Study of Dielectric Relaxation in Zn, Cd, and Hg, Ethanolamine Complexes

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The dielectric constant $\varepsilon`$ and dielectric loss $\varepsilon``$ for Zn(II), Cd(II) and Hg(II) ethanolamine complexes, which become semiconducting materials in their ligand structure, have been measured in the temperature (100-300K) and frequency (1kHz-13MHz). The temperature variation of $\varepsilon`$ and $\varepsilon``$ does not have a peak within the frequency range of the investigations, unlike many semiconducting glasses. Howevere, the imaginary parts, $M``$, of the dielectric modulus, $M*$, have peaks indicating Deby-type dielectric relaxation behaviour with a distribution of relaxation times. The relaxation behaviour is thermally activated with activation energy of about 0.3 eV.

1. Introduction:

Amino alcohol complexes have received much interest because of their applications in different fields such as buffers, catalysts, inhibitors, ion exchangers, additives in building materials, electroplating and dyes [1-6]. Recently, some of these materials with Monoethanolamine (MEA), Diethanolamine (DEA) and Triethanolamine (TEA) as ligand have been prepared and show glassy semiconductor materials [7 & 8]. Extensive studies on the structural chemistry, spectroscopic and thermal analysis of the amino-alcohol complexes were published [9-13]. The a.c electrical studies of the complexes reveal some structural details and add valuable complementary information relevant to electrical application of polymer materials. On the other hand, certain dielectric quantities or functions are employed more often than others depending on the particular field application. It is to be noted that different conduction mechanisms can exist in organometallic complexes. Some of them are well established such as electron hopping and polarization conduction. In the present paper, we report extensive studies of dielectric relaxation of the three octahedral Zn, Cd, and Hg (MEA)$_2$ complexes. It has shown that the gradual change from 3d to 5d electron (i.e from Zn to Hg) plays a major role in controlling their behaviour.

2. Experimental:

Detailed method of preparation of these complexes and their analytical data have been discussed in reference [14]. The solid metal-amino alcohol complexes were prepared by mixing the required weight of the metal salt (Zn SO$_4$, Cd SO$_4$ and Hg Cl$_2$) dissolved in the least amount of water with the calculated amount of the ligand saturated with ethanol. The mixture was refluxed for about 5 min. The complexes were precipitated and filtered, washed several time with a mixture of EtOH-H$_2$O solvent, then dried in vacuum desiccators over anhydrous CaCl$_2$. The complexes were pressed into discs of 10mm diameter and 1.0 mm thickness at a pressure of 0.9 G Pa. Silver paste was painted on the major faces of each test piece as electrodes. The capacitance C (ω), the phase angle φ, the loss factor tan δ, and the impedance Z (ω) were measured simultaneously at frequencies from 1kHz to 13MHz in the temperature range 100-300 K using LCR meter (4275A). The dielectric constant ε`, the dielectric loss ε`` and the dielectric modulus M* were calculated as discussed below. Carbon, Hydrogen, Nitrogen and sulphate contents were determined at the microanalytical center, Faculty of Science, Cairo University, EGYPT. The Zn, Cd, and Hg contents were done complexometrically [15]. All the analytical data as well as the dielectric relaxation data are collected in Table(1). Structural chemistry for the prepared octahedral complexes through this manuscript are summarized in Fig.(1).
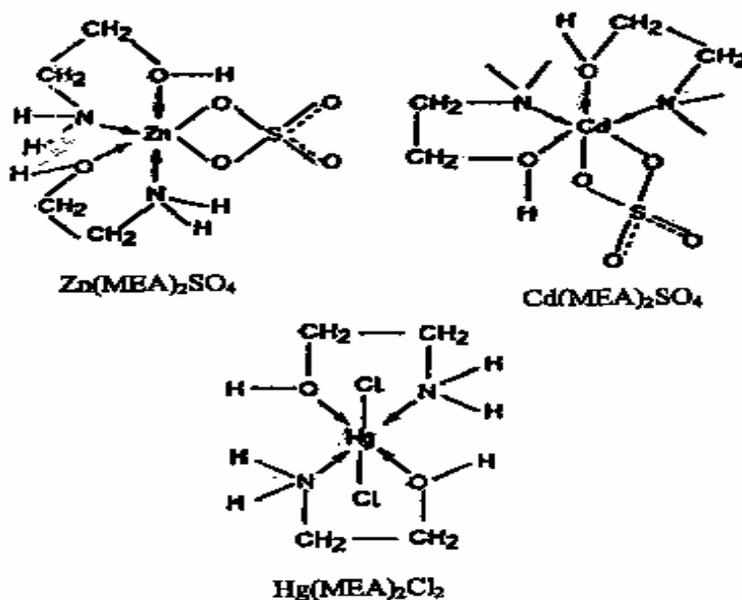
Fig.(1): Structural chemistry for Zn(MEA)$_2$SO$_4$, Cd(MEA)$_2$SO$_4$ and Hg(MEA)$_2$Cl$_2$ complexes.

