The use of hydrophobic deep eutectic solvents (HDES) for the extraction of valuable metals from aqueous electronic waste streams

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Abstract

The exponential growth of electronic waste (e-waste) has become a critical environmental concern, requiring innovative approaches for resource recovery. Among the valuable metals contained within the e-waste, copper holds particular significance due to its abundance and widespread application in electronic devices. Traditional extraction methods often involve environmentally detrimental processes and become ineffective in complex metal mixtures, leading to the necessity of selective, greener methods. Deep eutectic solvents (DES) can be defined as a class of solvents formed by the combination of two or more components, which have been reported as alternative solvents for various applications, with hydrophobic deep eutectic solvent (HDES), those that are immiscible with water, being reported as an innovative alternative solvent for extractions from water. The primary aim of the project is to evaluate the effect of using HDESs for the extraction of copper from complex aqueous electronic waste streams and use this understanding to improve the extraction system. 24 HDESs were assessed for their ability to extract copper from both a pure copper sulfate solution and a mixed metal e-waste lixiviant. While high copper removal from the mixed metal solution could be obtained with lidocaine based HDES, these formed a precipitate which contained a complex mixture of metals, likely as a result of the formation of metal complexes with lidocaine and carboxylate ligands. The HDES methyltrioctylammonium chloride : decanoic acid (N8881Cl : C10A) was found to be the most effective at extracting copper from the aqueous electronic waste stream without forming a precipitate. The molar ratio of the N8881Cl : C10A HDES system had a surprisingly large impact on extraction efficiency, with the optimal hydrogen bond acceptor : hydrogen bond donor (HBA:HBD) molar ratio of 2:1. A model was proposed for the molar ratio dependence of the extraction. Further, attempts to optimize the extraction conditions using DOE were unsuccessful with the optimized conditions proposed by the model not leading to the highest extraction yield. An attempt at the electrodeposition of copper and the recycling of the HDES was made. Finally, further investigation is required to elaborate the mechanisms dominating the copper extraction and optimize extraction conditions for enhanced metal extraction efficiency. By approaching a sustainable solution to copper extraction and recovery from e-waste, this study contributes to

advancing the field of resource recovery and environmental sustainability not only limited in metal but other material recycling.

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Abbreviations and Definitions

Deep eutectic solvent	DES
Hydrophobic deep eutectic solvent	HDES
Methyltrioctyl-ammonium chloride	$N_{8881}Cl$
Decanoic acid	$C_{10}A$
Design of Expert	DoE
Electronic waste	e-waste
Hydrogen bond acceptor	HBA
Hydrogen bond donor	HBD
Environmental Protection Agency	EPA
Dichloro diphenyl trichloro ethane (DDT)	DDT
Dodecanoic acid	$C_{12}A$
Volatile organic compound	VOC
Melting point	T_mS
Tetraheptylammonium	N_{7777}
Tetrabutylammonium	N_{4444}
Microwave Plasma-atomic emission spectroscopy	MP-AES
Fourier transform infrared spectroscopy	FTIR
High resolution mass spectrometer	HRMS
Dodecanol	$C_{12}OH$

1.Introduction

1.1 Green Chemistry

Green Chemistry is an emerging research area that developed the idea of a safer chemistry environment and focuses on reducing the use as well as the generation of hazardous substances in the design of products. The history of green chemistry can be traced back to 1962 when Rachel Carson wrote a book named Silent Spring, referred to the exposure of the harmful effects of pesticides, particularly DDT, on the environment, wildlife, and human health which raised awareness of the harm of chemical products or the chemical industry in both public and scientists.[1] In 1970, The US Environmental Protection Agency (EPA) was established by president Richard Nixon and dedicated to protecting environment and health.[1] In 1972, dichloro diphenyl trichloro ethane (DDT) was banned by EPA due to adverse effects such as being carcinogenic and environmentally persistent.[1] In the 1980s, the EPA and the chemical industry were aware that the design of the chemical processes can work to significantly reduce pollution.[1] In 1995, an annual award program was set up for scientists or chemists with novel inspiration in green chemistry.[1] Until 1998, Paul Anastas and John C Warner established a book "Green Chemistry: Theory and practice" that proposed 12 principles to help chemists work towards safer practices and reduced environmental impact which described in table 1 below. [1]

Table 1. Twelve principles of Green Chemistry and its description.

