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Electrical Conduction of Pth-Pvac Thin Films Doped With Bromine

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Abstract:

Thin solid films of PTh-PVAc doped withBromine (3.5, 5.5, 10.4, 14.9, 18.9 and 22.5 wt %) were synthesized by chemical oxidative polymerization method in order to study the ac conduction at various temperature ranges. The impedance spectra of PTh-PVAc doped with Bromine films (323-343K over frequencies from 0.1-200 KHz) found to consist of only one arc suggest various parameters such as relaxation time, bulk resistance, bulk capacitance, dielectric activation energy etc. Comparison of impedance spectra was done on the basis of various AC conduction parameters

Keywords: Poly(vinyl acetate) (PVAc), Polythiophene (PTh), Bromine, dc,ac

1. Introduction

These conjugating polymers thin films have been studied by many workers, because of special electrical properties, considerable thermal stability and oxidation resistance that are favorable in applications such as optoelectronic, biosensors, electro chromic displays and chemical sensors [1-3]. Roncali [4] surveyed the electrochemical synthesis and the electronic properties of substituted PThs in 1997. The overall review on chemical synthesis of PThs and applications as chemical sensors, organic memory devices, photo conductivity, etc., is given by many researchers [5,6]. Temperature-dependent conductivity, in the case of ion conducting solid electrolytes, is more completely explained by Vogel-Tamman-Fulcher (VTF) [7-9] rather than other models. Ryu et al. [10-11] predicted that PTh powder prepared by electrochemical method, shows better results than that prepared by the fast oxidation method. The present paper focuses on comparison in electrical properties of Polythiophene composite thin films doped with Bromine.

2. Experimental Procedures

2.1 Sample preparation

Thin solid films of PTh-PVAc doped withBromine (3.5, 5.5, 10.4, 14.9, 18.9 and 22.5 wt %) were synthesized by chemical oxidative polymerization method in order to study the ac conduction at various temperature ranges.

2.2 ac conductivity measurement

ac conductivity of the samples were recorded on LCR meter (Wayne Kerr, UK) having range of frequencies from 0.1-200 KHz at temperature in the range 323-343K with heating rate 1°C min^{-1}. A constant voltage is applied to the sample and corresponding impedance and phase angle was measured at constant temperature for all frequency range. ac conductivity of the pure PTh-PVAc sample and doped with different Bromine wt % was measured at various temperatures 323-343K by applying a wide range of frequencies from 0.1-200 KHz.

3. Results and discussion

3.1 ac conductivity of PTh-PVAc films doped with Bromine

Fig.3.1.1-3.1.3 shows Nyquist plots of the samples DD7, DD8 and DD9 and it is observed that the resistance of all the samples decreases with the rise of temperature. From the fig., it is observed that the sample shows similar trend of semicircle for temperature 323-343 K. Many researchers [12-15] reported a similar behavior in the Nyquist diagram. The impedance spectrum of PTh-PVAc films doped with Bromine is found to consist of only one arc.

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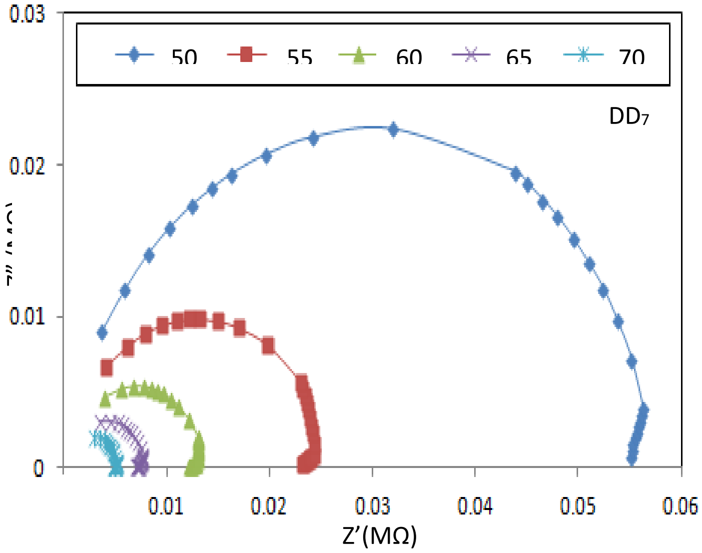

