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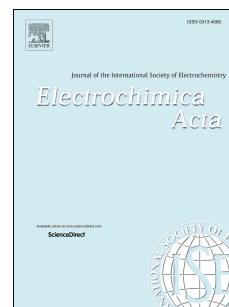
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Chemical and electrochemical properties of a hydrophobic deep eutectic solvent

S. Ruggeri^a, F. Poletti^a, C. Zanardi^a, L. Pigani^a, B. Zanfognini^a, E. Corsi^a, N. Dossi^b, M. Salomäki^{c,d}, H. Kivelä^{c,d}, J. Lukkari^{c,d}, F. Terzi^{a*}

^a Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via Campi 103, 41125 Modena (Italy).

^b Department of Agrifood, Environmental and Animal Science, University of Udine, Via Cotonificio 108, 33100 Udine (Italy).

^c Department of Chemistry, University of Turku, Vatselankatu 2, FI-20014, Turku (Finland).

^d Turku University Centre for Materials and Surfaces (MATSURF), University of Turku, Vatselankatu 2, FI-20014, Turku (Finland).

* Corresponding author; fabio.terzi@unimore.it

Abstract

Hydrophobic deep eutectic solvents (DESs) have been recently introduced and acknowledged to offer remarkable advantages over the common organic solvents, thanks to their biodegradability, low toxicity and low cost. In the present paper a first study of the electrochemical properties and extraction capabilities of a prototypical hydrophobic DES, based on tetrabutylammonium chloride-decanoic acid (1:2 molar ratio), is carried out. A small water content is shown to be advantageous as it dramatically affects the electrical conductivity and viscosity of the solvent, i.e. the parameters of fundamental importance in electrochemistry. A critical environmental pollutant, namely Cr(VI), has been successfully extracted from aqueous phase and amperometrically detected in the DES phase.

Keywords

Hydrophobic deep eutectic solvents; liquid-liquid extraction; metal extraction; Cr(VI)

1. Introduction

A Deep Eutectic Solvent (DES) is an eutectic mixture formed by a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) [1,2]. The interactions between these components lower the melting point of the mixture with respect to those of the individual components, leading to a liquid phase at room temperature. The odd nature of the hydrogen bond formed in similar compounds is discussed in ref. 1.

DESs are easy to prepare and offer several advantages [1,2], such as capability to solubilise different organic and inorganic species, high biodegradability, low toxicity and low cost. These features make them suitable for large-scale production, being effective alternatives to other solvents possessing some similar properties, such as ionic liquids.

Among the different types of DESs, the hydrophobic ones have emerged in recent years as promising alternatives to toxic and flammable organic solvents. However, only a few examples of such DESs have been reported so far (see ref. 3-10 and Table S1 and S2 in Supplementary Materials). Hydrophobic DESs are based on poorly water-soluble components, such as tetraalkylammonium salts [3], long chain carboxylic acids [4], menthol [5] and lidocaine [6]. The hydrophobic nature has been exploited mostly to extract species from biological materials or aqueous media, e.g., artemisin and polyprenyl acetates from *Artemisia annua* [7] and *Ginkgo biloba* leaves [4], synthetic pigments from beverages [8], as well as volatile fatty acids [3], pesticides [9], and few alkali and transition metal ions, e.g. In^{3+} [10] and Co^{2+} [6], from aqueous solutions.

In the present paper, a prototypical hydrophobic DES, namely a 1:2 molar mixture of tetrabutylammonium chloride (TBACl) and decanoic acid (DA), has been prepared and its relevant physico-chemical properties characterised. Although the role of water content is largely underrated for both hydrophobic and hydrophilic DESs, we could demonstrate that it induces dramatic changes in DESs' properties.

For the first time for hydrophobic DESs, the electrochemical behaviour has been studied. We demonstrate here that the addition of small water quantities to the hydrophobic DES dramatically improves its electrical conductivity, without the addition of any salt. Thanks to this property, DESs constitute particularly appealing green systems in electrochemistry, e.g. in sensing, electroremediation, and electrodeposition. In view of the possibilities in similar applications, we explored the electrochemical behaviour of ferrocene, a benchmark redox probe, and of Cr(VI) species, extracted from aqueous solution, in this solvent. Cr(VI) species have been selected in view of their importance in various industrial processes and their impact on the environment [11,12].

