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AC conductivity of polyemeraldine base

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Abstract. We report the results of our dielectric measurements carried out systematically on polyemeraldine base (PEB) in an Al–PEB–Al configuration, as functions of both frequency (5 Hz–13 MHz) and temperature (77–380 K). An attempt has also been made to understand the transport of charge in PEB in terms of the polaron-hopping model applicable to amorphous semiconductors. Analysis of the AC conductivity data indicates the operation of two relaxation mechanisms in this conducting polymer.

1. Introduction

Conducting polyaniline has recently attracted a great deal of interest because its electrical properties can be reversibly controlled by both protonation and doping by varying the oxidation state of the main chain. Its excellent stability coupled with a wide range of optical, electrical and electrochemical properties make polyaniline an attractive electronic material for a number of applications such as in displays, biosensors and batteries [1–8]. Depending upon the oxidation level, polyaniline can be synthesized in various forms such as leucoemeraldine, emeraldine base, nigraniline and pernigraniline states [9–13]. The emeraldine base (also referred to as polyemeraldine base (PEB)) differs substantially from other forms since its electrical conductivity $\sigma_T(\omega)$ can be easily varied from an 'insulating' to a 'metallic' state by doping it with a protonic acid such as HCl [14, 15]. Besides this, its valence and conduction bands are highly asymmetric with respect to the Fermi level, resulting in charge-conjugation asymmetry in the PEB [14]. Moreover, the nitrogen atoms and the carbon rings of the PEB lie in the conjugation path, making it a generalized polymer [15–21].

The mechanism of charge transport in PEB has attracted much attention in recent years. Magnetic susceptibility measurements carried out on PEB have revealed a linear variation in the Pauli magnetic susceptibility as a consequence of protonation [22]. It has been conjectured that non-linear defects such as solitons, polarons and also bipolarons make a significant contribution towards the observed electrical conductivity $\sigma_T(\omega)$ in PEB [23]. It has been shown that the temperature dependence of electrical conductivity in PEB is critically dependent upon the moisture contained in such an electronic material and can probably be explained by a model based on charging-energy-limited tunnelling between the granular metallic regions arising as a consequence of doping [16]. The results of both DC and AC conduction measurements carried out on PEB as functions of both temperature and frequency (1–10^7 Hz) support the hypothesis of hopping of the positively charged polarons and bipolarons or p-neutral polaron states in this conducting polymer. Very few models have been proposed in the literature to explain the phenomenon of charge transport in PEB. The present paper deals with the results of our dielectric measurements carried out systematically

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on PEB as functions of both temperature (77–380 K) and frequency (5 Hz–13 MHz). The detailed analysis of the observed experimental data indicates the operation of an interesting relaxation phenomenon in this conducting polymer.

2. Experimental details

Polyemeraldine salt was prepared by redox polymerization of aniline as reported earlier [6, 24]. It was undoped using aqueous NH_3 for 12 h and dried under dynamic vacuum for 24 h. The undoped polyaniline (i.e. PEB) so obtained was characterized by UV–visible and FTIR spectroscopy. The observed spectra were found to be consistent with the published literature [25, 26]. The DC electrical conductivity was measured using a four-point probe and was found to be 10^{-10} S cm^{-1}. The thickness of the pellets used for electrical conductivity measurements varied from 120 to 125 μm.

The Al–PEB–Al configuration was fabricated by vacuum (10^{-6} Torr) deposition of aluminium (99.9%). *I–V* characteristics were measured using an SI 1286 Schlumberger electrochemical interface. The voltage scan rate was maintained at 24 mV s^{-1} for the *I–V* measurements. Dielectric measurements were performed in the desired temperature range on the Al–PEB–Al configuration using an HP 4192A impedance analyser operating in the frequency range 5 Hz–13 MHz.

