Optical Properties of PVA:CdCl$_2$.H$_2$O Polymer Electrolytes

Omed Gh. Abdullah[1], Dana A. Tahir, Saro S. Ahmad, and Hawzhin T. Ahmad

Physics Department, Faculty of Science and Education Science, School of Science, University of Sulaimani, Kurdistan Region, Iraq.

Abstract: *Polymer electrolytes based on Polyvinyl alcohol – Cadmium Chloride were prepared by solution cast technique. Results of optical absorption, transmission spectra, refractive index, optical band gaps, optical conductance, single oscillator energy, dispersion energy, real and imaginary parts of dielectric constants studies are presented. The optical properties were obtained using UV-VIS Double Beam Spectrophotometer in the wavelength range (190-1100) nm. The optical transmittance at wavelength ≈ 190nm for pure PVA was nearly at 78%, while it was 50% for all doped samples. The optical transmittance was increased with increasing wavelength up to 98% for all films beyond ≈240nm. The calculated energy band gap changes from 6.42eV (pure PVA) to 5.80eV (PVA-20%CdCl$_2$.H$_2$O). The optical conductance and band-gap indicated that the films are almost transmitting within the visible range. The single oscillator expression has been used to obtain the information about disorder degree. The real and imaginary parts of dielectric constant of the doped films increases with increasing CdCl$_2$.H$_2$O concentration, and it shows decreases abruptly in the wavelength (200-220) nm, and finally becomes constant with increase in photon energy.*

Keywords : *polymer electrolytes; absorbance; transmittance; refractive index; optical conductance; dispersion energy; dielectric constant.*

I. Introduction

Essentially, the goal of material research is to create a new materials with properties for a particular application to understand the physical and chemical mechanisms that determine these properties. One method to modify the properties of matter is doping the polymers with different level of dopant [1]. Polymer based electrolytes are frequently studied for fundamental reasons and practical applications as well. The polymer electrolytes not only combine the advantageous properties of dopant and polymers, but also exhibit many new properties that single phase materials do not have [2]. The properties of a polymer may be improved and controlled substantially by adding suitable dopant [3].

Polyvinyl Alcohol (PVA) a polyhydroxy polymer, is typically used as glue, and as well as adhesive properties, exhibits good emulsifying and film-forming properties. It is also resistant to oil, grease and solvent[4]. Some metallic salts with Polyvinyl Alcohol (PVA) presents important variations in the optical absorption and the refractive index. The optical parameters of doped polymers are strongly dependent on the electronic configuration inside the electrolytes. In order to obtain materials with improved optical proprieties, it is necessary to understand and control the electronic mechanisms involved in the process [5].

In the present work the optical properties of Polyvinyl alcohol (PVA) films doped with different concentration of Cadmium Chloride (CdCl$_2$.H$_2$O) are investigated, in the UV/VIS region to understanding the mechanism of transitions and optical parameters which is relatively affected by processing conditions.

II. Experimental details

Films of Polyvinyl alcohol (PVA) - Cadmium Chloride (CdCl$_2$.H$_2$O) electrolytes were prepared by casting method. In this method $2gm$ of pure PVA supplied from Sigma-Aldrich company, has dissolved in $40ml$ of distilled water. For this solution different weight ratios of CdCl$_2$.H$_2$O (5, 10, 15, and 20) wt% were added to prepare solid polymer electrolytes. To obtain the complete dissolution a magnetic stirrer was used at 350 K for one hour. These homogenous solutions were casted in a glass dish (diameter of 5 cm). The whole assembly was placed in a dust free chamber and the solvent was allowed to evaporate slowly in open air at room temperature for one week. The thickness of the films was in the range of (0.045-0.10) mm. It was determined using micrometer at different places in each film and an average was taken.

