



Binary and ternary deep eutectic solvent mixtures: Influence on methylene blue electropolymerisation

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ABSTRACT

Binary and ternary deep eutectic solvent (DES) mixtures based on choline chloride, with ethylene glycol, oxalic acid, urea and fructose, were used for the first time as media for the electropolymerisation of poly(methylene blue) (PMB) on glassy carbon electrodes (GCEs) and GCEs modified with multiwalled carbon nanotubes (MWCNTs). The influence of different parameters such as DES composition, the presence of MWCNTs and/or perchlorate dopant, on the polymer film properties was evaluated. The polymer films electrodeposited in the different media were characterized by cyclic voltammetry and different voltammetric characteristics were observed depending on the electropolymerisation conditions. This knowledge was used to determine the best binary and ternary mixtures for polymer growth, with a view to electrochemical sensor applications. The PMB-based modified electrode with the best characteristics was tested for ascorbate sensing in order to demonstrate the usefulness of this platform.

1. Introduction

Deep eutectic solvents (DESs) are formed by two or more components that, in an appropriate ratio, are capable of stabilising hydrogen bond interactions to form an eutectic mixture with a melting point lower than that of the individual components. Commonly, DESs are prepared by mixing quaternary ammonium salts, which act as H-bond acceptors (HBAs) with H-bond donors (HBDs). DESs formed by choline chloride as HBA and ethylene glycol or urea as HBD, known as ethaline or reline, are the most widely used. In recent years, choline chloride has also been combined with other HBDs such as sugars or organic acids, leading to DES mixtures with good properties for applications such as extraction procedures or synthesis of nanomaterials [1,2]. DESs benefit from good properties such as low toxicity, simple preparation, low cost, biodegradability and a wide potential window [3]. For these reasons, the use of DESs in different applications, such as extraction procedures, electrodeposition of metals and alloys, semiconductors and polymers, has increased in recent years [3–5].

Conducting phenazine redox polymers are widely used for developing electrochemical sensors with improved analytical features. The combination of nanomaterials, such as multiwalled carbon nanotubes (MWCNT) or Fe₂O₃ nanoparticles, with redox polymers leads to an

enhancement of the selectivity and sensitivity of the sensor due to the synergistic effects between the nanomaterial and the polymer [6,7]. It has been demonstrated that the medium in which the polymer is synthesised influences the polymer film properties, such as the morphology and the conductivity. Recent papers have demonstrated the advantages of using a DES as the medium for the electrosynthesis of phenazine polymer films on the electrode surface as part of a sensor construction process [7,8]. To the best of our knowledge, the electrosynthesis of phenazine polymers in different DESs has been little explored. Besides this, indications have been given in the literature that the presence of more than one hydrogen bond donor can alter the morphology of electrodeposits [9] and can positively influence the extraction efficiency of lignins [10] and biomass conversion [11]. In the case of urea and water mixtures with choline chloride, the eutectic temperature varies by 50 °C according to the mole fraction of each HBD [12].

We seek to understand how the use of ternary DESs can influence the growth and electrochemical properties of polyphenazine films. Such knowledge could be useful for designing the best media for polymer growth, looking towards electrochemical sensor applications. Thus, in this work, formation of the phenazine polymer poly(methylene blue) (PMB) by electropolymerisation was investigated in different DESs. Eutectic mixtures based on choline chloride with one or two of ethylene

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glycol, urea, fructose and oxalic acid were evaluated. Additionally, the effect of the presence of MWCNTs was studied by carrying out the polymerisation on both glassy carbon electrodes (GCEs) and MWCNT/GCEs. PMB film-modified electrodes were characterized by cyclic voltammetry and the sensing of ascorbate was tested.

