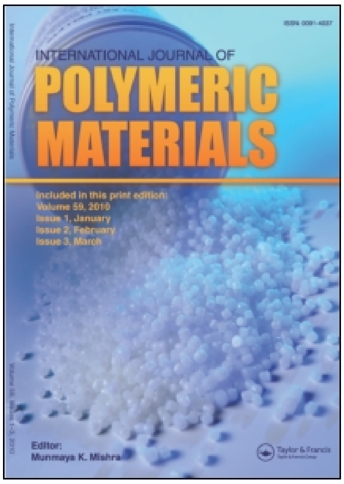

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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Abd-Alla M. A. Nada[a]; M. Fadly[b]; M. Dawy[c]
[a] Cellulose and Paper Dept., National Research Centre, Cairo, Egypt [b] Physics Dept., Faculty of Science, Helwan University, Cairo, Egypt [c] Physical Chemistry Dept., NRC, Cairo, Egypt

To cite this Article Nada, Abd-Alla M. A. , Fadly, M. and Dawy, M.(2000) 'Electrical Properties of Precipitated Lignins from Different Black Liquors', International Journal of Polymeric Materials, 45: 1, 149 — 168

To link to this Article: DOI: 10.1080/00914030008034875

URL: http://dx.doi.org/10.1080/00914030008034875

Intern. J. Polymeric Mater., 2000, Vol. 45, pp. 149–168
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Electrical Properties of Precipitated Lignins from Different Black Liquors

ABD-ALLA M. A. NADA[a], M. FADLY[b,*] and M. DAWY[c]

[a]*Cellulose and Paper Dept., National Research Centre, Dokki, Cairo, Egypt;*
[b]*Physics Dept., Faculty of Science, Helwan University, Helwan, Cairo, Egypt;*
[c]*Physical Chemistry Dept., NRC, Dokki, Cairo, Egypt*

(Received 28 June 1998)

Some corelations over the structure and dielectric properties of precipitated lignins from different waste black liquors of various modified soda and kraft pulping of bagasse have been discussed. The dielectric and the electrical properties at the same temperatures and frequencies ranges for the tested samples showed some differences which seems to be attributed to the difference in the structure and intermolecular interaction between lignin molecules. These differences are discussed on the basis of the molecular structure obtained from the infrared spectra. The conduction mechanism in the case of kraft and kraft sulfite lignins is due to electron transfer from the valence band to the conduction band by thermal activation.

Keywords: Lignins; electrical properties; waste black liquors; pulping

INTRODUCTION

Paper was produced by cooking of the lignocellulosic materials *e.g.*, wood and agricultural wastes *e.g.*, bagasse, rice straw, cotton stalks...*etc.*. There are many pulping process *e.g.*, conventional (soda–kraft and sulfite), nonconventional *e.g.*, alcell, phenols [1] and organosolv pulping [2]. A modified kraft pulping process by sodium sulfide–sulfite or addition of methanol in pulping process of bagasse was carried out [3].

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*Corresponding author.

To give more information about pulping process the infrared spectra of precipitated lignin (from the waste black lignin produced from these modified kraft pulping of bagasse) was also carried out to follow what happened in the molecular structure of lignin during the previous pulping process [4].

Lignin is a natural polymer made up of phenyl propane units bearing hydroxyl and methoxyl groups. The chemical composition of the precipitated lignin is highly dependent upon the method of pulping process. So, pulping of lignocellulose bagasse with soda and kraft process produces soda and kraft bagasse. The latter lignin contains sulphur in its structure [5].

Lignin is composed of *p*-hydroxy phenyl, syringyl and guaiacyl units which are connected in three dimensional macromolecules [6].

Lignin can be used with phenol to produce phenol lignin formaldehyde resin [7].

On the other hand lignin has a high dielectric properties [8]. The dielectric constant of lignin and cellulose was studied at different frequencies and temperatures [9].

The present work deals with the electrical properties and molecular structures of different lignins precipitated from the produced waste black liquor from bagasse pulped with modified kraft pulping process. Also the effect of the additives *e.g.*, methanol anthraquinone (AQ) in pulping liquor on the electrical properties of lignin is also investigated.

EXPERIMENTAL

Sample Preparation

Sugar cane bagasse was cooked by the following methods:

1. *Sugar pulping:* bagasse was cooked by 18% kraft in presence or absence of 0.1% AQ and methanol (20% from the total pulping liquor).
2. *Kraft pulping:* bagasse was cooked by using 13.5% NaOH and 4.5% Na_2S in presence and absence of 22% methanol.
3. *Kraft sulfite:* bagasse was cooked by using 13.5% NaOH + different percentage of sodium sulfite (5–40%) from the 4.5% weight of Na_2S.

All pulping process was carried out at 170°C for 2 hr using 45% lignin ratio in stainless steel cups of 2 liter capacity using electrically heated ethylene glycol bath.

Lignin was precipitated from the waste black lignin, produced after pulping process, using 10% H_2SO_4. Then lignin was filtered and washed till neutrality.

Dielectric Measurement

Specimen discs about 1.2 mm thickness and 1.2 cm diameter were prepared by compressing lignin powder at 10 ton/m^2. The disc surfaces were coated with silver paste to achieve better contact.

The dielectric measurements were carried out in the frequency range 0.3 – 100 kHz and in the temperature range 20 – 160°C using programable RCL meter (PM 6304). The sample was kept in thermostated chamber maintained at temperature within ±0.2°C. The heating rate was 0.5°C/min and the temperature was measured by a thermocouple kept close to the sample.

The infrared spectra was carried out using Jacco FT/IR 3000 E spectrophotometer. The samples were measured as KBr discs.

