

Dielectric response and electric properties of organic semiconducting phthalocyanine thin films

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Abstract: The dielectric function of some phthalocyanine compounds (ZnPc, H₂Pc, CuPc, and FePc) were investigated by analyzing the measured capacitance and loss tangent data. The real part of the dielectric constant, ϵ_1 , varies strongly with frequency and temperature. The frequency dependence was expressed as: $\epsilon_1 = A\omega^n$, where the index, n , assumes negative values ($n < 0$). In addition, the imaginary part of the dielectric constant, ϵ_2 , is also frequency and temperature dependent. Data analysis confirmed that $\epsilon_2 = B\omega^m$ with values of m less than zero. At low frequencies and all temperatures, a strong dependence is observed, while at higher frequencies, a moderate dependence is obvious especially for the Au-electrode sample. Qualitatively, the type of electrode material had little effect on the behavior of the dielectric constant but did affect its value.

Analysis of the AC conductivity dependence on frequency at different temperatures indicated that the correlated barrier hopping (CBH) model is the most suitable mechanism for the AC conduction behavior. Maximum barrier height, W , has been estimated for ZnPc with different electrode materials (Au and Al), and had values between 0.10 and 0.9 eV. For both electrode types, the maximum barrier height has strong frequency dependence at high frequency and low temperatures.

The relaxation time, τ , for ZnPc and FePc films increases with decreasing frequency. The activation energy was derived from the slopes of τ versus $1/T$ curves. At low temperatures, an activation energy value of about 0.01 eV and 0.04 eV was estimated for ZnPc and FePc, respectively. The low values of activation energy suggest that the hopping of charge carriers between localized states is the dominant mechanism.

Key words: organic semiconductor; dielectric function; evaporation; relaxation time

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1. Introduction

Recently, many research groups from all over the world have focused on studying the various properties of organic semiconductor thin films, bulk material or pellets. Metal-free and/or metal-substituted phthalocyanine systems are examples of such compounds. Phthalocyanines are aromatic and chemically stable compounds with semiconducting properties and also dense colors, which make them suitable for use as dyes and pigments in textile industries. In addition, many of these compounds have been technologically employed as gas sensors, solar cells, and opto-electronic devices^[1–3]. Phthalocyanine compounds such as NiPc, CoPc and CuPc have been intensively studied and then manufactured as gas sensing devices^[4–6]. Moreover, copper phthalocyanine, CuPc, has been utilized as a buffer-zone layer in the manufacture of white organic light emitting diodes^[7], while platinum phthalocyanine solution, PtPc, has been utilized to generate various types of optical switching devices^[8].

The effect of oxygen on the photovoltaic properties of organic solar cells consisting of zinc phthalocyanine, ZnPc, was thoroughly investigated by Kerp and Van Faassen^[9]. They observed a noticeable increment in the short-circuit current when increasing the partial O₂ pressure. In a comprehensive study on controlled p-doping of pigment layers, Pfeiffer *et al.*^[10] concluded that doping has the potential of both reducing the

series resistance and increasing the photo-voltage of organic solar cell in doped ZnPc donor-acceptor hetero-junctions. Gao and Kahn intensively investigated the electronic structure and current injection in p-doped ZnPc films^[11]. The possibility of using ZnPc thin layers as gas sensing devices was examined thoroughly by studying the effect of gases, either oxidizing (O₂ and NO₂) or reducing (H₂ and NH₃) gases, on the electrical conductivity of the sample^[12, 13].

A new promising and important era was opened recently for phthalocyanine compounds in biomedical and biophysical technology. Zinc phthalocyanine, ZnPc, is employed in medical applications due to its selective binding to tumor-selective antibodies, and it has been used in the synthesis of a novel compound applicable in photodynamic therapy^[14]. In addition, Gao and coworkers^[15] synthesized tetra-trifluoroethoxyl zinc phthalocyanine (an organic compound that can be dissolved in most organic solvents) that has the potential to be used in photodynamic cancer therapy. Fadel *et al.* used zinc phthalocyanine-loaded PLGA biodegradable nanoparticles for photodynamic therapy in tumor-bearing mice^[16].

In this study, the dielectric response and some of the AC electrical properties of some phthalocyanine compounds are investigated and analyzed over a wide range of temperature (90–470 K) and the frequency range between 0.1 to 20 kHz.