2. Experimental section

2.1 DES preparation

DESs with different water contents (DES1-4) were prepared using TBACl ($\geq 98\%$, TCI) and DA ($\geq 98\%$, Sigma Aldrich) in the 1:2 molar ratio [3]. A mixture of the components was heated in a water bath at 65°C for ca. 3 hours leading to the liquefaction of the two solids, and the formation of a liquid, homogeneous phase. Then, the mixture was left cooling to room temperature.

The driest DES (DES1 in Table 1) was prepared in an Ar atmosphere (Glovebox mBraun UNIlab Pro), where water and oxygen levels were < 4 ppm, using a procedure similar to that described above. DESs with higher water content (DES3 and DES4 in Table 1) were obtained by equilibrating the DES samples in an atmosphere saturated with water vapour at 30°C and 60°C , respectively, by leaving a DES aliquot of 10 to 15 g in the water-vapour saturated atmosphere, at constant temperature, overnight. Higher water content could be obtained, in principle, by increasing the temperature, but a phase separation occurs when the water content increases to ca. 2.6% w/w, the value attained at 75°C .

Aqueous solutions used throughout this work were prepared using water doubly distilled in quartz vessels (electrical conductivity $< 1.0\ \mu\text{S}/\text{cm}$) from a Distilon 2DQ system (Bhanu Scientific Instruments).

2.2. Determination of water content

The DES water contents have been measured using a Karl-Fischer titrator (Mettler-Toledo DL32 KF Coulometer). The electrolyte used as the titrating solution was Apura CombiCoulomat fritless (Merck), while precision and accuracy of the titrations were periodically checked using Hydranal-Eichstandard 5.0 (Riedel de Haen).

2.3. Density, viscosity, conductivity and pH

Density and dynamic viscosity measurements were conducted using an Anton Paar DMA 45 density meter and an Anton Paar AMVn automated microviscometer, respectively. Temperature was always kept constant at 25°C. The density of the different DES samples is ca. 0.9 g cm⁻³.

Conductivity measurements were performed at room temperature using an Orion 150Aplus conductivity meter, manufactured by Thermo Electron Corporation. Cell constant values have been periodically determined using solutions with known conductivity.

Measurements of the pH of the aqueous solutions were performed using a pH-510 instrument manufactured by XS Instruments. Calibration has been performed using standard solutions at pH 4.00, 7.00 and 10.00 at 25°C.

2.4. Electrochemical measurements

The electrochemical measurements were performed with an Autolab PGSTAT12 (Metrohm Ecochemie) potentiostat/galvanostat, in a single-compartment three-electrode cell containing 0.5 mL of DES, at room temperature.

Au and GC electrodes (diameter 1 mm, Cypress Systems) were used as bulk working electrodes. The GC electrode was polished using DP-Paste P 1 µm (Struers) on glass until a mirror-like surface was obtained and then sonicated for 5 min in pure ethanol. The Au electrode was polished using 0.1 µm alumina powder on DP-NAP-T Struers foil; in addition, in order to clean the surface, an electrochemical pre-treatment was performed by recording 50 voltammetric curves in ultrapure 0.5 M H₂SO₄ solution, from +1.55 to -0.30 V at 100 mV/s, using a Ag/AgCl (KCl 3.5 M) electrode as the reference electrode (Amel) and a 0.5 mm Pt wire as the auxiliary electrode.

The electrochemical behaviour of different electrodes in DESs was tested using a common reversible redox probe, namely ferrocene. Ferrocene solution was prepared by pouring 100 µL of DES into an Eppendorf tube and adding a small amount of ferrocene (a spatula tip). The mixture was then sonicated for five minutes. This procedure leads to a DES saturated with ferrocene, as a small amount of crystals is still left on the bottom. The

concentration of ferrocene is ca. 70 mM, as determined by mass spectroscopy experiments described in Section S9.

In the electrochemical investigations in DES, due to the nature of the solvent and the small volumes employed, a 0.5 mm Ag wire coated with AgCl was the reference electrode for bulk Au and GC working electrodes. In order to obtain a reproducible reference electrode, 3 cm long Ag wire was dipped in aqueous 0.1 M HCl and a constant potential of +0.90 V vs. Ag/AgCl (KCl 3.5 M) was applied for 600 s. The potential values given for GC and Au working electrodes are referred to this reference electrode.