3. Results and Discussions:

Ac response of a material can be expressed as complex impedance Z*, complex dielectric constant ε* and complex dielectric modulus M*. These functions are given as;

$$\varepsilon^* = \varepsilon` - i\,\varepsilon``$$
$$Z^* = Z` - i\,Z`` \tag{1}$$
$$M^* = M` + i\,M``$$

where $\varepsilon``/\varepsilon` = \tan\delta = M``/M` = Z``/Z`$ and tan δ is the loss factor, which gives directly the phase difference due to the absorption of energy.

The complex dielectric constant $\varepsilon^*(\omega)$ is related to the measured capacitance C(ω) as ; $\varepsilon(\omega) = C(\omega)d/\varepsilon_o A$, where A , d are the cross-section area and thickness of the sample respectively and ε_o is the permittivity of the free space. The real component ε` and the imaginary component ε`` of the complex dielectric constant ε*(ω) are related to the measured impedance Z and the phase angle φ as follows [16],

$$\varepsilon` = Z``/\omega|Z|^2 C_o$$
$$\varepsilon`` = Z`/\omega|Z|^2 C_o \tag{2}$$

where $Z` = |Z|\sin\varphi$, $Z`` = |Z|\cos\varphi$; $C_o = \varepsilon_o A/d$ is the air capacity and ω is the angular frequency (ω = 2πf). Hill and Jonscher [17,18] describe the complex permittivity as,

$$\varepsilon(\omega) = \varepsilon` - i\,\varepsilon`` - i\,(\sigma_{dc}/\omega) + \varepsilon(\infty) \tag{3}$$

where σ_{dc} is the zero frequency conductivity and $\varepsilon(\infty)$ is the limiting high frequency permittivity.

3.1. Variation of ε` with temperature and frequency:

Figure (2), shows the temperature dependence of the real part of the dielectric constant, ε`, at different frequencies, for the three samples. The inset of this figure represents the variation of ε` with frequencies. No peak in ε` as a function of temperature is observed (it should be noted that the solid lines in Fig.2 and other figures are guides for the eye). ε` varies very slowly with temperature to a temperature T_o , where T_o is a function of composition of the samples. It was found that T_o is approximately equal to half of the Debye temperature θ_D of the respective samples (see table 1). The values of θ_D are deduced from the dc conductivity data [8]. Above T_o, the values of ε` for all

samples increase with increase of temperature and decrease with increase of frequency. Such behaviour indicates a Debye –type dielectric relaxation process with relaxation frequency F_r , ($F_r = F_o \exp(-\Delta/k_BT) = 1/2\pi\tau$, τ being the relaxation time and F_o is the Debye phonon frequency, which may be related to T_o, k_B is the Boltzmann's constant and Δ is the activation energy for conduction). This relaxation process can be more resolved from the calculation of dielectric modulus, M^*, as discussed below. The observed values of ε` for Zn(MEA)$_2$SO$_4$ sample is much higher than other samples, which support the previous results of higher conductivity data than Cd or Hg –complexes [8]. The frequency dependence of ε` for the three samples decrease with increase of frequency. It should be noted that no maxima in ε` as a function of frequency is observed. The decay rate of ε` for Zn-complex is larger than Cd and Hg-complexes Fig. (2a).

Table (1): Analytical data for the prepared octahedral complexes

| Complex | Melting Point (K) | Weight (%) | | | | F_o (Hz) | Δ (eV) | T_o (K) | θ_D (K) |
		Metal	SO$_4$	Cl$_2$	Ligand				
Zn(MEA)$_2$SO$_4$	> 573	23	33.8	----	43.2	6.1×10^{11}	0.28	240	510
Cd(MEA)$_2$SO$_4$	>538	34.3	29	----	36.7	3.93×10^{10}	0.32	210	450
Hg(MEA)$_2$Cl$_2$	536	50.9	----	18.1	31	1.64×10^{11}	0.37	190	400

3.2. Temperature and frequency dependence of ε``:

Figure (3), shows the temperature dependence of dielectric loss, ε``, at different frequencies, which is similar to the behaviour of ε`. The frequency variation of ε`` at different temperature are shown in the inset of Fig.(3). For many semiconducting glasses, the dielectric relaxation time can be deduced from the observed peak when ε'and ε''are plotted as function of frequency [19]. As can be seen from Figures 2 and 3, ε` and ε`` for all samples do not have maxima when plotted as a function of temperature or frequency within the temperature range (100K-300K) and frequency range (1kHz-13MHz) of our investigations.

