

Comparative Electrical Studies of Lithium and Lithium Free-Phthalocyanine Complexes

A.M.Fathi*, Howida S. Mandour and A.H.Salama

Physical Chemistry Department, National Research Centre,
Dokki, Giza 12622, Egypt.

HYBRID inorganic-organic nanocomposite materials have various electrical and mechanical properties that make them used in many applications in areas of the electronic industry and have played as insulators and dielectrics. Conducting and semiconducting properties have stimulated their use in many novel applications. Among them new symmetrical Lithium phthalocyanine with different lithium concentrations were synthesized by urea fusion technique and characterized through the study of FTIR, and UV-visible spectra. The dielectric properties such as dielectric constant (ϵ') and dielectric loss (ϵ'') were studied for metal free phthalocyanine and Lithium phthalocyanine complexes with different concentration of lithium ions namely 0.01, 0.03 and 0.06 M. The studies were carried out at frequency range 100Hz-1MHz and within temperature range (280-440 K). It was observed that the dielectric constant of phthalocyanine complexes decrease with the increase of frequency and increase with increasing temperature signifying the semiconducting property. The decrease in energy gap with the coordination of metal ion suggests that the metal ion plays an important role in the electronic properties of the complexes.

Keywords: Phthalocyanine, Lithium, Dielectric constant, IR and UV.

Phthalocyanines (PCs) have been the study of a great deal for researches over 60 years. PCs have been appealing considerable attention as macrocyclic compounds, due to their odd physical and chemical properties^(1, 2). Due to their interesting properties they have been used successfully in many applications such as molecular electronic, semiconductor and solar cells in catalytic reaction^(3- 8), nonlinear optics⁽⁹⁻¹²⁾, gas sensor⁽¹³⁻¹⁵⁾ and photodynamic therapy (PDT) of cancer⁽¹⁶⁻¹⁸⁾, which is a very important association of photosensitizing drug and light for treatment of non-oncologic diseases and malignant tumors⁽¹⁹⁾.

It is worth to note that cobalt and nickel phthalocyanines may act as carcinogens⁽²⁰⁾ and there is a good advantage of using PDT that it can be demolished tumor selectively and does not harmful the surrounding tissues^(1,21).

*Corresponding author. Tel.: +20 233371383; fax: +20 233370931

- Address: National Research Centre, 33 El Bohouth St.(El-Tahrir St. former) - Dokki-Giza- P.O.12622 (Scopus affiliation ID 60014618)
- E-mail addresses: amfathi70@yahoo.com

Water soluble phthalocyanine and its complexes are considered to be the best aims for a new production of coatings and photosensitizers^(21,22). Since several decades the introduction of different central ions or substituents of PCs had been produced in both academic and applied fields which lead to changing of the physical and chemical properties of PCs⁽²³⁻²⁵⁾. Using of rare-earth elements to form PCs is very interesting because of their potential technical application such as molecular materials⁽²⁶⁾.

In the present work, we study the effect of lithium ion as central ion of phthalocyanine on the dielectric properties such as dielectric constant (ϵ') and dielectric loss (ϵ''). The dielectric measurements were passed out in the frequency 100Hz-5MHz and temperature range from 280 to 440 K with different concentration of lithium ions. To make a distinction of the prepared samples we study of FTIR and UV-visible spectra of the prepared samples.

Experimental

Synthesis of Metal Free Phthalocyanine (MF-Pc) and Lithium phthalocyanine (LiPc) complexes

Metal Free Phthalocyanine MF-Pc and Lithium phthalocyanine complexes were prepared by urea fusion technique which is a simple pathway by which phthalocyanine complexes can be obtained with high purity and recovery⁽²⁷⁾. About 8.88 gm (0.06 mole) of phthalic anhydride was added into a 500 ml flask, followed by 30 gm of urea, 0.2 gm of ammonium molybdate as reaction promoter (For preparing LiPc complexes, LiOH with concentrations of 0.01, 0.03 and 0.06 M were added respectively). The temperature was gradually raised to 190-200°C, and maintained for 4 hrs with continuous stirring. The reaction was cooled, boiled with distilled water many times. The precipitate was washed in sequence with 2% HCl, dilute alkali, 25% methanol and acetone. Final purification was done by drying the sample at 200°C for 3 hrs in dry oven by which any traces of impurities were sublimed. A blue colored of H₂PC (Dark green pigments of Li-Pc complexes) was obtained.

IR and UV measurements

The synthesized nano-phthalocyanine complexes were grinded in an agate mill until the desired grain size. It was investigated by IR spectra with the aid of JASCO 4600 model FTIR spectrometer. Also UV-Vis absorption spectra of the samples were recorded in the wavelength range of 190 to 800 nm and room temperature using a Jasco V360.