2. Experimental

Choline chloride, ethylene glycol, urea, D-fructose, methylene blue, nitric acid (65%), chitosan from crab shells, ascorbic acid and sodium hydroxide were supplied by Sigma-Aldrich, Germany. Perchloric acid (70%), potassium chloride and oxalic acid dihydrate were from Fluka, Switzerland. MWCNTs with 95% purity, diameter 30 ± 10 nm and 1–5 μm length were from Nanolab, USA. A Britton-Robinson (BR) buffer, prepared by mixing 0.040 M acetic acid (Carlo Erba), 0.040 M boric acid (Baker analysed) and 0.040 M phosphoric acid (Riedel-Haën), was used as supporting electrolyte for electrochemical characterization of the polymer films; the pH was adjusted by adding appropriate volumes of 1.0 M NaOH. Millipore Milli-Q nanopure water with resistivity ≥ 18 M Ω cm was used throughout this work. All experiments were carried out at room temperature (25 ± 1 °C).

Electrochemical experiments were performed using an Ivium CompactStat electrochemical analyser (Ivium Technologies, Netherlands) controlled by IviumSoft software. A three-electrode cell formed by a glassy carbon disc electrode (GCE) (1 mm diameter) as working electrode, a platinum wire as counter electrode and Ag/AgCl (3 M KCl) as reference electrode was used. A CRISON 2001 micro pH-meter (Crison, Spain) was used for pH measurements.

Prior to modification of the GCE, the MWCNTs were functionalized in nitric acid by the same procedure used in previous work on the polymerisation of MB in DESs [13]. In short, MWCNTs were dispersed in 5.0 M HNO₃ under mechanical stirring for 24 h. The functionalized MWCNTs were filtered and rinsed with ultrapure water until a neutral pH was attained and dried overnight at 80 °C. Dispersions of 1.0% MWCNT were prepared in 1.0% chitosan dissolved in 1.0% acetic acid aqueous solution. The mixtures were homogenised in an ultrasonic bath for 3 h. The dispersion was kept under refrigeration. Before modification, the GCE was mechanically polished with 1 μm particle size diamond spray on a polishing cloth, rinsed with ultrapure water and sonicated in ethanol for 10 min. A drop-casting procedure was used to modify the GCE. For this purpose, 1.0 μL of 1.0% MWCNT dispersion was dropped onto the electrode surface and dried at room temperature. The procedure was then repeated once.

Binary DES mixtures were prepared by mixing the HBA, choline chloride (ChCl), with different HBDs. These were: ethylene glycol (EG) in a 1:2 M ratio to give ethaline, urea in a 1:2 M ratio to give reline, oxalic acid (OA) in a 1:1 M ratio [10] and fructose (Fruc) in a 2:1 M ratio [10]. Ternary DES mixtures of ChCl:EG:OA in a 3:4:1 M ratio and ChCl:EG:urea in a 1.4:1.8:1 M ratio were prepared. ChCl:EG:Fruc ternary mixtures were made by mixing the binary DES mixtures of ChCl:EG (1:2 M ratio) and ChCl:Fruc (2:1 M ratio) and the following percentages of ChCl:EG in the ternary DES mixture were investigated: 4, 21, 50 and 84%. The binary and ternary mixtures were prepared as follows. First, ChCl was heated to 100 °C to evaporate any water. Then the HBDs were added and the mixture was held at 60 °C under mechanical stirring until a homogeneous solution was obtained. The DESs were cooled down to room temperature and were ready to use.

Polymerisation of MB was carried out in a DES containing 5 mM of monomer [8]. MB was also polymerised in 5 mM monomer solution formed by 90% DES plus 10% v/v of aqueous 0.1 M NaOH and 0.1 M HClO₄ added in this order to facilitate dissolution [8]. For comparison, polymerisation of MB was also carried out in aqueous solution containing 5 mM MB plus (0.1 M NaOH + 0.1 M HClO₄).

Poly(methylene blue) films were formed on the GCE and MWCNT/GCE by potential cycling between -0.6 V and $+1.0$ V at 150 mV s⁻¹ for 20 cycles in order to obtain uniform and reproducible films [8]. The

polymer films were characterized in BR buffer at pH 6.0 by cyclic voltammetry in the potential range from -0.4 to $+0.5$ V at 50 mV s⁻¹. Fixed potential amperometry was used for ascorbate sensing at $+0.2$ V vs. Ag/AgCl in 0.1 M KCl [8]. All experiments were carried out in triplicate to assess reproducibility.