The well-known method of displaying Debye type relaxation is by drawing a Cole-Cole plot. Cole and Cole [20] suggested that ε` as a function of ε`` gives important information about the distribution of relaxation times.
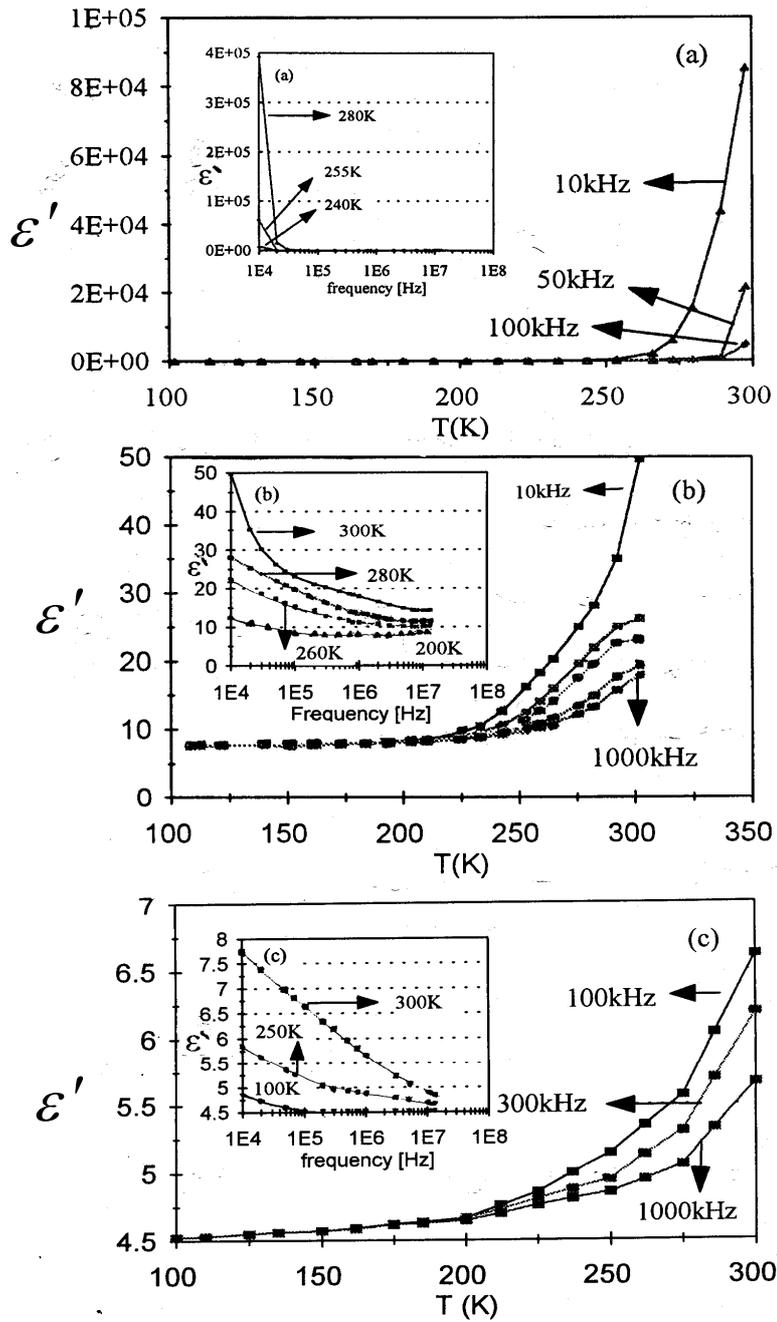
Fig.(2): Temperature dependence of dielectric constant εˋ at different frequencies for:

a) Zn(MEA)$_2$SO$_4$, b) Cd(MEA)$_2$SO$_4$ and

c) Hg(MEA)$_2$Cl$_2$ The insets represents the variation of εˋ with frequency at

different temperatures.