Fig.3.1.1

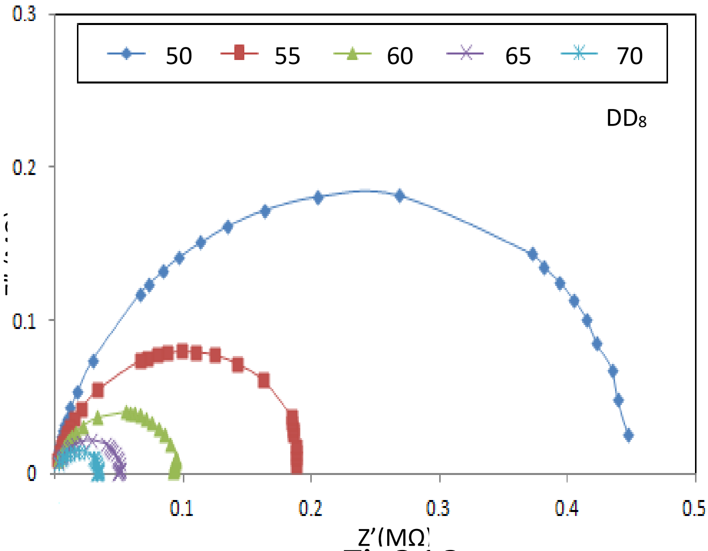

Fig.3.1.2

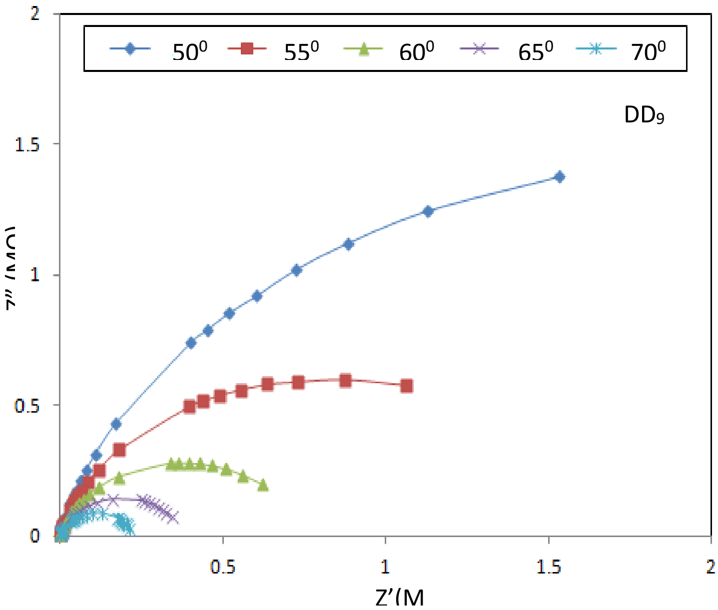

Fig.3.1.3

Also it may be argued that as the temperature increases for PTh-PVAc films doped with Bromine reduces the arc of semicircle indicating the increase in conductivity. The impedance spectra in figure 5.24 exhibited a single capacitive time constant at high frequencies and a finite length transport impedance with a permeable boundary at the low frequency end. The basic features of the spectra seem to be qualitatively similar to those obtained by Johnson et al. [14] for polythiophene films and Komura et al [23] for polypyrrole polystyrenesulfonate composite films. The arcs are found to be highly depressed for all films for different temperatures which indicate the distribution of relaxation times [15]. From the semicircle, the values of bulk resistance are calculated and noted in table 3.2.2. The variation of log f versus Z' at different temperature is as shown in fig 3.1.4-3.16.

