ELSEVIER

PII: S0032-3861(97)10285-3

Polymer Vol. 39 No. 15, pp. 3399–3404, 1998

0032-3861/98/$19.00+0.00

Dielectric relaxation in thin conducting polyaniline films

M. K. Ram, S. Annapoorni, S. S. Pandey and B. D. Malhotra*
Biomolecular Electronics and Conducting Polymer Research Group,
National Physical Laboratory, Dr K. S. Krishnan Road, New Delhi-110 012, India
(Received 29 April 1997; revised 18 August 1997)

The results of dielectric measurements carried out on polyemeraldine salt in an Al–polyemeraldine salt–Al configuration as function of frequency and temperature are reported. The analysis of the dielectric data obtained for Al–polyemeraldine salt–Al configuration shows the space-charge phenomenon. The mobility was obtained as a function of temperature and thickness of the sandwiched emeraldine salt, respectively. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyaniline; emeraldine salt; blocking contact)

INTRODUCTION

The charge transport mechanism in conducting polymers has been investigated in recent years using a number of experimental methods such as dielectric relaxation[1–3], ac conductivity[4] and photoconductivity techniques[5]. It has been proposed that nonlinear excitations such as solitons and polarons play an important role in the transport of electrical charge in conducting polymers[6–12]. Dielectric spectroscopy has been found to be a valuable experimental tool for understanding the phenomenon of charge transport in conducting polymers[13–15].

Among the various conducting polymers, polyaniline has become the subject of increasing interest due to its charge transport properties. Polyaniline that can be produced in its various oxidation states such as emeraldine base (EB), leucoemeraldine and polypernigraniline etc.[16–19], its excellent stability coupled with the ease of preparation has projected this electronic material towards a large number of potential applications[20–26]. The electronic state in this conducting polymer can be controlled by variation in protons by way of doping the EB by acids, converting it from an insulating state (conductivity $s = 10^{-14}$ S cm^{-1}) to a metallic state ($s = 5$ S cm^{-1}).

Philip *et al.*[27] have proposed a dimer model that explains the observed electrical conductivity of leucoemeraldine as a function of oxidation. Javadi *et al.*[27] have experimentally shown that a model based on granular polymeric metal particles and localization within metallic islands plays an important role in the frequency and temperature dependence of dielectric constant of polyaniline[28]. Further, the barriers present among the granular polymeric metal particles of emeraldine salt of polyaniline have been suggested to arise from the presence of crosslinks, chain ends and protonated amine groups (NH_2^+) etc. Zuo *et al.* have carried out various studies relating to both temperature dependence and electric field dependence of *s*, including the dependence of thermopower as a function of protonation level of polyaniline[29]. These studies have shown that the charge transport in EB is dominated by phase segregation with protonated and unprotonated regions, suggesting the operation of a charging-energy-limited-tunneling (CELT) mechanism in this system. Ram *et al.* have recently reported the results of ac conductivity studies carried out on EB in terms of a polarons-hopping model, which is applicable to amorphous semiconductors[30].

Space charge relaxation studies have been used to experimentally determine the mobility of charge carriers in thin films of organic conducting polymers[6]. In this paper, we report the results of our dielectric studies carried out on aluminium–polyaniline–aluminium (Al–PANI–Al) capacitor configuration in the frequency region from 10^3 to 10^7 Hz using blocking contacts on thin films of polyaniline. This data is used to determine the effect of both temperature and thickness of polyaniline on the mobility of charge carriers in polyaniline film.

EXPERIMENTAL DETAILS

Synthesis of EB used for preparation of thin films in the present investigation has been carried out using a standard procedure as reported in one of our earlier publications[21,31]. The EB (1 g) is stirred magnetically in 250 ml of *N*-methyl pyrrolidinone (NMP) (b.p. 202°C) at room temperature for about 8 h, and the blue solution is filtered through a Buchner funnel. This blue solution has been used to cast EB films on glass plates, and is heat treated at 160–170°C by a solution cast method for obtaining free standing films. These films are washed with acetone and protonated by inserting in 1 M aqueous HCl for about 48 h, and are then dried under dynamic vacuum for about 24 h. Films of various thicknesses (10–150 mm) of emeraldine salt thus obtained are annealed at 105°C for removal of any moisture in the sample. These polyaniline films are characterized by u.v–visible and *FT*i.r. spectroscopic techniques. The observed spectroscopic (u.v.–visible and i.r.) peaks have been found to be consistent with those published in the literature[31,32]. The electrical conductivity of the above polyaniline films, measured using the four-point-probe method, varies from 5 to 10 S cm^{-1}.

