Anal. Bioanal. Electrochem., Vol. 16, No. 10, 2024, 928-942
https://www.doi.org/10.22034/abec.2024.717550

Analytical & Bioanalytical Electrochemistry

Full Paper

New Electrochemical Sensors for Determination of Tamoxifen Based on Enhanced Polymer Nano Composite Deep Eutectic Solvent and Water Mixture as Ionophores

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Received: 4 July 2024 / Received in revised form: 29 September 2024 / Accepted: 14 October 2024 / Published online: 31 October 2024

Abstract- In recent decades, there has been a continuous rise in the worldwide demand for electrochemical electrodes, driven by their established advantages such as rapidity, cost-effectiveness, user-friendly nature, and practicality in comparison to alternative electrochemical methods. However, despite these advancements, there remains a pressing need to tailor electrode preparation methods to accommodate the diverse requirements of the pharmaceutical industry. A newly developed electrochemical method was described to produce three stable probes to measure tamoxifen citrate by a coated protective layer formed from ZnO nanocomposite polymer. This modified layer was prepared by drop-casting a solution of ethaline: oxaline: water on a polymer membrane. The modified membrane exhibited potential by less than 0.22 mV for 24 days. Different analytical measurements were examined to determine the optimization proposed electrode; it was found that the addition of polymer nanocomposite metals polymer mixed with deep eutectic solvents prompted high probe efficiency used for poor solubility drugs in water. The Nernstian slope was found to be good agreement measurements in Polyvinyl Pyrrolidine (PVP) electrode around 59.71±0.60 mV/decade while other electrodes slightly decreased at 58.88±0.23 mV/decade for Poly Ethylene Glycol (PEG) and 60.20±0.15 mV/decade recorded for polyvinylchloride (PVC) electrode. Tamoxifen samples in tablet form were found to be acceptable and accurate determinations in new electrochemical technique dependent on the preparation of different nanocomposite ZnO polymer molecules, with trace added of (1.5%, 2.0%, and 2.5%) weight percentage deep eutectic solvent water mixtures (DESs) as supporting permeation during hydrophobic membranes attributed to partition and pores mechanisms helped to ion pair diffusion.

Keywords- Tamoxifen citrate; Nanocomposite polymer; Deep eutectic solvents; Electrode; Pharmaceutical analysis

1. INTRODUCTION

Tamoxifen citrate (TC) is mainly contained chemical structure as [4-[(Z)-1,2-diphenylbut-1-enyl] phenoxy]-N,N-dimethylethanamine; 2 hydroxypropane-1,2,3-tricarboxylic acid.[1] In breast cancer Tamoxifen citrate found to be a good medication to block the growth of breast tumor tissue and reduces the probabilities of breast cancer for high-risk cases [1]. The main biological activity of tamoxifen originates from the metabolite endoxifen mostly formed by CYP2D6 hydroxilation of N-demethyltamoxifen. The chemical reaction occurs to interfere with the activity of estrogen in the breast tissues. The main compound structure for tamoxifen citrate is shown in figure.1. The most recommended dosage is 20 to 40 mg daily and the duration of endocrine therapy is dependent on the patient's menopausal status with ranges 5 to 10 years, while initial results from clinical recommendations in breast cancer advised lower uses range is 20 mg per day [2,3]. The widespread uses of TC for inter individual variability in therapeutic responses motivated extensive potential publications focused on finding different analytical improvement methods for measuring and controlling TC dosage in various samples such as high-performance liquid chromatography (HPLC) [4], polarography [5], potentiometry [6,7], voltammetry [8], thin layer chromatography (TLC) [9] gas chromatography (GC) [10], liquid chromatography–mass spectrometry (LC-MS) [11], gas chromatography– mass spectrometry (GC–MS) [12,13] capillary electrophoresis [14] and ion chromatography [15,16].

Recently, some manufactured electrochemical probes contained polymer membrane fabrication giving successful results in medical applications [17,18]. The highest significant outcomes for electrochemical polymers used are due to increasing the efficiency of the probe in terms of time, stability, availability, and reliability [19]. Polymer membrane fabrication is vital design to apply in the formation of many microprobes, the most popular additives macromolecules are Polyethylene glycol (PEG), Polyvinyl pyrrolidone (PVP) and Poly Ethylene Oxide (PEO). While membrane polymer in surfactant systems like in deep eutectic solvents water mixtures is a significant concept that can be functionalized as an acceptable uniform porous structure with good agreement for its hydrophilicity and solubility that can control microstructure of membranes [20-23]. This phenomenon can be applied with an additive of some active compounds such as Polyvinyl Pyrrolidine (PVP), Poly Ethylene Glycol (PEG), and Polyvinylchloride (PVC) with the assistance of DESs with nano metal oxides act as a selective agent thus preventing surface pouring by supporting the surface hydrophilicity [24-26]. In most cases, it could suffer from during phase transposition it nominates out along with the nonaqueous phase to the non-solvent part. This issue can be solved due to using Polyvinyl Pyrrolidine (PVP), Poly Ethylene Glycol (PEG), or polyvinylchloride (PVC) as blending grafted with DESs water mixtures or by immediately additive on the membrane surface [7]. This improvement chemical technique is very helpful in improving the efficiency of the sensor by modifying the hydrophilicity of membrane surfaces.