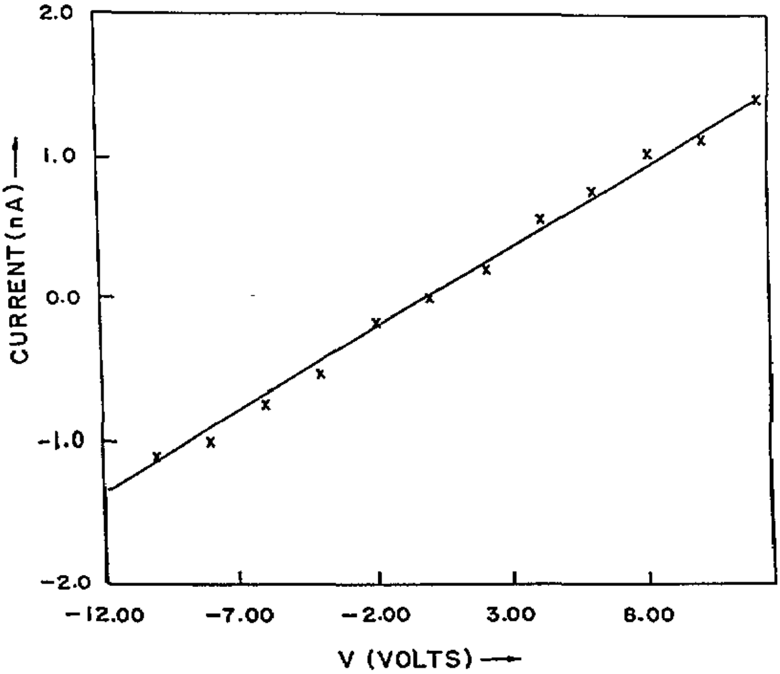

Figure 1. Variation in current *I* with voltage *V* of an Al–PEB–Al configuration.

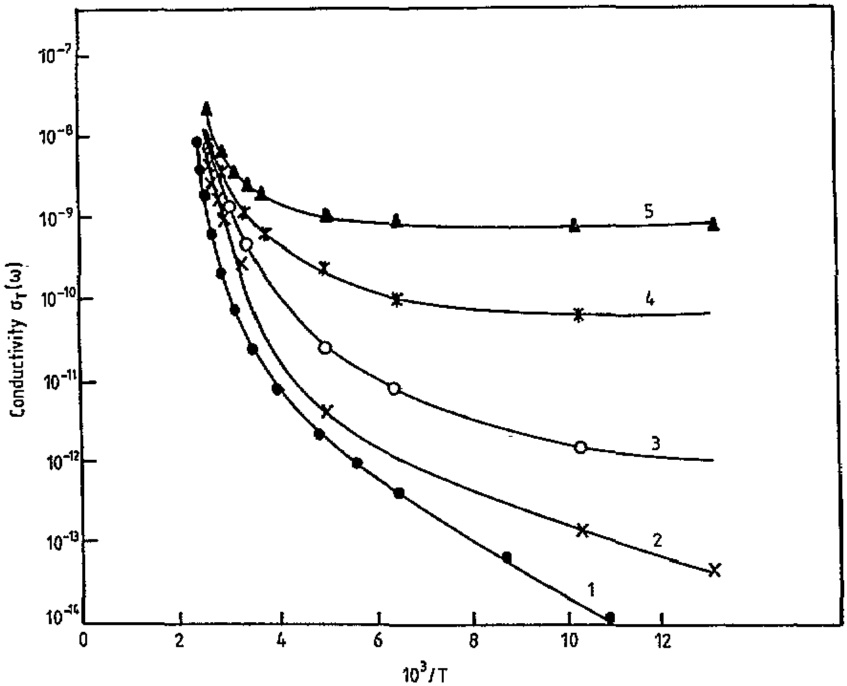

Figure 2. Variation in conductivity $\sigma_T(\omega)$ with temperature at various frequencies: curve 1, DC conductivity; curve 2, 100 Hz; curve 3, 1 kHz; curve 4, 10 kHz; curve 5, 100 kHz.

Table 1. Values of parameters.