Fig.(3): Temperature dependence of dielectric loss $\varepsilon^{``}$ at different frequencies for:
   a) $Zn(MEA)_2SO_4$, b) $Cd(MEA)_2SO_4$ and
   c) $Hg(MEA)_2Cl_2$. The insets represents the variation of $\varepsilon^{``}$ with frequency at

different temperatures.

The slope of the arc at $\varepsilon`` = 0$ is a measure of the extent of distribution of relaxation times. According to Cole and Cole, the complex dielectric is given by $\varepsilon^* = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/[1+(i\omega\tau)^{1-\beta}]$, where τ is the mean relaxation time , β is an empirical parameter lying between 0 and 1 , and ε_s and ε_∞ are the static and high frequency dielectric constants respectively. The slope of the Cole – Cole plot at $\varepsilon`` = 0$ gives the value of $(1-\beta)\pi/2$. For $\beta=0$, it leads to a single relaxation time, $\beta=1$ corresponds to an infinite distribution of relaxation times. We have plotted $\varepsilon``$ versus $\varepsilon`$ at different temperatures for all samples, but the data do not fit a semi-circular curve. According to Grant [21], the large value of high frequency capacitance or conductivity of the sample is responsible for such behaviour. In Fig.(4), we present the Cole-Cole plot for the three complexes at different temperature. From this figure, it is evident that β for the three samples is greater than zero and less than 1. From this deduction we first suggest that these complexes have a distribution of relaxation times. It is difficult to use this conventional method of estimating the relaxation frequency and the magnitude of the dispersion. Therefore, another approaches has been adopted. The relaxation process can be more clearly resolved from the calculation of dielectric modulus M*. Following Macedo et al [22], the real and the imaginary parts of dielectric modulus are related to $\varepsilon`$ and $\varepsilon``$ as,

$$M` = \varepsilon`/(\varepsilon`^2 + \varepsilon``^2)$$
$$M`` = \varepsilon``/(\varepsilon`^2 + \varepsilon``^2) \quad\quad\quad (4)$$

The dielectric modulus, M*, provides information particularly when the dc conductivity is large compared with the ac conductivity.

