ELECTROCHEMICAL STUDIES ON THE CORROSION BEHAVIOR OF

COMMON METALS IN EUTECTIC IONIC LIQUIDS

by

Rami Alhasan

A Thesis Presented to the Faculty of the American University of Sharjah College of Engineering in Partial Fulfillment of the Requirements for the Degree of

> Master of Science in Chemical Engineering

Sharjah, United Arab Emirates

May 2017

© 2017 Rami Alhasan. All rights reserved.

Approval Signatures

We, the undersigned, approve the Master's Thesis of Rami Alhasan. Thesis Title: Electrochemical Studies on the Corrosion Behavior of Common Metals in Eutectic Ionic Liquids.

Signature

Date of Signature (dd/mm/yyyy)

Dr. Taleb Hassan Ibrahim Professor, Department of Chemical Engineering Thesis Advisor

Dr. Nabil Abdel Jabbar Professor, Department of Chemical Engineering Thesis Co-Advisor

Dr. Amani Al-Othman Assistant Professor, Department of Chemical Engineering Thesis Committee Member

Dr. Mustafa Khamis Professor, Department of Biology, Chemistry and Environmental Sciences Thesis Committee Member

Dr. Naif Darwish Head, Department of Chemical Engineering

Dr. Mohamed El-Tarhuni Associate Dean for Graduate Affairs and Research, College of Engineering

Dr. Richard Schoephoerster Dean, College of Engineering

Dr. Khaled Assaleh Interim Vice Provost for Research and Graduate Studies

Acknowledgements

I would like to express my special gratitude and thanks to Dr. Taleb Ibrahim who guided me with all care and patience towards the completion of this thesis. Also, I would like to thank Dr. Nabil Abdel Jabbar, Dr. Amani Al-Othman, Dr. Mustafa Khamis and Dr. Paul Nancarrow who have been supportive of my thesis and who worked to provide me all the help needed.

Special thanks to Dr. Farouq S. Mjalli from Sultan Qaboos University in Oman for his invaluable input and help in the synthesis of the Deep Eutectic Solvents. Also, I would like to thank Dr. Fathia Mohammad and Eng. Mohammad Qasim for their insight and the brilliant lab support. I am really grateful to Eng. Faisal Khatri, Eng. Pierre Kawak and Eng. Mohammad Ashraf for their help in my lab work and reviewing my written thesis. I would like to give my thanks to my family especially my mother for the love and patience during this work.

I would like to thank the department of chemical engineering and Dr. Naif Darwish for offering me a graduate assistantship. Also, I would like acknowledge that this research was funded by the AUS Research grant FRG15-R-17.

Abstract

Recently, new green novel solvents called Deep Eutectic Solvents (DES) were investigated as substitute for none environmentally friendly organic solvents and ionic liquids that are used in many applications such as metal processing, organic synthesis, extraction and adsorption processes, and in medical and pharmaceutical researches. DES are biodegradable and eco-friendly solvents. However, their corrosivity is not well studied. Corrosion of metals is a major problem in the chemical, oil and gas industries. In this work, several DES were synthesized and their corrosivity towards mild steel, stainless steel and copper was investigated using electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and Cyclic Sweep (CS). DES were synthesized by mixing choline chloride with a hydrogen bond donor at 70°C for about an hour. The corrosivity of DES at three different temperatures (25 °C, 50 °C and 75 °C) and as a function moisture content (0%, 5% and 10%) was determined. In most of the observations, corrosion rate increases as temperature and moisture content increase. Moreover, the corrosion rate of stainless steel was found to be the lowest of the tested metals at all conditions which makes it a good material for different applications. It was concluded that urea and glycol based DES are good candidates as green solvents due to their low and resilient corrosion rate values.

Search Terms: Deep Eutectic Solvents, Choline Chloride, Corrosion, Copper, Steel.

Abstract		5
List of Fig	ures	8
List of Tab	les	.11
Abbreviati	ons	.12
Chapter 1.	Introduction	.13
Chapter 2.	DES Literature Review	.17
2.1 Dec	ep Eutectic Solvents (DES)	.17
2.2 Sug	gar-Based Deep Eutectic Solvents (SB-DES)	.19
2.3 Pro	perties of Deep Eutectic Solvent	.19
2.3.1	Freezing point of deep eutectic solvents	.19
2.3.2	Density of deep eutectic solvents.	.20
2.3.3	Viscosity of deep eutectic solvents	.20
2.3.4	Ionic conductivity of deep eutectic solvents	.21
2.3.5	Corrosivity of deep eutectic solvents.	.21
2.4.1	Metal processing	.22
	interm processing.	
2.4.2	Organic synthesis	.22
2.4.2 2.4.3	Organic synthesis Other applications of deep eutectic solvents	.22 .24
2.4.2 2.4.3 2.5 Env	Organic synthesis Other applications of deep eutectic solvents	.22 .24 .24
2.4.2 2.4.3 2.5 Env Chapter 3.	Organic synthesis Other applications of deep eutectic solvents vironmental Features of Deep Eutectic Solvents Corrosion and Electrochemical Testing	.22 .24 .24 .26
2.4.2 2.4.3 2.5 Env Chapter 3. 3.1 Con	Organic synthesis Other applications of deep eutectic solvents vironmental Features of Deep Eutectic Solvents Corrosion and Electrochemical Testing	.22 .24 .24 .26 .26
2.4.2 2.4.3 2.5 Env Chapter 3. 3.1 Con 3.2 Ele	Organic synthesis Other applications of deep eutectic solvents vironmental Features of Deep Eutectic Solvents Corrosion and Electrochemical Testing rosion Significance ctrochemical Testing Theory	.22 .24 .24 .26 .26 .27
2.4.2 2.4.3 2.5 Env Chapter 3. 3.1 Con 3.2 Ele 3.2.1	Organic synthesis Other applications of deep eutectic solvents vironmental Features of Deep Eutectic Solvents Corrosion and Electrochemical Testing trosion Significance ctrochemical Testing Theory Electrochemical impedance spectroscopy (EIS)	.22 .24 .24 .26 .26 .26 .27
2.4.2 2.4.3 2.5 Env Chapter 3. 3.1 Con 3.2 Ele 3.2.1 3.2.2	Organic synthesis Other applications of deep eutectic solvents vironmental Features of Deep Eutectic Solvents Corrosion and Electrochemical Testing trosion Significance ctrochemical Testing Theory Electrochemical impedance spectroscopy (EIS) Cyclic sweep (CS).	.22 .24 .26 .26 .27 .27 .27
2.4.2 2.4.3 2.5 Env Chapter 3. 3.1 Con 3.2 Ele 3.2.1 3.2.2 Chapter 4.	Organic synthesis Other applications of deep eutectic solvents vironmental Features of Deep Eutectic Solvents Corrosion and Electrochemical Testing rosion Significance ctrochemical Testing Theory Electrochemical impedance spectroscopy (EIS) Cyclic sweep (CS) Experimental Methodology	.22 .24 .26 .26 .27 .27 .27 .29 .32
2.4.2 2.4.3 2.5 Env Chapter 3. 3.1 Con 3.2 Ele 3.2.1 3.2.2 Chapter 4. 4.1 Rav	Organic synthesis Other applications of deep eutectic solvents vironmental Features of Deep Eutectic Solvents Corrosion and Electrochemical Testing corrosion Significance ctrochemical Testing Theory Electrochemical impedance spectroscopy (EIS). Cyclic sweep (CS). Experimental Methodology	.22 .24 .26 .26 .27 .27 .27 .29 .32
2.4.2 2.4.3 2.5 Env Chapter 3. 3.1 Con 3.2 Ele 3.2.1 3.2.2 Chapter 4. 4.1 Rav 4.2 DE	Organic synthesis Other applications of deep eutectic solvents vironmental Features of Deep Eutectic Solvents Corrosion and Electrochemical Testing corrosion Significance ctrochemical Testing Theory Electrochemical impedance spectroscopy (EIS). Cyclic sweep (CS). Experimental Methodology W Materials S Synthesis	.22 .24 .26 .26 .27 .27 .27 .29 .32 .32 .32
2.4.2 2.4.3 2.5 Env Chapter 3. 3.1 Con 3.2 Ele 3.2.1 3.2.2 Chapter 4. 4.1 Rav 4.2 DE Chapter 5.	Organic synthesis Other applications of deep eutectic solvents Vironmental Features of Deep Eutectic Solvents Corrosion and Electrochemical Testing Corrosion Significance crosion Significance ctrochemical Testing Theory Electrochemical impedance spectroscopy (EIS) Cyclic sweep (CS) Experimental Methodology S Synthesis Results and Discussions	.22 .24 .26 .26 .27 .27 .27 .29 .32 .32 .32 .33

Table of Contents

5.1.1	Glyceline results.	35			
5.1.2	Reline results.	42			
5.1.3	Trithaline results				
5.1.4	4 Ethaline results.				
5.1.5	Phenoline results	47			
5.1.6	Maloline results.	49			
5.2 Mil	ld Steel (MS) Testing Results	51			
5.2.1	Reline results.	51			
5.2.2	Phenoline results	53			
5.2.3	Glyceline results.	55			
5.2.4	Ethaline results.	57			
5.2.5	Trithaline results	59			
5.2.6	Maloline results.	60			
5.3 Sta	inless Steel (SS) Testing Results	62			
5.3.1	Reline results.	63			
5.3.2	Phenoline results	65			
5.3.3	Glyceline results.	66			
5.3.4	Ethaline results.	68			
5.3.5	Trithaline results	70			
5.3.6	Maloline results.	72			
5.4 Res	sults Comparison and Summary	74			
Chapter 6.	Conclusions	77			
References	S	78			
Appendix	A EIS and CS Results for Copper	84			
Appendix	B EIS and CS Results for Mild Steel (MS)	88			
Appendix	C EIS and CS Results for Stainless Steel (SS)	92			
Vita		96			

List of Figures

Figure 1. The major aspects that goal solvents should try to combine13
Figure 2. A representation of a binary system phase diagram forming a eutectic mixture
Figure 3. Typical structures of hydrogen bond donors utilized in DES
Figure 4. The Simplified Randles circuit diagram
Figure 5. An example of a Tafel plot used for estimating the corrosion current density
Figure 6. The structure of choline chloride (C ₅ H ₁₄ ClNO) salt32
Figure 7. The colorless ethaline DES synthesized in the lab
Figure 8. The glass cell designed for the electrochemical tests
Figure 9. Gill AC potentiostat employed in electrochemical testing
Figure 10. Temperature control of the electrochemical cell using a water bath
Figure 11. Corrosion rates of copper in Glyceline DES at different temperatures and water contents from the EIS test
Figure 12. Nyquist plots for copper in Glyceline at (a) pure (b) 5% water and (c) 10% water from the EIS test
Figure 13. Nyquist plots for copper in Glyceline at (a) 25 °C (b) 50 °C and (c) 75 °C from the EIS test
Figure 14. Corrosion rates of copper in Glyceline DES at different temperatures and water contents from the CS test
Figure 15. Cyclic sweep plots for copper in Glyceline at (a) pure (b) 5% water and (c) 10% water
Figure 16. Cyclic sweep plots for copper in Glyceline at (a) 25 °C (b) 50 °C and (c) 75 °C
Figure 17. Corrosion rates of copper in Reline DES at different temperatures and water contents from the EIS test
Figure 18. Corrosion rates of copper in Reline DES at different temperatures and water contents from the CS test
Figure 19. Corrosion rates of copper in Trithaline DES at different temperatures and water contents from the EIS test

Figure 20. Corrosion rates of copper in Trithaline DES at different temperatures and water contents from the CS test
Figure 21. Corrosion rates of copper in Ethaline DES at different temperatures and water contents from the EIS test
Figure 22. Corrosion rates of copper in Ethaline DES at different temperatures and water contents from the CS test
Figure 23. Corrosion rates of copper in Phenoline DES at different temperatures and water contents from the EIS test
Figure 24. Corrosion rates of copper in Phenoline DES at different temperatures and water contents from the CS test
Figure 25. Corrosion rates of copper in Maloline DES at different temperatures and water contents from the EIS test
Figure 26. Corrosion rates of copper in Maloline DES at different temperatures and water contents from the CS test
Figure 27. Corrosion rates of MS in Reline DES at different temperatures and water contents from the EIS test
Figure 28. Corrosion rates of MS in Reline DES at different temperatures and water contents from the CS test
Figure 29. Corrosion rates of MS in Phenoline DES at different temperatures and water contents from the EIS test
Figure 30. Corrosion rates of MS in Phenoline DES at different temperatures and water contents from the CS test
Figure 31. Corrosion rates of MS in Glyceline DES at different temperatures and water contents from the EIS test
Figure 32. Corrosion rates of MS in Glyceline DES at different temperatures and water contents from the CS test
Figure 33. Corrosion rates of MS in Ethaline DES at different temperatures and water contents from the EIS test
Figure 34. Corrosion rates of MS in Ethaline DES at different temperatures and water contents from the CS test
Figure 35. Corrosion rates of MS in Trithaline DES at different temperatures and water contents from the EIS test
Figure 36. Corrosion rates of MS in Trithaline DES at different temperatures and water contents from the CS test

Figure 37. Corrosion rates of MS in Maloline DES at different temperatures and water contents from the EIS test
Figure 38. Corrosion rates of MS in Maloline DES at different temperatures and water contents from the CS test
Figure 39. Corrosion rates of SS in Reline DES at different temperatures and water contents from the EIS test
Figure 40. Corrosion rates of SS in Reline DES at different temperatures and water contents from the CS test
Figure 41. Corrosion rates of SS in Phenoline DES at different temperatures and water contents from the EIS test
Figure 42. Corrosion rates of SS in Phenoline DES at different temperatures and water contents from the CS test
Figure 43. Corrosion rates of SS in Glyceline DES at different temperatures and water contents from the EIS test
Figure 44. Corrosion rates of SS in Glyceline DES at different temperatures and water contents from the CS test
Figure 45. Corrosion rates of SS in Ethaline DES at different temperatures and water contents from the EIS test
Figure 46. Corrosion rates of SS in Ethaline DES at different temperatures and water contents from the CS test
Figure 47. Corrosion rates of SS in Trithaline DES at different temperatures and water contents from the EIS test
Figure 48. Corrosion rates of SS in Trithaline DES at different temperatures and water contents from the CS test
Figure 49. Corrosion rates of SS in Maloline DES at different temperatures and water contents from the EIS test
Figure 50. Corrosion rates of SS in Maloline DES at different temperatures and water contents from the CS test