Samples	B (10^{-17} esu)	s, slope at 77 K	Frequency f (KHz)	$NC(E_F)$ (eV^{-1} cm^{-3}) $\alpha = 0.4A^0$	$\alpha = 1A^0$	$\alpha = 1.5A^0$
1	17.3	0.92	0.1	4.79×10^{20}	4.84×10^{19}	1.76×10^{19}
2	4.0	0.92	1.0	9.12×10^{20}	9.23×10^{19}	3.35×10^{19}
3	4.2	0.92	10.0	2.96×10^{20}	2.99×10^{20}	10.88×10^{19}
4	43.0	0.92	100.0	10.51×10^{23}	1.06×10^{23}	3.86×10^{22}

3. Results and discussion

Figure 1 shows the results of current–voltage (I–V) measurements conducted on an Al–PEB–Al structure, indicating a linear fit over a wide range of applied voltages. From these results, it can be tentatively concluded that there is no barrier formation, indicating the absence of any contact effect at the Al–PEB junctions. Figure 2 exhibits the variation in experimentally determined electrical conductivity $\sigma_T(\omega)$ of the Al–PEB–Al structure plotted as a function of $10^3/T$ at various frequencies 100 Hz, 1 kHz, 10 kHz and 100 kHz. It can be seen that the value of $\sigma_T(\omega)$ reaches a constant value at about 378 K. However, on decrease in the temperature of the PEB sample, $\sigma_T(\omega)$ shows an interesting behaviour. For example, in the frequency region 100 Hz–100 kHz, the variation in the AC conductivity $\sigma_{LT}(\omega)$ at low temperatures can be expressed as [27]

$$\sigma_{LT}(\omega) = BTW^s \tag{1}$$

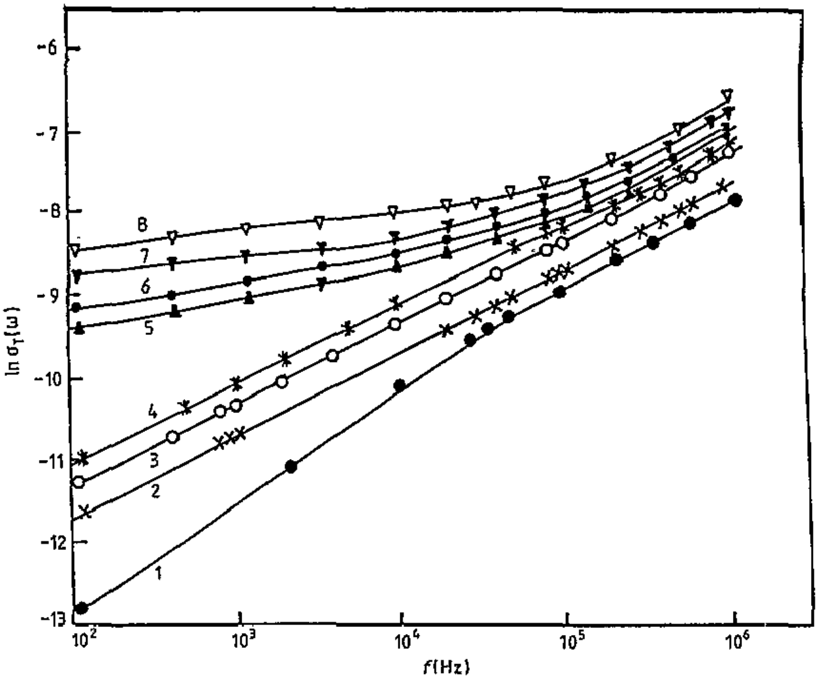

Figure 3. Variation in logarithmic conductivity $\ln[\sigma_T(\omega)]$ with frequency at various temperatures: curve 1, 77 K; curve 2, 150 K; curve 3, 202 K; curve 4, 273 K; curve 5, 300 K; curve 6, 323 K; curve 7, 346 K; curve 8, 378 K.

where the parameters B and s are independent of temperature T. Use of equation (1) with the AC conductivity data obtained at 77 K yields the value of s as 0.92, indicating the applicability of the hopping models proposed in the literature. The value of the parameter B (table 1) has been computed using this value (0.92) of s for the AC conductivity data (figure 2) obtained at 77 K in this frequency region using the following equation:

$$\sigma_T(\omega) = \tfrac{1}{3}\pi e^2 k_B T[N(E_F)]^2 \alpha^{-5}\omega[\ln(\nu_0/\omega)]^4 \qquad (2)$$

where k_B is the Boltzmann constant, e is the electronic charge, $\omega = 2\pi f$ (f being the measured frequency), ν_0 is the phonon-assisted frequency (10^{13} Hz for the amorphous system) and § $= \alpha^{-1} \rightarrow \alpha^{-1}$ is the localization length (it varies between 0.4 and 0.5 Å corresponding to the nearest-neighbour hopping); the values of the density $N(E_F)$ of states have been calculated and are given in table 1. The observed variation in the density $N(E_F)$ of states, as a function of the localization length α^{-1} testifies to the phenomenon of hopping of charges between polaron and bipolaron sites existing in the as-synethsized PEB. it is important to mention here that equation (1) is valid for the uncorrelated hops between the charge carriers considering that the contribution due to multiple hopping is negligible.