III. Results and Discussion

A Perkin Elmer lambda 25 UV–visible spectrophotometer was used to measure the absorption spectra of the samples in the wavelength range (190-1100) nm. The optical absorbance against the wavelength in the wavelength range (190–250) nm, and for pure PVA and different concentration of CdCl$_2$.H$_2$O are shown in Fig.1
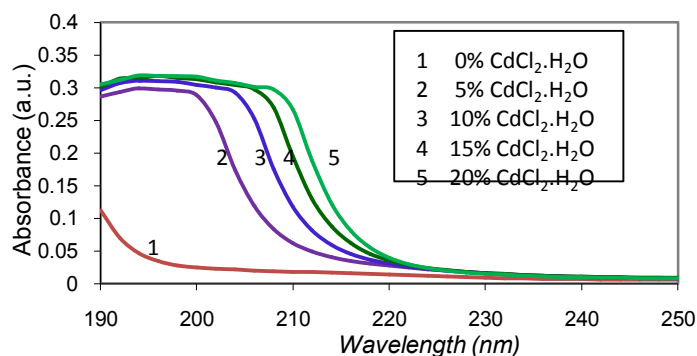
Fig.1: Absorption Spectra of PVA-CdCl$_2$.H$_2$O electrolytes films.

The absorbance spectrum shows a sharp increase in absorption at wavelength near to the absorption edge of the threshold wavelength for onset of absorption. The energy corresponding to this determines the band gap of the semiconductor material [6]. The CdCl$_2$.H$_2$O concentration caused significant increase of absorption edge in the wavelength range (190-230) nm. It can be seen that the absorption edge shifts towards higher wavelength upon the addition of salt concentration.

The ratio of radiant power transmitted (P) by a sample to the radiant power incident (P_0) on the sample is called the transmittance T:

$$T = \frac{P}{P_0} \qquad (1)$$

But, $P = P_0\, e^{\alpha t}$

$$T = e^{\alpha t} \qquad (2)$$

Where t is the thickness, and α is the optical absorption coefficient, which can be calculated from the measured absorbance (A), and thickness of the films by [7, 8]:

$$\alpha = 2.303 \frac{A}{t} \qquad (3)$$

The transmittance spectrum of samples in the wavelength range (190-250) nm, is shown in the Fig.2.
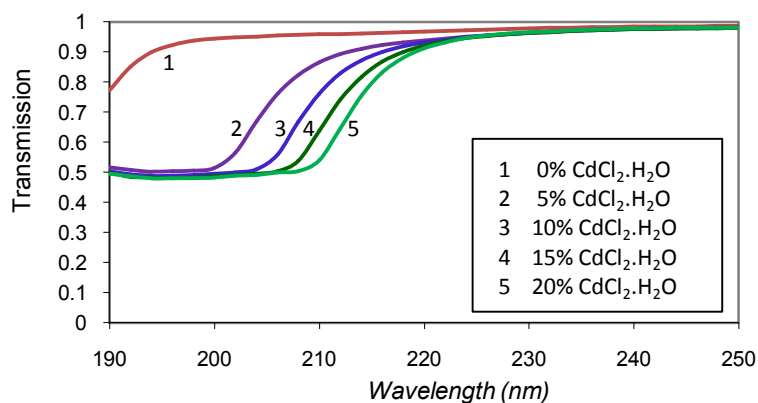

Fig.2: Transmittance Spectra of PVA-CdCl$_2$.H$_2$O electrolytes films.

The optical transmittance at wavelength ≈ 190nm for pure PVA was nearly at 78%, while it was 50% for all doped sample. The optical transmittance was increased with wavelength up to 98% for all films beyond ≈240nm.

The reflectance of the films has been found from Transmittance T and absorbance A using relationship [9]:

$$R = 1 - (T + A) \qquad (4)$$

At normal incidence, the relation between refractive index (n) of the film, and reflectance (R) are given by formula [10]:

$$R = \frac{(n-1)^2}{(n+1)^2} \qquad (5)$$

The above equation can be inverted and use the reflectance and transmittance at normal incidence for given wavelength to determine the refractive index. The real part of the refractive index (n) can be determined by:

