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Synthesis and characterization of metal complexes of cu (ii) and cd (ii) with poly vinyl alcohol and studied of electrical and optical properties

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Abstract

Metal complexes of Poly (vinyl alcohol) (PVA-oxi) with the formula $[M (PVA- oxi)_2 (Cl_2)_2]$ [M = Cu and Cd] were prepared using solution cast method. The atomic absorption; IR, UV-Vs spectroscopic techniques, molar ratio and molar conductance as well as the reduced viscosity of them were characterized. It was found that the prepared complexes were obtained from the ligand reaction with metal ions in a DMF solvent were ratio of metal: ligand (1:2) for complex Cu (II) ion and (1:1) for complexes Cd (II) ion. The results proved that the ligand (PVA-oxi) was bidentate ligand coordinated with metal ion through the oxygen atoms of carbonyl and hydroxylic groups of its chain, with an octahedral geometry around the metal ion Cu (II) complex and tetrahedron geometry for Cd (II) complex. The optical properties were examined using UV–Vis spectroscopy. The researchers studied the properties of the absorbance spectra, direct and indirect optical band gap energies of (PVA-oxi) and [M (PVA- oxi) 2 (Cl2)2] [M = Cu and Cd].Absorbance spectra, direct and indirect optical band gap energies were studied electrolyte for ligand and the prepared complexes. These band gap energies showed that the connection of the complexes is lower than of the ligand. The electrical conductivity of ligand and the prepared complexes electrolyte samples has been estimated by DC conductivity, which showed that the connection of the complexes was higher than the ligand.

Keywords: pva metal complexes; viscosity; molar ratio; flam atomic; u.v spectrum; ir spectrum; dc conductivity, band gap energies, optical properties

1. Introduction

Polymer materials are of great scientific and technological interest due to their unique optical, electronic, and mechanical properties. Polymer complexes have been given a great deal of interest in the recent years [1-3]. Synthesis of polymeric ligand and the selective chelation of specific metal ions is a field of active research [4]. The metal ions of polymer complexes have potential applications such as electrolytes [5], sensory [6], stabilizers [7] and semiconducting [8]. Polyvinyl alcohol is an important material in view of its wide-scaleapplications, such as biomaterials, biosensors, electrochemical sensors, membranes with selective permittivity, viscous medium for controlling the crystallization process of salts, for controlled drug delivery or catalytic systems, etc. Polyvinyl alcohol is non-toxic, non-carcinogenic, biodegradable, biocompatible, water-soluble, and non-expensive polymer. It could be also matrix for metal ions or salts in ecological composites [9, 10].

PVA is a potential material having a high dielectric strength, good charge storage capacity and dopant dependent electrical properties. It has carbon chain back bone with hydroxyl groups attached to methane carbons. The OH groups can be a source of hydrogen bonds and hence can assist in the formation of polymer complexes [11]. It has unique mechanical properties and shows both ionic and electronic conduction [12]. When polymers are doped with inorganic salts, they show remarkable change in their structural as well as in electrical properties. Polymer electrolytes containing divalent cations are suitable for electrochemical applications. Recently the PVA has doped with divalent metal salts like $CuCl_2$, $MnCl_2$ and $MgBr_2$etc.

These materials are used in different applications like magneto-optic data storages, reflective materials, optoelectronic devices, and photovoltaic cells [13]. Much has been done to improve the optical properties of polymer via producing new polymer materials through the support of polymers with metals, semiconductors, magnetic and carbon [14]. The most important polymer was polyvinyl alcohol (PVA), some of metal complexes of this polymer have been synthesized [15- 17]. The option of PVA as a host matrix is motivated by the opportunity to obtain highly transparent polymer materials with good optical properties. Equally, PVA has a carbon chain backbone, with hydroxyl groups attached to the carbon atoms [18]. Formed the copper or cadmium doped polyvinyl alcohol which has been used in multidimensional applications in holography optics and mechanically flexible systems [19].

