

Electrochemical Impedance Spectroscopy as a Novel Approach to Investigate the Influence of Metal Complexes on Electrical Properties of Poly(vinyl alcohol) (PVA) Composites

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In the current study, black tea leaves extract solution (TES) as a new green technique is used to fabricate metal-polyphenols complexes (X-polyphenols complex; X= Cu⁺², Ce⁺³, and Cd⁺²). The metal-complexes are integrated with poly (vinyl alcohol) (PVA) to prepare PVA composite films. The electrical properties of pure PVA and composites are characterized using the electrochemical impedance spectroscopy (EIS) method. The EIS data are fitted to the electrical equivalent circuit to evaluate the impedance parameters of pure PVA and composite films. The trend of DC conductivity is further verified by dielectric analysis. The electrical parameters are considerably improved upon incorporating with the metal-complexes. The effects of the metal-complexes on the modification of PVA are compared together. The PVA composite incorporated with the Cu⁺²-complex shows the highest DC conductivity and dielectric constant, which is important for application in electrochemical energy storage devices such as batteries and supercapacitors, in comparison with the Ce⁺³- and Cd⁺²-complexes.

Keywords: PVA polymer; Polyphenols, Extract tea solution; Ce(III)-, Cu(II)-, and Cd(II)-complexes; EIS study.

1. INTRODUCTION

Polymer composites with good electrical characteristics are imperative to prepare materials for possible applications such as energy storage devices for example batteries, supercapacitors, and fuel cells. Addition of inorganic nanoparticles (NPs) into polymers, which synthesis inorganic/ polymer nanocomposites (NCs) [1], is of industrial attention due to their potential uses in electrochemical energy storage devices. The nano-dopants are broadly used in polymers to enhance the electrical characteristics [1]. A range of physical and chemical techniques were widely used to prepare NPs such as flame-based aerosol techniques, arc-submerged NPs synthesis system, chemical treatment, hydrothermal, micro-emulsion method, solid-state methods, and sonochemical [2-5]. These methods need large energy generally or apply toxic compounds. Thus, the use of clean, biocompatible, and green methods for NPs preparation is imperative.

Extract of plant leaf was used to prepare metal NPs in the past years, where gold and silver ions were reduced to gold and silver NPs [6]. This is because extract plant leaves polyphenols (PPHS) have redox potential from +0.09 to +0.4 V [7] which can easily reduce silver ions to silver NPs (redox potentials of Ag^+/Ag is +0.8) and gold ions to gold NPs (redox potentials of Au^+/Au is +1.69 V). Wang et al. [8] prepared iron– PPHS complex with extract leaf of *Salvia officinalis*. They showed that the PPHS of the plant extract reduced silver cations and gold cations to silver NPs and gold NPs, though only chelated with iron to fabricate iron– PPHS complexes. Aziz et al. [9] prepared silver NPs using an extract solution of quince leaf. They showed that there was a reduction of silver ions to silver NPs in the conjugated double bonds medium of phenolic compounds in the quince leaves.

Though in this work, the redox potential of Cu^{2+}/Cu , Ce^{3+}/Ce , and Cd^{2+}/Cd is 0.33, -2.33, and -0.40 V [10], respectively, implying that the PPHS of extract tea plant can't reduce Cu^{2+} , Ce^{3+} , and Cd^{2+} ions to copper, cerium, and cadmium NPs. In this situation, the polyphenols are able to interact with the Cu^{2+} , Ce^{3+} , and Cd^{2+} ions to prepare Cu(II)-, Ce(III)-, and Cd(II)- PPHS complexes (Cu(II)-, Ce(III)-, and Cd(II)-complexes), respectively. Wang [11] prepared the iron– PPHS complex by eucalyptus leaf and showed that the redox potential of Fe^{2+}/Fe is -0.44 V. Thus, the plant polyphenols can't reduce iron ions to iron nanoparticles. They indicated that the PPHS of plant extract is able to chelate iron cations to prepare iron– PPHS complexes.

In this work, the green method was used to prepare Ce(III)-, Cu(II)-, and Cd(II)-complexes using black tea leaves extract solution (TES). The PPHS in the TES interacts with the Cu^{2+} , Ce^{3+} , and Cd^{2+} cations to synthesis Cu(II)-complex, Ce(III)-complex, and Cd(II)-complex, respectively. Zielinski et al. [12] showed that the key components of tea leaves are PPHS and caffeine. Thus, based on the previous studies [12-15], the proposed complex formations of Cu^{2+} , Ce^{3+} , and Cd^{2+} with the catechin, theanine, theaflavin, and caffeine of TES are shown in *Figure 1* and *Figure 2*. It is seen from the proposed structure for the Cu(II)-complex, Ce(III)-complex, and Cd(II)-complex formation that Cu^{2+} , Ce^{3+} , and Cd^{2+} are able to form complexation with catechin (see *Figure 1(3A)* and *Figure 2(3A)*), caffeine (see *Figure 1(3B)* and *Figure 2(3B)*), theaflavin (see *Figure 1(3C)* and *Figure 2(3C)*), and theanine (see *Figure 1(3D)* and *Figure 2(3D)*). In our previous work [16-20], it was shown that the addition of Cu(II)-complex, Ce(III)-complex, and Cd(II)-complex into PVA polymer electrolyte significantly expanded the amorphous phase. In addition, the electrolytes were used for application in

electrochemical double-layer capacitor (EDLC) devices. It was shown that the metal complexes noticeably improved the performance of the EDLC devices [16-20]. Poly (vinyl alcohol) (PVA) was used in this study as a host polymer due to its low cost and biodegradability [21] [22].

