

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Optical properties Study of New Films Derived from poly(vinyl chloride)- N-(4-Hydroxy-phenyl)-acetamide

Salam A. Mohammed^{1*}, Ali Hasan², Wasan A. Al-Taa'y³, Ahmed Ahmed⁴,
Majid Khalaf², and Emad Yousif².

¹College of Engineering and Architecture, University of Nizwa, Birkat Almouz, 616 Nizwa, Sultanate of Oman

³Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

³Department of Physics, College of Science, Al-Nahrain University, Baghdad, Iraq

⁴Polymer Research unit, College of Science, Al-Mustansiriyah University, Bagdad, Iraq.

ABSTRACT

The present study focused on modification of the optical properties of PVC films N-(4-Hydroxy-phenyl)-acetamide complexes. Films of modified Poly(vinyl chloride) with different transition metal complexes, Cu(II), Cd(II), Co(II), Zn(II) and Ni(II) have been prepared in order to evaluate the role of some transition metal complexes in the modification of optical properties of the polymer. The structure of these complexes has been characterized by FT-IR and UV-Vis spectrophotometry. The optical data analyzed and interpreted in terms of the theory of phonon assisted direct electronic transitions. According to energy gap data, the conductivity of PVC and the complexes were obtained.

Keywords: PVC, Transition metal complexes, Energy Gap, Optical properties.

**Corresponding author*

INTRODUCTION

Polymer science is, of course, driven by the desire to produce new materials for new application. Poly(vinyl chloride) (PVC) is one of the most versatile plastics. It is the second largest manufactured resin by volume worldwide [1]. Recently, scientists could modify PVC [2], by introduction aromatic and heterocyclic moieties through halogen displacement reaction [1]. The facial chlorine displacement from PVC indicated the possibility of easy anchoring of ligands to PVC matrix and the subsequent synthesis of immobilized transition metal complexes [3]. In recent years, studies on the electrical and optical properties of polymers have attracted much attention in view of their applications in optical devices with remarkable reflection, antireflection, interference and polarisation properties [4]. The biggest advantage of conductive polymers is their processibility [5]. The optical characteristics are extremely important not only for scientific knowledge but also for modern technology applications [6]. This article discloses the investigation of the effect of transition elements on the electrical properties of the Novel materials.

EXPERIMENTAL

Instrumentation:

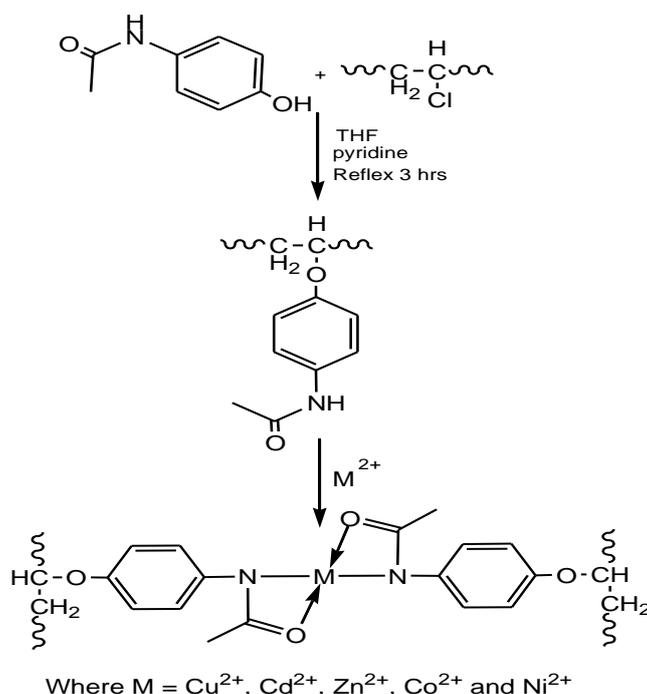
All the reagents, starting materials as well as solvents were purchased commercially and used without any further purification. The Fourier transformed infrared spectroscopy (FTIR) spectra were obtained in the range 4000-400 cm^{-1} using the KBr disc on FTIR 8300 Shimadzu spectrophotometer. UV-vis. Spectrums were measured using Shimadzu UV-Vis 160 A-Ultraviolet-visible spectrophotometer in range 200-1100 nm.