Electrical Measurements

To determine the dielectric properties, powders of the MF-Pc and LiPc complexes are compacted into disc of 12mm diameter under a pressure of about 10 N/cm². The temperature dependence of dielectric constant and loss will be determined at frequencies between 0.1 KHz and 5 MHz in the temperature range (298-423K) by means of a HI0KI3532 LCR Hi-Tester with a computer. In our experiments, the real and imaginary parts of the complex dielectric permittivity ϵ^*

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($\epsilon^* = \epsilon - j\epsilon''$) were obtained with the assumption that studied cell is equivalent to a circuit consisting of an ideal capacitance in parallel with a pure (ohmic) resistance R. The real part of the dielectric function (constant) ϵ' of MF-Pc and Li-Pc complexes with different concentration of Li^+ were calculated from the measured capacitance (C_p) according to the equation:

$$\epsilon' = \frac{C_p d}{\epsilon_0 A}$$

where d is the diameter of the disc, A is its cross section area and ϵ_0 is the dielectric constant of the vacuum (8.85×10^{-12})

Results and Discussion

FTIR spectra

From IR spectra (Fig. 1), it is clear that there is a broad band around 3730 cm^{-1} pointed to the presence of $-\text{CH}$ group and at 1590 cm^{-1} strong peak pointed for the presence of Ar C=C (stretching vibration of phenyl rings). Around 2360 cm^{-1} there is a medium peak which pointed to C=N, at 1035, 995, 920, 850, 830, 812, 805, 740, 700, 685, 590, 550, 540 cm^{-1} these peaks give indication to the presence of weak bands of C=N (vibration of pyrrole ring). Peak at 1225 cm^{-1} indicate the presence of strong peak for C=N, but at 1250 and 1358 cm^{-1} give a good evidence for presence of medium peak of C=N. At 1035 cm^{-1} there is a peak which indicated to the vibration of porphyrin ring for pyrrole unit.

The studies of lithium-phthalocyanine complexes show good adsorption properties for two strong regions, one of them at about 316-400 nm (B-band or solet band) which is attributed to $\pi-\pi^*$ transition from highest occupied molecular orbital (HOMO) to Lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring⁽²⁸⁻³⁰⁾. In this region, the shifting of wavelength of metal free-phthalocyanine may be due to decreasing the electron density at the inner nitrogen atoms depending on the electronegativity of the metal⁽³¹⁾.

All spectra for B-band are stronger than Q-band which appears at 665-700 nm and this reveal strong aggregation⁽³²⁾. The B-band is characteristic of metal-phthalocyanine absorption⁽³³⁾. The phthalocyanine principally absorb in this region because of the disruption in phthalocyanine π -system caused by the N atoms being in the meso-positions and the peripheral benzene rings that extend π -system⁽³⁴⁾.

Calculation of the band gap energy (E) is important in the semiconductors, so that the band gap energy of the prepared samples is calculated the extrapolation of the linear portion of the graph between the absorbance and wavelength⁽³⁵⁾ by using the following equation:

$$E = h \frac{C}{\lambda}$$

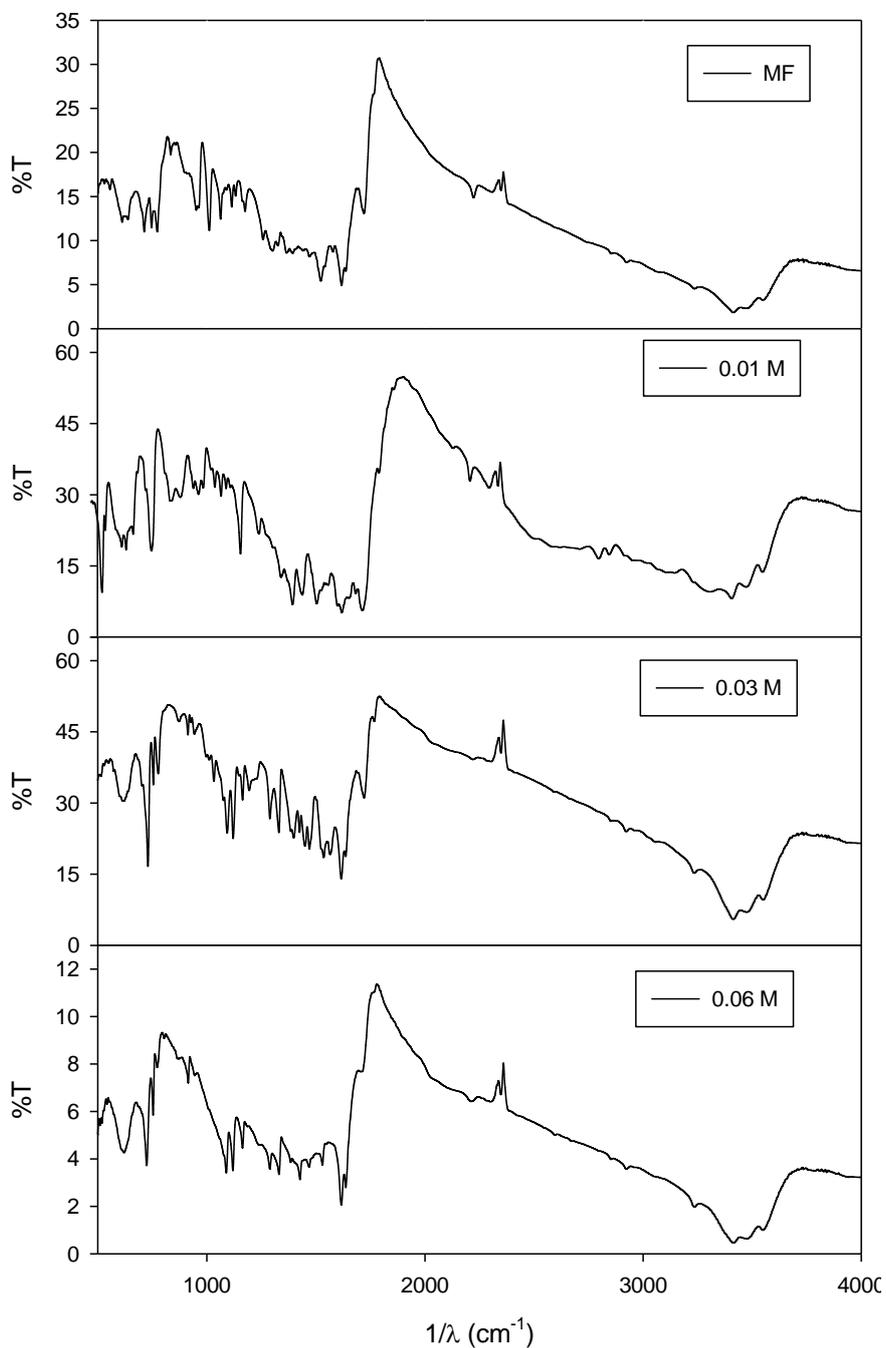


Fig. 1. IR spectra of metal free (MF) and different concentrations of Li-Pc complex.

UV-visible adsorption spectra

The sum of electronic, vibrational and rotational energies denotes the total energy of a molecule. The changes in the electronic energy of the molecule are produced from energy absorbed in the UV region. The resulting spectra acquired for MF-Pc and Li-Pc complexes with different Li ion concentration are revealed in Fig. 2.

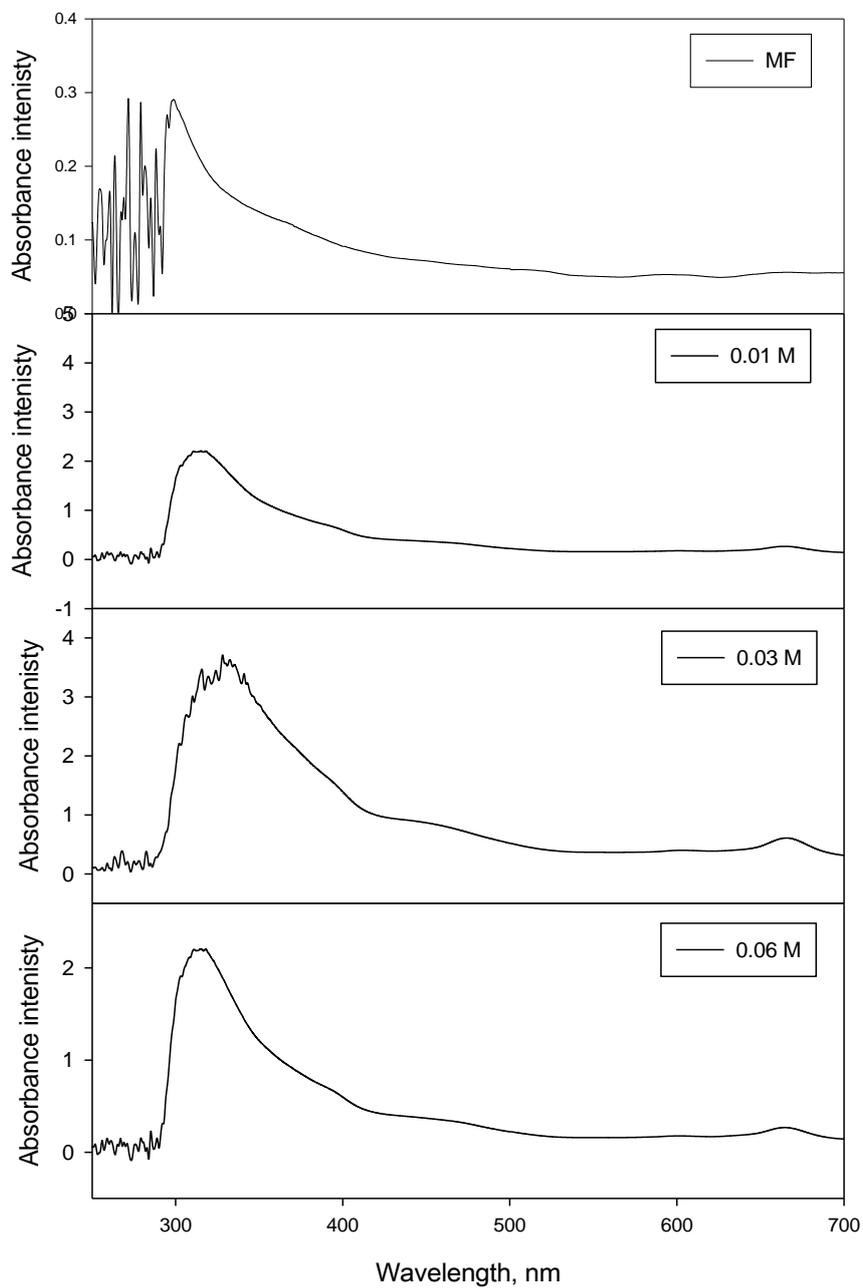


Fig.2. UV/Vis spectra of metal free (MF) and different concentrations of Li-Pc complex

