Cyclic Voltammetry of Iron (III) Acetylacetonate in Quaternary Ammonium and Phosphonium Based Deep Eutectic Solvents

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The electrochemical behaviour of commercially sourced iron (III) acetylacetonate is investigated in six different deep eutectic solvents (DESs) formed by means of hydrogen bonding between ammonium and phosphonium salts with glycerol, ethylene glycol and tri-ethylene glycol. Cyclic voltammetry (CV) is employed to determine kinetic and mass transport properties of the electrolytes. Diffusion coefficient, D, of the iron salt in all studied DESs is found to lie between 1.06×10^{-9} to 1.08×10^{-8} cm^2 s^{-1} (the salt does not dissolve in a DES prepared from choline chloride and glycerol while not producing any measurable CV peaks in a couple of others). The rate constant for electron transfer across the working electrode/DES interface is estimated to lie between 1.34×10^{-4} and 2.08×10^{-4} cm s^{-1}. From a range of criteria for electrolyte selection (peak potential separation near 59 mV for a one-electron transfer reaction, high diffusion coefficient and heterogeneous rate constant) only the ammonium based DESs prepared from choline chloride and ethylene glycol or tri-ethylene glycol appear to be worthy of further investigation.

1. INTRODUCTION

The importance of iron (III) acetylacetonate or Fe(acac)$_3$ has been emphasised to a small extent in the literature. Its main industrial uses stem from its catalytic applications in organic chemistry,

particularly with alkenes [1]. For instance, it has been known to catalyse the dimerization of isoprene to 1,5-dimethyl-1,5-cyclooctadiene and 2,5-dimethyl-1,5-cyclooctadiene [2]. It also found catalytic applications for the polymerization of 1,3-benzoxazine [3] as well as for reactions involved in the formation of 1,3-oxazolidine products [4]. Some properties of Fe(acac)$_3$ is tabulated below (Table 1) [5].

Table 1. Physical properties of iron acetylacetonate (as given in Wikipedia, the free encyclopaedia on the web)

CAS Number	14024-18-1	
Molecular formula	Fe(C$_5$H$_7$O$_2$)$_3$	
Molar mass	353.17 g mol^{-1}	
Manifestation	Red solid	
Density	5.24 g cm^{-3}	
Melting point	180–181 °C	
Boiling point	100 °C (at 13.00 kPa)	
Water Solubility	2 g L^{-1}	
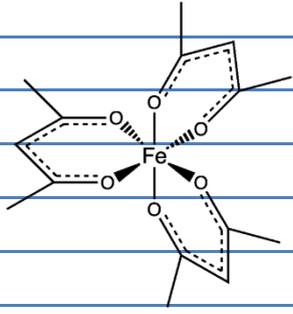
The application of Fe(acac)$_3$ with ionic liquids (ILs) seems to be scarce in the literature [6]. Fortunately, some electrochemistry has been reported for this material, whether directly [7] or indirectly [8]. Other metallic-based acetylacetonate salts have seen more applications as possible electrolytes for redox flow batteries since the late 1980s [9-15]. Detailed electrochemical kinetics as well as charge/discharge experiments in prototype cells has also been reported [16-20], but nothing seems to be available regarding their electrochemical properties in ILs as far as the authors are aware.

Having said that, ILs have also seen limited industrial applications as a consequence of high costs, low purity and toxicity [21,22]. Thus deep eutectic solvents (DESs) are in contention for replacing ILs [23-25]. They are basically organic-based salts that interact by means of metal halide bonds or hydrogen bonds along with the anion of a salt, as opposed to relying purely on electrostatic forces between anion and cation as in the case of conventional ILs. DESs with various hydrogen bond donors have been demonstrated using acids, amides, alcohols and metal halides [26,27]. These liquids can be prepared in a wholesome manner, some types are insensitive to atmospheric moisture and most importantly they are biodegradable due to which, the toxic nature of its constituents are reasonably well portrayed [21,27,28]. In addition, DESs have similar ionic conductivities as ILs [25] thereby eliminating the need to rely on supporting electrolytes for cyclic voltammetry (CV) studies.

In this work, the electrochemistry of Fe(acac)$_3$ is investigated in six DESs by means of CV. Prior to a detailed investigation upon this salt, a qualitative analysis on seven metallic based acetylacetonate salts is conducted in glycerol and tri-ethylene glycol-based DESs. Solubility and electrochemical data have not been reported for these salts in DESs before and this paper aspires to redress this issue.

2. EXPERIMENTAL SECTION

2.1. Chemical Reagents.

DESs from glycerol and tri-ethylene glycol were synthesised and used. The chemical structures of the salts and hydrogen bond donors are illustrated below (Figure 1) [21]. The chemical structure of a metal-based acetylacetonate salt (the metal atom is denoted as M) is also given in Figure 1 [9]. The molar ratio for synthesising the DESs and their physical properties are detailed in an earlier investigation [21] while their respective abbreviations are shown in Table 2.

Table 2. Abbreviations adopted in this paper for DESs synthesised from six different salts using ethylene glycol (EG), tri-ethylene glycol (TEG) and glycerol (G) as the hydrogen bond donors.

Salt	HBD	Molar ratio (salt:HBD)	Abbreviation	E_{OL} (V)	E_{RL} (V)
C_{19}	TEG	1:3	DES 1	+1.30	-1.35
ChCl	TEG	1:2	DES 2	+1.00	-1.30
C_{19}	G	1:3	DES 3	+1.10	-1.45
ChCl	G	1:2	DES 4	+1.10	-1.75
N,N	G	1:2	DES 5	+0.9	-1.25
ChCl	EG	1:2	DES 6	+1.0	-1.0

C_{19} = Methyltriphenylphosphonium bromide; ChCl = Choline chloride; TEG = Tri-ethylene glycol; G = Glycerol; EG = Ethylene glycol; N,N = ,N-diethylenethanol ammonium chloride; E_{OL} = oxidation potential limit in CV; E_{RL} = reduction potential limit.

The components for preparing the DESs were sourced from Sigma-Aldrich (> 99% purity) and Merck (N,N-diethylenethanol ammonium chloride, synthesis grade). The acetylacetonate salts of chromium, cobalt, manganese, copper, nickel (Merck, synthesis grade) iron and zinc (Sigma-Aldrich, 99% purity) were employed as received. Molecular sieves 4A were also supplied by Sigma-Aldrich for the purposes of drying the electrolytes. Ultra-pure nitrogen with less than 1 ppm of oxygen was provided by BOC (Guildford, Surrey, U.K.) and was passed through a column containing molecular sieves 4A in order to remove traces of moisture.

2.2. Synthesis of DESs.

The DESs were synthesised according to the procedure highlighted in the literature [29]. A jacketed cup reactor comprising of a magnetic stirrer was employed to homogenise the salt and hydrogen-bond donor at a specific temperature and atmospheric pressure until a colourless liquid was produced.
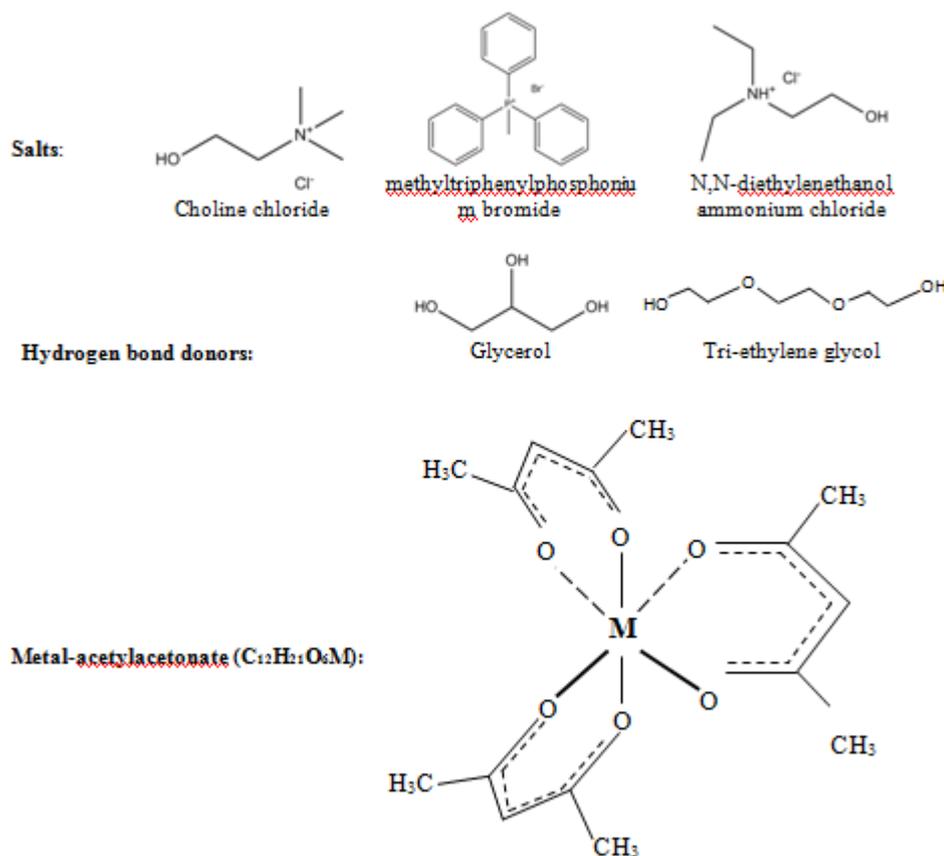
Figure 1. Structures of all the salts, the hydrogen bond donors [21] as well as a general representation of a typical metal-based acetylacetonate [9] (not to scale) used in this study are displayed.

Such experiments were conducted in a glove bag sourced from Sigma-Aldrich (Aldrich® AtmosBag) under a controlled moisture content of not more than 100 ppm. The physical properties of the DESs have been detailed in an earlier investigation [21].

2.3. Determination of solubility of metallic acetylacetonate salts.

Solubility of acetylacetonate salts in the DESs was determined gravimetrically after conducting dissolution experiments at 50 °C for 2 days by means of a magnetic stirrer and hot plate (Fisher Scientific) with in-built temperature settings [29]. All further experiments were conducted at room temperature. Chemicals were weighed on a Sartorius mass balance with an accuracy of ±0.1 mg.

2.4. Electrochemical set-up.

The three electrode cell was provided by Metrohm along with a glassy carbon macro working electrode of 3 mm outer diameter. The cell capacity was 100 mL with a PTFE lid of 15 mm thickness having five holes; three holes were provided for the electrodes (working, reference and counter), one for the nitrogen supply glass tube and one for the exhaust gas outlet tubing. Platinum (Pt) wire was employed as a counter electrode while a silver (Ag) wire acted as a quasi-reference electrode or

AgQRE (Advent Research Materials, UK). The AgQRE was immersed in 65% HNO_3 then rinsed thoroughly with water and ethanol prior to experiments. The glassy carbon working electrode was coated round its edges with PTFE. The working electrode was carefully polished before each electrochemical experiment with 0.25 μm alumina suspensions and cleansed thoroughly using de-ionised water and ethanol (Aldrich, synthesis grade). Electrochemical investigations were conducted at room temperature inside the glove bag using a computer-controlled Autolab potentiostat (Metrohm PGSTAT 302N) with Nova software .

In addition, all electrolytes were sparged with nitrogen for about 30 min prior to commencing CV experiments. After sparging, the gas supply was maintained continuously at the surface of the solution throughout the duration of all CV scans to minimise any opportunities for atmospheric oxygen to dissolve in the electrolyte and interfere with the experimental results.

Despite precautions to minimise moisture content, the hygroscopic nature of the DESs prompted us to measure this important parameter of each electrolyte after undergoing the drying procedure. Karl Fischer titrations were conducted by means of a Cou-Lo Aquamax KF moistness meter in the presence of Cou-Lo Formula A coulometric anodic as well as Cou-Lo Formula C coulometric cathodic solutions (G.R. Scientific, UK). Every DES sample was inoculated into the titration chamber by means of a 100 μL glass syringe having a 7 cm needle (S.G.E., UK). This syringe was washed with ethanol many times prior to being flushed with the DES that needed investigation. The DES was then inserted into the titration chamber to obtain a measurement of its moisture content.

3. RESULTS AND DISCUSSION

3.1. Metal acetylacetonate solubility in DESs.

Solubility experiments involved the dissolution of measured quantities of salt with the DES until clear saturates were obtained.

Table 3 illustrates the molar solubilities of all acetylactonate salts in six different DESs along with the range of moisture contents detected in them. DESs 1 and 4 had low viscosities and were easy to work with thereby allowing all experiments to be carried out at room temperature. However, DESs 3 and 5 had high viscosities, requiring constant heating to maintain their temperatures at 50 °C. If they were not heated then they tended to become semi-solid in nature, akin to a hair styling gel.

From these experiments it was clear that all salts had very poor solubilities with the exception of manganese and zinc acetylacetonates. Complexing agents such as cyanide or ammonia may be used to adjust metal speciation and thus control solubility of the acetylacetonate salts in future studies [30].

3.2. Electrochemical potential windows of DESs.

CVs were performed in a similar manner as mentioned in the literature [21] for all the DESs. The oxidative potential limit (Table 2) followed the trend of **DES 1 > DES 3 ≈ DES 4 > DES 2 ≈ DES 6 > DES 5** while the reductive potential limit was slightly different in terms of **DES 4 > DES 3 > DES 1 > DES 2 > DES 5 > DES 6**. The results in this work showed that for all DESs, the electrochemical

potential windows had shrunk in comparison to similar work reported in the literature [21] (CV with DESs made from tri-ethylene glycol appears to be scarce in the literature but based upon the results for DESs synthesised from glycerol and ethylene glycol [21], it was clear that the potential window had indeed shrunk). This issue was because of moisture (Table 3) that could not be eradicated despite the steps taken to do so and also due to the hygroscopic nature of the DESs. Such sensitivity to moisture does not fare well for the fate of such DESs because poor electrochemistry with increasing moisture content means the incorporation of expensive precautionary protocols that could limit their industrial applications.