Synthesis of modified polymer (PVC-L):

N-(4-Hydroxy-phenyl)-acetamide was added to (0.125g) poly(vinyl chloride) and five drop of pyridine in (25 mL) tetrahydrofuran (THF) was also added. A white precipitate was formed after refluxing the mixture for two hours. The modified polymer (PVC-L) was dried under vacuum [7].

Synthesis of PVC ligand complex:

Metal complexes of poly(vinyl chloride)-N-(4-Hydroxy-phenyl)-acetamide was prepared by the method described by Aliwi *et al.* [3]. Scheme 1, shows reactions for the synthesis of PVC-L- M^{II} polymer.



Scheme 1. Reaction for synthesis of PVC-L- $\text{M}(\text{II})$

Purification of Poly(vinyl Chloride):

Commercial Poly(vinyl chloride) (Petkim company, Turkey) was purified by re-precipitation from tetrahydrofuran (THF) solution in ethanol, then dried under reduced pressure at room temperature for 24 hours.

Films preparation:

0.5% concentrations of PVC and PVC-L-M^{II} solution in THF were used to prepare 40 micrometer thickness of polymer films, (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature for 24 hrs. film samples were further dried at room temperature for three hours under reduced pressure to remove the possible residual THF solvent. The optical absorbance (A) of the sample was measured as a function of wavelength (λ) it ranged from 200 - 900 nm by using computerized Shimadzu Uv-Vis 160A-Ultraviolet-spectrophotometer full-scale absorbance up to (2.5). The light sources are halogen lamp and socket-deuterium lamp. The detector is Si-photodiode and all measurements were performed at room temperature. UV-VIS absorption spectroscopies were made for prepared samples before and after modification. The spectra was used to carry out the energy gap by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ with (r) value (1/2) which indicates a transition of direct type. The linear portion was best fitted with $(r = 1/2)$ Energy gap shift for all samples plotted as a function to conjunction type [8].

RESULT AND DISCUSSION

The FTIR spectrum of the ligand (L) shows the following characteristic band, a weak band at 3111 cm^{-1} could be attributed (O-H), 2923 cm^{-1} observed related to (C-H) stretching, 1681 cm^{-1} could be attributed (C=O), the band at 1568 cm^{-1} related to (N-H) and the band at 921 cm^{-1} is related to (C-O). The FTIR graft polymer spectrum shows the following bands, a strong band at 609 cm^{-1} was observed which could be attributed to (C-Cl) band. Also the disappearance of (O-H) band at 3111 cm^{-1} good indicator for formation the PVC-L compound.

In the FTIR of the PVC-Complexes, the $\nu(\text{C=O})$ appeared at 1681 cm^{-1} in the modified PVC, was found to be shifted to lower wavelength number in the complexes, signifying that the coordination took place via the Oxygen atom of the Carbonyl group and a new bands appear in the range $(455-485)\text{ cm}^{-1}$ which could be attributed to (M-O) bond. Another new band appeared at $(425-463)\text{ cm}^{-1}$ attributed to (M-N), signifying that the coordination also took place via the nitrogen atom, this gives further evidences for the structures of complexes [9]. All important bands that appeared in the spectra of ligand, modified polymer and the complexes are given in Table 1.

Table 1. UV Absorption and IR bands of PVC-L and PVC-L-M(II)

Compounds	Electronic absorption peaks (nm)	Assignment	IR (cm^{-1})	Assignment
L	240 243	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	1616	C=O
			3111	O-H
			1616	C=C
			1568	N-H bending
PVC-L	276 290	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	1568	N-H bending
			605	C-Cl stretching
			3657	O-H
			1762	C=O
			1037	C-O
PVC-L-Ni(II)	276 388 510 596	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ Charge transfer (d-d)	3103	O-H
			609	C-Cl stretching
			1723	C=O

