Available online at **www.pelagiaresearchlibrary.com**

Pelagia Research Library

Der Chemica Sinica, 2012, 3(1): 204-209

ISSN: 0976-8505
CODEN (USA) CSHIA5

Dielectric studies of Phenylenediamine doped with organic acids

Snehal R. Kargirwar [a, b], *Sanjay R. Thakare [a], M. D. Choudhary [b]

[a]Department of Chemistry, Science College, Congress Nagar, Nagpur, India
[b]B. D. College of Engineering, Sevagram, Wardha, India

ABSTRACT

The polymer of aniline and its derivatives is one of the most widely researched electrically conductive polymers. Phenylenediamine doped with different concentrations of organic acids which act as dopant were prepared by chemical oxidation method. In this paper we have reported that as the concentration of dopant increases, ε' and ε" increases with temperature, may be attributable to free charge build up at the interface between the sample and the electrode (space-charge polarization).

Keywords : conducting polymer, phenylenediamine, dielectric study.

INTRODUCTION

The polyaniline (PANI) family of polymers has been the subject of increased investigation because of its electronic properties which can be modified by protonation, giving rise to unusual chemical, optical, electrochromic, and electrical properties in both insulating and conducting forms [1-3]. The polymer of aniline and its derivatives is one of the most widely researched electrically conductive polymers because of their easy preparation, high stability, good electrical conductivity, and high gas-separation ability. It is believed that the investigations of polymers synthesized from aromatic diamine are more attractive since they exhibit more novel multifunctionality than PANI. Phenylenediamines are a class of aniline derivatives having an extra $-NH_2$ group in the *o*-, *m*- or *p*-position. Although reports are available on polymerization of *m*- and *p*- isomers [4], *o*-phenylenediamine (OPD) is the most frequently studied member. Poly(*o*-phenylenediamine) (POPD) has apparently shown different characteristics of molecular structure and properties when compared with PANI [5]. It has been reported to be a highly aromatic polymer containing 2,3-diaminophenazine or quinoxaline repeat unit and exhibits unusually high thermostability [4,6,7] although a PANI like structure has also been proposed [8].

Little is known about the dielectric properties of conducting polymers associated with the conducting mechanism [9-11]. The charge transport mechanism of conducting polymer has been investigated in recent years using dielectric relaxation behavior and ac measurements; etc. [12-14]. Low frequency conductivity and dielectric relaxation measurement especially have proven to be valuable in giving additional information on the conduction mechanism as the *ac* conductivity measurement alone does not provide. The relaxation of an electric field in a charge carrier system is attributable to the charge hopping of mobile carriers, which can lead to both short-range (or local) *ac* conductivity and long-range dc conductivity. We have analyzed the experimental data by means of two different formalism complex permittivity ε' and permittivity loss ε".

1.2 Synthesis

Phenylenediamine (PDA), ammonium persulfate (APS), oxalic acid, picric acid, acetic acid, salicylic acid and benzoic acid were used as received. All chemicals were of analytical grade. 0.2M phenylenediamine and specific molar concentrations of oxalic acid (0.1M-0.4M) were dissolved in 100 ml deionized water with stirring at room temperature for 30 min. The stirring was then stopped and 50ml aqueous solution of 0.2M APS was added and the reaction was left for 12 hrs. The resulting PDA precipitate was washed with distilled water and methanol several times. Finally the product was dried in vacuum oven at 80^0C temperature for 12 hrs.

Similarly by keeping the monomer constant i.e. 0.2M Phenylenediamine and by varying the concentration of above organic acids were prepared by the above procedure.

1.3 Experimental Techniques:

The capacitance of the thin pellet of the polymers were measured by using direct reading of LCR bridge (Aplab-4910 D, Auto compute LCR-Q meter) of accuracy 0.01 PF, for the measurement of capacitance, at frequency 1KHz as a function of temperature.

