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Alternating-current conductivity and dielectric permittivity of polyaniline doped with β -naphthalene sulphonic acid

P Dutta, S Biswas and S K De

Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

E-mail: msskd@mahendra.iacs.res.in (S K De)

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Abstract

The alternating-current (ac) conductivity $\sigma(\omega)$ and the dielectric permittivity of polyaniline doped with β -naphthalene sulphonic acid (NSA) have been extensively studied in the temperature range of 300 K to 80 K and in the frequency range of 500 Hz to 10 MHz. The ac conductivity follows a power law in frequency, $\sigma(\omega) \propto \omega^s$, at high frequency, where s ($\simeq 0.85$ – 0.88) is nearly independent of temperature. At low temperature the ac conductivity spectra show saturations for frequencies of the order of 10^6 Hz. The ac conductivity exhibits a scaling behaviour in the form $\sigma(\omega)/\sigma_0 = 1 + (\omega/\omega_0)^n$ with $0.8 < n < 0.9$. The dielectric loss spectra reveal two peaks corresponding to two plateaus of $\sigma(\omega)$ at low and high frequencies. The broad and asymmetrical loss peaks of the dielectric spectra have been analysed on the basis of stretched-exponential decay of the electric field, $\phi(t) = \exp[-(t/\tau_0)^\beta]$, where $0 < \beta \leq 1$. The loss spectra at low temperatures collapse onto a single scaling curve determined by the height and position of the peak.

1. Introduction

The conducting polymer polyaniline (PANI) is a very promising material because it shows good environmental stability and is easy to process [1]. Protonation of PANI with organic acids such as camphor sulphonic acid (CSA) and dodecylbenzene sulphonic acid (DBSA) [2] improves its solubility in organic solvents. The formation of side chains by the functional group associated with the backbone of PANI leads to solubility in a variety of common organic solvents depending on the selection of functional group.

The transport properties of polymers become much more complicated due to the disorder originating from the random structure and inhomogeneous doping. The degree of disorder

depends mainly on the processing conditions and the dopants. Another difficulty in chain-like polymeric materials is the competition between intrachain and interchain process. The alternating-current (ac) conductivity, $\sigma(\omega)$, is an important experimental tool for identifying and quantify the contribution of each process due to its spectroscopic character. The most interesting feature is that the ac electrical properties of quite different disordered materials such as amorphous semiconductors, organic semiconductors, ionic glasses and conducting polymers reveal a common behaviour as a function of frequency [3]. The ac conductivity in most of the disordered solids satisfies the time-temperature superposition principle [4, 5]. The frequency and temperature dependence of the complex dielectric function, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, is important for determining the charge-transport mechanism [6]. Studies on the scaling behaviour of the ac conductivity for disordered conducting polymers are few [7]. In this paper, we have presented an extensive study of the charge transport and scaling properties of the ac conductivity and dielectric permittivity of PANI doped with β -naphthalene sulphonic acid as a function of frequency and temperature.

2. Experimental techniques

2.1. Sample preparation

Aniline (E Merck, India) monomer is polymerized in the presence of β -naphthalene sulphonic acid (NSA) at low temperature (0–5 °C) to produce polyaniline doped with NSA (PANI-NSA) by an *in situ* doping polymerization method [8]. Aniline monomer is distilled under reduced pressure. Ammonium persulphate (E Merck, Germany) is used as the oxidant and NSA as the dopant with their molar ratio 1:1. The molar ratio of aniline to NSA is also taken as 1:1 but in the reaction medium the concentrations of NSA for the different samples are 0.1, 0.5, 0.65, 1.0 M. For a particular NSA concentration the whole mixture is stirred magnetically at 0–5 °C for 24 h. The green precipitate is then washed with deionized water, methanol and ethyl ether several times and finally dried at room temperature in a dynamic vacuum for 48 h. The dried samples are ground and pelletized in a hydraulic press with a pressure up to four tons.

2.2. Measurements

The measurements are carried out with a Hewlett-Packard 4192A Impedance Analyzer. The samples are coated on two opposite sides with silver paint (supplied by Acheson Colloiden BV, Holland). Copper wires are cemented on both surfaces with silver paste and the specimen is mounted in a sample holder, the temperature of which can be varied over the range 80 to 350 K with a temperature control of ± 1 K. The capacitance (C) and the dissipation factor (D) are measured at various frequencies and temperatures. The ac conductivity (σ) and the real (ε') and imaginary parts (ε'') of the dielectric permittivity are calculated from the relations $G = D\omega C$, $\sigma = Gd/A$, $\varepsilon' = Cd/A$, $\varepsilon'' = \varepsilon'D$, where G is the conductance, A is the electrode area and d is the sample thickness.