$$n = \frac{[1 + \sqrt{R}]}{[1 - \sqrt{R}]} \qquad (6)$$

Fig.3 shows the variation of refractive index with incident photon energy for all samples. The refractive index of all samples was almost constant in low energy up to 5eV, and then increased with increase in photon energy, after that they becomes constant. Generally the cadmium chloride ($CdCl_2.H_2O$) concentration caused an increase in refractive index, especially in the energy range 5.5-6.2 eV. The refractive index of the dopant samples increase up to 2.6 and then they remain constant.
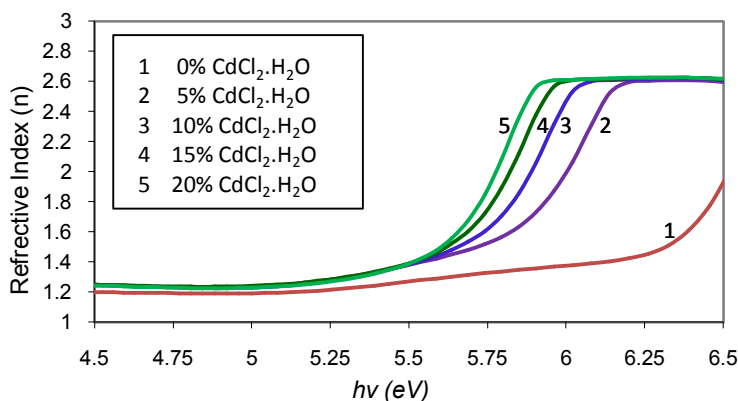

Fig.3: Change in Refractive Index with incident photon energy of PVA-CdCl₂.H₂O electrolytes films.

The UV-visible spectra of the material provide an important information about the details related with optical band gaps [11]. Plotting the graph between $(\alpha h v)^2$ versus photon energy $(h v)$ gives the value of direct band gap. The extrapolation of the straight line to $(\alpha h v)^2 = 0$, gives the value of the band gap as shown in Fig.4. From the UV-visible spectra, it is clear that the absorbance decreases with increase in wavelength. This decrease in the absorption indicates the presence of optical band gap in the material [6, 12]. The optical band gap of the films are presented in Table I, it is obvious, that the E_g decreases with increase salt concentration.
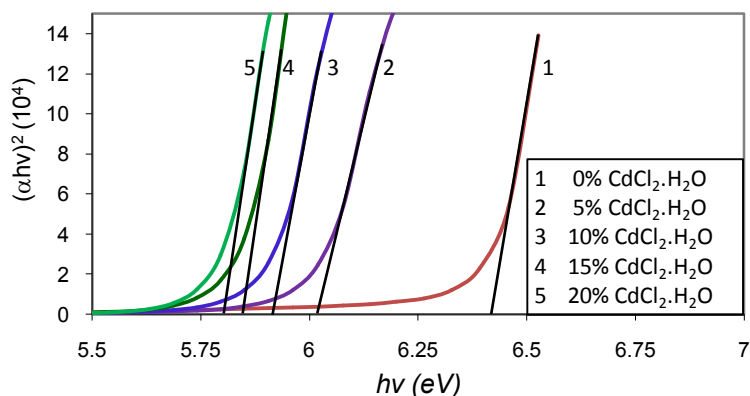

Fig.4: Variation of $(\alpha h v)^2$ as a function of photon energy (hv) of PVA-CdCl₂.H₂O electrolytes films.

The optical conductivity (σ) is obtained using the relation [6],

$$\sigma = \frac{\alpha n c}{4\pi} \qquad (7)$$

Where c is the velocity of light in the space; n is the refractive index and α is the absorption coefficient.