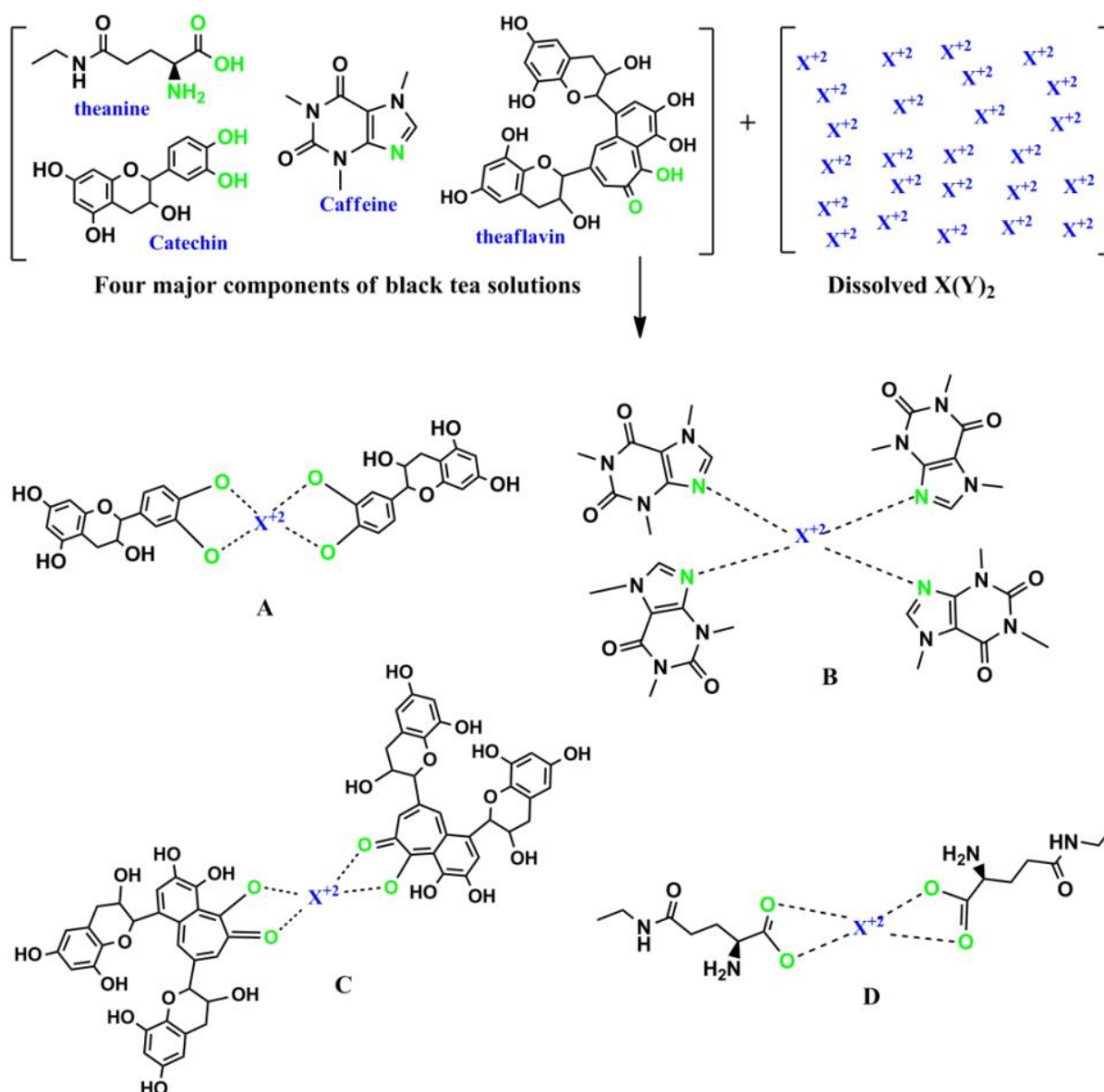


Figure 1. The proposed structure for the creation of Cu(II)-complexes and Cd(II)-complexes, where $X = Cu(II)$ and $Cd(II)$.

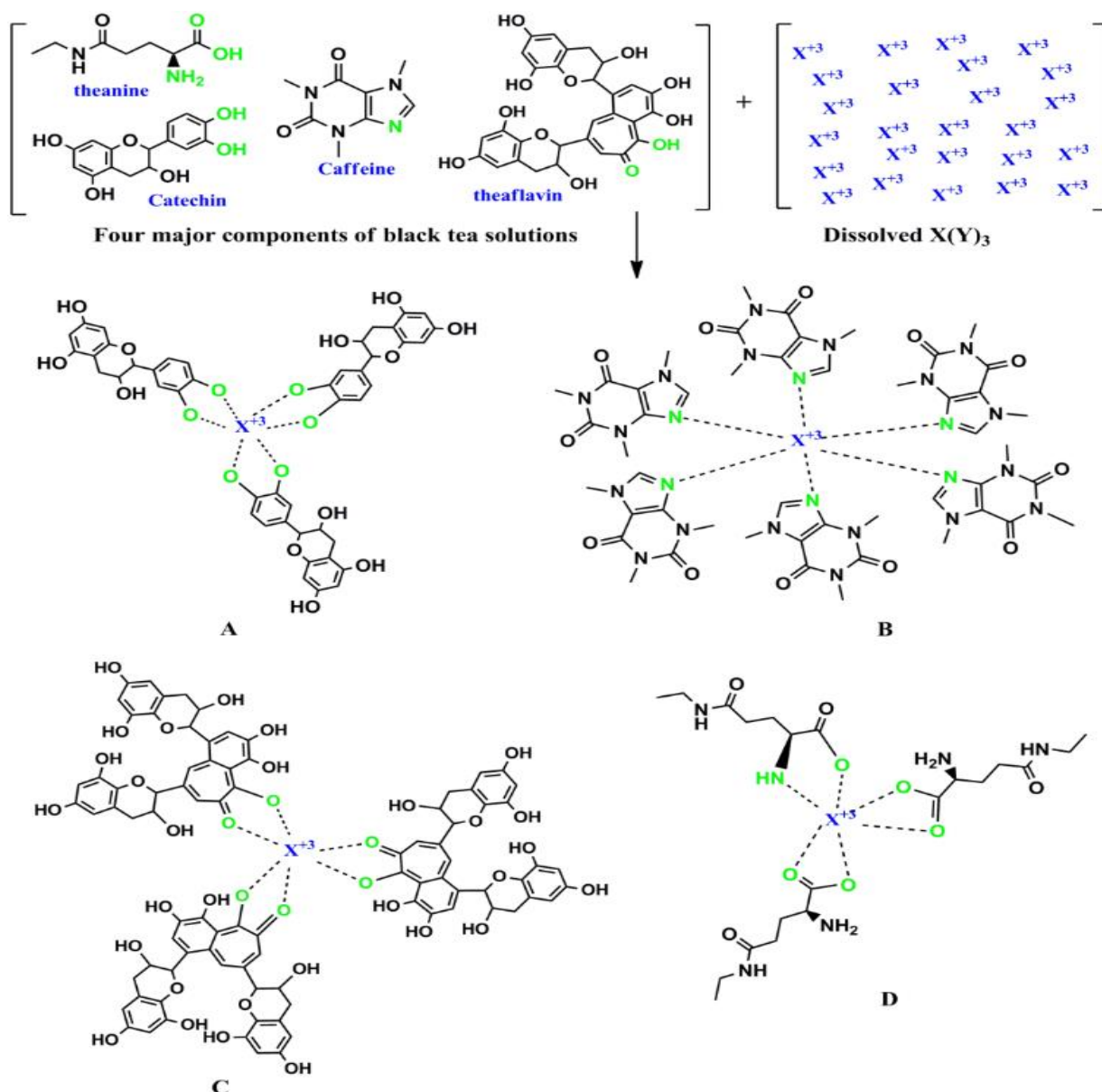


Figure 2. The proposed structure for the creation of Ce(III)-complexes, where $X = \text{Ce(III)}$.

This study tried to add the Cu(II)-complex, Ce(III)-complex, and Cd(II)-complex into the PVA to improve the electrical properties by increasing conductivity which is imperative for using PVA composites in the fabrication of electrochemical energy storage devices with high performance. Based on the current results, it was indicated that the Cu(II)-complex addition was better improved the electrical properties when added to PVA compared with the Cd(II)-complex and Ce(III)-complex.

2. MATERIALS AND METHODS

2.1. Materials

PVA with average molecular weight from 85000 to 124000, cadmium nitrate ($\text{Cd(NO}_3)_2$) with a molecular weight of 236.42 g/mol, cerium nitrate ($\text{Ce(NO}_3)_3$) with a molecular weight of 326.13

g/mol, and copper chloride (CuCl_2) with a molecular weight of 134.45 were purchased from Sigma-Aldrich (Kuala Lumpur, Malaysia). The black tea (BT) leaves were purchased from a nearby market.

2.2 Sample Preparation

TES was achieved using distilled water (DW). The procedure of the TES involved the addition of 50 g of BT leaves to 250 mL DT at nearly 90 °C while avoiding sun radiation exposure. The TES was filtrated after 10 minutes. For this purpose, Whatman filter paper with a pore radius of 20 μm was used to remove the residues during the filtration process. Then 10 g of each CuCl_2 , $\text{Ce}(\text{NO}_3)_3$, and $\text{Cd}(\text{NO}_3)_2$ were dissolved in 200 mL of DW separately. The fabrications of Cu(II)-complex, Ce(III)-complex, and Cd(II)-complex were performed by adding dissolved CuCl_2 , $\text{Ce}(\text{NO}_3)_3$, and $\text{Cd}(\text{NO}_3)_2$ to the TES separately at 80 °C. There was stirring the solutions for nearly 10 minutes. The creation of Cu(II)-complex, Ce(III)-complex, and Cd(II)-complex was confirmed when the dark color tea leaf solution converted to green color, and precipitation was formed like a cloud at the bottom of the beaker. The solutions with Cu(II)-complex, Ce(III)-complex, and Cd(II)-complex were kept and allowed to cool to room temperature (RT). The metal-complexes were washed with DT a number of times. Afterward, the metal-complexes were separately dispersed in 100 mL of DW.