In addition, disposable electrodes were employed, namely Pt (Micrux, ED-SE1-Pt) and boron doped diamond (BDD, Dropsens, DRP BDD10) electrodes. The relevant technical features are shown in Section S2 in Supplementary Materials. The potential values given for Pt and BDD working electrodes are referred to the reported reference electrode (Table S3 in the Supplementary Information). When using disposable electrodes, the electrochemical measurements in the DESs were performed by dropping 40 μ L of the DES onto the cell surface.

Voltammetric curves were recorded starting from open circuit potential (OCP), at 10 and 50 mVs^{-1} potential scan rate. In order to restore the diffusion layer, DESs have been stirred for 20 s between two subsequent potential sweeps, the working electrode being at OCP. All electrochemical tests have been carried out at room temperature, either in equilibrium with the atmosphere, i.e. in the presence of dissolved oxygen, or in deaerated solutions obtained by bubbling nitrogen through for 15 min.

2.5 Liquid-liquid extraction of metallic species

Liquid-liquid extractions were conducted using the prepared hydrophobic DESs as extractants at room temperature. An aqueous solution containing a salt of the metallic cation under investigation was mixed with 200 to 1000 μ L of DES in a 1:1 volume ratio in a centrifuge tube. The tube was vigorously shaken for 30 seconds and the mixture left still for some minutes until the phase separation of the DES and aqueous solutions was observed.

The aqueous solvent media for the extraction were ultrapure water, a 0.1 M buffer solution at pH 7 prepared from monobasic and dibasic potassium phosphate, 0.1 M HCl, 0.1 M H_2SO_4 and 0.1 M KOH. Species adopted for the extraction experiments were $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2$, NiCl_2 , $\text{Ni}(\text{NO}_3)_2$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$.

It is worth noticing that the nature of the Cr(VI) species in aqueous solution depends both on pH and concentration of the metal. Literature suggests that chromate ions are the most

abundant species above neutral pH [13] and a mixture of chromate, hydrogen chromate and dichromate ions is present in mildly acidic conditions.

3. Results and discussion

3.1 Electrochemical behaviour of hydrophobic DESs

In order to prepare DESs containing different amounts of water, four procedures have been adopted, as detailed in the Section 2.1. Electrical conductivity and dynamic viscosity of the hydrophobic DES under investigation, at different water contents, are reported in Table 1. The electrical conductivity of the solvents with water content below 2% w/w was found to be too low and their viscosity too high for a medium to be used in electrochemistry. Only DES4, with a water content of 2.4% w/w, displayed conductivity and viscosity suitable to lower the solution resistance to acceptable values and to allow effective mass transfer to and from the electrode surface. It was consequently used in the reported electrochemical studies, unless otherwise stated. As a possible explanation to these findings, water is supposed to disrupt the hydrogen bond interactions between the HBD and HBA in the DES, which increase ionic mobility within the medium.

The potential window, i.e. the values of the onset of the anodic and cathodic discharges of the solvent, has been determined at different electrode materials by linear sweep voltammetry (Table 2 and Figure S1 in Supplementary Materials). The available potential window between the anodic and cathodic solvent breakdown was quite wide, varying from ca. 1.5 V with Au and Pt electrodes to ca. 2.6 V with GC and BDD electrodes. The voltammetric tests were carried out in oxygen-containing solvents in order to simulate actual applicative conditions: the oxygen reduction peak is well detectable. The removal of oxygen by deaeration with nitrogen leads to the disappearance of this peak as discussed in Section 3.2.

Considering the DES formulation, the oxidation of chloride ions [14,15] could be responsible for the anodic limit; on the other hand, the cathodic limit may be ascribed to the reduction of carboxylic moieties or of tetrabutylammonium cations [14,15]. Reduction of water present in DESs cannot be excluded.