			1090	C-O
			445	Ni-O
			425	Zn-N
			3666	O-H
			618	C-Cl stretching
PVC-L-Zn(II)	270	$\pi \rightarrow \pi^*$	1720	C=O
	334	$n \rightarrow \pi^*$	1057	C-O
			435	Zn-O
			435	Zn-N
			3650	O-H
PVC-L-Cd(II)	267	$\pi \rightarrow \pi^*$	616	C-Cl stretching
	379	$n \rightarrow \pi^*$	1728	C=O
			1049	C-O
			485	Cd-O
			431	Zn-N
PVC-L-Cu(II)	235	$\pi \rightarrow \pi^*$	3645	O-H
	272	$\pi \rightarrow \pi^*$	619	C-Cl stretching
			1721	C=O
			1090	C-O
			430	Cu-O
		429	Zn-N	
PVC-L-Co(II)			3172	O-H
	281	$\pi \rightarrow \pi^*$	613.3	C-Cl
	350	$n \rightarrow \pi^*$	1755	C=O
	470	Charge transfer	1105	C-O
	514	(d-d)	515	Co-O
			430	Zn-N

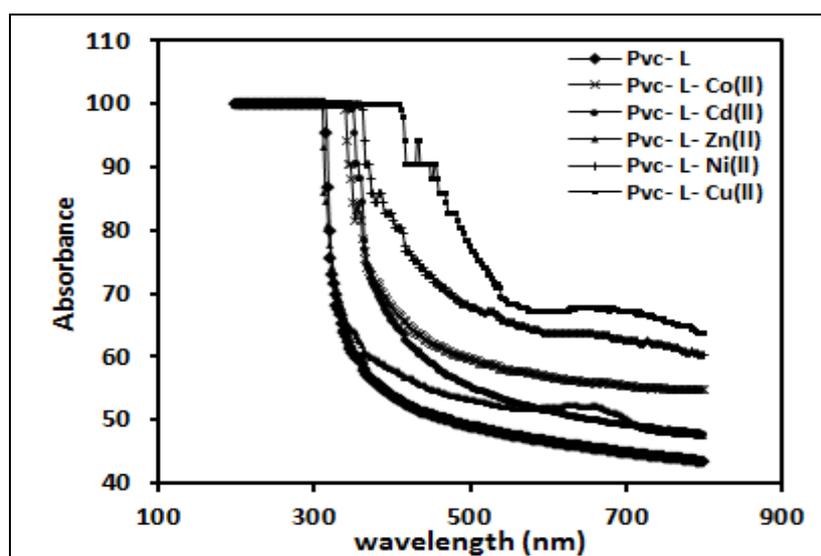


Figure 1. UV-VIS Spectra of the PVC Ligand and its Metal

Figure 1 and Table 1 show the electronic absorption bands for ligand and PVC-complexes. The bands are classified into three distinct groups: belong to ligand transitions appeared in the UV. region and d-d transitions appeared in the visible region and the third one is could be attributed to charge transfer These

transitions are assigned in relevance to the structures of complexes. The optical band gap of the modified films have been evaluated using the relation [10],

$$\alpha h\nu = A (h\nu - E_g)^n$$

where A is a constant, E_g is the optical band gap of the material and the exponent $n=1/2$ stands for the allowed direct transitions. The relation between $(\alpha h\nu)^2$ vs photon energy for modified and complex PVC are shown in Figures 2-7 for allowed transition. The difference in the values of energy gap could be attributed to the type of metal complexes[11].