3. Results and discussion

3.1. Alternating-current conductivity

The frequency-dependent total conductivity $\sigma(\omega)$ at various doping concentrations (c) is shown in figure 1. $\sigma(\omega)$ becomes much more prominent with the lowering of the doping concentration. The characteristic property of $\sigma(\omega)$ is independent of ω in low-frequency regions and almost equal to the direct-current (dc) conductivity. The ac conductivity starts to increase at the

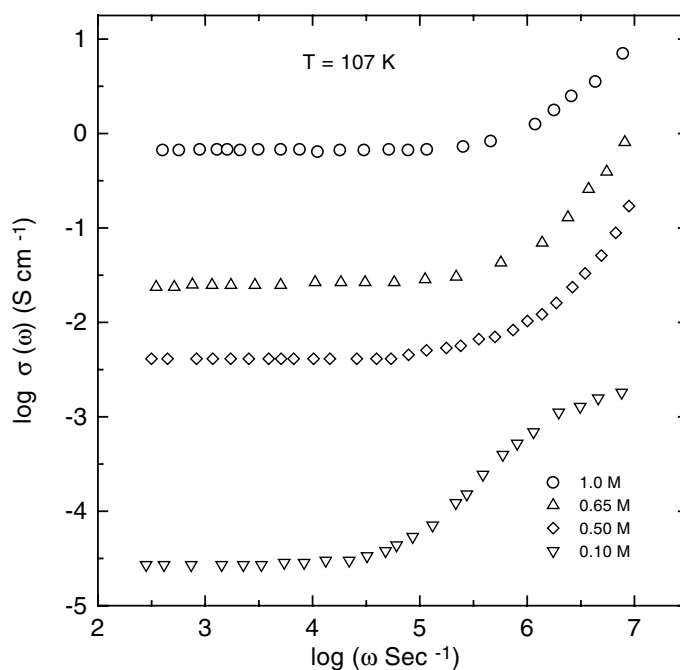


Figure 1. The frequency dependence of the conductivity for different NSA concentrations (c) at 107 K.

onset frequency, which increases with increase of the doping level. The increase of $\sigma(\omega)$ with frequency is due to the presence of various kinds of inhomogeneity present in the materials. The poor frequency dependence of $\sigma(\omega)$ at higher values of c indicates that more homogeneous materials are produced. We have extensively studied $\sigma(\omega)$ for the lowest doping concentration (0.1 M) at various temperatures as shown in figure 2, which indicates that $\sigma(\omega)$ is significant in the frequency range of our measurements only at low temperature. The ac conductivity is less temperature dependent than the dc conductivity in the temperature interval 110 K–300 K. The ac conductivity arises from the defect states. In the case of high disorder, the charge transfer between the defect states contributes to the ac conduction at low temperature. The most interesting observation is that the ac conductivity tends to attain a saturation value in the frequency range 10^6 – 10^7 Hz at low temperature for $c = 0.1$ M. The saturation frequency increases with increasing temperature.

The total measured conductivity at a given temperature and frequency arises from both dc and ac components:

$$\sigma(\omega) = \sigma_0 + \sigma_{ac}(\omega). \quad (1)$$

The ac conductivity $\sigma_{ac}(\omega)$ increases with the increase of the frequency for amorphous semi-conductors; it follows the power law

$$\sigma_{ac}(\omega) = A\omega^s \quad (2)$$

where A is a constant dependent on T and the frequency exponent $s \leq 1$. Equation (2) indicates that the value of s for a particular T can be evaluated from the slope of a $\log \sigma_{ac}(\omega)$ versus $\log \omega$ plot. The values of s remain almost constant (0.88–0.85) and are very close to 0.8, as observed for most of the amorphous semiconductors [9].