RESULTS AND DISCUSSION

• Dielectric Properties of Different Lignins

Figure 1 shows the dielectric constant ε' and dielectric loss ε'' of the different lignins at room temperature and in the frequency range 0.3 – 100 KHz. From this figure it is clear that ε' and ε'' (Figs. 1a and b) decrease by increasing the frequency for all the investigated samples. This can be attributed to the dielectric dispersion of the molecules as the orientation moments will not have time to develop. The molecule lag behind the field orientation and behave like a non-polar one. The soda lignin has the lowest dielectric properties and characterized by stability overall the frequency range. This may be attributed to the intermolecular hydrogen bonding between the hydroxyl groups forming very rigid system. This can be shown in the infrared spectra (Fig. 2) in which the OH band of soda lignin appeared at lower wave

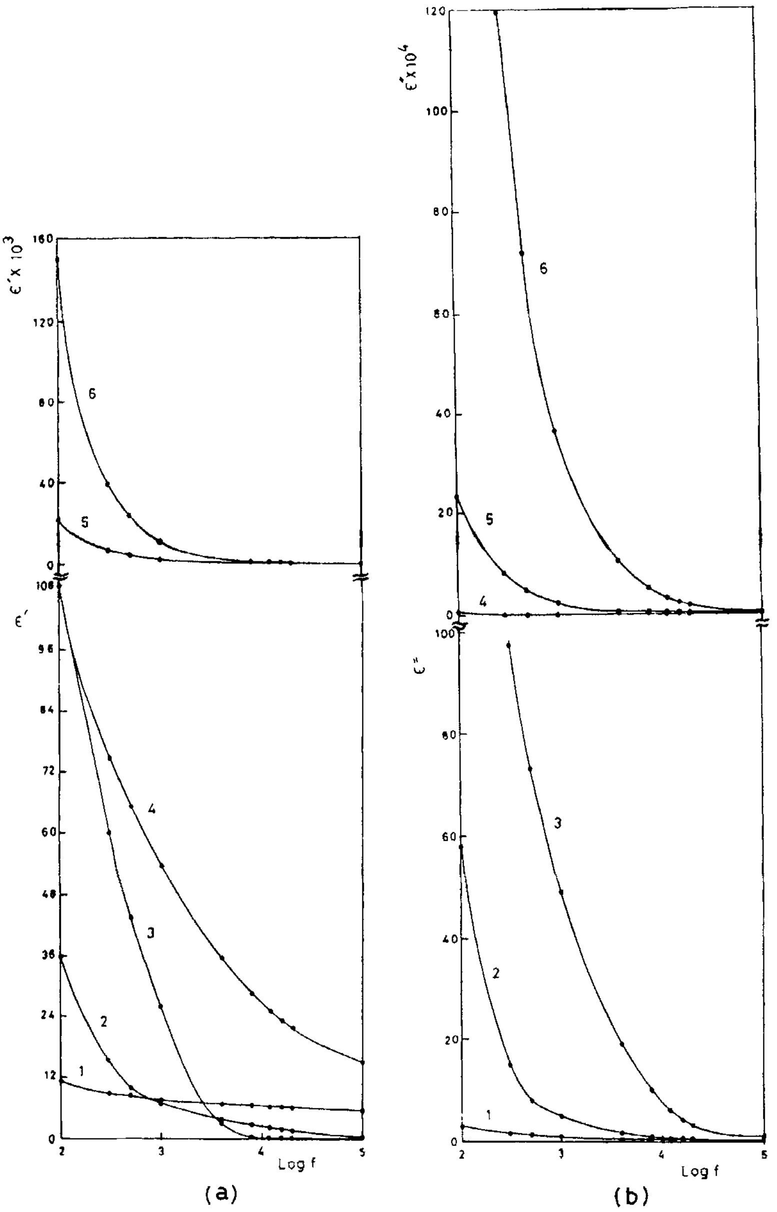

FIGURE 1 Relation between log *f* and (a) dielectric constant ε', (b) dielectric loss ε'' at room temperature for (1) soda lignin (2) soda + AQ + methanol lignin (3) soda methanol lignin (4) soda + AQ lignin (5) kraft lignin and (6) kraft sulfite lignin.

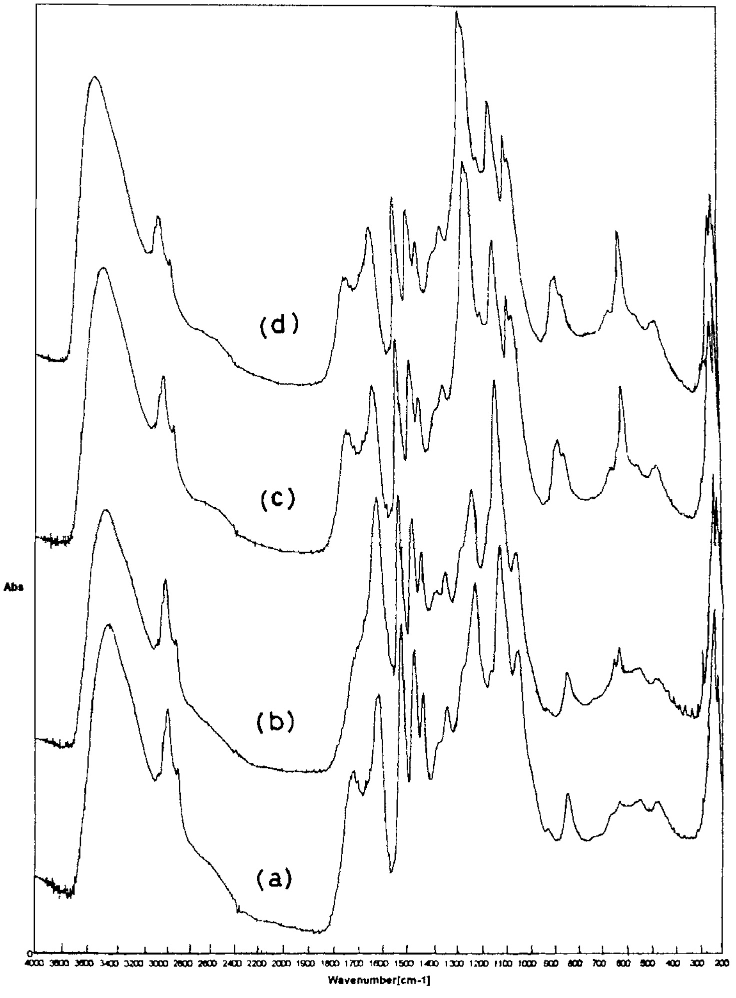

FIGURE 2 The infrared spectra of (a) soda lignin (b) soda methanol lignin (c) kraft lignin (d) kraft sulfite lignin.

number (3411 cm^{-1}) than soda methanol lignin (3421 cm^{-1}) and kraft sulfite lignin (3413 cm^{-1}).