The solution cast technique was used for the creation of the composites based on PVA doped by Cu(II)-complex, Ce(III)-complex, and Cd(II)-complex separately. Construction of the PVA solution involved the insertion of 1 g PVA to 40 mL DW, subsequently 60 minutes stirring with a magnetic stirrer at nearly 80 °C. Then the PVA solution was allowed to cool to RT. Finally, the 15-45 mL solution of Cu(II)-complex, Ce(III)-complex, and Cd(II)-complex in steps of 15 mL were separately added to the PVA homogeneous solution. The solutions were constantly stirred for nearly 50 minutes. The samples were coded as shown in **Table 1(a-c)**. In order for those films to be created, the mixtures were cast into Petri dishes and allowed to dry at RT. Before characterization, the films were kept in a desiccator containing blue silica gel for extra drying.

Table 1(a). The designations and compositions of PVA:Cd(II)-complex

Designation	Composition (PVA g: Cd(II)-complex mL)
Pure PVA	1:0
PVACd_1	1:15
PVACd_2	1:30
PVACd_3	1:45

Table 1(b). The designations and compositions of PVA:Ce(III)-complex

Designation	Composition (PVA g: Ce(III)-complex mL)
Pure PVA	1:0
PVACe_1	1:15
PVACe_2	1:30
PVACe_3	1:45

Table 1(c). The designations and compositions of PVA:Cu(II)-complex

Designation	Composition (PVA g: Cu(II)-complex mL)
Pure PVA	1:0
PVACu_1	1:15
PVACu_2	1:30
PVACu_3	1:45

2.3 Electrochemical Impedance Spectroscopy (EIS)

The impedance spectra of each system were obtained using electrochemical impedance spectroscopy (EIS) [3532-50 LCR HiTESTER (HIOKI)] in the frequency ranged from 50 Hz to 5 MHz. The fabricated samples were cut to circles 2 cm in diameter and then located between two stainless steel electrodes using spring pressure. The real (Z') and imaginary (Z'') parts of the complex impedance (Z^*) spectra were given by connecting the cell with a computer program.

3. RESULTS AND DISCUSSION

3.1 Electrical Properties

The impedance plots of pure PVA and composite films at ambient temperature are shown in Figures (3-6). The Cole-Cole plots consist of just a semicircle and the value of bulk resistance (R_b) is measured by the intersection between the semicircle curve and the real (horizontal) axis at the low-frequency region. The semicircle is associated with the conduction of charge carriers at the bulk of the systems [23-25]. Malathi et al. [26] reported that the bulk DC conductivity of a system is attributed to the parallel connection of R_b and bulk capacitance of the system. The semicircle is decreased as the concentrations of Ce(III)-, Cu(II)-, and Cd(II)-complexes increase to 30 and 45 mL. The increasing of the metal-complexes concentration to the systems enhanced the DC conductivity.

The electrical equivalent circuit (EEC) is usually employed in the analysis of impedance as it is rapid, straightforward, and produces a picture of each system [27]. In the current study, as the Cole-Cole plot for each sample consists of just a semicircle as displayed in Figures (3-6), the EEC is

interpreted by a parallel connection of R_b and a constant phase element (CPE) [28]. The impedance of CPE (Z_{CPE}) is represented as [28] [29]:

$$Z_{CPE} = \frac{1}{C\omega^p} \left[\cos\left(\frac{\pi p}{2}\right) - i \sin\left(\frac{\pi p}{2}\right) \right] \quad (1)$$

where ω , C , and p are the angular frequency, the capacitance of CPE , and linked to the plot departure from the axis. The Z_r and Z_i of the impedance associated with the EEC are represented as:

$$Z_r = \frac{R_b^2 C \omega^p \cos\left(\frac{\pi p}{2}\right) + R_b}{2R_b C \omega^p \cos\left(\frac{\pi p}{2}\right) + R_b^2 C^2 \omega^{2p} + 1} \quad (2)$$

$$Z_i = \frac{R_b^2 C \omega^p \sin\left(\frac{\pi p}{2}\right)}{2R_b C \omega^p \cos\left(\frac{\pi p}{2}\right) + R_b^2 C^2 \omega^{2p} + 1} \quad (3)$$

The EEC fitting parameters are indicated in **Table 2(a-c)**.

By taking the R_b and the thickness (t) for each film, the DC conductivity is measured using Eq.(4) [30-32],

$$\sigma_{dc} = \left(\frac{1}{R_b} \right) \times \left(\frac{t}{A} \right) \quad (4)$$

where A is the area of the stainless steel electrodes. The DC conductivity of each film and R_b values are shown in **Table 3(a-c)**.

The DC conductivity in the present work is higher than the previous work. For example, Ningaraju1 and Ravikumar [33] prepared PVA:graphite oxide (GO) polymer NCs with various GO wt.%. The authors showed that the DC conductivity of pure PVA is $1.63 \times 10^{-12} \text{ S cm}^{-1}$, whilst the DC conductivity of PVA/GO slowly increases as the GO amount increased and indicated maximum value at 0.4 wt.% of GO, which is $\sim 1.4 \times 10^{-10}$, and then decreased up to 1.0 wt.% of GO. As seen from **table 3(a-c)**, DC conductivity is higher when the highest concentration of Cu(II)-complex is added to PVA in comparison with Ce(III)-complex and Cd(II)-complex. In our previous work [16-20] it was indicated that Cu(II)-complex significantly improved amorphous phase when added to PVA compared with the Ce(III)-complex and Cd(II)-complex.

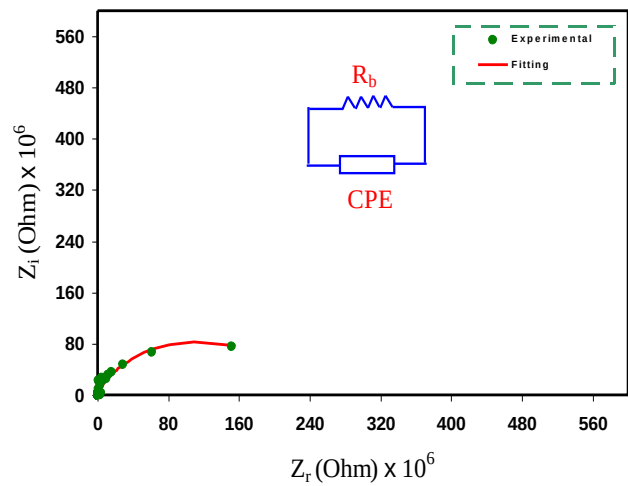
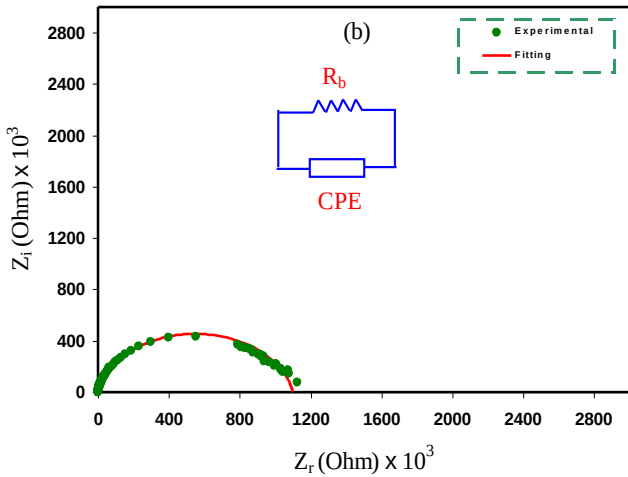
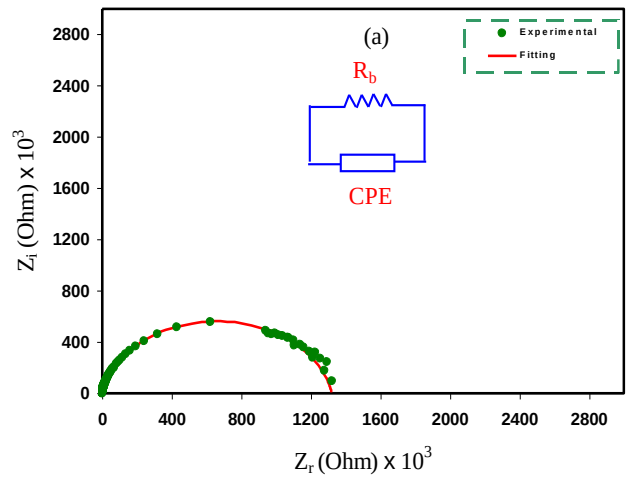