In this work, the modified method will address to preparation of accurate electrochemical probes for the determination of TC by enhancing additive nanocomposite polymer membranes based on trace amounts of water-deep eutectic solvent mixtures with acceptable performance to support medical applications and therapeutic drugs in breast cancer.

2. EXPERIMENTAL SECTION

2.1. Apparatus and reagents

A range of instrumental analyses was used to examine the chemical properties of developed electrodes. The SIRION SEM scanning electron microscope version was applied to identify the morphology of the surface membrane. An FTIR instrument (BRUKER–TENSOR–27) was conducted with spectrum wave numbers ranging from 500 to 3900 Cm^{-1}. A homemade working Pt wire electrode was used in all electrochemical measurements with an electrochemical analyzer (CHI 840C, USA). The setup of electrochemical cell was also used in a three-electrode system with saturated Ag/AgCl as a reference electrode and Pt wire as an assisting electrode platinum.

Two types of DESs solvent were prepared by mixing choline chloride (Fluka 99.9%) (1:2 mole ratio) with ethylene glycol (Fluka) to get an ethaline homogeneous solution after 2 hours with stirring and heating at 40 $^{\circ}C$. The same method was used to prepare oxaline solvent by mixing (1:1 mole ratio) of oxalic acid (Fluka 99.9%) and choline chloride with stirring for around 3 hours until obtained homogenies clear solution. All aqueous solutions were carried out in double-distilled water with pH 6.6–7.0 in acetate buffer. For membrane component, all chemicals in this study were used of analytical grade or higher purity and it was purchased from Fluka Company for Tetrahydrofuran (THF 99.99%), Molybdophosphoric acid (MPA) (Fluka 99.9%), Polyvinyl Pyrrolidine (PVP) 99.98%, Poly Ethylene Glycol (PEG) (Fluka 99.9%) and polyvinylchloride (PVC) (Fluka 98.9%), while, higher purity of benzoyl peroxide, o-nitrophenyl octyl ether, di-butyl phthalate, di-octyl phthalate, and di-butyl phosphate were purchased from Sigma-Aldrich without further purification, the ZnO nano prepared according to the literature method [20]. Pure tamoxifen citrate was used from State Company of drug industries and medical appliances. While, the pharmaceutical tablets formulated tamoxifen citrate was made from Wockhardt Made –India, Beta Drugs Ltdi India, and Actizapharma Company.

2.2. Electrochemical cells and equipment

A pH meter (WTW model PH720, Germany) was applied at room temperature (25±2 $^{\circ}C$) for all experiments for potentiometric measurement (Gallenkamp, USA) as the version for reference electrode used for water samples while; a homemade reference electrode of Ag-AgCl was constructed for measuring the photometric titration for an additive DESs samples. The

inner solution for the drug used in the constructive sensor is about 0.015 M of solution for tamoxifen.

2.3. Preparation of proposed membrane

Three membranes were prepared for each membrane 200 mL of 1.5×10^{-1} M TC solution and 200 ml of (1.5×10^{-1}, $1.25\times10^{-1,}$ and 3.5×10^{-1}) % weight of DESs and water mixture. The membranes were prepared by using Coatmaste 50 MC, Erichsen Testing Equipment. The polymer solution was dissolving 0.170 mg of powdered PVC 0.40 mg of plasticizer, and 0.040 mg of the ion pair in 8 mL THF. While 0.170 mg of PEG solution with 0.56 mg of plasticizer, 0.045 mg of the ion pair in 8 mL THF and the PVP polymer was dissolving 0.150 mg of powdered PVC 0.45 mg of plasticizer, and 0.045 mg of the ion pair in 7 mL THF. The produced polymer formed then added to a glass substrate and the proto-membrane was immersed in 0.15 nano ZnO solution mixed with polymer PVC, PEG, and PVP (25±1 ºC) for around 1 h. The resulting membranes then were washed with alcohol and the sample then soaked in the (ethaline: oxaline: water) solvent for 48 h the amount of the DESs sequentially immersing the membrane prepared separately. The construction (membrane) was connected to a glass tube with a diameter of approximately 8 mm in electrode construction [27]. A 1.0×10^{-2} M solution for TC was used as an interior solution in the Ag/AgCl reference electrode. The fabricated electrode was soaked for 24 h in 1.0×10^{-2} M medication solution by subsequent storage in a similar solution.

2.4. Calibrations

The calibration for each proposed electrode was tested by immersing the electrode into aliquots of 1.0×10^{-5} to 1.0×10^{-2} M tamoxifen citrate solution in a 50 ml-beaker. The potential was determined by plotting as a function logarithm concentration of tamoxifen citrate. The calibration curve was then used to calculate the unknown sample concentration of tamoxifen citrate.