The permittivity or real dielectric constant (ε') of the polymers was determined by the equation.

$$\varepsilon' = C\, d / \varepsilon_0 A$$

Where, C= capacitance of the polymer sample.
d = thickness of the pellet of polymer.
A = surface area of pellet.
ε_0 = permittivity in vacuum (8.854×10^{-12} F/m)

The dielectric loss (ε”) was calculated by the equation.

$$\varepsilon'' = \varepsilon' \tan \delta$$

Where tan δ = percentage dissipation factor

1.4 Observations and calculations

By the above procedure we have calculated for 0.1M to 0.4M concentration of oxalic acid with temperature but we have shown ε' and ε'' values and tabulated as follows as shown in table 1 and we have shown the figures of ε' vs ε'' of different concentrations of salicylic acid, acetic acid, benzoic acid and picric acid as shown in Fig.1-(a) to 1-(j)

Table 1 shows dielectric constant (ε') and dielectric loss (ε”) of PDA doped with 0.1M to 0.4M concentration of oxalic acid.

T	0.1M		0.2M		0.3M		0.4M	
^{0}C	**ε'**	**ε''**	**ε'**	**ε''**	**ε'**	**ε''**	**ε'**	**ε''**
100	1631.57	580.01	1411.00	347.70	1379.48	781.13	1897.67	2567.89
95	1568.55	521.28	1361.98	325.83	1267.45	583.80	1827.64	2296.04
90	1502.03	474.27	1337.47	306.47	1190.422	471.64	1743.61	1878.89
85	1435.50	414.04	1302.46	263.92	1099.39	395.74	1579.06	1291.135
80	1358.48	352.94	1277.95	248.33	1046.87	353.19	1460.01	925.23
75	1284.95	296.55	1256.94	226.06	987.35	309.22	1277.95	602.80
70	1235.93	254.20	1218.43	204.09	959.34	287.91	1228.93	553.07
65	1218.43	243.24	1211.43	195.39	931.33	263.08	1127.40	464.90
60	1179.91	223.04	1176.41	189.13	903.32	237.09	1022.36	378.93
55	1155.41	216.36	1172.91	181.00	882.31	229.41	994.35	353.10
50	1148.40	214.21	1148.40	174.26	840.29	210.49	920.82	282.46
45	1078.38	196.78	1109.89	162.26	833.29	194.69	882.31	267.28
40	1018.86	180.01	1078.38	153.39	827.69	177.61	870.05	250.73
35	997.854	172.34	1045.82	143.65	821.04	169.28	858.15	242.41

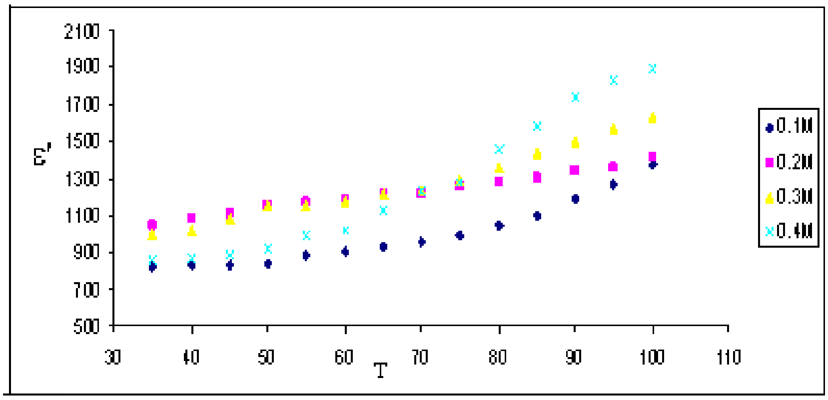

Fig. 1-a) shows permittivity constant of PDA doped with 0.1M to 0.4M concentration of oxalic acid

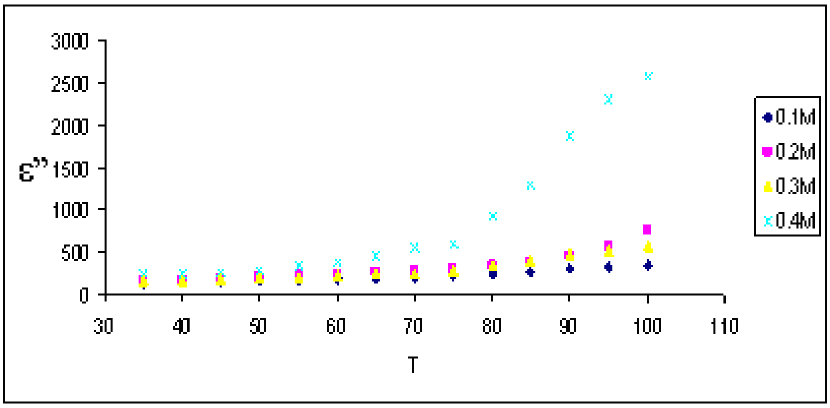

Fig. 1-b) shows permittivity loss of PDA doped with 0.1M to 0.4M concentration of oxalic acid