In this study, the researchers prepare PVO from PVA as ligand and reactions with Cu and Cd metal salt to form complexes of them and study their electrical properties such as conductivity for ligand and complexes. We also studied the structure and linear optical properties of pure PVA and Cu (II)/ Cd (II) complex of (PVA). Optical properties and parameters like absorbance and optical band gap were investigated

2. Materials and Method

Synthesis and Oxidation of the PVA

Stoichiometric amounts of high purity of polyvinyl alcohol (PVA) (Scharlau, 98%) and metal salts $CuCl_2$, $3H_2O$ and

$CdCl_2$, $4H_2O$, (Scharlau, 98%) were used. Distilled water was used as solvent. Concentration of hydrogen peroxide (H_2O_2) (Fluka, 99%) used in this work was 50%.

Oxidation of PVA

15.2 g (0.2 mmol) polyvinyl alcohol (PVA) with 36000 MW was dissolved completely in 100 ml distilled water as a solvent. Then, 20 ml of hydrogen peroxide (H_2O_2) with concentration = 20% vol was added from dropping funnel under constant stirring for 3h at temperature = 50-80 ^oC. The mixture was refluxed for 3 h. The homogeneous solutions were evaporated and the oxidized polymer spread by Reutery device and left to dry slowly in oven at 50^oC for 24h. Finally, the films were ready to be investigated,

Synthesis of oxidized PVO-Complexes ([Cu (PVA-oxi)$_2Cl_2$] and [Cd(PVA-oxi)$_2Cl_2$])

0.501 g (2 mmol) of oxidized PVA was dissolved in 10 ml DMF, and then 0.2118 g (1 mmol) of metal salt ($CuCl_2$, $3H_2O$ or $CdCl_2$, $4H_2O$) in DMF in each case being added at pH 6.7. The mixture was heated under reflux for about10 h. Colored products were formed in neutral or slightly basic solution. The products were filtered and purified by washing with ethanol, then dried at 50^oC in an oven overnight. Finally, the films were ready for calculating the melting point and other characterizations.

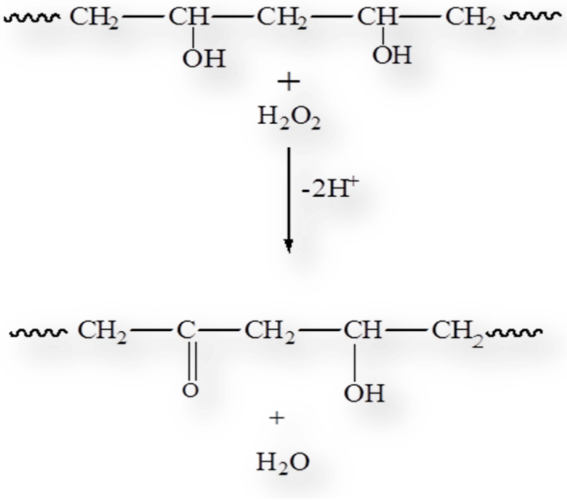
Characterizations

The optical transmission and absorption spectra of PVA and PVO-Complexes ([Cu (PVA-oxi) $_{2Cl2}$] and [Cd (PVA-oxi) $_{2Cl2}$] were recorded using a UV-Vis spectrophotometer (Hitachi U3900 with software of Varian Cary 50). The electrical conductivity measurements of samples were carried out using (conductivity meter and 3540 PH).