Table 3. Solubilities of seven acetylacetonate salts in six different DESs prepared as per recommendations in the literature [21,23,25].

Salt	Solubility (M)						Moisture content (ppm)
	DES 1	DES 2[*]	DES 3[*]	DES 4	DES 5[*]	DES 6[$]	
Chromium (III) acetylacetonate	0.004	0.000	0.001	0.000	0.000	0.000	750-789
Manganese (II) acetylacetonate	0.017	0.071	0.035	0.006	0.035	0.018	347-369
Cobalt (III) acetylacetonate	0.004	0.001	0.002	0.001	0.001	0.005	367-391
Copper (II) acetylacetonate	0.004	0.001	0.000	0.000	0.001	0.005	246-285
Nickel (II) acetylacetonate	0.006	0.001	0.020	0.000	0.009	0.001	278-304
Iron (III) acetylacetonate	0.001	0.005	0.001	0.000	0.001	0.002	359-413
Zinc acetylacetonate hydrate	0.800	0.630	0.190	0.450	0.800	0.010	1143-1250

[*]Experiments with DESs 2, 3 and 5 had to be carried out at 50 ^{o}C due to their high viscosities. [$] Results obtained from a DES prepared from choline chloride ethylene glycol for comparison purposes.

3.3. Cyclic voltammetry experiments.

The potential scan of the CV (scan rate of 0.1 V/s) commenced from the open circuit potential to ensure that products formed at the anodic and/or the cathodic limits could not meddle with the values obtained during scan reversal [31]. At first, the CV of the DESs was carried out to determine the background potential scan response commencing from potentials corresponding to anodic values leading to cathodic measurements and ultimately reverting back to the initial denomination. The observation of a sharp current increase for both oxidation as well as reduction limits may be caused by the decomposition of the DES at the potential thresholds [31]. Similar phenomena was also common with investigations performed using IL solvents [32]. After that, the CV of all active electrolytes was performed. For all cyclic voltammograms presented in this work, scans of both the electro-active species and the background electrolyte (i.e., the DES) were plotted together in the same graph as illustrated below.
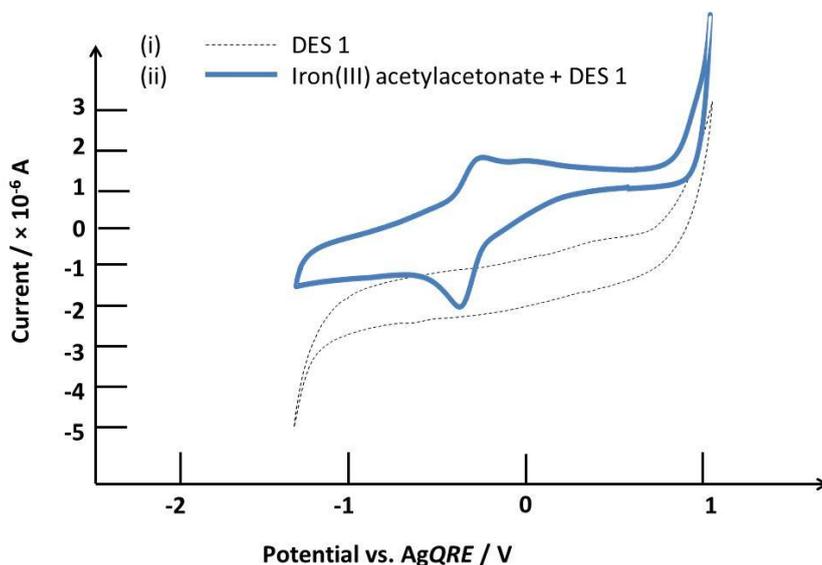
Figure 2. CVs at a scan rate of 0.1 V/s using GC working electrode at 35 °C of (i) DES 1; and (ii) 1 mM iron (III) acetylacetonate dissolved in DES 1.

Figure 2 shows a representative CV of iron (III) acetylacetonate dissolved in DES 1. This happens to be the only metallic acetylacetonate compound that has distinct peaks in their CVs thereby allowing their electrochemical kinetics to be ascertained. This result is consistent with that reported in the literature [33]. The CVs of other acetylacetonate based salts are given in the Appendix. The information in the Appendix highlights some compounds of cobalt, nickel, copper and zinc that have CV peaks but they are not as distinct as for iron to be further analysed. However, iron only showed decent results for three DESs (DES 1, DES 2 and DES 6) and thus these were chosen for further kinetic evaluation.

3.4. Quantitative results from CV of iron (III) acetylacetonates.
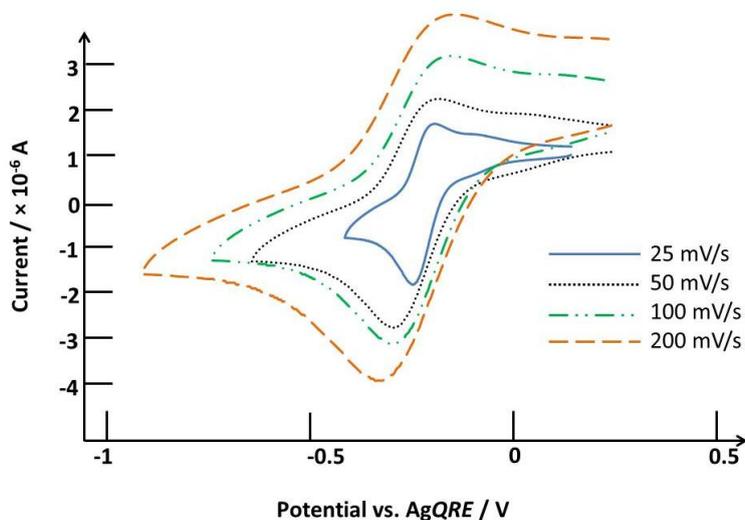
Figure 3. Cyclic voltammetry of the reduction of 1 mM iron (III) acetylacetonate dissolved in DES 2 at varying scan rates using a glassy carbon working electrode.

Figure 3 shows cyclic voltammograms for the redox reaction of 1 mM solution of $Fe(acac)_3$ in DES 1 on a glassy carbon electrode at four diverse scan rates extending from 25 to 200 mV/s (the figures for $Fe(acac)_3$ in two other DESs investigated are not shown as they were similar). As mentioned earlier, all CVs are reported against an AgQRE and a Pt counter electrode. The scan rate dependence indicates that the oxidation of $[Fe(acac)_3]$ to $[Fe(acac)_3]^+$ in DESs follows eq. (1).

$$[Fe(acac)_3] \rightleftharpoons [Fe(acac)_3]^+ + e^-$$

(1)
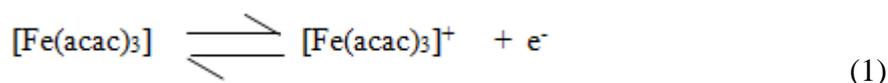
Important quantitative data acquired from CVs of DESs such as values of the $E_{1/2}$ (reversible half wave potential) estimated from $(E_{pa} + E_{pc})/2$ (the average of anodic and cathodic peak potentials), $\Delta E_p = E_{pa} - E_{pc}$ (the peak–to–peak potential separation), i_{pa}/i_{pc} (anodic peak current divided by cathodic peak current) and $W_{1/2}$ (the peak width at half-height) for both oxidation and reduction processes [21], are shown in Table 4. For all investigated DESs, the cathodic and anodic peak currents increased with magnifying scan rate and $i_{pa}/i_{pc}=1.0$ (i.e., the ratio of peak currents for the forward and reverse scans was close to unity) and remained oblivious to the scan rate. The peak potential separation (ΔE_p) from CVs conducted at distinctive scan rates was approximately 0.07 V. A rapid, reversible, one-electron transfer would principally have a $\Delta E_p = 0.059$ V at 298 K. The difference from this ideal value at increasing concentrations and scan rates in the tested DESs was ascribed to the occurrence of uncompensated solution resistance [34,35]. In addition it was observed that for different scan rates the $E_{1/2}$ and $W_{1/2}$ remained constant.

Table 4. Cyclic voltammetric data for oxidation of ferrocene in DESs

DESs	v / ($V.s^{-1}$)	i_{pa}/i_{pc}	ΔE_p / (mV)	$E_{1/2}$ / (mV)	$W_{1/2}(mV)$	
					Oxidized species	Reduced species
DES 1	0.025	1.12	77	186	227	271
	0.050	1.08	77	188	242	278
	0.100	0.95	77	186	253	271
	0.200	0.90	77	186	249	269
DES 2	0.025	1.02	71	179	239	240
	0.050	0.96	73	183	245	239
	0.100	0.98	75	181	245	258
	0.200	1.08	75	180	249	248
	0.025	0.92	75	159	225	220
DES 6[*]	0.050	1.06	78	162	235	219
	0.100	1.08	82	161	235	228
	0.200	1.05	80	160	230	224

[*] This DES was made from ChCl and EG at 1:2 molar ratio

The potential of a redox couple could be estimated in an enhanced manner by means of the half-wave potential ($E_{1/2}$) instead of the cathodic (E_{pc}) or anodic peak (E_{pa}) potentials, since both E_{pa}

and E_{pc} varied in response to the scan rates while $E_{1/2}$ remained oblivious to this independent variable; as was expected for an estimated reversible system. It was found that $E_{1/2}$ shifted towards progressive potentials conforming to: **DES 6 > DES 2 > DES 1**. This order revealed that the oxidation of $[Fe(acac)_3]$ to $[Fe(acac)_3]^+$ became more arduous on changing from DES2 to DES1.
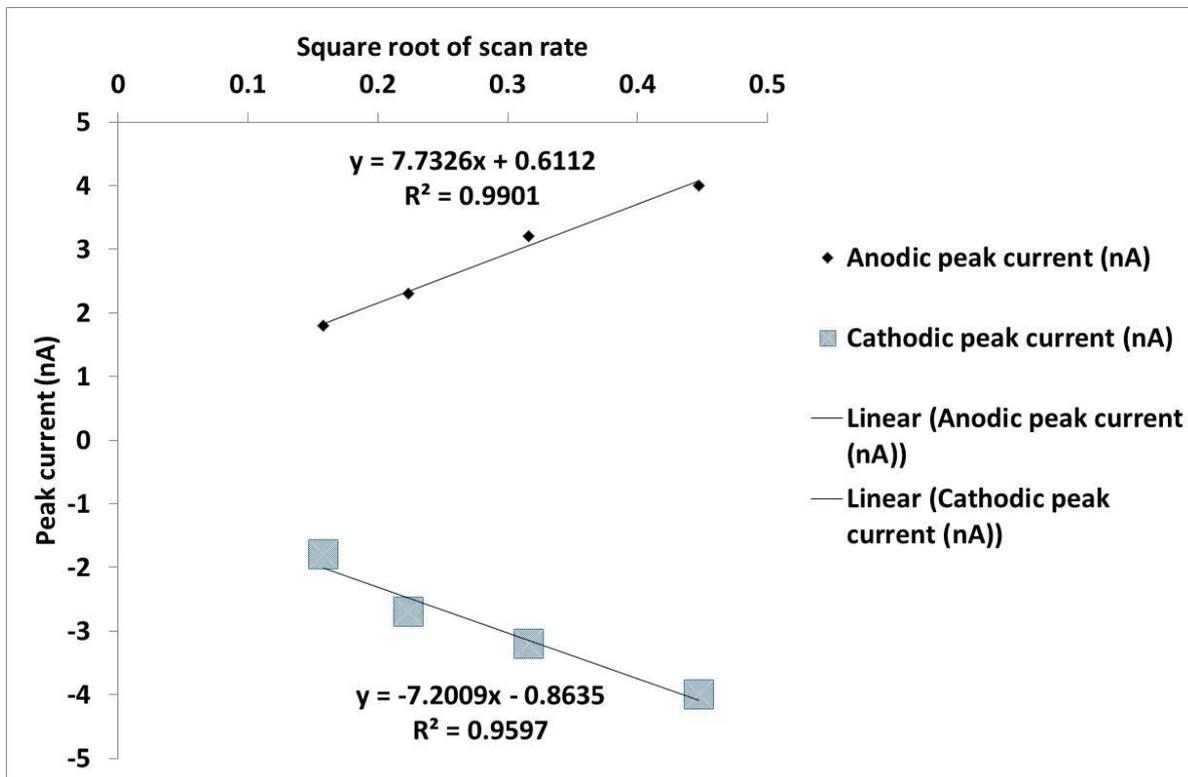

Figure 4. Linear dependence of peak current vs. square root of scan rates for 1 mM $[Fe(acac)_3]/[Fe(acac)_3]^+$ using a Pt electrode in DES 2.

In consideration of the above scenario, an assumption about the electrochemical reversibility of $[Fe(acac)_3]/[Fe(acac)_3]^+$ at the respective scan rates was made in order to calculate the diffusion coefficients of $Fe(acac)_3$ and $Fe(acac)_3^+$ in the DESs. The peak current was found to vary in a linear manner in response to the square root of the scan rate on glassy carbon electrodes (Figure 4). This confirmed that the process was mainly regulated by the diffusion of $[Fe(acac)_3]/[Fe(acac)_3]^+$ in DES 2 (plots of other DESs are not shown).

Table 5. Concentration-dependent diffusion coefficients of $Fe(acac)_3$ in DESs as well as their rate constants

DESs	D (cm^2 s^{-1})	k_s (cm s^{-1})
DES 1	$1.06 \times 10^{-9}(\pm 0.08)$	$1.34 \times 10^{-4}(\pm 0.03)$
DES 2	$2.42 \times 10^{-9}(\pm 0.07)$	$1.52 \times 10^{-4}(\pm 0.02)$
DES 6	$1.08 \times 10^{-8}(\pm 0.09)$	$2.08 \times 10^{-4}(\pm 0.06)$

The diffusion coefficients (*D*) were computed by means of the Randles-Sevcik equation (Eq. 2) [21], which postulates that mass transfer takes place mainly by diffusion (*D* values are shown in Table 5). As per the Randles-Sevcik equation, i_{pa} and i_{pc} are proportional to $v^{1/2}$ and thus a graph of i_{pa} or i_{pc} against $v^{1/2}$ shows a straight line response whose slope may be employed to estimate diffusion coefficients.

$$i_p = 0.4463 \, nFAC(nFvD/RT)^{1/2} \tag{2}$$

where i_p represents the peak current (A), *n* is equivalent to the number of electrons transferred in the electrochemical process (electron stoichiometry), *A* is the electrode area (cm^2), *D* is the diffusion coefficient of the electroactive species (cm^2 s^{-1}), *v* is the potential scan rate (V s^{-1}), C_O is the bulk concentration of the electroactive species (mol cm^{-3}), *R* is the universal gas constant (J mol^{-1} K^{-1}), *T* is the absolute temperature (K) and *F* is Faraday's constant (C mol^{-1}).