Al–PANI–Al capacitor configurations used for dielectric measurements were fabricated by vacuum deposition

---

* To whom correspondence should be addressed

(10^{-6} Torr) of aluminium (99.9%). Current–voltage (*I–V*) characteristics of Al–PANI–graphite and Al–PANI–Al capacitor configurations were experimentally determined using a Keithley (617) electrometer. Both the dielectric and the capacitance measurements have been performed on various Al–PANI–Al configurations, having different thicknesses of polyaniline at a signal voltage of 0.1 V, with different dc bias (0, 50, 100 and 200 mV), using an HP 4192A impedance analyser operating in the frequency range 5–13 MHz.

THEORY

Organic semiconducting polymers are known to exhibit similar *I–V* characteristics and capacitance–voltage (*C–V*) characteristics as their inorganic counterparts. *I–V* and *C–V* characteristics have recently been reported for various metal/polyaniline junctions[6,22].

Formation of space charge in a polyaniline film is illustrated in *Figure 1a*. The resulting electric field and the charge distribution inside the sample are shown in *Figure 1b* and *c*, respectively. As a result of the presence of a strong bias across the sample, the ions in the sample align towards their respective electrodes. Moreover, due to the blocking nature of the aluminium electrodes[6,21,30], there is no injection or extraction of charge carriers into the PANI region. Thus a space charge near the electrodes and the depletion region inside the sample is created. This results in an electric field gradient across the sample (*Figure 1b* and *c*).

Keeping in view the blocking nature of (Al) electrodes with polyaniline, the theoretical basis for the interpretation of the dielectric data has been proposed. The equation of motion for the space charge boundary (*Figure 1*), when an alternating voltage is superposed on the existing bias, has been used.

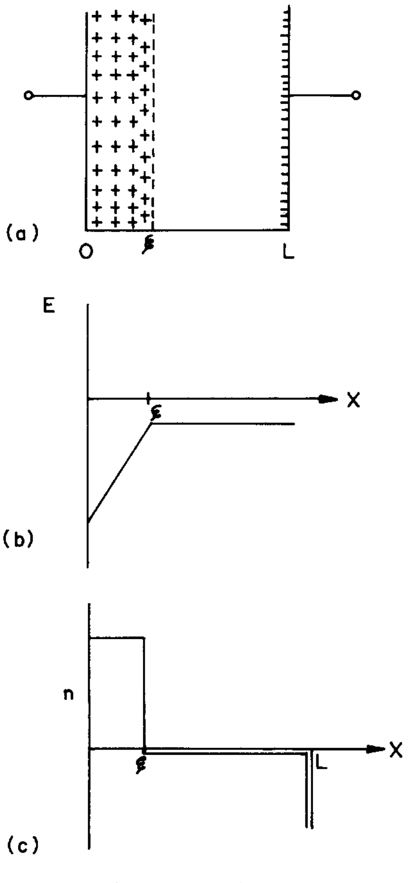

Figure 1 (a) Formation of space charge in a polyaniline (emeraldine salt) film. (b) The electric field gradient in a polyaniline (emeraldine salt) film. (c) Variation of carrier concentration in a polyaniline (emeraldine salt) film under the influence of space charge

We make a simplifying assumption by considering the movement of the space charge boundary at the cathodic region. Further, the width of the anodic space-charge region is also ignored as an approximation. Coelho[33] has discussed in detail the analysis and derivation of polarization, based on such an approximation.

Let the space charge region be limited to $0 < x < \xi$, as shown in *Figure 1*. The electric field intensity *E*, in the region $\xi < x < L$, is approximately given by

$$\mathrm{E}(\xi) = (1/L)[V_s - (ne/2\epsilon\epsilon_0)^2\xi] \qquad (1)$$

where ϵ_0 is the permittivity in free space, *e* is the magnitude of the electronic charge, ϵ is the high frequency permittivity, V_s is the static bias across the sample, and *n* is the concentration of charge carriers.

The equation governing the movement of the space charge boundary made of charges with mobility μ can be written as:

$$\mathrm{d}\xi/\mathrm{d}t = -\mu\mathrm{E}(\xi) \qquad (2)$$

For a constant static bias $V = V_s$, the final position of the boundary ξ_s is given by;

$$\xi_s = [(2\epsilon\epsilon_0/ne)V_s]^{1/2} \qquad (3)$$

In a situation where a steady bias is superposed by a small ac component $V = V_0\exp(i\omega t)$, the capacitance is given by;

$$C = C_{ae}[(\alpha^2 + \beta^3)]/(\alpha^2 + \beta^2)] \qquad (4)$$

where $C_{ae} = \epsilon\epsilon_0 A/L$ and *A* is the area of the electrode.