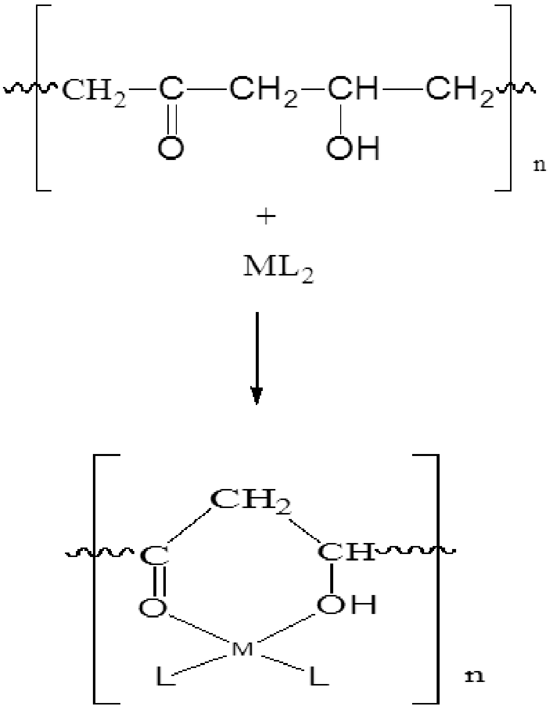
3. Results and Discussion

Partial oxidant (PVO) from PVA and hydrogen peroxide at (60-100 ^oC) was prepared to form a mixture of carbonyl and hydroxyl group in the polymeric chains as shown in scheme (1). Metals Complexes preparations from reaction of (PVA–oxi) and metal ions as shown in scheme (2, 3).

Scheme (1) preparation of PVO from poly vinyl alcohol (PVA)



Scheme (2) preparation of Metal complexes Molar ratio (1:1) ML1 (Metal: Ligand)



Scheme (3) preparation of Metal complexes Molar ratio (1:2) ML2 (Metal: Ligand)

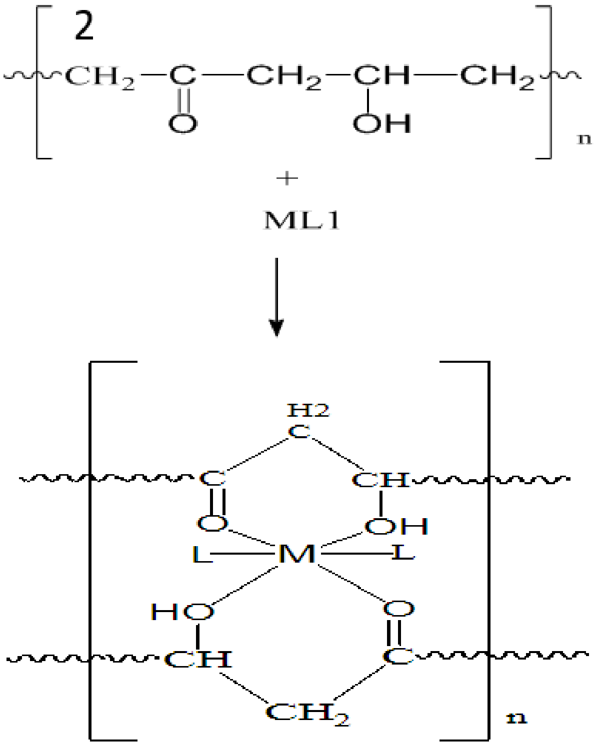


Table (1) shows the physical properties of ligand and metal complexes which show the different of colors between the complexes prepared and ligand and the melting point of all the prepared (PVA–oxi) metal complexes were higher than

360 °C. This indicates that the presence of metal ion increases the thermal stability of the polymer.

Table 1: Physical properties of ligand and metal complexes

compound	**Color**	**M. P. C° (decom.)**	**Yield%**	**$_{red}$η At 0.5gmdL/**
(PVA-oxi)	White-yellow	**240**	84	0.48
[Cu(PVA-oxi)$_2$Cl$_2$]	Yellow-green	*>360*	73	1.1
[Cd(PVA-oxi) Cl$_2$]	Prone-black	*>360*	81	0.92

Viscosity

Viscosities were measured of all the prepared (PVA–oxi) complexes in DMF as a solvent at 30°C, was measured at 0.5 % concentration. Viscosities of (PVA–oxi) complexes are listed in table (1). The viscosity of ligand and complexes get increased with increasing molecular weight. This is consistent with the literatures [20, 21], so that these results support the proposed molecular formulas.