Nicholson's method [36] was the first approach used to evaluate the heterogeneous rate constant (k_s) using data from CV of redox couples. Anodic and cathodic peak separations from a background were subtracted from a voltammogram for the simple one electron transfer reaction and further used to determine ψ from which k_s was estimated using eq. 3:

$$\psi = \frac{k_S}{(\pi a D_O)^{1/2}} \tag{3}$$

Where $a=nFv/RT$, D_O is the diffusion coefficient, *v* is the scan rate while all other symbols have their standard meanings [21]. For this experiment the data was obtained at 298.15 K, C = 1.00 mM, $v = 0.1$ V s^{-1} and thus linear diffusion was expected to dominate. Once diffusion coefficients are determined for an electrochemically reversible system, k_s may be determined from cyclic voltammograms obtained at a range of scan rates and by fitting the perceived peak separation changes to tabulated values [21,36]. The values of the heterogeneous rate constant were determined as 1.34×10^{-4}, 1.52×10^{-4} and 2.08×10^{-4} cm s^{-1} in DES1, DES2 and DES 6, respectively. Upon comparison of k_s values, it can be inferred that the rate constants for ammonium based DESs were greater than those for phosphonium based ones, which was also confirmed from experiments performed on the same DESs using ferrocene [21].

4. CONCLUSIONS

Six different DESs prepared from hydrogen bond donors of ethylene glycol, tri-ethylene glycol and glycerol were evaluated as solvents for seven different commercially sourced metallic acetylacetonate salts. Cyclic voltammetry showed that only the iron (III) acetylacetonate gave reasonable peaks that could be used to estimate diffusion coefficients and electrochemical rate constants in three out of six DESs. It was concluded that the ammonium based DES gave better electrochemical kinetics (2.08×10^{-4} cm s^{-1}) in comparison to its phosphonium counterpart (1.34×10^{-4} cm s^{-1}) thereby suggesting further work to be more dedicated on the former mainly. The result was altogether not surprising because the viscosity of ammonium based DESs was discovered to be lower than that of phosphonium DESs in previous investigations.

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APPENDIX
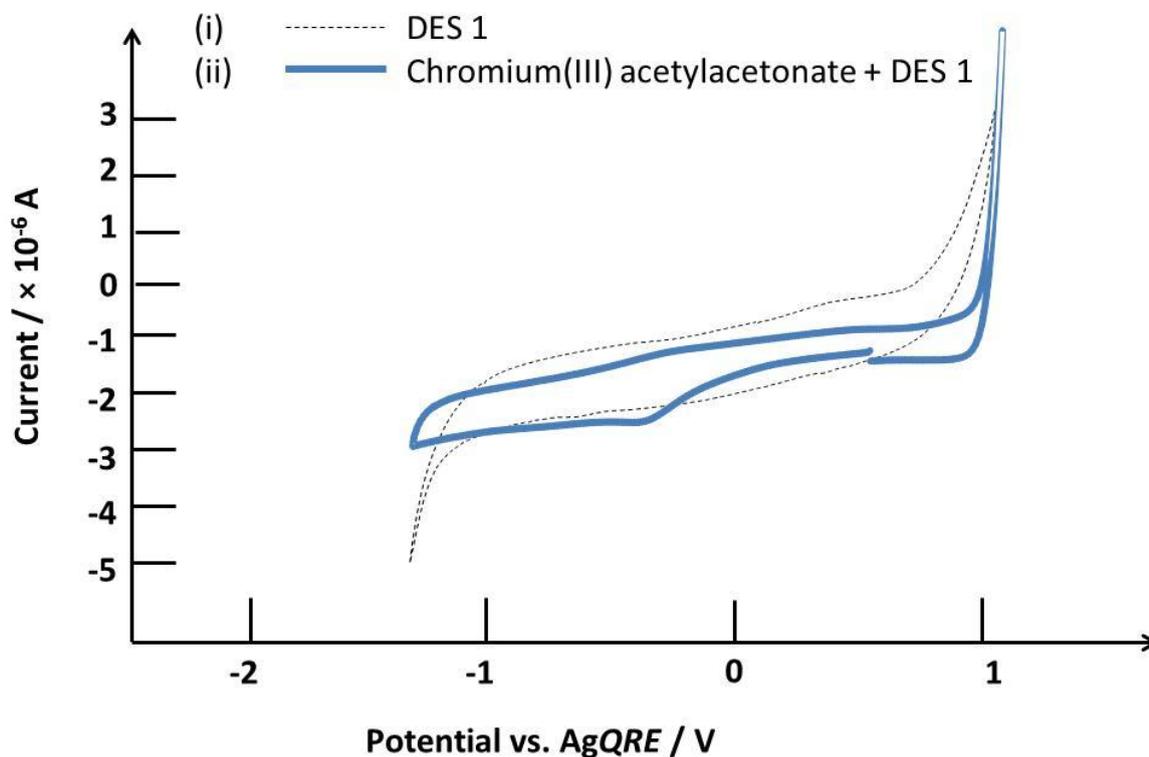
Figure A1 (a). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 °C of (i) DES 1; and (ii) 1 mM chromium (III) acetylacetonate dissolved in DES 1.
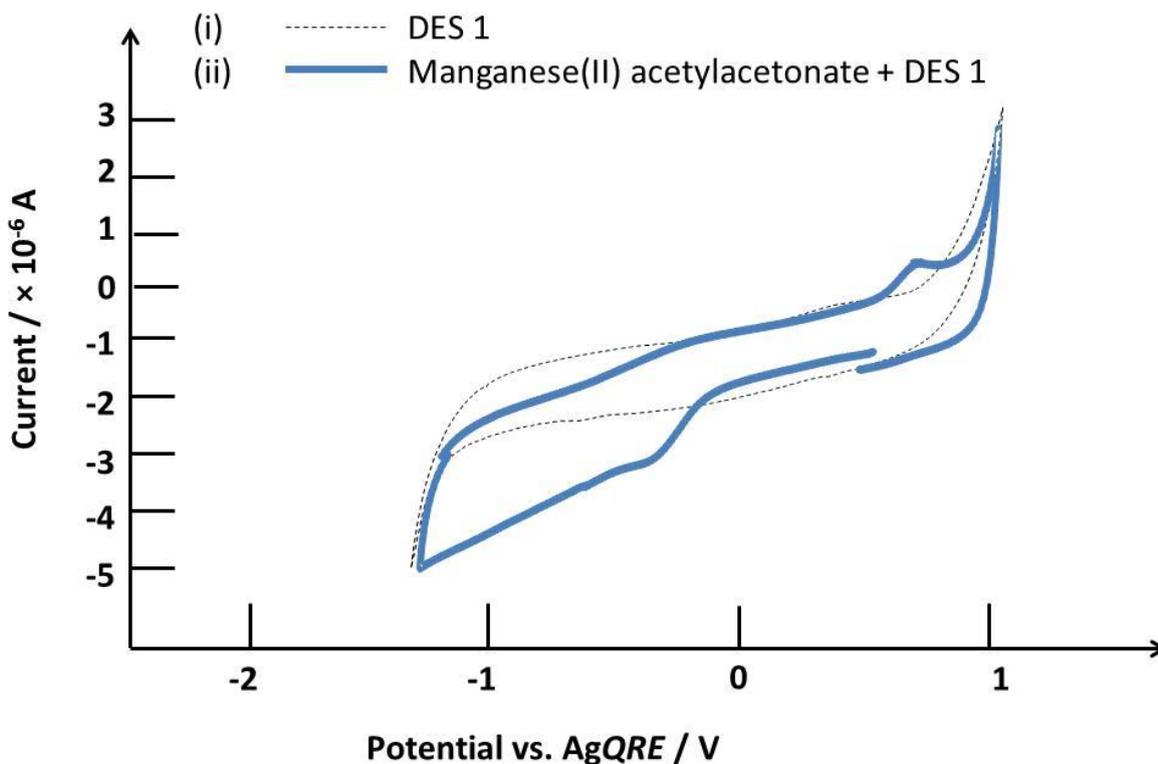
Figure A1 (b). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 °C of (i) DES 1; and (ii) 1 mM manganese (II) acetylacetonate dissolved in DES 1.
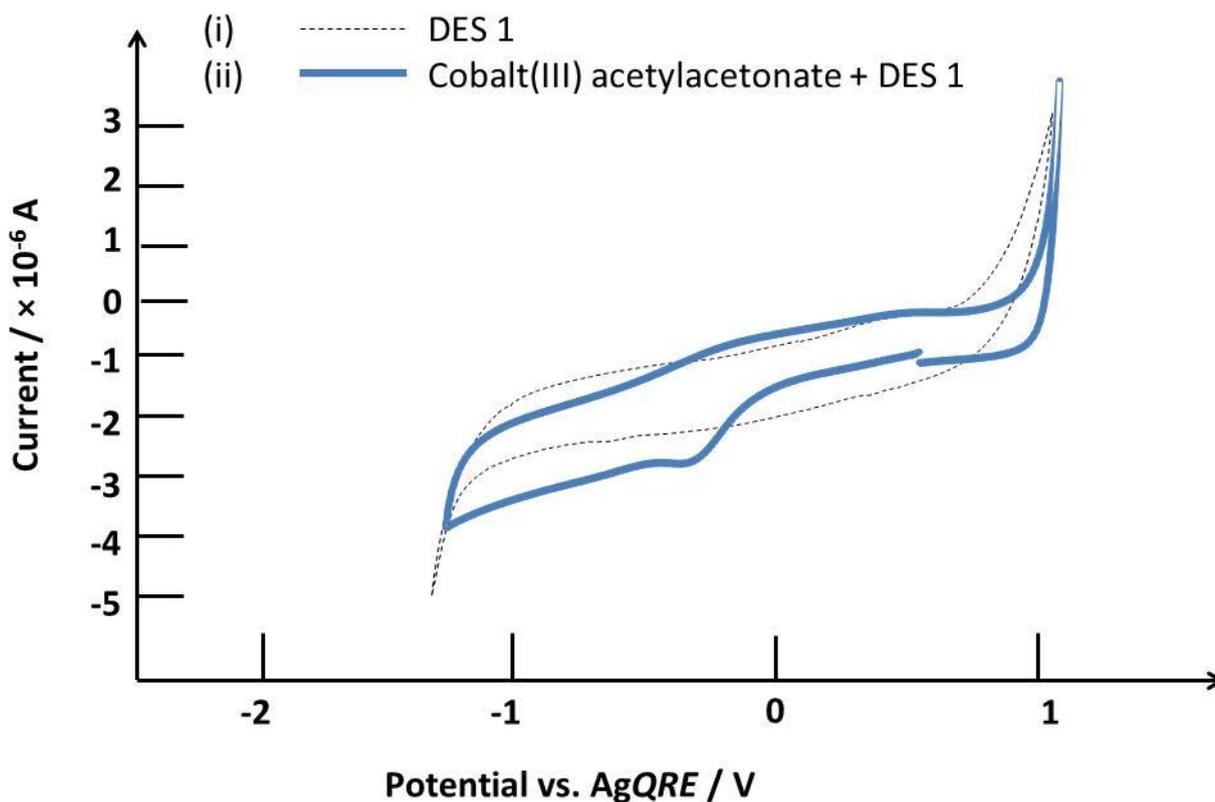