Features of the charge transfer processes in hydrophobic DES4 were evaluated by studying the electrochemical behaviour of ferrocene, a prototypical reversibly oxidised probe (Figure 1 and Figure S2 in Supplementary Materials). The voltammetric behaviour was repeatable and reproducible at all four electrodes, as shown by negligible differences exhibited over 10 subsequent potential scans and between three different electrodes. The

peak-to-peak separation of the cathodic and anodic peaks was larger than 60 mV, which is a typical value for a reversible one-electron redox couple (Table S4 in Supplementary Materials). The peak potential difference at 10 mV/s sweep rate varied between 100 mV and 300 mV, and was the smallest on BDD and GC electrodes. At higher sweep rate of 50 mV/s, the potential separation increased but was still relatively small, especially with Au and BDD electrodes. Similar peak-to-peak separations have been observed in ionic liquids and hydrophilic DESs [16]. Even though the peak separation in voltammograms of Figure 2 increased with scan rate, the redox potential, calculated as the half sum of the anodic and cathodic peak potentials, did not change, because the anodic and cathodic peaks are shifted by the same amount. A linear relationship between the anodic peak current and the square root of the potential scan rate (Figure S3 in Supplementary Materials) shows that the charge transfer process is diffusion controlled. It may be interesting to note that the cathodic to anodic peak current ratio, after a proper background subtraction, is ca. 1.25, which suggests sorption of ferricinium ion on the electrode surface.

The apparent quasi-reversible behaviour of the ferrocene/ferricinium redox couple supports the possibility to adopt DES4 in electrochemical applications. Based on experiments using three separate electrodes, the best reproducibility was observed with the bulk GC electrode (Figure 1), and, therefore, further investigations were carried out using GC, even though it did not display the highest reversibility toward ferricinium ion/ferrocene redox couple.

In order to show the effect of water content, voltammograms of ferrocene solution at the different amount of water content proper of DES1, DES2, DES4 were recorded. Figure 3 shows that the lower the water content of the DES the larger the peak separation and the lower the current, which can be ascribed to decreased conductivity, inducing ohmic drop, and increased viscosity, lowering the rate of mass transfer. An anodic shift of the formal redox potential of ferrocene was also evident with lower water content, which implies some form of destabilisation of ferricinium ion in drier DES. However, we could not find reliable explanation to the redox potential shift of the ferrocene/ferricinium couple [17], based on the properties of the different DESs.

In order to use the DES in extraction processes we first had to understand how it behaved in contact with various aqueous phases. Therefore, we have equilibrated DES4 with equal volumes of aqueous phases of different ion content and pH. The changes occurring in the DES composition are largely neglected in the literature reports published so far.

Initially, 1 ml of DES4 was shaken with 1 ml of ultrapure water and the phases were allowed to separate. The chloride ion content of the aqueous phase after extraction was

determined by the Mohr's titration method, and the amount of TBA and DA was estimated by quantitative NMR (see Sections S5 and S6 in Supplementary Materials). The concentrations of both chloride and TBA ions were close to each other, and can be assumed equal within the experimental error limits. This suggests that TBACl was extracted predominantly as an ion pair. The concentrations of TBA and Cl^- in the aqueous phase were large, close to 1 M, which shows that a significant fraction of TBACl in DES was extracted into water. This was also evidenced by the increase of the volume of the aqueous phase. On the other hand, only ca. 1% of DA was transferred to the aqueous phase, and the observed decrease of pH of the aqueous phase, down to 2.5, can be explained by the deprotonation of DA. The TBACl/DA ratio in the water-saturated DES phase decreased, but the mixture was still a clear liquid and its melting point was still below the room temperature. In addition, the aqueous phase became cloudy, due to the formation of an emulsion: the concentrations of TBACl and DA were above the relevant critical aggregation concentration [18,19]. In principle, the use of a DES based on an alkyl ammonium salt possessing longer alkyl chains would reduce the loss of cations into the aqueous phase but, at the same time, may be supposed to reduce conductivity and to increase viscosity.

Upon contact with strongly acidic aqueous solutions (0.1 M), DES4 formed a gel (Figure S6 in Supplementary Materials). Similar results were obtained using both HCl and H_2SO_4 , suggesting that the nature of the anion in the acidic solution did not play a role. The hydrated protons may interfere with chloride ions bridging TBA and DA *via* hydrogen bonding, which destabilizes the internal structure of the DES. The gel was liquefied by mild heating at ca. 30°C but, after cooling down to room temperature, it reformed. No jellification was observed by contact with neutral and alkaline aqueous solutions.