List of Tables

Table 1. Freezing points of some ChCl – HBD mixtures and pure HBD melting temperatures
Table 2. Examples of using ChCl+urea DES as a solvent and a catalyst in organic synthesis reactions. 23
Table 3. Examples using SB-DES in organic synthesis. 24
Table 4. EIS parameters obtained using Glyceline on copper. 36
Table 5. CS parameters obtained for copper in Glyceline
Table 6. Corrosion rate range comparison at different temperatures
Table 7. Corrosion rate range comparison at different water contents. 76
Table 8. EIS and CS parameters obtained using Glyceline on copper
Table 9. EIS and CS parameters obtained using Reline on copper. 85
Table 10. EIS and CS parameters obtained using Trithaline on copper
Table 11. EIS and CS parameters obtained using Ethaline on copper
Table 12. EIS and CS parameters obtained using Phenoline on copper
Table 13. EIS and CS parameters obtained using Maloline on copper
Table 14. EIS and CS parameters obtained using Reline on MS
Table 15. EIS and CS parameters obtained using Phenoline on MS
Table 16. EIS and CS parameters obtained using Glyceline on MS90
Table 17. EIS and CS parameters obtained using Ethaline on MS90
Table 18. EIS and CS parameters obtained using Trithaline on MS91
Table 19. EIS and CS parameters obtained using Maloline on MS91
Table 20. EIS and CS parameters obtained using Reline on SS
Table 21. EIS and CS parameters obtained using Phenoline on SS
Table 22. EIS and CS parameters obtained using Glyceline on SS
Table 23. EIS and CS parameters obtained using Ethaline on SS
Table 24. EIS and CS parameters obtained using Trithaline on SS
Table 25. EIS and CS parameters obtained using Maloline on SS

Abbreviations

- \mathbf{CR} Corrosion rate
- CS Cyclic Sweep
- **DES** Deep eutectic solvents
- **EIS** Electrochemical impedance spectroscopy
- $\boldsymbol{HBD}-\boldsymbol{Hydrogen} \text{ bond donor}$
- IL Ionic liquid
- MS Mild steel
- **SB-DES** Sugar based deep eutectic solvents
- **SS** Stainless steel

Chapter 1. Introduction

In recent years, increasing attention has been paid to reducing the environmental problems and sustaining our energy, water and food resources. This can be done by utilizing "green" technologies which focus on decreasing environmental impact using eco-friendly materials. In solvents industry, the goal solvent should have a high performance in the chemical and engineering aspects, as well as a low negative influence on environment, health and safety features. The higher the intersection between the three circles shown in Figure 1, the more precious the solvent would be.



Figure 1. The major aspects that goal solvents should try to combine [1].

The conventional solvents have two main problems: (i) Great quantities are needed. (ii) Relatively high volatility that causes loss of solvent or air pollution. In recent decades, studies and experiments have been made in order to replace organic solvents. These methods involve the application of easily recyclable systems such as supercritical CO₂ (scCO₂) or fluorous solvents, using no solvent at all, or the utilization of non-volatile systems like Ionic Liquids (ILs) [2].

Ionic Liquids (ILs) have been viewed as the new alternative solvents that provide variety of options in chemical processing and have good environmental properties. The standard way to define an ionic liquid is "an ionic media which is in the liquid state at a temperature less than 100 °C. ILs work smoothly under a wider range

of low temperatures and pressures compared to traditional solvents. Also, ILs withstand moisture, have thermal stability and they are nonvolatile with almost no vapor pressure. ILs consist of bulky and asymmetrical cationic and anionic parts. The approximately countless combinations of cations and anions means the IL properties can be tailored for a certain requirement and that is why they are called "designer solvents" [3-7]. The first ionic liquid, ethyl ammonium nitrate, ([EtNH₃][NO₃]; melting point: 13-14 °C) was reported in 1914 [8]. Since then, ionic liquids (ILs) were broadly studied in a wide range of applications such as: organic catalysis [9], desulfurization of fuel [10], CO₂ capture [11], electrochemistry [12], and processing of precious metal [13]. On the other hand, ILs suffer some disadvantages like other solvents such as: synthesis difficulties that ends up disturbing the purity of ILs, poor biodegradability with high toxicity, and relatively high cost [14-17].

Deep eutectic solvents (DES) are considered as a novel alternative class of ILs in order to overcome aforementioned limitations. The DES are defined as mixtures of two or more components, which at a certain atomic or molecular ratio called eutectic point, possess a lower melting point than any of the individual components [18] as shown in Figure 2 [19].



Figure 2. A representation of a binary system phase diagram forming a eutectic mixture [19].

One of the significant advantages of the DES is the simplicity of synthesis. The liquid forms simply by mixing the two components with moderate heating as the reaction is endothermic. Another key advantage of DES is that they are simple mixtures of well-known chemicals so that they do not have to be listed as new ones because they return to their essential components upon excessive dilution in water.

The first paper on DES was only published in 2001 [20], so it is obvious that they are still at early stages compared to ILs. In distinction to ILs, which are made up of one type of discrete anion and cation, the DES systems are formed from a eutectic mixture of Lewis and Bronsted acids and bases. The leading applications of DES are reaction media and metal processing. DES have been used as substitute media for metals that are usually hard to plate or process, or include environmentally hazardous processes. Also, DES serve as an environmentally kind alternative to organic solvents in organic synthesis [21]. In addition, DES are employed as sustainable media for the development of functional and well-defined nanoscale materials concerning metalorganic frameworks, shape-controlled nanoparticles, hierarchal porous carbons, colloidal assemblies, and DNA/RNA architectures [22]. Furthermore, biomaterials solubility such as chitin and cellulose in DES was lately reported strongly along with the use of DES in extraction processes [23-27].

The DES properties in terms of biodegradability are merely dependent on the materials used. Consequently, natural-based DES can be created by using primary metabolites, such as amino acids, choline derivatives, organic acids or sugars [28]. These DES completely accomplish the green chemistry values.

While there is a big number of constituents and loads of DES that have been discussed in literature, the formation mechanism is not yet fully understood. The melting point depression is reflected by combining the hydrogen bond interactions, entropy change, and lattice energy effects. As the three parameters are contributing simultaneously, it is a challenging process to predict the viable formation, and the possible intermolecular interactions [18].

Although many studies tackled different properties of DES, only recent work of Abbott et al. [29] discussed the corrosion characteristics of some metals in DES. So it is clear that this area is new and needs a lot of research as corrosion is known to be one of the most expensive problems in industry and due to it billions of dirhams are spent yearly for repair and maintenance of equipment.

This work aims to study the corrosion effect of different metals in some selected DES. Operating conditions manipulated will be DES type, water content and temperature. The tests will be operated and evaluated under well-established corrosion related techniques and tools. Including this introduction, the thesis is divided into 6 chapters. The second chapter will introduce the reader to the types and properties of DES. It will also highlight some of the applications and environmental aspects of DES. The third chapter begins with corrosion significance and then moves to a background about electrochemical tests that were carried out. The fourth chapter discusses the experimental set up that was employed to prepare for testing. The fifth chapter presents the results of the two electrochemical tests for different metals, DES, temperatures, and water contents. Finally, the conclusions of this thesis work are presented in chapter six.

Chapter 2. DES Literature Review

2.1 Deep Eutectic Solvents (DES)

A eutectic system is a blend of chemicals or components that converts to a single compound which solidifies at a lower melting temperature than any of the initial components as shown in Figure 2. Eutectic systems that undergoes a huge melting point depression (around 200 °C) are called deep eutectic solvents (DES) [14]. In contrast to ionic liquids (ILs), which are made up of a cation and a complex anion or the opposite, DES contain a cation, an anion and a complexing agent [30].

The first aluminum-based ionic liquids that were reported in the 1950s by Hurley et al. [31], and until the 1990s no other metal salts were used to produce ionic liquids. Abbott et al. [20, 32] and Sun et al. [33, 34] displayed that eutectic mixtures of zinc halides and quaternary ammonium halides also have melting points near the ambient conditions. A broad range of other salts and organic compounds that form eutectic mixtures with quaternary ammonium salts has been further discussed and reported after that. The general formula to express a eutectic solvent is:

Cat^+X^- . zY

where Cat^+ is in any ammonium, phosphonium or sulfonium cation, and X^- is a halide anion (usually Cl⁻). They are based on equilibria between X^- and a Lewis or Bronsted acid *Y*, and *z* is the number of *Y* molecules which complex X^- . So the principle is that the complexing agent "*Y*" just needs to be able to complex the simple anion to effectively delocalize the charge and decrease the interaction with the cation. The eutectic solvents mentioned can be split into three types depending on the complexing agent used [18-20, 31-39]:

Eutectic Type 1:	$Y = MCl_x$	and	M = Zn, Sn, Fe, Au, In.
Eutectic Type 2:	$Y = MCl_x \cdot yH_2O$	and	M = Cr, Co, Cu, Ni, Fe.
Eutectic Type 3:	$Y = \mathbf{R}\mathbf{Z}$	and	$Z = CONH_2$, COOH, OH.

This work focusses on type three of DES. The first "type three" DES was reported by Abbott et al. in 2003 [38] and phase diagram was documented by mixing urea and choline chloride at different compositions. Urea and choline chloride (ChCl) have a melting temperature of 134 °C and 302 °C, respectively. The eutectic point was found to be at 1:2 molar ratio of ChCl-urea. As this combination has a freezing point of 12 °C, it is liquid at room temperature. Abbott et al. detailed that this freezing point depression must be happening as a result of the interaction between urea molecules and the chloride ion. In addition, homogeneous liquids can merely be formed by interacting with compounds capable of creating hydrogen bonds with chloride ions. And this can be applied to a range of hydrogen bond donors (HBDs) for instance amines, acids, and alcohols. Some of the common structures of HBDs are shown in Figure 3.



Figure 3. Typical structures of hydrogen bond donors utilized in DES [14].

DES are easily produced by mixing the components and heating them up under stirring. The purity of the produced mixture depends mainly on the purity of the initial components. Other advantages of DES are inflammability, non-volatility and close to inertness for water reactions in many cases [14]. Some freezing points of choline chloride with HBDs are shown in Table 1 [18, 38, 40].

HBD	T _f in °C	T _m [∗] in °C
Urea	12	134
1-Methyl urea	29	93
Acetamide	51	80
Malonic acid	10	135
Oxalic acid	34	190
Phenylacetic acid	25	77
Ethylene glycol	-66	-13

Table 1. Freezing points (Tf) of some ChCl – HBD mixtures and pure HBD melting temperatures (Tm *).

2.2 Sugar-Based Deep Eutectic Solvents (SB-DES)

Carbohydrates were revealed as appropriate mixing companions for lowmelting systems [21, 41]. Also, carbohydrates are the major part of all biomass which means they are renewable and the most dominant feedstock on earth. Carbohydrates are insoluble in all solvents with the exception of water, which is a major weakness regarding their usage [42]. Another drawback for these sugar-based DES is that they suffer at melting points in the range 65-85 °C, which restrict their application at moderate temperatures.

2.3 **Properties of Deep Eutectic Solvent**

As mentioned before, a tremendous number of deep eutectic solvents (DES) exists so they can be tailored to match a desired physical or chemical property like freezing point, density, viscosity, conductivity or corrosivity. These major properties are detailed and discussed in this section.

2.3.1 Freezing point of deep eutectic solvents. The freezing point of DES depends on the selection of mixture of organic salt and HBD. For example, the freezing point of a mixture of choline salt DES joined with urea increases in the following order F^- (1 °C)- NO₃ ⁻ (4 °C)- Cl⁻ (12 °C)- BF₄ ⁻ (67 °C) indicating that a correlation exists between the salt and the hydrogen bond strength. Nuclear magnetic resonance (NMR)

spectroscopy displayed the existence of a hydrogen bond network within the eutectic mixtures. Also, a tough cross-correlation between the fluoride anion of ChF and the NH₂ groups of the urea molecule in DES was detected by Heteronuclear Overhauser Effect Spectroscopy (HOESY) measurements [38]. However, the composition of DES or the molar ratio of salt to HBD has no clear relation with freezing temperature. For example, composition of 1:2 like ChCl-urea, phenylpropionic acid and phenylacetic acid, in which two molecules of carboxylic acid are required to complex one chloride anion, show a lower freezing point compared to dicarboxylic acids such as oxalic or succinic acid, with a composition of 1:1. An exception to this is the malonic acid which is a dicarboxylic acid but has a lower freezing point than ChCl-urea mixture. Abbott et al. proposed that this freezing point depression depends on the lattice energies of each DES, the interaction of the salt's anion and HBD, and the change in entropy due to forming a liquid [18].

2.3.2 Density of deep eutectic solvents. Overall, the densities of deep eutectic solvents (DES) are higher than the density of water. They are analogous to ILs' densities which are in the range between 1.1 g/cm³ and 2.4 g/cm³ [43]. The density depends on molecular grouping and packing of DES [44]. Mjalli et al. suggested a technique to evaluate the DES density at different temperatures. The average of absolute relative percentage error (ARPE) was calculated for all the DES tested and was found to be around 1.9% after comparison between the measured densities and the predicted ones. In Addition, the authors discovered that the salt and HBD types and the composition (mole ratio) of both compounds had a substantial effect on the reported properties like the density [45].

In most cases, the increase in temperature results a reduction in the density of DES. This reduction is due to the creation of space which causes fast molecular movement at high temperatures [40]. Furthermore, the density is affected by the water content and as percentage of water gets higher, the density will decrease [46].

2.3.3 Viscosity of deep eutectic solvents. The viscosity is very important factor for practical application and it controls the usage of DES in many industries. Most DES own a fairly high viscosity at room temperature compared to traditional solvents [14, 46]. And as temperature increases, the viscosity of DES decreases following an Arrhenius-like behavior. Also, the water content has a similar effect as the temperature.

The viscosity is linked to free volume and the probability of finding holes of appropriate dimensions for movement of the solvent ions or molecules [30]. The availability of a widespread hydrogen bond network can results in a lower motion of species inside the mixture which ultimately gives a higher viscosity values for DES. Likewise, some minor forces like electrostatic force or van der Waals interactions may result in high viscosity values [14, 46]. Moreover, the composition plays different roles for different DES with regards to viscosity. For instance, the viscosity decreases with increasing choline chloride amount for ChCl-glycerol mixtures but mixtures of choline chloride and ethylene glycol have the reverse effect [30].