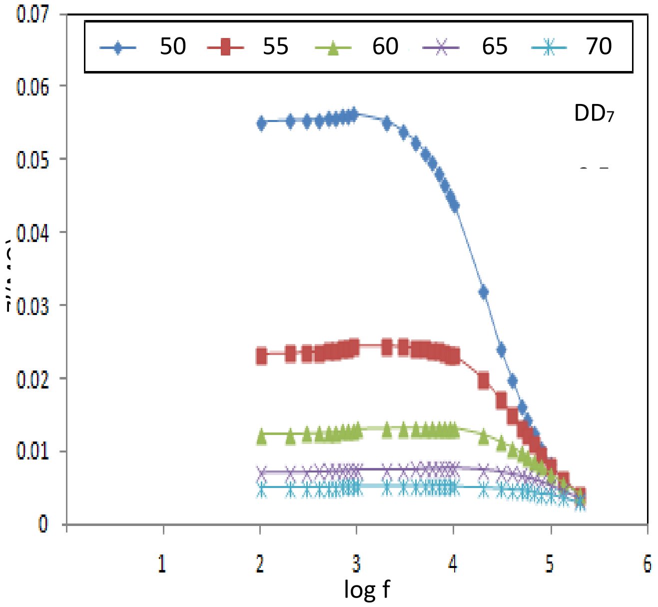

Fig.3.1.4

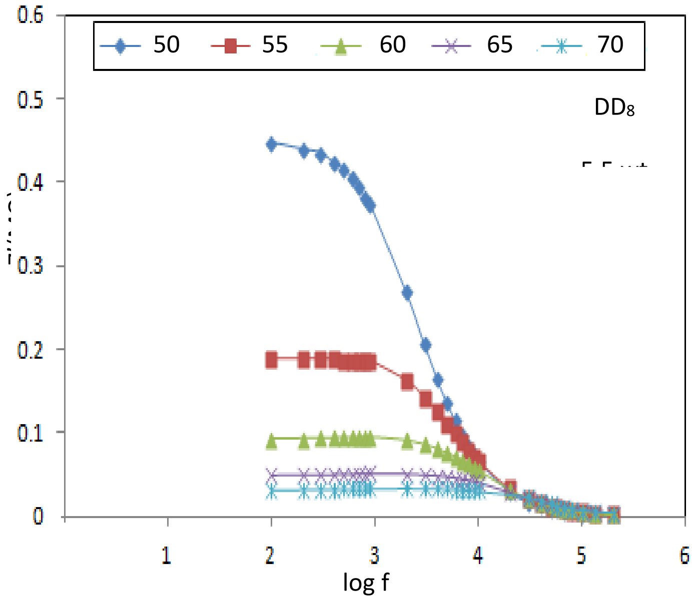

Fig.3.1.5

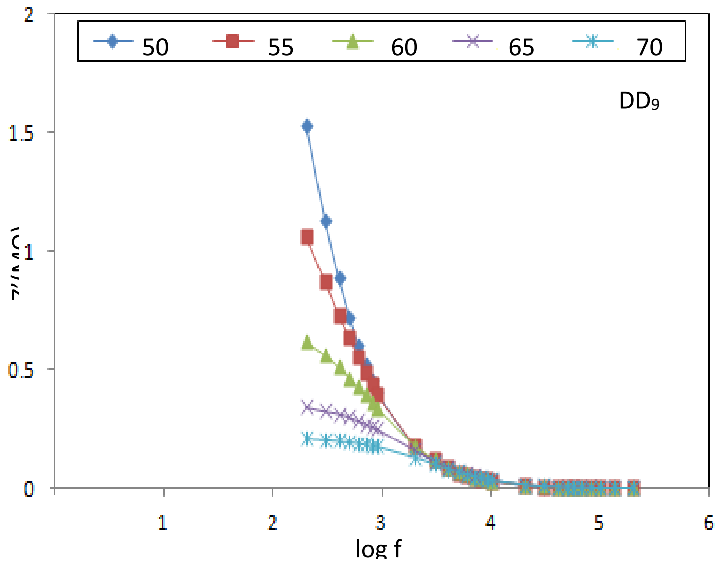

Fig.3.1.6

From the figure it is observed that the pure PTh-PVAc sample shows the wide variation of resistance with all frequencies. The resistance of the sample is found to be decreased with increase in frequency. Also as the concentration of the dopant Bromine is increasing, the sample constitutes much lesser resistance for increasing frequencies. The magnitude decreases on increasing temperature in the low frequency range which merges in the high-frequency region irrespective of temperature. This nature may be due to the release of space charge [16].