3.2 Liquid-liquid extraction of Cr(VI)

The use of DES4 for the liquid-liquid extraction of Cr(VI) species from aqueous solutions was considered. Cr(VI) aqueous solutions are strongly coloured and the occurrence of extraction can be easily checked by naked eye, even at 0.1 mM initial aqueous concentration. When the extraction was carried out from 5 and 50 mM aqueous unbuffered solutions (mildly acidic, pH of 4.1 and 4.5, respectively), the Cr(VI) ions were quantitatively transferred to DES4, as shown by the orange colour of DES and the resulting colourless aqueous solution (Figure 4). Similar results were observed in case of phosphate buffer solutions at pH 7 (Figure S7 in Supplementary Materials); on the contrary, only partial extraction is observed using 0.1 M NaOH solutions.

An extraction from 500 mM Cr(VI) solution (unbuffered pH 5.6) was far from being quantitative, as shown by the orange colour of the aqueous phase after the extraction. In this case, part of DES formed a separate liquid phase at the bottom of the tube, with a density higher than that of the aqueous solution. An estimation of the maximum Cr(VI) concentration in the DES phase was at least 50 mM. This value is higher than those reported for other materials suggested for the Cr(VI) removal from aqueous solutions in remediation [11]. In the case of 50mM initial concentration, UV-Vis spectroscopy (Section S8 in Supplementary Materials) revealed that the residual concentration of Cr(VI) species in aqueous solution is below 0.01 mM: the extraction efficiency exceeds 99%. The success of extraction can be attributed to the high affinity of TBA to Cr(VI) [20]. TBA and chromate form a strong ion pair in acidic aqueous solutions but its stability is weak under basic conditions, which can explain the failure of extraction in 0.1 M NaOH. TBA has also previously been used for the extraction of Cr(VI) from aqueous media and proved to work best in acidic conditions [21]. It is noteworthy that after ca. 12 hours the DES phase became blue in colour, suggesting that Cr(VI) species have been reduced to Cr(III) by the DES components. This reaction would be favoured by the stabilization of Cr(III) as a chloride complex [22]. This process meets the requirement to reduce Cr(VI) after the extraction process in order to lower its toxicity [11].

Finally, the electrochemical behaviour of Cr(VI) species in DES was studied after the extraction process carried out in ambient atmosphere. These experiments are necessary to the development of procedures for in-line amperometric sensing, as well as for electroremediation, suitable to operate directly in DES. The voltammograms on bulk GC electrode show, for the first time, that a metallic species, namely Cr(VI), is electroactive in a hydrophobic DES. The voltammograms exhibit a cathodic peak at ca. -0.90 V vs. Ag/AgCl, which partially overlaps the oxygen reduction (Figure 5). Deaeration of DES decreases the height of the cathodic peak more than expected from the sum of Cr(VI) and oxygen reduction, suggesting that the two processes interact [23].

3.3 Liquid-liquid extraction of other metallic species

Additional liquid-liquid extraction tests were carried out using other metallic species, namely Cu(II), Ni(II) and Cr(III), at different concentrations (50 and 500 mM). The metal ions were dissolved in an unbuffered aqueous phase. Similarly to Cr(VI), all the metal species were selected considering their importance in industrial processes and impact on the environment if released [18,19]. The results of extraction experiments of the listed cations are reported in Table 3. In the case of Cu(II) similar results have been obtained for

chloride and nitrate salts: jellification was observed at 50 mM while a minimal quantity was extracted at 500 mM concentration level. As to Ni(II), jellification was observed only in the case of NiCl₂ at the lowest concentration level. The efficiency of the extraction seemed to be negligible in the case of NiCl₂ at 500 mM concentration level, Ni(NO₃)₂ and CrCl₃. These results were confirmed by ICP-MS experiments: the final concentration of Ni(II) and Cr(III) species in DES4 did not exceed ca. 0.1 mM, i.e. a tiny fraction of the value in aqueous solution. Hence, we can conclude that selective extraction of Cr(VI) species is feasible.