IR spectrum

Figures (1) shows the bonds absorbency of IR spectrum for each of the ligand and metal complexes. The predominant O–H vibrational band of ligand at 3420 cm^{-1} is shift towards the high wave numbers and appeared at 3432 for Cu^{+2} complex and 3453 for Cd^{+2} complex. It gives strong indication of specific interactions between the ligand and metal salts. The band of C-OH appeared in the ligand at (1077) cm^{-1} is shifted towards the high wave numbers and appeared at (1280, 1319) cm^{-1} for complexes of Cu and Cd respectively. The band of C=O appeared in the ligand at 1740 cm^{-1} is shifted towards the low wave numbers and appeared at (1705, 1691) cm^{-1} for complexes of Cu and Cd respectively. The bands of M-O appeared at (519, 440) cm^{-1} for metal complexes but disappeared in the ligand [22]. Table (2) shows the bonds absorbency of IR spectrum for each of the ligand and metal complexes.

Table 2: IR spectrum of ligand and metal complexes

compound	**V (OH)**	**V (C=O)**	**V (C-OH)**	**V(C-H)**	**V (M-OH)**	**V (M-O)**
Ligand (PVA-oxi)	3420	1740	1077	3000	-	-
[Cu(PVA-oxi)$_2$Cl$_2$]	3432	1705	1280	2910	1079	519
[Cd(PVA-oxi)Cl$_2$]	3453	1691	1319	2988	1039	440

U.V spectrum

Table (3) and Figure (3) show U.V. spectrum for each of the ligand and metal complexes prepared. These show two peaks at 226 nm and this band is attributed to intra ligand π-π* transition. Another band of lower intensity appeared near the visible region (335 nm) and this band was attributed to n- π*.but these bands ware shifted toward high wavelength [23, 24].

Table *3*: UV -spectrum of ligand and metal complexes

Complex	**Band(I) (V$_1$)**		**Band(II) (V$_2$)**		**Band(III) (V$_3$)**	
	maxλ nm	**υcm1**	**maxλ nm**	**υcm1**	**maxλ nm**	**υcm1**
PVA-oxi)(	276	36231	335	29850	---	---
[Cu(PVA-oxi)$_2$Cl$_2$]	406	24630	885	11299	982	10183
[Cd(PVA-oxi)Cl$_2$]	330	30303	635	15748	990	10101

Determine the compositions of the proposed complexes

Molar ratio

Table (4) shows the UV absorption, with the molar ratio M/L of the metal complexes being prepared. Figure (2) shows plots of absorbance against molar ratio of each complex notes. Through these drawings the absorbance increases as the molar ratio increased to a certain point at it's the prove absorption with molar ratio. This can be attributed to the stability of the complexes in their solutions. It is clear from our study of curves percentage molar ions elements with legend (PVO) that complexes consisting of 2:1 per mole for ion of copper (II) and 1:1 per mole for ion of cadmium (II).