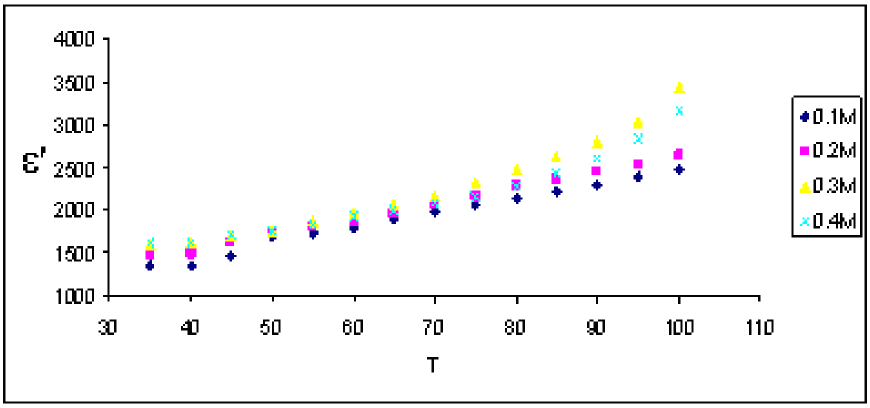

Fig. 1-(c) shows permittivity constant of PDA doped with 0.1M to 0.4M concentration of salicylic acid

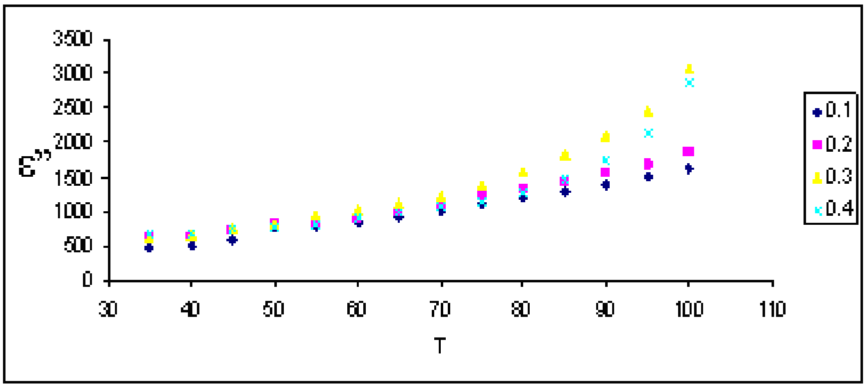

Fig. 1-(d) shows permittivity loss of PDA doped with 0.1M to 0.4M concentration of salicylic acid

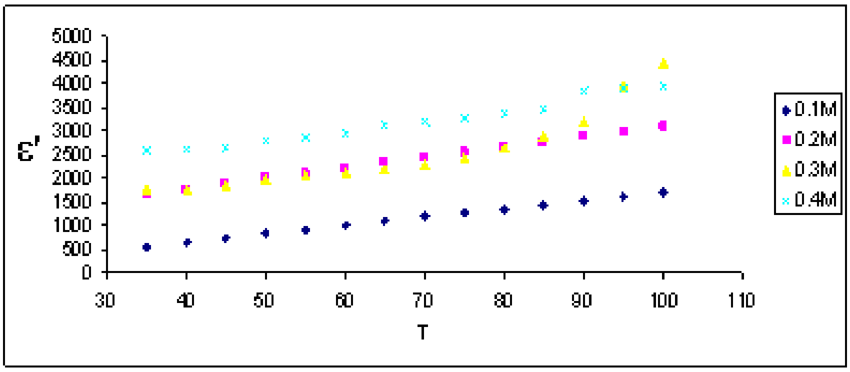

Fig. 1-(e) shows permittivity constant of PDA doped with 0.1M to 0.4M concentration of acetic acid