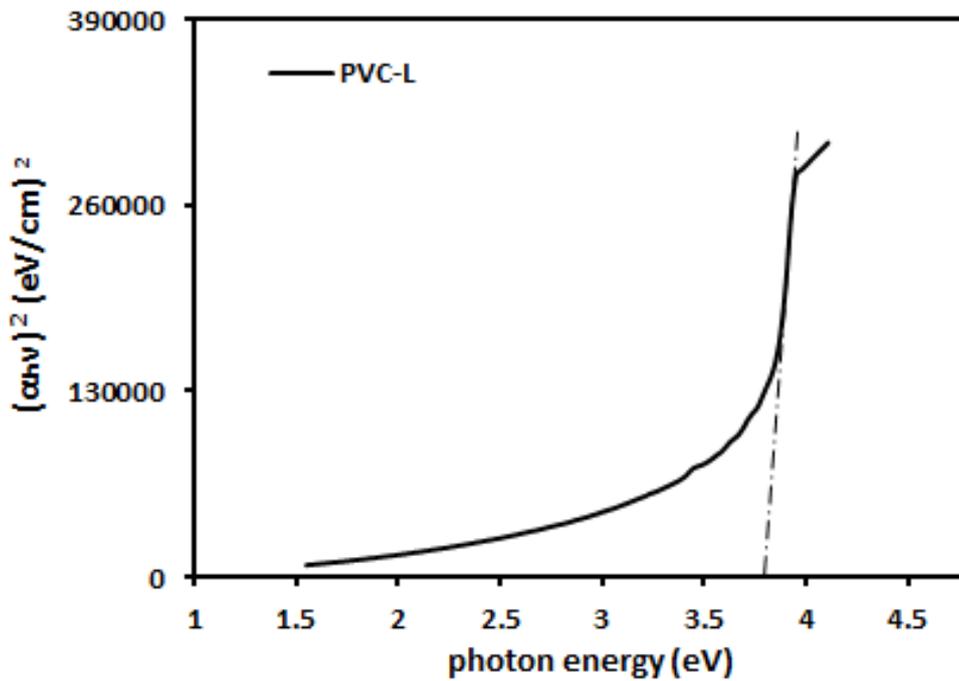


Figure 2. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L

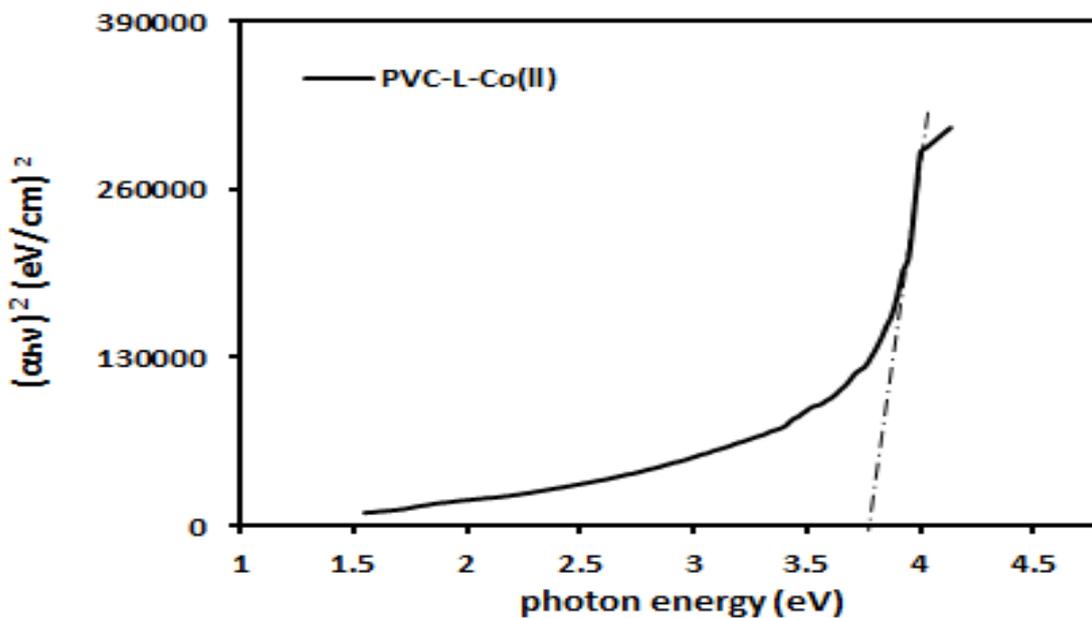


Figure 3. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Co(II)