Figure A1 (c). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 °C of (i) DES 1; and (ii) 1 mM cobalt (III) acetylacetonate dissolved in DES 1.
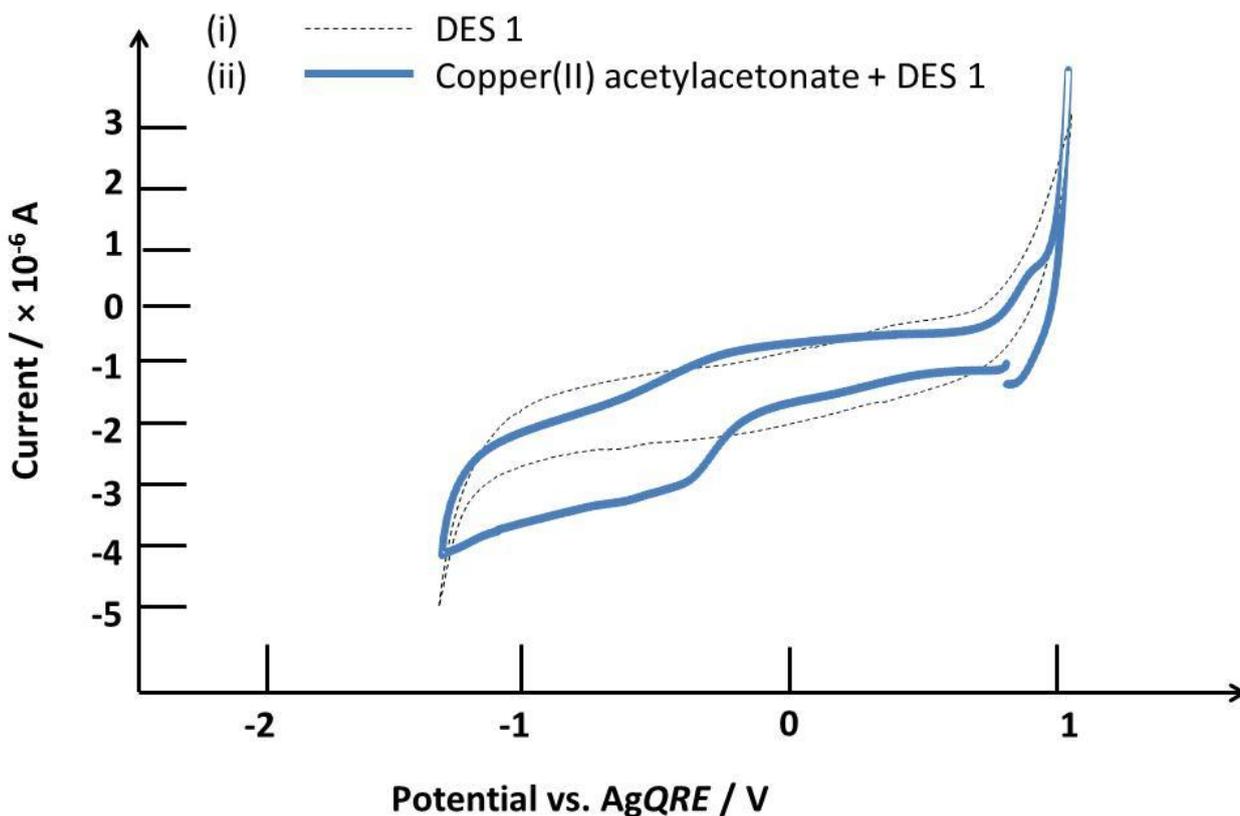
Figure A1 (d). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 °C of (i) DES 1; and (ii) 1 mM copper (II) acetylacetonate dissolved in DES 1.
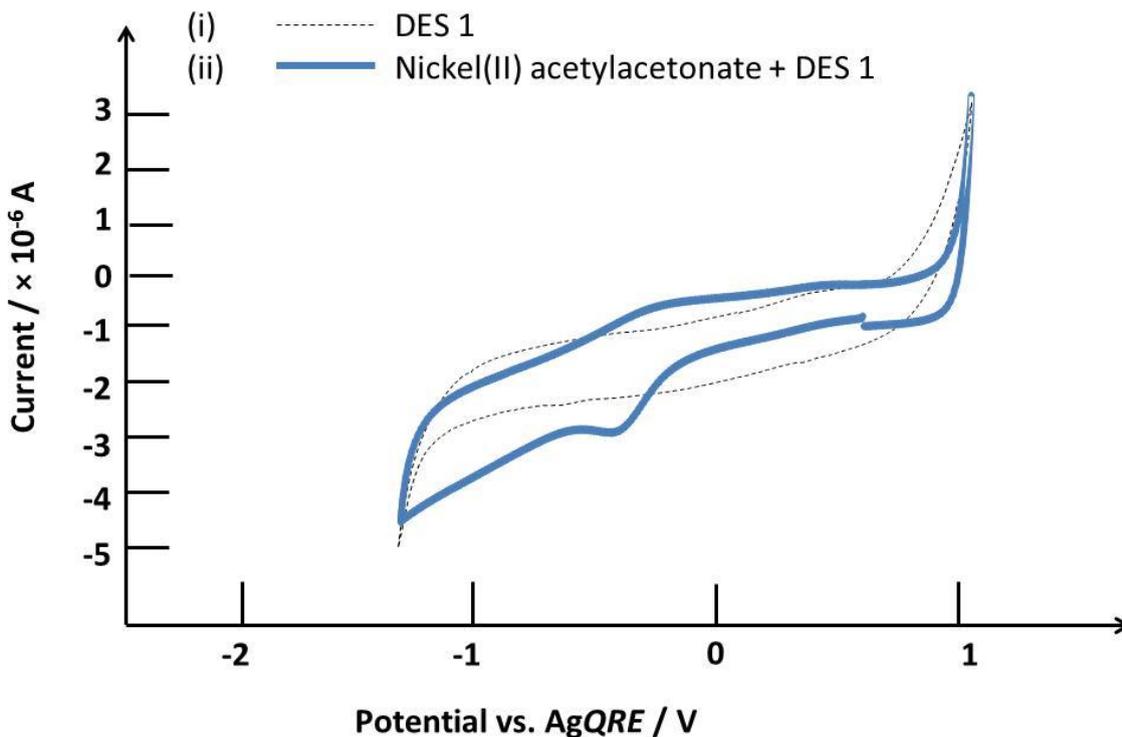
Figure A1 (e). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 °C of (i) DES 1; and (ii) 1 mM nickel (II) acetylacetonate dissolved in DES 1.
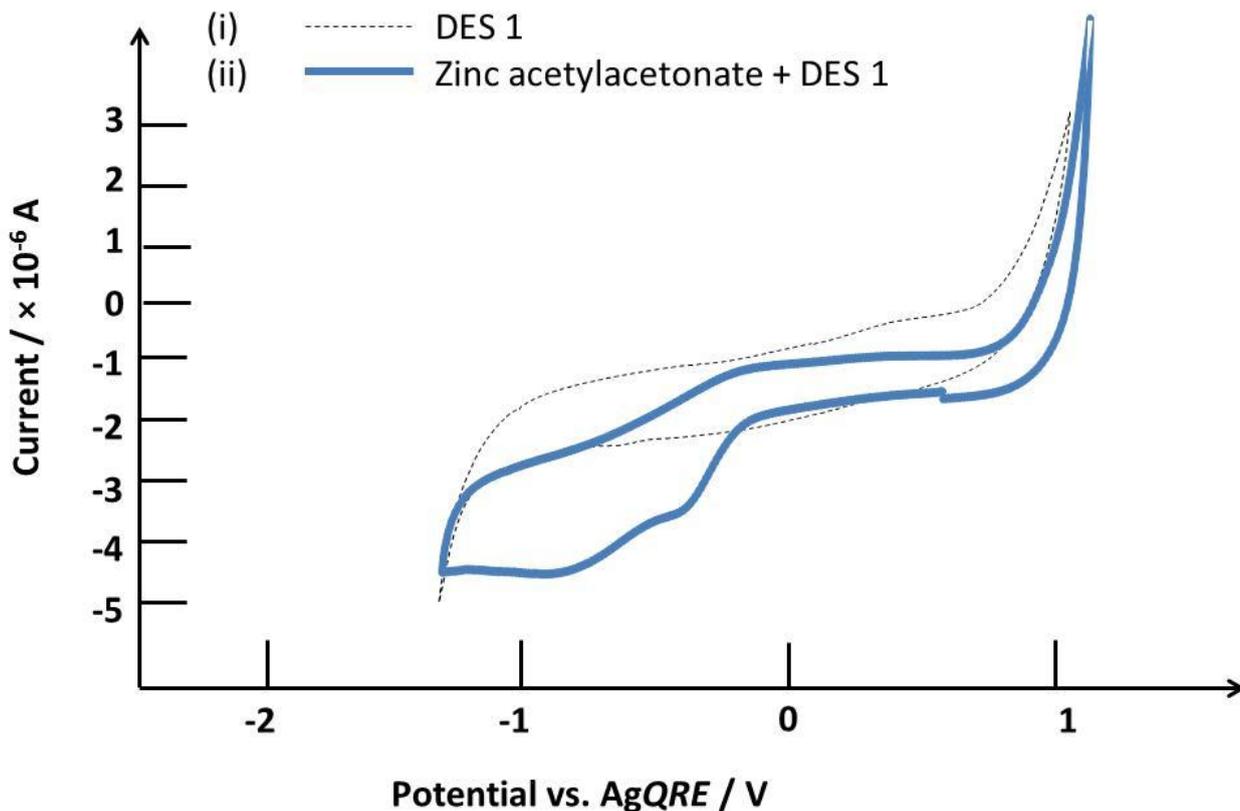
Figure A1 (f). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 ^{o}C of (i) DES 1; and (ii) 1 mM zinc acetylacetonate dissolved in DES 1.
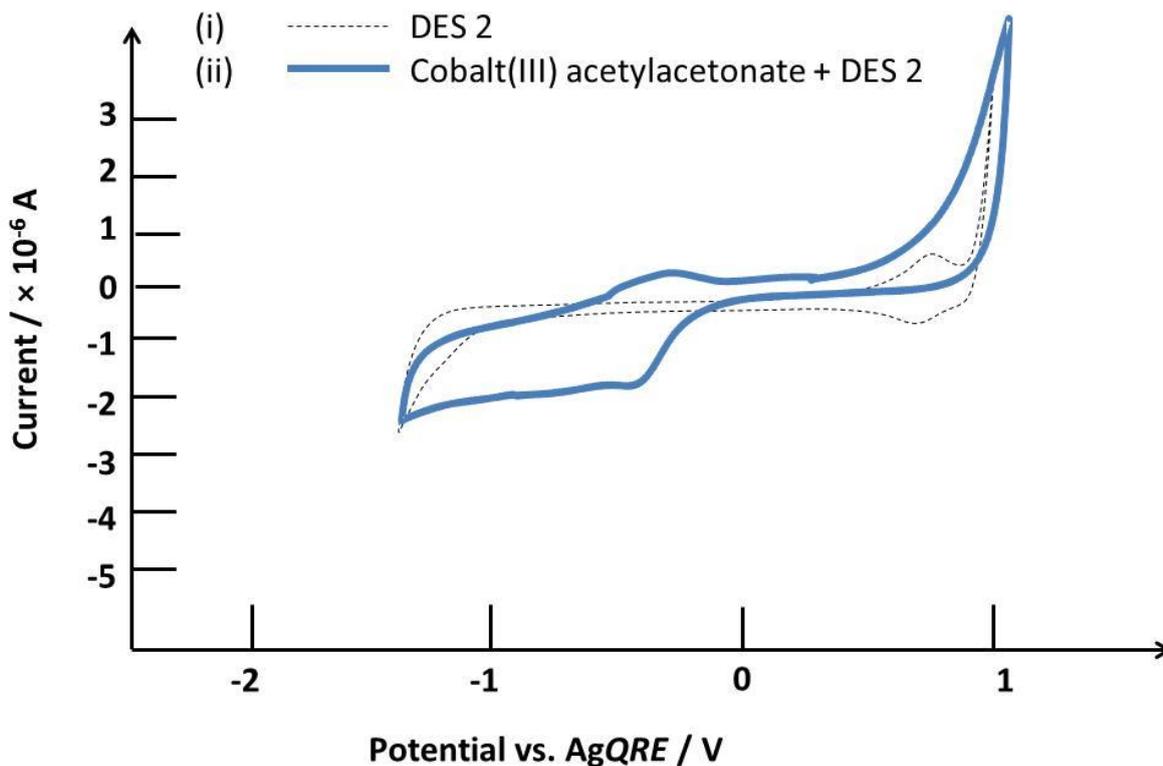
Figure A2 (a). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 ^{o}C of (i) DES 2; and (ii) 1 mM cobalt (III) acetylacetonate dissolved in DES 2.
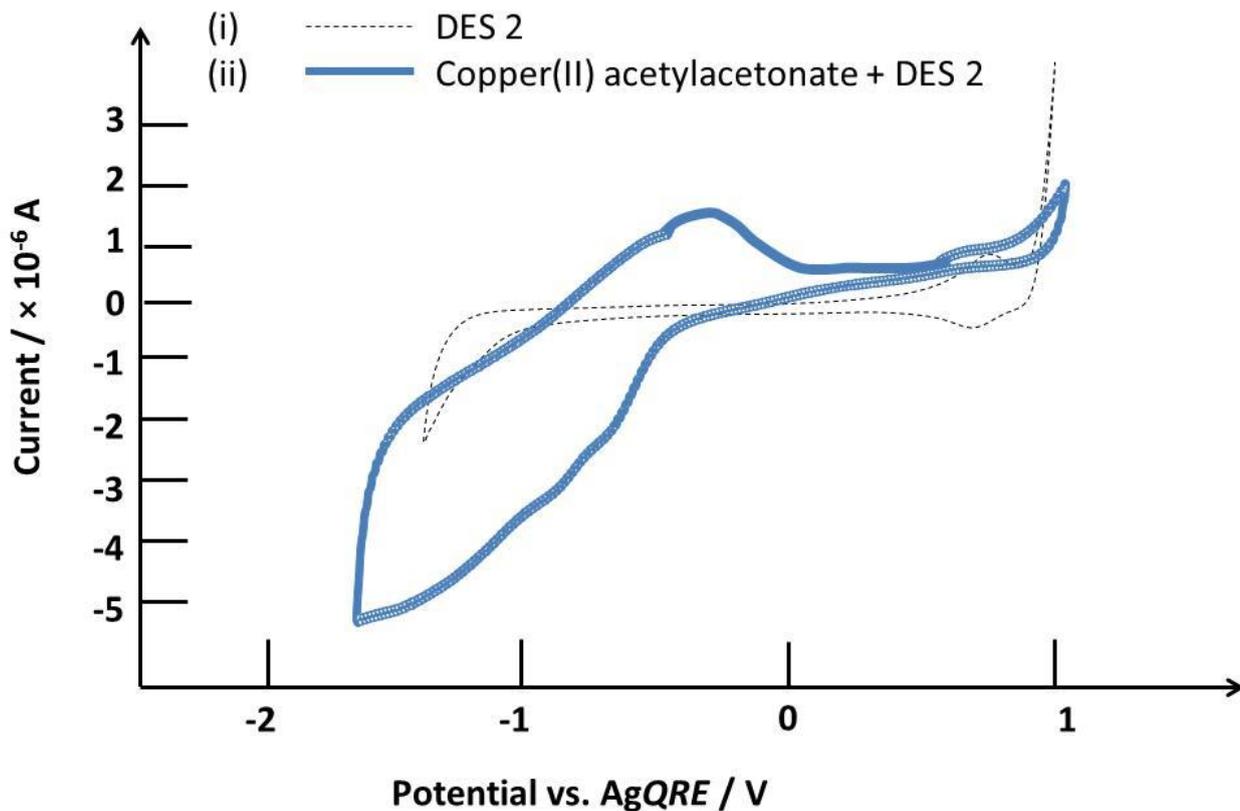
Figure A2 (b). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 ^{o}C of (i) DES 2; and (ii) 1 mM copper (II) acetylacetonate dissolved in DES 2.
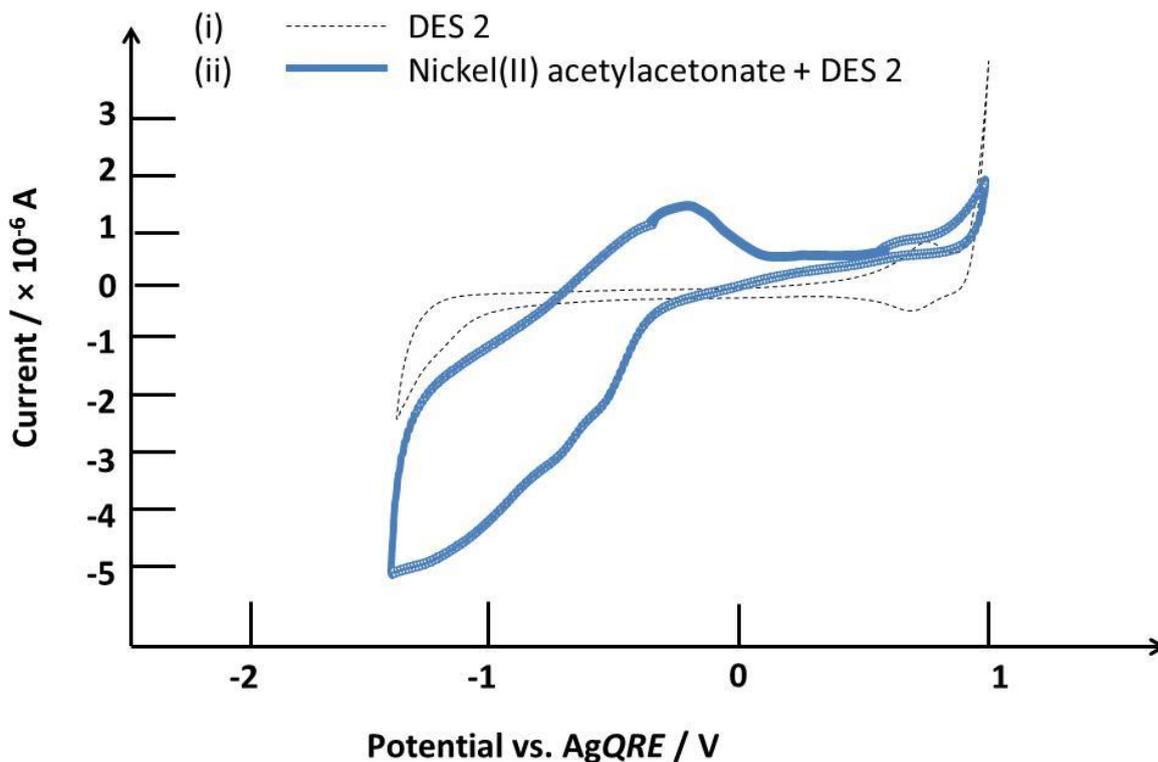