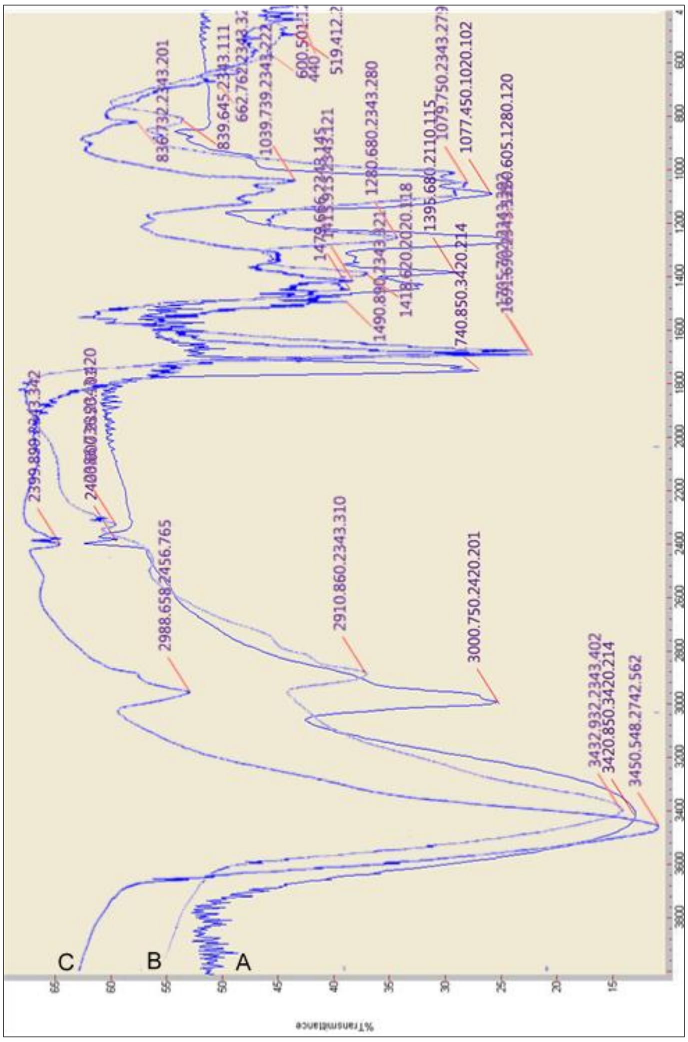


Fig 1: IR Spectrum for (A) (PVO), (B) Cd (PVO-complex), (C) Cu (PVO-complex)

Table *4*: Absorption of complex solutions at the wavelengths corresponding of the molar ratio (ligand: metal) at the molar concentration (1×10^{-5})

M:L	Absorbance of Complex		M:L	Absorbance of Complex	
	Cu(II)	Cd(II)		Cu(II)	Cd(II)
1:0.25	0.283	0.122	1:2.00	0.783	0.507
1:0.50	0.351	0.237	1:2.25	0.798	0.521
1:0.75	0.423	0.341	1:2.50	0.803	0.529
1:1.00	0.492	0.461	1:2.75	0.812	0.542
1:1.25	0.561	0.468	1:3.00	0.825	0.554
1:1.50	0.649	0.488	1:3.25	0.838	-
1:1.75	0.709	0.498	1:3.50	0.849	-

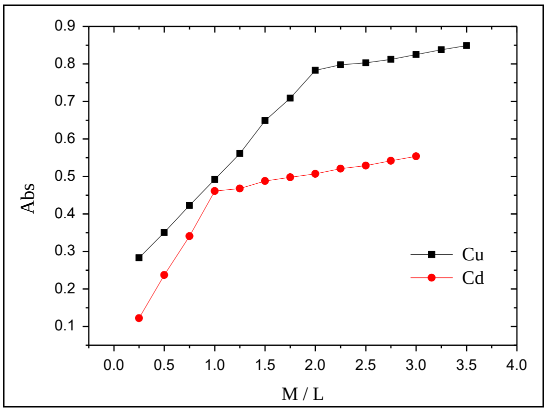


Fig 2: Molar ratio for (1) Cd (PVO-complex), (2)Cu(PVO-complex)

Flam atomic absorption technique

This technique is used to determine the percent of metal in metal complexes proportion comparing them with the calculated ratios theoretically as shown in table (5),which shows the great convergence between the values of theoretical and practical, which confirms the correctness ratios molar of (Ligand: metal) and thus support the proposed formulas of the complexes being prepared

Table 5: Molar conductivity and flame atomic absorption (M%), of metal complexes

NO	Complex	A_m(S.meL^{-1} Cm)$^{-2}$	Metal %	
		In DMF	Calc.	Exp.
2	[Cu(PVA-oxi)$_2$Cl$_2$]	7.22	22.8	20.5
8	[Cd(PVA-oxi) Cl$_2$]	6.74	43.4	32.1

Electrical Conductivity Molar

Using electrical conductivity of molar solutions is widely used in chemistry of coordinating to know the status of the ionic compound in the solution [25].The findings of this study, as shown in table (5), prove that the complexes are non-electrolytes in DMF so that it supports the proposed molecular formulas. The values obtained are consistent with the provisions contained in the literature [20].

