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Electrochemical Investigation of the Extraction of Cobalt (II) Ions at Liquid/Liquid Micro-Interface

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Abstract

Electrochemistry at the micro-interface between two immiscible electrolyte solutions (ITIES) has become an important and powerful platform for electroanalytical investigations. Recently, single µITIES, like a liquid/liquid interface formed at the tip of a micropipette, emerged as a sensitive electrochemical platform for the versatile applications. In this investigation, Acorga M5640 was used as an extractant or facilitator for Co and Ni metal extraction or transfer across the 1, 2-dichloroethane (DCE)/water micro-interface supported by a micropipette using cyclic voltammetry (CV) techniques. Investigations were carried out at different pHs values and at different concentrations of Acorga. It was found that Co^{2+} ions transferred across the DCE/water interface and the better response was achieved at pH 9.0 and in 10% of Acorga in DCE organic phase. However, no response of Co^{2+} ions was noticed in mixed organic solvent of 1-butanol and DCE. In contrast, no voltametric response was found for Ni^{2+} ions across the studied ITIES.

Keywords: Electrochemistry, ITIES, micropipette, cyclic voltammetry, Acorga M5640.

1 Introduction

Separation or extraction of metals from solutions is a challenging task. Solvent extraction has been an extensively used method for the analytical investigation of separation of metals. In the conventional solvent extraction method, the use of extractants or ionophores either in organic solvents or in aqueous phase is an important industrial technique for the recovery and refining of metals from dilute solutions (Benedetto et al., 1995; Brooks, 1993; Ismael & Tondre, 1994; Matsuyama et al., 1996).

Electro-assisted extraction across a liquid/liquid interface can be a novel method for metal extraction. David J. Schffrin and his group (Bustero et al., 1998) reported the successful separation of Ni^{2+}, $Cu^{2+,}$ and Cd^{2+} ions at ITIES. They used 2, 2'; 6', 2"-terpyridine as an extractant or facilitator in organic solvent 2-heptanone. Additionally, the transfer of heavy and transition metal ions (Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}) at a water/2-octanone interface facilitated by terpyridine has been reported by Cheng and Schffrin (Cheng & Schiffrin, 1997). Terpyridine is also used to transfer metal ions Fe, Co, Ni, Cu, and Zn at water/2-octanone interface (Alemu et al., 1990).

Acorga M5640 is one of the most widely used effective solvents for the recovery of copper from aqueous solutions (Alguacil et al., 2012; Sridhar & Verma, 2011; Vander Linden & De Ketelaere, 1998; Wang et al., 2019; Yang et al., 2016). Figure 1.1 shows that Acorga M5640 consists of 5-nonylsalicylaldoxime (5-nonyl-2-hydroxy-benzaldoxime) as an active substance and a fatty ester as a modifier (Agarwal et al., 2012; Yang et al., 2016) and is highly selective for copper over iron (Agarwal et al., 2010; Wang et al., 2019; Yang et al., 2016). Yang et al. (Yang et al., 2016) used 10% (v/v) Acorga M5640 and 2% (v/v) trialkyl phosphine oxides (TRPO) for copper and nickel extraction and reported that more than 99.96% of copper could be recovered from the solution.

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In this investigation, initially, Acorga M5640 was used as an extractant or facilitator for Co^{2+} and Ni^{2+} ions transfer across the DCE/water micro-interface supported by a micropipette. Acorga was added to the organic solvent, DCE in different compositions and cyclic voltammetry was applied to observe the Co^{2+} and Ni^{2+} ions transfer at various aqueous phase pHs. Mixed organic solvent (DCE and 1-decanol) was also utilized to characterize the liquid/liquid interface.