Figure A2 (c). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 ^{o}C of (i) DES 2; and (ii) 1 mM nickel (II) acetylacetonate dissolved in DES 2.
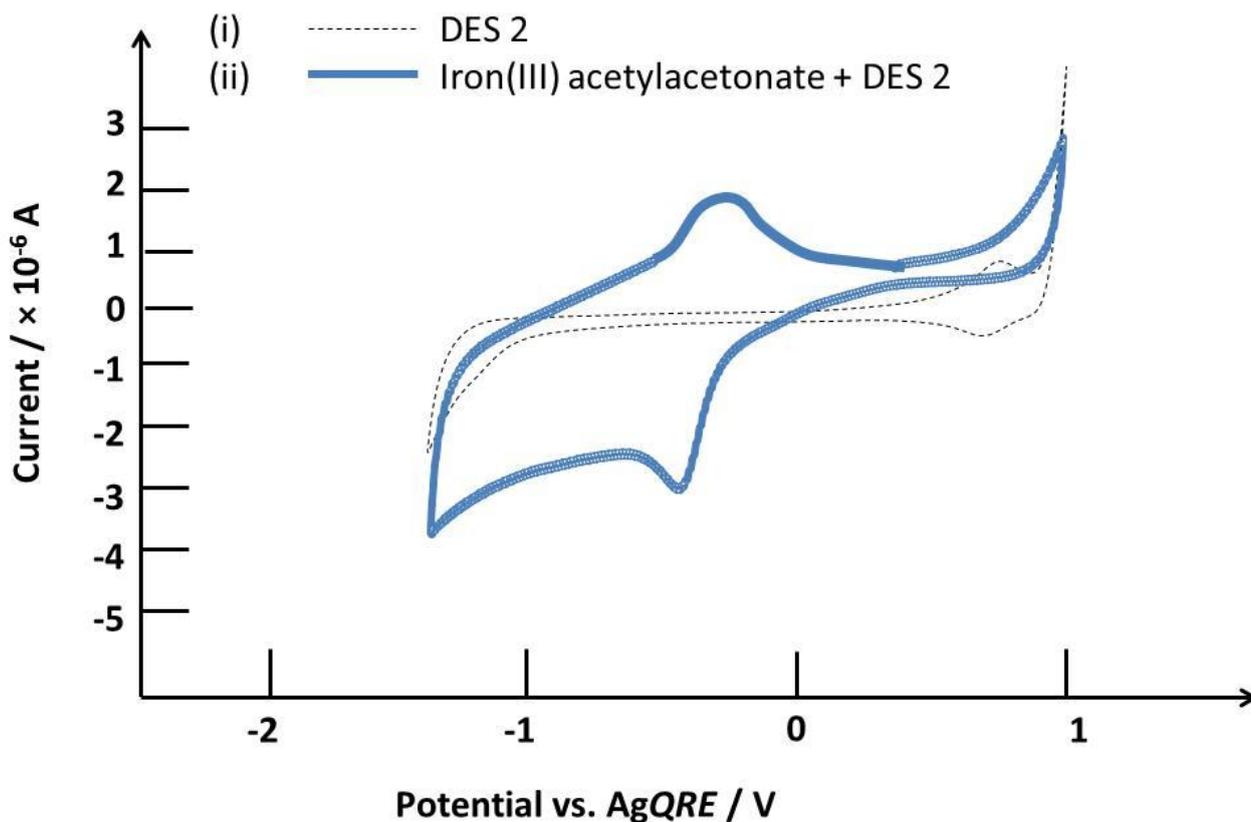
Figure A2 (d). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 ^{o}C of (i) DES 2; and (ii) 1 mM iron (III) acetylacetonate dissolved in DES 2.
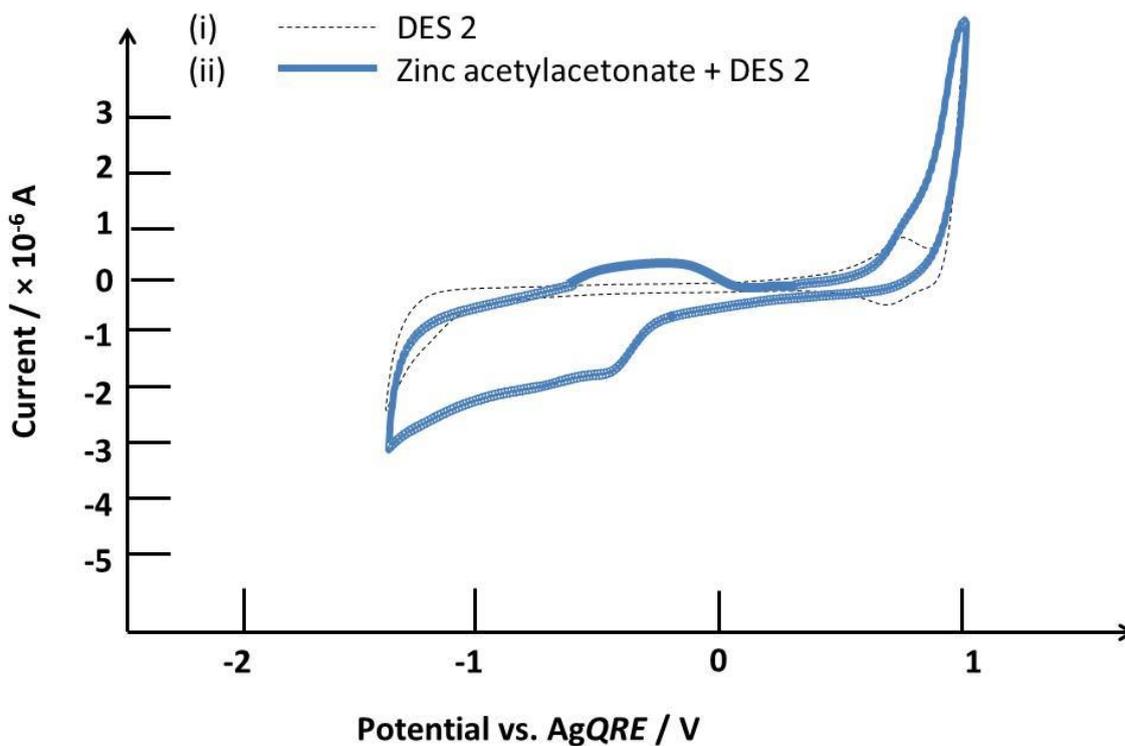