Figure 3. EIS for pure PVA



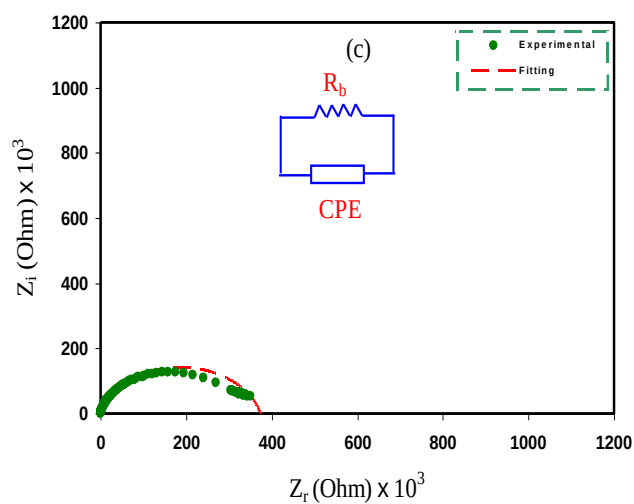
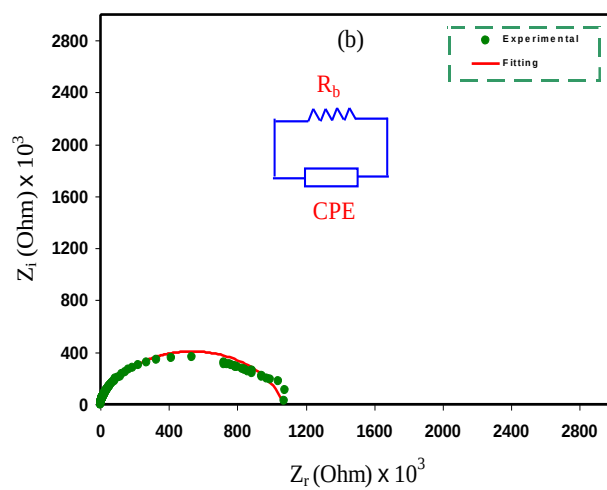
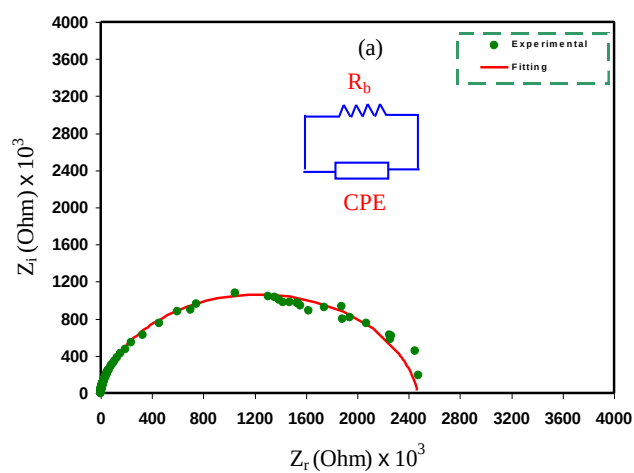


Figure 4. EIS for (a) PVACd_1, (b) PVACd_2, and (c) PVACd_3 films.



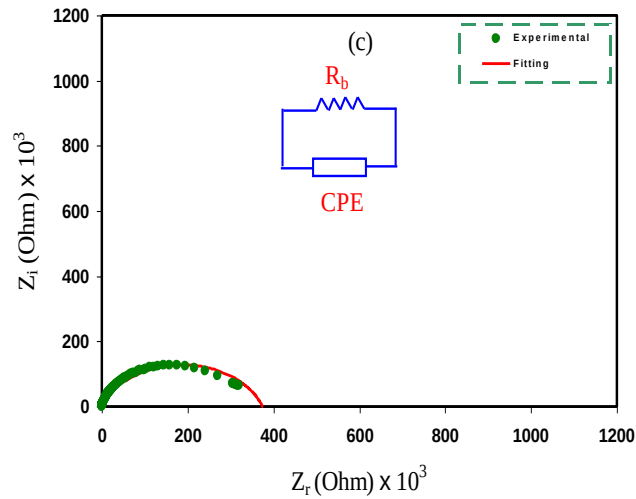
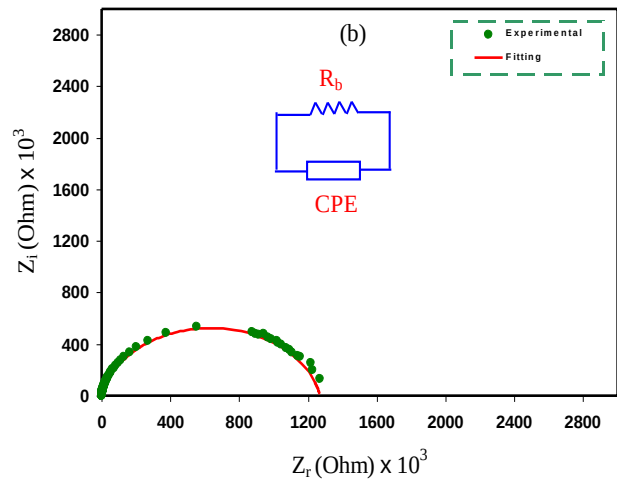
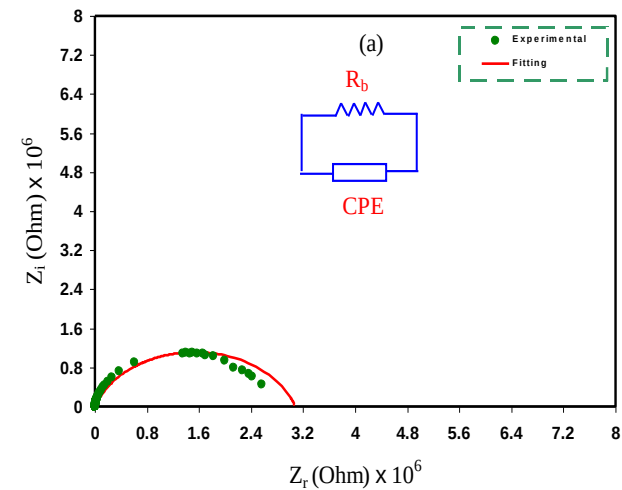


Figure 5. EIS for (a) PVACe₁, (b) PVACe₂, and (c) PVACe₃ films.