It is worth noticing that the use of buffered solutions for the extraction experiments is problematic; as to phosphate buffer, Cu(II), Ni(II) and Cr(III) phosphates are poorly soluble and precipitation of hydroxides is observed in alkaline conditions. Finally, similar extraction experiments were carried out using a conventional anionic redox probe, namely Fe(CN)₆⁴⁻. Quantitative extraction from unbuffered aqueous solutions was obtained using concentrations of 1 and 5 mM (pH 6.69 and 7.17, respectively).

4. Conclusions

New insights on the physico-chemical properties of a prototypical hydrophobic DES, based on TBACl and DA, are reported. In particular, the viscosity and electrical conductivity are strongly dependent on the water content of the DES. The electrochemical behaviour of a hydrophobic DES is investigated for the first time and the DES is employed to extract Cr(VI) species from an aqueous phase. The extracted metal species are electroactive in DES, opening the possibility to develop in-line amperometric sensors suitable for monitoring the extraction process and electroremediation reactors. The extraction of Cr(VI) from aqueous phase is effective and the maximum concentration in DES is quite high. Spontaneous reduction to Cr(III) occurs.

5. References

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Captions

Figure 1 – Voltammetric responses of a GC electrode in the ferrocene-saturated DES4 at 50 mVs⁻¹ potential scan rate. Three replicates are shown.

Figure 2 – Voltammetric responses for DES4 in presence of ferrocene at different scan rates on a GC electrode.

Figure 3 – Electrochemical responses of ferrocene on a GC electrode employing four DESs with different water content, 50 mV s⁻¹ potential scan rate.

Figure 4 – Extraction in DES4 from an aqueous solution of Cr(VI) species at different concentrations: 5 mM (A), 50 mM (B) and 500 mM (C).

Figure 5 – Voltammetric responses of a GC electrode in the DES4 containing Cr(VI) at 10 mVs⁻¹ potential scan rate.

Table 1 – Dynamic viscosity and conductivity of the investigated DESs. Standard deviations are in parenthesis.

Table 2 – Anodic and cathodic potential limits of DES4. The reference potential to which the reported values are referred is given in Table S3 in the Supplementary Materials.

Table 3 – Results of the extraction experiments. Initial pH values of the solutions before extraction are also reported.

| DES | Preparation method | Dynamic viscosity (mPa s) | Conductivity ($\mu\text{S/cm}$) | Water content (% w/w) |
|------|---|---------------------------|-----------------------------------|-----------------------|
| DES1 | Anhydrous | 429 (9) | Not available | 0.014 (0.008) |
| DES2 | Equilibrium with atmosphere | 403 (17) | 40.5 (3.53) | 0.11 (0.07) |
| DES3 | Equilibrium with water-vapour saturated at 30°C | 113 (1) | 341 (30) | 1.70 (0.03) |
| DES4 | Equilibrium with water-vapour saturated at 60°C | 81 (10) | 445 (46) | 2.4 (0.2) |

Table 1

| Electrode | Anodic limit (V) | Cathodic limit (V) | Onset of the O_2 reduction peak (V) |
|-----------|------------------|--------------------|--|
| GC | +1.30 | -1.30 | -0.30 |
| Au | +0.70 | -0.85 | -0.40 |
| Pt | +0.60 | -0.75 | -0.20 |
| BDD | +1.30 | -1.35 | -0.30 |

Table 2

| Salt | Concentration (mM) | pH |
|----------------------------|--------------------|------|
| CuCl_2 | 50 | 4.25 |
| | 500 | 3.02 |
| $\text{Cu}(\text{NO}_3)_2$ | 50 | 4.02 |
| | 500 | 3.03 |
| NiCl_2 | 50 | 6.06 |
| | 500 | 4.18 |
| $\text{Ni}(\text{NO}_3)_2$ | 50 | 4.84 |
| | 500 | 4.72 |
| CrCl_3 | 50 | 3.22 |
| | 500 | 1.57 |