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2. Experimental

Samples in the form of Au–metal–Pc–Au, or Al–metal–Pc–Al sandwich structures have been prepared using a fine powder of phthalocyanine (purity $\sim 98\%$) supplied by Fluka AG. Six samples, each of an active area of $1.2 \times 10^{-5} \text{ m}^2$, were sequentially deposited onto pre-cleaned Corning microscope slides at room temperature. A sequential masking system^[17] was employed to prevent breaking the vacuum during the deposition process. The background pressure was held approximately at 10^{-3} Pa during the deposition of both the ZnPc film and the Au electrode layers. The gold electrodes were evaporated from a molybdenum boat at a deposition rate of 0.5 nm/s , while zinc phthalocyanine, ZnPc, utilized a covered tantalum boat and a deposition rate of 0.9 nm/s . Deposition of the second Au electrodes was initially at a lower rate of 0.1 nm/s in order to avoid thermal damage to the underlying phthalocyanine films. Under such deposition conditions, and like many other metal–phthalocyanine compounds, the films assume an α -phase polycrystalline structure^[18]. During the deposition process, a conventional quartz crystal system was employed for continuous monitoring of the deposition rates and film thickness.

The AC electrical measurements were made in a secondary vacuum system at a pressure of about 10^{-3} Pa . A homemade liquid nitrogen cryostat was used for electrical measurements. The sample temperature was measured using a chromel–alumel thermocouple attached to a Fluke K/J digital thermometer. A stabilized power supply incorporated with a Keithley 617 electrometer was connected to the sample using very short leads, and measurements were recorded via a microprocessor. The sample temperature was varied and stabilized by controlling the heating and cooling rates. Capacitance, loss tangent and conductance are measured in the frequency range of 0.1 to 20 kHz and temperature between 90 – 470 K using a Hewlett-Packard (4276A) LCZ meter equipped with a four-terminal test fixture.

3. Results and discussion

The capacitance of phthalocyanine thin films was measured as a function of temperature and frequency. Figure 1 displays the variation of capacitance, C_m , on the inverse of film thickness, $1/d$, for ZnPc thin films. An approximate linear relation between these two parameters is apparent, and therefore, the system may be analyzed in terms of a parallel plate capacitor^[19]. The measured capacitance, C_m , is therefore, given by:

$$C_m = \frac{\varepsilon_0 \varepsilon_r A}{d}, \quad (1)$$

where ε_0 is the permittivity of free space while ε_r is the relative permittivity of the dielectric material, and A ($= 1.2 \times 10^{-5} \text{ m}^2$) is the effective area of the capacitor. The measured capacitance depends only on the geometry of the film and on the permittivity of the material, ZnPc. As can be clearly seen from the figure, the fitted line does not pass through the origin, and hence an additional parallel capacitance, C_p , of approximately 0.5 nF should be added to the measured one. The overall capacitance, C , is therefore the sum of the sample capacitance, C_m , and the parallel one, C_p , thus;

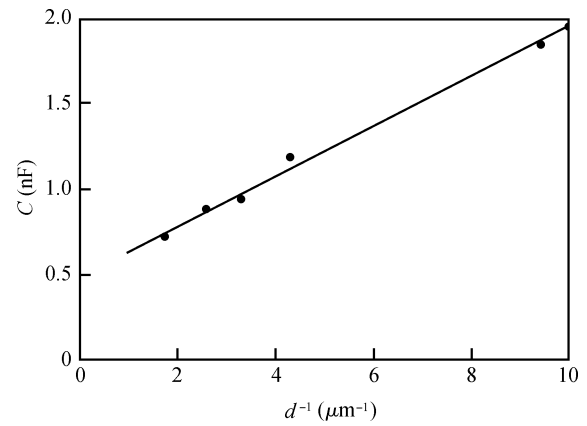


Fig. 1. Dependence of capacitance of ZnPc-films on the inverse of sample thickness at constant frequency of 1 kHz .

$$C = C_m + C_p = \frac{\varepsilon_0 \varepsilon_r A}{d} + C_p. \quad (2)$$

By determining the slope of the line ($\sim \varepsilon_0 \varepsilon_r A$), the permittivity of ZnPc, $\varepsilon \approx 1.4 \times 10^{-11} \text{ F/m}$, was estimated, while the intercept, C_p , may be due to instrumental features and/or edge effects. This derived permittivity value is considerably lower than the value of ε ($\approx 3.2 \times 10^{-11} \text{ F/m}$) for copper phthalocyanine CuPc^[20, 21]. The low value of ε observed for ZnPc is probably due to submicroscopic inhomogeneities, small grain size, impurities, and to the low packing density of the specimen.