The dielectric loss tan(δ) is given by;

$$\tan\delta = \beta(\beta - 1)\alpha/\beta^3 + \alpha^2) \qquad (5)$$

where α and β are dimensionless variables defined as

$$\alpha = \omega L^2/2\mu V_s \qquad (6)$$

and

$$\beta = (neL^2/\epsilon\epsilon_0 V_s)^{1/2} = L/\xi_s \qquad (7)$$

From equation (5) it is clear that tan(δ) is maximum when

$$\alpha^2 = \beta^3 \qquad (8)$$

From equation (8), the mobility μ of the charge carriers can be written as

$$\mu = [\omega_m^4\epsilon^3\epsilon_0^3L^2/n^3e^3V_s]^{1/4} \qquad (9)$$

where ω_m is the frequency at which the dielectric loss is maximum and V_s is the static bias across the film.

RESULTS AND DISCUSSION

Figure 2a shows the results of our *I–V* measurements on Al–PANI–graphite and Al–PANI–Al configuration fabricated using a given thickness (30 μm) of polyaniline. From this figure, one can clearly see that Al makes a Schottky contact with polyaniline (curve 1), whereas it forms rectifying contacts on both sides of the Al–PANI–Al configuration. In the light of this result, *I–V* measurements (*Figure 2b*) on Al–PANI–Al configurations have been carried out for various thicknesses (15, 32, 45, 54 and 145 μm) of polyaniline at room temperature. From these results, it can perhaps be concluded that Al shows the rectifying behaviour in all Al–PANI–Al configurations. *Figure 3* gives the variation of capacitance with frequency measured for a number of Al–PANI–Al structures with varying thickness of polyaniline at room temperature at 100 mV dc bias. The value of the capacitance gradually decreases with increase in frequency resulting into a resonance behaviour at 680 kHz for all Al–PANI–Al

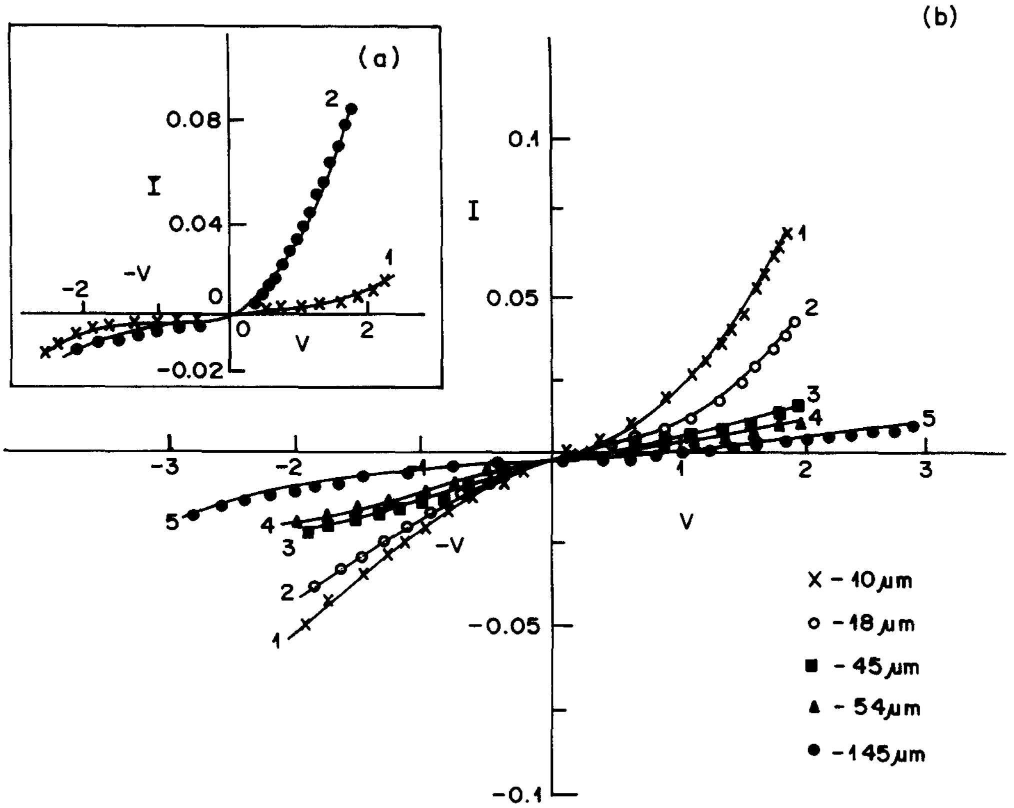

Figure 2 (a) Variation of current, I (mA)–voltage, V (volts) for Al–PANI (emeraldine salt)–graphite and (×) Al–PANI (emeraldine salt)–Al configurations. (b) Variation of current, I (mA)–voltage, V (volts) characteristics in Al–PANI (emeraldine salt)–Al configuration as a function of thickness: curve 1 (10 μm); curve (18 μm); curve 3 (45 μm); curve 4 (54 μm); curve 5 (145 μm)