3. Results and discussion

3.1. Polymerisation of MB on a GCE in different DES media

Previous studies have demonstrated the significant effect of additives, such as a second HBD, salts or acids, on polymer film characteristics [11]. Thus, the influence of the composition of DES mixtures on the electropolymerisation of PMB on a GCE was investigated. Cyclic voltammograms (CVs) during potential cycling electropolymerisation of MB on a GCE in ChCl:Fruc and ChCl:EG:Fruc containing 21% of ChCl:EG in the absence and presence of perchlorate dopant (from 0.1 M NaOH + 0.1 M HClO₄) are shown in Fig. 1. As can be seen, polymerisation occurs via radical cation formation in one step at potentials higher than $+0.4$ V in ChCl:Fruc and ChCl:Fruc + dopant, and at $+0.8$ V in ChCl:EG:Fruc and ethaline, reline, ChCl:OA, ChCl:EG:urea and ChCl:EG:OA with and without dopant (not shown). In ChCl:EG:Fruc with dopant, the polymerisation occurs via radical cation formation in two steps at $+0.25$ V and $+0.58$ V. A redox couple assigned to the oxidation and reduction of the polymer and the monomer units trapped in the PMB film was observed in all the polymerisation media. As can be seen in Fig. 1A–D for ChCl:EG:Fruc and ChCl:Fruc, the anodic peak decreases and shifts to more positive values due to the changes that happen on the electrode surface because of the formation of a polymer film. This behaviour of the anodic peak was not observed in pure ethaline and ChCl:OA and ChCl:EG:OA with or without dopant, since the anodic peak current and potential did not change after the first cycle.

In all DESs, the potential of the cathodic peaks remained constant and the cathodic current decreased. The polymerisation profile in ChCl:Fruc (Fig. 1A and C) presents two cathodic peaks at about -0.1 V and $+0.15$ V related to the reduction of the adsorbed monomer and the diffusion-controlled reduction of dimers or oligomers formed during the polymerisation, respectively. After 20 cycles, the highest anodic current density was observed in ChCl:EG:Fruc with dopant (94 ± 5 $\mu\text{A cm}^{-2}$, $n = 3$). No anodic and cathodic peaks were observed when PMB films were formed in (0.1 M NaOH + 0.1 M HClO₄) aqueous solution.

PMB films formed in the different DESs and aqueous solution were tested by CV in BR buffer at pH 6.0. The voltammograms (Fig. S1 (Supplementary information)) show a well-defined redox couple that corresponds to the polymer film formed on the electrode surface. The values of the anodic peak current densities are shown in Fig. 2 and it can be seen that the highest currents were obtained when PMB films were electropolymerised in ternary DES mixtures formed by ChCl, ethylene glycol, fructose or urea.

This behaviour may be attributed to the interaction between the two HBDs facilitating diffusion of the monomer and thence the amount of polymer electrodeposited on the electrode surface. As expected, higher current densities were also observed when perchlorate dopant was added to the DES mixture since its presence leads to higher ionic strength and, thus, an increase in the mobility of the positively charged MB monomer. Higher currents were obtained using ChCl:EG:Fruc as the medium for PMB formation than were obtained in aqueous media (Fig. 2B), demonstrating the advantages of using DESs in the electropolymerisation of MB.

3.2. Polymerisation of MB on a GCE in different ChCl:EG:Fruc media

According to the results shown above, better PMB films were obtained in ternary DES mixtures. For this reason, the influence of the composition of the DES formed by ChCl:EG:Fruc on the electropolymerisation was evaluated. For this purpose, different percentages