Figure 3 shows the variation in AC conductivity $\sigma_T(\omega)$ experimentally obtained with frequency from 100 Hz to 1 MHz at various temperatures 77, 150, 202, 273, 300, 323, 346 and 378 K, respectively. It can be seen from figure 3 that the value of the slope decreases as the PEB is raised to a higher temperature. It can thus be concluded that the contribution of hopping conductivity $\sigma_{LT}(\omega)$ to $\sigma_T(\omega)$ becomes less predominant at elevated temperatures owing to the presence of induced dipoles arising as a result of Debye-type relaxation in

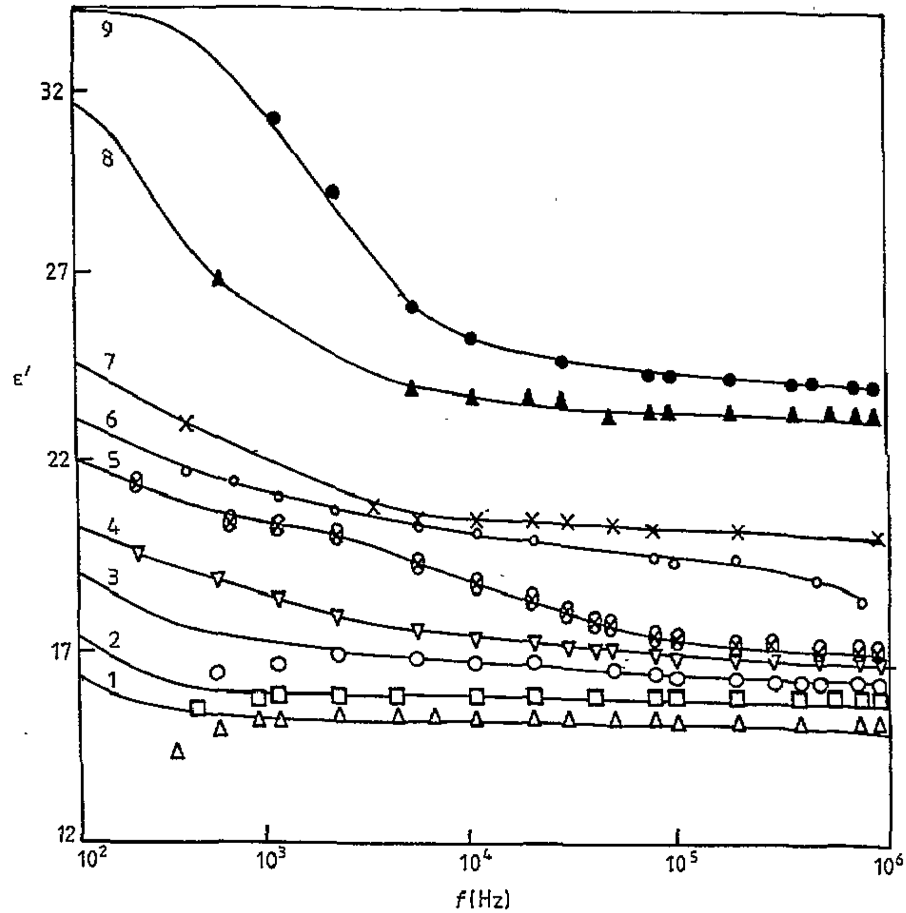

Figure 4. Variation in the real part ϵ' of the dielectric constant with frequency at various temperatures: curve 1, 77 K; curve 2, 138 K; curve 3, 150 K; curve 4, 202 K; curve 5, 273 K; curve 6, 300 K; curve 7, 323 K; curve 8, 346 K; curve 9, 378 K.