Figure A2 (e). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 ^{o}C of (i) DES 2; and (ii) 1 mM zinc acetylacetonate dissolved in DES 2.
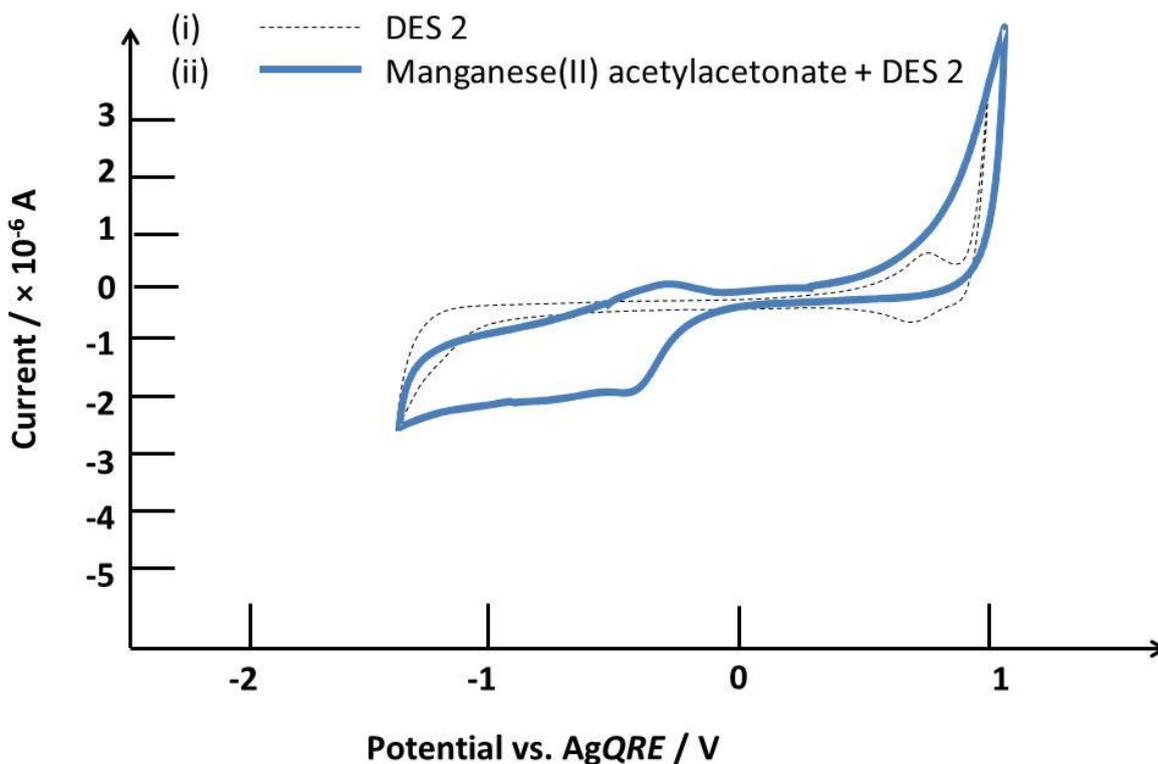
Figure A2 (f). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 ^{o}C of (i) DES 2; and (ii) 1 mM manganese (II) acetylacetonate dissolved in DES 2.
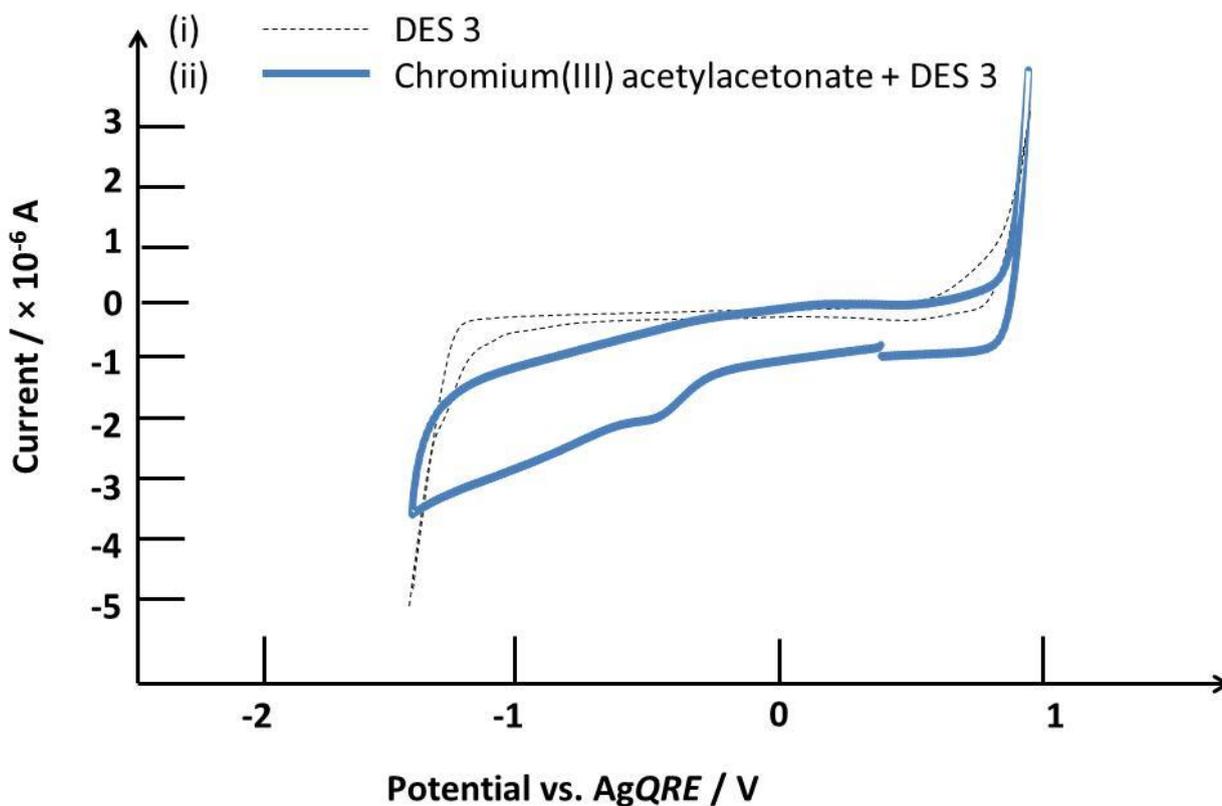
Figure A3 (a). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 ^{o}C of (i) DES 3; and (ii) 1 mM chromium (III) acetylacetonate dissolved in DES 3.
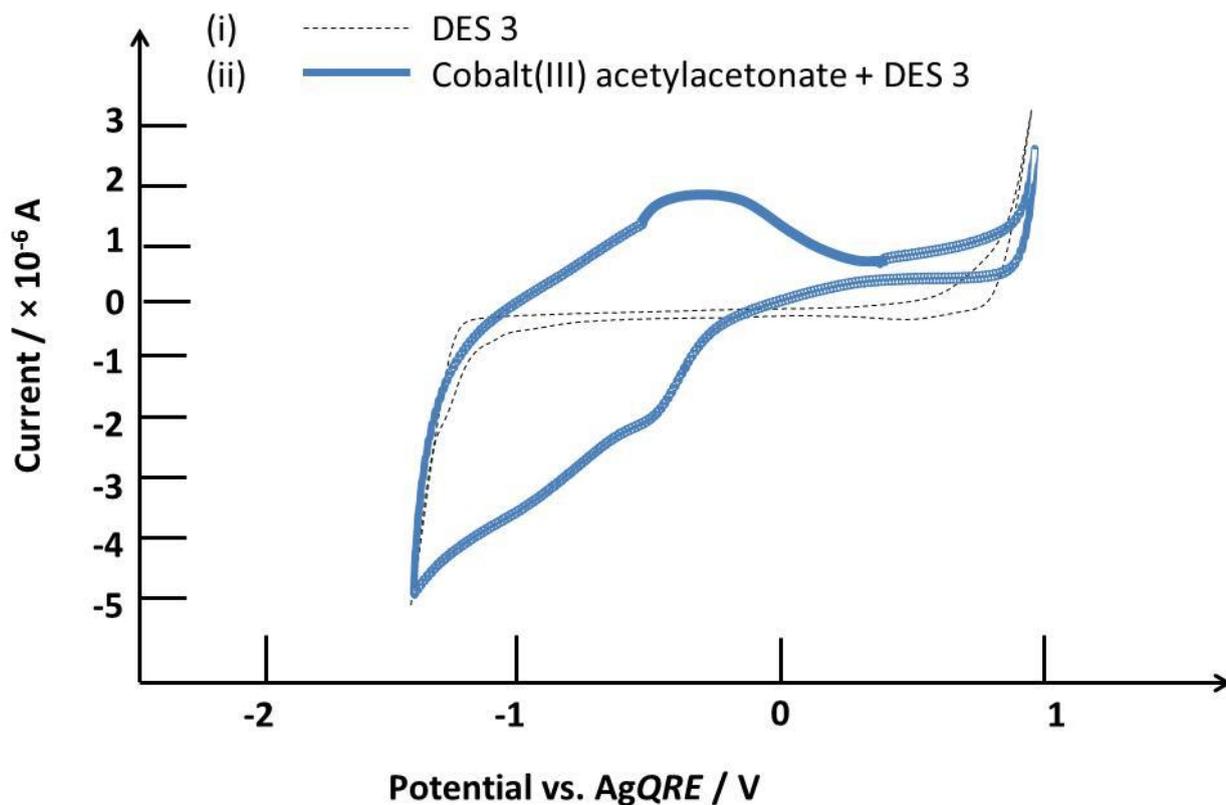
Figure A3 (b). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 °C of (i) DES 3; and (ii) 1 mM cobalt (III) acetylacetonate dissolved in DES 3.
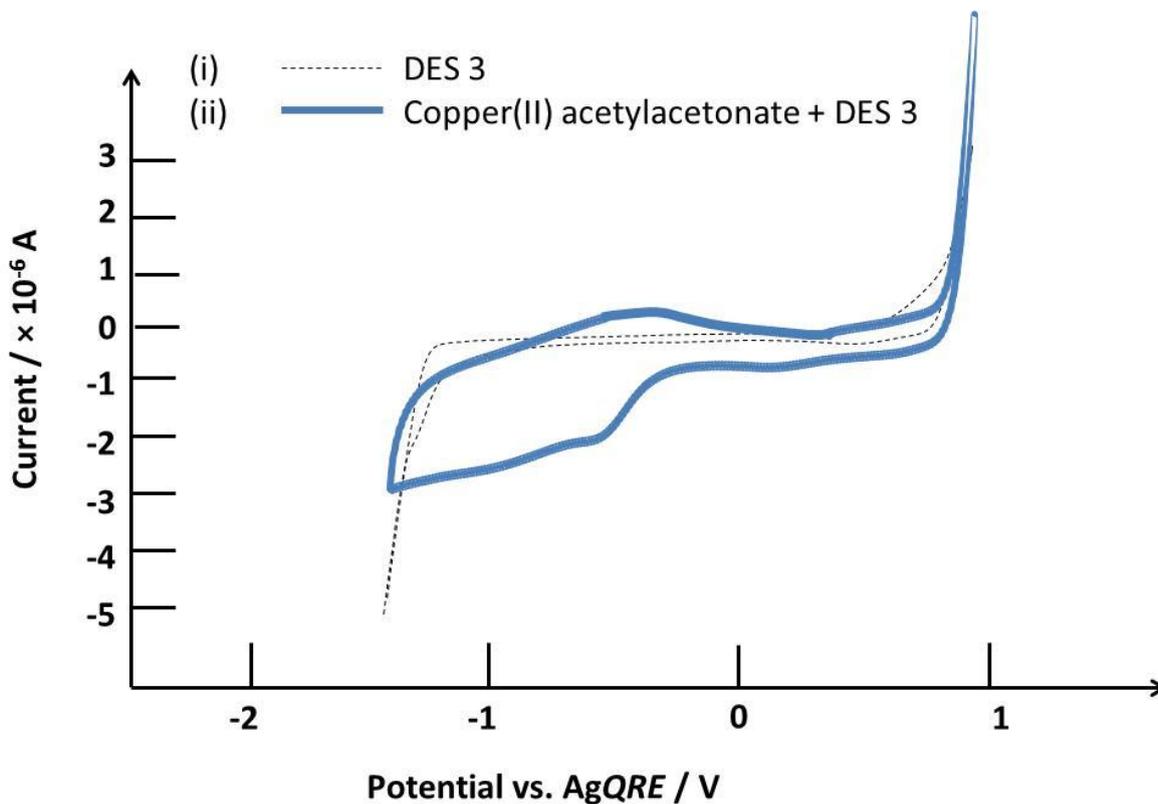
Figure A3 (c). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 °C of (i) DES 3; and (ii) 1 mM copper (II) acetylacetonate dissolved in DES 3.
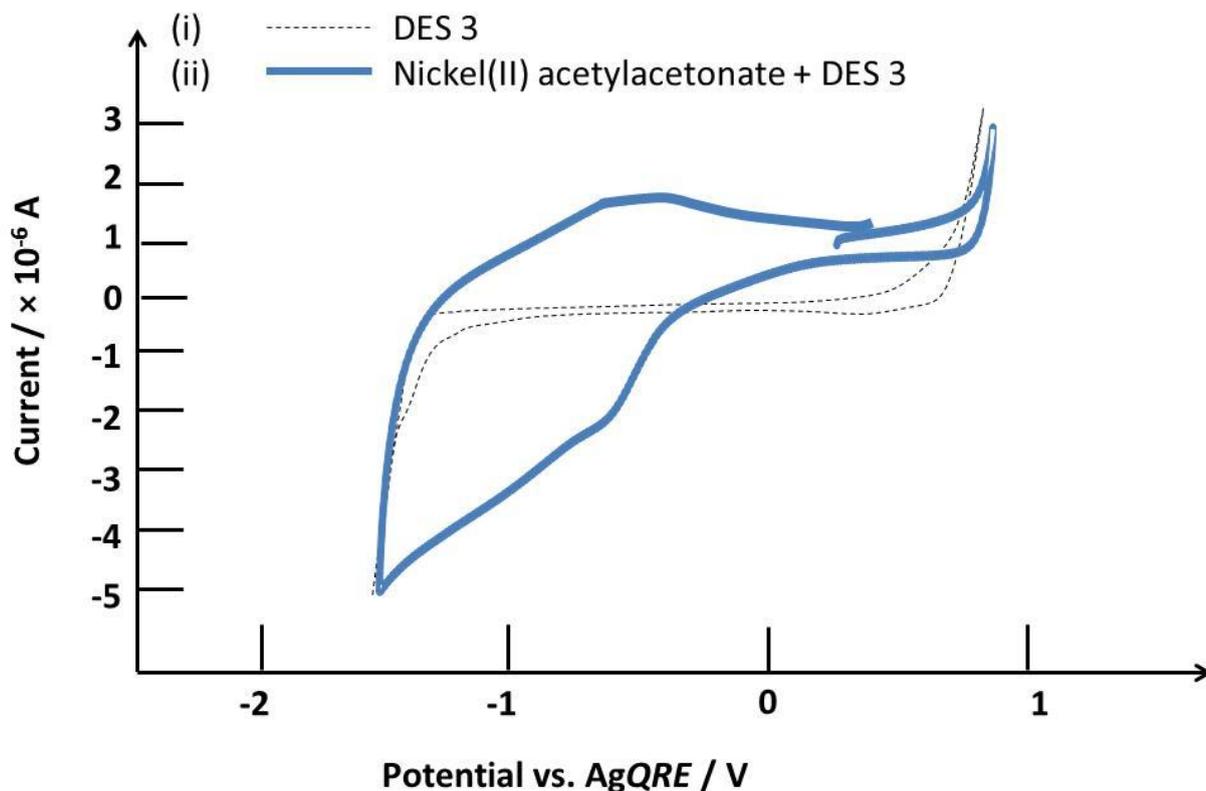
**Figure A3 (d).** CVs at a scan rate of 0.1 V/s using GC working electrode at 50 $^{\circ}$C of (i) DES 3; and (ii) 1 mM nickel (II) acetylacetonate dissolved in DES 3.
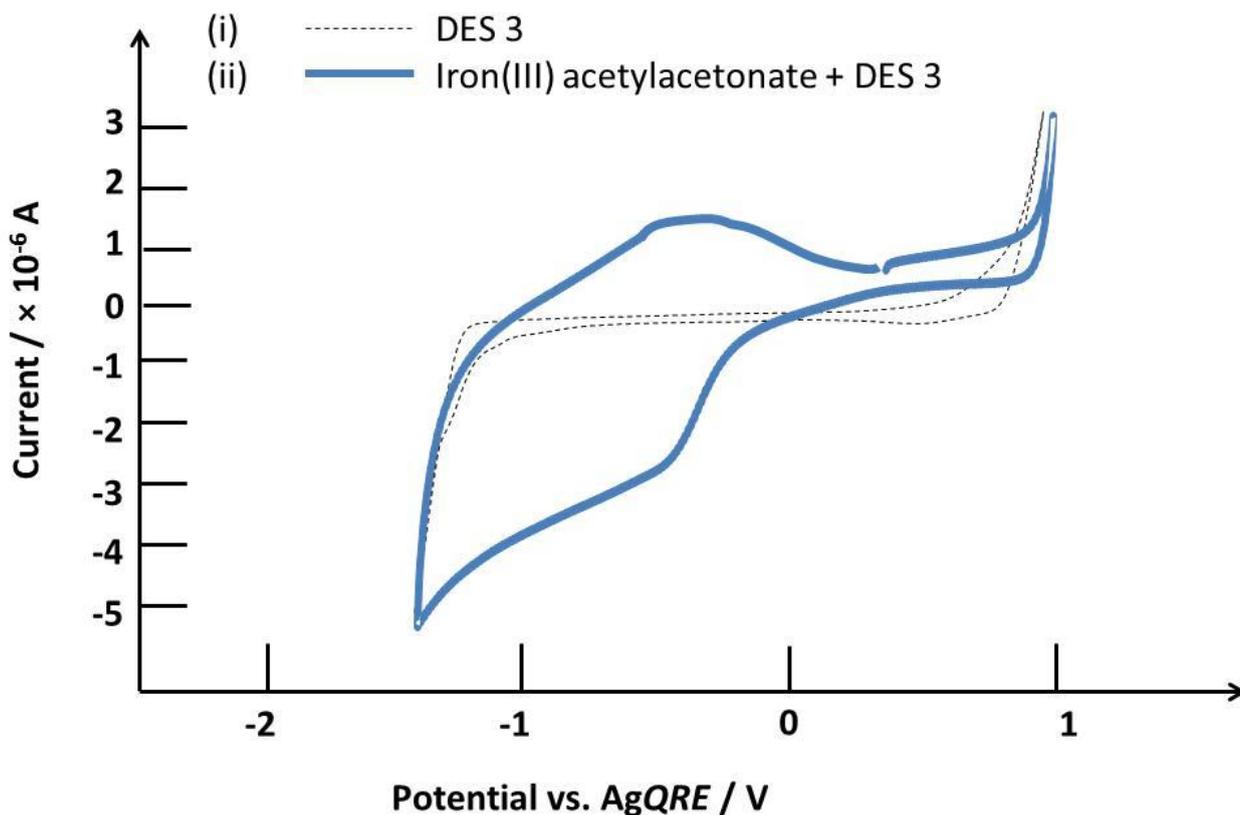
Figure A3 (e). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 $^{\circ}$C of (i) DES 3; and (ii) 1 mM iron (III) acetylacetonate dissolved in DES 3.
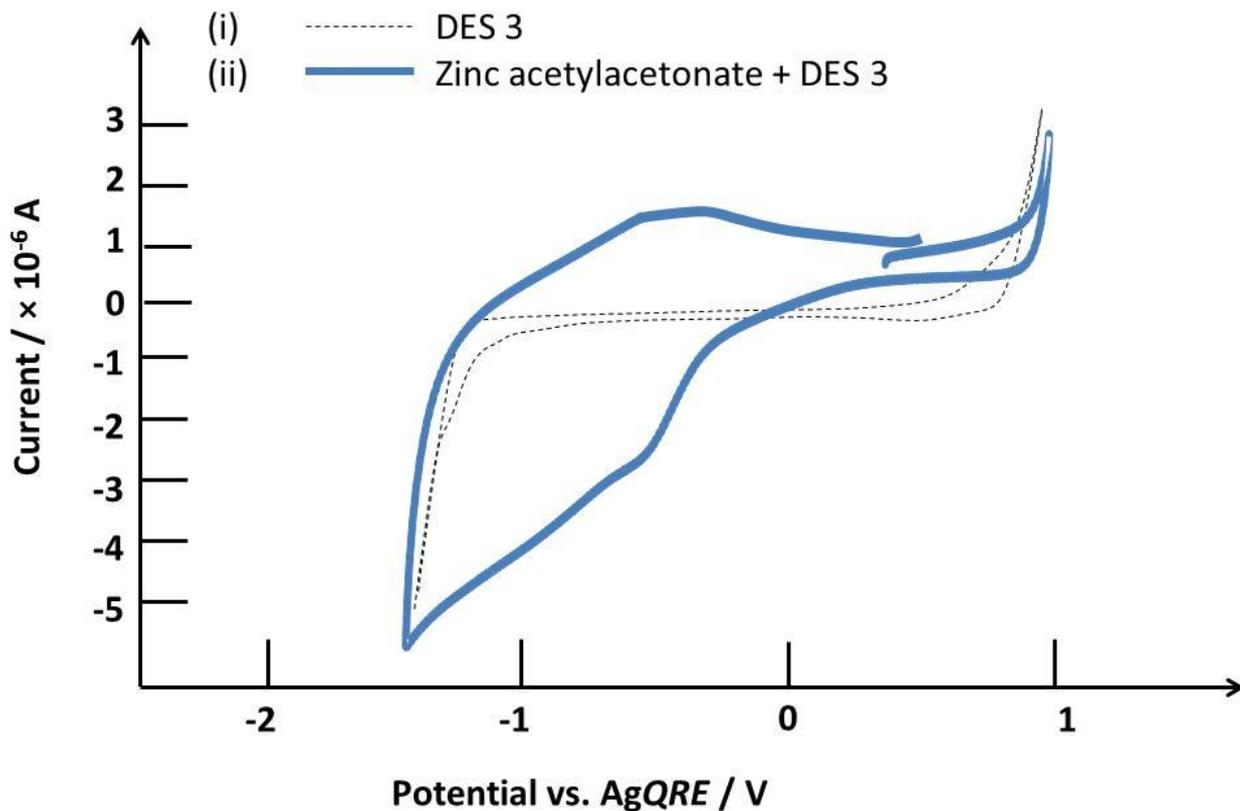
Figure A3 (f). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 $^{\circ}$C of (i) DES 3; and (ii) 1 mM zinc acetylacetonate dissolved in DES 3.
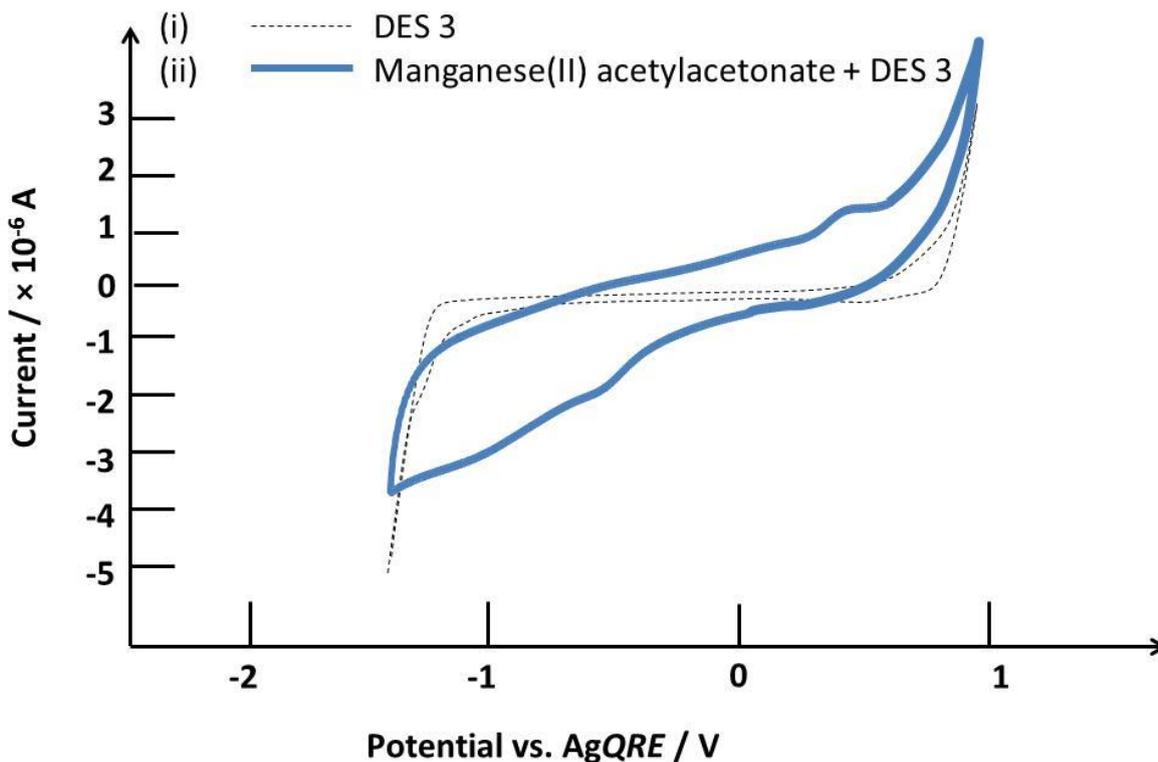