2.5. Sample analysis

Sires of real samples (urine) taken from different patients to direct analysis of proteomics in human urine. Tamoxifen citrate was dissolved in urine without further additions to obtain 1 M stock solution. A range of standard additions was used from stock solutions a 15 mL of 0.1 M Phosphate-Buffered Saline (PBS) at pH 7.4.

2.6. Selectivity coefficient

The K_{MPM} assumption was determined to examine the efficacy of the proposed electrode in the presence of different ions by measuring the selectivity coefficient ($K^{pot}_{A,B}$). The matched

potential method (MPM) was used to compare the potential recorded in the presence of interfacing ions with a reference solution until the same electrode potential was read. The K_{MPM} assumption is important to measure the selectivity coefficient of each interference ion and the ratio factor is obtained between the primary ions and interfering ion activity, this was applied with the assumption illustrated in equation (1) below:

$$K_{MPM} = \Delta\, a_{2\,A}/a_{1\,B} \qquad (1)$$

where a_1 is the activity of the reference solution, a_2 is the activity of the primary solution, and the interfering solutions are represented as a_B which is given in the same ΔE [28].

3. RESULTS AND DISCUSSION

3.1. Chemical structure of the membrane surface

In order to address the prepared membrane and the chemical bonds in the DES/polymer/ZnO nanoparticles, the FTIR spectrum was studied in all membranes, which is illustrated in Figure 3. The spectrum data showed the appearance of a peak at 3290 cm^{-1} is due to OH groups in the polymer backbone, while the peaks at 29343 cm^{-1} and 957 cm^{-1} are respectively related to CH_2 symmetric and asymmetric stretching. The observed of peak at 1416 cm^{-1} is according to C–C stretching.

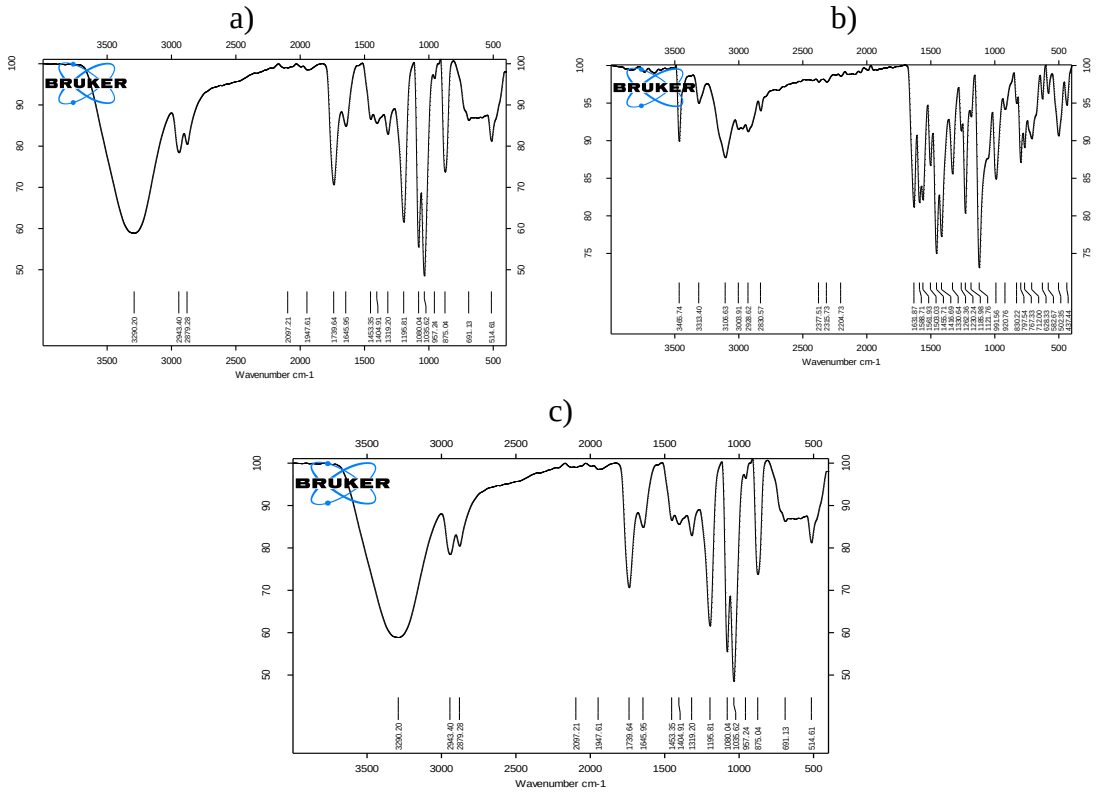

Figure 1. FTIR spectra of a) PVPE b) PEGE c) PVCE with nano composite ZnO membrane in DESs

The chemical band of Zn-O stretching is observed at 514 cm^{-1}. The interactions between ZnO and polymer molecules play an important function in obtaining intermolecular interaction to increase the activity of the surface proposed membrane. The addition of DESs/water molecules in the solution allows complete interaction between the nanoparticles and the polymer and also suggests the occurrence of dispersion nanoparticles and avoiding agglomerates. The addition of DESs is increasing the hydrophobicity which is increasing the tendency of non-polar molecules to form more aggregates active surface in the membrane. The chemical reaction of DESs with nano ZnO/polymer as is known from Figure 3. There is a broad absorbance peak at 3350 cm^{-1}, related to the overlap of amine groups (–N–H) in DESs (oxaline) and a characteristic peak of the carbonyl group (–C═O) in the oxalic acid groups.