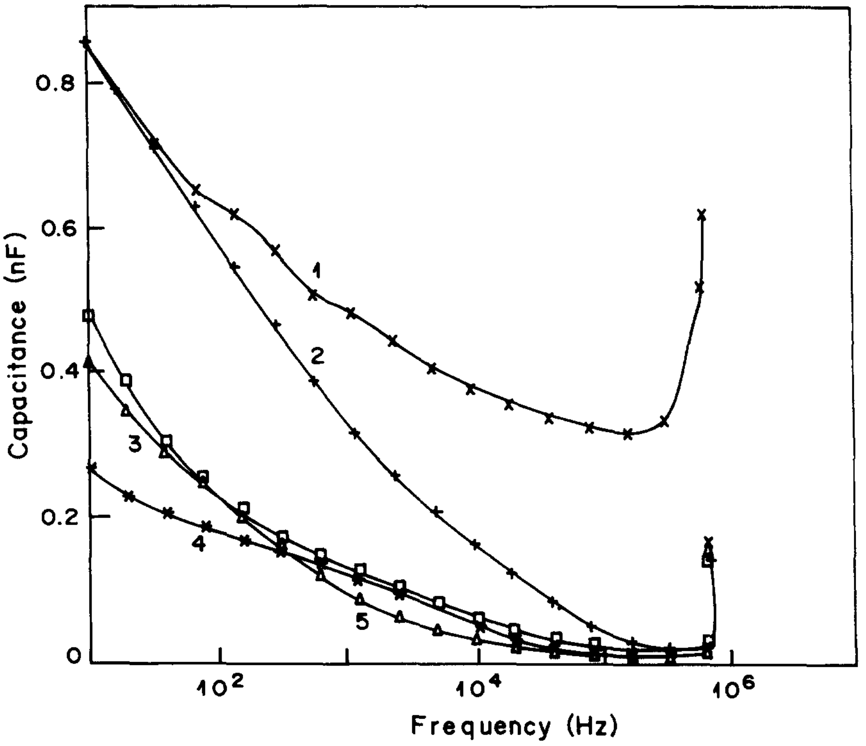

Figure 3 Variation of differential capacitance (nF) with logarithmic frequency for Al–PANI (emeraldine salt)–Al configuration at static bias of 100 mV as a function of thickness: curve 1 (10 μm); curve 2 (18 μm); curve 3 (45 μm); curve 4 (54 μm); curve 5 (145 μm)

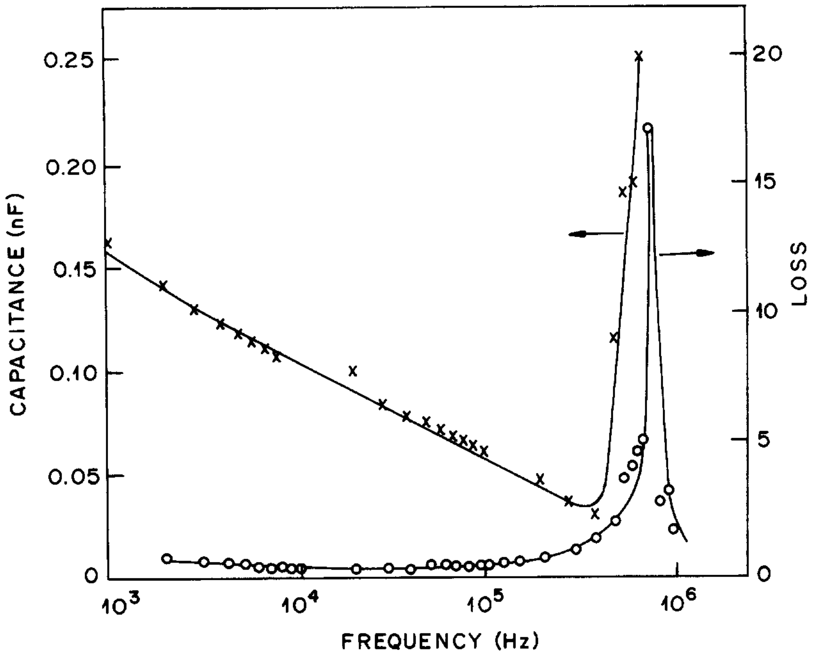

Figure 4 Variation of differential capacitance (nF) (×) and dielectric loss (O) with logarithmic frequency obtained at 0 bias