On the other hand the dielectric constant ε' and dielectric loss ε'' values of kraft and kraft-sulfite lignins are very high. This is due to the presence of S in their molecular structure. Also, the dielectric properties of kraft sulfite lignin is higher than kraft lignin. This can be attributed to the presence of —SO_3H group beside —SH in the structure of kraft sulfite lignin. This can be seen from the infrared spectra of the kraft and kraft sulfite lignin in which the C—S vibrational band appeared at 625 and $630\,cm^{-1}$ for C—S in kraft lignin and SO_3H for kraft sulfite lignin. The band intensity of C—S at $625\,cm^{-1}$ is higher than that at $630\,cm^{-1}$ of C—S and C—SO_3H. These bands do not appear in the infrared spectra of soda and soda methanol lignin. These groups increase the polarity and mobility of the side chain of lignin molecules. However, the presence of the sulfur in the lignin structure decreases the intermolecular interaction than in soda lignin which has no sulfur in its structure. For these reasons, the kraft and kraft sulfite lignins can be considered as semiconductor materials.

• Effect of Temperature on the d.c. Electrical Resistivity

Figure 3 shows $\log\rho$ against 1000/T. From this figure it is clear that kraft and kraft sulfite lignins have electrical resistivity of 40.22×10^6 and $0.44 \times 10^6\ \Omega^{-1}\,cm^{-1}$ respectively. Kraft lignin shows a small decrease of resistivity by increasing temperature to about 124°C after which the resistivity shows a linear rapid decrease. The activation energies in the two regions are $E_1 = 0.045$ and $E_2 = 1.984\,eV$. For kraft sulfite lignin, its electrical resistivity shows two regions in which the resistivity decreases linearly by increasing temperature, with activation energies of $E_1 = 1.297$ and $E_2 = 0.389\,eV$. The inspection of this figures reflects the semiconducting behaviour of these two lignins.

• Mechanism of the Conduction Process

Further information concerning the solid state properties was obtained by considering the type and mechanism of the conduction process. This can be achieved by studying the effect of temperature on the mobility μ and the number of current carriers N which take part in the conduction process. The number of change carriers can be obtained by calculating the Fermi distribution function and the density of state function [10–11]. The product of the two functions

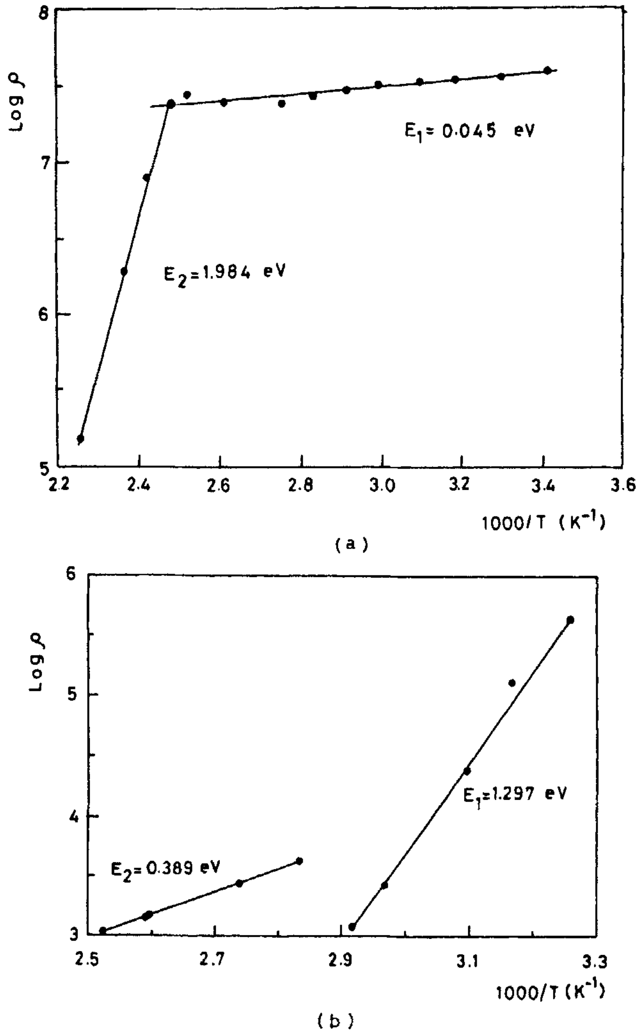

FIGURE 3 Relation of log ρ against 1000/T for (a) kraft lignin and (b) kraft sulfite lignin.

gives the actual number of carriers per cubic meter N. The mobility of the change carriers μ ($cm^2\ V^{-1}s^{-1}$) is also calculated using the single model relation [12].

$$\sigma = Ne\mu$$

where σ is the electrical conductivity ($\Omega^{-1}\text{cm}^{-1}$) and e is the electronic charge.

The effect of temperature on the number of carriers and their mobilities for kraft and kraft sulfite lignins is shown in Figures 4 and 5 respectively. Inspection of the figures shows that the drift mobility decreases with increasing temperature while the density of carriers increases with increasing temperature. This indicates that the activation process is due to the electron transfer from the valence band to the conduction band by thermal activation.

Dissipation factor ($\tan\delta$) of all the investigated lignins over the frequency range 0.3–100 kHz is shown in Figure 6. It is clear, in