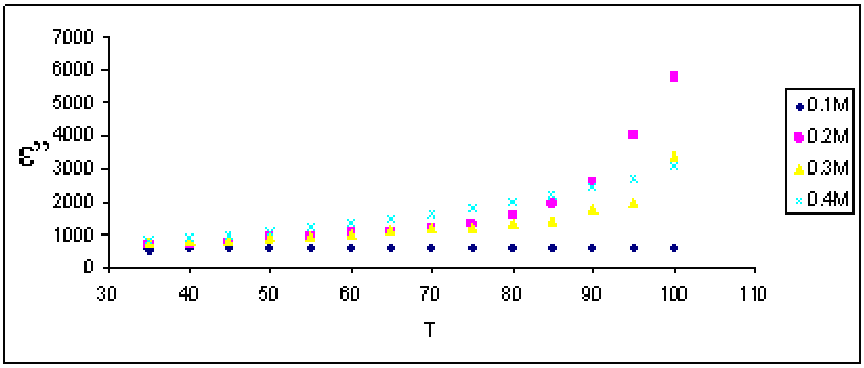

Fig. 1-(f) shows permittivity loss of PDA doped with 0.1M to 0.4M concentration of acetic acid

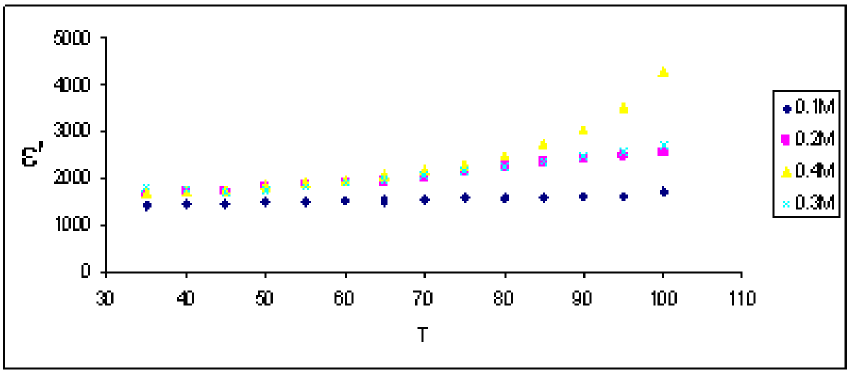

Fig. 1-(g) shows permittivity constant of PDA doped with 0.1M to 0.4M concentration of benzoic acid

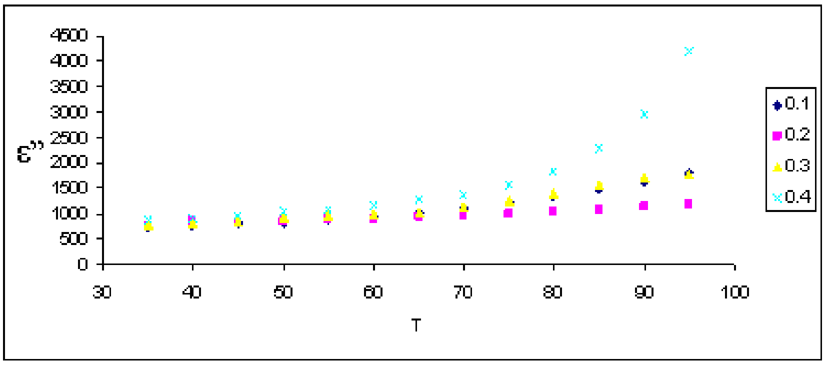

Fig. 1-(h) shows permittivity loss of PDA doped with 0.1M to 0.4M concentration of benzoic acid

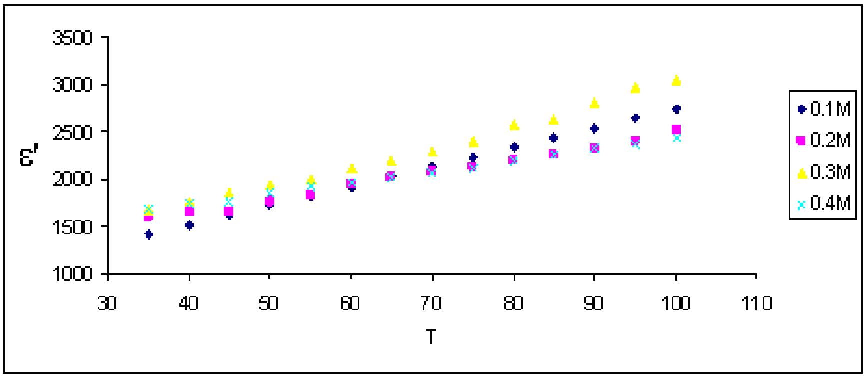

Fig. 1-(i) shows permittivity constant of PDA doped with 0.1M to 0.4M concentration of picric acid