Figure A3 (g). CVs at a scan rate of 0.1 V/s using GC working electrode at 50 $^{\circ}$C of (i) DES 3; and (ii) 1 mM manganese (II) acetylacetonate dissolved in DES 3.
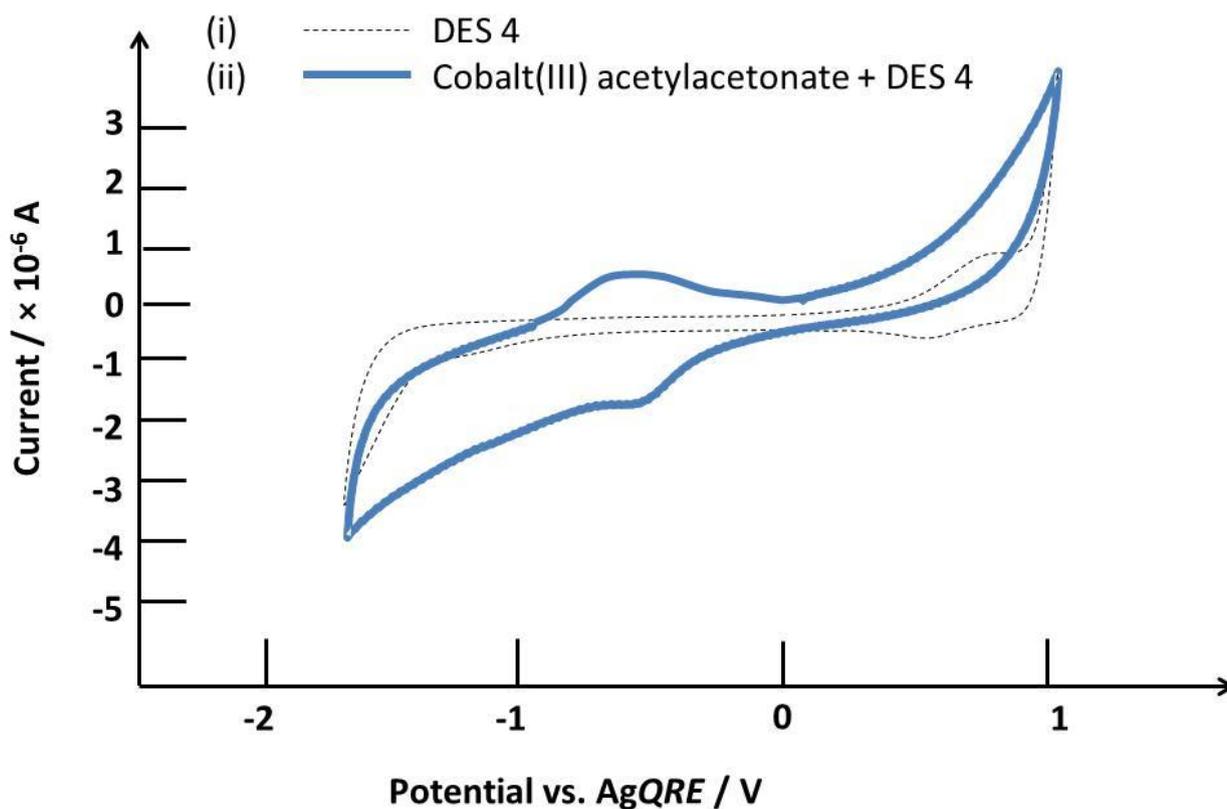
Figure A4 (a). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 $^{\circ}$C of (i) DES 4; and (ii) 1 mM cobalt (III) acetylacetonate dissolved in DES 4.
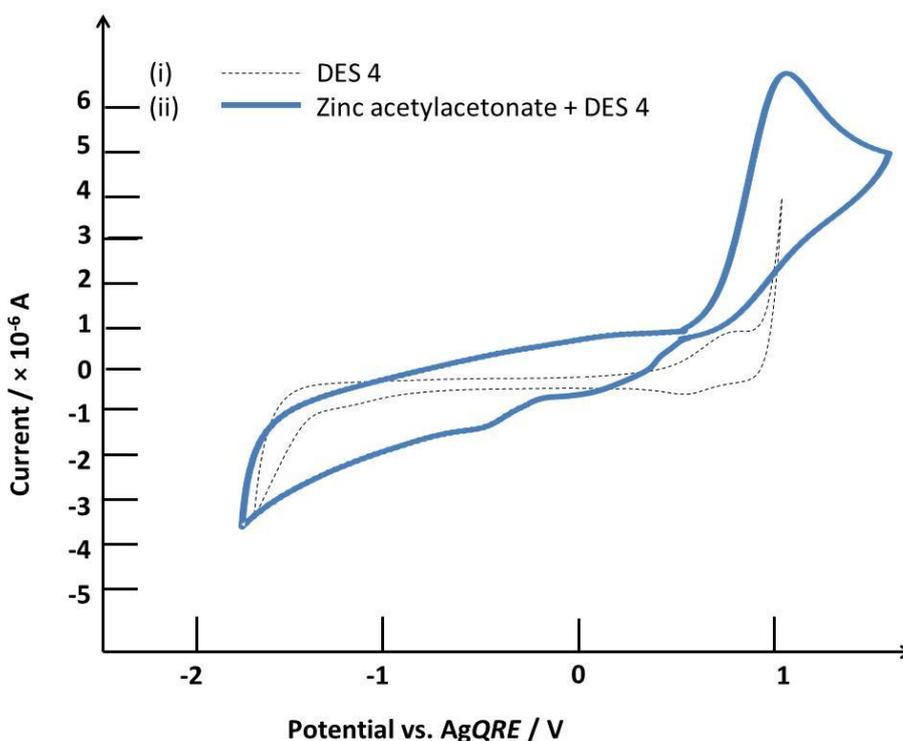
Figure A4 (b). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 $^{\circ}$C of (i) DES 4; and (ii) 1 mM zinc acetylacetonate dissolved in DES 4.
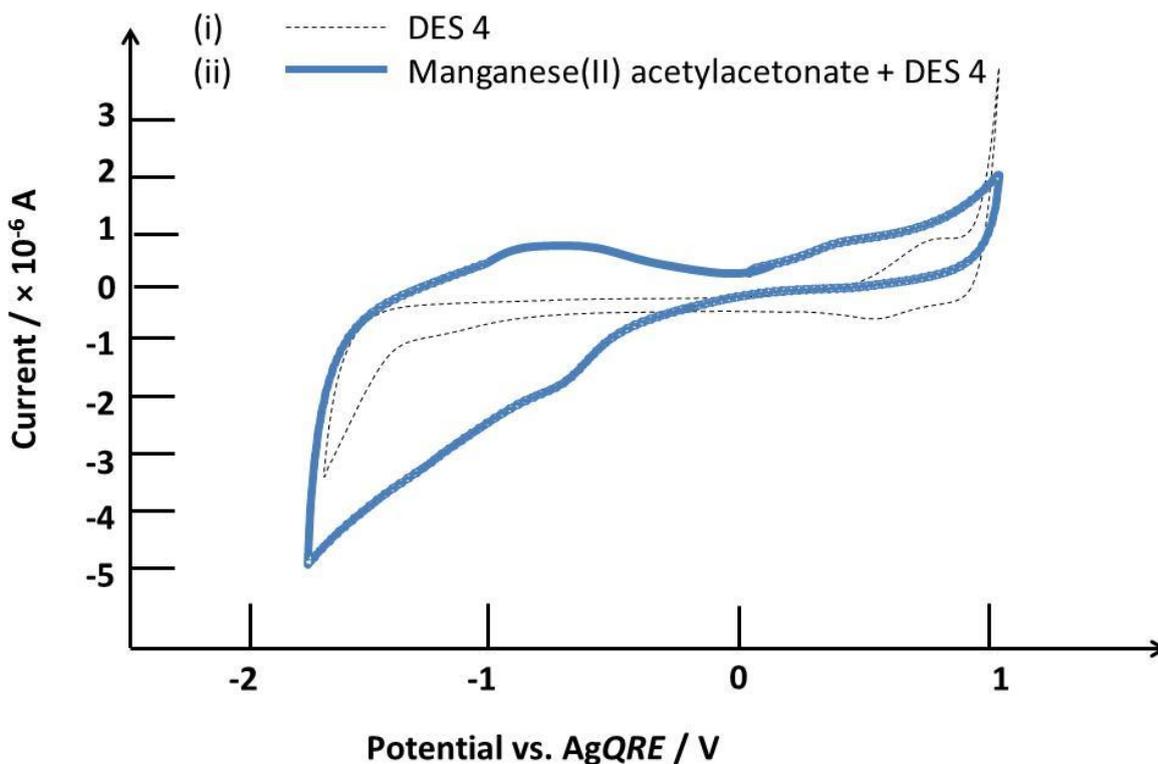
Figure A4 (c). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 ^{o}C of (i) DES 4; and (ii) 1 mM manganese (II) acetylacetonate dissolved in DES 4.
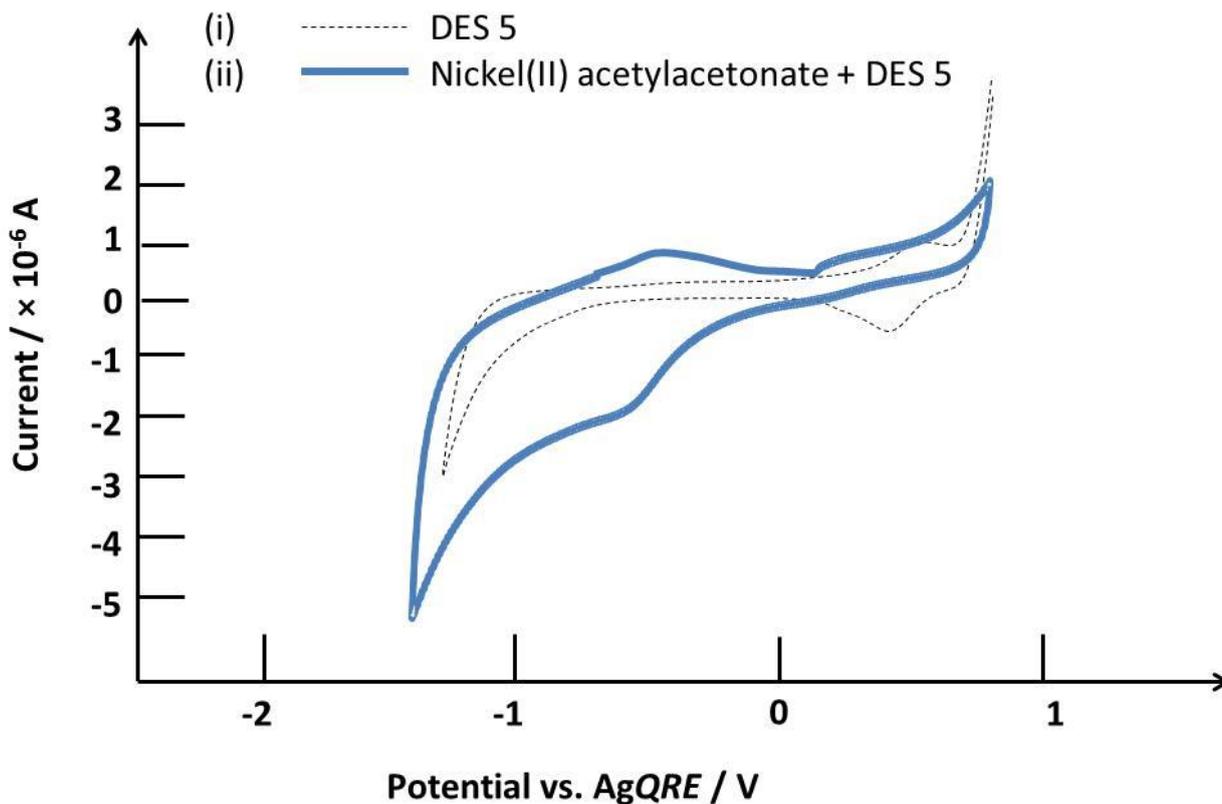