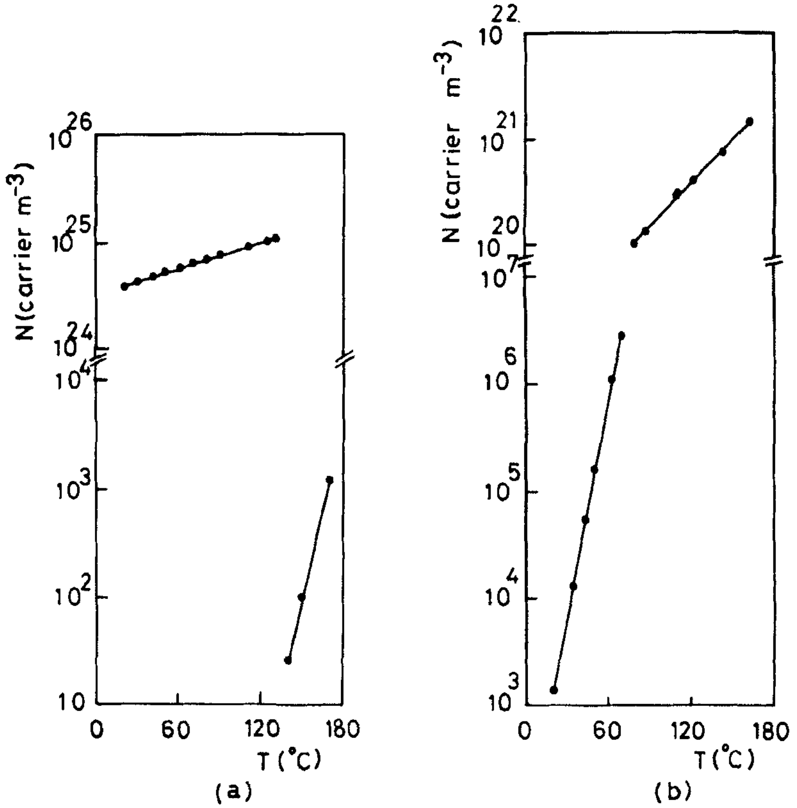

FIGURE 4 Effect of temperature on the number of carriers for (a) kraft lignin and (b) kraft sulfite lignin.

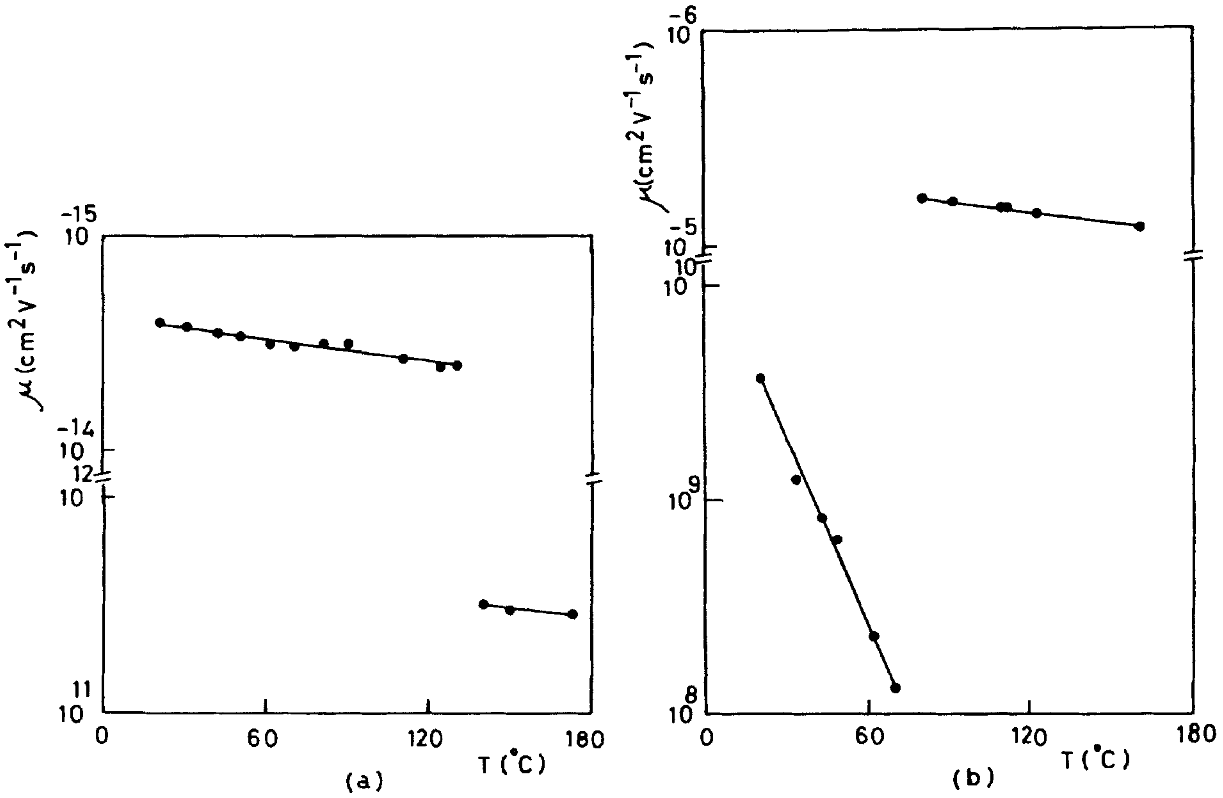

FIGURE 5 Effect of temperature on the carrier mobility for (a) kraft lignin and (b) kraft sulfite lignin.