The determination of the AC dielectric constant ($\varepsilon = \varepsilon_1 - i\varepsilon_2$) allows us to study and analyze the behavior of the complex dielectric function. The real part of the dielectric function (constant), ε_1 , of some metal–phthalocyanine thin films was calculated from the measured capacitance $\{\varepsilon_1 = C_m d / \varepsilon_0 A\}$ at all temperatures and frequencies under consideration. The calculated real part of the dielectric constant as a function of temperature and frequency is displayed in Fig. 2. Figure 2(a) shows the variation of ε_1 as a function of T at fixed frequencies for CuPc film of thickness $0.4 \mu\text{m}$, while Figure 2(b) displays the variation of ε_1 as a function of f at different fixed temperatures for ZnPc.

As can be clearly observed from Fig. 2, the real part of the dielectric constant, ε_1 , increases at temperatures above room temperature and low frequencies, while at low temperatures and high frequencies it saturates to a constant value. The real part of the dielectric constant, ε_1 , shows a steady variation with temperatures above 270 K . The same behavior of the dielectric function was also observed in ZnPc thin films^[22]. There is a good agreement between values of the real part of dielectric constant and the temperature variations with CoPc pellets^[23]. A large increase in ε_1 with temperature is observed in CoPc above room temperature followed by an abrupt decrease at temperatures higher than 370 K . This behavior was explained in terms of nonadmic polarization, which arises from the steep increase in the number of free carriers with increasing temperatures^[23].

The real part of the dielectric constant is strongly frequency dependent above room temperature, as can be seen in Fig. 2. Qualitatively, the present study shows that the behav-

Table 1. Dependence of the index n on temperature at various frequency ranges as obtained from the real part of dielectric constant for ZnPc with both aluminum and gold contact electrodes.

T (K)	Frequency range (kHz)					
	Al-electrodes			Au-electrodes		
	0.1–1	1.5–10	10–20	0.1–1	1–8	8–20
93				–0.01	–0.01	–0.01
192	–0.04	–0.015	–0.015	–0.01	–0.01	–0.01
263				–0.04	–0.018	–0.013
274	–0.06	–0.02	–0.02			
293	–0.36	–0.07	–0.08	–0.18	–0.05	–0.02
309	–0.17	–0.06	–0.04			
333	–0.17	–0.08	–0.05	–0.298	–0.17	–0.03
353	–0.47	–0.13	–0.06	–0.31	–0.22	–0.09
373	–0.64	–0.20	–0.1	–0.48	–0.25	–0.13
393				–0.58	–0.32	–0.18
415				–0.59	–0.56	–0.27

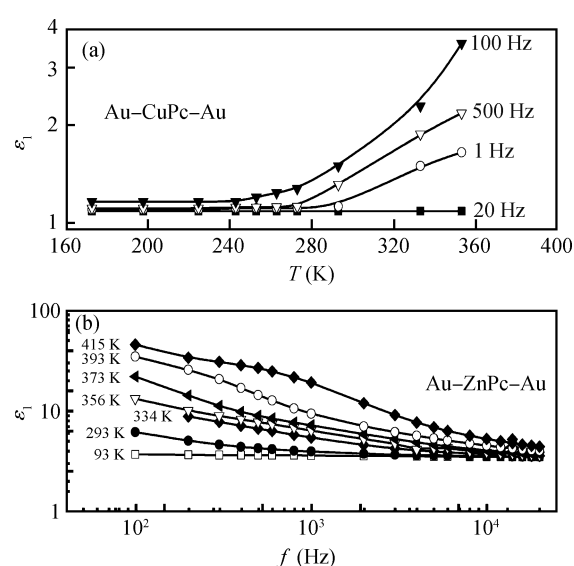


Fig. 2. Variation of the relative dielectric constant, ϵ_1 , on frequency and temperature. (a) Dependence on temperature at fixed frequencies for CuPc. (b) Dependence of ϵ_1 on frequency for ZnPc sample at fixed temperatures.

ior of the ZnPc samples with different electrode materials (Al or Au) is almost the same over the entire frequency range of study. The real part of the dielectric constant, ϵ_1 , shows strong frequency dependence below 5 kHz, particularly at temperatures above room temperature, while above this frequency and for all temperatures, the value of ϵ_1 becomes almost constant. The dielectric constant value of ϵ_1 of the Au-electrode sample has lower value than that of the Al-electrode, and this may be attributed to packing density of the sample, impurities, and film thickness variation. In addition, the formation of a space-charge layer due to charge accumulation within the Pc layer and the probable formation of Al_2O_3 during deposition will be of great influence on the values of ϵ_1 [24, 25]. Similar behavior of ϵ_1 has been also observed in other phthalocyanine compounds such as CoPc thin films [26] and CoPc pellets [23].