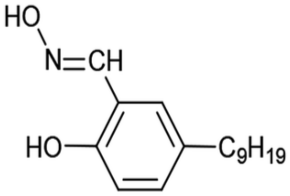

Figure 1.1: *Structure of Acorga M5640*

2 Experimental

2.1 Reagents

Acorga M5640 was supplied by Cytec Australia. All other reagents were purchased from Sigma-Aldrich Australia Ltd. and used as received unless otherwise indicated. The organic electrolyte bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) was prepared by metathesis of equimolar amounts of bis(triphenylphosphoranylidene)ammonium chloride (BTPPACl) and potassium tetrakis(4-chlorophenyl)borate (KTPBCl) as reported earlier (Lee et al., 1997). BTPPATPBCl (0.01 M) solutions were prepared in 1,2-dichloroethane (DCE). Chlorotrimethylsilane was used for silanization of pipettes. All aqueous solutions (e.g. LiCl solution) were prepared in purified water from a USF Purelab plus UV (resistivity: 18.2 MΩ cm). 10 mM $CoSO_4.7H_2O$ and 10 mM $NiSO_4.6H_2O$ were prepared as stock solution**.**

2.2 Electrochemical cell

Electrochemical measurements were conducted by using an Autolab PGSTAT302N electrochemical analyzer (Metrohm Autolab, Utrecht, The Netherlands) running with NOVA software. The organic electrolyte phase was introduced into the pipette which reached to the tip and the organic reference solution (saturated BTPPACl in 10 mM LiCl) was placed on the top of the organic phase. Then the pipette was immersed into the aqueous phase so that an ITIES formed at the tip of the pipette. As this was a miniaturized interface, a two-electrodes system was employed for this electrochemical cell. An Ag/AgCl electrode was in the aqueous solution and another Ag/AgCl electrode was in the organic reference solution. The micro-interface was polarised by imposing a potential difference between these two electrodes. Unless stated otherwise, 10 mVs^{-1} scan rate was applied to carry out the cyclic voltammetry (CV) experiments. The pH of the aqueous LiCl solution was adjusted by adding NaOH or HCl solution dropwise. The cell is illustrated in the following scheme.

Ag | AgCl | Sat'd BTPPACl in 10 mM LiCl | 10 mM BTPPATPBCl in DCE + x % acorga || x μM $CoSO_4$ / $NiSO_4$ in 10 mM LiCl at diff. pH | AgCl | Ag

3 Results and discussion

3.1 Detection of Co^{2+} ions at ITIES by applying Cyclic Voltammetry

The transfer of cobalt ions across the micro-interface between water and DCE formed at the tip of a glass micropipette was studied by cyclic voltammetry to analyze the electrochemical behaviour of Co^{2+} at different aqueous phase pHs. Acorga M5640 was added to the organic phase at different percentages to examine the impact on the transfer processes. pH of the aqueous solutions also varied to examine that which pH was good for Co^{2+} transfer. The cyclic voltammograms started from a low potential and the forward scan was in a positive direction. The potential window is limited by the transfer of background electrolytes at low and high potentials. Figure 3.1.1 shows the CVs of tetraethylammonium ion (TEA^+) transfer to check the interface without Acorga and with 50% Acorga in the organic phase. Without Acorga (only the DCE organic phase), figure 3.1.1 shows that the blank response is good and that 40 µM TEA^+ gave an ideal voltammetric response. However, when 50% Acorga was added in the DCE phase, the figure shows that the blank scan became very resistant. It might because of the Acorga molecules blocked the interface, which was ascribed to the molecules could not transfer across the ITIES. Figure 3.1.1 also shows that there was no response for 80 µM TEA^+. This phenomenon suggests that the interface became blocked with Acorga molecules.

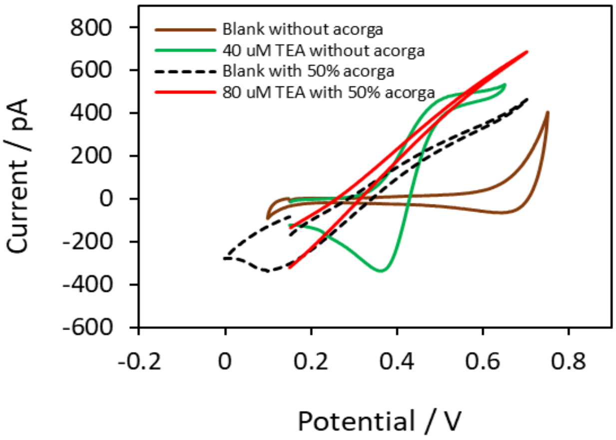

Figure 3.1.1: *The brown CV response for the blank with DCE only in the organic phase, the green CV is for 40 µM* TEA^+ *response in that ITIES, the black dashed line CV is for DCE with 50% Acorga and the red one is for 80 µM* TEA^+ *across the interface with Acorga.*