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Calculation of the band gap energy (E) is important in the semiconductors, so that the band gap energy of the prepared samples is calculated by the extrapolation of the linear portion of the graph between the absorbance and wavelength⁽³⁵⁾ by using the following equation:

$$E = h \frac{C}{\lambda}$$

Where h is Planck's constant (6.626×10^{-34} J.s), C is the speed of light (3.0×10^8 m/s), λ is the cut off wavelength and $1 \text{ eV} = 1.6 \times 10^{-19}$ J. The spectral data recorded showed strong cut off at 286 nm, 285 nm, 477 nm and 407 nm for MF-Pc, 0.01M Li-Pc, 0.03M LiPc and 0.06M Li-Pc respectively. Referring to the data recorded in Table (1), it is obvious that the presence of lithium ion as central metal in phthalocyanine macromolecule decreases the band gap energy. Moreover, as the concentration of lithium ion increases the band gap energy decreases significantly; this can be referred to the small ionic radii of lithium ion.

TABLE 1. Band gap energy of different concentrations of the samples.

Samples	E (eV)
MF- Pc	4.346591
0.01M Li-Pc	4.361842
0.03M Li-Pc	2.606132

Dielectric investigation

The dielectric properties of the metal free and lithium phthalocyanine complexes were studied in frequency range 100Hz-5MHz and within temperature range 280-440K. The dielectric constant (ϵ') of metal-free phthalocyanine (H₂PC) and phthalocyanine complexes with different concentrations of lithium ions (0.01, 0.03 and 0.06 M) were measured as a function of frequency and temperature as shown in Fig. 3. The dielectric constant increases with increasing temperature and decreases with increasing frequency; this behavior can be due to the interfacial polarization which is called Maxwell-Wagner Sillars, MWS which is a famous theory in the heterogeneous structure of compound. Also this can be attributed to the donation of the conductivity on the dielectric constant⁽³⁶⁾.

According to Koops's⁽³⁷⁾ the main donation to the dielectric constant at low frequency comes from the grain boundaries which have a high dielectric constant. On the other hand, at high frequency the dielectric behavior is controlled by the grains which have small dielectric constant, so the decrease of ϵ' may be related to the electrical relaxation processes⁽³⁸⁾. It is noticeable that, the values of dielectric constant (ϵ') measured at high temperature (423K) and low frequency (50 Hz) for MF-Pc and Li-Pc with 0.01, 0.03 and 0.06 M Li ion concentration were 13.2, 1188, 828 and 466 , respectively which indicate the increase in dielectric constant (ϵ') of the Pc with the presence of metal ion. It is noticeable that the dispersion of dielectric constant (ϵ') begins at very low frequency for MF-Pc and when the lithium ion introduced to the Pc molecule, it begins at about 1 KHz.

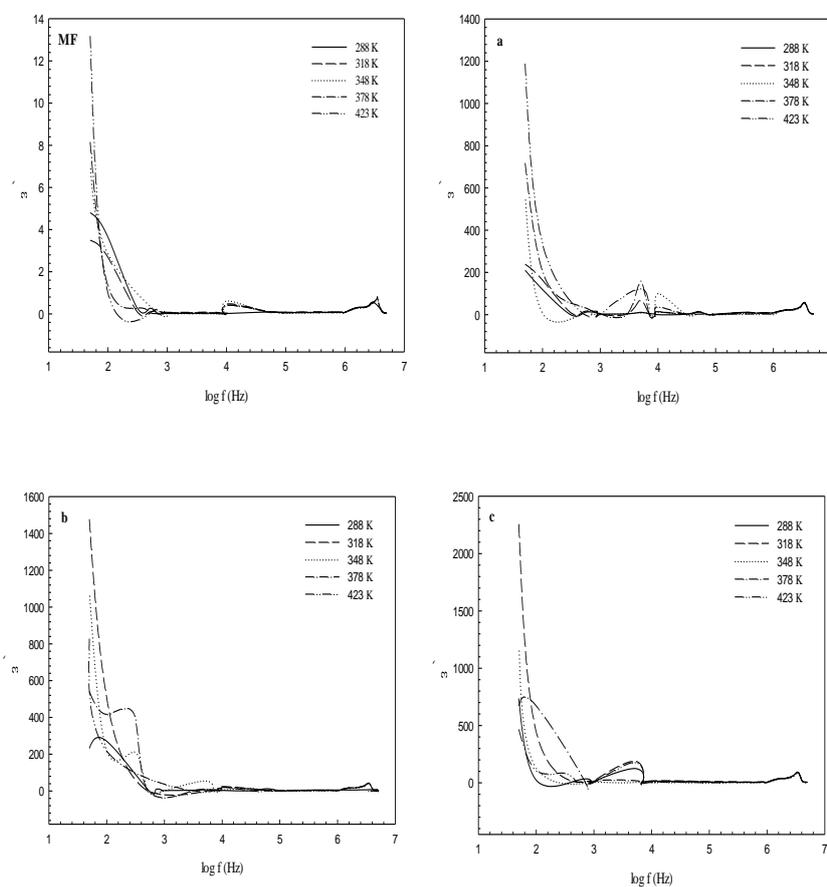


Fig.3. Relation between $\log f$ (Hz) and dielectric constant (ϵ') as a function of frequency at different temperature and at different lithium concentrations (MF metal free a 0.01M, b 0.03M and c 0.06 M) .