Fig.5 shows the variation of optical conductivity with the incident photon energy. The optical conductivity is constant up to 5.5eV of photon energy after that it increases with increase in photon energy. The increased optical conductivity at high photon energies is due to high absorbance of film in that region. The optical conductance and band gap indicated that the films are transmittance within the visible range.
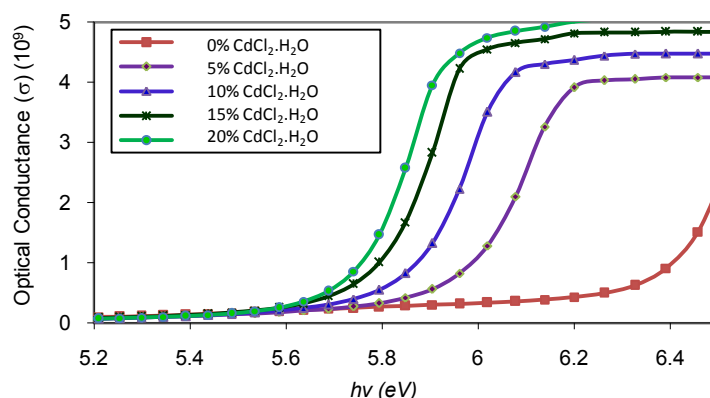
Fig.5: Optical conductivity of PVA-CdCl$_2$.H$_2$O electrolytes films.

The dispersion data of the refractive index can be calculated by single-oscillator model. Which developed by Wemple and Didomenico [13]:

$$(n^2 - 1)^{-1} = \frac{E_o{}^2 - (hv)^2}{E_d E_o} \qquad (8)$$

where E_o is the single oscillator energy, and E_d is the dispersion energy, which measures the average strength of inter band transitions [14].

Plotting $(n^2 - 1)^{-1}$ versus $(hv)^2$ as shown in Fig(6), allows one to determine the oscillating parameters E_o and E_d, by fitting a linear function to the data, the slope of the line represented $(-1/(E_o E_d))$, and (E_o/E_d) determined from intercept on the vertical axis. The values obtained for the oscillating parameters are listed in Table I.
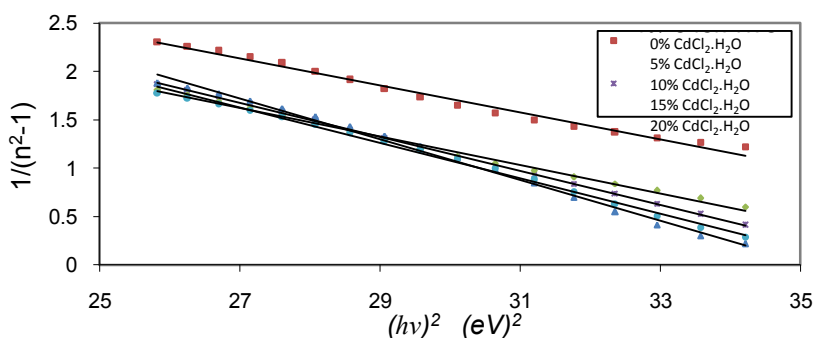
Fig.6: Plots of $1/(n^2 - 1)$ verse $(hv)^2$ for different CdCl$_2$.H$_2$O concentration.

The single-oscillator energy E_o and dispersion energy E_d are related to the optical energy band gap (Fig.4), they are decreases as CdCl$_2$.H$_2$O concentration increase. Since the dispersion energy E_d, measures the average strength of inter-band optical transitions [15], we expect the decrease of bound strength by increasing the CdCl$_2$.H$_2$O concentration, which lead to increases in degree of disorder.

Based on single-oscillator model the moment of optical spectra (M_{-1}) and (M_{-3}) can be determined from the following relations [14]:

$$E_o{}^2 = \frac{M_{-1}}{M_{-3}} \quad ; \quad E_d{}^2 = \frac{(M_{-1})^3}{M_{-3}} \qquad (9)$$

The obtained (M_{-1}) and (M_{-3}) are both increases as CdCl$_2$.H$_2$O concentration increased as shown in Table (I). The optical moments are related to the macroscopic quantities like dielectric constants, effective number of valence electrons in the investigated material [14, 16].

Table (I): The Wemple-Didomenico oscillating parameters.