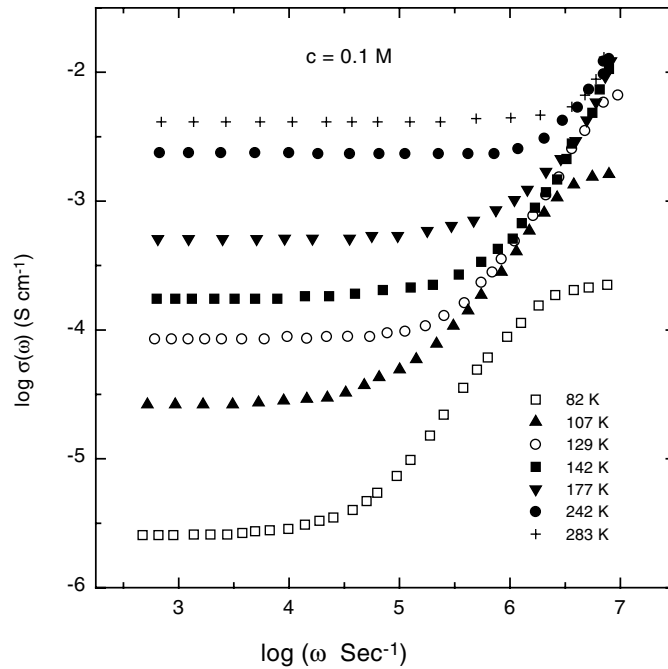


Figure 2. The frequency dependence of the conductivity at various temperatures for $c = 0.1$ M.

The various theoretical models for the microscopic relaxation process in ac conduction are generally described as quantum mechanical tunnelling or classical hopping on the basis of the classical pair approximation [3]. The charge carriers in all of these models are either electrons or polarons. The tunnelling or hopping occurs between a pair of localized states randomly distributed in space and energy. In the electron tunnelling model, the frequency exponent s is given by [3]

$$s = 1 + \frac{4}{\ln(\omega\tau_{ph})} \quad (3)$$

where τ_{ph} is the characteristic phonon frequency. The exponent s is independent of temperature but decreases with increase of the frequency. The minimum value of s corresponding to the maximum experimental frequency is 0.66, which implies that the saturation nature of the ac conductivity in the high-frequency region cannot be explained by this model.

In the case of small-polaron tunnelling, the frequency exponent is [3]

$$s = 1 + \frac{4}{\ln(\omega\tau_0) + W_H/kT} \quad (4)$$

where W_H is the activation energy of the polaron. At low temperature, s decreases rapidly with increase of the frequency. The observed saturation frequency is about 10^6 s⁻¹ and if we assume $W_H/kT = 16$ and $\tau_0 \sim 10^{-13}$ s⁻¹, then equation (4) yields $s \rightarrow 0$. As a result of this, the contribution of the small-polaron tunnelling to the ac conductivity tends to zero at low T and high frequency. Dyre [10] developed a model based on random free-energy barriers within the continuous-time random-walk approximation and obtained s as

$$s = 1 - \frac{2}{\ln(\omega\tau)} \quad (5)$$

where τ is the typical minimum hopping time. The correlated-barrier and random-free-energy-barrier hopping models predict that s varies inversely with temperature ($s \rightarrow 1$ as $T \rightarrow 0$) which contradicts our experimental results.

The scaling behaviour of the ac conductivity in disordered solids is a unique property. During the last few years, the scaling nature of $\sigma(\omega)$ for ionic glasses [4, 5, 11] has been studied. The main aim in studying this property is to choose the appropriate scaled frequency ω/ω_0 , so that the scaled conductivity $\sigma(\omega)/\sigma_0$ falls onto a single master curve at different temperatures and compositions for a particular solid. Barton, Nakajima and Namikawa (BNN) [12] established a relation between the dc conductivity σ_0 and dielectric loss peak frequency ω_p :

$$\sigma_0 = p\varepsilon_0 \Delta\varepsilon \omega_p \quad (6)$$

where p is a numerical constant ~ 1 and $\Delta\varepsilon = \varepsilon(0) - \varepsilon_\infty$ is the dielectric loss strength. The BNN relation suggests that the master curve can be represented by

$$\frac{\sigma(\omega)}{\sigma_0} = F\left(\frac{c\omega}{\sigma_0}\right) \quad (7)$$

where c depends on the charge-carrier concentration and temperature. Recently Sidebottom [5] predicted that a scaling of the form

$$\frac{\sigma(\omega)}{\sigma_0} = F\left(\frac{\varepsilon_0 \Delta\varepsilon \omega}{\sigma_0}\right) \quad (8)$$