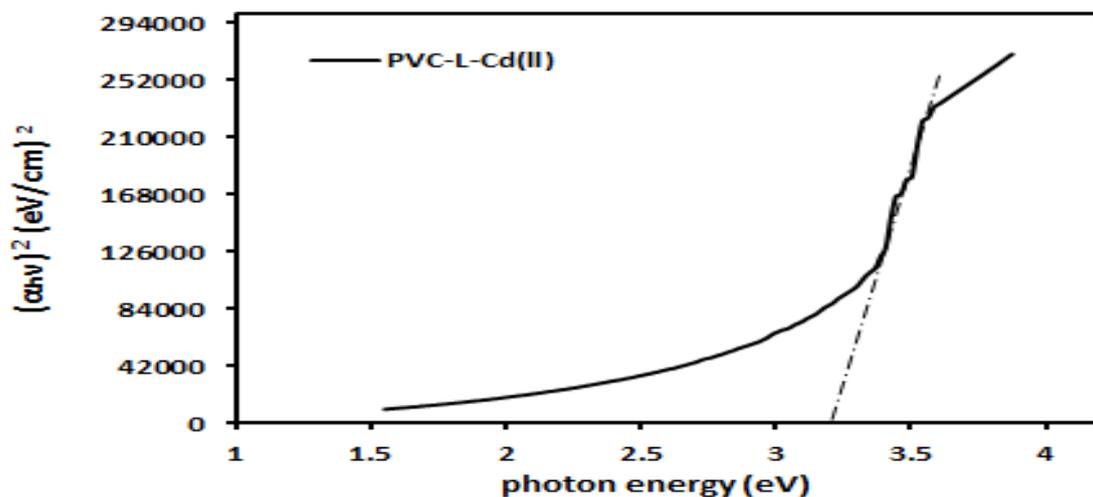


Figure 4. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Cd(II)

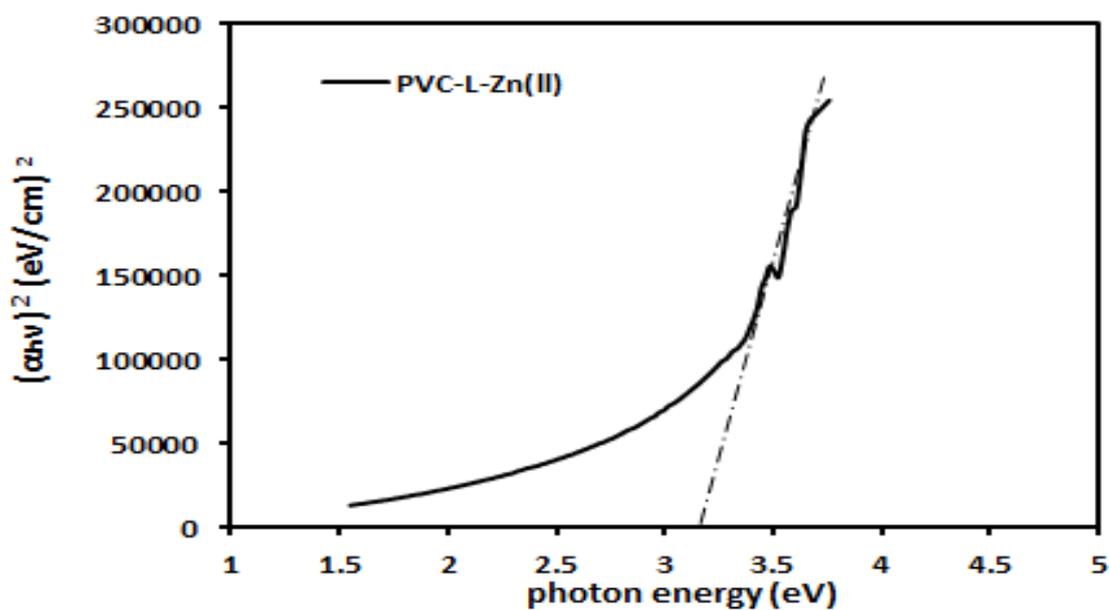


Figure 5. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Zn(II)