the PEB. In fact, it is possible to describe the variation in experimentally observed AC conductivity $\sigma_{\mathrm{HT}}(\omega)$ at higher temperatures as

$$\sigma_{\mathrm{HT}}(\omega) = \frac{\omega\varepsilon_0(\epsilon_0 - \epsilon_\infty)[1 + (f/f_0)^{1-\alpha}\cos(\alpha\pi/2)]}{1 + 2(f/f_0)^{1-\alpha}\sin(\alpha\pi/2) + (f/f_0)^{2(1-\alpha)}} \tag{3}$$

where ϵ_0 and ϵ_∞ are the low- and high-frequency dielectric constants, respectively, and ε_0 is the space-charge permittivity. These results are in keeping with the reported observation that the temperature dependence of the AC conductivity $\sigma_T(\omega)$ shows a higher increase at low frequencies (100 Hz–1 kHz) than higher frequencies (10–100 kHz). According to Pike [28] and Elliott [29] the temperature dependence of s can be expressed as

$$1 - s = 6k_{\mathrm{B}}T/W \tag{4}$$

where W is the activation energy and k_{B} is Boltzmann's constant. Using equation (4), the value of s has been found to be 0.4 which is inconsistent with the experimentally obtained

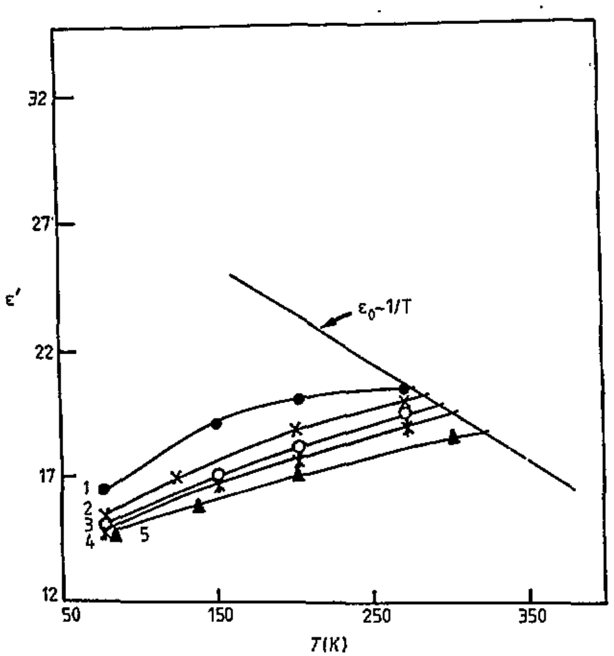

Figure 5. Variation in the real part ϵ' of the dielectric constant with temperature at various frequencies: curve 1, 100 Hz; curve 2, 1 kHz; curve 3, 10 kHz; curve 4, 100 kHz; curve 5, 1 MHz.

value (0.92). These results imply that the phenomenon of interpolaron hopping cannot perhaps explain the observed variation in $\sigma_T(\omega)$ at higher temperatures (273 K $< T <$ 378 K).

Figure 4 exhibits the variation in the real part ϵ' of the relative permittivity with frequency experimentally obtained at various temperatures 77, 138, 150, 202, 273, 300, 323, 346 and 378 K. The observed low dispersion in figure 4 indicates the absence of any inhomogeneities arising owing to Maxwell-Wagner polarization. Further, the absence of any surface barrier at the Al–PEB–Al junction rules out the effect of any surface polarization. The observed increase in dispersion with increased temperature confirms our earlier observation that AC conduction in the PEB base is a true bulk effect.

Figure 5 has been obtained by plotting the variation in the real part ϵ' of the relative permittivity of PEB with temperature T obtained with various frequencies 100 Hz, 10 kHz, 10 kHz and 1 MHz. A simple analysis of these data indicates that ϵ_0 is inversely proportional to temperature T. The measured value of ϵ_0 at these frequencies shows a saturation region in PEB at higher temperatures. From these results the value of ϵ_∞ has been estimated as 11.2 [30].