2.3.4 Ionic conductivity of deep eutectic solvents. There is a solid relationship between conductivity and viscosity in general. DES show low conductivity values at room temperature (lower than 2 mS/cm) owing to their high viscosity readings [14]. Further, the same Arrhenius-like behavior is obtained with respect to temperature analogous to the viscosity relation with temperature. Regarding the composition, another similar behavior to viscosity is reported. For example, continual addition of choline cloride to glycerol-based DES increases the conductivity from 0.74 mS/cm for a molar ratio of 1:4 ChCl – glycerol to 1.30 mS/cm for a molar ratio of 1:2 ChCl – glycerol. This occurs due to the gradual decrease in viscosity and subsequently more available charge carriers in the liquid electrolytes [47].

2.3.5 Corrosivity of deep eutectic solvents. Abbott et al. have recently reported a preliminary study on the corrosion rates of different metals including steel, nickel and aluminum [29]. They used water miscible DES such as Reline (ChCl+urea), Ethaline (ChCl+ethylene glycol), Glyceline (ChCl+glycerol) and Oxaline (ChCl+oxalic acid) to test the change in corrosion rate at different water content. The corrosion rate was evaluated using two techniques: linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). The corrosion rate based on Tafel slopes in the LSV was very low for Ethaline, Glyceline and Reline but very high for Oxaline. Also, Tafel slopes suggest that the cathodic process is rate limiting. Another finding is that glycol-based DES are relatively insensitive to the addition of water so they would be suitable as lubricants for marine environments. EIS showed that Ni and Al form a passivating layer after a slow initial corrosion.

2.4 Applications of Deep Eutectic Solvents

As the deep eutectic solvents (DES) are in the liquid phase at room temperature, they have been employed in many solvent applications. Also, they work as good lubricants at moderate temperatures. This section discusses some of the major applications for DES.

2.4.1 Metal processing. One of the major applications of DES recently is electroplating and electropolishing which is reducing the surface roughness by controlled corrosion and increases the optical reflectivity. Nearly all electroplating processes are based on aqueous acidic or basic solutions and some minor applications actually use organic solvents. The main restrictions for these systems are their electrochemical performance and stability, because limited potential windows result in evolution of gas which will cause hydrogen embrittlement and passivation. The DES overcome these problems in addition to some key advantages to other non-aqueous solvents and ILs. First, the metal salts have high solubility in DES which increase their electrochemical performance [48]. Also, they are tolerant to water content, cheap and biodegradable [14, 49, 50]. In electropolishing of 316 stainless steel, a mixture of choline chloride and ethylene glycol has been reported by Abbott et al [51]. The results were successful and the electropolishing liquid was non-corrosive, also air and moisture stable.

In metal extraction, a eutectic mixture of choline chloride and urea was used to solubilize metal oxide which are typically insoluble in non-aqueous solvents as mentioned before. Nevertheless, ChCl+urea mixture was able to dissolve numerous of the metal oxides like ZnO, Cu₂O or NiO. Further, ligands like urea, thiourea and oxalate were utilized to complex different types of metals and also involved in DES synthesis. Yet, these mixtures are fully water miscible and their usage for two phase extraction would not work [52, 53].

2.4.2 Organic synthesis. The selection of solvents is vital in organic synthesis processes. The solvents are the prime source of waste, hence, non-toxic choices are very essential to get an environmentally benign waste. So picking DES would be a wise choice as a solvent and it is used as a catalyst as well in some applications. For instance, a mixture of choline chloride and urea was used as solvent and a catalyst for

bromination, Perkin condensation reaction, and reduction of epoxides as shown in Table 2. These reactions typically demand severe conditions including elevated temperatures, strong acids, and toxic solvents. On the other hand, using DES as solvents, which are not toxic or acidic, made the reaction run faster and at lower temperatures [54-56].

 Table 2. Examples of using ChCl+urea DES as a solvent and a catalyst in organic synthesis reactions.



Another green solvents that can also be used as reaction media are the Sugarbased DES. Nevertheless, their usage is still narrow because of their high viscosity values, high melting points and the effect of high temperature on the sugar structure. Some examples for reactions involving SB-DES are presented in Table 3 [21, 41, 57].





2.4.3 Other applications of deep eutectic solvents. Recently, the popularity of DES has rapidly increased, consequently, they are being used and tested for a wide range of applications and processes [48]. An innovative field for DES is using them as for the development of functional and well-defined nanoscale materials concerning metal-organic frameworks, shape-controlled nanoparticles, hierarchally porous carbons, colloidal assemblies, and DNA/RNA architectures [22]. In the pharmaceutical area, they were tested as potential drug solubilization vehicles [15].

DES are tested as biomass solvents for chitin, cellulose and lignocellulose [23, 24, 58]. DES were also used as extraction media for azeotropic mixtures like extracting glycerol from biodiesel [27]. In addition, DES were reported in CO₂ adsorption and they enhanced the adsorption by a microporous anionic framework [59].

2.5 Environmental Features of Deep Eutectic Solvents

Organic solvents generally endanger are toxic, hazardous while handling and environmentally non-friendly. As a result, multiple "greener" ways were proposed to substitute them in chemical processes for instance water, supercritical fluids (CO₂) or Ionic Liquids (ILs). Nonetheless, defining any of those solvents as "Green Solvents" is still debatable [60]. But recently, deep eutectic solvents (DES) are stepping up to that title as it will be shown in this section.

As DES possess lower vapor pressures than various organic solvents, no emission to the atmosphere is expected. Also, DES are made up of nontoxic, natural and environmentally gentle materials [48]. Choline chloride that is mostly used in type three DES, is an organic salt that is biocompatible and an important source of vitamin B4 for chicken feed. It also has some key functions in the human body as a micronutrient [61].

Further, urea, an important hydrogen bond donor (HBD) of DES is not toxic to the human body and can be readily excreted in the urine [62]. In addition, Matthijs et al. did a study on the environmental influence of ChCl+ethylene glycol DES in electroplating. The two constituents were not harmful to the environment and readily biodegradable, with the resultant DES (Ethaline) also biodegradable [63]. Furthermore, sugars (glucose, fructose, etc.), carboxylic acids (malonic acid, oxalic acid, etc.), and amino acids are considered as friendly and biodegradable in the environment and they can be used to synthesis DES [18, 28, 41, 58].

Chapter 3. Corrosion and Electrochemical Testing

3.1 Corrosion Significance

In today's world, the term "Corrosion" has a very great significance looking at the huge effects it has in our lives. From small metallic screws to large applications, corrosion can be seen everywhere. Scientists and engineers have been working out for a long time to combat corrosion but no optimum measures have yet been discovered. The prominence of this issue can be seen from the emerging of an entire new field just to understand and combat corrosion titled "Corrosion Science and Engineering" [64].

Corrosion in simple words is the deterioration of materials by chemical interaction with the environment. The term is seldom applied to plastic pipes, wood and concrete too but usually it only refers to metallic corrosion. Corrosion is often referred to as extractive metallurgy in reverse because corrosion takes place when similar amount of energies required to extract a metal are present. Due to the presence of these energies, the same chemical reaction takes place, but in the opposite direction they return the metal to its combined state in chemical compounds that are somewhat identical to the minerals they were extracted from [64].

The most important cost of corrosion are the economic costs induced to prevent applications from degradation due to this phenomenon. A survey by the Department of Commerce in the United States says that approximately \$70 billion was spent for corrosion in 1976. These numbers have now reached around \$126 billion per year in today's time. Hence it can be seen that economic costs of Corrosion are enormous. In several cases, it is seen that the cost to avoid corrosion to certain equipment are much costlier than the equipment itself [64].

However along with these direct costs, several indirect costs also come into play. These indirect costs are as follows [64]:

 Plant Downtime: The loss incurred due to the shutdown of the plant because of corrosion, since the plant becomes inoperable if some vital part corrodes and stops functioning. Also the labor and equipment required to replace these parts contribute to costs.

- 2) Loss of Product: The pipelines or tanks that corrode get damaged and basically become unusable which incurs indirect cost. Usually replacing these equipment is very expensive and time consuming. Since time is money, it costs the firm a lot. Along with these environmental hazards due to leakage of hazardous substances should also be taken into consideration as paying fines or compensating for this will cost too.
- Loss of Efficiency: Corrosion on equipment's surfaces also reduces their efficiencies. For eg. The heat transfer would reduce significantly if the tubing of a heat exchanges corroded.
- Contamination: Some soluble corrosion products can spoil the overall composition of the chemical products being prepared industries such as soaps, dyes, pharmaceuticals etc.
- 5) Overdesign: To have appropriate measures keeping corrosion in mind, extra resources are wasted and extra power is wasted for the moving parts. Overdesign is done since firms do not have the adequate corrosion rate information.

3.2 Electrochemical Testing Theory

To execute electrochemical testing for the selected metals, a GILL AC potentiostat from ACM Instruments was used. The electrochemical experiments were conducted by this potentiostat are electrochemical impedance spectroscopy (EIS) and cyclic sweep polarization (CS). This section gives a brief background about the theory behind these tests.

3.2.1 Electrochemical impedance spectroscopy (EIS). One of the key tests that analyzes capacitive and resistive characteristics of many corrosion cells is the EIS or AC Impedance test that uses a scan of certain test frequencies. It has been broadly used as a dominant tool for characterizing corrosion processes and checking the performance of protective coatings. EIS is a non-destructive technique of electrochemical testing which can determine the corrosion kinetics and that's why the CS test was conducted directly after it each run [65]. The EIS experiments were piloted between a frequency of 0.1 Hz, and a finish frequency of 1000 Hz with a 20mV-amplitude peak to peak. The cell impedance response ought to be linear as it is does not

dependent on the perturbation amplitude. Using a very small amplitude commonly results a high noise in the signal. On the other hand, a large amplitude might end up with a non-linear response in an AC impedance testing [65].

One of most commonly models used in EIS experiments is the Simplified Randles circuit. It consists of a solution resistance (R_{sol}), a double layer capacitor (C_{dl}) in parallel with a charge transfer or polarization resistance (R_{ct} or R_p). Besides being an easy useful model, it is considered a starting point for further complex EIS models and circuits. The equivalent Randles circuit is shown in Figure 4 [66, 67].



Figure 4. The Simplified Randles circuit diagram.

The Impedance (*Z*) consists of a real and an imaginary part where Z = Z' + jZ''. When the real part is plotted on the x-axis and the imaginary one is plotted on the yaxis of a chart, The resultant plot is called a "Nyquist Plot" [66, 67].

The typical Nyquist plot for a Simplified Randles circuit takes the shape of a semicircle. The GILL AC potentiostat software provides a fitting tool for the data to be used to fit the generated raw data into a semicircle shape. By reading the value on the x-axis (real) at high frequency intercept, the solution resistance (R_{sol}) can be found. This intercept is near the origin of the Nyquist plot. The other x-axis (real) intercept value at the low frequency is the sum of the charge transfer resistance (R_{ct}) and the solution resistance (R_{sol}). Therefore, the diameter of the semicircle essentially is the charge transfer or polarization resistance (R_{ct} or R_p) [66, 67].

The double layer occurs on the interface between the working electrode and the surrounding electrolyte liquid. It is formed when ions from the solution are adsorbed onto the surface of the electrode. The electrode potential, the operating temperature, ionic concentrations in the electrolyte, layers of oxide, surface roughness, are all factors affecting the double layer capacitance (C_{dl}) [66, 67].

Every time an electrode potential is pushed away from the open-circuit potential value that is called "polarizing" the electrode. A polarized electrode can cause a flow of current at the electrode surface by electrochemical reactions. In uniform corrosion cells, the open circuit potential is controlled by an equilibrium between the reactions generate a cathodic current and the others that generate an anodic one. When the cathodic and anodic currents are equal, the equilibrium state is reached and this potential is called a mixed potential. While the electrode is under active corrosion, the corrosion current is equal to the current of either of the reactions [64].

The Stern-Geary equation relates the polarization resistance (R_p) that was estimated from the Nyquist plot to the corrosion current which can be used to calculate the corrosion rate [64]:

$$i_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{R_p}$$

Where:

 i_{corr} is the corrosion current density. β_a is the anodic Tafel constant. R_p is the polarization resistance. β_b is the cathodic Tafel constant.

2.303 is a constant to switch between the natural logarithm and the base-10 one.

3.2.2 Cyclic sweep (CS). The mixed potential theory described in the previous section can be used to derive the polarization resistance method in the CS plots. The generated polarization plots in the CS test is obtained from [64]:

$$i_{app,c} = i_c - i_a$$

 $i_{app,a} = i_a - i_c$

Where:

- *ic* is the current density of the cathodic reaction
- i_a is the current density of the anodic reaction
- *i*_{*app,c*} is the applied cathodic current density
- *iapp*,*a* is the applied anodic current density

Also, when corrosion polarization occurs from the corrosion potential, two potential changes from the corrosion potential at steady-state can be defined [64]:

$$\varepsilon_c = \beta_c \log \frac{i_c}{i_{corr}}$$
 $\varepsilon_a = \beta_a \log \frac{i_a}{i_{corr}}$

Where:

 ε_c is the cathodic overvoltage ε_a is the anodic overvoltage

 β_a is the cathodic Tafel constant β_c is the anodic Tafel constant

*i*_{corr} is the corrosion current density

Using the exponential form and combining with $i_{app,c}$ equation:

$$i_{app,c} = i_{corr} (10^{-\frac{\varepsilon_c}{\beta_c}} - 10^{-\frac{\varepsilon_a}{\beta_a}})$$

Now the polarization resistance (R_p) can be found by differentiation:

$$R_p = \left[\frac{d\varepsilon}{di_{app}}\right]_{\varepsilon \to 0} = \left[\frac{\Delta\varepsilon}{\Delta i_{app}}\right]_{\varepsilon \to 0}$$

From this the Stern-Geary equation is found:

$$i_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{R_p}$$

In the Tafel plot, the intersection between the anodic and cathodic Tafel slopes indicates the value of the corrosion current density as seen in Figure 5.

The corrosion current density can be transformed to the corrosion rate:

$$CR = 3272 \frac{i_{corr}.EW}{d.A}$$

Where:

CR is the corrosion rate in mm/year

*i*corr is the corrosion current density in amperes

EW is the equivalent weight in g/equivalent

d is the density of metal in g/cm^3

A is the sample area exposed to corrosive environment in cm^2



3272 is a constant in mm/(amperes.cm.year)

Figure 5. An example of a Tafel plot used for estimating the corrosion current density.

The CS experiment was conducted between -150 mV to +150 mV around the polarization resistance (R_p) with a sweep rate of 20 mV/min. The generated plot is called the Tafel plot. The cathodic region of the Tafel plot is scanned from -150 mV to 0 mV while the anodic region is from 0 mV to +150 mV.