The percentage of Acorga was then decreased from 50% to 10%. Figure 3.1.2 shows the TEA^+ response with 10% Acorga in the organic phase. The black dashed voltammogram is for the background voltammogram where no Acorga was added. The green voltammogram is also for the background with 10% Acorga in the organic phase, DCE. It shows that the background CV response with Acorga was changed and the potential window was narrowed at a higher potential region. However, it is considerably good and stable compared to the blank achieved with 50% Acorga as can be found in figure 3.1.1. Then 60 µM TEA^+ was added in the aqueous solution to check the ion transfer behaviour of this ITIES. The red cyclic voltammogram is for the transfer of the TEA^+ and its shape looks like an ideal transfer of TEA^+ at the DCE/water interface, which indicates that the system was working well.

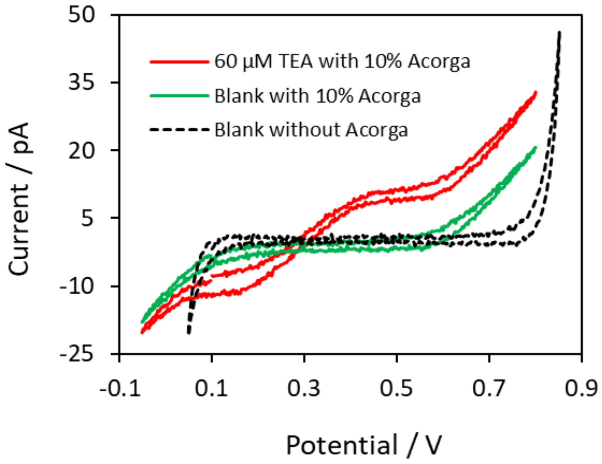

Figure 3.1.2: *The black dotted voltammogram is the response for the background electrolytes without Acorga, the green one is also for the background electrolytes with 10% Acorga at DCE organic phase and the red CV is for the 60 µM TEA$^+$ transfer at ITIES with 10% Acorga in DCE.*

3.2 pH effect

To investigate the electrochemical properties of metal ion, cobalt (Co^{2+}) at the ITIES we applied cyclic voltammetry technique at different pH of the aqueous solutions. In Figure 3.2.1, the CV response for 10 mM $CoSO_4$ shows that at pH 3.5, no phenomenon of Co^{2+} ions transfer happened at ITIES.

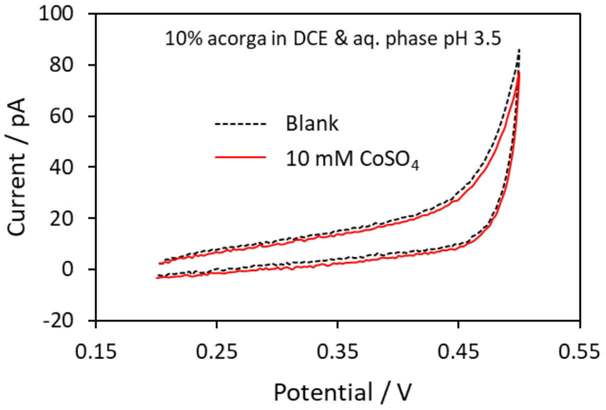

Figure 3.2.1: *Cyclic voltammogram of background electrolytes (black) and 10 mM $CoSO_4$ in aqueous phase (red) at pH 3.5 with 10% Acorga in organic phase. The diameter of the tip of the pipette was 10 µm.*

Similar result was obtained at a higher pH 11. Figure 3.2.2 shows the cyclic voltammograms of background electrolytes (black) and 10 mM $CoSO_4$ (red). The two CVs were identical, which suggests that no response for Co^{2+} ion transfers happened at ITIES at pH 11.