Figure 6 gives the variation in the imaginary part ϵ'' of the dielectric constant of PEB with frequency at various temperatures 77, 138, 150, 202, 273, 300, 323, 346, 358 and 378 K. The observed low dispersion in ϵ'' with frequency and the absence of any resonance peak further confirms the non-existence of any inhomogeneities including the barrier effect in the Al–PEB–Al structure. However, the observed increase in ϵ'' with temperature at low frequencies (100 Hz–1 kHz) can be understood to arise from the increased value of $\sigma_T(\omega)$ since $\epsilon'' = \sigma_T(\omega)/\omega\epsilon_0$. It is significant to note that at $T = 376$ K, the observed dielectric loss ϵ'' in PEB does not obey the usual trend. This can perhaps be attributed to the structural

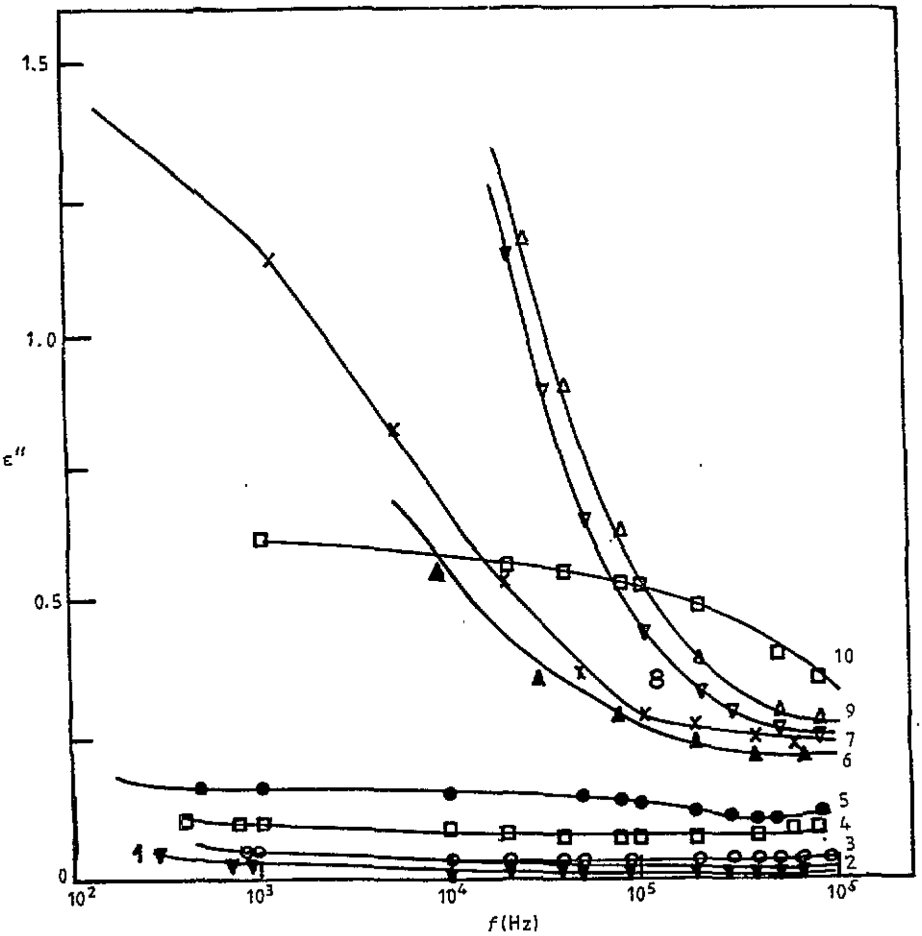

Figure 6. Variation in the imaginary part ϵ'' of the dielectric constant with frequency f at various temperatures: curve 1, 77 K; curve 2, 138 K; curve 3, 150 K; curve 4, 202 K; curve 5, 273 K; curve 6, 300 K; curve 7, 323 K; curve 8, 346 K; curve 9, 358 K; curve 10, 378 K.

changes in PEB brought about as a result of temperature variation.

Figure 7 shows the variation in the real part ϵ' of the dielectric permittivity with $\omega\epsilon''$, indicating the existence of two relaxation times. The first relaxation time occurs in the low-frequency region (100 Hz–10 kHz) whereas the second relaxation time may be ascribed to the higher-frequency region (10 kHz–1 MHz). These results are in conformity with our earlier observations (figures 2–5) relating to the presence of a multiple-relaxation phenomenon. The absence of any loss peaks and the observed larger dispersion at low frequencies follows the usual law (seen in the higher-frequency response), resulting in a smaller value of the exponent.