Analysis of the curves of ϵ_1 as a function of frequency was found to obey a power law relation of the form:

$$\epsilon_1 = A\omega^n, \quad (3)$$

where ω is the angular frequency, A is a constant, and the index, n , assumes negative values ($n < 0$). This index is not constant; it varies with frequency and temperature. The values of n were derived from the slope of the curves of Fig. 2. A linear dependence of $\log \epsilon_1$ and $\log f$ over the relevant frequency range is observed. The derived values of n over the whole frequency range at different fixed temperatures for samples with Al and Au electrodes are presented in Table 1. For both electrodes, the values of index n at low temperatures below (192 K) are almost constant for the whole range, above this temperature, n increases with increasing frequency.

The large values of the dielectric constant at low frequencies and at higher temperatures may not be an indication for spontaneous polarization [27]. At low frequencies, electrons can hop easily out of the sites with low free energy barriers in the electric field direction and tend to accumulate at sites with high free energy barriers. This leads to a net polarization of the dielectric medium and therefore higher dielectric constant values [28]. However, at high frequency, the charge carriers will no longer be able to relax as rapidly as the time-variation of the field, so the charge oscillation will begin to lag behind this field, resulting in a decrease of dielectric constant [29].

The loss tangent, $\tan \delta$ (which is a measure of the dissipated energy in the sample), was measured for H_2Pc and many metal-phthalocyanine samples over a wide range of frequency and temperature. The imaginary part of the dielectric function was estimated according to the relation:

$$\epsilon_2 = \epsilon_1 \tan \delta. \quad (4)$$

The calculated values of ϵ_2 for ZnPc, CuPc, FePc, and H_2Pc compounds were studied as a function of temperature and frequency. Figure 3 displays the frequency dependence of ϵ_2 for H_2Pc sample at different fixed temperatures. A strong frequency dependence of ϵ_2 is evident from the figure. The values of ϵ_2 increase with temperature up to 300 K, then starts to decrease due to nomadic polarization and to the partial exhaustion of oxygen molecules from the sample. The analysis of the obtained values of ϵ_2 as a function of frequency showed that it follows a power law relation ($\epsilon_2 = B\omega^m$). The power index, m , was calculated from the slopes of the fitted straight lines of $\log \epsilon_2$ versus $\log \omega$. For all temperatures of interest, the index m assumes negative values ($m < 0$).

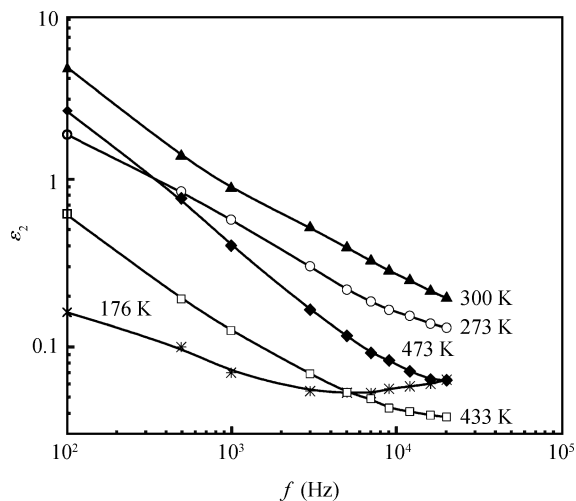


Fig. 3. Dependence of the imaginary part of dielectric function, ϵ_2 , on frequency for an H_2Pc thin film at different fixed temperatures.

Table 2. Variation of index m for H_2Pc at different temperatures in a frequency ranges.