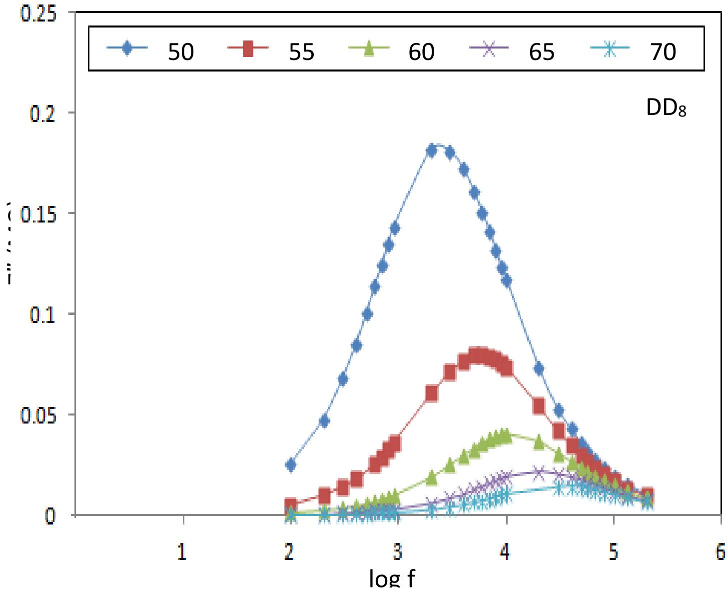

Fig.3.1.7

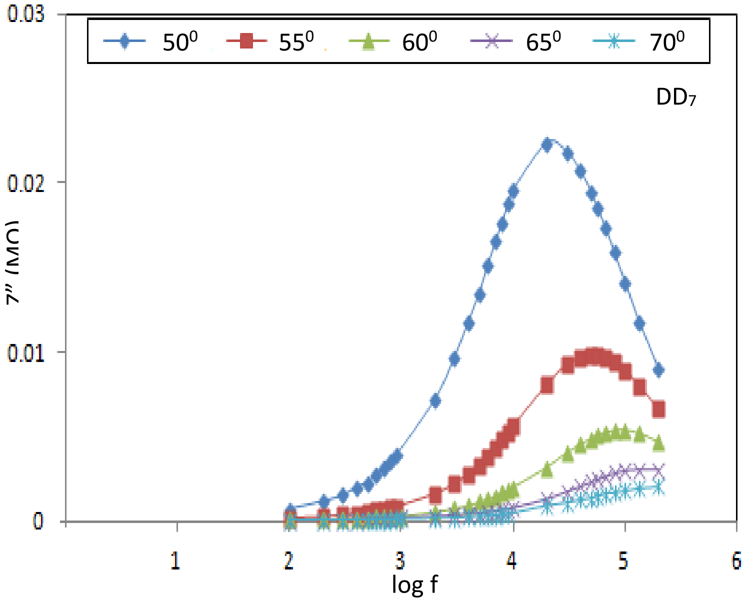

Fig.3.1.8

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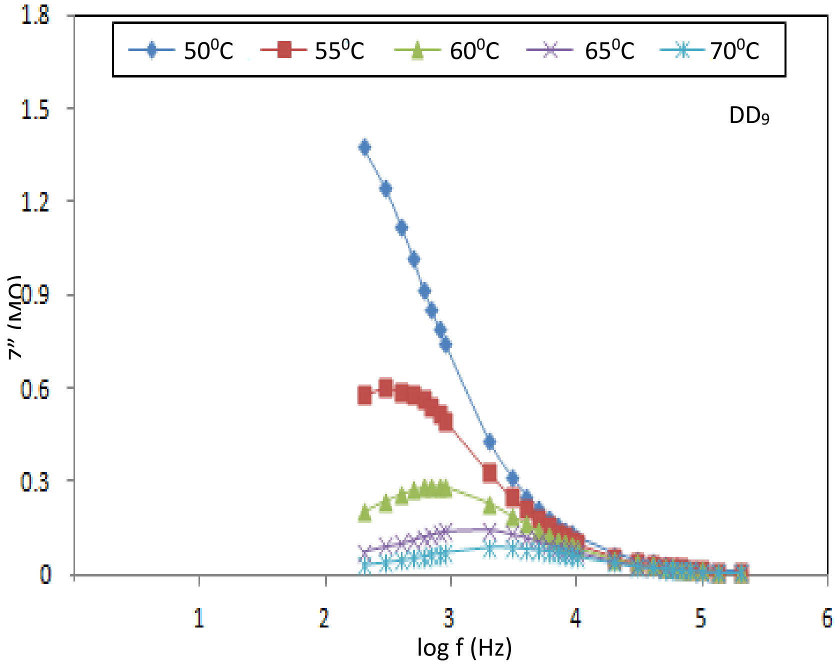
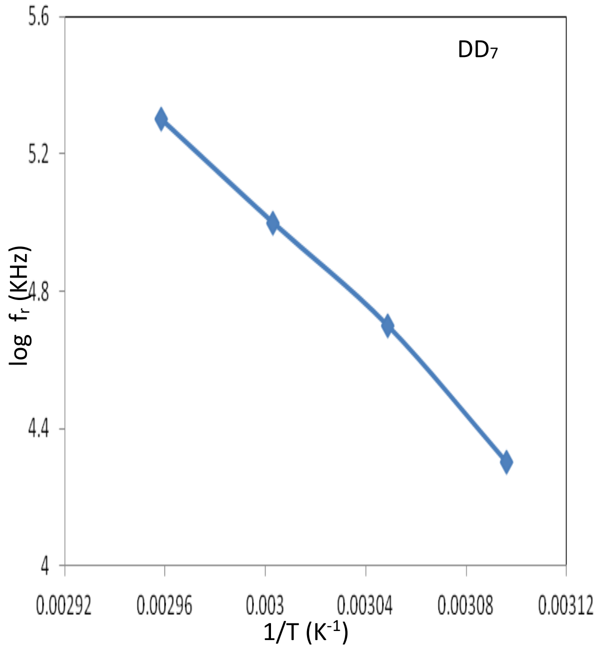