3.2. Characterization of membrane

Addressing morphology and shape of surfaces modified membranes are important functions to understand the electrochemical behavior of the probe and it can give official details about optimization of electrodes [20].

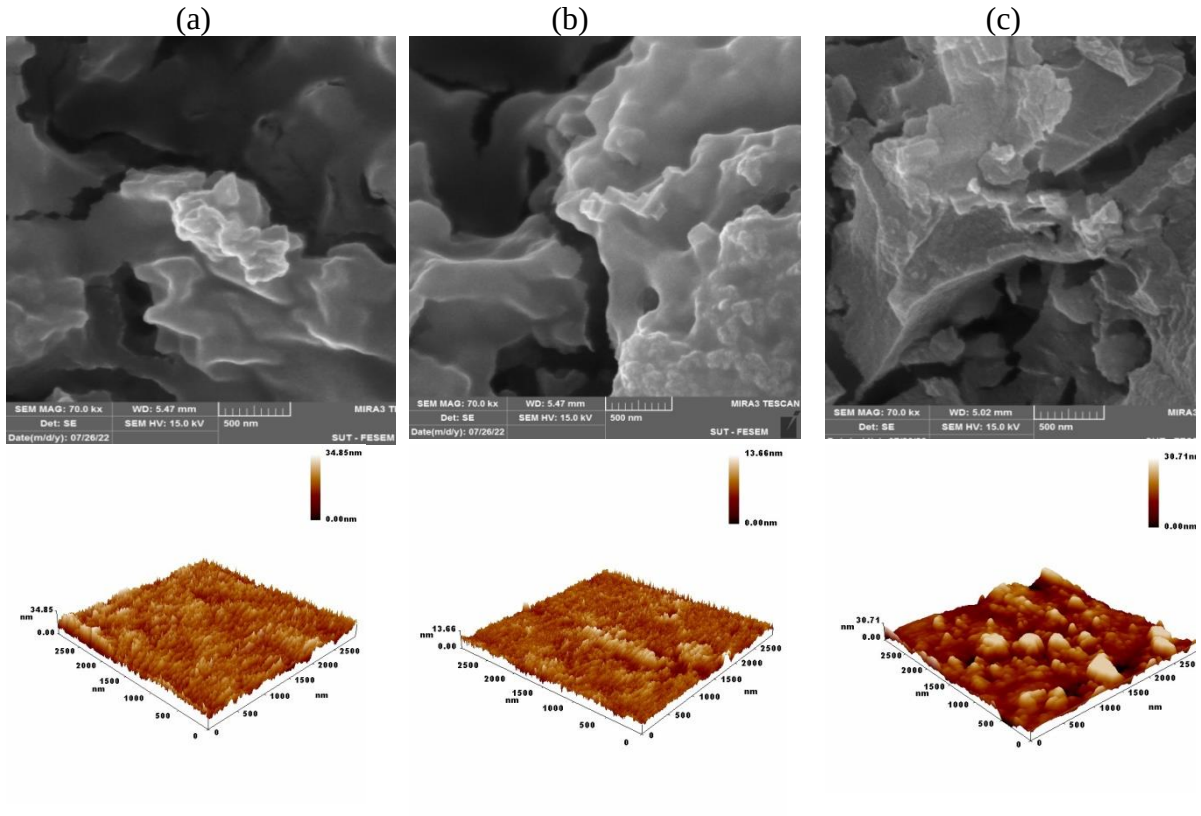

Figure 2. SEM, AFM images showing the morphology of proposed membrane electrodes a) PVPE b) PEGE c) PVCE in 0.25 weight % of DES (1 oxaline: 1 water)

The Scanning electron microscopy (SEM) images of Polyvinyl Pyrrolidine (PVP), Poly Ethylene Glycol (PEG), and polyvinylchloride (PVC) surface membranes in developed

electrodes are shown in Figure 4. It is observed significant differences in surface morphologies between the three proposed electrochemical membranes. The PVC electrode appears as glossy and crimp sheet-like stacked layers. The SEM image of PEG and PVP electrodes in Figure 2 (a) and (b) depicts a denser surface with a relatively larger area. The denser surface formation is attributed to supporting the selectivity of the membrane toward electrode efficiency that penetrates and eventually fills up. This is also caused by acting as an ion carrier between the membrane conductive molecules and the surface resulting in a larger specific surface area with a more rapid electron transfer rate.

The transport mechanism of PVPE, PEGE, and PVCE membranes are important factor in determining the effect of DESs solvent in nanofiltrations. AFM is the main instrument to understand the reliably predict the ion selectivity of these membranes. From data in Figure 2 different image surfaces affect their microstructure by changing the type of the polymer, although all types in these images have the same DESs additive molecules, which evident that the combination of a polymer through these membranes has been attempted to be modeled and this mostly is related to the membrane composition microstructures and the type of the solvent used.