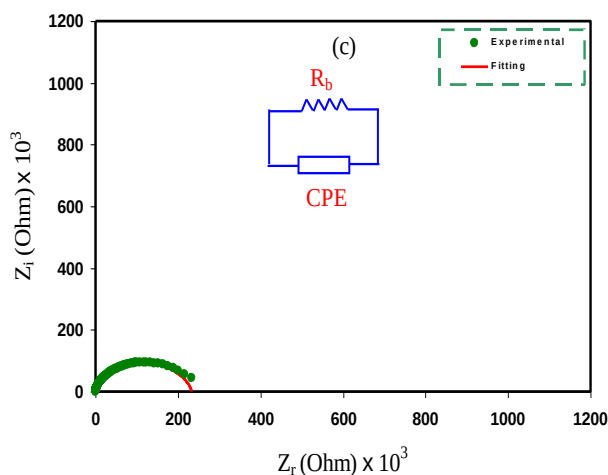


Figure 6. EIS for (a) PVACu_1, (b) PVACu_2, and (c) PVACu_3 films.

Table 2(a). The EEC fitting parameters for PVA: Cd(II)-complex films at RT.

Sample	P(rad)	$K (F^{-1})$	$C (F)$
Pure PVA	0.79	3.6×10^{10}	2.78×10^{-11}
PVACd_1	0.89	3.5×10^{10}	2.86×10^{-11}
PVACd_2	0.87	3.4×10^{10}	2.94×10^{-11}
PVACd_3	0.82	3.3×10^{10}	3.03×10^{-11}

Table 2(b). The EEC fitting parameters for PVA: Ce(III)-complex films at RT.

Sample	P(rad)	$K (F^{-1})$	$C (F)$
Pure PVA	0.79	3.6×10^{10}	2.78×10^{-11}
PVACe_1	0.89	3.6×10^{10}	2.78×10^{-11}
PVACe_2	0.82	3.1×10^{10}	3.23×10^{-11}
PVACe_3	0.76	2.8×10^{10}	3.57×10^{-11}

Table 2(c). The EEC fitting parameters for PVA:Cu(II)-complex films at RT.

Sample	P(rad)	$K (F^{-1})$	$C (F)$
Pure PVA	0.79	3.6×10^{10}	2.78×10^{-11}
PVACu_1	0.79	4.8×10^{10}	2.08×10^{-11}
PVACu_2	0.87	3.2×10^{10}	3.13×10^{-11}
PVACu_3	0.84	3.0×10^{10}	3.33×10^{-11}

Table 3(a). DC conductivity of the PVA:Cd(II)-complexes at RT.

Designation	Composition (PVA g: Cd(II)-complex mL)	$R_b (\Omega)$	DC conductivity($S\ cm^{-1}$)
PVACd_0	1:0	2.3×10^8	2.87×10^{-11}
PVACd_1	1:15	1.31×10^6	3.8×10^{-9}
PVACd_2	1:30	1.09×10^6	5.08×10^{-9}
PVACd_3	1:45	3.67×10^5	1.86×10^{-8}

Table 3(b). DC conductivity of the PVA:Ce(III)-complexes at RT.

Designation	Composition (PVA g: Ce(III)-complex mL)	$R_b (\Omega)$	DC conductivity($S\ cm^{-1}$)
Pure PVA	1:0	2.3×10^8	2.87×10^{-11}
PVACe_1	1:15	2.46×10^6	4.65×10^{-9}
PVACe_2	1:30	1.05×10^6	1.54×10^{-8}
PVACe_3	1:45	3.63×10^5	4.80×10^{-8}

Table 3(c). DC conductivity of the PVA:Cu(II)-complexes at RT.

Designation	Composition (PVA g: Cu(II)-complex mL)	R _b (Ω)	DC conductivity(S cm ⁻¹)
Pure PVA	1:0	2.3×10^8	2.87×10^{-11}
PVACu_1	1:15	3.05×10^6	3.91×10^{-9}
PVACu_2	1:30	1.24×10^6	1.31×10^{-8}
PVACu_3	1:45	2.27×10^5	7.71×10^{-8}

3.2 Dielectric Study

Dielectric studies are able of providing information relating to conductivity trend. Dielectric constant (ϵ_r) refers to the stored charge and dielectric loss (ϵ_i) refers to the energy losses for migrating charge carriers when the electric field polarity reversed quickly [34] [35]. In this work, ϵ_r and ϵ_i values were measured using Eq.s (5 and 6) [36] [37]:

$$\epsilon_r = \left[\frac{Z_i}{\omega C_0 (Z_r^2 + Z_i^2)} \right] \quad (5)$$

$$\epsilon_i = \left[\frac{Z_r}{\omega C_0 (Z_r^2 + Z_i^2)} \right] \quad (6)$$

where C_0 and ω are the capacitance in free space and radial frequency. Figures 7-9(a, b), show the frequency dependence of ϵ_r and ϵ_i for the pure PVA and PVA/ Ce(III)-, Cu(II)-, and Cd(II)-complexes systems at RT. In these systems, the increasing Ce(III)-, Cu(II)-, and Cd(II)-complexes concentrations into PVA increase the values of ϵ_r and ϵ_i . Aziz [38] also noticed these modifications. There is a large value of ϵ_r at the region of low frequency as a result of the charge species accumulation. However, at the region of higher frequency, there is a large electric field periodic reversal, which lessens the influence of carriers towards the ϵ_r .

The DC conductivity and ϵ_r relation are expressed qualitatively. The DC conductivity is written by [39-49]:

$$\sigma_{dc} = nq\mu \quad (7)$$

where n is the density of carriers, q is a charge (1.6×10^{-19} C), and μ is the carrier's mobility. From Eq.(7), both of the μ and n rise when the concentrations of Ce(III)-, Cu(II)-, and Cd(II)-complexes increased from 15 to 45 mL. The value of n is associated with the dissociation energy (U) and ϵ_r which is described using ($n = n_0 \exp(-U/\epsilon_r k_B T)$), where T and K_B are the absolute temperatures and Boltzmann constant. The increase in ϵ_r as a result of the addition of Ce(III)-, Cu(II)-, and Cd(II)-complexes increases the DC conductivity by increasing n [39-49].