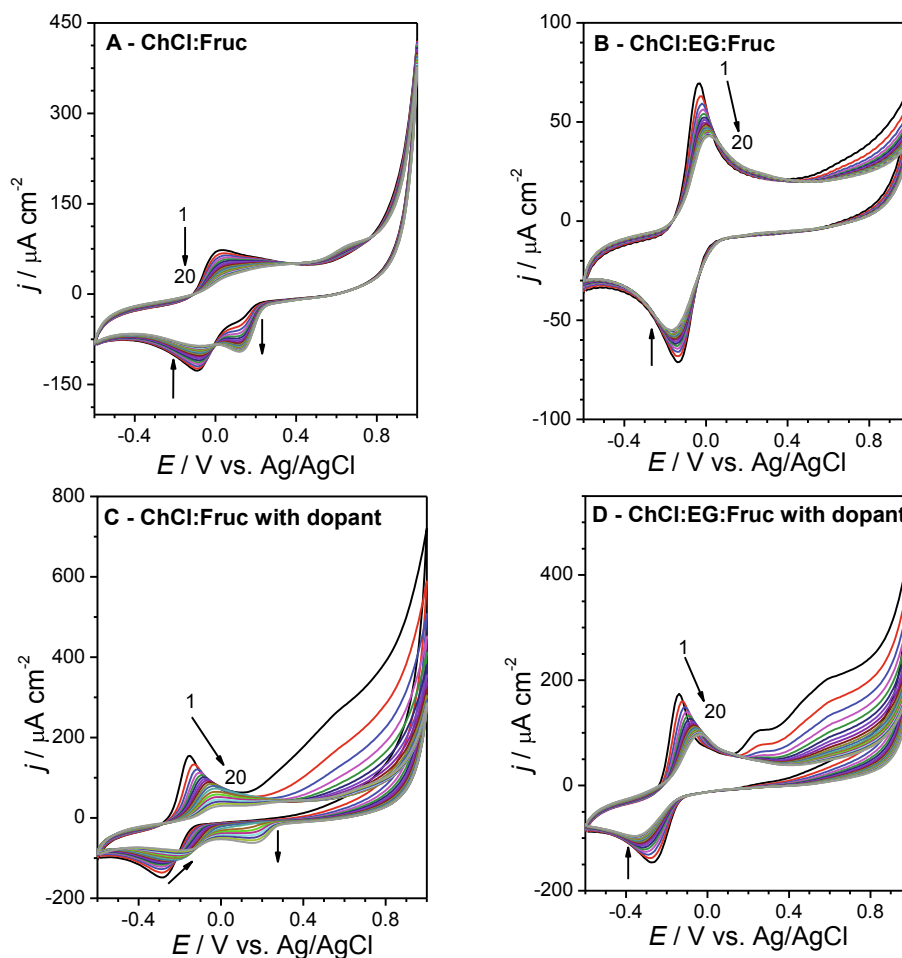


Fig. 1. Potential cycling electropolymerisation of 5 mM of MB on a GCE in (A) ChCl:Fruc, (B) ChCl:EG:Fruc, (C) ChCl:Fruc + (0.1 M NaOH + 0.1 M HClO₄) dopant, (D) ChCl:EG:Fruc + (0.1 M NaOH + 0.1 M HClO₄) dopant.

