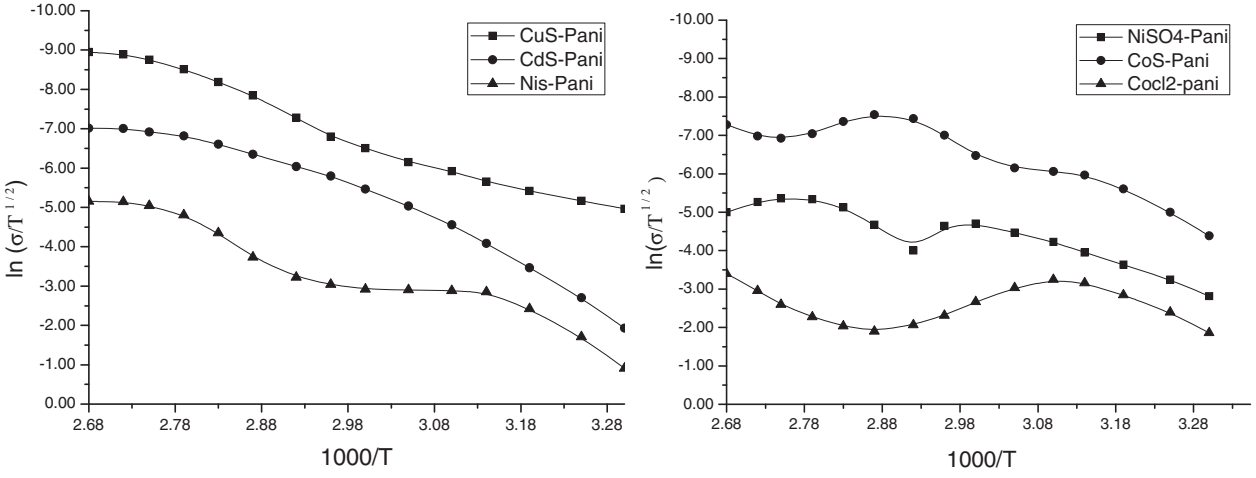

Figure 5. The temperature dependence of conductivity (σ) plot, $\ln(\sigma/T^{1/2})$ vs. $1000/T$ for different transition metal Pani composites.

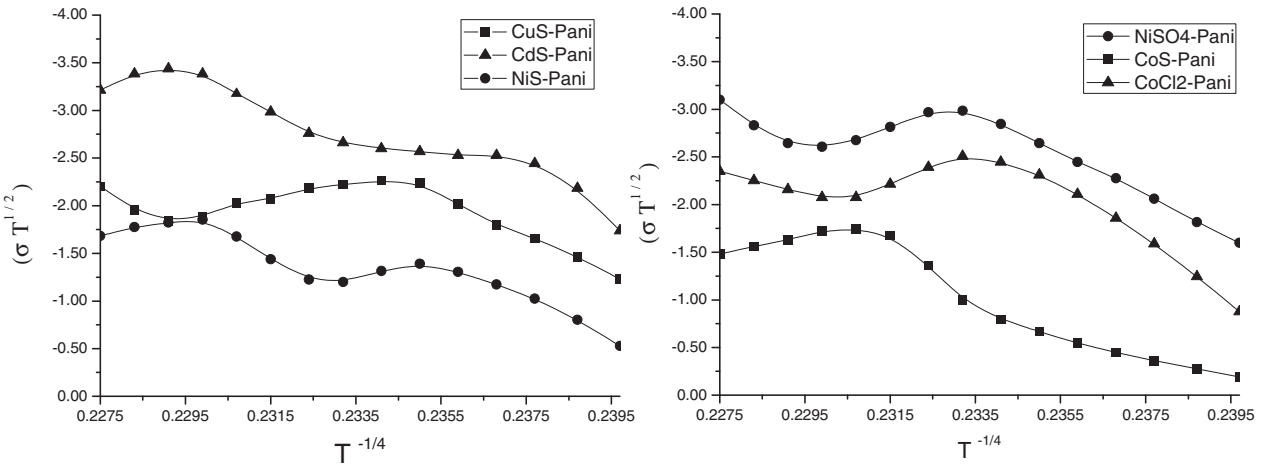

Figure 6. The temperature dependence of conductivity (σ) plot, $\ln(\sigma T^{1/2})$ vs. $T^{-1/4}$ for different transition metal Pani composites.

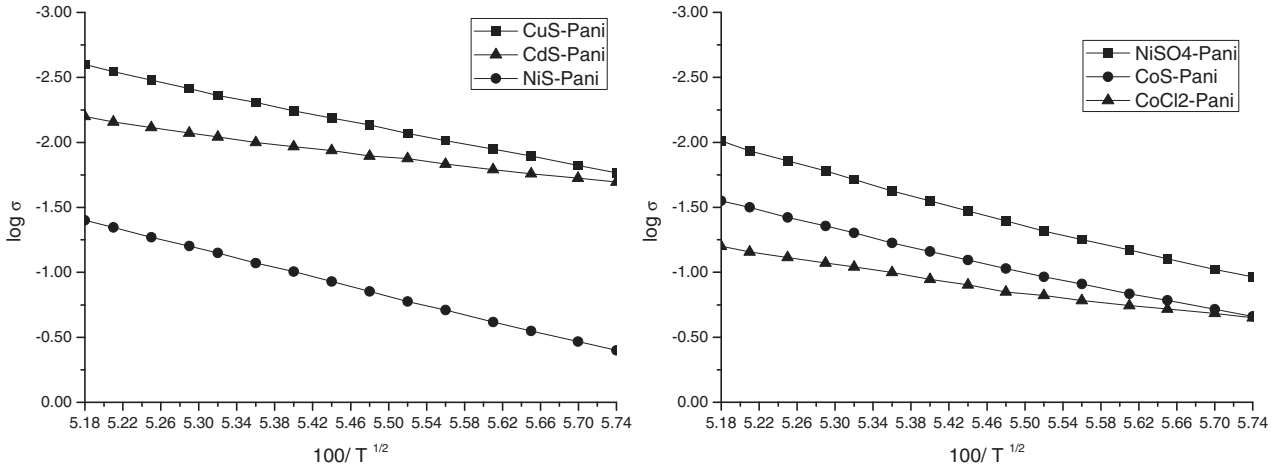

Figure 7. The temperature dependence of conductivity (σ) plot, $\log\sigma$ vs. $100/T^{1/2}$ for different transition metal Pani composites.

salt composites was found to be increased when compared to pure aniline due to its increase in crystallinity. It was also observed that the presence of electron withdrawing group decreases the conductivity and activation energy.

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