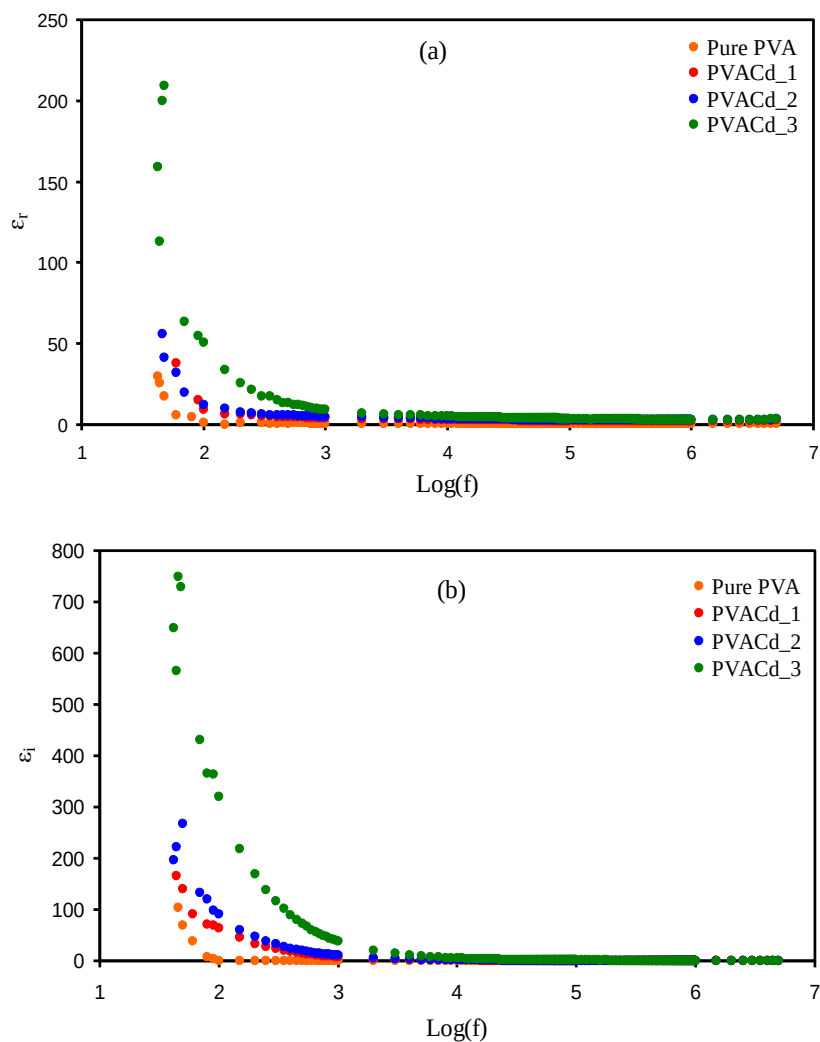
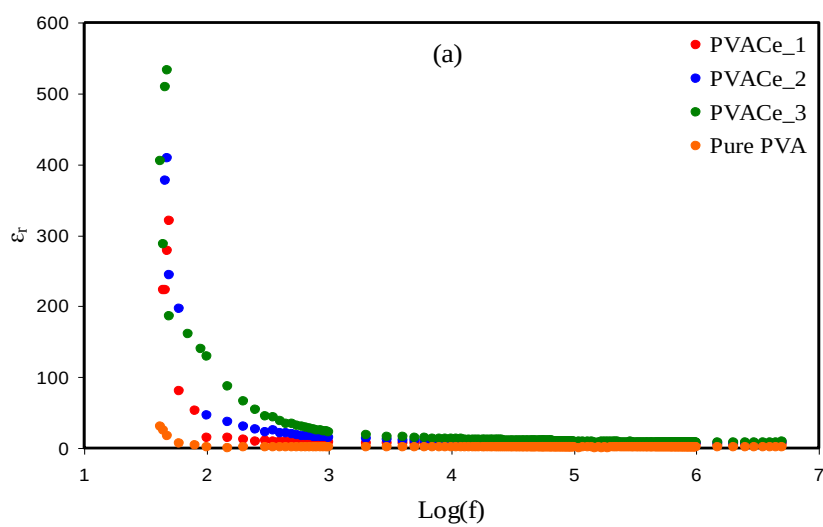


Figure 7. Complex dielectric constant (a) $\epsilon_r \nu \log(f)$ and (b) $\epsilon_i \nu \log(f)$ for PVA:Cd(II)-complex films.



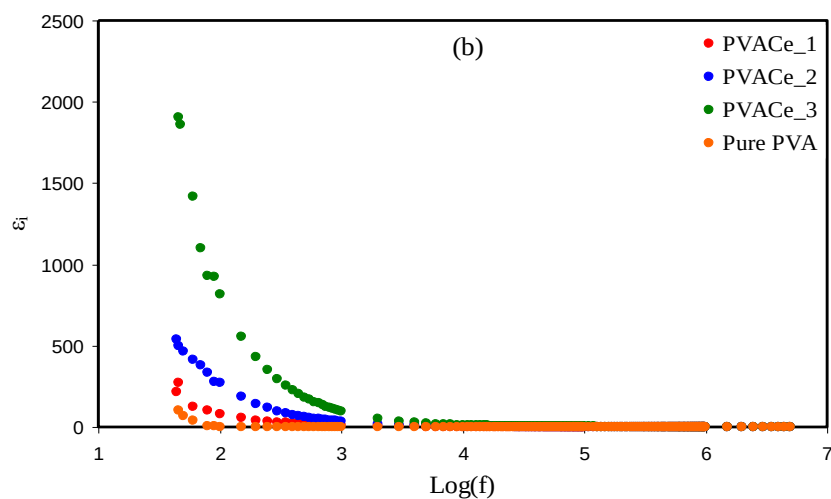


Figure 8. Complex dielectric constant (a) ϵ_r v $\log(f)$ and (b) ϵ_i v $\log(f)$ for PVA:Ce(III)-complex films.

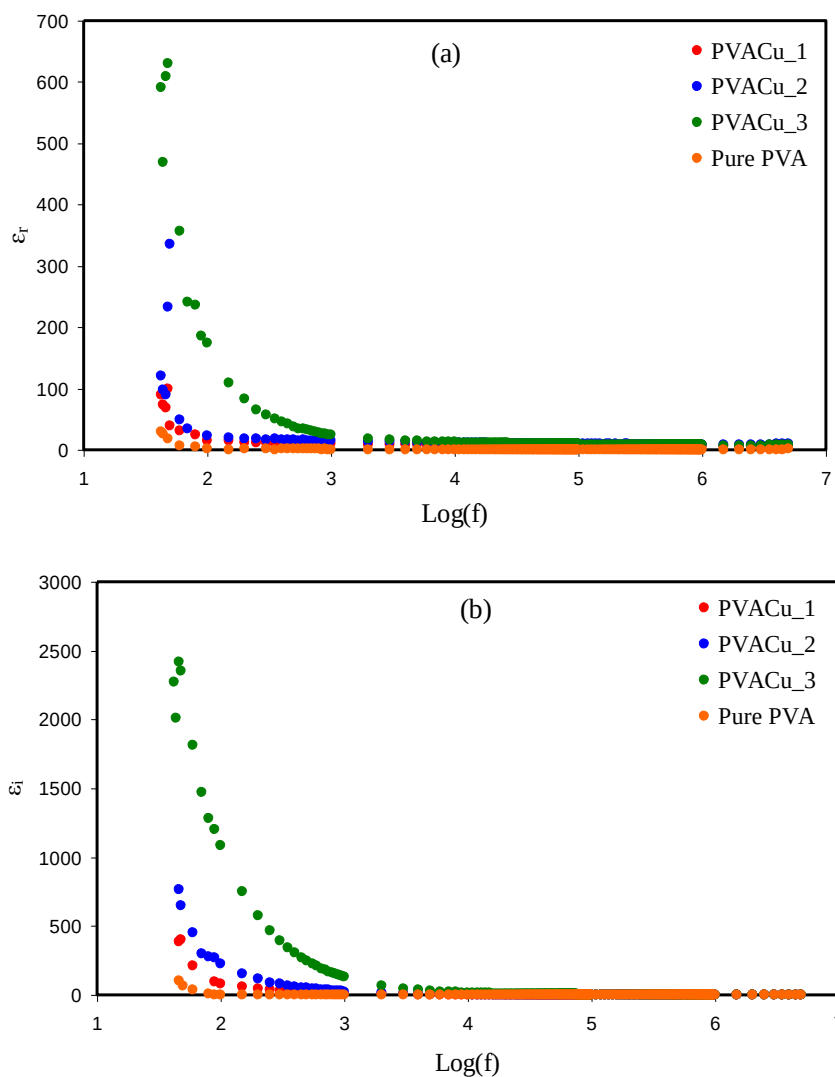


Figure 9. Complex dielectric constant (a) ϵ_r v $\log(f)$ and (b) ϵ_i v $\log(f)$ for PVA:Cu(II)-complex films.