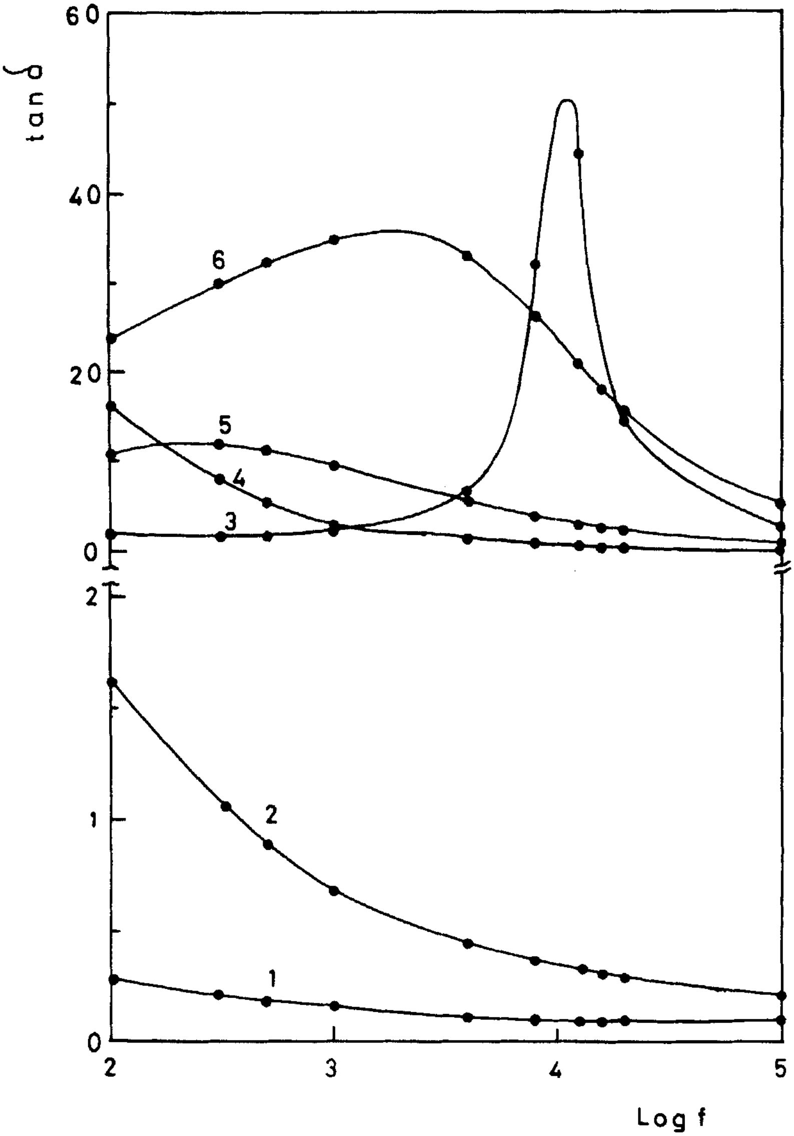

FIGURE 6 Relation between dissipation factor tan δ and log *f* at room temperature for (1) soda lignin (2) soda + AQ + methanol lignin (3) soda methanol lignin (4) soda + AQ lignin (5) kraft lignin and (6) kraft sulfite lignin.

general, that the dissipation factor decreases by increasing the frequency except for kraft, kraft sulfite and soda methanol lignins. These latter three lignins show a maximum values of tan δ at 0.3, 2.5 and 11 kHz respectively. The presence of S and SO_3H in the lignin polymer decreases the energy of relaxation due to the increase of mobility of the side chain of lignin. The methanol soda lignin has also this phenomena *i.e.*, decreasing degradation as well as hydroxyl groups. From the infrared spectra it is clear that the absorbance of the etheric band at $1120\,cm^{-1}$ has a lower value in case of methanol soda lignin (4.2) than other lignins (8.9, 9.5 and 8.5). This also causes an increase in the phenol hydroxyl group of methanol soda lignin. This will shift the relaxation process to high frequencies.

For quantitative studies of the dielectric behaviour, the effect of temperature on the dielectric constant ε', dielectric loss ε'' and dissipation factor tan δ at different frequencies for soda, kraft, kraft sulfite, soda methanol and soda + AQ + methanol lignins are taken into consideration, Figures 7–11. These figures show that the dielectric constants ε' and ε'' of soda, kraft, kraft sulfite, soda methanol and soda + AQ + methanol lignins have maximum values at (60–85), 110, 80, (40–130) and 80°C respectively. This may be due to the increase of degradation of lignin molecules. These maxima decrease by increasing frequency. These temperatures reflect a qualitative sequence for the energy of the intermolecular interaction. The maximum intensity of the dielectric constant ε' at a frequency of 1 kHz has the following values: 22.6, 25.8×10^4, 9.4×10^5, 0.6 and 16.2 for soda, kraft, kraft sulfite, soda methanol and soda + AQ + methanol lignins respectively, (Figs. 7–11). The kraft and kraft sulfite has the higher dielectric constant at 1 kHz than the other lignins due to the presence of S in the lignin molecules. On the other hand the soda methanol lignin has the lowest ε' (0.6) at 1 kHz due to its high degradation during the pulping process. Also the soda methanol lignin is characterized by its lower absorbance of the methoxyl band (14) than the soda (19) and Kraft (19) lignin. This causes an increase in the phenol hydroxyl groups. This will induce also a high mobility of the functional group of soda methanol lignin (Fig. 2).

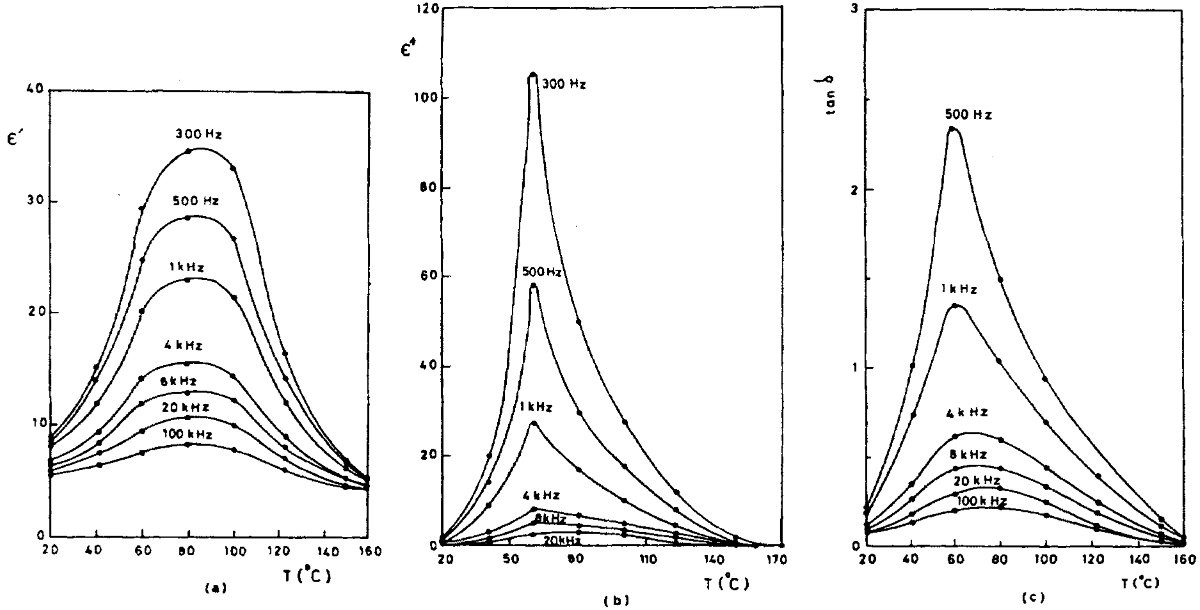

FIGURE 7 Effect of temperature on (a) the dielectric factor ε', (b) dielectric loss ε'' and (c) dissipation factor $\tan\delta$ at different frequencies for soda lignin.