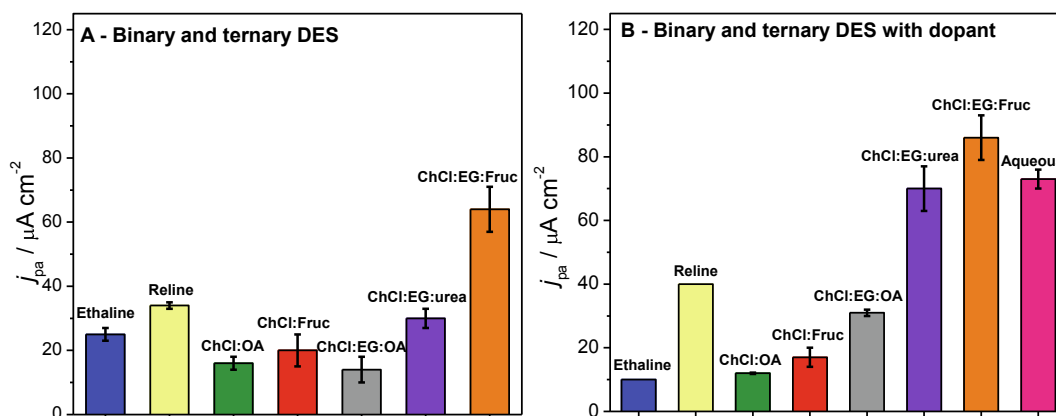


Fig. 2. Anodic peak current densities, j_{pa} , from CVs recorded in BR buffer at pH 6.0, of the different PMB films obtained in (A) DES and (B) DES + (0.1 M NaOH + 0.1 M HClO₄). DES: (blue bar) ethaline, (yellow bar) reline, (green bar) ChCl:OA, (red bar) ChCl:Fruc, (grey bar) ChCl:EG:OA, (violet bar) ChCl:EG:urea, (orange bar) ChCl:EG:Fruc and (pink bar) aqueous solution. Note: Fig. S1 shows the CVs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(4%, 21%, 50%, and 84%) of ChCl:EG in the ChCl:EG:Fruc mixture, with and without perchlorate dopant, were tested. After 20 cycles of polymerisation, higher peak current densities were observed in the presence of dopant, in the following (increasing) order: 94 ± 5 , 131 ± 11 , 155 ± 19 and $180 \pm 8 \mu\text{A cm}^{-2}$ ($n = 3$) for PMB film in ChCl:EG:Fruc with 21%, 84% 4% and 50% of ChCl:EG, respectively.

GCEs modified with PMB films prepared in DESs with different percentages of ChCl:EG were characterized by CV in a BR buffer. Fig. 3 shows a plot of peak current vs. percentage of ChCl:EG. As can be seen, better results were obtained when ChCl:EG was added to ChCl:EG:Fruc at any of the tested percentages than those obtained in ethaline (100% of ChCl:EG) or ChCl:Fruc (0% of ChCl:EG). This confirms that the presence

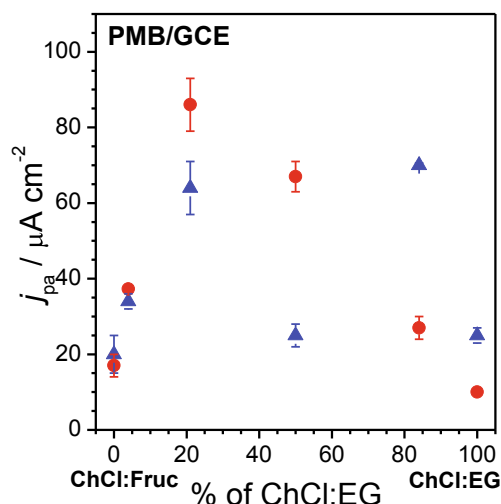


Fig. 3. Effect of the percentage of ChCl:EG in ChCl:EG:Fruc mixture on the anodic peak current density of a GCE modified with PMB film obtained (▲) in the absence and (●) in the presence of (0.1 M NaOH + 0.1 M HClO₄). CV conditions: BR buffer pH 6 at 50 mV s⁻¹.

of the second HBD enhances the polymer film currents. As the ChCl:EG percentage increases, the difference in the currents obtained in the presence and absence of dopant becomes greater. This may be due to the differences in the viscosity of the different ChCl:EG:Fruc mixtures [14]. The species expected to be present in the monomer solution are Ch⁺, Fruc₂Cl⁻, EG₂Cl⁻ and Na⁺ and ClO₄⁻ in the solutions containing dopant [15]. The small differences in the anodic current observed in the presence and absence of dopant at ChCl:EG percentages lower than 21% are explained by the limited ion mobility and consequent ineffective ion doping/dedoping process due to the high viscosity of the DES.

At ChCl:EG percentages of 84 and 100%, higher anodic current densities were observed in the absence of dopant, indicating that in this case the presence of Na⁺ and ClO₄⁻ ions worsens the PMB film properties. This may be explained by competition between the different ions present in the solution to be incorporated in the polymer matrix [15]. The highest anodic current densities were observed at a percentage of 21% ChCl:EG in the presence of dopant. Thus, these conditions are the most favourable for obtaining PMB films on GCEs.