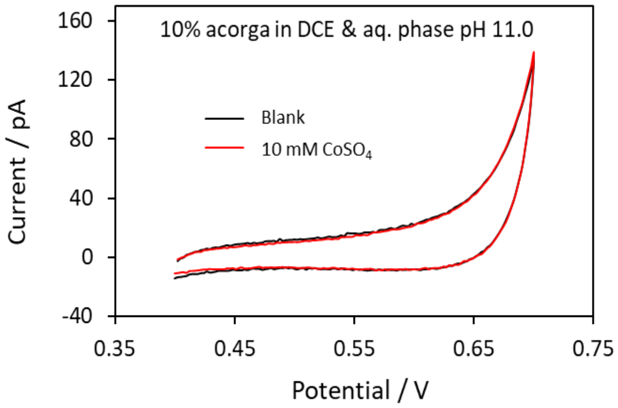

Figure 3.2.2: *Cyclic voltammogram of background electrolytes (black) and 10 mM* $CoSO_4$ *in aqueous phase (red) at pH 11.0 with 10% Acorga in organic phase. The diameter of the tip of the pipette was 10 µm.*

At pH 6.0, the Co^{2+} ions gave a response at ITIES with 10% Acorga in the organic phase. At this pH, when potential was applied the Co^{2+} ions transferred between the two phases. Figure 3.2.3 shows the cyclic voltammograms of 0.2, 0.5, 1.0 5.0, and 10.0 mM Co^{2+} ions. It also shows that the current increased up to the concentration of Co^{2+} at 5 mM.

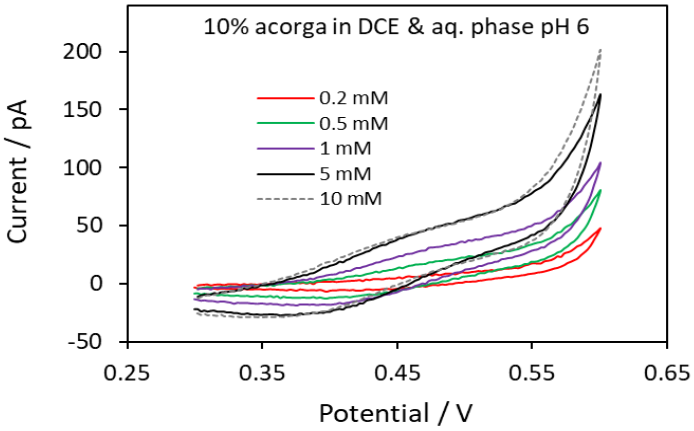

Figure 3.2.3: *Cyclic voltammograms of 0.2, 0.5, 1, 5 and 10 mM* $CoSO_4$ *at pH 6 with 10% Acorga in organic phase. The diameter of the tip of the pipette was 10 µm.*

The Co^{2+} ions' electrochemical properties across the ITIES at pH 9.0 was also examined and it was found that, a slightly higher response was observed at this pH compared to the response was achieved at pH 6. Figure 3.2.4 shows the background subtracted CVs of 3 mM and 15 mM $CoSO_4$ with the presence of 10% Acorga in the organic phase. The shape of the voltammogram for Co^{2+} transfer at the ITIES did not match with any ideal voltammogram observed at ITIES. From the Figures 3.2.4 and 3.2.3, it can be seen that the transfer started around 0.35 V, and the current increased linearly until it reached the background electrolyte transfer. Normally, a forward transfer process at a micro-ITIES formed at the tip of a pipette occurs with radial diffusion control (from outside to the inside of the pipette) and gives a sigmoidal voltammogram or a steady state current (as seen for TEA^+ transfer in Figures 3.1.1 and 3.1.2). However, in this case, Co^{2+} gave almost a linear increase in current.

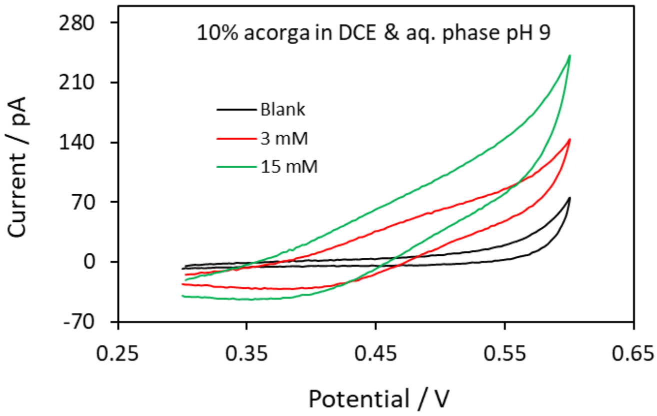

Figure 3.2.4: *Background subtracted cyclic voltammograms of 3 mM and 15 mM $CoSO_4$ at pH 9.0 with 10% Acorga in organic phase. The diameter of the tip of the pipette was 10 µm.*