structures. *Figure 4* shows the results of the capacitance measurements conducted on desired Al–PANI–Al configurations at 0 V bias fabricated using polyaniline films. The slow decrease of capacitance with frequency coupled with the observed resonance at 680 kHz (*Figures 3 and 4*) indicates the presence of space charge polarization in the Al–PANI–Al structures. *Figure 5a* and *b* exhibit the results of the systematic studies carried out on a given Al–PANI–Al structure relating to both dielectric loss and capacitance as a function of frequency at various bias voltages (50, 100 and 200 mV). The observed increase in the value of both capacitance (*Figure 5a*) and dielectric loss (*Figure 5b*) with bias voltage indicates the increased density of charge region of Al–PANI–Al configuration. Interestingly, the resonance occurs at the same frequency (*Figure 5a* and *b*) as indicated in (*Figure 4*).

Figure 6a shows the variation of imaginary part of the dielectric constant ϵ'' as a function of ω. One can clearly see (*Figure 6a*) the presence of two relaxation times in polyaniline. The values of these relaxation times have been calculated and are found to be 1 and 0.3 ms, respectively. *Figure 6b* is the Cole–Cole plot obtained at 120, 290, 323 and 373.6 K, respectively. The marked deviation (scew type) from semi-circle to arc, as seen in *Figure 6b*, points out to the operation of a complex relaxation behaviour in this typical system arising due to presence of charge carriers and their conductivity. Consequently, one can express complex permittivity as

$$\epsilon^* = \epsilon + [(\epsilon_0 - \epsilon_\alpha)/1 + i\omega)] - i\sigma \qquad (10)$$

where ϵ_0 is the static dielectric constant, T is the relaxation time, ϵ_α is the instantaneous dielectric permittivity, δ is the conductivity of the medium, and ω is the angular frequency. The observed skew type behaviour (*Figure 6b*) can probably be understood to arise both from the conduction of various charge carriers and their resulting dipoles.

The nature of the semi-circle (i.e. skew type) indicates the presence of different relaxation states. Further, the relaxation time obtained from the Cole–Cole plot is found to be dependent on temperature and obeys the following

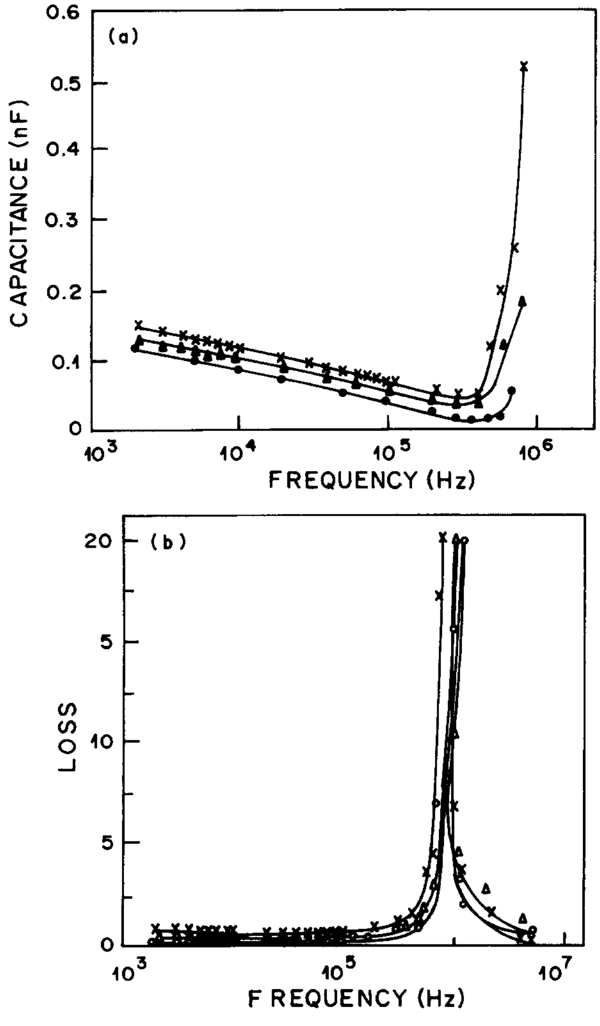

Figure 5 (a) Variation of differential capacitance (nF) with logarithmic frequency (Hz) for Al–PANI (emeraldine salt)–Al at various bias voltages, 50 mV (0), 100 mV (Pt) and 200 mV (×). (b) variation of dielectric loss with logarithmic frequency (Hz) for the Al–PANI (emeraldine salt)–Al at various bias voltages: 50 mV (0); 100 mv (△); 200 mV (×)