Colour code

XXXX jellification

XXXX partial extraction

XXXX no jellification, no extraction

Table 3

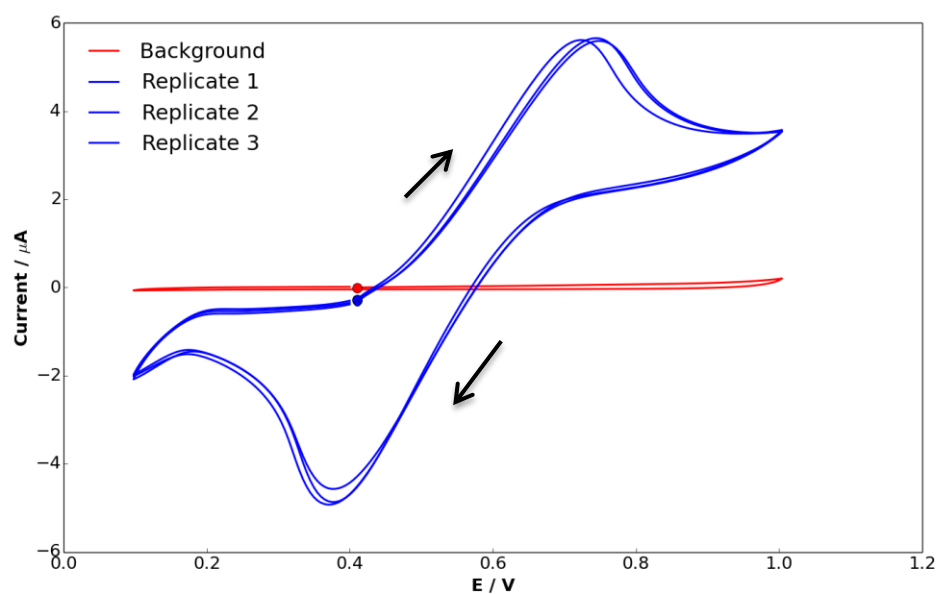


Figure 1 – Voltammetric responses of a GC electrode in the ferrocene-saturated DES4 at 50 mVs^{-1} potential scan rate. Three replicates are shown.

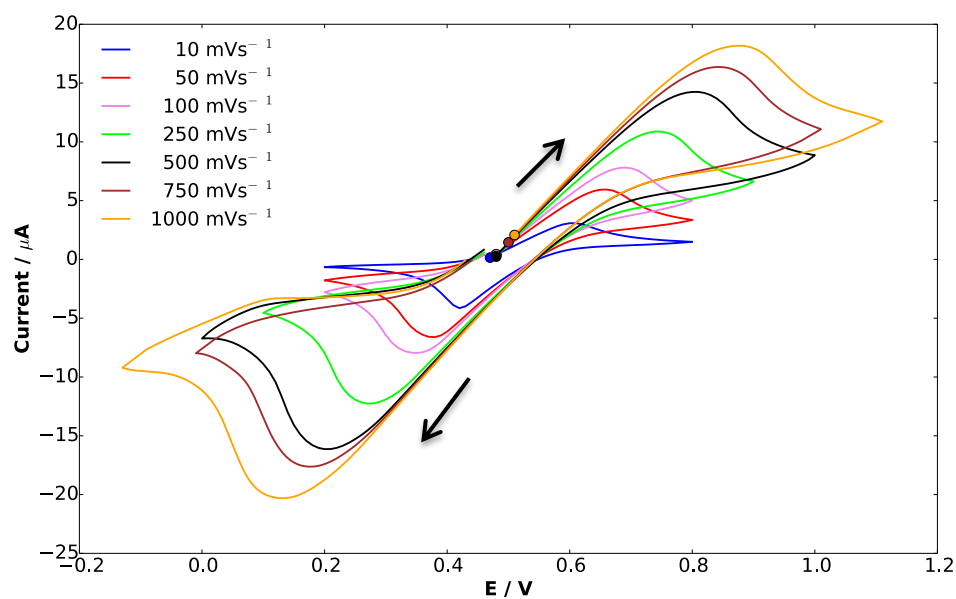


Figure 2 – Voltammetric responses for DES4 in presence of ferrocene at different scan rates on a GC electrode.