Fig.3.1.9



The reduction in barrier properties of the materials with rise in temperature may be a responsible factor for enhancement of a.c. conductivity of the materials at higher frequencies [17-18]. Further, in the low frequency region, there is a decrease in magnitude with rise in temperature showing negative temperature coefficient of resistance (NTCR) behavior [19]. This behavior is changed drastically in the high frequency region showing complete merger of plot above a certain fixed frequency. The variation of log f versus Z" is as shown in fig.3.1.7-3.1.9 which shows asymmetric peaks at different temperatures. Each peak is associated with a maximum frequency called as relaxation frequency. As the temperature increases the relaxation frequency is found to be shifting towards higher frequency [20-21]. The relaxation frequency (fr) follows the Arrhenius behavior as same in **equation no 3.2.1**. This equation is explored to find out the dielectric relaxation activation energy (ΔE) and relaxation time (τ).

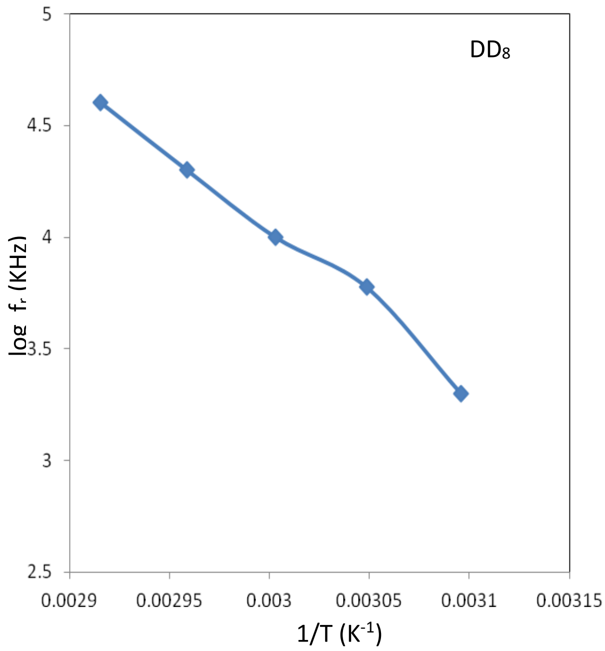


Fig 3.1.10

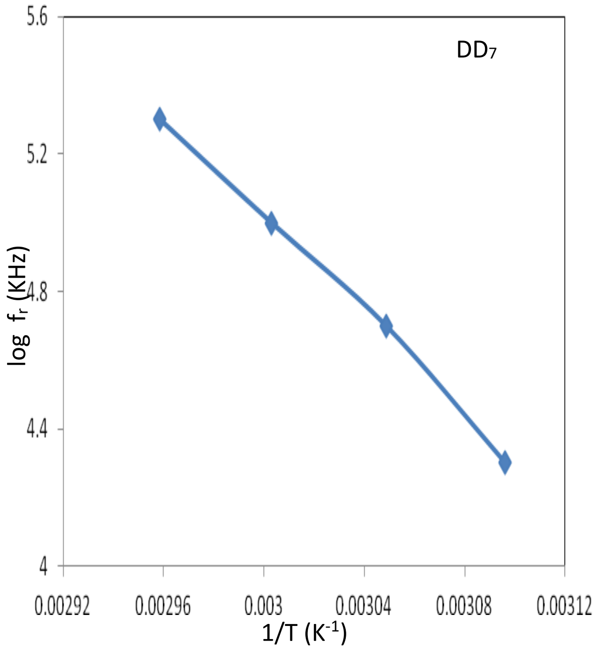


Fig 3.1.11

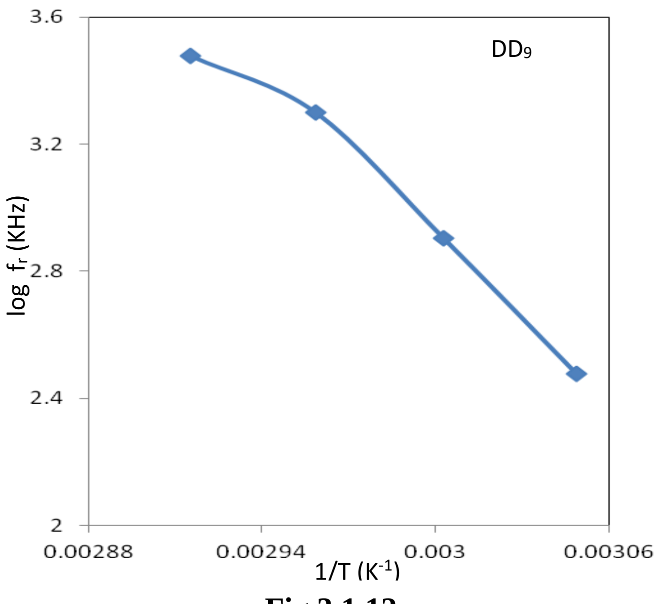


Fig 3.1.12

The variation of 1/T versus log fr for samples DD7, DD8 and DD9 in fig.3.1.10-3.1.12. shows a straight line nature [20-22]. The values of peak frequencies (log f) are plotted against the 1/T as shown in fig 3.2.10-3.2.12. From this straight lines dielectric relaxation activation energy (ΔE) and relaxation time (τ) is calculated and tabulated in table 3.1.1.

Table 3.1.1: Dielectric relaxation activation energy and Relaxation time of PTh-PVAc with doped Bromine

Sr.No.	Bromine wt %	ΔE (eV)	τ (μs)
1	3.5	0.6224	2.51
2	5.5	0.5985	17.78
3	10.4	0.6619	199.52

From the table it is observed that, dielectric relaxation activation energy and relaxation time is maximum for the sample 10.4 wt % of Bromine and minimum for 3.5 wt % of Bromine.