Arrhenious equation:

$$T = T_0 \exp[E_a'/k_B T] \tag{11}$$

where E_a' is the activation energy, and k_B is the Boltzmann constant. The activation energies E_a' of conduction calculated using equation (11) have been found to be 0.042 and 0.028 eV respectively, implying some relaxation of dipoles in polyaniline. *Figure 7b* shows the Cole–Cole plots obtained at various temperatures (120, 290, 323 and 373 K). The observed shift of the Cole–Cole plot with increase in temperature indicates the presence of multiple relaxation in the given Al–PANI–Al configuration. Moreover, the departure from skew behaviour beyond 0.3 μF (curve 2, *Figure 7b*) seen in the Cole–Cole plot signifies the contribution originating from the Al contact in the given Al–PANI–Al configuration. Similar behaviour in the various other Cole–Cole plots (*Figure 6b*) can also be seen. The contact effect may perhaps arise due to the Schottky junction formed as a result of evaporation of aluminum on polyaniline films.

Figure 7a exhibits the variation of dielectric loss obtained at different temperatures as a function of frequency. The relaxation phenomenon observed is similar to that of damping of dipole oscillators. Although, the shapes of loss profiles are similar, the shift in the frequency at which the dielectric loss maximum occurs can perhaps be attributed to the increased number of charge carriers. At a higher temperature, the shift of the dielectric loss peak is probably due to the increased number of induced dipoles in the Al–PANI–Al configuration. Such induced dipoles are likely to be oriented in the direction of the applied electric field at higher frequency.

Figure 7b exhibits the plot of $1/C^2$ as a function of applied voltage. The slope of the observed curve can be used to calculate the magnitude of carrier concentration that has been found to be $n = 10^{18}$ cm^{-3} [21].

Figure 8a shows the variation of mobility obtained as a function of temperature using equation (9). The value of mobility increases slowly up to 300 K, whereafter a sharp and sudden increase at about 340 K can be clearly seen, indicating that polyaniline perhaps undergoes a glass–rubber transition at this temperature[32]. The value of mobility, μ, in polyaniline calculated at 300 K has been found to be 9.6×10^{-6} cm^2 V^{-1} s^{-1}. The low value of mobility, 9.6×10^{-6} cm^2 V^{-1} s^{-1}, compared to that obtained for polypyrrole may perhaps be attributed to the existence of increased number defects in polyaniline. The variation of mobility, μ, calculated as a function of thickness of polyaniline film, has been shown in *Figure 8b*. The value

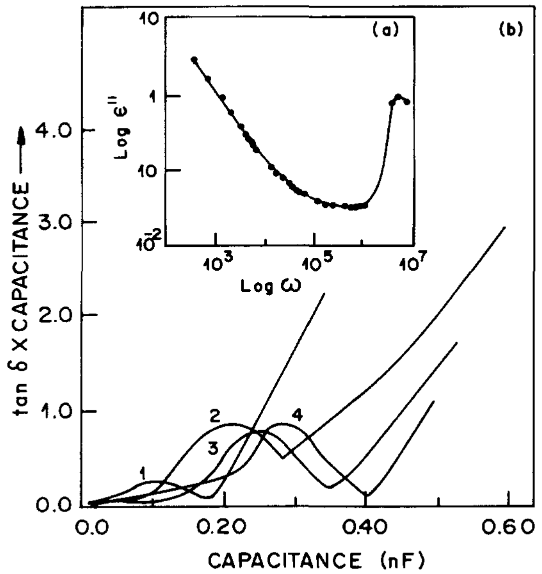

Figure 6 (a) Variation of imaginary part of ϵ'' as a function of ω ($= 2\pi f$) at 290 K on the logarithmic scale. (b) Cole–Cole plot for Al–PANI (emeraldine salt)–Al as a function of temperature: curve 1 (120 K); curve 2 (290 K); curve 3 (323 K); curve 4 (373.6 K)

