

Synthesis and Characterization of some Metalions (II) Complexes of Poly vinyl alcohol and Studied some Physical Properties

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Abstract

Metal complexes of Poly (vinyl alcohol) (PVA-oxi) with the formula $[M(PVA-oxi)_2(NO_3)_2]$ $[M = Fe(II), Co(II) \text{ and } Ni(II)]$ and metal complex with formula $[M(PVA-oxi)_2Cl_2]$ $[M = Cr(II), Mn(II), Hg(II), Zr(II), Zn(II) \text{ and } Pd(II)]$ were prepared using solution cast method. The atomic absorption, IR, UV-Vs spectroscopic techniques, molar ratio and molar conductance as well as the relative viscosity were characterized. It was found that the prepared complexes are obtained from the ligand reaction with metal ions in a DMF solvent were ratio of metal: ligand (1:2) for the complexes of $[Co(II), Cr(II), Mn(II), Fe(II), Zr(II), Ni(II)]$ ions and (1:1) for the complexes of $[Zn(II), Pd(II), Hg(II)]$ ions were obtained. The results showed that the ligand (PVA-oxi) was bidentate ligand coordinated with metal ions through the oxygen atoms of carbonyl and hydroxlic groups of its chain their octahedral geometry for $[Co(II), Cr(II), Mn(II), Fe(II), Zr(II), Ni(II)]$ complexes while their tetrahedral geometry for $[Zn(II), Pd(II), Hg(II)]$ complexes. The conductivity of the ligand and the prepared complexes were studied, which showed that the connection of the complexes is higher than the ligand and ion Zn (II) had the highest conductivity. Ion Fe(II) showed the lowest conductivity.

المخلص

تم في هذا البحث تحضير معقدات لبولي فابنيل الكحول (PVA) مع بعض العناصر الانتقالية ، وذلك بتفاعل الاملاح الثنائية لهذه العناصر وهي املاح النترات ل $[M = Fe(II), Co(II), Ni(II)]$ واملاح الكلوريدات ل $[M = Cr(II), Mn(II), Hg(II), Zr(II), Zn(II), Pd(II)]$ مع متعدد فانيل الكحول المؤكسد اكسدة جزية والذي يعمل كليجند وكانت الصيغة العامة للمعقدات هي $[M(PVA-oxi)_2(NO_3)_2]$ و $[M(PVA-oxi)_2Cl_2]$ على الترتيب تم التعرف على هذه المعقدات باستخدام طيف الاشعة فوق البنفسجية- المرئية وطيف الاشعة تحت الحمراء ، والامتصاص الذري ، والتوصيلية المولارية ، واللزوجة النسبية . وقد وجد ان المعقدات المحضرة يتم الحصول عليها من مفاعلة الليجند مع الايون الفلزي في مذيب DMF بنسبة 2:1 للايونات $[Co(II), Cr(II), Mn(II), Fe(II), Zr(II), Ni(II)]$ ، وان الليجند يسلك سلوك الليجندات ثنائية السن مع الايونات وذلك من خلال التناسق مع ذرة الاكسجين من جهة ومع مجموعة الهيدروكسيل من جهة اخرى يكون الشكل الهندسي لمعقدتها هو ثماني السطوح اما معقدات الايونات التالية $[Zn(II), Pd(II), Hg(II)]$ فقد تم الحصول عليها بنسبة 1:1 وشكلها الهندسي هو رباعي هرمي . ايضا تم دراسة التوصيلية للليجند والمعقدات المحضرة والتي بينت ان توصيلة المعقدات اعلى من الليجند وان اعلى توصيلة هي لايون $(Zn(II))$. ثم $(Hg(II))$ وان اقل توصيلية هي ل $(Fe(II))$.

Keywords: PVA metal complexes; Viscosity; Molar ratio; Flam atomic; U.V spectrum; IR spectrum; DC conductivity.

1- Introduction

In recent years the polymer complexes have been given a great deal of attention [1-3]. The selective chelation of specific metal ions and polymer ligand synthesis is a field of active research [4]. More potential applications of the metal ions of polymer complexes have been a bear such as science as catalytic, conductive, luminescent, magnetic, porous, chiral or non-linear optical materials [5-8].