Figure 3.2.5 shows the background subtracted CVs of 0.2, 0.5, 1.0, 3.0, 5.0, 10.0 and 15.0 mM $CoSO_4$. Earlier it was observed that at pH 6.0, the current increased up to 5 mM $CoSO_4$ (Figure 3.2.3). In contrast, at pH 9.0, Figure 3.2.5 shows that the current increased linearly with the concentration studied. Therefore, from the investigation of four different pH, it has been found that at a very low pH value of 3.5 and at a very high pH value of 11.0, the Co^{2+} ions was not found to cross the ITIES. Whereas at pH 6.0 and pH 9.0, Co^{2+} ions found to transfer across the ITIES and peak current observed was a bit higher at pH 9.0 than that of pH 6.0.

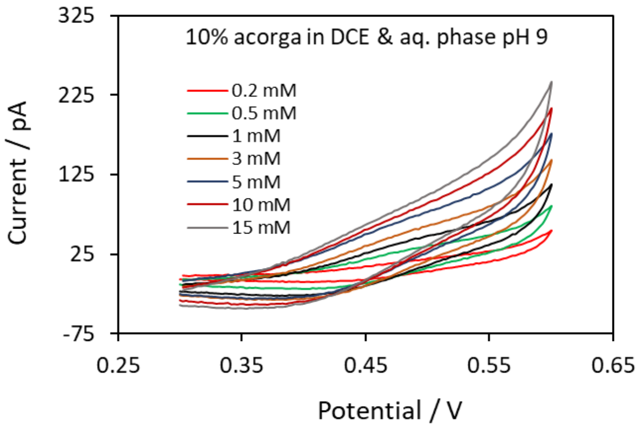

Figure 3.2.5: *Background subtracted cyclic voltammograms of 0.2, 0.5, 1, 3, 5, 10 and 15 mM $CoSO_4$ at pH 9.0 with 10% Acorga in organic phase. The diameter of the tip of the pipette was 10 µm.*

As at pH 9.0 Co^{2+} ions provided the comparatively better response, so, at this pH, an investigation was carried out to find out the better composition made out of Acorga and DCE that worked in a better way for Co^{2+} ion transfer. Figure 3.2.6 shows the voltammogram for 15 mM $CoSO_4$ transfer with 5% Acorga in the organic phase. If the CVs of Co^{2+} ion transfer with 5% Acorga and with 10% Acorga (Figure 3.2.4) in the organic phase were compared, then it can clearly be found that, the current response for Co^{2+} ion transfer with 10% Acorga was higher than the current with 5% Acorga utilizing the same micro size interface.

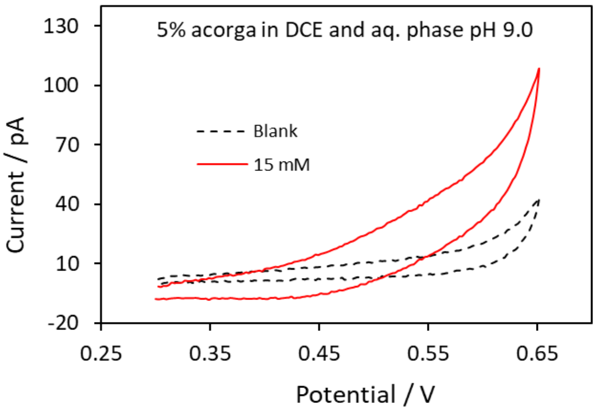

Figure 3.2.6: *Cyclic voltammograms of 15 mM $CoSO_4$ (red) and CV for background electrolytes (blank) at pH 9.0 with 5% Acorga in organic phase. The diameter of the tip of the pipette was 10 µm.*

Figure 3.2.7 shows the background subtracted CVs of 0.1, 0.5, 1, 2, 4, 10, and 15 mM Co^{2+} ions transfer at the micro-ITIES with 5% Acorga in the organic phase. Like the transfer with 10% Acorga (Figure 3.2.5), in this case, also, the current response increased linearly with concentrations. But mentioned earlier (Figure 3.2.5) that this current response~~s~~ are lower than that of the current responses with 10% Acorga.