Figure 4 clarifies the variation of dielectric constant as a function of temperature at 3 frequency values (100 Hz, 100 KHz and 1 MHz) for metal free phthalocyanine and lithium-phthalocyanine with different concentrations of lithium ions. For 0.01M, the dielectric constant increased give up one value which indicates the presence of one transition phase. While at concentrations (0.03 M and 0.06 M) the dielectric constant interprets two values means that there are two transition phases. The change of α -phase to β -phase begin at 320 K and concluded 390 K, this could be due to that the polarization increases with temperature⁽³⁹⁻⁴¹⁾.

These phenomena may be related to the migration of electrons or ions over distances of microns. Also, as the temperature increases, the bound charge carriers get enough excitation thermal energy to be able to complete the variation in the external field more clearly. This turn raises their benefaction to the polarization leading to an increase of dielectric constant⁽⁴²⁾.

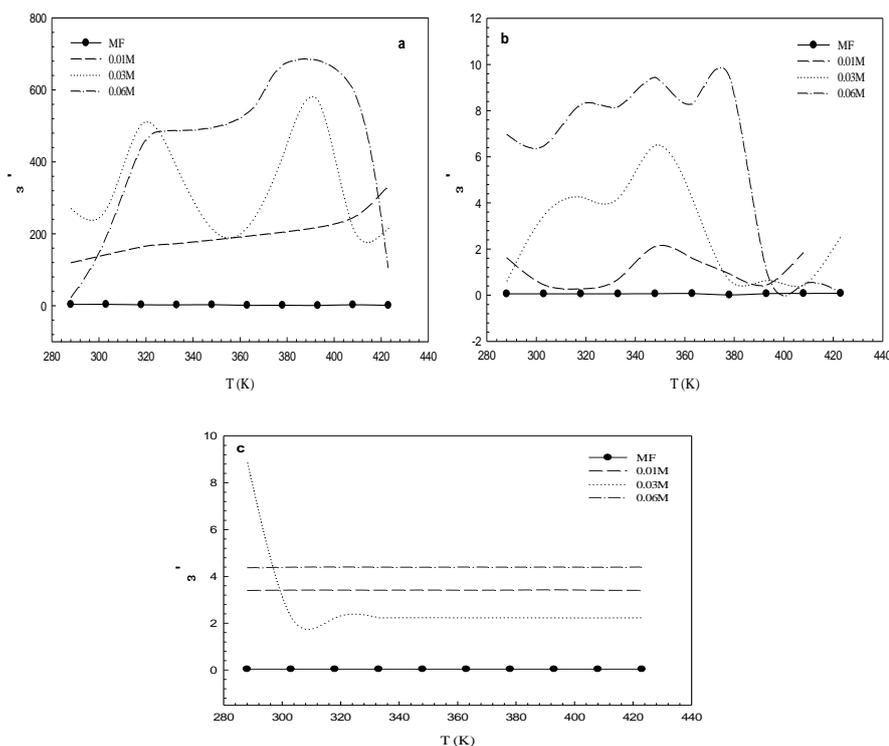


Fig.4. Relation between dielectric constant ϵ' and temperature T (K) at selected frequency (a 100Hz, b 100KHz and c 1MHz) for metal free (MF) and different concentrations of Li-Pc complex .

Dielectric loss (ϵ'') for MF-Pc and its Li-Pc complexes as a function of

frequency were displayed in Fig. 5. The dielectric absorption bands appear in all samples. The frequencies corresponding to the maximum energy loss (f_m) are used to evaluate the relaxation time (τ) from the relation:

$$\tau = \frac{1}{2\pi f_m}$$

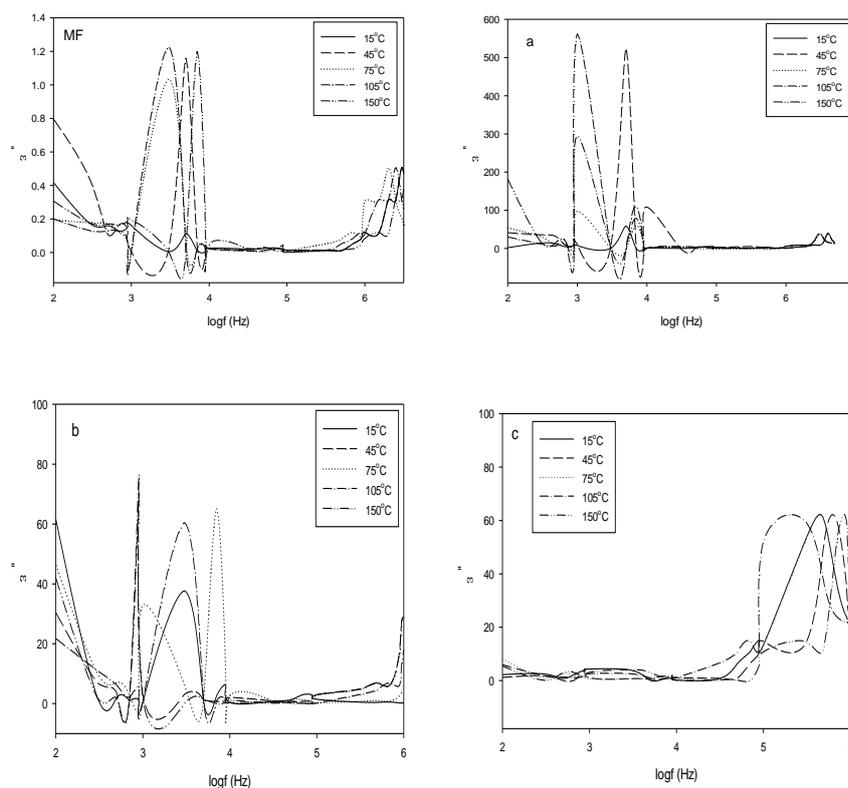


Fig.5. Relation between dielectric loss ϵ'' and $\log f$ (Hz) as a function of temperature at different lithium concentrations (MF metal free a 0.01M, b 0.03M and c 0.06 M).

Generally, it was found that in heterocyclic compounds in the solid state, there are two loss regions. One of them described by a loss peak located at temperature above the glass transition point is because of α -relaxation and the other described by a flat loss maximum extending over a wide temperature range below the transition point is because of β -relaxation. It was proposed that the reason of β -relaxation is the motion of polar side groups in the amorphous phase and the local in nature. Assuming that the crystalline phase contains various

kinds of defectiveness, the motion associated with the β -relaxation would be possible even in such crystalline defects.

The relaxation time increases from 2.3×10^{-5} s for MF-Pc to 1.6×10^{-4} s for 0.01 & 0.03 M LiPC and then decreases to 1.9×10^{-7} s for 0.06 M LiPC and the values of the dielectric loss are generally high especially for 0.01 M LiPC. These indicate the semiconducting property of these complexes. Moreover, the decrease of τ and dielectric loss is attributed to the presence of Lithium ions with its small ionic radii which can lead to increase in the number of electrons. While the losses decrease at high frequency is because of the decrease in the dc-conductance.

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The relaxation process in all these complexes can be considered as β -relaxation initiated from the lattice defects due to the electron transfer which leads to the formation of charge centers as polar bonds, groups or sites possessing orientation polarization.

Relation between capacitance and different concentration of lithium ions [Li^+] at selected frequency as a function of temperature was illustrated in Fig. 6 which elucidates that the smaller capacitance predicts smaller charge, this is due to smaller concentration and ofcourse less diffusion of ions⁽⁴³⁾.

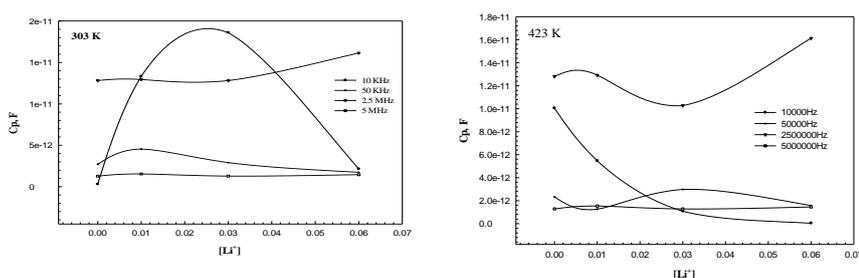


Fig.6. Relation between capacitance and different concentration of lithium ions [Li^+] at selected frequency as a function of temperature.

Fig. 7 represents the frequency dependence of the real part (Z) of the complex

impedance at different temperature. The decrease in impedance of low frequency by increasing the temperature followed by impedance saturation of high frequency was observed for all complexes which proving the semiconducting property of the complexes and suggesting mixed type of polarization (electronic, orientation and dipole).