A plot of M`` versus temperature should give a maximum at the temperature for which the dielectric relaxation frequency is equal to the measuring frequency, (as will be shown down). We have plotted M` as a function of temperature for the complexes at different frequencies (Fig.5). From this figure, we observed that, at lower temperature, M` tends to a constant value for all frequencies. This dependence indicates that the dielectric constant of the samples is thermally activated. The imaginary part, M``, was calculated and plotted as a function of temperature at different frequencies. An example is shown in Fig.(6). For $Zn(MEA)_2SO_4$ sample. The data in Fig.(6). Show maxima which shift to higher temperature for higher frequencies. Similar dependence of temperature and frequency variation of M`` is also showed maxima for other samples. The value of the temperature at the position of the maximum in (M``T) plots corresponds to the temperature at which the measuring frequency is equal to the relaxation frequency F_r.
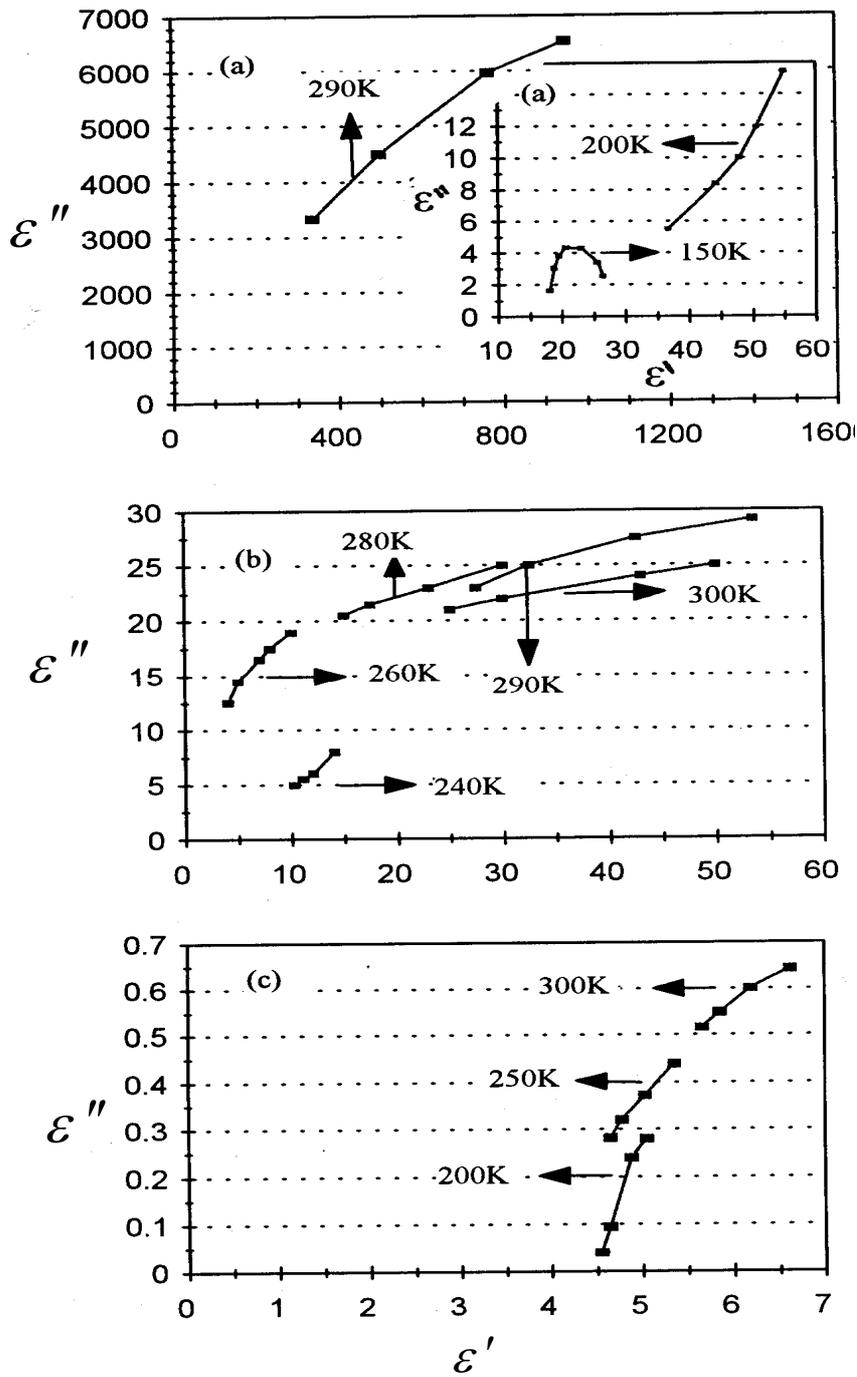
Fig.(4): Cole-Cole plots at different temperatures for : a) $Zn(MEA)_2SO_4$,
b) $Cd(MEA)_2SO_4$ and c) $Hg(MEA)_2Cl_2$ complexes.
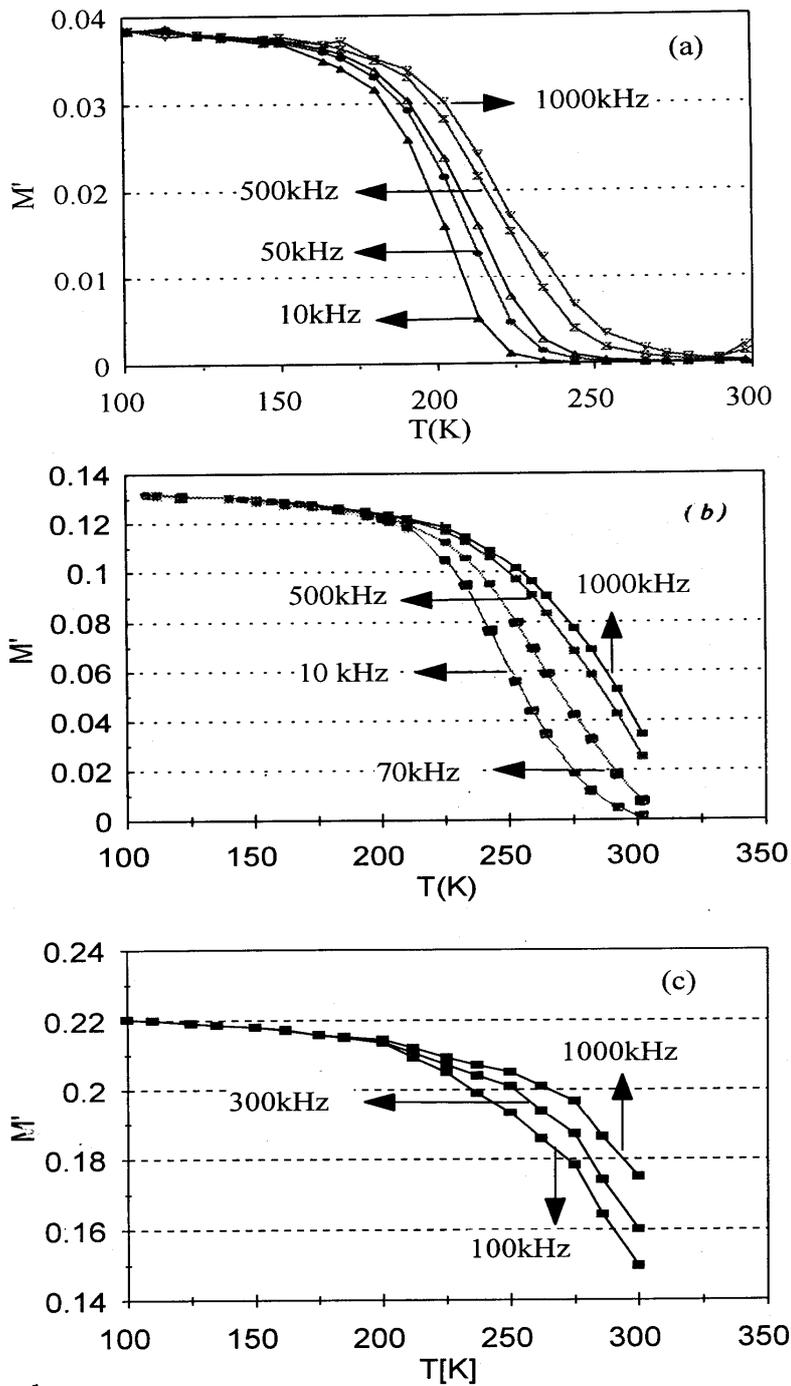
Fig.(5): Temperature dependence of dielectric modulus M` at different frequencies for
a) $Zn(MEA)_2SO_4$, b) $Cd(MEA)_2SO_4$ and c) $Hg(MEA)_2SO_4$ complexes.
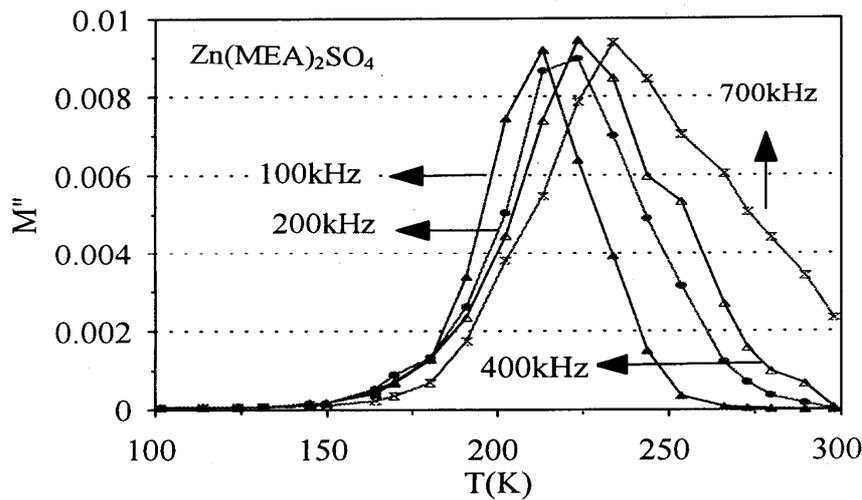
Fig.(6): Temperature dependence of imaginary part M`` at different frequencies for :
Zn(MEA)$_2$SO$_4$ complex.