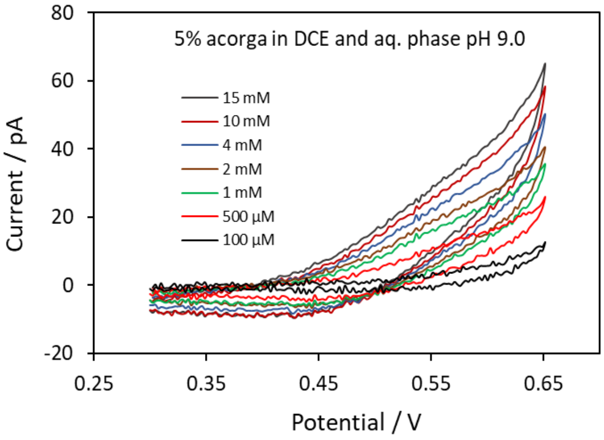

Figure 3.2.7: *Background subtracted cyclic voltammograms of 0.1, 0.5, 1, 2, 4, 10 and 15 mM $CoSO_4$ at pH 9.0 with 5% Acorga in organic phase. The diameter of the tip of the pipette was 10 µm.*

A similar experiment was carried out with 1% Acorga in the organic phase. Figure 3.2.8 shows the CVs of 0.1, 0.4, 2, 8, and 15 mM Co^{2+} ions transfer at the micro ITIES with 1% Acorga in the organic phase. It is obvious form the CV that, the current response again decreased with the decrease of Acorga in the organic phase.

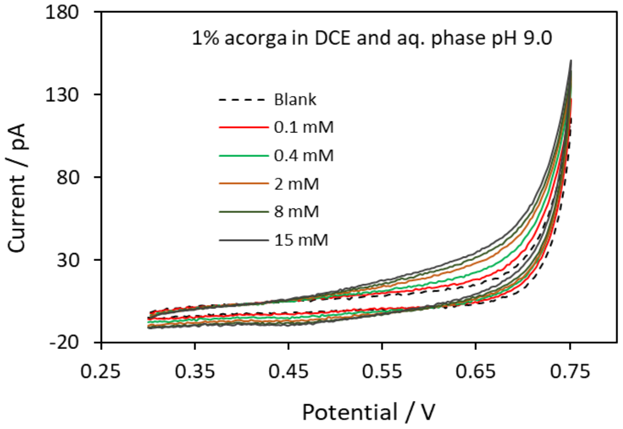

Figure 3.2.8: *Background subtracted cyclic voltammograms of 0.1, 0.4, 2, 8 and 15 mM* $CoSO_4$ *at pH 9.0 with 1% Acorga in organic phase. The diameter of the tip of the pipette was 10 µm.*

3.3 Mixed organic solvent

Conventionally, the ITIES is formed with a relatively more dense organic solvent than the aqueous phase and with relative permittivity around 10 - 15. A variety of organic solvents like nitrobenzene (NB), 1,2-dichloroethane (DCE), acetophenone, 1,2-dichlorobenzene (DCB), 1,6-dichlorohexane and 1,1-dichlorobutane are widely used in electrochemical studies at ITIES. There are some limitations for the wider applications of these solvents and toxicity is one of them. For the last two decades, the application of mixed organic solvents has attracted attention, because the opportunity of using lower-density organic solvents with lower toxicity and as well as achieving a higher permittivity. In this study, 1-decanol was mixed with DCE in the organic phase to explore the electrochemical properties of such an ITIES and the transfer behaviour of Co^{2+} ions across that newly modified ITIES. All the experiments utilizing the mixed organic solvents have been performed at pH 9.0, as at this pH the better response was found for Co^{2+} ions. Figure 3.3.1 shows the CVs of background electrolytes and 10 mM $CoSO_4$, where 20% 1-decanol was mixed in the DCE organic phase with 10% Acorga. The CV shows that no signal or response was observed for Co^{2+} ion transfer. The potential window was also narrower as compared to DCE organic phase only.