In order to obtain information about the surface and interfacial characteristics of the PMB films formed in the different media, the polymer films were also characterized by electrochemical impedance spectroscopy. Examples of impedance spectra for 84% ChCl:EG are given in the electronic [supplementary material](#) in Fig. S2A and clearly illustrate the effect of dopant in reducing the impedance values and slightly altering the profile of the complex plane plot.

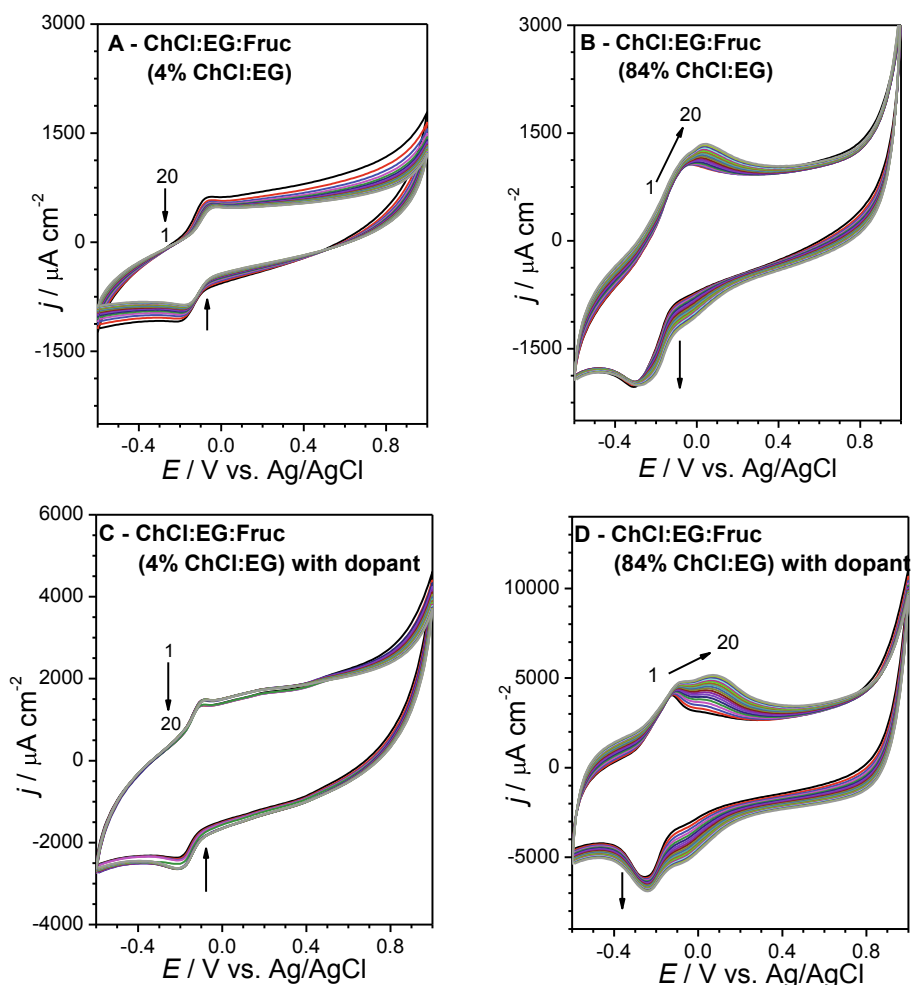


Fig. 4. Potential cycling electropolymerisation of 5 mM of MB on MWCNT/GCE in (A) ChCl:EG:Fruc with 4% ChCl:EG, (B) pure ChCl:EG:Fruc with 84% ChCl:EG, (C) ChCl:EG:Fruc with 4% ChCl:EG + (0.1 M NaOH + 0.1 M HClO₄), (D) ChCl:EG:Fruc with 84% ChCl:EG + (0.1 M NaOH + 0.1 M HClO₄).