T (K)	Frequency range (kHz)		
	0.1–1	1–8	8–20
273	–0.52	–0.59	–0.32
300	–0.67	–0.55	–0.48
433	–0.66	–0.42	–0.16
473	–0.81	–0.74	–0.46

Table 2 shows the variation of the power index, m , with temperature. It is obvious from the table that the values of m decrease almost linearly with the temperature. At low frequencies and at a specific temperature, the values of ϵ_2 are much higher than those values observed at high frequencies. Such dependence of ϵ_2 on frequency is typically associated with energy losses by conduction. Under the influence of an electric field at high temperature, electrons move easily through the network and conduction losses increase. At lower temperatures and higher frequencies, the capacity for mobility becomes lower, and conduction losses decrease^[29].

Qualitatively, the variation of ϵ_2 as a function of temperature at different fixed frequencies is almost the same for all the phthalocyanine compounds under consideration. However, in some phthalocyanine compounds (as in H_2Pc or $NiPc$), a peak is observed in ϵ_2 versus T . This peak was attributed to a probable nomadic polarization in the sample^[23] and to exhaustion of oxygen molecules out of the H_2Pc sample^[31, 32]. Nevertheless, in this study $ZnPc$, $CuPc$ and $FePc$ samples did not show any peak in ϵ_2 –temperature curves. Apparently, the preparation conditions, sample thickness, and the presence of impurities such as O_2 (which acts as acceptor) will have a noticeable effect on the electrical and dielectric properties of phthalocyanine compounds. However, annealing the sample or heating it to high temperatures will stabilize such properties due to oxygen desorption and to partial structural transformation^[26, 31–33]. The increase of the observed values of the real part, ϵ_1 , and the imaginary part, ϵ_2 , with temperature may be accredited to the enhanced conductivity through the thermal excitation of the charge carriers. Such behavior will greatly af-

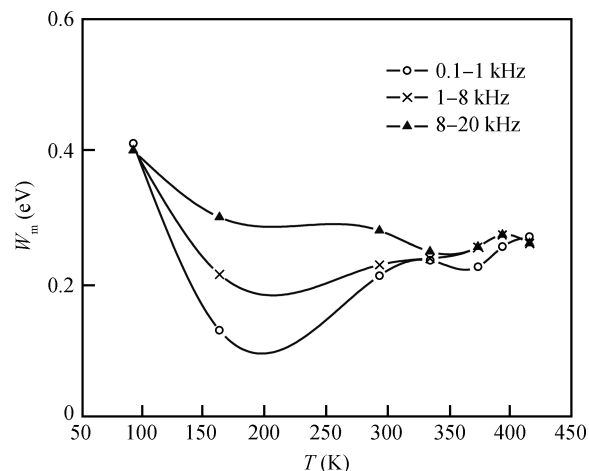


Fig. 4. Dependence of maximum barrier height, W_m , on temperature at various frequency ranges for $ZnPc$ with Au-electrodes.

fect the conductivity of the sample, hence the dielectric properties^[34].

The frequency dependence of the AC conductivity ($\sigma_{ac} = A'\omega^s$) is used to assess the frequency exponent index, s ^[33–36]. The obtained experimental results of the AC conductivity were analyzed with various theoretical models and the correlated barrier hopping (CBH) model was found to be the appropriate mechanism for the electron transport in phthalocyanine films^[36]. Application of the CBH model reveals that the electronic conduction takes place via single or bipolaron hopping processes in the whole temperature range of study. According to the CBH model, the index, s , is related to maximum barrier height, W_m to first order approximation as^[36]:

$$s = 1 - \frac{6k_B T}{W_m}, \quad (5)$$

where k_B is the Boltzmann's constant and T is the temperature. The maximum barrier height W_m at infinite separation, which is called the "polaron binding energy", i.e. the binding energy of the carrier in its localized sites^[36]. For a bipolaron W_m is approximately, equal to the band gap width, while for single polaron its value is equal to a quarter of the optical band gap^[37].

For most metal-phthalocyanine compounds, the experimental value of the index, s , is temperature dependent and has values less or equal to unity ($s \leq 1$). Such behavior of s is an indication of a dominant hopping conduction process over that frequency and temperature range^[22, 26, 31, 33–34]. The value of s increases towards unity as the temperature tends to zero indicating the dominance of a CBH model as a transport mechanism in many organic and/or in inorganic systems^[22, 33, 34, 38–40].