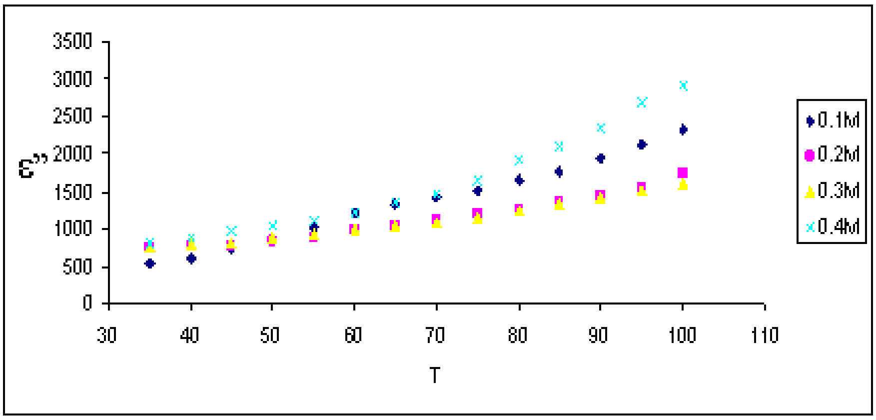

Fig. 1-(j) shows permittivity loss of PDA doped with 0.1M to 0.4M concentration of picric acid

RESULTS AND DISCUSSION

It has been observed that the variation of ε' and ε" with temperature is nonlinear. These curves show the existence of relaxation during the change of temperature. It has been observed that as the concentration of dopant increases, ε' and ε" increases with temperature, may be attributable to free charge build up at the interface between the sample and the electrode (space-charge polarization). It has been observed that at higher temperature ε' shows higher value for 0.1M concentration of organic acids as compared to 0.4M concentration and ε" shows lower value for 0.1M concentration as compared to 0.4M concentration. As the temperature decreases it shows similar results.

CONCLUSION

It has been observed that as the concentration of dopant increases, ε' and ε" increases with temperature, may be attributable to free charge build up at the interface between the sample and the electrode (space-charge polarization).

Acknowledgement
The authors express their gratitude to Physics Department, Shivaji Science College, Nagpur for providing LCR meter bridge for dielectric study.

REFERENCES

[1] Pouget J P, Jozefowicz M E, Epstein A J, Tang X and Macdiarmid A G, *Macromolecules*, 24 (**1991**) 779.
[2] Baughman R H, Wolf J F, Eckhardt H and Shacklette L W, *Synth Met*. 25 (**1998**) 121.
[3] Heeger A J, *Faraday Discuss Chem Soc*, 88 (**1989**) 1.
[4] Cataldo F, *Eur. Polym. J.* 32 (**1996**) 43.
[5] Li X G, Huang M R, Duan W and Yang Y L, *Chem. Rev*. 102 (**2002**) 2925.
[6] Premasiri A H and Euler W B, Macromol. *Chem. Phys.* 196 (**1995**) 3655.
[7] Chan H S O, Ng S C, Hor T S A, Sun J, Tan K L and Tan B T G, *Eur. Polym. J.* 27 (**1991**) 1303.
[8] Yano J, *J. Polym. Sci. Part A: Polym. Chem*. 33 (**1995**) 2435.
[9] Singh R, Arora V, Tandon R P, Mansingh A and Chandra S. *Synth Met*. 104 (**1999**) 137.
[10] Zuo F, Angelopolous M, Macdiarmid A G, Epstein A J. *Phys Rev B*, 39 (**1989**) 3570.
[11] Singh R, Narula A K, and Tandon R P, *Synth Met*, 82 (**1996**) 245.
[12] Capacciooli S, Lucchesi M, Rolla P A and Ruggeri G. *J Phys: Condens Matter*, 10, (**1998**) 5595.
[13] Ram M K, Annapoorni S, Pandey S S and Malhotra B D. *Polymer*, 39 (**1998**) 3399.
[14] Moon G H and Seung I S, *J Appl Polym Sci* 82 (**2001**) 2760.