Table 3.1.2: Bulk resistance and Bulk capacitance of PTh-PVAc doped with Bromine at different temperature

Bromine wt %	323K		328K		333K		338K		343K	
	R_b(KΩ)	C_b(pF)	R_b(KΩ)	C_b(pF)	R_b(KΩ)	C_b(pF)	R_b(KΩ)	C_b(pF)	R_b(KΩ)	C_b(pF)
3.5	57	139.7	24.2	131.6	13	153.1	7.9	150.2	5.3	-
5.5	450	176.9	185	172.1	98	180.3	51.8	153.7	35	113.7
10.4	3800	-	1700	312.2	750	303.3	380	209.5	225	235.1

The values of bulk resistance (Rb) and bulk capacitance (Cb) at peak frequencies are noted in table 3.1.2.From the table it is observed that the bulk resistance of the sample is decreasing as the temperature increases but the bulk capacitance of the samples almost remain constant at all temperature. The bulk capacitance is found maximum for the sample with 10.4 wt % of dopant Bromine.

4. Conclusion

The impedance spectra of PTh-PVAc for the samples 5.5, 10.4, 14.9 and 22.5 wt % of Bromine dopant consist of only one arc which may be taken to mean that the conduction processes have identical time constants. The variation of real axis Z' with log f shows negative temperature coefficient of resistance (NTCR). The variation of imaginary axis Z" versus log f shows asymmetric peaks at different temperatures that lead to Debye type of relaxation. On the basis of impedance spectra various parameters such as relaxation time, bulk resistance, bulk capacitance, dielectric activation energy etc. are calculated. Dielectric relaxation activation energy and relaxation time is maximum for 5.5wt% of Bromine and minimum for 10.4 wt % of Bromine. The bulk capacitance is found to be maximum for the sample with 5.5 wt % Bromine. Dielectric relaxation activation energy and relaxation time is minimum for 5.5 wt % of Bromine. The bulk capacitance is found to be maximum for the sample with 10.4 wt % Bromine.

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