From analyzing spectrums illustrated above, molar ratio methods, atomic absorption and electrical conductivity molar of legand and metal complexes preparation are compared with the display in the literatures [26]. The ratio of metal:ligand obtained are (1:2) for both complex of Cu(II) ion provide additional evidence for the approximate octahedralconfiguration Scheme (3) and (1:1) for both complex of Cd(II), ion provide additional evidence for the approximate square configuration Scheme (2).

Optical properties

The UV–visible absorption spectra of PVA containing and PVO-Complexes ([Cu (PVA-oxi)$_2$Cl$_2$] and [Cd(PVA-oxi)$_2$Cl$_2$]were shown in Figure 3. Absorbance spectra of all sample exhibits broad band (200–400 nm) with clear two peaks found at around 276 nm for PVA containing and this band is attributed to ligand π- π* transition so that it corresponds to the spectral bands of PVA [26-27]. Absorbance spectra of PVO-Complexes ([Cu (PVA-oxi)$_2$Cl$_2$] and [Cd(PVA-oxi)$_2$Cl$_2$] showed single peak at around 380 and 320 nm respectively. Another band of lower intensity appeared near the visible region (335 nm). This band was attributed to n- π*, but these bands ware shifted toward higherwavelength. The absorption edge, where a sharp absorption decrease was in the region $200 < \lambda < 450$ nm, red shifted to a lower photon energy (a higher wavelength), which indicates a decrease in the optical band gap as the filler content in the polymer matrix increases [28].

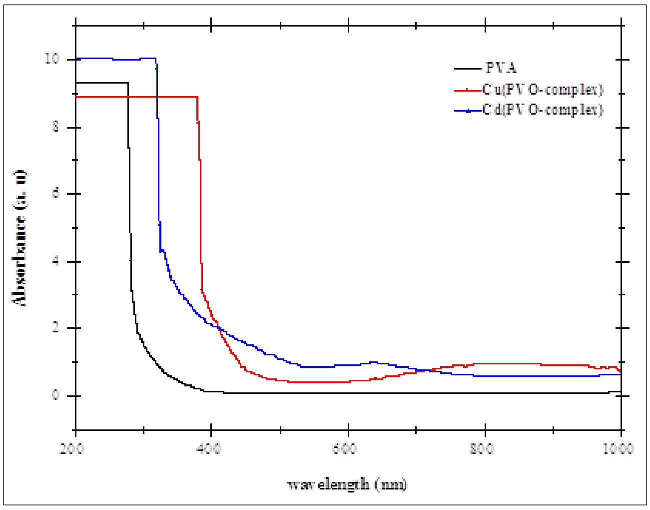


Fig 3: UV Spectrum for (I) (PVO), (II) Cd (PVO-complex), (III) Cu (PVO- complex)

As seen in Figure 3, intensity of the absorbance spectra for [Cd (PVA-oxi)$_2$Cl$_2$] was the highest. The increase in the absorption intensity and decrease in the optical band gap may be due to a larger absorption increment associated with the charge transfer transition [29] or refers to increase the inter/intra molecular hydrogen bonding [30]. The absorption coefficient α can be determined as a function of wavelength using the formula [31]:

$$\alpha \approx 2.303\ A / d \quad (1)$$

Where *A* is the absorbance, *d* is the thickness of the sample.

The optical band gap energy E_g of the samples was calculated using Tauc plot method and the fallow Equation [32]:

$$(\alpha\ .h\nu)^n = B\left(h\nu - E_g\right) \quad (2)$$

where $h\nu$ is the photon energy, *B* is a constant depends on electron and hole effective masses of materials and the exponent *n* depends on the type of transition: it can be equal to 1/2, 2, 3/2 or 3 for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. The variation of $(\alpha\cdot h\nu)^2$ (for direct) and $(\alpha\cdot h\nu)^{1/2}$ (for indirect) versus $h\nu$ is plotted and the straight line range of these plots are extended on $h\nu$ axis to obtain the values of optical direct and indirect band gap E_g of the samples as is illustrated in Figure 4. Direct and indirect transition Eg values were obtained for the pure PVA and PVA-complexes are listed in Table 6.