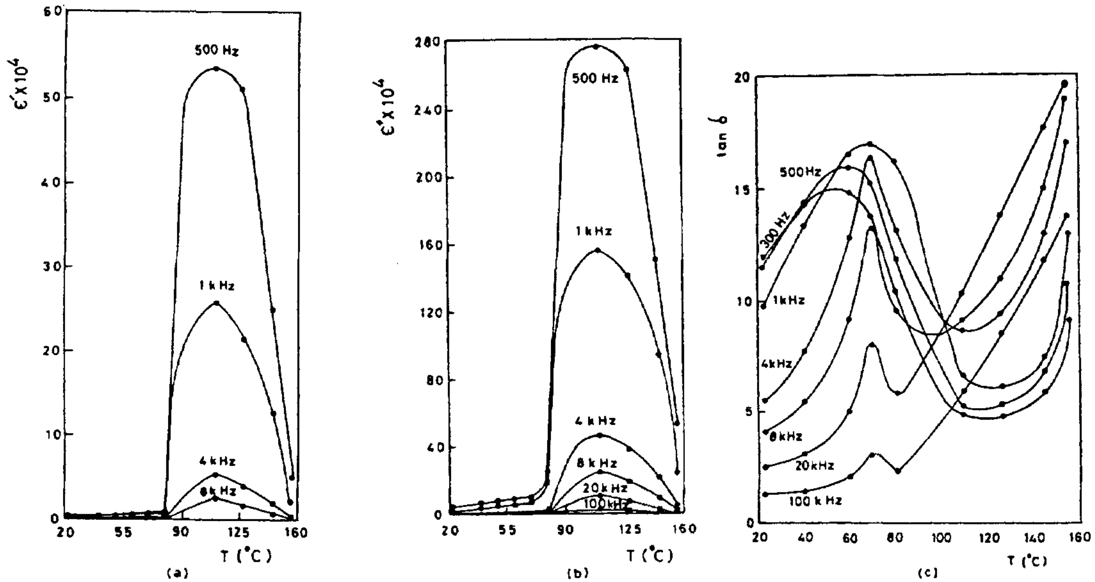

FIGURE 8 Effect of temperature on (a) the dielectric constant ε', (b) dielectric loss ε'' and (c) dissipation factor $\tan\delta$ at different frequencies for kraft lignin.

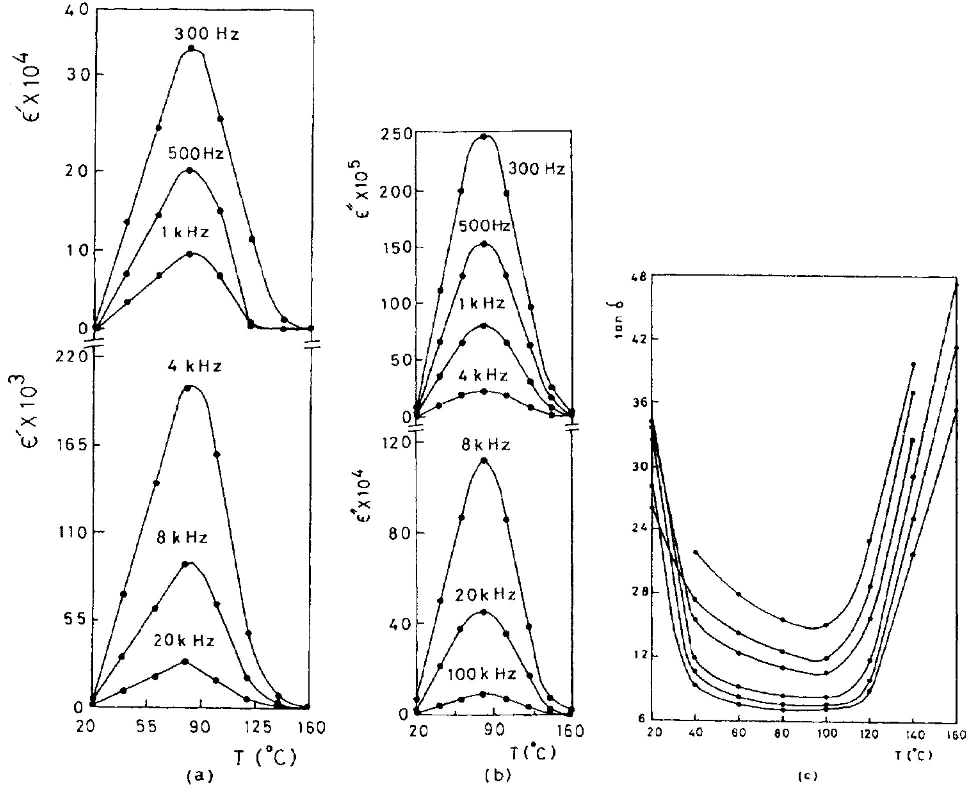

FIGURE 9 Effect of temperature on (a) the dielectric constant ε', (b) dielectric loss ε'' and (c) dissipation factor $\tan\delta$ at different frequencies for kraft sulfite lignin.