3.3. Transmission electron microscopy (TEM)

Due to their excellent advantages in specifying membrane properties, TEM instrument has been used to achieve selective membranes in a range of deep eutectic additive mixtures. It has been found that the 0.25% DESs are an interesting ratio to enhancing the activity of the proposed electrodes. From the data in Figure 5, it can be clearly noted that the membranes have different layers that become disordered and the structure becomes less densely packed with less amount of DESs molecules; this indicates that the transport mechanism is possibly neither only solution-diffusion nor only pore flow. The type of the polymer is also affected due to the differences in microstructure membranes formed in each prepared membrane with nanometal oxides (ZnO) as shown in Figure 5 (a) and (c).

The densely packed polymer is shaped slowly more interconnected and less densely packed further from the membrane surface such as in PVC membrane.

3.4. Membrane surface charge

A surface charge property is greatly contributed on membrane retention and selectivity from membrane to ions. Zeta potential is the main parameter for describing properties of surface charge measurement during electrochemical applications. In this work, different Zeta potential measurements were examined in order to compare the efficiency of the surface charge of proposed membranes which is presented in Figure 3. It can be seen that PVP, PEG, and PVC membrane surfaces give higher negative charges with the addition of DESs solutions, and the highest value was found to be 0.35 wt. % at pH around (5.5 - 6.0) for PVP and PEG electrodes

than in PVC, it is interesting to see gradual decreases of the absolute values with increasing of pH values.

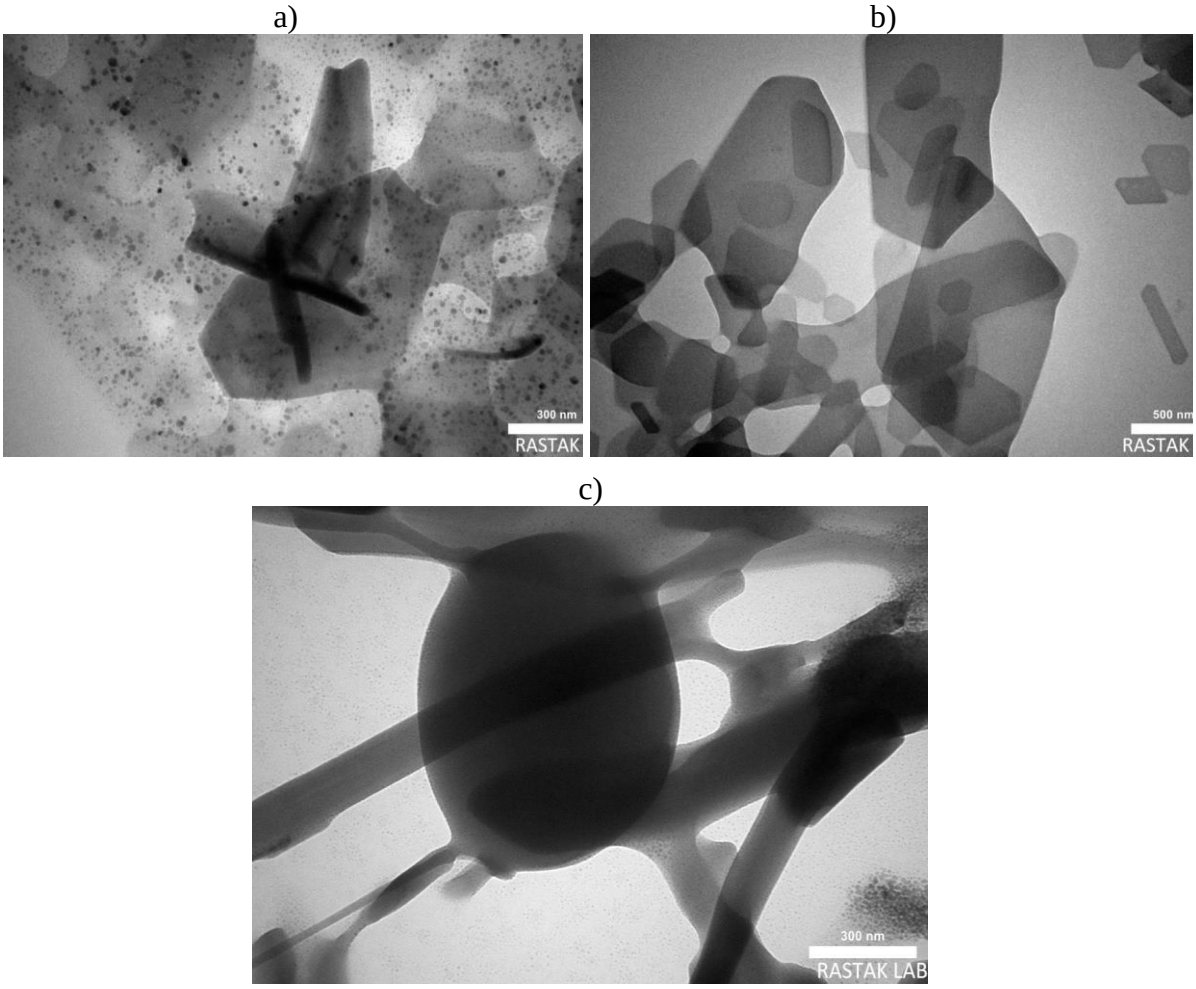

Figure 3. TEM images for ion conductive membrane in nanocomposite zinc oxide proposed membrane with **(a)** PEGE **(b)** PVPE **(c)** PVCE electrodes in 0.25 weight % of DES (1 oxaline: 1 water)