3.3. Polymerisation on MWCNT/GCE

The influence of the substrate for polymerisation on polymer growth and properties was also evaluated. For this purpose, the polymerisation was also carried out on MWCNT/GCE in ethaline (ChCl:EG 100%), ChCl:Fruc (ChCl:EG 0%) and in ChCl:EG:Fruc with percentages of ChCl:EG in the mixture of 4, 21 50 and 84%, in the presence and absence of perchlorate dopant. The presence of MWCNTs on the electrode surface leads to an increase in the stability of the PMB film (after 10 min in aqueous solution, loss of 100% of the initial current on PMB/GCE and 30% on PMB/MWCNT/GCE). The polymerisation profiles also change on MWCNT/GCE; this can be expected due to the interactions between the nanomaterial and the polymer. Good polymerisation profiles were observed in DESs with percentages of ChCl:EG of 50, 84 and 100%, since an increase in the anodic and cathodic peak currents with the number of cycles was observed (Fig. 4B and D). For percentages of 0, 4 and 21% of ChCl:EG, there was a decrease in the anodic and cathodic currents (Fig. 4A and C).

After 20 polymerisation cycles, higher anodic currents were obtained in all DESs in the presence of the dopant, obtaining the highest current densities in ethaline + 0.1 M NaOH + 0.1 M HClO₄ (2312 ± 99 $\mu\text{A cm}^{-2}$, $n = 3$) and ChCl:EG:Fruc (84% of ChCl:EG) + 0.1 M NaOH + 0.1 M HClO₄ (2273 ± 369 $\mu\text{A cm}^{-2}$, $n = 3$). An increase in the anodic peak current with the number of cycles was observed when the PMB film was obtained in (0.1 M NaOH + 0.1 M HClO₄) aqueous solution, with a current density of 1726 ± 225 $\mu\text{A cm}^{-2}$ ($n = 3$) after 20 cycles. Figs. S3A and B show CVs of PMB films, electro synthesised on MWCNT/GCE in different DESs and aqueous solution, recorded in BR buffer at pH 6.0. Well-defined anodic and cathodic peaks are obtained in DES media. In aqueous media, the redox couple was not observed; thus, the use of DES improves the PMB film properties. Also, the PMB films electrodeposited on MWCNT/GCE presented higher currents than those formed on GCE. These results demonstrate the synergistic effect between the nanomaterial and the polymer.

As can be seen in Fig. 5, for 100% ChCl:EG a significant increase in the anodic peak current was observed when the dopant was added. This is expected, since as the viscosity of the DES decreases, the effectiveness of the doping/dedoping process increases. The doping/dedoping process was also affected by the amount of the species present in the monomer solution, which change depending on the percentage of ChCl:EG. This explains the different behaviour in the absence and presence of the

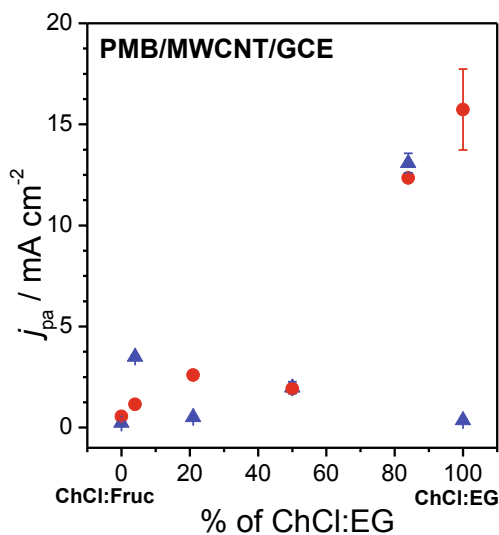


Fig. 5. Plot of anodic peak current, j_{pa} , vs. % of ChCl:EG from CVs at PMB/MWCNT/GCE recorded in BR buffer solution, pH 6.0 at 50 mV s⁻¹ (Fig. S2A and S2B) obtained (▲) in the absence and (●) presence of (0.1 M NaOH + 0.1 M HClO₄).

dopant at the different ChCl:EG percentages. The highest anodic current densities were obtained for PMB films synthesised in pure ChCl:EG:Fruc containing 84% of ChCl:EG (13083 ± 486 $\mu\text{A cm}^{-2}$, $n = 3$) and in ethaline with dopant (15732 ± 2432 $\mu\text{A cm}^{-2}$, $n = 3$). As for PMB formed on GCE, examples of impedance spectra for 84% ChCl:EG are given in the electronic supplementary material, Fig. S2B, and show the large effect of MWCNTs in reducing the impedance, whilst the effect of the dopant is rather small for 84% ChCl:EG.