It can be seen from Table 6 that the optical band gap for pure PVA is equal to 3.98 eV, which decreases to 2.88 eV and 2.83 eVfor PVA-Cu and PVA-Cd respectively for direct transition. These data coincide with the results of the previous work [33] for a PVA/CuI polymer electrolyte, where the optical band gap for pure PVA was equal to 3.39 eV: it decreases to 2.12 eV for a PVA doped with 10 wt % CuI. The decrease in the optical band gap is an indicator of the change in the structure of the polymer matrix and is associated with the creation of localized states in the band gap [34- 35].

Table 6: Optical band gap energy (Eg) for the prepared (I) (PVO), (II) Cd (PVO-complex), (III) Cu (PVO- complex)

sample	E_g(eV)(direct)	E_g (eV)(indirect)
PVA	3.98	2.75
Cu(PVO-complex)	2.88	2.41
Cd(PVO-complex)	2.83	1.43

Electrical properties

The DC conductivity values of the electrolytes are calculated by using the equation [36]:

$$\sigma_{DC} = l/AR_b \quad (3)$$

where *l* is the thickness, *A* is the area of the electrolyte film and R_b is the bulk resistance of the electrolyte film. The DC resistance against weight for (PVO), Cu-(PVO-complex) and Cd-(PVO-complex)can be discussed as presented in Figure 5. The room-temperature resistance and the conductivity are summarized in Table (7). The room-temperature resistance decreased in metals complexes compounds; however, conductivity increased is compared with (PVA-oxi). The resistivity values indicate variation in the charge carrier's concentration. Conductivity results (Table 7) showed that all samples are semiconductors. This means DC conductivity of PVA has been significantly improved by addition of Cu or Cd.

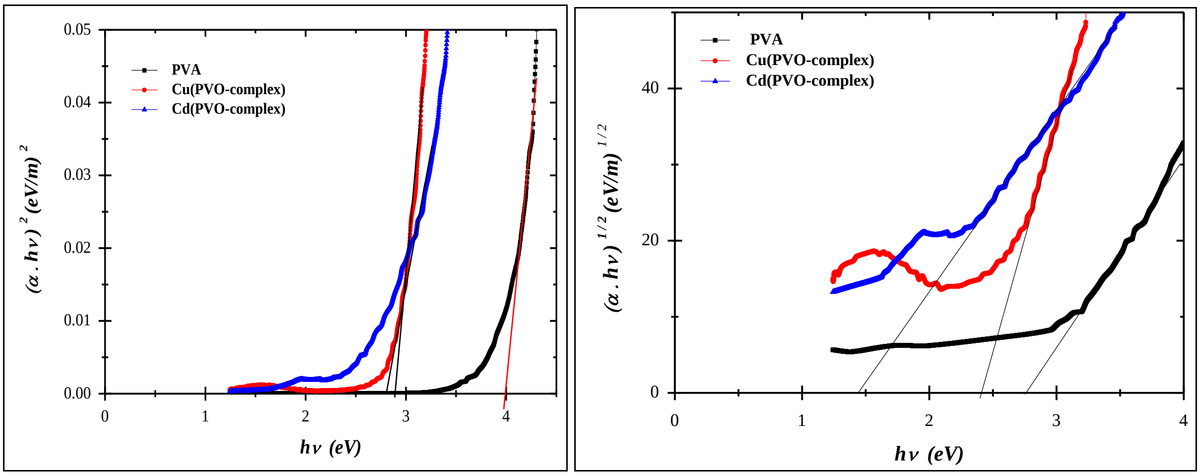


Fig 4: Optical band gap energy (Eg) for the prepared (I)(PVO), (II) Cd(PVO-complex), (III)Cu(PVO- complex) (a) direct transition band gap, (b) indirect transition band gap