Another notification is that the additive of molecular nanocomposite polymer strongly changes the activity of surface charge in all creation membrane types. The linear change in zeta potential with pH values for all membranes indicated that the surfaces have a negative charge as a result of anion adsorption from the solvent. In the same context, it is also seen that PEG and PVC have small increases in the negative charge of the surface membrane compared to PVP electrode membrane. These specified that adsorption of nanocomposite metals developed the efficiency for major benefits by applying PEG and PVC than other membrane types used.

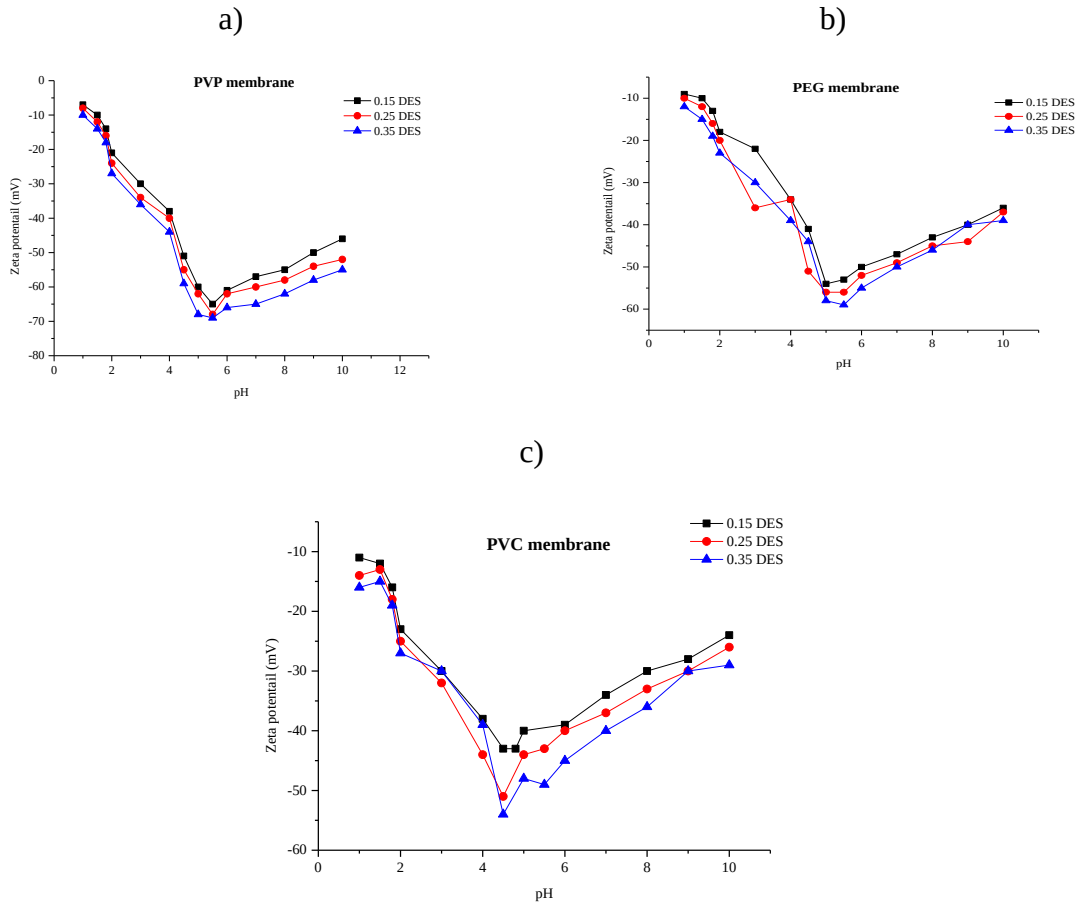

Figure 4. Zeta potential of ion conductive membranes for (a) PVP electrode (b) PEG electrode (c) PVC electrode in various concentrations (0.15 wt. %, 0.25 wt.%, and 0.35 wt.%) of (1 oxaline: 1 water)

3.5. Chemical characterization of Membranes surface

The specific membrane is generally prepared by using a suitable plasticized polymer to form suitable ionophores. Each type of polymer in the electrode has specific properties to improve the diffusional mobility of the analysts associated with the appropriate plasticizer to enhance the electro activity of the complex used. Here, a PVP, PEG, and PVC added with nano ZnO and DESs solvent increased the probability of getting an agreement long time and Nernstain responses near to ideal reference electrode. For each electrode, it was activated the probe by soaking it in tamoxifen solution for 24 hours. A comparison study has been examined between each electrode with linearity responses to Nernstian slope by preparing different concentrations of (8.1×10^{-4} - 8.0×10^{-2}, 6.0×10^{-5} - 1.0×10^{-2} and 3.0×10^{-5}- 1.0×10^{-2}) M O-NPO tamoxifen anodes in (PVPE, PEGE, and PVC) electrodes respectively. It found to be an agreement behavior of PVPE, PEGE with ZnO layer in DESs together as a diagnostic sensor indicating real sample concentrations with loss ±0.0302 mV, than PVC electrode, this indicated that the membrane turned out to be in contact with solutions.