Figure 8 is the Cole–Cole plot obtained at 330 K for the Al–PEB–Al configuration. The marked deviation (skew type) from a semicircle indicates the operation of a complex behaviour in this typical system. The observed skew-type behaviour can be understood to result from the motion of charge carriers such as polarons and bipolarons in the PEB. These results are similar to those observed for Al–PANI(HCl-doped)–Al structures and indicate the presence of multiple relaxation in PEB in this frequency region (100 Hz–1 MHz) [24].

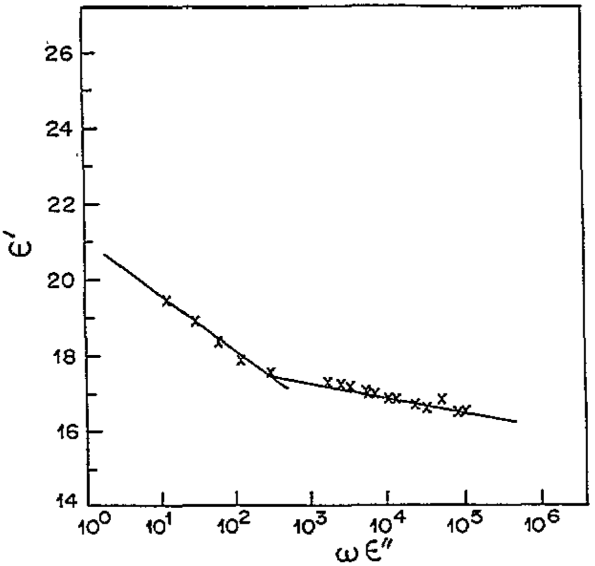

Figure 7. Variation in the real part ϵ' of the dielectric constant with $\omega\epsilon''$ where $\omega = 2\pi f$.

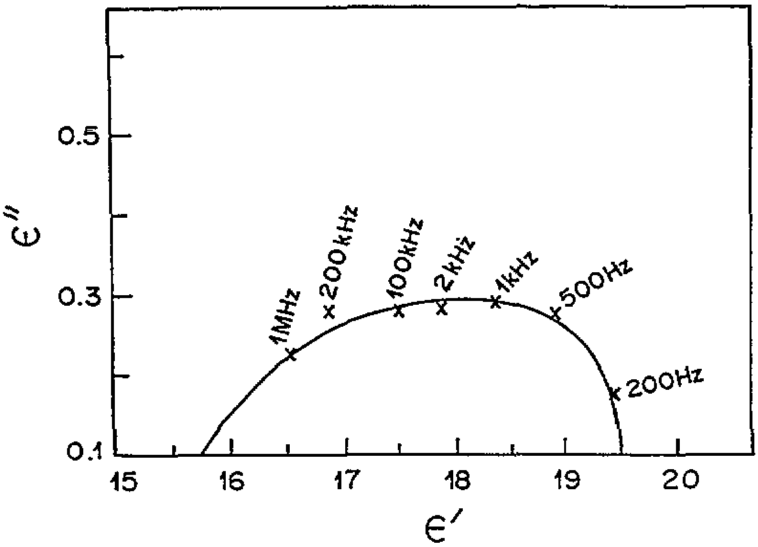

Figure 8. Variation in the imaginary part ϵ'' of the dielectric constant with the real part ϵ' of the dielectric constant (Cole–Cole plot) obtained at a temperature $T = 330$ K.

An attempt has been made to compute the value of $\sigma_T(\omega)$ at a given temperature by expressing $\sigma_T(\omega)$ as

$$\sigma_T(\omega) = \sigma_{\mathrm{LT}}(\omega) + \sigma_{\mathrm{HT}}(\omega). \quad (5)$$

Using equations (2), (4) and (5), the value of $\sigma_T(\omega)$ has been computed and the results are shown in figure 9 which also contains the experimentally determined values of AC