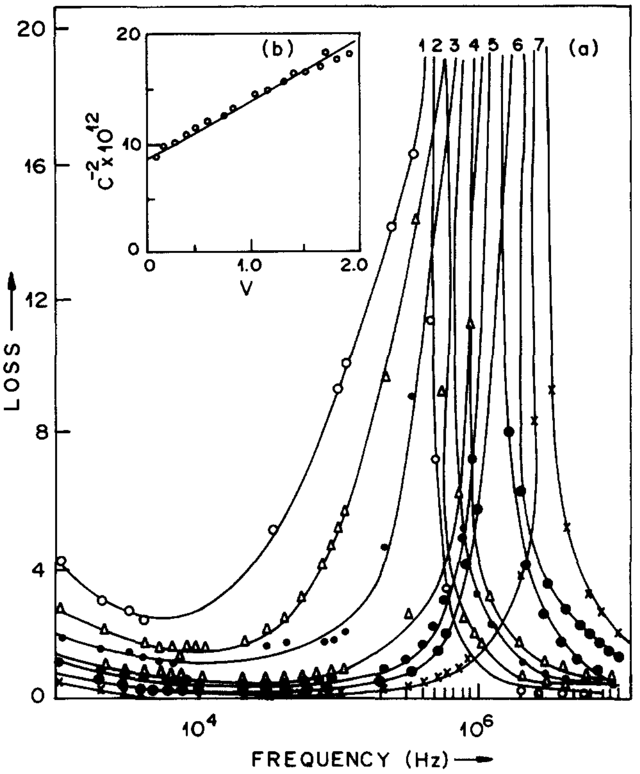

Figure 7 (a) Variation of dielectric loss with logarithmic frequency (Hz) at different temperatures for Al–PANI (emeraldine salt)–Al at a static bias (100 mV): curve 1 (120 K); curve 2 (133 K); curve 3 (213 K); curve 4 (290 K); curve 5 (232 K); curve 6 (363 K); curve 7 (373.6 K). (b) Variation of $1/C^2$ (F^{-2}) of Al–PANI (emeraldine salt)–Al configuration as a function of applied voltage (volts)

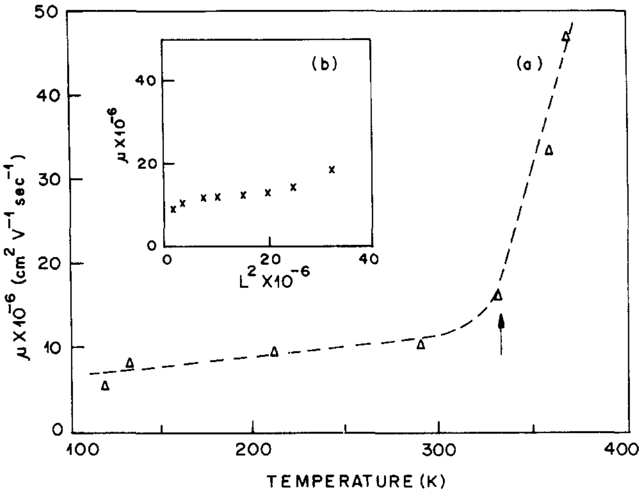

Figure 8 (a) Variation of mobility (cm^2 V s^{-1}) for Al–PANI (emeraldine salt)–Al structures observed with thickness (m^2). (b) Variation of mobility (observed for Al–PANI (emeraldine salt)–Al configuration (cm^2 V s^{-1}) with temperature (K)

of slope obtained as ≤ 2 indicates the presence of space charge polarization[28,29].

CONCLUSIONS

The results of dielectric relaxation studies carried out on Al–PANI–Al capacitor configurations have shown that the movement of charge carriers under the influence of an electric field gives rise to the space charge phenomenon, leading to interfacial polarization. Further, the observed shifts of Cole–Cole with increasing temperature indicates the presence of multiple relaxation in the Al–PANI–Al capacitor configuration. The relaxation phenomenon seen in this configuration has been attributed to the damping of dipole oscillators originating due to the application of external electric field.

The mobility, μ, of charge carriers has been calculated using the approximation to space charge theories. The increase in the value of mobility both with increasing temperature and thickness observed in case of Al–PANI–Al configuration support the formation of space charge in doped polyaniline.

ACKNOWLEDGEMENTS

We are grateful to Professor E. S. R. Gopal, Director, NPL, for the constant encouragement and his continued interest in this work. We thank Dr Subhas Chandra for many valuable discussions. Thanks are also due to Dr N. S. Sundaresan for his suggestions during preparation of this manuscript. One of us, M. K. Ram, thanks the CSIR (India) for the financial support. Financial support received under the India–US fund, Project No. DST/USIF/404/93 is gratefully acknowledged.