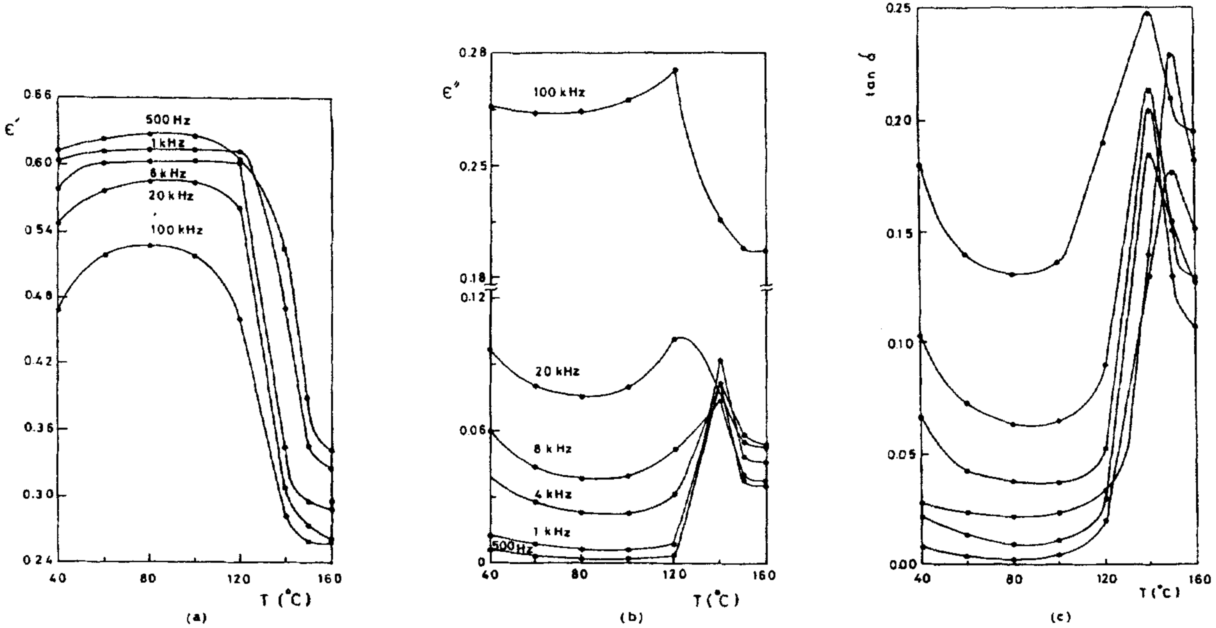

FIGURE 10 Effect of temperature on (a) the dielectric constant ε', (b) dielectric loss ε'' and (c) dissipation factor $\tan\delta$ at different frequencies for soda methanol lignin.

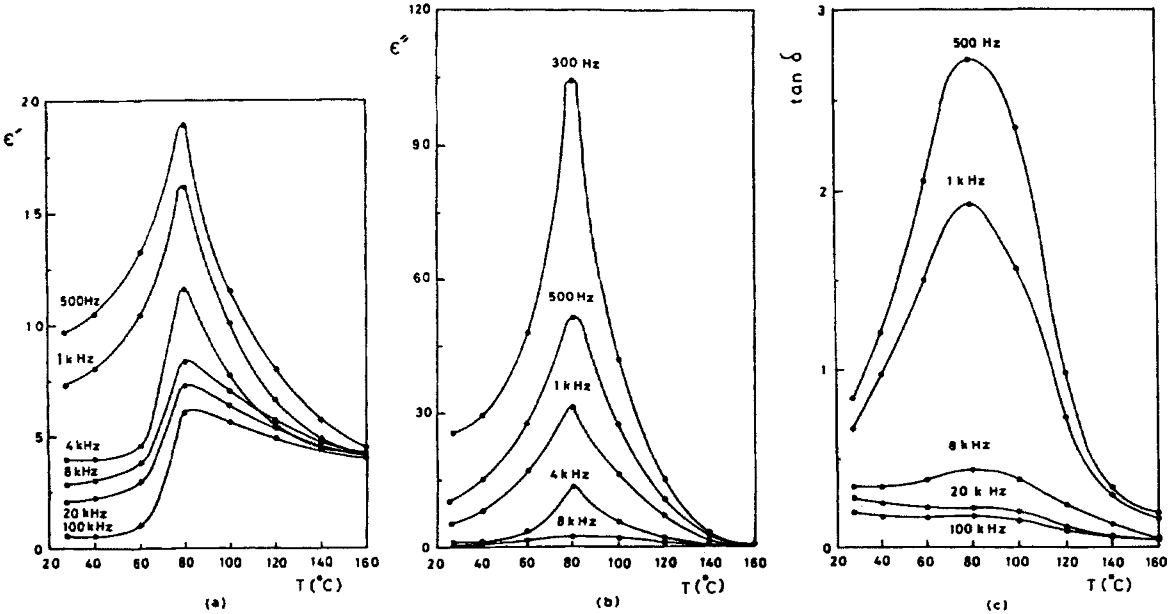

FIGURE 11 Effect of temperature on (a) the dielectric constant ε', (b) dielectric loss ε'' and (c) dissipation factor $\tan\delta$ at different frequencies for soda + AQ + methanol lignin.

• Effect of Temperature on the Dielectric Properties of Different Lignins

Figures 12–14 show the effect of temperature on the relaxation of kraft, kraft sulfite and soda methanol lignins. It is clear from these

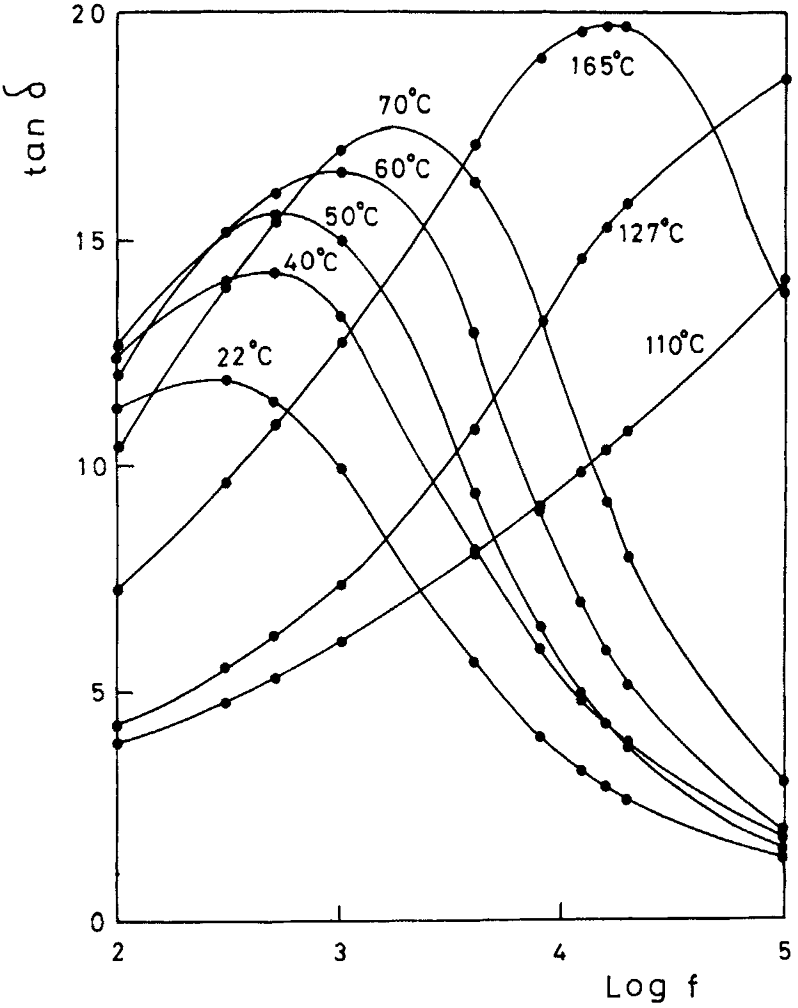

FIGURE 12 Relation between the dissipation factor tan δ and log ρ at different temperatures for kraft lignin.