Figure A5 (a). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 ^{o}C of (i) DES 5; and (ii) 1 mM nickel (II) acetylacetonate dissolved in DES 5.
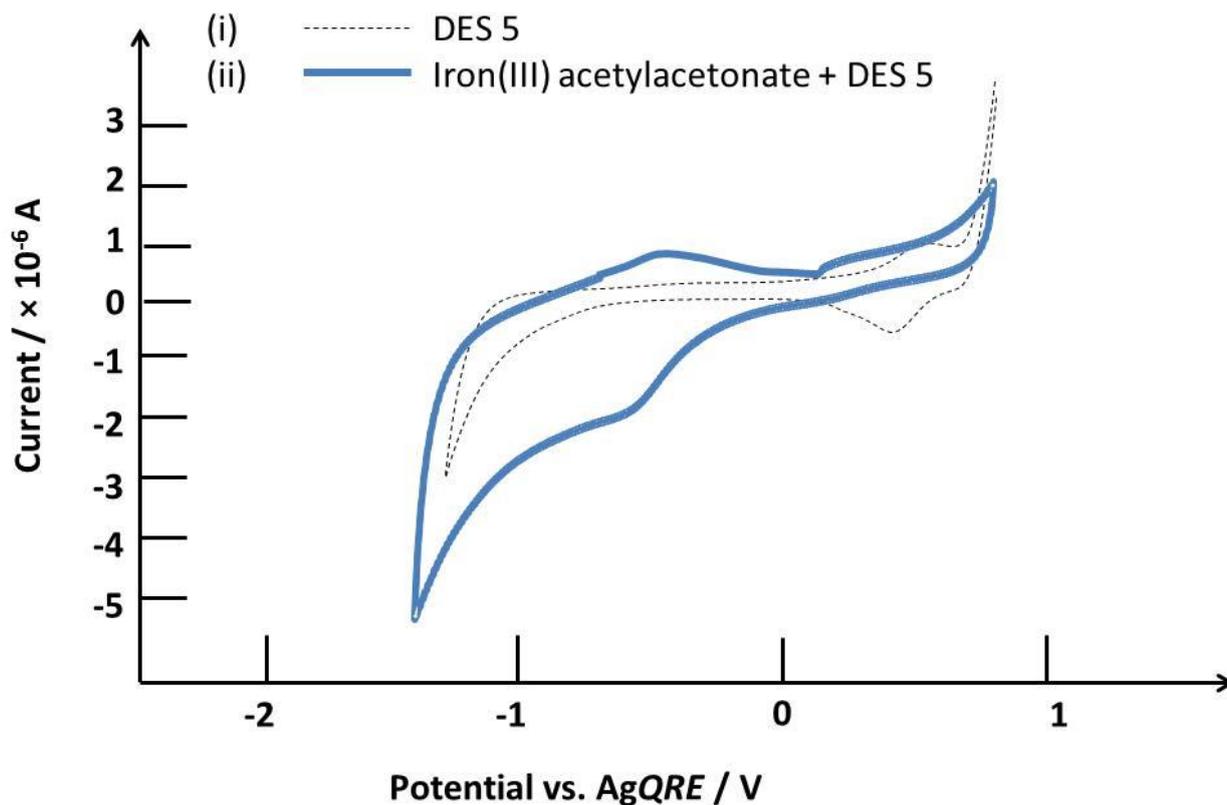
Figure A5 (b). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 ^{o}C of (i) DES 5; and (ii) 1 mM iron (III) acetylacetonate dissolved in DES 5.
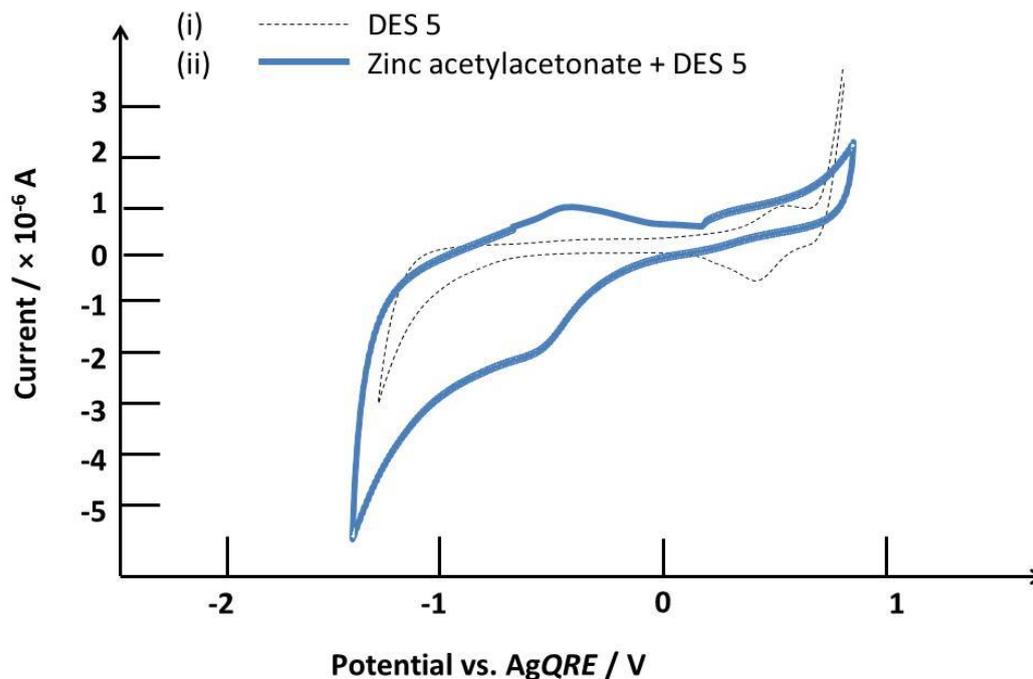

Figure A5 (c). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 ^{o}C of (i) DES 5; and (ii) 1 mM zinc acetylacetonate dissolved in DES 5.
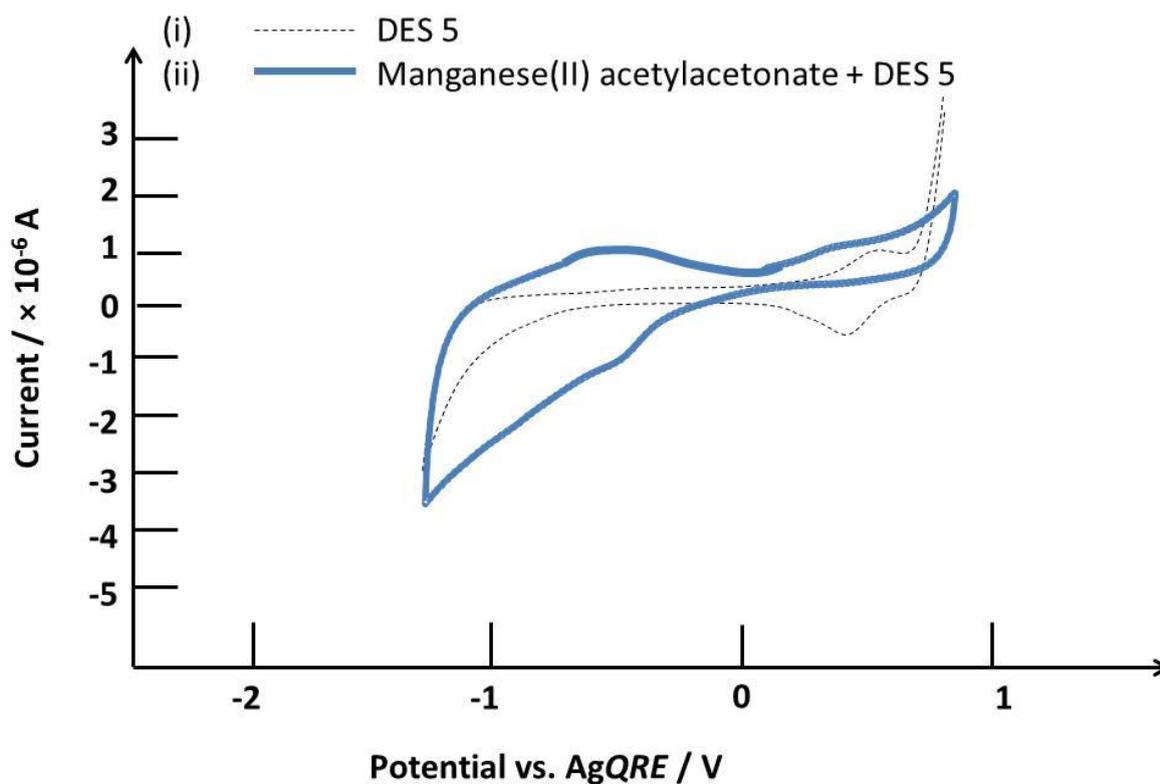
Figure A5 (d). CVs at a scan rate of 0.1 V/s using GC working electrode at 35 °C of (i) DES 5; and (ii) 1 mM manganese (II) acetylacetonate dissolved in DES 5.