Table 1. Characterization of tamoxifen citrate ion elective membrane electrodes

Parameters	**Electrode PVP**	**Electrode PVC**	**Electrode PEG**
Slope (mV/decade)	59.71±0.60	60.02 ± 0.15	58.88 ± 0.23
Limited detection / M	3.20×10^{-6}	2.23×10^{-6}	4.20×10^{-6}
Correlation Coefficient	0.9981	0.9955	0.9985
Linear range / mol.L^{-1}	1×10^{-6}-1.0×10^{-2}	1×10^{-6}-1.0×10^{-2}	1×10^{-5}-1.0×10^{-2}
pH range	2.9-5.8	4.2-5.4	5.2-6.3
Time /sec	29	31	33
Regression equation Y = mX + b	Y=24.981 ln(x) +313.2	Y=24.094 ln(x) +302.1	Y=24.024 ln(x) + 289
Time /day	22	18	24

Data in Table 1 represented characterization and reproducibility of the constructed electrodes at room temperature. The slope of all three electrodes gives good agreement measurements, for PVP electrode it was found around 59.71±0.60 mV than other electrodes the other slopes have slightly decreased to 58.88 ± 0.23, and 60.02 ±0.15 mV per decade for PVPE, PEGE, and PVPE individually. According to the acceptable linear response with stable potential measurement, it is true to apply these electrodes in measuring tamoxifen citrate.

3.6. Validity of the constructed electrodes

The effect of accumulation time is responsible part in the peak sensitivity and intensity of the electrochemically active drug molecule and this could significantly describe the stability of the proposed electrode to reach equilibrium. An interesting observation was observed in the stability of 10^{-3} M tamoxifen citrate solution results at 29, 31, and 33 seconds for PEG, PVP, and PVC separately as shown in Figure 3. The PVC electrode showed less response than other electrodes with non-linearity and these error bars could happen due to uncertain results of the linear response with the Nernstian equation. This also observed uncertain measurements in the location of potentiometric titration of the order of potential values; these differences are around (±3.4 m V e.m.f) [29]. However, in PEGE electrode changes in the potential for concentrations of TC solutions give a slight deviation in analytical measurements above around (±0.4 m V e.m.f) in 0.01M.

Figure 5(a) showed the slight change in the potential of PVPE and PEGE compared to magnification potential measurements observed in PVCE, this behavior was logical owing to previous studies [30-32].

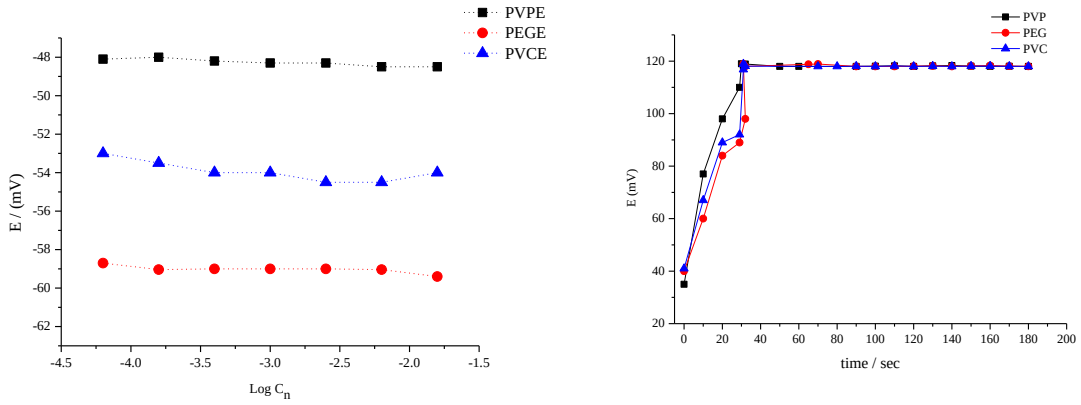

Figure 5. (a) Potential dependenyc for PEG, PVP, and PVC fabricated electrode (b) Time dependent 10^{-3} M of TC to reach equilibrium; in the presence of 0.25 wt. % of ethaline: oxaline: water mixture

3.7. Effect of inferencing Ions

Having shown that the addition of NPs-polymer in membrane caused to increased selectivity of the electrode towards tamoxifen concentrations; it is essential to determine the selectivity of the proposed electrodes in the presence of different in inorganic anions. Series of interfering ions added in to solution as described in table 2. Selectivity coefficients ($k_{potODH.}$,B) were calaculated by measuring the activity ratio of interfering ions and primary one . It can be given an acceptable data with main concept of electrode performance.[29] The results showed good selectivity for tamoxifen solutions in presence of range amount of inorganic anions.