The observed peaks in (M``-T) plots indicates Debye-type relaxation behaviour [23]. Moreover, the imaginary part of dielectric modulus M`` are plotted in Fig.(7). as a function of frequency at different temperature. The relaxation time is defined as the inverse of angular frequency at the maximum of the M`` ($\omega\tau = 1$). It has proposed [24,25] that, if full width at half maximum is equal to 1.14 decade, then the peak is said to be an ideal Debye peak (i.e having single relaxation time) and if it is more than 1.14 decades, the relaxation times for different processes are comparable. Fig.(7). shows the spectroscopic plot of M`` vs log F for Zn(MEA)$_2$SO$_4$ complex at different temperatures. It has observed that full width at half maxima is in the range of 1.9 to 2.6 in the temperature region 300K – 210K, which is larger than an ideal Debye peak. This indicates that there is a distribution of relaxation times or/and there is more than one relaxation process involved. At temperature less than 210K, the observed peaks has width at half maxima much less than 1.14, involves one relaxation behaviour. The separate peaks in Fig.(7). corresponding to orientational polarization which involves short range movement of the electronic charge carriers may occur beyond the frequency range of measurements [26] .
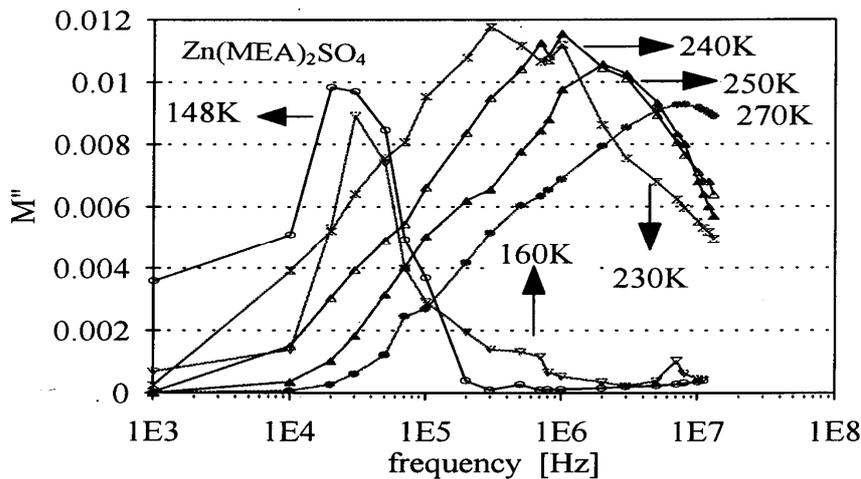
Fig.(7): M``versus F in log-log scale at different temperatures for Zn(MEA)$_2$SO$_4$.