Table 7: The room-temperature resistance, conductivity and activation energy

sample	Wight	Resistant (Ω)	Conductivity (Ω.cm)	Activation energy (eV)
PVA	72	***923×10^9***	***3.1×10^{-14}***	0.67
Cu(PVO complex)	***277***	$197x\ 10^6$	***1.2×10^{-10}***	3.61
Cd(PVO-complex)	***254***	$14.3x\ 10^6$	***2.02×10^{-9}***	1.94

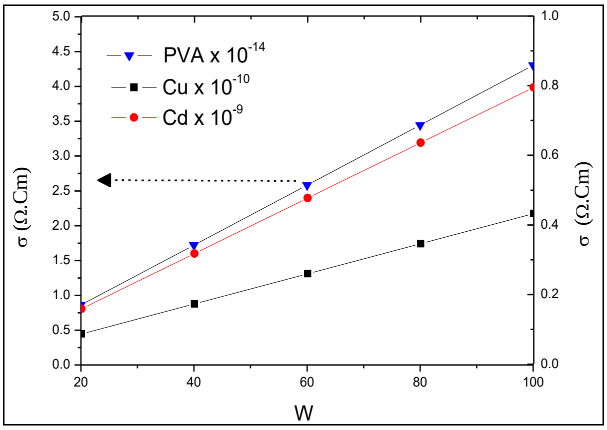


Fig 5: Resistance against weight for (PVO), Cu-(PVO-complex) and Cd-(PVO-complex)

According to the thermally activated flux creep model, the dissipated energy in the tail part of the resistivity plot is defined by an Arrhenius-type equation:

$$\rho(H, T) = \rho_0 \exp[-U(H) / k_B T] \quad (4)$$

Where U is the flux pinning energy or activation energy for flux creep that depends on the temperature (T) and magnetic field (H), ρ_0 is the pre-exponential factor or simply the pre-factor, and k_B is Boltzmann constant. The activation energy are summarized in Table (7)..

Conclusions

In this study, two salts of ions of Cu(II) and Cd(II) were prepared from the reaction of the salts with ligand (PVA -oxi). Some physical properties such as melting point MP C^o and reduced viscosity were studied for two complexes and the ligand, which showed that the complexes had a high boiling point from ligand they high from 360C^o. also reduced, viscosity of the complexes are higher than the ligand. The complexes and ligand were identified using FTIR technique, which showed that the shift towards the high wave numbers to C-OH and OH bands, and the UV-Visible technique showed shift of two bands (π- π*, n-π*)towards the high wave numbers. We also use the molecular ratio, the flam atomic absorption technique and the molar conductivity method in the recognition of the structure of the complexes and the ratio of the complexes of preparation to ligand they are shown 2:1 ligand to ion complex and structure of ions Cu (II) is octahedral and that the ratio of ligand to ion complexes 1:1 and structure of ions Cd (II) is tetrahedron.The optical of ligand and complexes were investigated. The absorbance spectra of all samples exhibits broad band (200–400 nm) with clear two peaks found at around 276 nm for PVA containing so this band is attributed to ligand π- π* transition.. Absorbance spectra of PVO-Complexes ([Cu $(PVA\text{-}oxi)_2Cl_2$] and [Cd$(PVA\text{-}oxi)_2Cl_2$] showed single peak at around 380 and 320 nm respectively. Another band of lower intensity appeared near the visible region (335 nm) so this band was attributed to n-π*, but these bands ware shifted towards higher wavelength. The absorption edge, where a sharp absorption decrease was in the region $200 < \lambda < 450$ nm, red shifted to a lower photon energy, which indicates a decrease in the optical band gap as the filler content in the polymer matrix increases. The direct optical band gap energies for pure PVA is equal to 3.98 eV, which decreases to 2.88 eV and 2.83 eVfor PVA-Cu and PVA-Cd respectively. This decrease in the optical band gap is an indicator of the change in the structure of the polymer matrix and is associated with the creation of localized states in the band gap. The conductivity of two complexes and ligand was studied at room temperature, which showed increased conductivity and decreased the resistance of the prepared ions compared to ligand.

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