CdCl$_2$.H$_2$O %	E_g (eV)	E_d (eV)	E_o (eV)	M_{-1} (eV)^2	M_{-3} (eV)^2
0	6.42	1.5389	4.6751	0.3292	0.0151
5	6.02	1.3831	4.1079	0.3367	0.0200
10	5.92	1.2699	3.7499	0.3386	0.0241
15	5.85	1.5191	4.4782	0.3392	0.0169
20	5.80	1.3661	4.0219	0.3397	0.0210

The dielectric constant can be obtained theoretically, since it was related to the absorption coefficient. The real part (ε_r) and the imaginary part (ε_i) of the dielectric constant, was obtained using relation [17]:

$$\varepsilon_r = n^2 - k^2 \qquad (10)$$
$$\varepsilon_i = 2nk \qquad (11)$$

Where n is the refractive index of the films and k is the extinction coefficient given by [17]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (12)$$

Where λ is the wavelength of the incident light. The imaginary part of dielectric constant, represents loss factor or energy absorbed.

So the complex dielectric constant (ε^*) is expressed as [18]:

$$\varepsilon^* = \varepsilon_r - i\,\varepsilon_i \qquad (13)$$

Fig.7(a&b) illustrate the variation of real part and imaginary part of the dielectric constant as a function of CdCl₂.H₂O concentration, for different frequency in the region of absorption edge. The real and imaginary part of the dielectric constant increases slowly with salt concentration, while they decrease with increase of wavelength, and they are almost constant in the visible region.
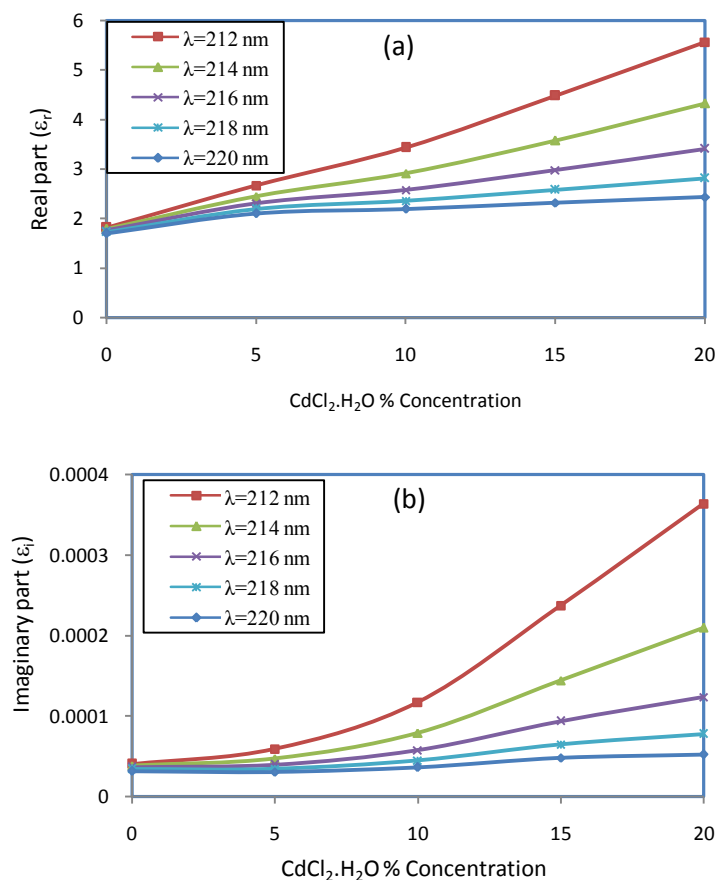

Fig.7: (a) Real part and (b) Imaginary part of dielectric constant as a function of CdCl₂.H₂O concentration.

IV. Conclusions

In this work the effect of cadmium chloride concentration on optical properties of Polyvinyl alcohol film was demonstrated. The optical behavior of the samples shows that the films almost transmitting in the visible region. The cadmium chloride content caused increase in the absorbance at the near infrared domain, with high transmittance at the same region. The data explain the relationship between refractive index, real and imaginary parts of dielectric constants and optical conductance. Information about disorder degree and optical band gap of the films has been obtained from Wemple-DiDomenico model. The results have shown that the single oscillator energy E_o and the dispersion energy E_d, of the samples are strongly dependent on the CdCl₂.H₂O concentrations.

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