3.4. Ascorbate sensing on PMB/MWCNT/GCE

To evaluate the usefulness of the PMB/MWCNT/GCE sensor obtained in the ternary DES mixture, ChCl:EG:Fruc with 84% of ChCl:EG, the model analyte ascorbate was determined by fixed potential amperometry at +0.2 V vs. Ag/AgCl in 0.1 M KCl. For comparison, ascorbate was also determined using the PMB/MWCNT/GCE sensors prepared in ethaline and in aqueous (0.1 M NaOH + 0.1 M HClO₄). Calibration plots are shown in Fig. S4. The modified electrode obtained in the ternary mixture presents a significantly higher sensitivity (73.0 $\mu\text{A cm}^{-2} \mu\text{M}^{-1}$, RSD = 2%, $n = 3$) for the determination of ascorbate than that obtained in ethaline (0.385 $\mu\text{A cm}^{-2} \mu\text{M}^{-1}$, RSD = 2%, $n = 3$) and aqueous + dopant (0.19 $\mu\text{A cm}^{-2} \mu\text{M}^{-1}$, RSD = 6%, $n = 3$). A LOD of 5.6 μM was obtained using PMB/MWCNT/GCE in the ternary mixture, this value being two and three times lower than that obtained when PMB films were formed in ethaline and aqueous solution (0.1 M NaOH + 0.1 M HClO₄), respectively. These results confirm the advantages of using DESs and pure ternary DES mixtures. The LOD obtained with the PMB prepared in the ternary DES mixture is of the same order of magnitude as previously reported for ascorbate sensing using PMB sensors obtained in ethaline with dopant [8]. This indicates that the presence of the second HBD leads to a much higher sensitivity and a lower detection limit than can be obtained by adding an acid dopant to binary DES mixtures.

4. Conclusions

PMB was synthesised successfully in binary and ternary DES mixtures based on choline chloride, ethylene glycol, oxalic acid, urea and fructose on GCE and on MWCNT/GCE, in the absence and presence of perchlorate dopant. The polymerisation medium and the substrate influence the polymer film growth and properties. Higher currents and better stability of the PMB film were observed on the MWCNT/GCE substrate, being more appropriate for sensor applications. Polymerisation on both GCE and MWCNT/GCE, in ternary DESs based on choline chloride plus ethylene glycol and urea or fructose, improved the electrochemical properties of the PMB films. The presence of a second hydrogen bond donor tuned the DES characteristics, leading to polymer films with different properties.

More detailed investigation of polymerisation in ChCl:EG:Fruc showed that PMB films grown on GCE and MWCNT/GCE in ChCl:EG:Fruc containing 84% of ChCl:EG presented an anodic peak current higher and comparable, respectively, to that obtained in ethaline + (0.1 M NaOH + 0.1 M HClO₄). PMB/MWCNT/GCE sensors prepared in ChCl:EG:Fruc with 84% of ChCl:EG have excellent analytical characteristics for the determination of the model analyte ascorbate, which are significantly better than those from two-component DESs.

This study has shown that the use of ternary DES mixtures leads to improved film characteristics, opening up new perspectives for the preparation of polymer-modified electrodes for electrochemical sensors with enhanced analytical parameters. It can be foreseen that this approach will have wide appeal in the future.

CRediT authorship contribution statement

Lucía Abad-Gil: Investigation, Writing - original draft. **Jesus R. Procopio:** Supervision, Writing - review & editing. **Christopher M.A. Brett:** Conceptualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2021.106967>.

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