Table 2. Selectivity coefficient value with different interfering ions in (TC) electrode

$K_{A,B}$ in (10^{-3} M) TC solution .			
Ion Interference	Electrode PVP	Electrode PEG	Electrode PVC
Li^{+}	1.0131×10^{-2}	1.1068×10^{-2}	1.0615×10^{-2}
Na^{+}	3.6732×10^{-2}	3.0610×10^{-2}	3.4544×10^{-2}
K^{+}	1.0029×10^{-2}	1.1017×10^{-2}	1.6503×10^{-2}
Mg^{2+}	5.3433×10^{-3}	5.4668×10^{-3}	5.0310×10^{-3}
Ca^{2+}	6.1923×10^{-3}	6.1155×10^{-3}	6.2126×10^{-3}
Zn^{2+}	4.0289×10^{-3}	4.8913×10^{-3}	4.7115×10^{-3}
Fe^{3+}	5.4211×10^{-4}	5.3401×10^{-4}	5.1179×10^{-4}
Cr^{3+}	6.1980×10^{-4}	6.9701×10^{-4}	6.1344×10^{-4}
Al^{3+}	4.1221×10^{-4}	4.0993×10^{-4}	4.675×10^{-4}

3.8. The application of the fabricated electrode

The validity of the proposed electrodes was tested by using direct, multi-standard, potentiometric methods (SAMS), and standard (SAM) methods to determine the concentration of tamoxifen solutions. Two different concentrations of tamoxifen solution were prepared once in 10^{-3} M and 10^{-3} M. Based on data in Table 3. the PVPE was recorded mostly the same in PEGE with small differences values as shown in Table 4. Subsequently, PVCE gives lower indication responses than other electrodes. In all electrodes, the titration with the potentiometric method assessed good linearity with a low limit of detection at room temperature. The statistical analytical data in Tables 3, 4, and 5 emphasized that the current work provides authorization access to apply with other analyte medical solutions. By comparing with previous studies,[8] a study modified electrochemical electrode to get limits of delectation 0.025 µg mL^{-1} with acceptable accuracy in spite of using a long process with additive methanol and 0.1 M of H_2SO_4; their data indicated electroanalytical signals with oxidative signal peak. In the same manner, an electrochemistry group produced a carbon paste electrode with alumina-carbon core-shell in vanadium oxide nanoparticles using cyclic voltammetry and differential pulse techniques. They also assumed that the addition of conductive electrolytes could possibly participate in the quantification of the tamoxifen drug. The current results achieved better documentation within the approval range of higher accuracy and less error bar than those values observed in carbon core sell electrodes.[15] The determination of TC concentrations was carried out in some pharmaceutical forms. Table 3 represents a variety of analytical parameters of measuring TC concentrations by PVPE, PEGE, and PVCE, it is observed excellent measurements for most TC samples and it gives good convention electrodes that can be considered to use for the determination of different pharmaceutical samples [15].

Table 3. Determination of TC in tablets under optimum conditions (n = 3)

Direct Potentiometric Methods for TC in 1.00×10^{-3} M			
Tablet (Beta Drugs Ltdi (TC 20 mg)	Electrode PVPE	Electrode PEGE	Electrode PVCE
Concentration of TC (M)	9.8121×10^{-3}	9.6423×10^{-3}	9.5014×10^{-3}
Recovery %	98.01	97.54	96.23
Error %	-1.29	-1.06	-1.31
Tablet Wockhardt made (tamoxifen citrate 20 mg)	Electrode PVPE	Electrode PEGE	Electrode PVCE
Concentration of TC (M)	9.105×10^{-3}	9.245×10^{-3}	9.382×10^{-3}
Recovery %	97.00	98.73	96.12
Error %	-1.02	-1.18	-1.86
Tablet tamoxifen citrate 4 mg		Reference method [21]	
Recovery %		85.3	
Error %		0.61	

4. CONCLUSION

Three different approaches proposed focused on modified membranes allow improving the sensitivity of traditional potentiometric electrodes. The main idea of the work is dependent on mixing ZnO nanocomposite polymer with a plasticizer in different DESs solvent phases. Each assumed electrode is described by the Nernst equation. The resulting slopes for all electrodes refer to providing an extremely sensitive and selective method for the determination of tamoxifen. The proposed method verified a new, simple, inexpensive, and portable tool to use for broad concentrations of tamoxifen measurement in urine samples with accurate analytical performances. The best experimental data exhibited significant selective activity toward tamoxifen concentrations by PEGE, PVPE with polymer nano ZnO composite in wt. 0.25 %DESs. This electrochemical method can practically be used in different medical pharmaceutical applications with rapid and highly sensitive measurements.

Acknowledgments

Authors would like to thank Department of Chemistry in College of Science at Al-Nahrain University for supporting this research and Department of Postgraduate Affairs at University of Baghdad.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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