Chapter 4. Experimental Methodology

4.1 Raw Materials

Choline chloride salt (ChCl) (98-100%) was purchased from EMD Millipore Co., USA. It has a molecular weight of 139.62. ChCl structure is shown in Figure 6. The IUPAC name for choline chloride is 2-hydroxyethyltrimethylammonium chloride.



Figure 6. The structure of choline chloride (C₅H₁₄ClNO) salt.

LabChem Inc. supplied five of the chemically pure HBDs. Those are urea (ChCl : urea is 1:2), ethylene glycol (ChCl : ethylene glycol is 1:2), glycerol (ChCl : glycerol is 1:2), malonic acid (ChCl : malonic acid is 1:1), and phenol (ChCl : phenol is 1:3). Triethylen glycol extra pure (ChCl : triethylene glycol is 1:3) was purchased from SchartauChemie S.A., Spain.

Rectangular copper panels were acquired from AL RABIH TRDG. CO. L.L.C. and then they were cut into smaller rectangular pieces. The copper panels have a composition of 99.99 % Cu.

Also, rectangular mild steel panels were acquired from PRO TEST PANELS LTD. and then they were cut into smaller rectangular pieces. The mild steel panels have a percent composition of 0.037 C, 0.001 Si, 0.151 Mn, 0.0090 P, 0.0140 S, 0.017 Cr, 0.028 Ni, 0.001 Mo, 0.0028 N, and Fe makes up the balance of the MS.

In addition, rectangular stainless steel 316 panels were acquired from AL RABIH TRDG. CO. L.L.C. and then they were cut into smaller rectangular pieces. The stainless steel panels have a percent composition of 0.021 C, 0.51 Si, 0.95 Mn, 0.033 P, 0.001 S, 16.8 Cr, 10 Ni, 2.03 Mo, 0.039 N, and Fe makes up the balance of the SS 316.

4.2 DES Synthesis

The DES are all prepared in the same way. First, the common salt Choline chloride (ChCl) should be dried at 70-80 °C for 24 hours. After that, using a beaker of a good size a certain amount of ChCl and another the hydrogen bond doner (HBD) were added. In this step, the molar ratio of choline chloride to HBD must be satisfied. Then, the beaker was fixed at the center of a magnetic heating plate. The temperature was set at 70 °C and mixing speed at a minimum of 300 rpm. The beaker is left for 1 hour and up to 2 hours for big amounts to ensure homogeneity of the resultant DES. Finally, to sealed glass bottles and labelled like shown in Figure 7.



Figure 7. The colorless ethaline DES synthesized in the lab.

4.3 Corrosion Testing Setup

For electrochemical testing, a small cell was designed to perform the electrochemical experiments as shown in Figure 8.



Figure 8. The glass cell designed for the electrochemical tests.

A three electrode cell system is used for measuring the corrosion rate of a metal sample that is immersed in the DES. The working electrode (WE) is the metal specimen to be tested whose surface area will corrode. The reference electrode (RE) is a saturated calomel electrode that contains potassium chloride and the potential of WE will be measured with respect to it. The auxiliary electrode (AE) is a platinum wire which transmits current through the DES, either to or from the WE. A Gill AC potentiostat, which is shown in Figure 9, connects the three electrodes and is connected to the computer.



Figure 9. Gill AC potentiostat employed in electrochemical testing.

For each test, DES was added first then desired water amount was well mixed. After that, the cell Teflon cover with all electrodes was attached. Then the cell was placed in a water bath as shown in Figure 10 and the electrodes were connected to the potentiostat. Finally, in the Gill AC software, the type of metal, surface area and tests parameters were set and the experiment started.



Figure 10. Temperature control of the electrochemical cell using a water bath.

Chapter 5. Results and Discussions

The results of the electrochemical experiments for the 3 selected metals are presented in this section. The results for each metal are divided into six separate sections which contain the results from the EIS and CS tests. All the results are discussed and justified depending on corrosion related references [64, 66-68] and the Abbott et al. research observations [29].

5.1 Copper Testing Results

The six DES were used to investigate their corrosion effect on copper. The experiments were conducted at 25 °C, 50 °C and 75 °C. Also, three different water contents: pure, 5% water and 10% water were tested at each of the three temperatures. For each run, EIS and CS tests were carried out and the results are presented in this section. Note that all corrosion rates in this section are in mm/year.

5.1.1 Glyceline results. Glyceline, which is the mixture produced by mixing choline chloride with glycerol, was tested on copper. This section presents its electrochemical results.

5.1.1.1 Electrochemical impedance spectroscopy results for copper in glyceline. The EIS test was used to investigate the corrosion of copper metal in the glyceline DES. The corrosion rates of copper can be seen in Figure 11. It can be seen that increasing the water content at constant temperature, increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature also increases the corrosion rate. Also, it can be noticed that this DES has a narrow range of corrosion rates.

The results in Table 4 are the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the water content at a fixed temperature or increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of copper have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the copper surface.



Figure 11. Corrosion rates of copper in Glyceline DES at different temperatures and water contents from the EIS test.

	т	R _{sol}	R _{ct}	C _{dl}	EIS-CR
	I	(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mm/year)
pure	25	378.6	6401	0.0086	0.0631
	50	125.3	2804	0.0556	0.1412
	75	37.06	1466	0.2104	0.3672
5%	25	200.4	3594	0.0259	0.1044
water	50	63.40	1495	0.0916	0.2606
	75	12.39	1311	0.3425	0.4633
10%	25	99.00	2058	0.0175	0.1803
water	50	35.24	1357	0.1474	0.3374
	75	10.37	1153	0.3562	0.5491

Table 4. EIS parameters obtained using Glyceline on copper.

The parameters in Table 4 were obtained from the Nyquist plots in Figures 12 and 13 by fitting them to a semi-circle shape using the Gill AC software. In Figure 12, the semi-circle diameter, which is the charge transfer resistance (R_{ct}), decreased with increasing the temperature. In Figure 13, the semi-circle diameter, which is the charge transfer resistance (R_{ct}), also decreased with increasing the water content. This is again due to a thinner protective film being formed on the copper surface.


Figure 12. Nyquist plots for copper in Glyceline at (a) pure (b) 5% water and (c) 10% water from the EIS test.

5.1.1.2 Cyclic sweep results for copper in glyceline. The CS test was also used to investigate the corrosion of copper metal in the glyceline DES. The corrosion rates of copper can be seen in Figure 14. It can be seen that increasing the water content at constant temperature, increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature also increases the corrosion rate. This



trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.

Figure 13. Nyquist plots for copper in Glyceline at (a) 25 °C (b) 50 °C and (c) 75 °C from the EIS test.

The results in Table 5 are the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one and it has a bigger change with

temperature. The reason for that could be that the glyceline DES does not affect the anodic corrosion reaction.



Figure 14. Corrosion rates of copper in Glyceline DES at different temperatures and water contents from the CS test.

The parameters in Table 5 were obtained from the CS plot in Figures 15 and 16. These figures show the change in the cathodic and anodic behaviour of copper in glyceline. This in turn describes hydrogen reduction and metal oxidation associated with the corrosion process.

	Т	$E_{corr}(\mathbf{mV})$	b ₂ (mV)	b _c (mV)	Cyclic-CR
	_		~a (+)		(mm/year)
pure	25	-451	65.9	105.4	0.0699
	50	-481	61.0	121.0	0.1663
	75	-516	70.0	254.9	0.3619
5% water	25	-434	60.7	104.1	0.1002
	50	-461	57.8	145.7	0.2772
	75	-495	71.6	391.2	0.5140
10% water	25	-413	54.8	93.90	0.2073
	50	-443	59.7	150.0	0.4113
	75	-478	71.8	404.9	0.6607

Table 5. CS parameters obtained for copper in Glyceline.



Figure 15. Cyclic sweep plots for copper in Glyceline at (a) pure (b) 5% water and (c) 10% water.

In Figure 15, it can be noticed that changing the temperature shifts the curve towards a higher corrosion current density. This is accompanied by a large change in the cathodic slope. And the trend is similar for the compositions (pure, 5% water and 10% water).



Figure 16. Cyclic sweep plots for copper in Glyceline at (a) 25 °C (b) 50 °C and (c) 75 °C.

On the other hand, Figure 16 shows that changing the temperature at a fixed water content has a slight effect on the curves. The Tafel slopes remained almost unchanged but a small shift to a higher corrosion current density is observed.

5.1.2 Reline results. Reline, which is the mixture produced by mixing choline chloride with urea, was tested on copper. This section presents its electrochemical results.

5.1.2.1 Electrochemical impedance spectroscopy results for copper in reline. The EIS test was used to investigate the corrosion of copper metal in the reline DES. The corrosion rates of copper can be seen in Figure 17. It can be seen that increasing the water content at constant temperature, increased the corrosion rate. However, high temperatures had more effect in that increment. In addition, it was observed that at a fixed water content, increasing the temperature also increases the corrosion rate.



Figure 17. Corrosion rates of copper in Reline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 9 in Appendix A is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the water content at a fixed temperature or increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of copper have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the copper surface.

5.1.2.2 Cyclic sweep results for copper in reline. The CS test was also used to investigate the corrosion of copper metal in the reline DES. The corrosion rates of

copper can be seen in Figure 18. It can be seen that increasing the water content at constant temperature, increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature also increases the corrosion rate. This trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.



Figure 18. Corrosion rates of copper in Reline DES at different temperatures and water contents from the CS test.

The second half of the results in Table 9 in Appendix A is the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one and it has a bigger change with temperature. The reason for that could be that the reline DES does not affect the anodic corrosion reaction. The cyclic sweep curves had a shift towards a higher corrosion current density when the temperature or the water content was increased.

5.1.3 Trithaline results. Trithaline, which is the mixture produced by mixing choline chloride with triethylene glycol, was tested on copper. This section presents its electrochemical results.

5.1.3.1 Electrochemical impedance spectroscopy results for copper in *trithaline*. The EIS test was used to investigate the corrosion of copper metal in the trithaline DES. The corrosion rates of copper can be seen in Figure 19. It can be seen that increasing the water content at constant temperature, very slightly increased the

corrosion rate. However, high temperatures had more effect in that increment. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate.



Figure 19. Corrosion rates of copper in Trithaline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 10 in Appendix A is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the water content at a fixed temperature or increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of copper have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the copper surface.

5.1.3.2 Cyclic sweep results for copper in trithaline. The CS test was also used to investigate the corrosion of copper metal in the trithaline DES. The corrosion rates of copper can be seen in Figure 20. It can be seen that increasing the water content at constant temperature, increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature also increases the corrosion rate. This trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed and the big

jump in the 10% water content results from the pure and 5% water. However, the results are within a close range.



Figure 20. Corrosion rates of copper in Trithaline DES at different temperatures and water contents from the CS test.

The second half of the results in Table 10 in Appendix A is the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one and it has a bigger change with temperature. The reason for that could be that the trithaline DES does not affect the anodic corrosion reaction. The cyclic sweep curves had a shift towards a higher corrosion current density when the temperature or the water content was increased.

5.1.4 Ethaline results. Ethaline, which is the mixture produced by mixing choline chloride with ethylene glycol, was tested on copper. This section presents its electrochemical results.

5.1.4.1 Electrochemical impedance spectroscopy results for copper in ethaline. The EIS test was used to investigate the corrosion of copper metal in the ethaline DES. The corrosion rates of copper can be seen in Figure 21. It can be seen that increasing the water content at constant temperature, somewhat increased the corrosion rate. However, high temperatures had more effect in that increment. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate.



Figure 21. Corrosion rates of copper in Ethaline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 11 in Appendix A is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the water content at a fixed temperature or increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of copper have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the copper surface.

5.1.4.2 Cyclic sweep results for copper in ethaline. The CS test was also used to investigate the corrosion of copper metal in the Ethaline DES. The corrosion rates of copper can be seen in Figure 22. It can be seen that increasing the water content at constant temperature, increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature also increases the corrosion rate. This trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.

The second half of the results in Table 11 in Appendix A is the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one and it has a bigger change with temperature. The reason for that could be that the ethaline DES does not affect the anodic corrosion reaction. The cyclic sweep

curves had a shift towards a higher corrosion current density when the temperature or the water content was increased.



Figure 22. Corrosion rates of copper in Ethaline DES at different temperatures and water contents from the CS test.

5.1.5 Phenoline results. Phenoline, which is the mixture produced by mixing choline chloride with phenol, was tested on copper. This section presents its electrochemical results.

5.1.5.1 Electrochemical impedance spectroscopy results for copper in phenoline. The EIS test was used to investigate the corrosion of copper metal in the phenoline DES. The corrosion rates of copper can be seen in Figure 23. It can be seen that increasing the water content at constant temperature, slightly decreased the corrosion rate. However, high temperatures had more effect in that decrement. This is a unique trend for the phenoline DES. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate.

The first half of the results in Table 12 in Appendix A is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the water content at a fixed temperature resulted a slight increase then a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of copper have approximately a constant retention time in this case. While increasing the temperature resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the second process intermediates from the dissolution of copper have approximately a constant retention time in this case. While increasing the

the double layer capacitance (C_{dl}). The increase in double layer capacitance can be due to a thinner protective film being formed on the copper surface.



Figure 23. Corrosion rates of copper in Phenoline DES at different temperatures and water contents from the EIS test.

5.1.5.2 Cyclic sweep results for copper in phenoline. The CS test was also used to investigate the corrosion of copper metal in the phenoline DES. The corrosion rates of copper can be seen in Figure 24. It can be seen that increasing the water content at constant temperature, very slightly decreased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature also increases the corrosion rate. This trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.

The second half of the results in Table 12 in Appendix A is the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one and it has a bigger change with temperature. The reason for that could be that the phenoline DES does not affect the anodic corrosion reaction. The cyclic sweep curves had a shift towards a higher corrosion current density when the temperature or the water content was increased. However, between 5% and 10% water content, the change is very small and can be considered as a negligible difference.



Figure 24. Corrosion rates of copper in Phenoline DES at different temperatures and water contents from the CS test.

5.1.6 Maloline results. Maloline, which is the mixture produced by mixing choline chloride with malonic acid, was tested on copper. This section presents its electrochemical results.

5.1.6.1 Electrochemical impedance spectroscopy results for copper in maloline. The EIS test was used to investigate the corrosion of copper metal in the maloline DES. The corrosion rates of copper can be seen in Figure 25. It can be seen that increasing the water content at constant temperature, significantly increased the corrosion rate. However, high temperatures had more effect in that increment. In addition, it was observed that at a fixed water content, increasing the temperature dramatically increases the corrosion rate.