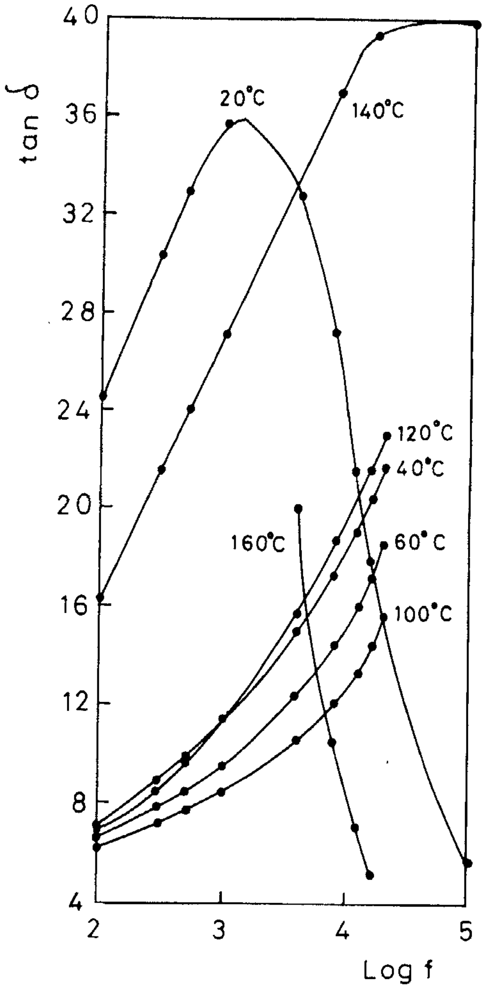

FIGURE 13 Relation between the dissipation factor tan δ and log ρ at different temperatures for kraft sulfite lignin.

figures that the maximum of relaxation is shifted toward higher frequency by increasing temperature. This can be explained by the decrease in intermolecular interaction between the molecules of lignin in its polymer structure.

In case of kraft sulfite and soda methanol lignins the maximum relaxations are shifted towards high frequency (out of the investigated range) by increasing temperature.

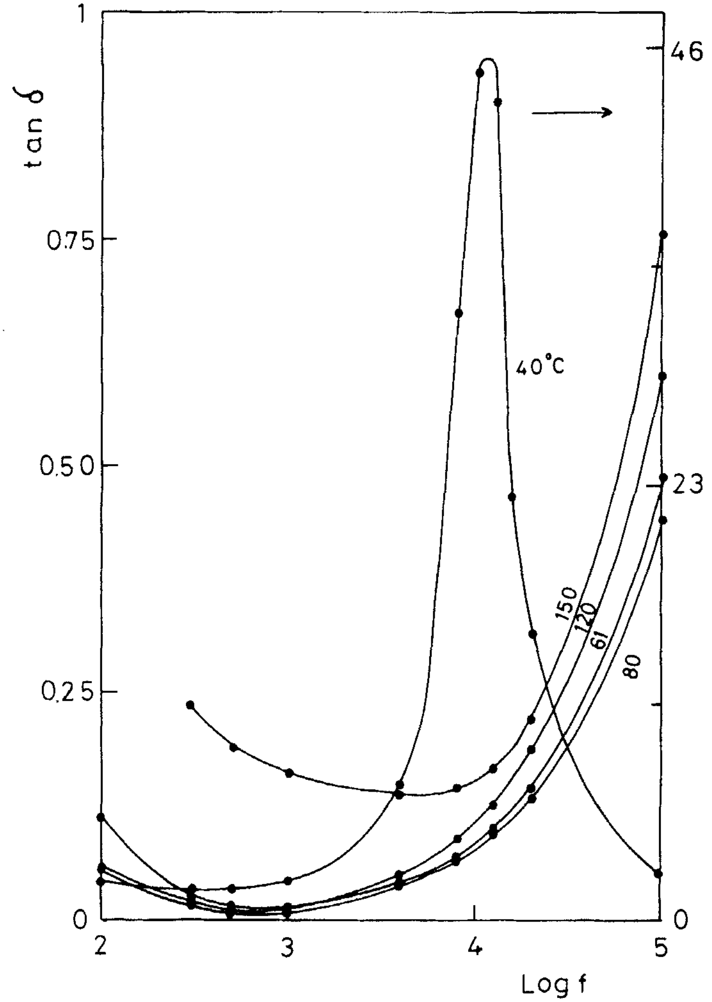

FIGURE 14 Relation between the dissipation factor $\tan\delta$ and $\log\rho$ at different temperatures for soda methanol lignin.

CONCLUSION

The molecular structure of different lignins plays an important role on their dielectric properties. Presence of sulfur in the structure of kraft and kraft sulfite lignins decreases their dielectric constants and their electrical resistivity are in the range semiconductor materials.

The drift mobility of the charge carriers for kraft and kraft sulfite lignins decreases with increasing temperature while the density of carriers has the opposite trend. This indicates that the activation process is due to electron transfer from the valence band to the conduction band by thermal activation.

Activation energies of kraft and kraft sulfite lignins have been calculated. There are two values for each lignin E_1 and E_2 for low and high temperature range respectively.

They are $E_1 = 0.045$, $1.297\,\text{eV}$ and $E_2 = 1.984$, $0.389\,\text{eV}$ for kraft and kraft sulfite lignins respectively.

The dissipation factor of different lignins decreases by increasing frequency except for kraft, kraft sulfite and soda methanol lignins.

Presence of S and SO_3H groups in kraft and kraft sulfite lignins decreases the energy of relaxation.

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