is more universal. The present reduced ac spectra $\sigma(\omega)/\sigma_0$ at different temperatures as a function of $\varepsilon_0 \Delta\varepsilon \omega/\sigma_0$ fail to collapse onto a common curve. Summerfield [13], considering the extended pair approximation, proposed the scaling law as

$$\frac{\sigma(\omega)}{\sigma_0} = F\left(\frac{A\omega}{\sigma_0 T}\right) \quad (9)$$

where A depends on the charge-carrier concentration only. Our experimental $\sigma(\omega)/\sigma_0$ data plotted as a function of $\omega/\sigma_0 T$ do not superpose into a single curve. The ac transport in disordered materials is described by a hopping mechanism. Schroder and Dyre [4] have shown that the scaling form of equation (8) is more general and is based on a symmetric hopping model. Monte Carlo calculations [14] within the hopping transport model in the presence of site energy disorder show that the scaling relation (9) is always valid at sufficiently low temperatures.

The scaling behaviour of the ac conductivity $\sigma(\omega)$ can be described by the following relation:

$$\frac{\sigma(\omega)}{\sigma_0} = 1 + (\omega/\omega_0)^n \quad (10)$$

where n is a constant and ω_0 is a characteristic frequency. This equation predicts that $\sigma(\omega)$ starts to rise when the applied frequency is greater than ω_0 . Almond and West [15] have suggested such a relation to interpret the ac conductivity in disordered materials. Recently, it has been found that the universality of $\sigma(\omega)$ for polyaniline–cellulose acetate blends [7] can be well represented by this scaling formula. The values of σ_0 , ω_0 and n have been calculated from the best-fit curves at different temperatures. The value of n varies from 0.8 to 0.9 over the whole temperature range. From figure 3, it is observed that the reduced conductivity $\sigma(\omega)/\sigma_0$ follows the above scaling behaviour except in the saturation region.

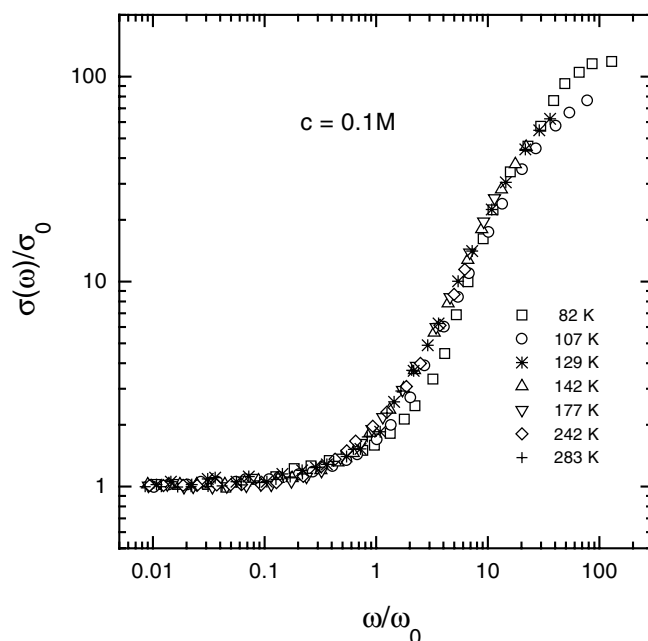


Figure 3. Scaling of the reduced conductivity versus the reduced frequency at various temperatures for $c = 0.1$ M.

3.2. Dielectric permittivity

The frequency dependence of the real part $\epsilon'(\omega)$ of the dielectric permittivity is presented in figure 4 at several temperatures. $\epsilon'(\omega)$ increases with decreasing frequency and increasing temperature. It falls off rapidly after a certain frequency which is generally the onset frequency of the ac conductivity. $\epsilon'(\omega)$ exhibits plateaus: $\epsilon(0)$ at low frequency and ϵ_∞ at high frequency. The value of $\epsilon'(\omega)$ is high at low frequency and high temperature. This may be due to space-charge polarization [16] which is built up at the interface between the sample and the electrode.