The first half of the results in Table 13 in Appendix A is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the water content at a fixed temperature or increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of copper have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the copper surface.



Figure 25. Corrosion rates of copper in Maloline DES at different temperatures and water contents from the EIS test.

5.1.6.2 Cyclic sweep results for copper in maloline. The CS test was also used to investigate the corrosion of copper metal in the maloline DES. The corrosion rates of copper can be seen in Figure 26.



Figure 26. Corrosion rates of copper in Maloline DES at different temperatures and water contents from the CS test.

It can be seen that increasing the water content at constant temperature, increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature significantly increases the corrosion rate. This trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.

The second half of the results in Table 13 in Appendix A is the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one and it has a bigger change with temperature. The reason for that could be that the ethaline DES does not affect the anodic corrosion reaction. The cyclic sweep curves had a shift towards a higher corrosion current density when the temperature or the water content was increased.

5.2 Mild Steel (MS) Testing Results

The same six DES were used to investigate their corrosion effect on MS. Similarly, the experiments for each DES were conducted at 25 °C, 50 °C and 75 °C. Also, each DES was tested at three different water contents: pure, 5% water and 10% water, and this was implemented at each of the three temperatures. For each run, EIS and CS tests were carried out and the results are presented in this section. Note that some corrosion rates in this section are in μ m/year and others are in mm/year.

5.2.1 Reline results. Reline, which is the mixture produced by mixing choline chloride with urea, was tested on MS. This section presents its electrochemical results.

5.2.1.1 Electrochemical impedance spectroscopy results for MS in reline. The EIS test was used to investigate the corrosion of MS metal in the reline DES. The corrosion rates of mild steel can be seen in Figure 27. It can be seen that increasing the water content at constant temperature, increased the corrosion rate. However, high temperatures had more effect in that increment. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate especially at elevated temperature.

The first half of the results in Table 14 in Appendix B is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the water content at a fixed temperature or increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}) especially at elevated temperature. This indicates that the electrochemical process intermediates from the dissolution of MS have low retention

time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the MS surface.



Figure 27. Corrosion rates of MS in Reline DES at different temperatures and water contents from the EIS test.

5.2.1.2 Cyclic sweep results for MS in reline. The CS test was also used to investigate the corrosion of MS metal in the reline DES. The corrosion rates of mild steel can be seen in Figure 28. It can be seen that increasing the water content at constant temperature, increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate. This trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.

The second half of the results in Table 14 in Appendix B is the CS test parameters. It can be seen that the anodic Tafel slope (b_a) has a greater value than cathodic one and it has a bigger change with temperature. The reason for that could be that the reline DES affects the anodic corrosion reaction. However, a clear trend of the change of the Tafel slopes with temperature and water content could not be obtained. This might be due to the very viscous nature of reline and the increased corrosion resistivity of MS compared to copper. Nevertheless, the cyclic sweep curves had a clear shift towards a higher corrosion current density when the temperature or the water content was increased.



Figure 28. Corrosion rates of MS in Reline DES at different temperatures and water contents from the CS test.

5.2.2 Phenoline results. Phenoline, which is the mixture produced by mixing choline chloride with phenol, was tested on MS. This section presents its electrochemical results.

5.2.2.1 Electrochemical impedance spectroscopy results for MS in phenoline. The EIS test was used to investigate the corrosion of MS metal in the phenoline DES. The corrosion rates of mild steel can be seen in Figure 29. It can be seen that increasing the water content at constant temperature, slightly increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate.

The first half of the results in Table 15 in Appendix B is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}) especially at elevated temperature. This indicates that the electrochemical process intermediates from the dissolution of MS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the MS surface. However, increasing the water content had a negligible effect on the values.



Figure 29. Corrosion rates of MS in Phenoline DES at different temperatures and water contents from the EIS test.

5.2.2.2 Cyclic sweep results for MS in phenoline. The CS test was also used to investigate the corrosion of MS metal in the phenoline DES. The corrosion rates of mild steel can be seen in Figure 30.



Figure 30. Corrosion rates of MS in Phenoline DES at different temperatures and water contents from the CS test.

It can be seen that increasing the water content at constant temperature, very slightly increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate. This trend is in

agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.

The second half of the results in Table 15 in Appendix B is the CS test parameters. It can be seen that the anodic Tafel slope (b_a) has a greater value than cathodic one, which can be considered constant at all times, and it has a bigger change with temperature. The reason for that could be that the phenoline DES affects the anodic corrosion reaction. The cyclic sweep curves had a slight shift towards a higher corrosion current density when the temperature or the water content was increased.

5.2.3 Glyceline results. Glyceline, which is the mixture produced by mixing choline chloride with glycerol, was tested on MS. This section presents its electrochemical results.

5.2.3.1 Electrochemical impedance spectroscopy results for MS in glyceline. The EIS test was used to investigate the corrosion of MS metal in the glyceline DES. The corrosion rates of mild steel can be seen in Figure 31. It can be seen that increasing the water content at constant temperature, slightly increased the corrosion rate. However, elevated temperature had more effect in this case. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate.



Figure 31. Corrosion rates of MS in Glyceline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 16 in Appendix B is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content or increasing the water content at a fixed temperature resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}) especially at low temperature. This indicates that the electrochemical process intermediates from the dissolution of MS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the MS surface.

5.2.3.2 Cyclic sweep results for MS in glyceline. The CS test was also used to investigate the corrosion of MS metal in the glyceline DES. The corrosion rates of mild steel can be seen in Figure 32. It can be seen that increasing the water content at constant temperature, slightly increased the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate especially going from 5% to 10% water content. This trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.



Figure 32. Corrosion rates of MS in Glyceline DES at different temperatures and water contents from the CS test.

The second half of the results in Table 16 in Appendix B is the CS test parameters. It can be seen that when water is added to glyceline, the cathodic Tafel slope (b_c) has a greater value than anodic one at all times and it has a bigger change with temperature. The reason for that could be that the glyceline DES does not affect the anodic corrosion reaction. However, both Tafel slopes are changing for pure glyceline, but again the cathodic one is greater. The cyclic sweep curves had a shift towards a higher corrosion current density when the temperature or the water content was increased.

5.2.4 Ethaline results. Ethaline, which is the mixture produced by mixing choline chloride with ethylene glycol, was tested on MS. This section presents its electrochemical results.

5.2.4.1 Electrochemical impedance spectroscopy results for MS in ethaline. The EIS test was used to investigate the corrosion of MS metal in the ethaline DES. The corrosion rates of mild steel can be seen in Figure 33. It can be seen that increasing the water content at constant temperature significantly increases the corrosion rate. However, elevated temperature had more effect in this case. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate dramatically.



Figure 33. Corrosion rates of MS in Ethaline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 17 in Appendix B is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that

the electrochemical process intermediates from the dissolution of MS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the MS surface.

5.2.4.2 Cyclic sweep results for MS in ethaline. The CS test was also used to investigate the corrosion of MS metal in the ethaline DES. The corrosion rates of mild steel can be seen in Figure 34. It can be seen that increasing the water content at constant temperature or increasing the temperature at constant water content, increased the corrosion rate. This trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.



Figure 34. Corrosion rates of MS in Ethaline DES at different temperatures and water contents from the CS test.

The second half of the results in Table 17 in Appendix B is the CS test parameters. It can be seen that when water is added to ethaline, the cathodic Tafel slope (b_c) has a greater value than anodic one at all times and it has a bigger change with temperature. The reason for that could be that the ethaline DES does not affect the anodic corrosion reaction. However, both Tafel slopes are changing for pure ethaline, but again the cathodic one is greater. The only anomaly to this behavior is the values at 50 °C for pure ethaline which could be due to experimental errors. The cyclic sweep curves had a shift towards a higher corrosion current density when the temperature or the water content was increased.

5.2.5 Trithaline results. Trithaline, which is the mixture produced by mixing choline chloride with triethylene glycol, was tested on MS. This section presents its electrochemical results.

5.2.5.1 Electrochemical impedance spectroscopy results for MS in trithaline. The EIS test was used to investigate the corrosion of MS metal in the trithaline DES. The corrosion rates of mild steel can be seen in Figure 35. It can be seen that increasing the water content at constant temperature increases the corrosion rate. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate.



Figure 35. Corrosion rates of MS in Trithaline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 18 in Appendix B is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of MS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the MS surface. However, it can be noticed that the change in C_{dl} is negligible at constant temperature.

5.2.5.2 Cyclic sweep results for MS in trithaline. The CS test was also used to investigate the corrosion of MS metal in the trithaline DES. The corrosion rates of mild steel can be seen in Figure 36. It can be seen that increasing the water content at constant temperature or increasing the temperature at constant water content, increased the corrosion rate. However, the water content effect is very small compared to the temperature effect. This trend is in agreement to the corrosion rate results determined by the EIS experiments with a difference in the magnitude of the corresponding values observed.

The second half of the results in Table 18 in Appendix B is the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one at all times and it has a bigger change with temperature. The reason for that could be that the trithaline DES does not affect the anodic corrosion reaction. However, both Tafel slopes have close values at constant temperature which indicate that the water content effect is minimal. The cyclic sweep curves had a shift towards a higher corrosion current density when the temperature or the water content was increased.



Figure 36. Corrosion rates of MS in Trithaline DES at different temperatures and water contents from the CS test.

5.2.6 Maloline results. Maloline, which is the mixture produced by mixing choline chloride with malonic acid, was tested on MS. This section presents its electrochemical results.

5.2.6.1 Electrochemical impedance spectroscopy results for MS in maloline. The EIS test was used to investigate the corrosion of MS metal in the maloline DES. The corrosion rates of mild steel can be seen in Figure 37. It can be seen that increasing the water content at constant temperature increases the corrosion rate especially at elevated temperatures. In addition, it was observed that at a fixed water content, increasing the temperature increases the corrosion rate especially at 10% water content were the increment was significant.

The first half of the results in Table 19 in Appendix B is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content or increasing the water content at constant temperature resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of MS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the MS surface.



Figure 37. Corrosion rates of MS in Maloline DES at different temperatures and water contents from the EIS test.

5.2.6.2 Cyclic sweep results for MS in maloline. The CS test was also used to investigate the corrosion of MS metal in the maloline DES. The corrosion rates of mild steel can be seen in Figure 38. It can be seen that increasing the water content at constant temperature or increasing the temperature at constant water content, increased the corrosion rate. This trend is in close agreement to the corrosion rate results determined

by the EIS experiments with a very small difference in the magnitude of the corresponding values observed.

The second half of the results in Table 19 in Appendix B is the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one at all times. The reason for that could be that the maloline DES has lower effect on the anodic corrosion reaction. However, both Tafel slopes are changing with temperature and water content. So, both anodic and cathodic reactions affected the system. The cyclic sweep curves had a shift towards a higher corrosion current density when the temperature or the water content was increased. Overall, maloline had the highest corrosion rate results for MS especially at high temperature and water content.



Figure 38. Corrosion rates of MS in Maloline DES at different temperatures and water contents from the CS test.

5.3 Stainless Steel (SS) Testing Results

The same six DES were used once again to investigate their corrosion effect on SS. Similarly, the experiments for each DES were conducted at 25 °C, 50 °C and 75 °C. Also, each DES was tested at three different water contents: pure, 5% water and 10% water, and this was implemented at each of the three temperatures. For each run, EIS and CS tests were carried out and the results are presented in this section. Note that all corrosion rates in this section are in μ m/year.

5.3.1 Reline results. Reline, which is the mixture produced by mixing choline chloride with urea, was tested on SS. This section presents its electrochemical results.

5.3.1.1 Electrochemical impedance spectroscopy results for SS in reline. The EIS test was used to investigate the corrosion of SS metal in the reline DES. The corrosion rates of stainless steel can be seen in Figure 39. It can be seen increasing the water content at constant temperature increases the corrosion rate. The only anomaly to this trend is the value at 5% water content and 50 °C where its corrosion rate was higher than that at 10% water content. However, the error bar suggests that this might be due to experimental errors. In addition, it can be noticed that increasing the temperature at constant water content increases the corrosion rate.



Figure 39. Corrosion rates of SS in Reline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 20 in Appendix C is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content or increasing the water content at constant temperature resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of SS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the SS surface.

5.3.1.2 Cyclic sweep results for SS in reline. The CS test was also used to investigate the corrosion of SS metal in the reline DES. The corrosion rates of stainless steel can be seen in Figure 40. It can be seen that increasing the water content at constant temperature or increasing the temperature at constant water content, increased the corrosion rate. Generally, this trend is in agreement to the corrosion rate results determined by the EIS experiments with a very small difference in the magnitude of the corresponding values observed. However, two anomalies were found. One is at 5% water content and 50 °C and the other is at 10% water content and 25 °C. The two values had a wide error range and this might be due to the viscous nature of reline and the very slow corrosion reactions with SS that makes it difficult to obtain a reading through the electrodes.



Figure 40. Corrosion rates of SS in Reline DES at different temperatures and water contents from the CS test.

The second half of the results in Table 20 in Appendix C is the CS test parameters. It can be seen that the anodic Tafel slope (b_a) has a greater value than cathodic one at all times. The reason for that could be that the reline DES has higher effect on the anodic corrosion reaction as the cathodic Tafel slope had a slight change when the conditions are modified. Most of the cyclic sweep curve had a shift towards a higher corrosion current density when the temperature or the water content was increased. Overall, reline had the lowest and narrowest corrosion rate results for SS even at high temperature and water content.

5.3.2 Phenoline results. Phenoline, which is the mixture produced by mixing choline chloride with phenol, was tested on SS. This section presents its electrochemical results.

5.3.2.1 Electrochemical impedance spectroscopy results for SS in phenoline. The EIS test was used to investigate the corrosion of SS metal in the phenoline DES. The corrosion rates of stainless steel can be seen in Figure 41. It can be seen increasing the water content at constant temperature slightly decreases the corrosion rate. Also, the results at 5% and 10% water content and very close which indicates that water had minimal effect on phenoline. On the other hand, it can be noticed that increasing the temperature at constant water content always increases the corrosion rate.



Figure 41. Corrosion rates of SS in Phenoline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 21 in Appendix C is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of SS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the SS surface. However, the water content had relatively a small effect on the results.

5.3.2.2 Cyclic sweep results for SS in phenoline. The CS test was also used to investigate the corrosion of SS metal in the phenoline DES. The corrosion rates of stainless steel can be seen in Figure 42. It can be seen increasing the water content at constant temperature slightly decreases the corrosion rate. On the other hand, it can be noticed that increasing the temperature at constant water content always increases the corrosion rate.