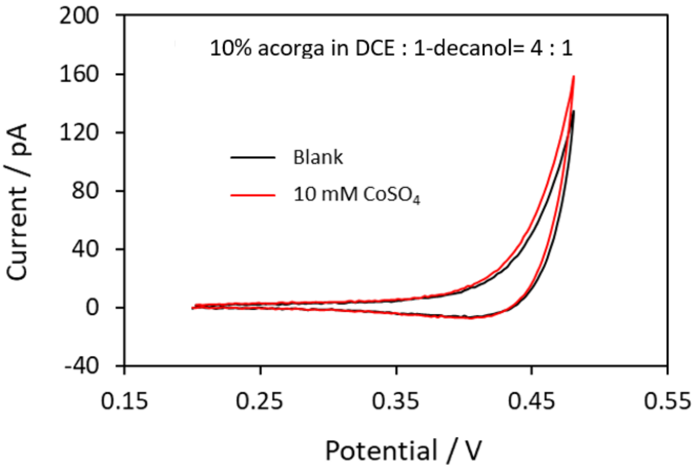

Figure 3.3.1: *Cyclic voltammogram of background electrolytes (black) and 10 mM* $CoSO_4$ *in aqueous phase (red) with mixed organic solvents (10% Acorga in DCE:1-decanol = 4:1) at pH 9.0. The diameter of the tip of the pipette was 10 µm.*

The percentage of 1-decanol was increased from 20% to 50% in the organic phase. Figure 3.3.2 shows the CVs of background electrolytes and 10 mM $CoSO_4$ in that interface. In this case, no signal or response was observed for Co^{2+} ion transfer as well and the potential window became more narrow than the potential window found at 20% 1-decanol.

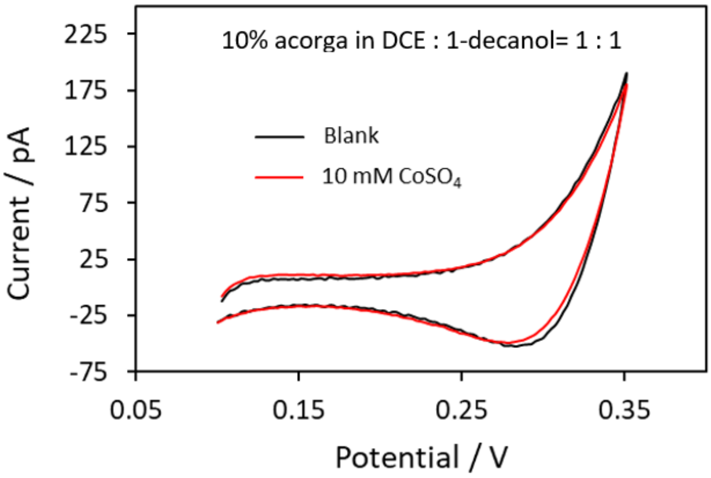

Figure 3.3.2: *Cyclic voltammogram of background electrolytes (black) and 10 mM $CoSO_4$ in aqueous phase (red) with mixed organic solvents (10% Acorga in DCE:1-decanol = 1:1) at pH 9.0. The diameter of the tip of the pipette was 10 µm.*

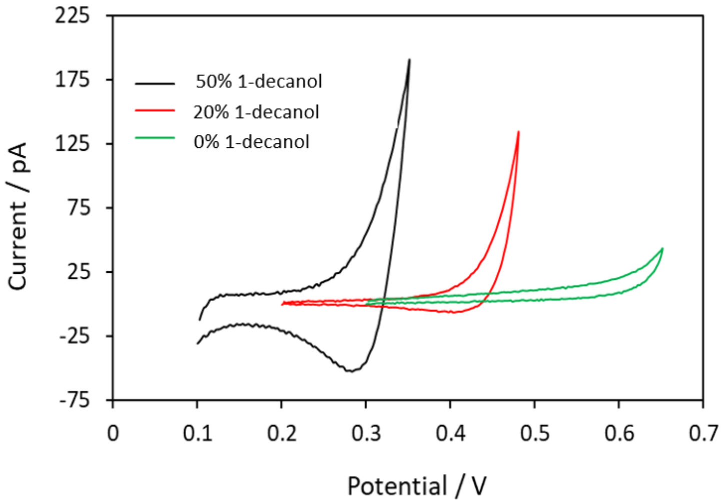

Figure 3.3.3: *Cyclic voltammogram of background electrolytes at different composition of organic phase. The green on is for only DCE, the red one is for 20% 1-decanol and the black one is for 50% 1-propanol. The aqueous phase pH was 9.0 and diameter of the tip of the pipette was 10 µm.*