The frequency dependence of the imaginary component of the dielectric function $\epsilon''(\omega)$ is shown in figure 5 at different temperatures. The double peaks are observed at low and high frequencies. The small peak arises from the cumulative dipole moment of the main chain [17, 18]. The peak with large amplitude is due to the local orientation of the individual dipole moment associated with the relatively large and rigid sulphonate dopant. The peaks are not symmetrical on the logarithmic scale of the frequency. The frequency of the maximum loss shifts towards higher frequency with increase of temperature. The amplitude of the loss peak increases with decrease of temperature in the low-frequency region while at high frequency it is almost independent of temperature. The temperature dependence of the loss peak frequency ω_p shows the Arrhenius-type behaviour

$$\omega_p = \omega_{p0} \exp\left(-\frac{E}{kT}\right) \quad (11)$$

where ω_{p0} is a constant, k is the Boltzmann constant, E is the activation energy. The estimated value of E is 0.059 eV for the high-frequency relaxation process. The ac conductivity can be evaluated from the imaginary part of the dielectric function, $\sigma(\omega) = \epsilon_0 \omega \epsilon''(\omega)$. In the high-frequency region we have obtained $\epsilon''(\omega) \sim \omega^{-0.81}$, which explains $\sigma(\omega)$ showing saturation behaviour.

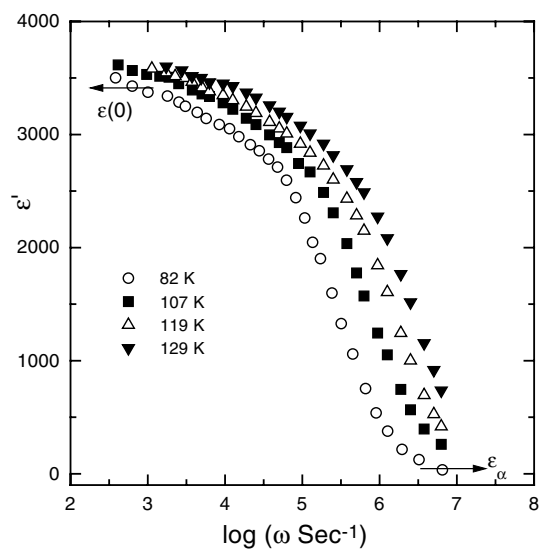


Figure 4. The real part of the permittivity versus the frequency at different temperatures for $c = 0.1$ M.

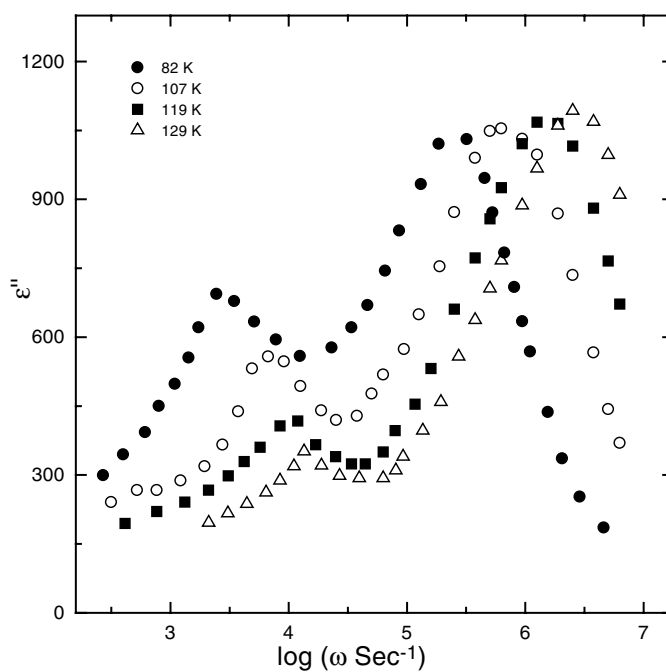


Figure 5. The imaginary part of the permittivity versus the frequency at different temperatures for $c = 0.1$ M.

The broad and asymmetrical shapes of the dielectric permittivity are generally described by Cole–Cole [19], Cole–Davidson [20], Kohlrausch–William–Watts (KWW) [21] functions. The shape of the peak is quite different from Debye behaviour [22]. To explore the relaxation

behaviour we have used the complex dielectric permittivity as follows:

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon(0) - \varepsilon_\infty} = \int_0^\infty -\frac{d\phi(t)}{dt} \exp(-i\omega t) dt \quad (12)$$

with the decay function of electric field given by the KWW function [23]:

$$\phi(t) = \exp -(t/\tau_0)^\beta \quad (13)$$

where $0 < \beta \leq 1$. The exponent β determines the degree of non-Debye behaviour as $\beta = 1$ for Debye model. Both peaks have been fitted to equation (12). It has been observed that the relaxation modes corresponding to the two peaks can be described by the KWW function with significant overlap as shown in figure 6. The best-fit values of β for the small and large peaks are 0.825 and 0.583 respectively.