REFERENCES

1. Legros, F. and Fourrier-Lamer, A., *Mat. Res. Bull.*, 1984, **19**, 1109.
2. Chrobeczek, J. A. and Summerfield, S., *J. Physics Colloid*, 1984, **44**(C3), 103.
3. Mammone, R. J. and Binder, M., *J. Electro. Chem. Soc.*, 1990, **137**(7), 2135.
4. Zuo, F., Angelopoulos, M., Macdiarmid, A. G. and Epstein, A. J., *Phys. Rev.*, 1989, **B 39**, 3570.
5. Annapoorni, S., Sundaresan, N. S., Pandey, S. S. and Malhotra, B. D., *J. Appl. Phys.*, 1993, **74**(3), 1.
6. Beladakere, N. N., Misra, S. C. K., Ram, M. K., Rout, D. K., Gupta, R., Malhotra, B. D. and Chandra, S., *J. Phys. (Condens. Matter)*, 1992, **4**, 5747.
7. Javadi, H. H., Angelopolous, M., MacDiarmid, A. G. and Epstein, A. J., *Synth. Metals*, 1988, **26**, 1.
8. Heeger, A. J., *Faraday Discuss. Chem. Soc.*, 1989, **88**, 1.
9. Su, W. P., Schrieffer, J. R. and Heeger, A. J., *Phys. Rev. Lett.*, 1979, **42**, 1698.
10. Rice, M. J., *Phys. Lett.*, 1979, **71A**, 152.
11. Campbell, D. K. and Bishop, R., *Phys. Rev.*, 1981, **B 24**, 859.
12. Heeger, A. J., Kevelson, S. and Schrieffer, J. R., *Reviews of Mod. Phys.*, 1980, **60**, 781.
13. Bugamayer, P. and Murray, W., in *Handbook of Conducting Polymers*, T. A. Skotheim (ed.), Dekker, New York, 1986, **1**, 507.
14. Kivelson, S., *Phys. Rev.*, 1982, **B25**, 3799.
15. MacDiarmid, A. G., Chiang, J. C., Richter, A. F. and Epstein, A. G., *Synth. Metals*, 1987, **18**, 285.
16. Ray, A., Asturias, G. E., Khershner, D. L., Richter, A. F., MacDiamrid, A. G. and Heeger, A. J., *Synth. Metals*, 1989, **29E**, 141.
17. Boudreaux, D. S., Chance, R. R., Wolf, J. F., Shacklette, L. W., Bredas, J. L., Andre, T. J. M. and Silbey, R., *Chem. Phys.*, 1986, **85**(8), 4584.
18. Monkman, A. P. and Adams, P., *Synth. Metals*, 1991, **40**, 87.
19. Epstein, A. J., Ginder, J. M., Zuo, F., Woo, H. S., Tanner, D. B., Richter, A. F., Angelopoulos, M., Huang, W. S. and MacDiarmid, A. G., *Synth. Metals*, 1987, **21**, 63.
20. Pandey, S. S., Misra, S. C. K., Malhotra, B. D. and Chandra, S., *J. Appl. Pol. Sci.*, 1992, **44**, 911.
21. Ram, M. K., Annapoorni, S. and Malhotra, B. D., *J. Appl. Pol. Sci.*, 1996, **46**, 407.
22. Misra, S. C. K., Ram, M. K., Pandey, S. S., Malhotra, B. D. and Chandra, S., *Appl. Phys. Lett.*, 1992, **61**(10), 1219.
23. Genies, E. M., Bayle, A., Lapkowski, M. M. and Tsintavis, A. C., *Synth. Metals*, 1990, **36**, 139.
24. Beladakere, N. N., Ram, M. K., Annapoorni, S., Pandey S. S., Malhotra, B. D., Pratt, F. L. and Hayes, W., unpublished results.
25. Ram, M. K., Optical and electrical properties of conducting polymer films. Ph.D. thesis, Birla Institute of Technology and Science, Pilani, Rajasthan, India, 1995.
26. Ram, M. K. and Malhotra, B. D., *Polymer*, 1996, **37**, 4801.
27. Philips, P. and WU, H., *Science*, 1991, **252**, 1805.
28. Javadi, H. H. S., Zuo, F., Angelopoulos, M., MacDiarmid, A. G. and Epstein, A. J., *Mol. Cryst. Liq. Cyst.*, 1988, **160**, 225.
29. Zuo, F., Angelopoulos, M., MacDiarmid, A. G. and Epstein, A. G., *Phys. Rev.*, 1987, **B36**, 3475.
30. Ram, M. K., Mehrotra, R., Pandey, S. S. and Malhotra, B. D., *J. Phys. (Condens. Matter)*, 1994, **6**, 8913.
31. Ram, M. K., Gowri, R. and Malhotra, B. D., *J. Appl. Pol. Sci.*, 1997, **63**, 141.
32. Pandey, S. S., Annapoorni, S. and Malhotra, B. D., *Macromolecules*, 1993, **26**(1), 3190.
33. Coehlo, R., 1979, *Physics of Dielectrics for the Engineer*. Elsevier, New York.