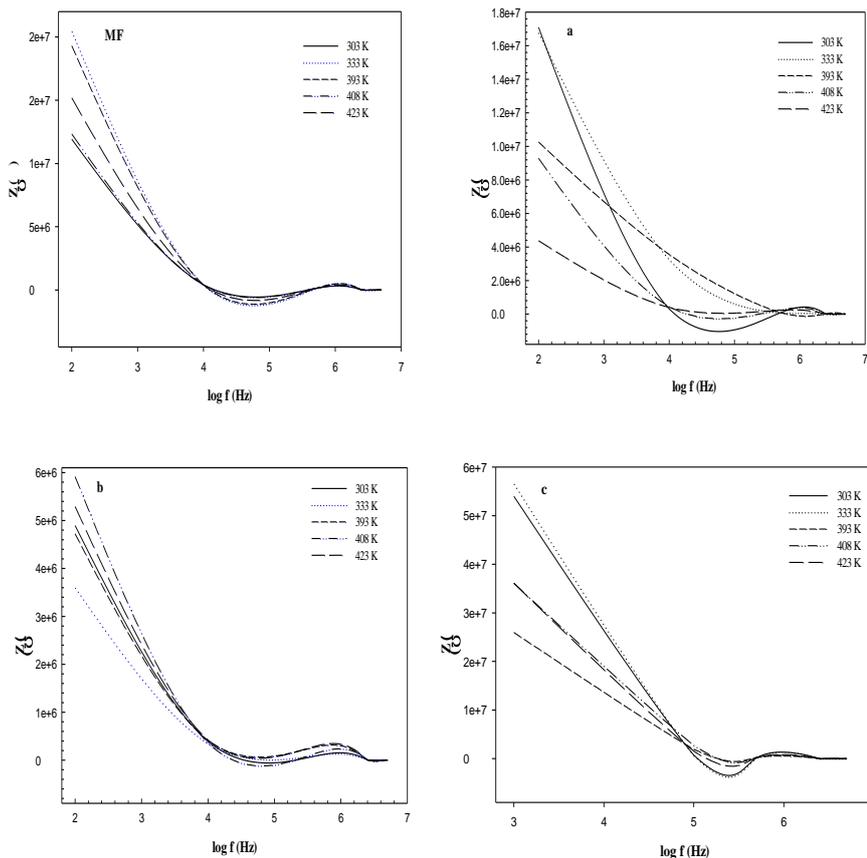


Fig.7. Relation between $\log f$ (Hz) and Z (Ω) as a function of temperature for metal free (MF) and different concentrations of Li-Pc complex (a) 0.01M, (b) 0.03M & (c) 0.06M.

References

1. Moser, F. H. and Thomas, L. A. , *Phthalocyanine Compounds*. Reinhold Pub. Co, New York (1963).

2. **Merey, S., Bekaroglu, O.**, *J. Chem. Soc., Dalton Trans.*, 4503(1999).
3. **Moser F. and Thomas, A. H.** The Phthalocyanines, CRC press, 1-2 (1983).
4. **Leznoff, C.C. and Lever, A.B.P.** (editors), *Phthalocyanines Properties and Applications*, VCH, New York, vols. 1-4 (1989–1996).
5. **McKeown, N.B.** *Phthalocyanine Materials: Synthesis, Structure and Functions*, Cambridge University Press, (1998).
6. **Bedioui, F.**, *Coord. Chem. Rev.*, **144**, 39(1998).
7. **Yılmaz, Y., Özer, M., Kani, İ. and Bekaroğlu, Ö.**, *Catal. Lett.*, **130**, 642(2009).
8. **Sorokin, A. B. and Kudrik, E. V.**, *Catal.Today*, **159**, 37(2011).
9. **Simon, J. and Bossoul, P.** In: *Phthalocyanines/Properties and Applications*, II ; Lezno_, C. C.; Lever, A. B. P., Eds., VCH: Weinheim, Germany (1989).
10. **Lukyanets, E.A.** *Electronic Spectra of Phthalocyanines and Related Compounds*; Tcherkassy: Moscow, USSR, (1989).
11. **Kobayashi, N., Lezno, C. C. and Lever, A. B. P.**, Eds., *Phthalocyanines Properties and Applications*, II ; VCH:Weinheim, Germany, (1993).
12. **Lezno, C.C. and Lever, A.B.P.**, Eds., *Phthalocyanines Properties and Applications*, I-V; VCH: Weinheim, Germany, (1996).
13. **Açıkbaş, Y., Eyyapan, M., Ceyhan, T., Çapan, R. and Bekaroğlu, Ö.**, *Sens. Actuators, B*, **123**, 1017(2007).
14. **Özer, M., Altındal, A., Özkaya, A. R. and Bekaroğlu, Ö.**, *Dalton Trans.*, issue **17**, 3175(2009).
15. **Wang, B., Zuo, X., Wu, Y., Chen, Z., He, C. and Duan, W.**, *Sens. Actuators, B*, **152**, 191(2011).
16. **Capella, M. A. and Capella, L. S.**, *J. Biomed. Sci.*, **10**, 361(2003).
17. **Vrounraets, M. B., Visser, G. W., Snow, G. B. and Van Dongen, G. A.**, *Anticancer Res.*, **23**, 505(2003).
18. **Marino, J. Vior, M. C. G., Dicolino, L. E., Roguin, L. P. and Awruch, J.**, *Eur. J. Med. Chem.*, **45**, 4129(2010).
19. **Bonnett, R.**, *Chem. Soc.*, **24**, 19(1995).
20. **Singh, P. and Ravindra, N. M.**, *Journal of Materials Science*, **45**, 4013(2010).
21. **Moser, J.G.**, *Photodynamic Tumor Therapy-2nd and 3rd Generation Photosensitizers*. Harwood academic publishers, Amsterdam (1998).