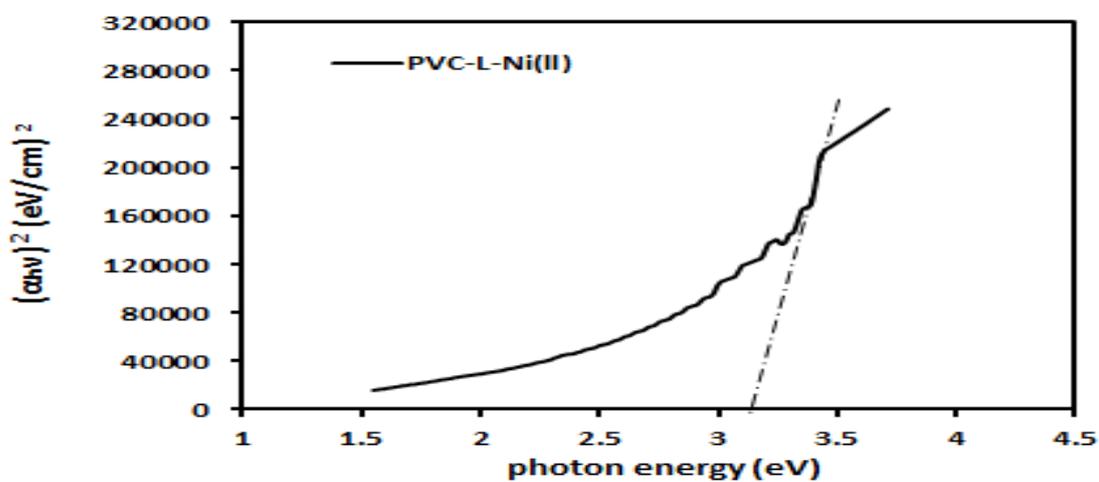


Figure 6. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Ni(II)

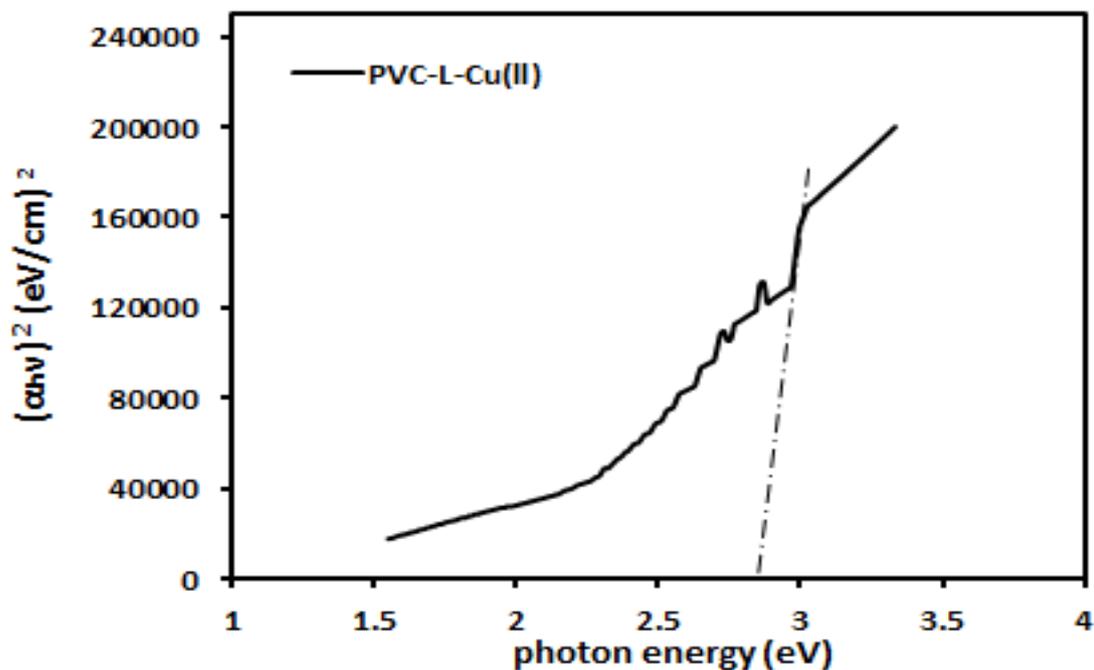


Figure 7. Allowed direct transition $(\alpha h\nu)^2$ vs energy for PVC-L-Cu(II)