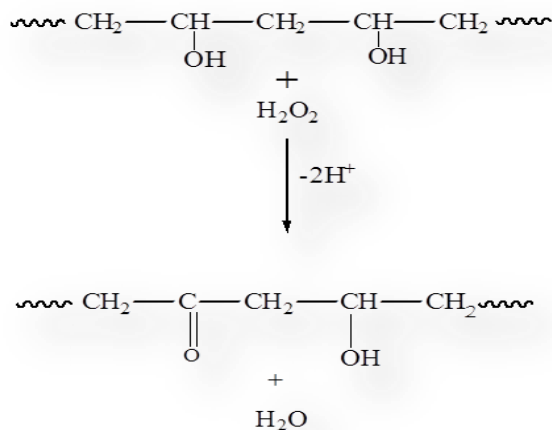
Poly (vinyl alcohol) is an important material in view of its large-scale applications, such as biomaterials, biosensors, electrochemical sensors, membranes with selective permittivity, viscous medium for controlling the crystallization process of salts, for controlled drug delivery or catalytic systems, etc. Because it is a 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].

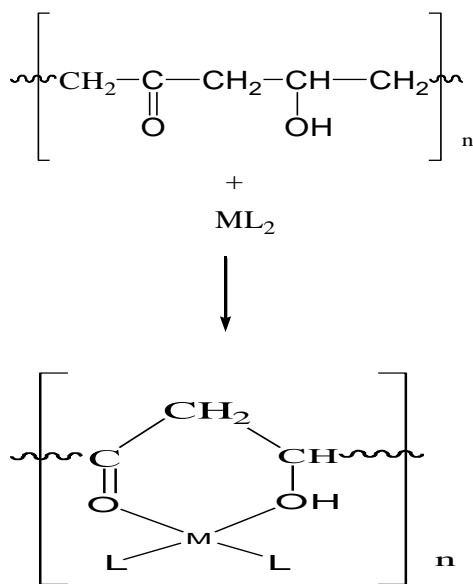
PVA is a potential material having a high dielectric strength, good charge storage capacity and dopant dependent electrical properties. It has carbon chain back bone with hydroxyl groups attached to methane carbons. These O-H groups can be a source of hydrogen bonding and therefore, assist the formation of polymer complexes [11]. It has excellent mechanical properties and shows both ionic and electronic conduction [12]. When polymers are doped with inorganic salts, they show appreciable change in their structural as well as electrical properties. Polymer electrolytes containing divalent cations are suitable for electrochemical applications. The most important polymer was polyvinyl alcohol (PVA), some of metal complexes of this polymer have been synthesized [13, 14]. The Cu(II) complex of (PVA) in a

neutral or slightly basic solution [15]. In this study, we prepare PVO from PVA as ligand and reactions with a number of metal salt to form complexes of them and study of some physical properties as electrical properties for ligand and complexes.

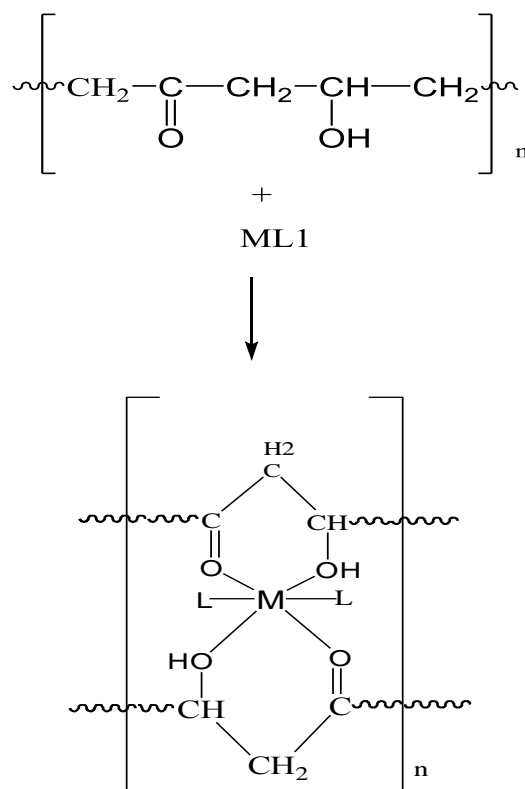
Scheme(1) preparation of PVO from poly vinyl alcohol (PVA)



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).



2- Materials and method

2.1 Materials

Stoichiometric amounts of high purity of polyvinyl alcohol (PVA)(Scharlau, 98 %) and metal salts (Scharlau, 98 %) were used. Distilled water was used as a solvent. Concentration of hydrogen peroxide (H_2O_2) (Fluka, 99 %) was used in this work (50%).