In-order to confirm the recorded values of relaxation rate F_r from the maxima in (M``-T) and (M``- F) plots, a double–logarithmic plots of permitivity (ε` and ε``) as a function of frequency are constructed for the investigated samples. An example is shown in Fig.(8). It can be seen that the imaginary component $\varepsilon$`` shows a power law behaviour ε`` $\alpha$ $(F/F_r)^{-n}$ as observed in many transition metal glasses [27]. Where $F_r$ has a position near the intersection point between $\varepsilon$` and $\varepsilon$`` and n is the power exponent depends on temperature and frequency region. It was found from Fig.(8) that F_r is approximately equal to the values obtained from maxima in both (M``- T) and (M``- F) plots. Also, the lower frequency region in Fig.(8)., ε`` are increased with a higher rate. In this case, there is no contribution from dc conductivity term in Eqn. (3), as explained by Hill and Jonscher [17]. The temperature dependence of the observed relaxation rate F_r (Figs. (6 - 8)) for the Zn– ,Cd– and Hg–complexes are given in the form of Arrhenius plots in Fig.(9). From this Figure there is an evidence for activated processes with activation energy of about 0.3 eV, which is approximately equal to the values deduced from dc conductivity [8]. For Zn(MEA)$_2$SO$_4$ sample, Fig.(9) shows a distribution of relaxation times at temperature higher than 210K with activation energy 0.28eV and one relaxation behaviour at temperature less than 210K with activation energy equal to 0.09eV. This lower value of activation energy may be due to the activation from the donor level to the conduction band i.e. extrinsic behaviour. It can be seen from Fig.(9) that, Cd– and Hg–complexes needs measurements at frequencies less than 1kHz in-order to observe relaxation behaviuor at temperature less than 200K.
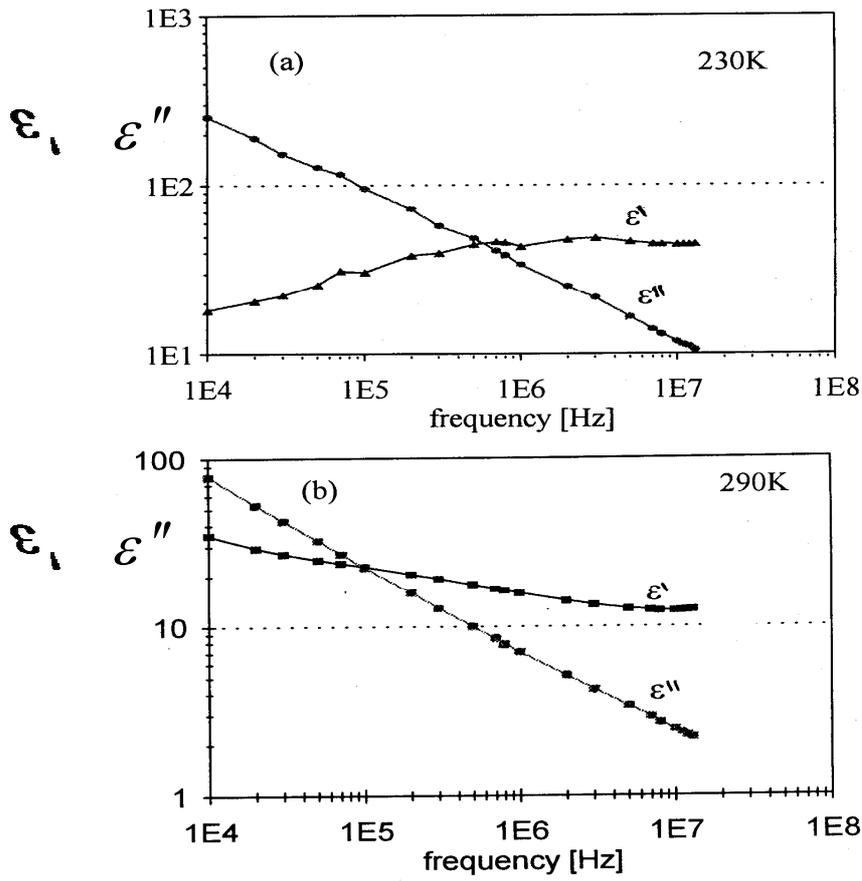
Fig.(8): Log-log plot of the permittivity ($\varepsilon`$, $\varepsilon``$) as a function of frequency for
   a) $Zn(MEA)_2SO_4$ and b) $Cd(MEA)_2SO_4$.
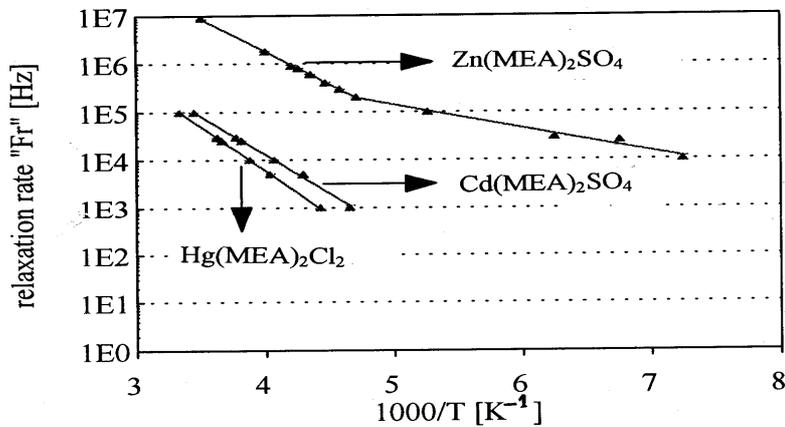
Fig.(9): The temperature dependence of the relaxation rate F_r in $Zn(MEA)_2SO_4$, $Cd(MEA)_2SO_4$
   and $Hg(MEA)_2Cl_2$ complexes in the form of Arrhenius plot (equation 5).