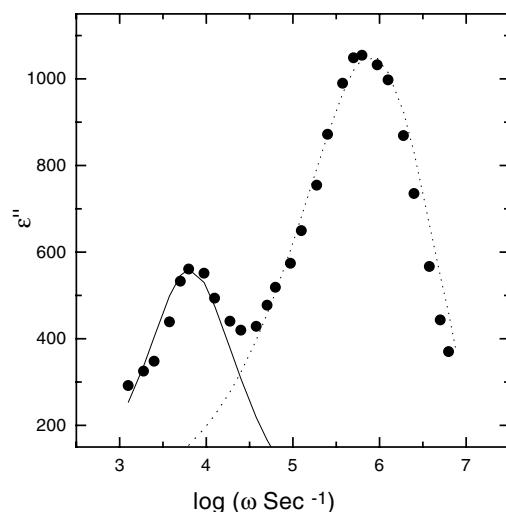


Figure 6. An illustration of the fitting procedure for the imaginary part of the permittivity with the KWW function at $c = 0.1$ M. The solid and dashed curves are for β -values of 0.825 and 0.583 respectively.

The dielectric loss function $\varepsilon''(\omega)$ is scaled by its maximum value, ε''_{max} , and the frequency, ω , by loss peak frequency ω_p at different temperatures in the high-frequency region. It is observed that the scaled $\varepsilon''(\omega)/\varepsilon''_{max}$ superpose on a single master curve as shown in figure 7. The master curve is well represented by the stretched-exponential function $\phi(t)$ with $\beta = 0.583$. The superposition of all curves at various temperatures suggests that the dielectric relaxation process is independent of temperature.

4. Conclusions

Comprehensive studies on the ac conductivity and dielectric permittivity of polyaniline doped with β -naphthalene sulphonic acid have been performed. The ac conductivity obeys a power law in frequency and becomes constant in the smaller-frequency region (10^6 Hz)—as compared to the phonon frequency (10^{12} Hz). The ac conductivity has been explained qualitatively by quantum mechanical tunnelling and satisfies the time–temperature superposition principle except in the saturation region. The dielectric loss spectrum at high frequency exhibits scaling behaviour and is well described by the stretched-exponential KWW function. Most of the

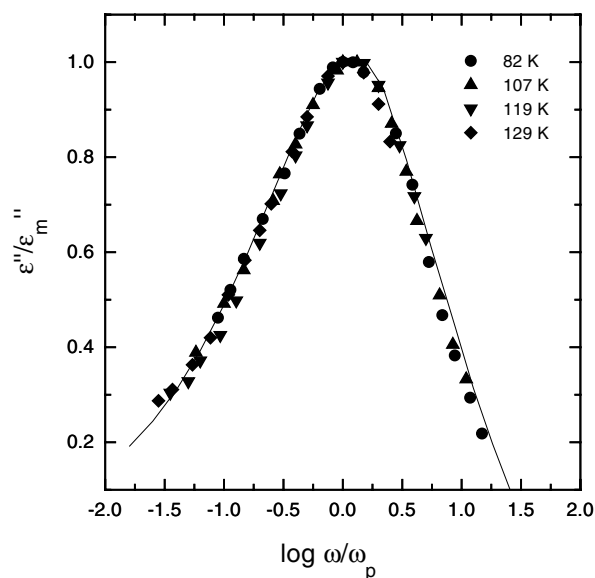


Figure 7. The master curve of dielectric loss at high frequency for different temperatures at $c = 0.1$ M.

theoretical models of $\sigma(\omega)$ in disordered materials are developed by considering the maximum jump frequency to be infinity. The present observation of saturation behaviour of $\sigma(\omega)$ in the frequency region of 10^6 Hz suggests that more studies are essential in order to understand the experimentally observed characteristic features of $\sigma(\omega)$ spectra taking into account the finite value of the maximum jump frequency.

Acknowledgments

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