2.2 Synthesis

2.2.1 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 3 hours at temperature = 50-80 oC. The mixture was refluxed for 3 hrs. The homogeneous solutions were evaporated and the oxidized polymer spread by Reutery device and left to dry slowly in oven at 50 oC for 24 hrs. Finally, the films were ready for characterizations.

2.2.2 Synthesis of oxidized PVO-Complexes: 0.501 g (2 mmol) of oxidized PVA was dissolved in 10 ml DMF, and then 0.2118 g (1 mmol) of metal salt ($\text{M}(\text{PVA-oxi})_2(\text{NO}_3)_2$] or ($\text{M}(\text{PVA-oxi})_2\text{Cl}_2$) in DMF in each case was added at pH 6.7. The mixture was heated under reflux for about 10 hrs. 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 over night.

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 | - | - |
| [Co (PVA–oxi) ₂ (NO ₃) ₂] | 3433 | 1720 | 1284 | 2919 | 1080 | 560 |
| [Ni (PVA–oxi) ₂ (NO ₃) ₂] | 3450 | 1700 | 1285 | 2888 | 1082 | 510 |
| [Fe(PVA–oxi) ₂ (NO ₃) ₂] | 3425 | 1710 | 1272 | 2930 | 1075 | 600 |
| [Mn(PVA–oxi) ₂ Cl ₂] | 3445 | 1680 | 1310 | 2959 | 1120 | 640 |
| [Cr(PVA–oxi) ₂ Cl ₂] | 3423 | 1673 | 1277 | 2922 | 1041 | 583 |
| [Zn (PVA–oxi)Cl ₂] | 3440 | 1695 | 1354 | 2920 | 1060 | 576 |
| [Zr (PVA–oxi) ₂ Cl ₂] | 3439 | 1681 | 1225 | 2921 | 1063 | 500 |
| [Hg (PVA–oxi)Cl ₂] | 3441 | 1687 | 1281 | 2990 | 1087 | 439 |
| [Pd (PVA–oxi)Cl ₂] | 3430 | 1674 | 1241 | 2900 | 1046 | 520 |

Table 3. UV -spectrum of ligand and metal complexes

| Complex | Band(I) (V ₁) | | Band(II) (V ₂) | | Band(III) (V ₃) | |
|---|------------------------------|------------------------|-------------------------------|------------------------|--------------------------------|------------------------|
| | λ_{\max} nm | $\nu_{\text{cm}^{-1}}$ | λ_{\max} nm | $\nu_{\text{cm}^{-1}}$ | λ_{\max} nm | $\nu_{\text{cm}^{-1}}$ |
| (PVA–oxi) | 276 | 36231 | 335 | 29850 | --- | --- |
| [Co(PVA–oxi) ₂ (NO ₃) ₂] | 355 | 28169 | 403 | 24813 | 600 | 16666 |
| [Ni(PVA–oxi) ₂ (NO ₃) ₂] | 418 | 23923 | 603 | 16583 | 710 | 14084 |
| [Fe(PVA–oxi) ₂ (NO ₃) ₂] | 382 | 12195 | 408 | 24259 | 691 | 14471 |
| [Mn(PVA–oxi) ₂ Cl ₂] | 305 | 32786 | 595 | 16806 | --- | --- |
| [Cr(PVA–oxi) ₂ Cl ₂] | 315 | 31746 | 588 | 17006 | --- | --- |
| [Zn(PVA–oxi)Cl ₂] | 408 | 24509 | 650 | 15384 | 835 | 11976 |
| [Zr(PVA–oxi) ₂ Cl ₂] | 310 | 32258 | 415 | 24096 | 687 | 14556 |
| [Hg(PVA–oxi) Cl ₂] | 310 | 32258 | 590 | 16949 | --- | --- |
| [Pd(PVA–oxi)Cl ₂] | 317 | 31545 | 416 | 24038 | 643 | 15552 |

vibration respectively but the same bands of metal complexes appeared at higher frequencies in the range 3453-3420 cm^{-1} and 1225-1354 cm^{-1} respectively while the carbonyl group in the ligand exhibited a band at 1740 cm^{-1} . This band was shifted to lower frequencies by 80-40 cm^{-1} in the metal complexes giving evidence for the coordination to metal ion. Also the bands of M-O appeared between (400-700) cm^{-1} for metal complexes but disappeared in the ligand [18, 19].