As seen from Figures 7-9(a), the dielectric constant is noticeably increased after Cu(II)-complex included in PVA in comparison with the Ce(III)- and Cd(II)-complexes. In our earlier studies [17-19] it was indicated that when the Cu(II)-complex inserted into the plasticized PVA electrolyte, the dielectric constant of the electrolyte with Cu(II)-complex is higher compared with the Ce(III)- and Cd(II)-complexes. A high dielectric constant material is mainly used for supercapacitor applications. For example, in our earlier studies [17-19] it was presented that when Cu(II)-the complex was included in the PVA electrolyte, the electrolyte was used for application in EDLC devices with high performance and high energy density in the battery energy density range.

3.3 Electric Modulus Study

The real (M_r) and imaginary (M_i) parts of the electric modulus versus frequency are shown in figures 10-13(a, b) for the pure PVA and PVA/ Ce(III)-, Cu(II)-, and Cd(II)-complexes composites.

Eq.s (8) and (9) were used to measure the M_r and M_i of complex electric modulus (M^*) [50] [51].

$$M_r = \left[\frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} \right] = \omega C_o Z_i \quad (8)$$

$$M_i = \left[\frac{\varepsilon_i}{(\varepsilon_r^2 + \varepsilon_i^2)} \right] = \omega C_o Z_r \quad (9)$$

In the above equations, ε_r and ε_i refer to the real and imaginary parts of permittivity respectively.

Figure 10(a, b) shows the values of M_r and M_i for pure PVA. It can be seen in Figures 11-13(a) that the values of M_r become smaller at a lower frequency and they eventually become zero thus indicating the elimination of polarization [49]. On the other hand, the values of M_r increase with increment in frequency, and maximum value M_∞ is obtained at maximum frequency. This can be due to the fact that the relaxation phenomenon spans over different frequency values [38] [52] [53]. The dispersion noticed is basically as of the conductivity relaxation spanning over different frequencies and points towards the relaxation time existence that must occur with a loss peak in the figure presenting the imaginary part of the dielectric modulus against frequency (Figures 11-13(b)). It can be seen that M_i has a smaller value at lower frequency. This can be due to the increased capacitance value which is associated with the effect of polarization [54-56]. Figures 11-13 (a) show that no peak is present in the M_r and this can be because of the reason that M_r in the M^* is equivalent to ε_r in the complex permittivity (ε^*) that is M_r shows the potential of the substance for energy storage.

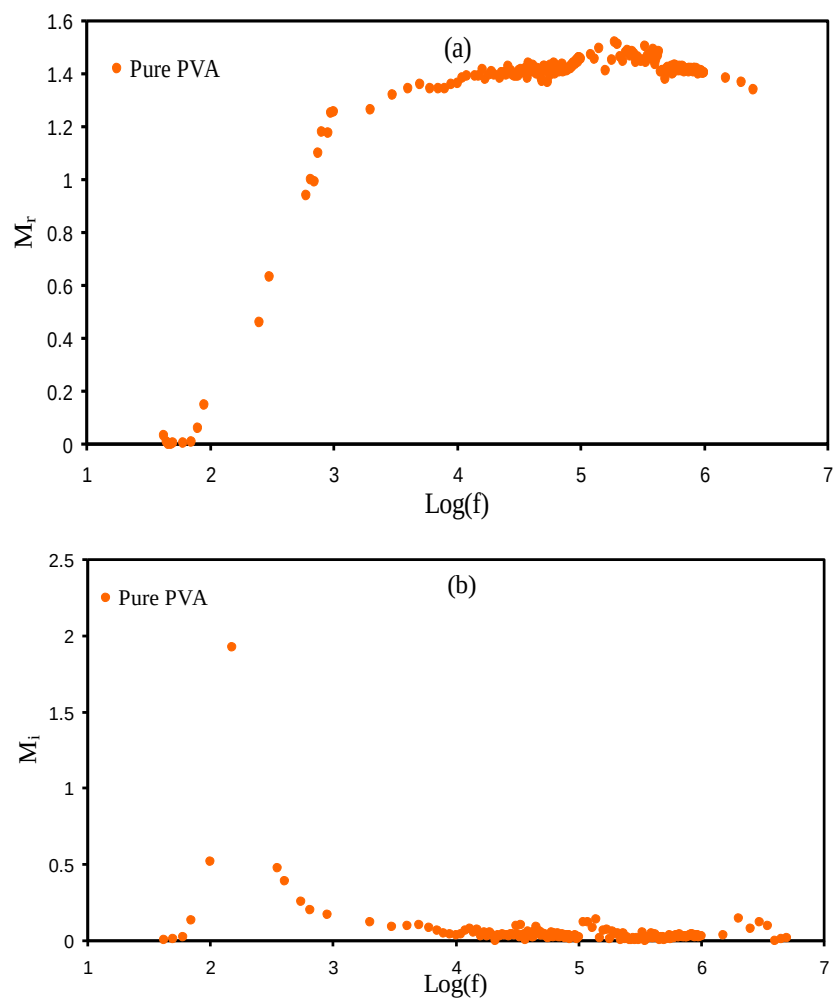
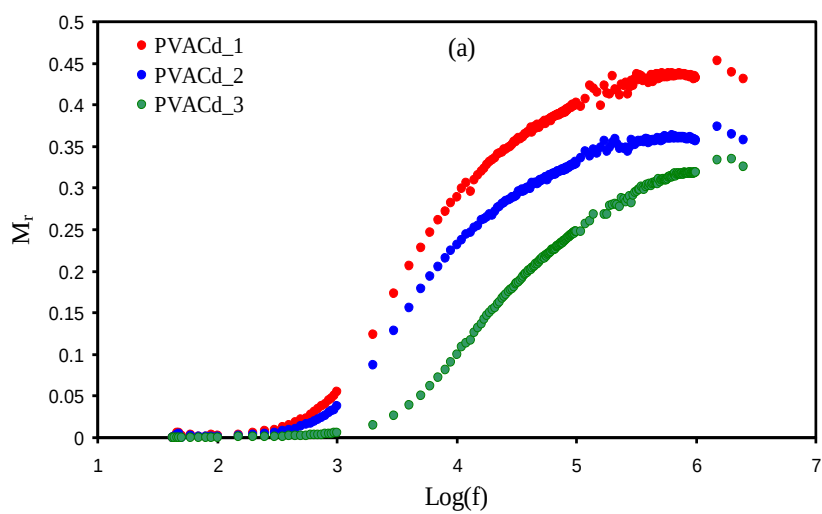


Figure 10. Plots of electric modulus (a) M_r vs. $\log(f)$ and (b) M_i vs. $\log(f)$ for pure PVA.



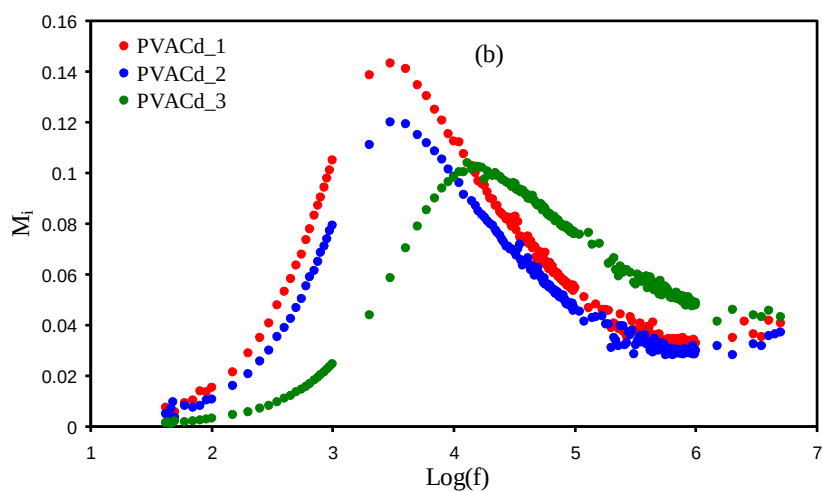


Figure 11. Plots of electric modulus (a) M_r vs. $\log(f)$ and (b) M_i vs. $\log(f)$ for Cd(II)-complex composites.