The second half of the results in Table 21 in Appendix C is the CS test parameters. It can be seen that the anodic Tafel slope (b_a) has a greater value than cathodic one at all times. The reason for that could be that the phenoline DES has higher effect on the anodic corrosion reaction as the cathodic Tafel slope had a slight change when the conditions are modified. The only anomaly to this is the result at 5% water and 50 °C where b_a was smaller than b_c . This might be due some experimental errors in the test. Most of the cyclic sweep curve had a shift towards a higher corrosion current density when the temperature was increased and they remained almost constant with changing the water content.



Figure 42. Corrosion rates of SS in Phenoline DES at different temperatures and water contents from the CS test.

5.3.3 Glyceline results. Glyceline, which is the mixture produced by mixing choline chloride with glycerol, was tested on SS. This section presents its electrochemical results.

5.3.3.1 Electrochemical impedance spectroscopy results for SS in glyceline. The EIS test was used to investigate the corrosion of SS metal in the glyceline DES. The corrosion rates of stainless steel can be seen in Figure 43. It can be seen that increasing the water content would increase the corrosion rate values especially at high temperatures. However, the corrosion rate values remained almost constant between 25 and 50 °C before increasing at 75 °C.



Figure 43. Corrosion rates of SS in Glyceline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 22 in Appendix C is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of SS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the SS surface. However, the water content had relatively a small effect on the results for all temperatures.

5.3.3.2 Cyclic sweep results for SS in glyceline. The CS test was also used to investigate the corrosion of SS metal in the glyceline DES. The corrosion rates of stainless steel can be seen in Figure 44. It can be seen that increasing the temperature had almost no effect while going from 25 to 50 °C but going to 75 °C increased the corrosion rate value. Generally, this trend is in agreement to the corrosion rate results

determined by the EIS experiments with a very small difference in the magnitude of the corresponding values observed.



Figure 44. Corrosion rates of SS in Glyceline DES at different temperatures and water contents from the CS test.

The second half of the results in Table 22 in Appendix C is the CS test parameters. It can be seen that the anodic Tafel slope (b_a) has a greater value than cathodic one at 25 and 50 °C. The reason for that could be that the glyceline DES has higher effect on the anodic corrosion reaction as the cathodic Tafel slope had a slight change when the conditions are modified. However, the case is reversed at 75 °C where the cathodic reaction is more dominant. The cyclic sweep curve had a shift towards a higher corrosion current density when the temperature was increased to 75 °C and they remained relatively constant with changing the water content.

5.3.4 Ethaline results. Ethaline, which is the mixture produced by mixing choline chloride with ethylene glycol, was tested on SS. This section presents its electrochemical results.

5.3.4.1 Electrochemical impedance spectroscopy results for SS in ethaline. The EIS test was used to investigate the corrosion of SS metal in the ethaline DES. The corrosion rates of stainless steel can be seen in Figure 45. It can be seen that increasing the water content had a very slight and negligible effect on the corrosion rate values. On the other hand, the corrosion rate values remained almost constant between 25 and 50 °C before increasing at 75 °C similar to the behavior of glyceline.



Figure 45. Corrosion rates of SS in Ethaline DES at different temperatures and water contents from the EIS test.

The first half of the results in Table 23 in Appendix C is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of SS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the SS surface. However, the water content had relatively a small effect on the results for all temperatures.

5.3.4.2 Cyclic sweep results for SS in ethaline. The CS test was also used to investigate the corrosion of SS metal in the ethaline DES. The corrosion rates of stainless steel can be seen in Figure 46. It can be seen that water content had a very small effect on the corrosion rate values at 25 and 50 °C but it increased the corrosion at 75 °C when it was increased. Also, increasing the temperature resulted an increment in the corrosion rate of SS.

The second half of the results in Table 23 in Appendix C is the CS test parameters. It can be seen that the anodic Tafel slope (b_a) has a greater value than cathodic one at 25 °C. The reason for that could be that the ethaline DES has higher effect on the anodic corrosion reaction as the cathodic Tafel slope had a slight change when the conditions are modified. However, the case is reversed at 50 and 75 °C where

the cathodic reaction is more dominant. The cyclic sweep curve had a shift towards a higher corrosion current density when the temperature was increased and they remained relatively constant with changing the water content at low temperatures.



Figure 46. Corrosion rates of SS in Ethaline DES at different temperatures and water contents from the CS test.

5.3.5 Trithaline results. Trithaline, which is the mixture produced by mixing choline chloride with triethylene glycol, was tested on SS. This section presents its electrochemical results.

5.3.5.1 Electrochemical impedance spectroscopy results for SS in trithaline. The EIS test was used to investigate the corrosion of SS metal in the trithaline DES. The corrosion rates of stainless steel can be seen in Figure 47. It can be seen that increasing the water content decreased the corrosion rate at all temperatures. However, increasing the temperature increased the corrosion rate values at all times.

The first half of the results in Table 24 in Appendix C is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of SS have low retention time in this case. The increase in double layer capacitance can be due to a thinner

protective film being formed on the SS surface. However, the water content had a proportional relationship with charge transfer resistance (R_{ct}).



Figure 47. Corrosion rates of SS in Trithaline DES at different temperatures and water contents from the EIS test.

5.3.5.2 Cyclic sweep results for SS in trithaline. The CS test was also used to investigate the corrosion of SS metal in the trithaline DES. The corrosion rates of stainless steel can be seen in Figure 48.



Figure 48. Corrosion rates of SS in Trithaline DES at different temperatures and water contents from the CS test.

It can be seen that increasing the water content decreased the corrosion rate at all temperatures. However, increasing the temperature increased the corrosion rate values at all times. Generally, this trend is in agreement to the corrosion rate results determined by the EIS experiments with a very small difference in the magnitude of the corresponding values observed.

The second half of the results in Table 24 in Appendix C is the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one at all times. The reason for that could be that the trithaline DES has lower effect on the anodic corrosion reaction as the anodic Tafel slope had a slight change when the conditions are modified. The cyclic sweep curve had a shift towards a higher corrosion current density when the temperature was increased. On the other hand, they shifted towards a lower corrosion current density when the water content was increased.

5.3.6 Maloline results. Maloline, which is the mixture produced by mixing choline chloride with malonic acid, was tested on SS. This section presents its electrochemical results.

5.3.6.1 Electrochemical impedance spectroscopy results for SS in maloline. The EIS test was used to investigate the corrosion of SS metal in the maloline DES. The corrosion rates of stainless steel can be seen in Figure 49.



Figure 49. Corrosion rates of SS in Maloline DES at different temperatures and water contents from the EIS test.
It can be seen that increasing the water content increased the corrosion rate values at all temperatures. The effect was more significant at high temperatures. Also, increasing the temperature increased the corrosion rate values and the effect was more significant at 10% water content.

The first half of the results in Table 25 in Appendix C is the EIS test parameters. They are the Randles circuit parts described in Chapter 3. It can be seen that increasing the temperature at a fixed water content or increasing the water content at a constant temperature resulted a decrease in the charge transfer resistance (R_{ct}) and an increase in the double layer capacitance (C_{dl}). This indicates that the electrochemical process intermediates from the dissolution of SS have low retention time in this case. The increase in double layer capacitance can be due to a thinner protective film being formed on the SS surface.

5.3.6.2 Cyclic sweep results for SS in maloline. The CS test was also used to investigate the corrosion of SS metal in the maloline DES. The corrosion rates of stainless steel can be seen in Figure 50.



Figure 50. Corrosion rates of SS in Maloline DES at different temperatures and water contents from the CS test.

It can be seen that increasing the water content increased the corrosion rate values at all temperatures. The effect was more significant at high temperatures. Also, increasing the temperature increased the corrosion rate values and the effect was more significant at 10% water content. Generally, this trend is in agreement to the corrosion rate results determined by the EIS experiments with a very small difference in the magnitude of the corresponding values observed.

The second half of the results in Table 25 in Appendix C is the CS test parameters. It can be seen that the cathodic Tafel slope (b_c) has a greater value than anodic one at all times. The reason for that could be that the maloline DES has lower effect on the anodic corrosion reaction as the anodic Tafel slope had a slight change when the conditions are modified. The cyclic sweep curve had a shift towards a higher corrosion current density when the temperature or the water content was increased.

5.4 **Results Comparison and Summary**

The results were arranged starting from the highest corroding metal (copper) to the lowest corroding one (stainless steel) for any fixed DES as can be seen in Tables 6 and 7. Copper is known for higher thermal and electrical conductivity compared to steel. This might be the reason for the higher corrosion rates obtained compared to the mild and stainless steel values. However, forming copper alloys might be one of the ways to increase its corrosion resistance. The difference between mild steel and stainless steel arises from the composition and alloying the steel. Stainless steel showed more corrosion resistance due to the high percentage of chromium (Cr = 16.8%). Chromium is commonly known to be the main reason for increasing corrosion resistivity of steel alloys. In addition, the current density is further reduced with the addition of Mo and Ni to Cr [64, 68].

For copper, the DES can be arranged from the lowest to the highest overall corrosion rates as the following: glyceline, reline, trithaline, ethaline, phenoline and maloline. Although reline had lower corrosion rate values than glyceline for copper at 25 °C, glyceline values did not increase as much as reline ones with temperature, and that is why glyceline had the first place here. In terms of mild steel, the order would be as follows: reline, glyceline, ethaline, trithaline, phenoline and maloline. Finally, the stainless steel observations give the following: reline, phenoline, glyceline, ethaline, trithaline, maloline. From the reported results, it can be noticed that the urea and glycol based DES had the lowest corrosion rate values in most cases compared to the malonic acid or the phenol based ones. An exception to that is the phenoline with stainless steel

which showed the high resistivity of stainless steel to the relatively corrosive DES. Also, maloline DES showed high sensitivity to the increase of temperature and water content. It had the highest corrosion rate values in most of the cases especially at 75 °C.

Metal	T (°C)	min CR	max CR
	25	24.700 μm/yr	2.096 mm/yr
	DES	Reline	Phenoline
C	50	75.900 μm/yr	4.631 mm/yr
Copper	DES	Reline	Phenoline
	75	252.10 μm/yr	16.230 mm/yr
	DES	Reline	Maloline
	25	0.0220 μm/yr	0.8440 mm/yr
	DES	Reline	Phenoline
MG	50	0.0373 μm/yr	2.4210 mm/yr
IVIS	DES	Reline	Phenoline
	75	1.0725 μm/yr	16.670 mm/yr
	DES	Reline	Maloline
	25	0.0065 µm/yr	0.0119 mm/yr
	DES	Reline	Maloline
88	50	0.0735 µm/yr	0.3156 mm/yr
88	DES	Reline	Maloline
	75	0.2470 μm/yr	1.6621 mm/yr
	DES	Reline	Maloline

Table 6. Corrosion rate range comparison at different temperatures.

In terms of temperature, the general trend is that increasing the temperature causes the corrosion rate values to increase. Although some DES with certain metals had a slight change with temperature, but the overall results make it safe to conclude that the temperature increase is 'bad' for metals. This happens due to the enhanced and improved dissolution kinetics and the decrement of the passivity on the metal surface whenever the temperature is elevated [68]. Also, the viscosity of DES decreases with increasing the temperature as mentioned in Chapter 2. The decrement in viscosity would increase the ionic conductivity of the DES which means the corrosion rate values would increase.

Metal	wc%	min CR	max CR
	0	24.700 µm/yr	7.0020 mm/yr
	DES	Reline	Phenoline
C	5	45.270 μm/yr	12.350 mm/yr
Copper	DES	Reline	Maloline
	10	114.80 µm/yr	16.230 mm/yr
	DES	Reline	Maloline
	0	0.0220 µm/yr	4.0870 mm/yr
	DES	Reline	Maloline
MC	5	0.1979 μm/yr	8.8690 mm/yr
IVIS	DES	Reline	Maloline
	10	2.0110 μm/yr	16.670 mm/yr
	DES	Reline	Maloline
	0	0.0195 µm/yr	0.2772 mm/yr
	DES	Reline	Maloline
88	5	0.1225 µm/yr	1.0960 mm/yr
80	DES	Reline	Maloline
	10	0.1760 µm/yr	1.6621 mm/yr
	DES	Ethaline	Maloline

 Table 7. Corrosion rate range comparison at different water contents.

Chapter 6. Conclusions

Deep Eutectic Solvents (DES) have emerged as the novel ecofriendly alternative to the traditional solvents used in industry. Although they are being used and implemented in a wide range of chemical, mechanical and medical applications, their corrosion behavior with common metals is not well established and not researched enough in the literature. Since corrosion of metals is one of the costly problems in industry, this thesis aimed to fill part of this gap and to propose good candidates that would have low corrosion attributes. Six DES were readily synthesized in the lab and were tested by electrochemical methods to predict the corrosion characteristics towards copper, mild steel and stainless steel.

DES were easy to synthesize as the process involves knowing the eutectic point of the mixture, purchase the relatively cheap raw materials, and mixing and heating at about 70 °C. This gives them an advantage over the mainstream ionic liquids that are quite expensive.

The electrochemical tests conducted (EIS and CS) are widely used by researchers for determining the corrosion rate and its related parameters. One of the major advantages of EIS over CS is that it is a non-destructive method. This allows for CS test to run directly after EIS one gets over. Both EIS and CS tests gave similar trends in almost every case with a difference in the magnitude of the calculated corrosion rate, which was previously observed in many research articles.

Stainless steel results make it safe to choose it as the best corrosion resisting metal of the three metals that were tested in this study. However, mild steel had some low corrosion rates with certain DES like reline and glyceline. For these cases, it might be wiser to choose the cheaper steel metal. That choice also depends on the corrosion allowance for the equipment.

In terms of the DES, the urea and glycol based ones are good candidates for green-low-corrosion solvents. It was noticed that reline and glyceline had low corrosion rates and more resilience and flexibility towards changes in temperature and water content if compared to other DES. However, as reline was observed to be viscous at room temperature, it would be advisable to use glyceline for low temperatures and reline for the elevated ones.