The maximum barrier height, W_m , dependence on temperature at different frequency ranges is illustrated in Fig. 4 for a $ZnPc$ sample with Au electrodes. Qualitatively, the behavior of W_m is the same irrespective of type of the electrode material. The maximum barrier height increases with increasing frequency and decreases with temperature increase up to about 200 K. Above this temperature, W_m starts to increase up to room temperature, then it almost saturates to a constant value. The accumulation of charge carriers within traps at low

Table 3. Maximum barrier height, W_m , values for Au–ZnPc–Au and Al–ZnPc–Al thin film.

T (K)	Frequency range (kHz)				
	Al-electrodes		Au-electrodes		
	0.5–4.5	5–20	0.1–1	1–8	8–20
93			0.411	0.405	0.401
163			0.135	0.216	0.301
193	0.832				
273	0.543				
295	0.441	0.857	0.214	0.230	0.281
310	0.335	0.488			
333	0.357	0.507	0.227	0.220	0.221
353	0.281	0.332			
375	0.206	0.236	0.227	0.227	0.227
393			0.257	0.275	0.257
415			0.272	0.262	0.262

temperatures may increase the barrier height above 200 K. At low temperatures, W_m is strongly frequency dependent, while a weak frequency dependence is observed at higher temperatures. Quantitatively, the values of W_m for Al-electrodes are higher than for Au-electrodes due to the possible formation of a very thin Al_2O_3 layer during deposition^[31, 33]. It is evident that the value of W_m depends on the electrode material since some elements provide ohmic contacts while others provide blocking contacts^[3, 20, 21]. In addition, film thickness, impurity concentration (such as O_2), charge accumulation, and their distribution within traps will have a huge effect on the value of optical barrier height. In the present study, the Al-electrode gave an ohmic contact behavior since the deposition of all layers took place without breaking the vacuum^[17]. Table 3 displays the values of barrier height width for both Al- and Au–ZnPc samples at different temperatures and frequencies.

The calculated values of W_m of the present study agree well with those observed in ZnPc^[22]. In addition, a qualitative agreement is observed with the W_m values of inorganic compound Ga_2S_3 – Ga_2Se_3 ^[40]. The present results indicate that the conduction mechanism may be resulted by bipolaron or mixed with a single polaron hopping process. Thus, we invoke the correlated barrier-hopping (CBH) model to explain the observed behavior of W_m . In the CBH model, the electrons in charged defect states hop over the coulomb barrier of the height given as $W_C = W_m - (ne^2/\pi\epsilon_1\epsilon_0R)$ ^[38].

The relaxation time, τ , was calculated by using the relation given in^[36–38, 41]

$$\tau = \frac{\epsilon_2}{(\epsilon_1 - \epsilon_\infty)\omega}, \quad (6)$$

where ϵ_1 (ϵ_2) is the real (imaginary) part of the dielectric constant, ω is the angular frequency, and, ϵ_∞ is the optical dielectric constant (at very high frequency). The optical dielectric constant (ϵ_∞) values were determined by extrapolating the curves of ϵ_1 versus frequency. Above 15 kHz, the values of ϵ_∞ saturates to a constant value at any specific temperature. The variation of relaxation time as a function of frequency and temperature is displayed in Fig. 5. As can be clearly seen from the figure, τ is strongly dependent on both frequency and temperature. Figure 5 (a) displays the dependence of τ on frequency at different fixed constant temperatures for the iron phthalocyanine, FePc, sample. In general, the relaxation time for both ZnPc and FePc decreased with increasing frequency up to