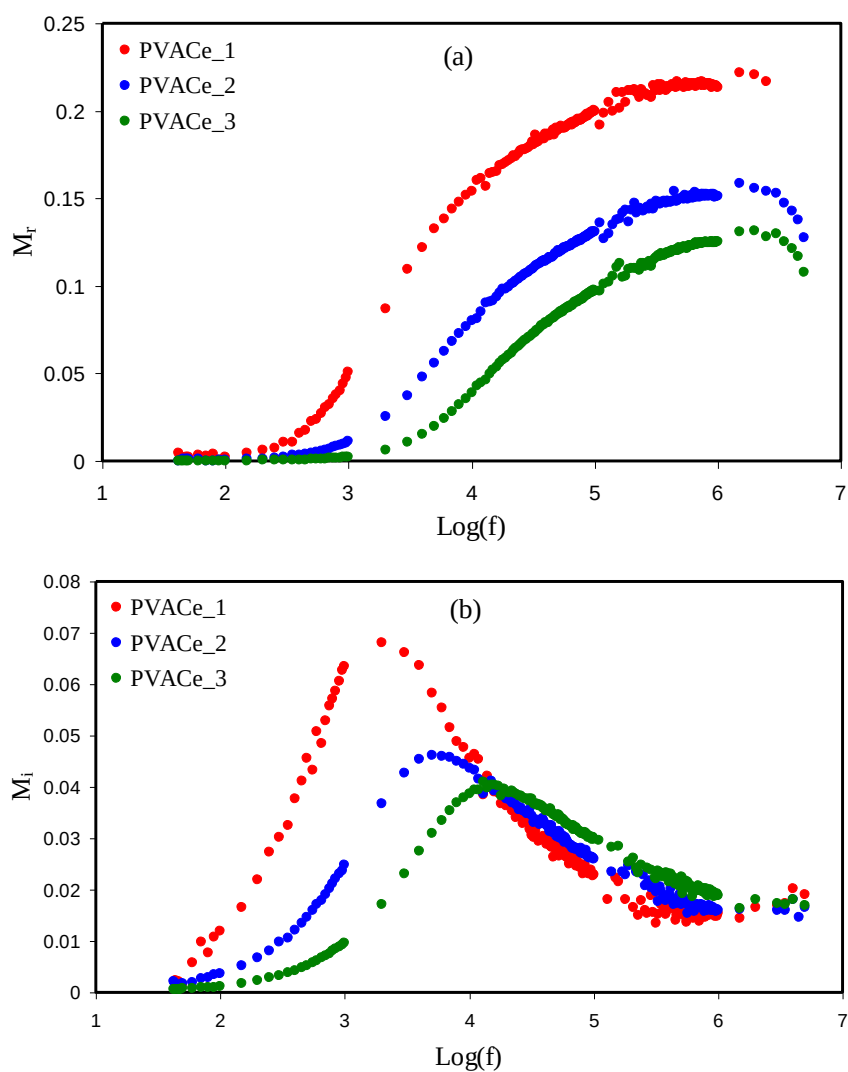


Figure 12. Plots of electric modulus (a) M_r vs. $\log(f)$ and (b) M_i vs. $\log(f)$ for Ce(III)-complex composites.

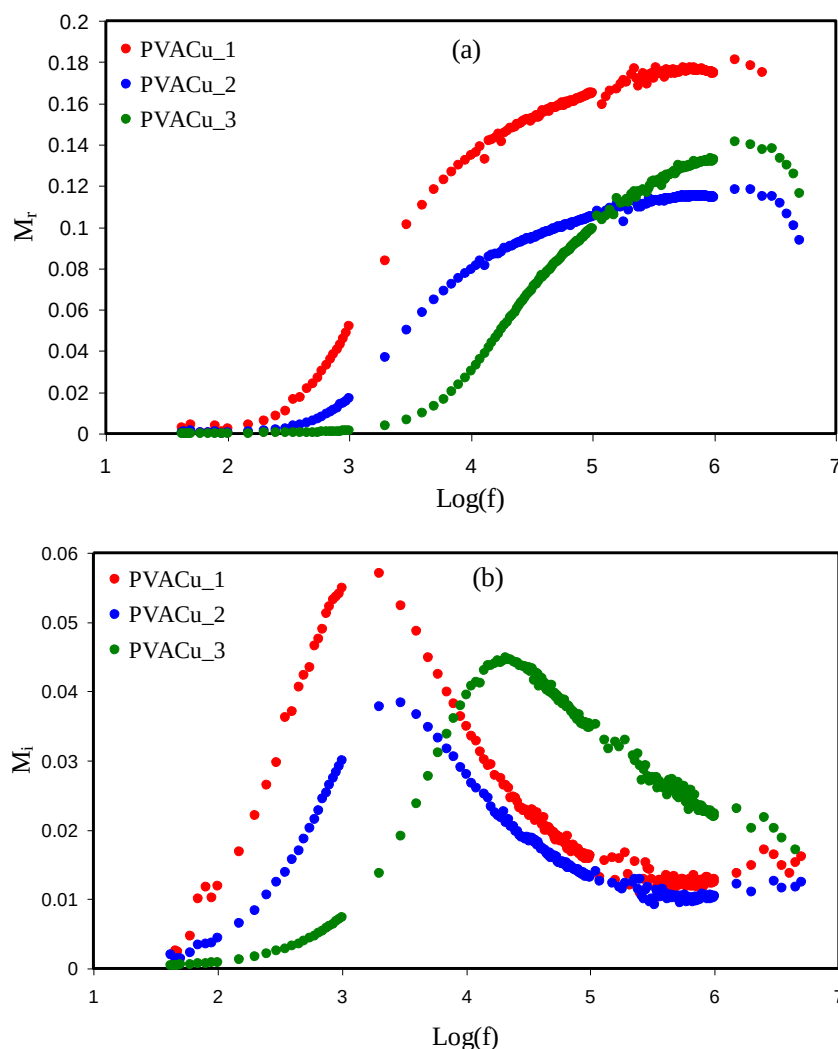


Figure 13. Plots of electric modulus (a) M_r vs. $\log(f)$ and (b) M_i vs. $\log(f)$ for Cu(II)-complex composites.

4. CONCLUSION

In the current work, TES as a novel green technique was used to prepare Cu(II)-complex, Ce(III)-complexes, and Cd(II)-complex. The metal-complexes were combined with PVA to prepare composite films. The pure PVA and composites were characterized using the EIS method. The EIS data were fitted to a relevant electrical equivalent circuit to evaluate the impedance parameters of pure PVA and composite films. The maximum value DC conductivity of 7.71×10^{-8} was obtained for the PVA doped with the highest concentration of Cu(II)-complex. The trend of DC conductivity was further verified by dielectric analysis. The electrical parameters were considerably improved upon incorporating with the metal-complexes. The influences of the metal-complexes on the PVA modification were compared together. The PVA composite doped with the 45 mL Cu(II)-complex shows the highest dielectric constant and conductivity, which is vital for application in energy storage devices such as batteries and supercapacitors, in comparison with the Ce(III)- and Cd(II)-complexes.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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