References

- R. Gani, C. Jiménez-González, and D. J. C. Constable, "Method for selection of solvents for promotion of organic reactions," *Computers and Chemical Engineering*, vol. 29, no. 7, pp. 1661-1676, 2005.
- [2] J. H. Clark and S. J. Tavener, "Alternative Solvents: Shades of Green," *Organic Process Research & Development,* vol. 11, no. 1, pp. 149-155, 2007.
- [3] P. S. Kulkarni, L. C. Branco, J. G. Crespo, M. C. Nunes, A. Raymundo, and C. A. M. Afonso, "Comparison of physicochemical properties of new ionic liquids based on imidazolium, quaternary ammonium, and guanidinium cations," *Chemistry-A European Journal*, vol. 13, no. 30, pp. 8478-8488, 2007.
- [4] J. F. Brennecke and E. J. Maginn, "Ionic liquids: Innovative fluids for chemical processing," *AIChE Journal*, vol. 47, no. 11, pp. 2384-2389, 2001.
- [5] A. Mohammad, D. Inamuddin, and SpringerLink, *Green Solvents II: Properties and Applications of Ionic Liquids*. Dordrecht: Springer Netherlands, 2012.
- [6] Z. F. Fei, T. J. Geldbach, D. B. Zhao, and P. J. Dyson, "From dysfunction to bis-function: On the design and applications of functionalised ionic liquids," *Chemistry-A European Journal*, vol. 12, no. 8, pp. 2122-2130, 2006.
- [7] C. B. Yue, D. Fang, L. Liu, and T. F. Yi, "Synthesis and application of taskspecific ionic liquids used as catalysts and/or solvents in organic unit reactions," *Journal of Molecular Liquids*, vol. 163, no. 3, pp. 99-121, 2011.
- [8] P. Walden, "Molecular weights and electrical conductivity of several fused salts," *Bull. Acad. Imper. Sci.(St. Petersburg)*, vol. 8, pp. 405-422, 1914.
- [9] H. Zhao and S. V. Malhotra, "Applications of ionic liquids in organic synthesis," *Aldrichimica Acta*, vol. 35, no. 3, pp. 75-83, 2002.
- [10] S. G. Zhang and Z. C. Zhang, "Novel properties of ionic liquids in selective sulfur removal from fuels at room temperature," *Green Chemistry*, vol. 4, no. 4, pp. 376-379, 2002.
- [11] C. M. Wang *et al.*, "The strategies for improving carbon dioxide chemisorption by functionalized ionic liquids," *RSC Advances*, vol. 3, no. 36, pp. 15518-15527, 2013.
- [12] K. J. Stevenson, H. Ohno, Ed. *Electrochemical Aspects of Ionic Liquids*, 2nd ed. John Wiley & Sons, 2011, p. 485.
- [13] J. A. Whitehead, G. A. Lawrance, and A. McCluskey, "'Green' leaching: recyclable and selective leaching of gold-bearing ore in an ionic liquid," *Green Chemistry*, vol. 6, no. 7, pp. 313-315, 2004.

- [14] Q. H. Zhang, K. D. Vigier, S. Royer, and F. Jerome, "Deep eutectic solvents: syntheses, properties and applications," *Chemical Society Reviews*, vol. 41, no. 21, pp. 7108-7146, 2012.
- [15] H. G. Morrison, C. C. Sun, and S. Neervannan, "Characterization of thermal behavior of deep eutectic solvents and their potential as drug solubilization vehicles," *International Journal of Pharmaceutics*, vol. 378, no. 1, pp. 136-139, 2009.
- [16] K.-K. Kow and K. Sirat, "Novel manganese(II)-based deep eutectic solvents: Synthesis and physical properties analysis," *Chinese Chemical Letters*, vol. 26, no. 10, pp. 1311-1314, 2015.
- [17] F. S. G. Bagh, K. Shahbaz, F. S. Mjalli, M. A. Hashim, and I. M. AlNashef, "Zinc (II) chloride-based deep eutectic solvents for application as electrolytes: Preparation and characterization," *Journal of Molecular Liquids*, vol. 204, pp. 76-83, 2015.
- [18] A. P. Abbott, D. Boothby, G. Capper, D. L. Davies, and R. K. Rasheed, "Deep eutectic solvents formed between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids," *Journal of the American Chemical Society*, vol. 126, no. 29, pp. 9142-9147, 2004.
- [19] F. Endres, D. MacFarlane, and A. Abbott, *Electrodeposition from Ionic Liquids*. John Wiley & Sons, 2008.
- [20] A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed, and V. Tambyrajah, "Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains," *Chemical Communications*, vol. 1, no. 19, pp. 2010-2011, 2001.
- [21] C. Russ and B. Konig, "Low melting mixtures in organic synthesis an alternative to ionic liquids?," *Green Chemistry*, vol. 14, no. 11, pp. 2969-2982, 2012.
- [22] D. V. Wagle, H. Zhao, and G. A. Baker, "Deep Eutectic Solvents: Sustainable Media for Nanoscale and Functional Materials," *Accounts of Chemical Research*, vol. 47, no. 8, pp. 2299-2308, 2014.
- [23] M. Sharma, C. Mukesh, D. Mondal, and K. Prasad, "Dissolution of [small alpha]-chitin in deep eutectic solvents," *RSC Advances*, vol. 3, no. 39, pp. 18149-18155, 2013.
- [24] C. Mukesh, D. Mondal, M. Sharma, and K. Prasad, "Choline chloride-thiourea, a deep eutectic solvent for the production of chitin nanofibers," *Carbohydrate Polymers*, vol. 103, pp. 466-471, 2014.
- [25] A. P. Abbott, P. M. Cullis, M. J. Gibson, R. C. Harris, and E. Raven, "Extraction of glycerol from biodiesel into a eutectic based ionic liquid," *Green Chemistry*, vol. 9, no. 8, pp. 868-872, 2007.

- [26] Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, and Y. H. Choi, "Ionic Liquids and Deep Eutectic Solvents in Natural Products Research: Mixtures of Solids as Extraction Solvents," *Journal of Natural Products*, vol. 76, no. 11, pp. 2162-2173, 2013.
- [27] F. S. Oliveira, A. B. Pereiro, L. P. N. Rebelo, and I. M. Marrucho, "Deep eutectic solvents as extraction media for azeotropic mixtures," *Green Chemistry*, vol. 15, no. 5, pp. 1326-1330, 2013.
- [28] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R. L. Reis, and A. R. C. Duarte, "Natural Deep Eutectic Solvents – Solvents for the 21st Century," ACS Sustainable Chemistry & Engineering, vol. 2, no. 5, pp. 1063-1071, 2014.
- [29] A. P. Abbott, E. I. Ahmed, R. C. Harris, and K. S. Ryder, "Evaluating water miscible deep eutectic solvents (DESs) and ionic liquids as potential lubricants," *Green Chemistry*, vol. 16, no. 9, pp. 4156-4161, 2014.
- [30] A. P. Abbott, R. C. Harris, and K. S. Ryder, "Application of Hole Theory to Define Ionic Liquids by their Transport Properties[†]," *The Journal of Physical Chemistry B*, vol. 111, no. 18, pp. 4910-4913, 2007.
- [31] F. Hurley and T. WIer, "The Electrodeposition of Aluminum from Nonaqueous Solutions at Room Temperature," *Electrochem. Soc.*, vol. 98, no. 5, pp. 207-212, 1951.
- [32] A. P. Abbott, G. Capper, D. L. Davies, and R. Rasheed, "Ionic liquids based upon metal halide/substituted quaternary ammonium salt mixtures," *Inorganic Chemistry*, vol. 43, no. 11, pp. 3447-3452, 2004.
- [33] S.-I. Hsiu, J.-F. Huang, I. W. Sun, C.-H. Yuan, and J. Shiea, "Lewis acidity dependency of the electrochemical window of zinc chloride–1-ethyl-3methylimidazolium chloride ionic liquids," *Electrochimica Acta*, vol. 47, no. 27, pp. 4367-4372, 2002.
- [34] Y.-F. Lin and I. W. Sun, "Electrodeposition of zinc from a Lewis acidic zinc chloride-1-ethyl-3-methylimidazolium chloride molten salt," *Electrochimica Acta*, vol. 44, no. 16, pp. 2771-2777, 1999.
- [35] W. G. Xu, X. M. Lu, Q. G. Zhang, J. S. Gui, and J. Z. Yang, "Studies on the thermodynamic properties of the ionic liquid BMIGaCl4," *Chinese Journal of Chemistry*, vol. 24, no. 3, pp. 331-335, 2006.
- [36] J. Z. Yang, P. Tian, L. L. He, and W. G. Xu, "Studies on room temperature ionic liquid InCl3-EMIC," *Fluid Phase Equilibria*, vol. 204, no. 2, pp. 295-302, 2003.
- [37] A. P. Abbott, G. Capper, D. L. Davies, and R. K. Rasheed, "Ionic liquid analogues formed from hydrated metal salts," *Chemistry-A European Journal*, vol. 10, no. 15, pp. 3769-3774, 2004.

- [38] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, and V. Tambyrajah, "Novel solvent properties of choline chloride/urea mixtures," *Chemical Ccommunications*, vol. 1, no. 1, pp. 70-71, 2003.
- [39] A. P. Abbott, G. Capper, B. G. Swain, and D. A. Wheeler, "Electropolishing of stainless steel in an ionic liquid," *Transactions of the Institute of Metal Finishing*, vol. 83, no. 1, pp. 51-53, 2005.
- [40] K. Shahbaz, F. S. Mjalli, M. A. Hashim, and I. M. AlNashef, "Prediction of deep eutectic solvents densities at different temperatures," *Thermochimica Acta*, vol. 515, no. 1, pp. 67-72, 2011.
- [41] G. Imperato, E. Eibler, J. Niedermaier, and B. Konig, "Low-melting sugar-ureasalt mixtures as solvents for Diels-Alder reactions," *Chemical Communications*, vol. 36, no. 9, pp. 1170-1172, 2005.
- [42] M. E. Zakrzewska, E. Bogel-Łukasik, and R. Bogel-Łukasik, "Solubility of Carbohydrates in Ionic Liquids," *Energy & Fuels*, vol. 24, no. 2, pp. 737-745, 2010.
- [43] P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, second ed. *Wiley*-VCH, 2008.
- [44] A. P. Abbott, J. C. Barron, K. S. Ryder, and D. Wilson, "Eutectic-Based Ionic Liquids with Metal-Containing Anions and Cations," *Chemistry – A European Journal*, vol. 13, no. 22, pp. 6495-6501, 2007.
- [45] M. A. Kareem, F. S. Mjalli, M. A. Hashim, and I. M. AlNashef, "Phosphonium-Based Ionic Liquids Analogues and Their Physical Properties," *Journal of Chemical & Engineering Data*, vol. 55, no. 11, pp. 4632-4637, 2010.
- [46] A. Yadav, S. Trivedi, R. Rai, and S. Pandey, "Densities and dynamic viscosities of (choline chloride + glycerol) deep eutectic solvent and its aqueous mixtures in the temperature range (283.15–363.15) K," *Fluid Phase Equilibria*, vol. 367, pp. 135-142, 2014.
- [47] A. P. Abbott, R. C. Harris, K. S. Ryder, C. D'Agostino, L. F. Gladden, and M. D. Mantle, "Glycerol eutectics as sustainable solvent systems," *Green Chemistry*, vol. 13, no. 1, pp. 82-90, 2011.
- [48] E. L. Smith, A. P. Abbott, and K. S. Ryder, "Deep Eutectic Solvents (DESs) and Their Applications," *Chemical Reviews*, vol. 114, no. 21, pp. 11060-11082, 2014.
- [49] K. Izutsu, "Overview of Electrochemical Techniques," in *Electrochemistry in Nonaqueous Solutions*: Wiley-VCH Verlag GmbH & Co. KGaA, 2009, pp. 111-170.
- [50] K. Izutsu, "Electrochemistry in Clean Solvents," in *Electrochemistry in Nonaqueous Solutions*: Wiley-VCH Verlag GmbH & Co. KGaA, 2009, pp. 355-384.

- [51] A. P. Abbott, G. Capper, K. J. McKenzie, and K. S. Ryder, "Voltammetric and impedance studies of the electropolishing of type 316 stainless steel in a choline chloride based ionic liquid," *Electrochimica Acta*, vol. 51, no. 21, pp. 4420-4425, 2006.
- [52] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, and P. Shikotra, "Selective Extraction of Metals from Mixed Oxide Matrixes Using Choline-Based Ionic Liquids," *Inorganic Chemistry*, vol. 44, no. 19, pp. 6497-6499, 2005.
- [53] A. P. Abbott, G. Frisch, J. Hartley, and K. S. Ryder, "Processing of metals and metal oxides using ionic liquids," *Green Chemistry*, vol. 13, no. 3, pp. 471-481, 2011.
- [54] S. B. Phadtare and G. S. Shankarling, "Halogenation reactions in biodegradable solvent: Efficient bromination of substituted 1-aminoanthra-9,10-quinone in deep eutectic solvent (choline chloride : urea)," *Green Chemistry*, vol. 12, no. 3, pp. 458-462, 2010.
- [55] P. M. Pawar, K. J. Jarag, and G. S. Shankarling, "Environmentally benign and energy efficient methodology for condensation: an interesting facet to the classical Perkin reaction," *Green Chemistry*, vol. 13, no. 8, pp. 2130-2134, 2011.
- [56] N. Azizi, E. Batebi, S. Bagherpour, and H. Ghafuri, "Natural deep eutectic salt promoted regioselective reduction of epoxides and carbonyl compounds," *RSC Advances*, vol. 2, no. 6, pp. 2289-2293, 2012.
- [57] C. Russ, F. Ilgen, C. Reil, C. Luff, A. Haji Begli, and B. Konig, "Efficient preparation of [small beta]-d-glucosyl and [small beta]-d-mannosyl ureas and other N-glucosides in carbohydrate melts," *Green Chemistry*, vol. 13, no. 1, pp. 156-161, 2011.
- [58] M. Francisco, A. van den Bruinhorst, and M. C. Kroon, "New natural and renewable low transition temperature mixtures (LTTMs): screening as solvents for lignocellulosic biomass processing," *Green Chemistry*, vol. 14, no. 8, pp. 2153-2157, 2012.
- [59] S. Chen, J. Zhang, T. Wu, P. Feng, and X. Bu, "Multiroute Synthesis of Porous Anionic Frameworks and Size-Tunable Extraframework Organic Cation-Controlled Gas Sorption Properties," *Journal of the American Chemical Society*, vol. 131, no. 44, pp. 16027-16029, 2009.
- [60] M. Deetlefs and K. R. Seddon, "Assessing the greenness of some typical laboratory ionic liquid preparations," *Green Chemistry*, vol. 12, no. 1, pp. 17-30, 2010.
- [61] J. K. Blusztajn, "Choline, a Vital Amine," *Science*, vol. 281, no. 5378, pp. 794-795, 1998.