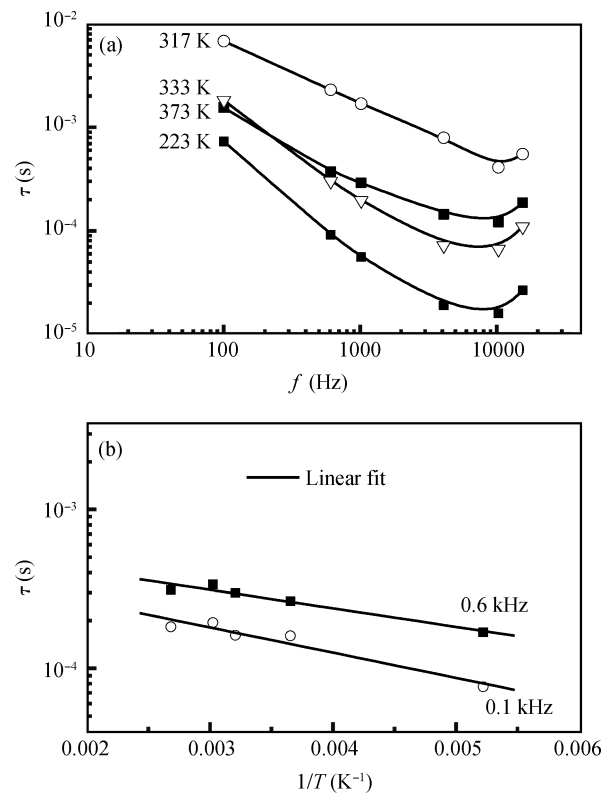


Fig. 5. Dependence of relaxation time on (a) frequency, and on (b) reciprocal of temperature for ZnPc-sample with Al-electrodes.

about 10 kHz, then a small increase in τ is observed. The estimated values of τ for the ZnPc sample are comparable, but not the same as those for the FePc sample. This discrepancy may be attributed to growth conditions, sample packing fraction, charge carrier concentrations and their distribution, and differences in sample thickness. The values of relaxation time and their dependence with temperature and frequency have a good qualitative agreement with glassy a-Se–Te–Ga system^[37], and ZnPc^[22, 38, 42].

For many compounds, it is well established that relaxation time is related to a thermally activated process according to the relation of the form^[36, 37, 41]

$$\tau = \tau_\infty \exp\left(-\frac{E_r}{k_B T}\right), \quad (7)$$

where τ_{∞} ($\sim 10^{-13}$ s) is a characteristic relaxation time which is in the order of an atom vibrational period at very high (infinite) temperature^[22, 36, 37], and E_r is the activation energy for relaxation. The dependence of $\ln\tau$ on reciprocal temperature, $1/T$, for the ZnPc sample at different fixed frequencies is depicted in Fig. 5(b). The data fits well to a straight line, indicating an exponential variation of τ with temperature, as expected from Eq. (7). The determination of the slope of each curve allowed us to estimate the activation energy of the charge carrier, and it was found to be around 0.01 eV. Similarly, an activation energy of about 0.04 eV was calculated for the FePc sample. The low values of activation energy are consistent with the hopping of charge carriers between localized states^[36, 43, 44]. Such low values of activation energy were observed in some inorganic materials like AlN_x ^[45], and ZnO ^[46], and also in many metal-phthalocyanine compounds like ZnPc^[22, 33, 34, 42], MgPc^[47], CuPc^[48] and FePc^[49].

4. Summary and conclusions

The dielectric function of some phthalocyanine compounds (ZnPc, H_2Pc , CuPc, and FePc) were investigated by analyzing the measured capacitance and loss tangent data. The real (imaginary) part of dielectric constant, ϵ_1 (ϵ_2) is found to vary with frequency and temperature. Qualitatively, the type of electrode material had no effect on the behavior of the dielectric constant, but quantitatively the values are different. The formation of a very thin insulating Al_2O_3 layer between the Al-electrode and the phthalocyanine layer will change the value of the dielectric constant. Also, film thickness, impurity concentration, and carrier distribution will affect ϵ .

The maximum barrier height, W_m , has been estimated for the ZnPc sample with different electrodes, (Au or Al), and found to be in the range between 0.10 and 0.90 eV. For both electrode-materials, W_m variation with temperature and frequency depends on the range of consideration. The observed values of W_m of Al-ZnPc-Al are higher than those values for the Au-ZnPc-Au sample and it may be due to the formation of an Al_2O_3 thin layer during deposition.

The relaxation time, τ , for ZnPc and FePc films is found to depend on both frequency and temperature. For both compounds, the relaxation time decreases with increasing frequency up to about 10 kHz and then a small increase is observed. The observed low value of activation energy suggests that the hopping of charge carriers between localized states is the dominant mechanism.

In general, the behavior of the dielectric properties of the different phthalocyanine compounds is qualitatively almost the same, but there are some differences in their values. Such variation could be related to the type of electrode material, impurity concentration, sample thickness, packing fraction, and growth conditions.

In conclusion, the results of this study, in conjunction with the AC- and DC-electrical measurements of H_2Pc , FePc, CuPc, ZnPc, and CoPc, suggest that more research efforts are needed to fully understand phthalocyanine-compound systems. The proposed investigation should cover a wider frequency range and include other phases such as β - and γ -modification. In addition, the study may take into account the preparation conditions, film growth, electrode material type, and sample aging.

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