22. **Alpatova, N.M. and Ovsyannikova, E.V.**, In: *Electropolymerization: Concepts, Materials and Application*, Cosnier, S. and Karyakin, A., Eds., Weinheim: Wiley, p. 111(2010).
23. **Bekaroğlu, Ö.**, *Struct. Bonding*, **135**, 105(2010).
24. **Shen, X., Jiang, X., Huang, C., Zhang, H. and Huong, Z.** *Tetrahedron*, **66**, 9041(2010).
25. **Yabaş, E., Sülü, M., Saydam, S., Dumludağ F., Salih, B. and Bekaroğlu, Ö.**, *Inorg. Chim.Acta.*, **365**, 340(2011).
26. **Bao, M., Wang, R., Rintoul, L., Liu, Q., Arnold, D.P., Ma, C. and Jiang, J.**, *Polyhedron*, **25**,1195(2006).
27. **Salama, A.H. and Fathi, A.M.**, *Silicon Journal*, DOI 10.1007/s12633-016-9481-1. (2016).
28. **Yazıcı, A., Ateş, D., Bekaroğlu, Ö. and Kobayashi, N.** *J. Porphyrins Phthalocyanines*, **10**,1140 (2006).
29. **Edwards, L. and Gouterman, M.**, *J. Mol. Spectrosc.* **33**, 292(1970).
30. **Ambily, S. and Menon, C.S.**, *Thin Solid Films* **347**, 284(1999).
31. **Eckut, H. and Schier, A.**, *Angew. Chem. Intern.*, Ed. English 2, p.280(1981).
32. **Kobayashi, N., Yishiyama, N., Ohya, T. and Sato, M.**, *J. Chem. Soc., Chem. Commun.*, issue 5, 390(1987) .
33. **Davidson, A.T.** *J. Chem. Phys.*, **77**, 168 (1982).
34. **Allen, C. Sharman, W. J. Van Lier, J. Porph. Phthal.**, **5**, 161. (2001).
35. **Hoffman, M. Martin, S. Choi, W. W. and Bahnemann, D.** Environmental applications of semiconductor photo catalysis. *Chemical Review*, **95**, pp. 69-96(1995).
36. **Darwish, W.M. Abd El-Ghaffar, M.A. Turkey, G.M.** *J. Inorg. Organomet. Polym.*, **24**, 858(2014).
37. **Koops, C.**, *Phys. Rev.*, **83**, 121 (1951).
38. **Varshney, D., Kumar, A. and Verma, K.**, *Journal of Alloys and Compounds*. **509**, 8421 (2011).
39. **Jonscher, A. K.** *J. Mater. Sci.*, **16**, 2037 (1981).
40. **Lucia, E. A. Verderame, F. D.** *J. Chem. Phys.*, **48**, 2674 (1968).
41. **Riad, A. S. Korayem, M. T. Abdel-Malik, T. G.** *Physica B* **270**, 140 (1999).
42. **Anantharaman, M. R. Sindhu, S. Jagatheesan, S. Molini, K. A and Kurian, P. J.** *Egypt. J. Chem.* **59**, No. 6 (2016)

Phys. D: Appl. Phys., **32**, 1801 (1999).

43. **Ozoemena, K. I. Nyokong, T. Nkosi, D. Chambrier, I. Cook M.J.**, *Electrochim. Acta*, **52**, 4132 (2007).

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مقارنة للدراسات الكهربائية لمعدقات الفيثالوسيانين الحر و متراكباته مع الليثيوم

أحلام محمد فتحى, هويدا سيد مندور و عالية حسنى سلامة

قسم الكيمياء الفيزيائية- المركز القومي للبحوث- الجيزة -مصر.

المواد المركبة المهجنة النانومترية المكونة من مواد عضوية وغير عضوية لها العديد من الخواص الكهربائية والميكانيكية التي تجعلها تلعب دورا هاما كعوازل أو أشباه موصلات في العديد من التطبيقات مثل الصناعات الالكترونية، وحافز لتفاعلات الخلايا الشمسية، البصريات اللاخطية والمستشعرات الغازية. كما حفزت خواص التوصيل وشبه التوصيل استخدامها في العديد من التطبيقات الجديدة، ومن بين هذه المواد تم تحضير متراكب فيثالوسيانين الليثيوم المتمثل بتركيزات مختلفة بواسطة تقنية انصهار البوريا. ولقد تم إثبات التركيب لهذه المتراكبات عن طريق مطياف الأشعة تحت الحمراء والفرق بنفسجية. وأيضا تمت دراسة خصائص ثابت العزل للفيثالوسيانين الحر ومتراكباته مع الليثيوم بتركيزات مختلفة من الليثيوم علي مدى التردد من 100 إلي 1000 هرتز ومدى درجة الحرارة من 280 إلي 440 درجة كلفن. ولوحظ أن ثابت العزل الكهربائي لمتراكبات الفيثالوسيانين ينخفض مع زيادة التردد ويزيد مع زيادة درجة الحرارة مما يدل علي أن له خاصية شبة توصيل. والانخفاض الملاحظ في قيم في فجوة الطاقة لهذه المتراكبات يثبت اقتراح أن الأيون الفلزي يلعب دورا هاما في الخواص الكهربائية لهذه المتراكبات.