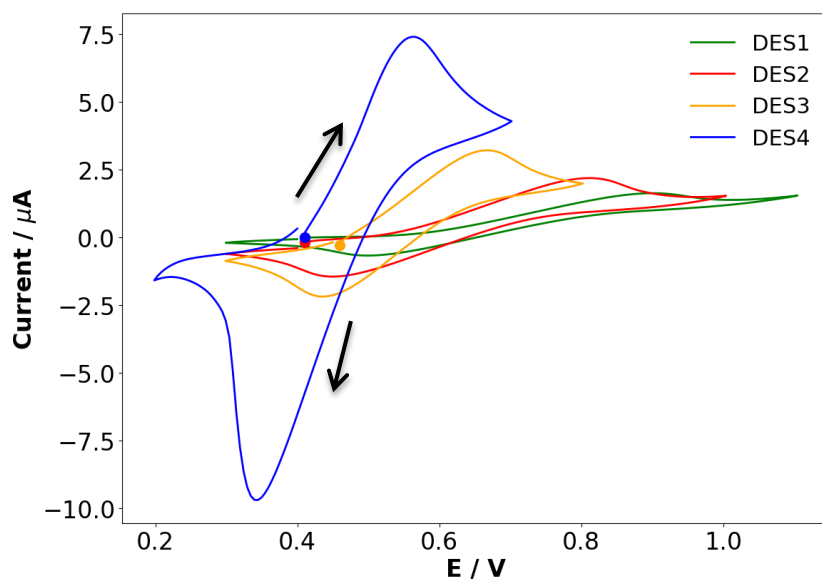


Figure 3 – Electrochemical responses of ferrocene on a GC electrode employing ~~three~~ four DESs with different water content, 50 mV s⁻¹ potential scan rate.

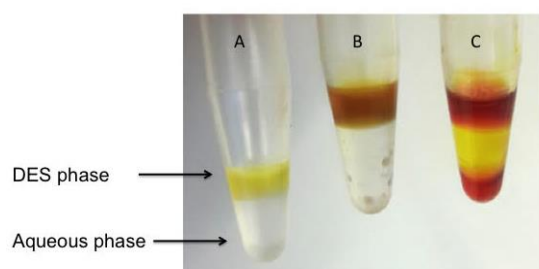


Figure 4 – Extraction in DES4 from an aqueous solution of Cr(VI) species at different concentrations: 5 mM (A), 50 mM (B) and 500 mM (C).

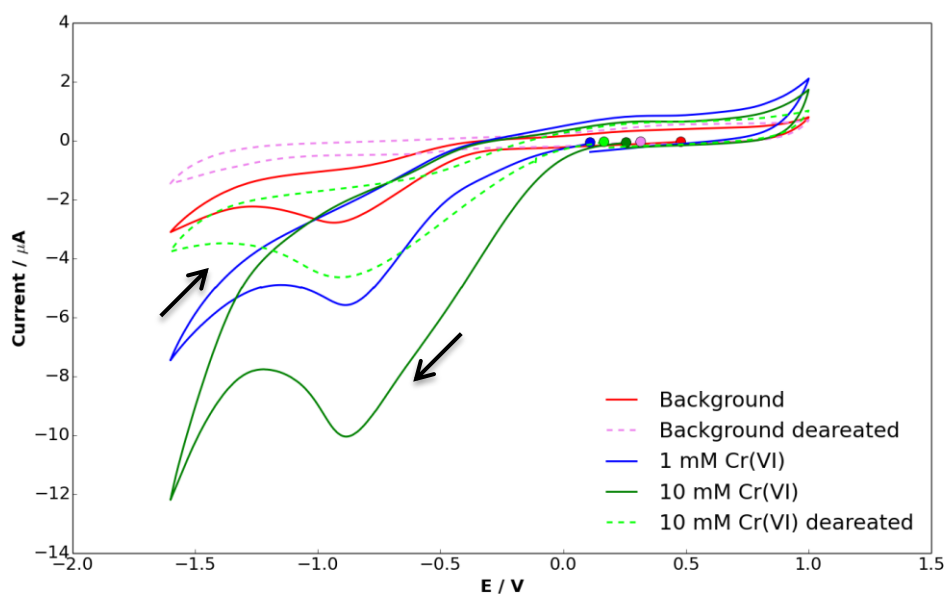


Figure 5 – Voltammetric responses of a GC electrode in the DES4 containing Cr(VI) at 10 mVs⁻¹ potential scan rate.