- [62] A. A. Jackson, "Urea as a nutrient: bioavailability and role in nitrogen economy.," *Archives of Disease in Childhood*, vol. 70, no. 1, pp. 3-4, 1994.
- [63] K. Haerens, E. Matthijs, A. Chmielarz, and B. Van der Bruggen, "The use of ionic liquids based on choline chloride for metal deposition: A green alternative?," *Journal of Environmental Management*, vol. 90, no. 11, pp. 3245-3252, 2009.
- [64] D. Jones, *Principles and Prevention of Corrosion*, second ed. Pearson, 2014.
- [65] M. O. a. M. Poelman. (2012). Use of Electrochemical Impedance Spectroscopy (EIS) for the Evaluation of Electrocoatings Performances. Available: http://cdn.intechopen.com/pdfs/26668/InTech-Use_of_electrochemical_impedance_spectroscopy_eis_for_the_evaluation_of _electrocoatings_performances.pdf. Accessed April, 2017.
- [66] E. Barsoukov and J. R. Macdonald, *Impedance Spectroscopy; Theory, Experiment, and Applications*, second ed. Wiley, 2005.
- [67] A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, second ed. Wiley, 2001.
- [68] Z. Ahmad, *Principles of Corrosion Engineering and Corrosion Control*, First ed. Butterworth-Heinemann, 2006.

Appendix A

EIS and CS Results for Copper

1- Glyceline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
	•	(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	378.6	6401	0.0086	-451	65.9	105.4
pure	50	125.3	2804	0.0556	-481	61	121
	75	37.06	1466	0.2104	-516	70	254.9
5%	25	200.4	3594	0.0259	-434	60.7	104.1
water	50	63.4	1495	0.0916	-461	57.8	145.7
water	75	12.39	1311	0.3425	-495	71.6	391.2
10%	25	99	2058	0.0175	-413	54.8	93.9
water	50	35.24	1357	0.1474	-443	59.7	150
,, atci	75	10.37	1153	0.3562	-478	71.8	404.9

Table 8. EIS and CS parameters obtained using Glyceline on copper.

2- Reline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
	1	(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	890.6	14440	0.0165	-498	57.3	78.3
pure	50	125.7	4532	0.0582	-533	56.6	113.4
	75	55.41	2012	0.0468	-547	63.8	164.5
5%	25	74.49	6552	0.0622	-468	41	79.2
water	50	49.58	2263	0.0799	-489	58.6	125.5
Water	75	22.87	668.5	0.1228	-519	66	264.1
10%	25	19.48	2655	0.0924	-422	44.8	121
water	50	18.91	762.9	0.1531	-465	56.7	131.7
,, ater	75	11.38	311.7	0.2616	-491	66.7	263.5

Table 9. EIS and CS parameters obtained using Reline on copper.

3- Trithaline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	275.3	3005	0.0576	-488	68.3	121.5
pure	50	109.6	818.5	0.1864	-494	74.5	197.4
	75	52.13	255.9	0.5009	-506	87.6	334.8
5%	25	191	1976	0.0924	-465	65.3	117.1
water	50	82.83	759.9	0.3064	-471	74.9	247
water	75	39.44	227.7	0.6059	-483	87.4	443.1
10%	25	129	1544	0.1258	-446	59.5	111.2
water	50	57.3	635.4	0.3611	-456	75.9	272.6
water	75	32.2	217.4	0.6215	-471	90.2	517.6

Table 10. EIS and CS parameters obtained using Trithaline on copper.

4- Ethaline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
	1	(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	20.1	2759	0.0873	-464	45.3	103.4
pure	50	25.41	679.5	0.2037	-467	58.7	169.3
	75	13.6	216.1	0.5235	-499	62.3	189.5
5%	25	24.42	1693	0.1155	-447	48.7	93.87
water	50	15.54	579.1	0.2673	-465	60.1	191.2
Water	75	9.744	209.2	0.7649	-484	64.9	241.6
10%	25	19.57	1304	0.1665	-429	54.6	115.4
water	50	13.14	457.7	0.3659	-446	66.3	267.2
, ator	75	5.874	210.1	1.5231	-464	74.6	391.7

Table 11. EIS and CS parameters obtained using Ethaline on copper.

5- Phenoline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
	I	(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	0.07598	405	0.5554	-304	57.5	181.8
pure	50	0.5578	213.9	1.7712	-320	66.5	283.2
	75	1.122	161.2	3.8769	-342	67.1	333.6
5%	25	0.528	413.9	0.5477	-300	56.9	185.6
water	50	1.076	303.8	1.7232	-316	66.8	294.6
, ator	75	1.385	186.9	3.0833	-337	67.6	308.9
10%	25	1.646	431.8	0.5128	-297	57.2	185.5
water	50	1.7	274	1.5208	-310	64.2	256.8
, acci	75	1.221	164.7	2.8709	-332	65	356.8

Table 12. EIS and CS parameters obtained using Phenoline on copper.

6- Maloline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
	I	(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	956.6	7418	0.1126	-449	70.1	119.3
pure	50	314.7	1924	0.3458	-429	81.4	157.1
	75	117.7	139.7	0.5532	-412	125.6	239.2
5% water	25	329.4	2091	0.2155	-389	68.9	107.9
	50	105.5	271.4	0.3349	-383	81.6	146.1
water	75	49.42	49.45	0.5685	-388	104.8	309.4
10% water	25	140.4	611.9	0.2410	-361	61.8	123.5
	50	55.04	109.8	0.3797	-362	80.4	143.1
	75	24.53	38.61	1.0859	-372	95.4	281.6

Appendix B

EIS and CS Results for Mild Steel (MS)

1- Reline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
	-	(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	992.4	4309000	0.0011	-288	417.4	67.7
pure	50	194.8	4069000	0.0018	-154	332.8	61.5
	75	66.9	340300	0.0046	-158	303.9	87.3
5%	25	134.9	998300	0.0025	-275	471.3	74.5
water	50	40.23	101400	0.0026	-200	537.7	104.8
water	75	19.44	52890	0.0382	-324	218.7	167.9
10%	25	44.91	119500	0.0048	-345	202.4	133.8
water	50	27.96	58390	0.0075	-339	263.6	195.5
water	75	11.1	19140	0.0528	-285	885.7	133.4

Table 14. EIS and CS parameters obtained using Reline on MS.

2- Phenoline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	4.445	1913	0.0766	-630	86.4	503
pure	50	4.245	745.7	0.1313	-680	73.9	504.2
	75	2.599	323.6	0.2609	-676	67.8	415.1
5%	25	4.216	1169	0.0882	-635	84.1	490.2
water	50	3.445	577.1	0.1206	-673	75.7	512
,, acci	75	3.689	366.4	0.1817	-680	70.6	506.3
10%	25	4.083	1103	0.0870	-636	84.8	544.3
water	50	5.123	522.2	0.1419	-679	76.6	542.5
	75	2.728	336.1	0.2058	-683	69.7	450.3

Table 15. EIS and CS parameters obtained using Phenoline on MS.

3- Glyceline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
	1	(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	429.8	207300	0.0018	-356	131.7	121.3
pure	50	123.1	51530	0.0069	-383	106.9	177.4
	75	41.97	12650	0.0189	-411	70.5	363.6
5%	25	151.8	140300	0.0070	-389	57.1	210.5
J70 water	50	54.55	29490	0.0117	-404	50.7	283
water	75	27.03	9373	0.0290	-465	49.8	553.7
10%	25	123.7	91760	0.0177	-398	60	183.8
water	50	38.06	28490	0.0163	-448	53.4	298.2
water	75	19.94	7573	0.0287	-475	49.1	661.9

Table 16. EIS and CS parameters obtained using Glyceline on MS.

4- Ethaline

	т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
	1	(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	54.82	113100	0.0077	-362	96.8	123.7
pure	50	30.41	19140	0.0148	-385	308	191.1
	75	14.84	3460	0.0244	-411	138.8	247.9
5%	25	41.58	40780	0.0114	-421	65.4	143.2
water	50	19.09	7500	0.0191	-429	80.9	251.6
,, acci	75	17.79	2016	0.0311	-465	69.3	758.4
10%	25	37.27	38130	0.0189	-396	60.5	115.6
water	50	20.13	4741	0.0222	-435	63.4	312.6
	75	9.78	1422	0.0893	-483	65.8	655.6

Table 17. EIS and CS parameters obtained using Ethaline on MS.

5- Trithaline

	Т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	350.1	69900	0.0152	-408	51.2	308.7
pure	50	148.7	5287	0.0239	-527	68	418.4
	75	60.1	2229	0.0400	-595	79.7	442.5
5%	25	212.3	26270	0.0148	-523	61.7	289.1
	50	105.4	4209	0.0235	-575	72.1	353.7
water	75	52.5	1441	0.0341	-604	101	383.4
10% water	25	134.6	17500	0.0136	-541	59.1	283.9
	50	84.65	3163	0.0299	-579	71.8	353.3
water	75	38.32	1167	0.0498	-601	74.5	443

Table 18. EIS and CS parameters obtained using Trithaline on MS.

6- Maloline

	Т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	1579	5260	0.0204	-423	133.1	211.2
pure	50	474.2	937.8	0.0266	-422	139.7	202.6
	75	141.8	124.2	0.0474	-439	191.2	223.2
5%	25	527.9	2596	0.0169	-414	103.6	167.1
water	50	146.9	481	0.0298	-430	122.1	185.5
,, acci	75	73.61	66.78	0.0577	-433	217.1	250.6
10% water	25	223.9	1236	0.0229	-421	90.5	151.2
	50	64.51	212	0.0390	-430	130	212.4
, ator	75	28.94	29.76	0.0887	-429	191.6	217.9

Table 19. EIS and CS parameters obtained using Maloline on MS.

Appendix C

EIS and CS Results for Stainless Steel (SS)

1- Reline

	Т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	671.7	2243000	0.0010	-294	559.6	68.1
pure	50	62.26	630300	0.0031	-220	401.6	59.2
	75	51.66	191600	0.0055	-177	261.7	65.1
5% water	25	176.4	2367000	0.0026	-239	498.5	51.9
	50	42.3	219800	0.0052	-240	429.5	63.5
, all a	75	17.06	136500	0.0078	-164	181.4	53.9
10% water	25	81.64	513600	0.0046	-327	559.3	87.2
	50	19.26	256100	0.0076	-238	455.9	58.5
	75	15.29	121700	0.0085	-120	256	68.8

Table 20. EIS and CS parameters obtained using Reline on SS.

2- Phenoline

	т	R _{sol}	Rct	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	5.209	216800	0.0105	-123	514.5	88.3
pure	50	2.624	84510	0.0181	-106	379.4	90.4
	75	1.054	58010	0.0381	-76	304.3	77.6
5%	25	4.679	166200	0.0087	-121	240.4	84.6
	50	2.915	74200	0.0174	-99	52.9	77.4
water	75	0.6227	56030	0.0261	-74	305.4	72
10% water	25	4.034	317800	0.0081	-122	415.3	83.3
	50	2.417	146600	0.0162	-95	358.5	86.5
	75	0.7885	65490	0.0225	-71	352.5	77.4

Table 21. EIS and CS parameters obtained using Phenoline on SS.

3- Glyceline

	Т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	276.5	139400	0.0042	-215	212.8	40.3
pure	50	99.05	144700	0.0081	-192	85.8	84.6
	75	60.64	42960	0.0132	-200	61	159.7
5% water	25	228.9	126200	0.0049	-308	505.6	72.9
	50	41.1	130600	0.0080	-166	114.7	96.7
, ator	75	38.63	38950	0.0151	-184	58.5	200
10% water	25	102.8	135400	0.0045	-313	821.7	91.7
	50	35.71	224300	0.0092	-96	108.4	97.2
	75	33.69	37400	0.0160	-143	93.9	195.2

Table 22. EIS and CS parameters obtained using Glyceline on SS.

4- Ethaline

	Т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	53.28	367900	0.0038	-312	331.4	69.3
pure	50	33.44	144500	0.0073	-238	68.2	98.6
	75	11.87	35600	0.0202	-185	72.3	130.4
50/	25	46.46	435900	0.0047	-158	417.2	69.5
water	50	19.4	144400	0.0068	-157	65.6	97.6
water	75	10.29	31230	0.0152	-167	70.8	131.5
10% water	25	33.58	418800	0.0051	-175	376.7	78.8
	50	16.16	105800	0.0124	-151	97.6	100
	75	7.797	32530	0.0162	-173	72.4	125.3

Table 23. EIS and CS parameters obtained using Ethaline on SS.

5- Trithaline

	Т	R _{sol}	R _{ct}	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	315.8	65910	0.0128	-146	55.6	146.8
pure	50	139.7	22320	0.0204	-141	88.6	264.8
	75	60.27	30340	0.0325	-156	77.2	333.4
5%	25	276.6	334600	0.0122	-57	39.2	103.8
water	50	104	104500	0.0318	-68	92.2	258.1
water	75	55.59	24610	0.0281	-126	91.9	283
10% water	25	231.4	296400	0.0140	26.5	65.7	101.8
	50	82.42	84870	0.0223	-40.3	88.3	180.6
	75	46.09	52660	0.0272	-102	79.6	238.1

Table 24. EIS and CS parameters obtained using Trithaline on SS.

6- Maloline

	Т	R _{sol}	Rct	C _{dl}	Ecorr	ba	bc
		(ohms.cm ²)	(ohms.cm ²)	(mF/cm ²)	(mV)	(mV)	(mV)
	25	1377	92130	0.0197	-231	76	96.3
pure	50	388.2	7492	0.0272	-221	76.9	124.5
	75	146	1845	0.0392	-227	78.15	170.5
5%	25	324.6	39340	0.0239	-250	82.3	122.6
	50	122.2	2927	0.0348	-240	66.3	141.5
, all a	75	53.91	509.1	0.0733	-262	57.4	153.6
10% water	25	160.5	23240	0.0257	-256	71.3	113.6
	50	67.69	1505	0.0494	-257	56.6	141.3
	75	50.67	270.3	0.0855	-280	68	157

Table 25. EIS and CS parameters obtained using Maloline on SS.

Vita

Rami Alhasan was born in 1991, in Sharjah, in the United Arab Emirates. He was educated in local private schools till the 8th grade then moved to Jordan. He graduated from Al-Ittihad Secondary School in 2009. After that he enrolled in the University of Jordan and obtained his bachelor's degree in Chemical Engineering in 2014. He was an elected member at the Students Union through the academic year 2011/2012.

Mr. Alhasan moved to the United Arab Emirates in April 2014 and worked in Dubai for 5 months as a chemical engineer. After that he received a graduate assistantship at the American University of Sharjah and worked as a laboratory assistant for 2 years while studying for the Master's degree in Chemical Engineering.

Ms. Alhasan is a member of the Jordanian Engineers Association.