3.3 U.V spectrum

Table (3) and Figure (2) show U.V. spectrum for each of the ligand and metal complexes prepared. They show two peaks at 226 nm. This band is attributed to intra ligand $\pi \rightarrow \pi^*$ transition. Another band of a lower intensity appeared near the visible region (335 nm). This band was attributed to $n \rightarrow \pi^*$ but these bands were shifted toward high wave length [20,21].

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

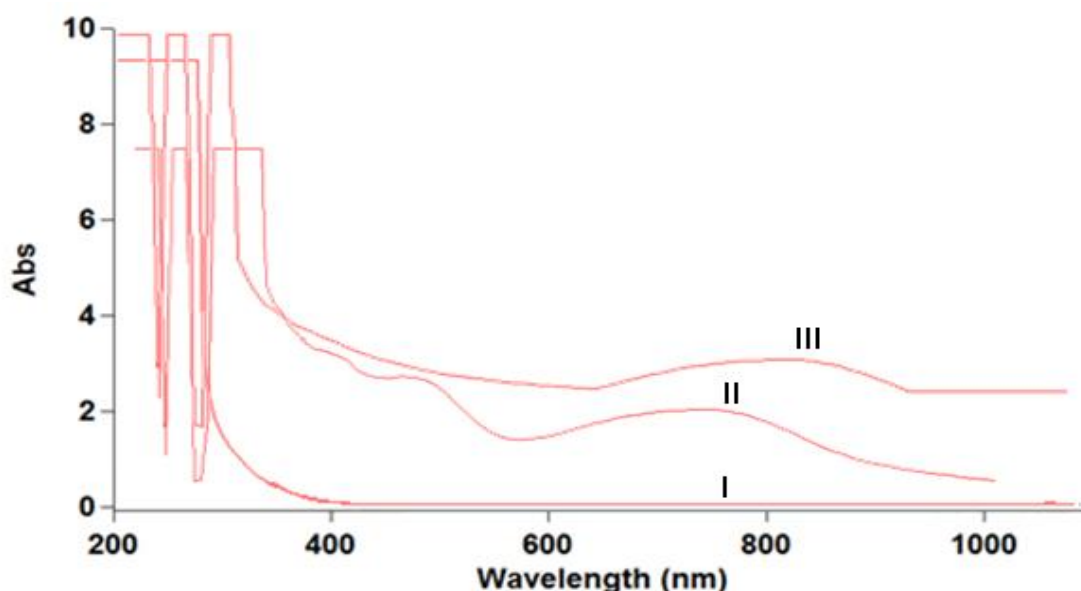
| M:L | Co(II) | Ni(II) | Fe(II) | Mn(II) | Cr(II) | Zn(II) | Zr(II) | Hg(II) | Pd(II) |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1:0.25 | 0.156 | 0.213 | 0.139 | 0.125 | 0.101 | 0.145 | 0.185 | 0.103 | 0.179 |
| 1:0.50 | 0.198 | 0.264 | 0.174 | 0.169 | 0.145 | 0.174 | 0.221 | 0.212 | 0.342 |
| 1:0.75 | 0.224 | 0.312 | 0.253 | 0.214 | 0.174 | 0.222 | 0.256 | 0.307 | 0.469 |
| 1:1.00 | 0.265 | 0.379 | 0.317 | 0.264 | 0.222 | 0.238 | 0.291 | 0.425 | 0.622 |
| 1:1.25 | 0.297 | 0.412 | 0.374 | 0.318 | 0.238 | 0.301 | 0.326 | 0.441 | 0.628 |
| 1:1.50 | 0.335 | 0.443 | 0.438 | 0.354 | 0.301 | 0.369 | 0.361 | 0.453 | 0.644 |
| 1:1.75 | 0.368 | 0.503 | 0.493 | 0.422 | 0.369 | 0.387 | 0.396 | 0.459 | 0.651 |
| 1:2.00 | 0.401 | 0.550 | 0.542 | 0.467 | 0.387 | 0.408 | 0.431 | 0.460 | 0.662 |
| 1:2.25 | 0.418 | 0.561 | 0.556 | 0.501 | 0.408 | 0.432 | 0.461 | 0.479 | 0.671 |
| 1:2.50 | 0.425 | 0.573 | 0.575 | 0.522 | 0.432 | 0.452 | 0.473 | 0.492 | 0.681 |
| 1:2.75 | 0.436 | 0.582 | 0.593 | 0.541 | 0.452 | 0.472 | 0.481 | 0.505 | 0.692 |
| 1:3.00 | 0.449 | 0.595 | 0.612 | 0.556 | 0.472 | 0.493 | 0.493 | 0.512 | 0.703 |
| 1:3.25 | 0.458 | 0.612 | 0.628 | 0.581 | 0.493 | - | 0.501 | - | - |
| 1:3.50 | 0.460 | 0.623 | 0.639 | 0.597 | 0.101 | - | 0.512 | - | - |