Figure 3.3.3 shows the CVs of background electrolytes for different compositions of the organic phase. It shows that as the 1-decanol was added to the organic phase the potential window shifted towards the left or the lower potential. The working potential window became shorter in a continuous manner as more 1-decanol was added to the organic phase.

3.4 Detection of Ni^{2+} ions at ITIES by applying Cyclic Voltammetry

The transfer of Ni^{2+} ions was investigated at liquid/liquid interface with 10% Acorga in the DCE organic phase and the pH of the aqueous phase chosen was 9.0, as Co^{2+} ions provided the better response at these conditions. The identical experimental conditions were utilized for Ni^{2+} ions transfer and detection at the micro-ITIES. However, in this case, no response was observed for Ni^{2+} ions. Figure 3.4.1 shows the cyclic voltammograms of background electrolytes (black) and aqueous 5 mM $NiSO_4$ (red). This figure shows that there was no electrochemical response observed for nickel at this studied ITIES.

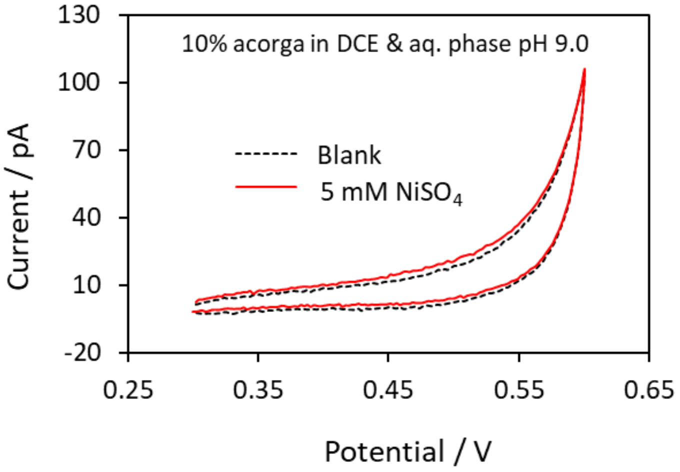

Figure 3.4.1: *Cyclic voltammogram of background electrolytes (black) and 5 mM* $NiSO_4$ *in aqueous phase (red) at pH 9.0 with 10% Acorga in organic phase. The diameter of the tip of the pipette was 10 µm.*

4 Conclusion

In this study, the extraction of metal ions Co^{2+} and Ni^{2+} with the aid of Acorga M5640 was investigated at liquid/liquid micro-interface by applying cyclic voltammetry technique. Different percentages of Acorga were added into the organic phase DCE and various pH values of the aqueous solution were utilized to investigate the suitable conditions for extracting/transferring the studied ions. When the percentage of Acorga was much higher, nearly 50%, no response was observed, even no TEA^+ transfer happened across the ITIES. This phenomenon suggests that the liquid/liquid interface was nearly blocked by the presence of 50% Acorga. The electrochemical investigation was performed for 10%, 5%, and 1% Acorga as well and it was observed that the Co^{2+} ions response for 10% Acorga in DCE was the best. From the pH investigations of aqueous solutions, it was found that the Co^{2+} ions response at pH 9.0 was better than any other studied pH. On the contrary, no transfer of Co^{2+} ions was noticed at relatively lower or higher pH values for instance, pH 3.5 & pH 11.0. A mixed organic solvent of 1-butanol & DCE was also investigated to observe the effect of it’s on the ITIES. It has been found that no transfer of Co^{2+} ions across the ITIES was observed when 1-butanol was present in the organic phase. Additionally, the resulting potential window decreased with an increased amount of 1-butanol in organic phase.

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