Conclusion:

From Cole-Cole plots dielectric measurements seems to be Debye type with distribution of relaxation time. Temperature dependence of dielectric constant shows that $\varepsilon`$ increased with a higher rate above certain temperature which indicates dipole polarization mechanism. At low temperature, the real part of dielectric modulus $M`$ is constant over the frequency range 1kHz - 13MHz indicates that the dielectric constant is thermally activated process. A separate peaks are observed in the temperature and frequency dependent of $M``$ with a half width greater than 1.14 in the temperature range 210K to 300K, indicates again a distribution of relaxation time while at T <210K , the observed peaks has a half width less than 1.14 indicates single relaxation behaviour. The separate peaks in $M``$ vs log F reveals the presence of orientational polarization. This is caused due to hopping of charge carriers among defect complexes within the bulk. The temperature dependence of the relaxation rate F_r (Fig.9.) shows two relaxation conduction mechanisms in Zn(MEA)2SO4 complex with activation energy 0.28eV at temperature higher than 210K which is due to thermal activated hopping of electronic charge carriers. Below 210K the activation energy becomes 0.09eV. The present of oxygen in octahedral structure may occur a vacancies, these vacancies may act as a donor, which is responsible for low activation energy at low temperatures. The values of activation energy deduced from dielectric relaxation are approximately equal to that obtained from dc conductivity measurements. Both activation energy and the characteristic phonon frequency F_o are listed in Table(1).

Ac conductivity measurements for these complexes will be published soon in a separate article.

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