3.4 Determining the compositions of the proposed complexes

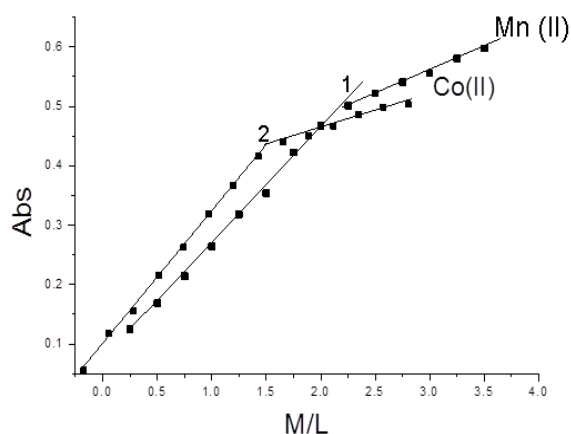
3.4.1 Molar ratio method

In this method, absorption spectrum U.V. at different concentration ratios (M/L) was used. Table (4) shows the UV absorption, with the molar ratio M/L of the metal complexes prepared. Figures (3) shows plots of absorbance against molar

ratio of each complex notes through these drawings that the absorbance increases as the molar ratio increased to a certain point to prove absorption with molar ratio. That is attributed to the stability of the complexes in their solutions [18-23]. It is clear from our study of curves percentage molar ions elements with ligand (PVO) that complexes consisting of 2:1 per mole of ions of cobalt (II), nickel (II), iron (II), chromium (II), zirconium (II), and manganese (II) and 1:1 per mole of ions of a zinc (II), mercury (II) and palladium (II).



Figure(2): UV Spectrum for (I) (PVO), (II) Co(PVO-complex), (III) Mn(PVO-complex)



Figure(3): Molar ratio for (1) Co(PVO-complex), (2) Mn(PVO-complex)

| Complex | flame atomic absorptionMetal % | | $A_m(S.meL^{-1}Cm)^{-2}$ |
|---|--------------------------------|-------|--------------------------|
| | Calc. | Exp. | In DMSO |
| [Co(PVA-oxi) ₂ (NO ₃) ₂] | 16.37 | 19.6 | 11.33 |
| [Ni(PVA-oxi) ₂ (NO ₃) ₂] | 16.61 | 19.8 | 8.89 |
| [Fe(PVA-oxi) ₂ (NO ₃) ₂] | 16.12 | 19.10 | 7.56 |
| [Mn(PVA-oxi) ₂ Cl ₂] | 20.07 | 18.3 | 8.24 |
| [Cr(PVA-oxi) ₂ Cl ₂] | 19.1 | 17.8 | 9.11 |
| [Zn(PVA-oxi)Cl ₂] | 31.24 | 29.2 | 5.48 |
| [Zr(PVA-oxi) ₂ Cl ₂] | 29.7 | 26.5 | 10.35 |
| [Hg(PVA-oxi)Cl ₂] | 58.3 | - | 6.65 |
| [Pd(PVA-oxi)Cl ₂] | 42.33 | - | 5.12 |

3.4.2 Flam atomic absorption technique

This technique is used to determine the percentage of metal in Metal complexes proportion and compared with the calculated ratios theoretically as shown in table (5) which shows the great convergence between the values of theoretical and practical ratios; which confirms the correctness ratios molar of (Ligand: metal) and thus supports the proposed formulas of the complexes prepared.

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

3.4.3 Electrical conductivity molar

Using electrical conductivity of molar solutions to know the status of the ionic compound in the solution [22] is widely used in chemistry of coordination. The findings through this study are described in Table (5) which shows that, all the complexes are non-electrolytes in DMSO, have given these results supporting the proposed molecular formulas. The values obtained are consistent with the provisions contained in the literature [16].