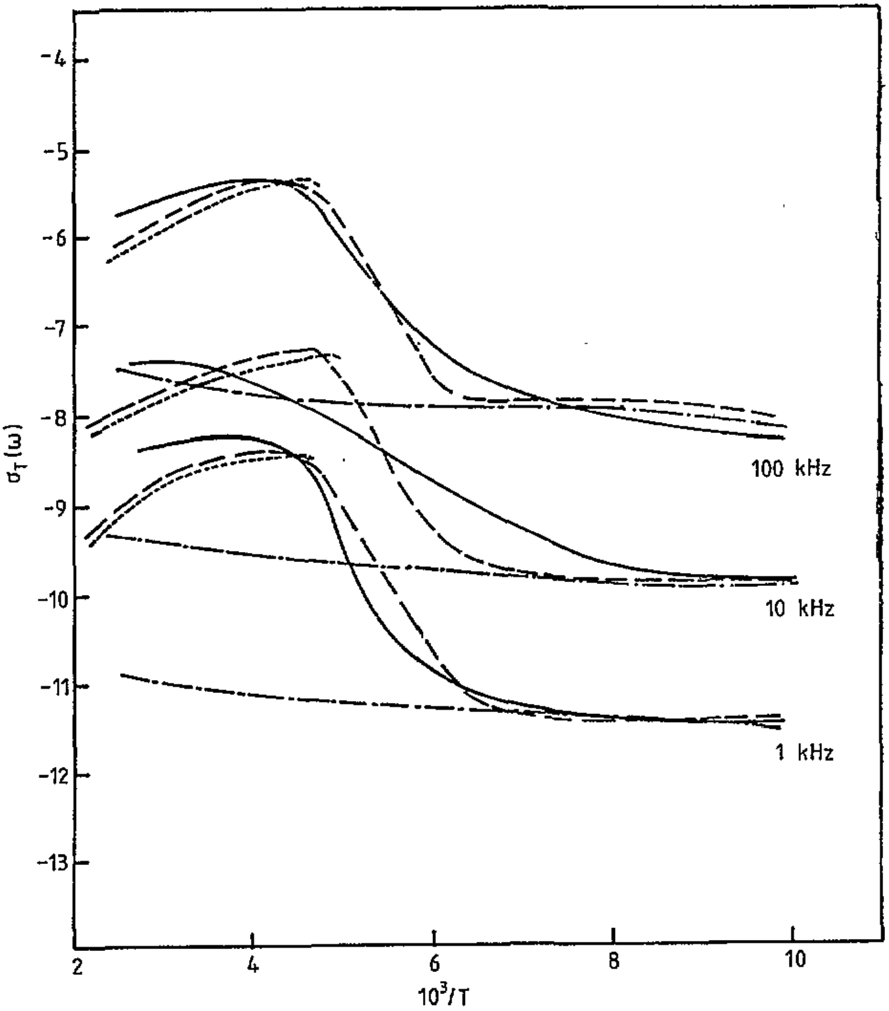

Figure 9. Variation in AC conductivity $\sigma_T(\omega)$ with $10^3/T$ at 1, 10 and 100 kHz: ----, $\sigma_{LT}(\omega)$; — · —, $\sigma_{HT}(\omega)$; – – –, experimental $\sigma_{LT}(\omega) + \sigma_{HT}(\omega)$; ——, calculated $\sigma_{LT}(\omega) + \sigma_{HT}(\omega)$.

conductivity. The excellent agreement between the experimental and the calculated values of AC conductivity $\sigma_T(\omega)$ shows that the AC conduction in PEB can be explained using the existing models applicable to amorphous semiconductors.

4. Conclusions

The results of AC conductivity measurements carried out on the Al–PEB–Al configuration demonstrate the operation of two relaxation mechanisms in PEB. The temperature dependence of AC conductivity $\sigma_T(\omega)$ of PEB has been explained by expressing the measured AC conductivity $\sigma_T(\omega)$ as a sum of $\sigma_{LT}(\omega)$ and $\sigma_{HT}(\omega)$ arising from two different temperature regimes. $\sigma_{HT}(\omega)$ is dominant at higher temperature whereas at low temperatures the contribution to $\sigma_T(\omega)$ from $\sigma_{LT}(\omega)$ is larger. In order to delineate further the phenomenon of AC conduction, the effect of annealing on PEB in both bulk and film forms should be systematically investigated using similar studies.

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