The effect of the metal complexes addition on the values of activation energies is investigated and the result are shown in Table 2. In addition, the shift in the energy gap could be attributed to the formation of polarons and bipolarons. The evidence of polar on formation is made that the reaction in band to band transitions due to the shifting the band density of state toward the energy gap. This observation is not like doping of conventional semiconductor when the band to band absorption strength dose not affected by the formation of dopant state in the energy gap. The effect of modification and complex formation on the values of activation energies was investigated and the results shown in Table 2.

Table 2. Indicate the energy band gap according to the direct allowed transition

Sample	E_g (ev)
PVC-L	3.8
PVC-L-Co(II)	3.72
PVC-L-Cd(II)	3.2
PVC-L-Zn(II)	3.16
PVC-L-Ni(II)	3.12
PVC-L-Cu(II)	2.85

The results presented in Figures 2-7 indicate the existence of two bipolaron bands in the energy gap. The first one represents the transition from valance band to bonding bipolaron band. The second band represents the transition from valance band to anti- bonding bipolaron band which is in a good agreement with results are obtained by other workers [12]. Conductivity measurement of PVC with additive can obtain by adopting the data of energy gap [13-15], (see Table 2 and Figures 2-7). The conductivity measurement for PVC in the presence of additive increase in the following order:

$$PVC-L-Cu(II) > PVC-L-Ni(II) > PVC-L-Zn(II) > PVC-L-Cd(II) > PVC-L-Co(II) > PVC$$

CONCLUSION

The study on the effect of PVC modification with N-(4-Hydroxy-phenyl)-acetamide complexes, the repeating units on its optical properties has shown that the energy gap of modified polymers decreases in comparison with that of pure.



ACKNOWLEDGMENTS

The authors extend their appreciation to the Al-Nahrain University, University of Nizwa and University of Al-Mustansiriyah University for continued support.

REFERENCES

- [1] Claudiu L, Edina R, Bogdan M, Teodora Z, Gheorghe H. UPB Sci Bull Series B 2010; 72: 127–140.
- [2] Moulay S. Progr. Polymer Sci 2010; 35: 303-331.
- [3] Aliwi M, Yousif E, Otaiwi, A. Iraqi J Polymers 2005 10: 53-64.
- [4] Reddy V, Zhu Q, Mail L, Chen W. J App Electrochem 2006 36: 1051-1056.
- [5] Hashim H, Abdallh M, Yousif E. J. Al-Nahrain Uni. (Science) 2012 15: 40-45..
- [6] Yousif E, Abdul Nabi M, Hameed A, Salih, N, Salimon J. Journal of Al-Nahrain University 2010 13: 30-35.
- [7] Witwit N. Euro J Chem 2014 5: 652-656.
- [8] Yousif E, Hassan O, Otaiwi A, Farina, Y. Iraqi Journal of Polymers 2008 12: 5-78.
- [9] Nakamoto K. Infrared of Inorganic and Coordination Compounds. 6th Edition, John Wiley, New York, 1997, pp. 484.
- [10] Pankove J. Optical Processes in Semiconductors, Dover, New York, 1975.
- [11] Yousif E, Aliwi S, Abdul Nabi M. J. Al-Nahrain Univ 2005 8: 22-26.
- [12] Al-Daeif Y, Yousif E, Abdul Nabi M. J. Al-Nahrain Univ. (Science) 2012 15: 79-83.
- [13] Salimon J, Salih N, Ahmed A, Yousif E. Int J Chem Tech Res 2011 3: 981-987.
- [14] Yousif E, Abdallh M, Hashim H, Salih N, Salimon J, Abdallh B, Win Y. Int J Ind Chem 2013 4: 1-8.
- [15] Abdallh . J. Al-Nahrain Univ (Science) 2013 16: 24-29.