From analysis, spectrums were illustrated above, molar ratio methods, atomic absorption and electrical conductivity molar of legend: and matel complexes preparation and compare

with the display in the literatures [16, 20]. The ratio of metal:ligand obtained are (1:2) for both complexes of [Co(II), Cr(II), Mn(II), Fe(II), Zr(II), Ni(II)] ions provide additional evidence for the approximate tetrahedrons configuration Scheme (3) and (1:1) for both complexes of [Zn(II), Pd(II), Hg(II)] ions provide additional evidence for the approximate square configuration Scheme (2).

The room-temperature resistance and the conductivity are summarized in Table (6). Sample (PVA-oxi) showed the highest room temperature resistance ($923 \times 10^9 \Omega$) and the lowest conductivity ($3.1 \times 10^{-14} \Omega \cdot \text{cm}$). For metal complex compounds sample [Cr(PVA-oxi) $_2$ Cl $_2$] showed the highest room temperature resistance ($1.8 \times 10^9 \Omega$) and the lowest conductivity ($1.6 \times 10^{-11} \Omega \cdot \text{cm}$). However sample [Zr(PVA-oxi) $_2$ Cl $_2$] showed the highest conductivity ($2.6 \times 10^{-8} \Omega \cdot \text{cm}$). For metal complex compounds sample [Co(PVA-oxi) $_2$ (NO $_3$) $_2$] showed the highest room temperature resistance ($18 \times 10^8 \Omega$) and the lowest conductivity ($1.6 \times 10^{-11} \Omega \cdot \text{cm}$). However sample [Ni(PVA-oxi) $_2$ (NO $_3$) $_2$] showed the highest conductivity ($3.8 \times 10^{-10} \Omega \cdot \text{cm}$).

Table 6. The room-temperature resistance and the conductivity for ligand (PVO) and metal complexes at room temperature (25 Co)

| Compound | R (Ω) | σ ($\Omega \cdot \text{cm}$) |
|-------------------------------------|--------------------|---------------------------------------|
| (PVA-oxi) | 923×10^9 | 3.1×10^{-14} |
| [Co(PVA-oxi) $_2$ (NO $_3$) $_2$] | 18×10^8 | 1.6×10^{-11} |
| [Ni(PVA-oxi) $_2$ (NO $_3$) $_2$] | 7.5×10^7 | 3.8×10^{-10} |
| [Fe(PVA-oxi) $_2$ (NO $_3$) $_2$] | 185×10^6 | 1.2×10^{-11} |
| [Mn(PVA-oxi) $_2$ Cl $_2$] | 156×10^7 | 1.4×10^{-11} |
| [Cr(PVA-oxi) $_2$ Cl $_2$] | 1.8×10^9 | 1.6×10^{-11} |
| [Zn(PVA-oxi)Cl $_2$] | 189×10^6 | 1.1×10^{-10} |
| [Zr(PVA-oxi) $_2$ Cl $_2$] | 1.1×10^6 | 2.6×10^{-8} |
| [Hg(PVA-oxi)Cl $_2$] | 15.2×10^6 | 1.9×10^{-9} |
| [Pd(PVA-oxi)Cl $_2$] | 88.5×10^6 | 3.2×10^{-10} |

The room-temperature resistance decreased in metal complex compounds, however, conductivity increased comparing with (PVA-oxi). The resistivity values indicate variation in the charge carrier's concentration. Conductivity results (Table 6) showed that all samples are semiconductors.

4-Conclusion

In this study, various salts of some of the two-ion transition elements were prepared from the reaction of these salts with ligand (PVA -oxi). Some physical properties such as melting point MP Co and red viscosity were studied for each of the prepared complexes and the ligand which showed that the complexes had a high boiling point from ligand they high from 360 also red, viscosity of the complexes also 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 ($\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$) towards the high wave numbers. Also were made using the molecular ratio, the flame 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 [Co (II), Cr (II) Mn (II), Fe (II), Zr (II), Ni (II)] are octahedral and that the ratio of ligand to ion complexes 1:1 and structure of ions [Zn(II), Pd(II) Hg(II)] tetrahedron. The conductivity of all complexes and ligand was studied at room temperature, which showed increased conductivity and decreased the resistance of the prepared ions compared to ligand and the highest conductivity was in Zn (II). Then Hg (II) and the lowest connectivity was in Fe (II).

5-References

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