Principle	Description
1. Prevention	It is better to prevent waste than to treat waste after it is formed
2. Atom Economy	Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Syntheses	Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment
4. Designing Safer Chemicals	Chemical products should be designed to achieve their desired function while minimizing toxicity.
5. Safer Solvents and Auxiliaries	The use of auxiliary substances (e.g., solvents, separation agents) should be minimized, and, whenever possible, benign substances should be used.
6. Design for Energy Efficiency	Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized
7. Use of Renewable Feedstocks	A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.
8. Reduce Derivatives	Unnecessary derivatization should be avoided whenever possible.
9. Catalysis	Catalytic reagents are superior to stoichiometric reagents.
10. Design for Degradation	Chemical products should be designed so that at the end of their function, they break down into innocuous degradation products and do not persist in the environment.
11. Real-time Analysis for Pollution Prevention	Analytical methodologies need to be further developed to allow for real-time, in-process

	monitoring and control prior to the formation of hazardous substances.
12.Inherently Safer Chemistry for Accident Prevention	Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

These twelve principles are employed as the foundation for designing chemical products and processes, including every aspect of the entire life-cycle; from the efficiency and safety of the reaction itself, to the toxicity and biodegradability of products and reagents, through to the use of fossil carbon.[1,2]

Waste prevention, the first principle out of the twelve aims, means it is preferable to stop the formation of waste rather than to clear it up after it has occurred. Chemical waste can be defined as any unnecessary or excessive use of a chemical which, if released into the air, water, or land, could be harmful to human health and the environment.

Atom economy is a measures the efficiency of a chemical reaction by assessing the proportion of reactant atoms that become part of the desired product. Barry Trost introduced the concept of Atom Efficiency, also called Atom Economy (AE) in 1990.[2] When designing a new chemical product or process, maximizing the incorporation of all materials is highly recommended. The ideal chemical reaction would maximize the use of all the atoms involved in it, but in reality, most of the chemical reactions have 100% AE but still generate waste.

While Baylis-Hillman reaction is currently an ideal chemical process that has 100% atom economy and has no byproduct, Wittig reaction has only 18.5% of the atom economy which is extremely low in contrast to the Baylis-Hillman reaction.[3] The Wittig reaction leads to an abundance of byproducts that is toxic and not environmentally friendly, which requires extra cost of method and energy to handle the undesired chemical waste.[3] These solvent waste proved that solvents are not incorporated in the product and hence development on minimization of toxic solvent should be sought.

AE is a way of measuring waste but excludes important factors such solvents. Moreover, in terms of the understanding of chemical waste, Roger Sheldon introduced a metric known as the environmental impact factor (E-factor) in 1992 in order to quantify the amount of waste generated per kilogram of product.[2] The E-factor has now been applied to many industries examine how inefficient some industrial processes have been performed. The early synthesis of ethylene oxide through a chlorohydrin intermediate is a well-known example, with E-Factor equal to 5 indicated that 5 kg of waste was produced for every kilogram were generated. With the synthesis route modified to use molecular oxygen and removing the necessity for chlorine, the E-Factor changed to 0.3. The change in the E-Factor do not directly contribute by changing to the benign reactant as it does not affect the E-factor unless there are other benefits in the process, it is in addition to the use of a more benign oxygen than chloride. When waste or byproducts are inevitable in the generation of new products or chemical reactions, it's crucial to explore viable and innovative solutions.

However, solvents are used in large quantities for many chemical processes and so it is critical to address the safety and environmental impact of these components. Researchers on this basis have explored and designed a variety of novel solvents that have been proposed as green solvent. They are supercritical fluids, ionic liquid, deep eutectic solvent, switchable solvent, water and bio-based solvent. Deep eutectic solvents as one of the developing alternative green solvents will be investigated further on the later discussion.

1.1.1 Alternative solvent

Solvents in chemistry are generally used for extraction, catalysts, dissolving reactants, separation, and purifying reaction products, making it become a vital character in commercial manufacturing and industries.[4] With inappropriate post-treatment of the harmful, toxic, and environmentally damaging volatile organic compound (VOC), it can cause risks to both living environment and human health. Alternative solvents, solvents designed with the intention of being greener and more sustainable, have been increasingly developed in the early 21st century. As mentioned previously, alternative solvents such as ionic liquid, deep eutectic solvent, supercritical fluid, switchable solvents, and bio-based solvents are being considered as a replacement solution to VOC as they target on avoiding the detrimental environmental and health effects due to their biodegradability and volatility, opening up an innovative solvent development.[5,6] However, with promising properties of alternative solvents, each of these classes of solvent have their own challenges, for example, some ionic liquids are expensive and their toxicity is either an issue or unknown in many cases.

Ionic liquid (ILs), as one of the widely explored alternative solvent are salts that have low melting points of below 100°C.[7,8] The first IL, ethanolammonium nitrate, was prepared by Gabriel and Weiner in 1888.[7–9] The characteristics of ILs have led to them being investigated as potentially greener solvents, which includes negligible vapour pressure, ease of recyclability, high thermal and chemical stability, low flammability, and electricity conductivity.[8,10] The two figures below show the commonly used cations and anions in ILs.[11] In synthesis of the ILs, they are generally made of an organic cation and either organic or inorganic anion. The choice of ions in ILs is the main source of tunability as it can modify their thermophysical and chemical properties, leading them to a significant interest in this area. Nevertheless, not all of the ILs are “green” due to the toxicity and biodegradability of some ions that have been chosen, hence, the development for greener alternatives to ILs lead to a new subset of ILs called deep eutectic solvents being explored.[11]

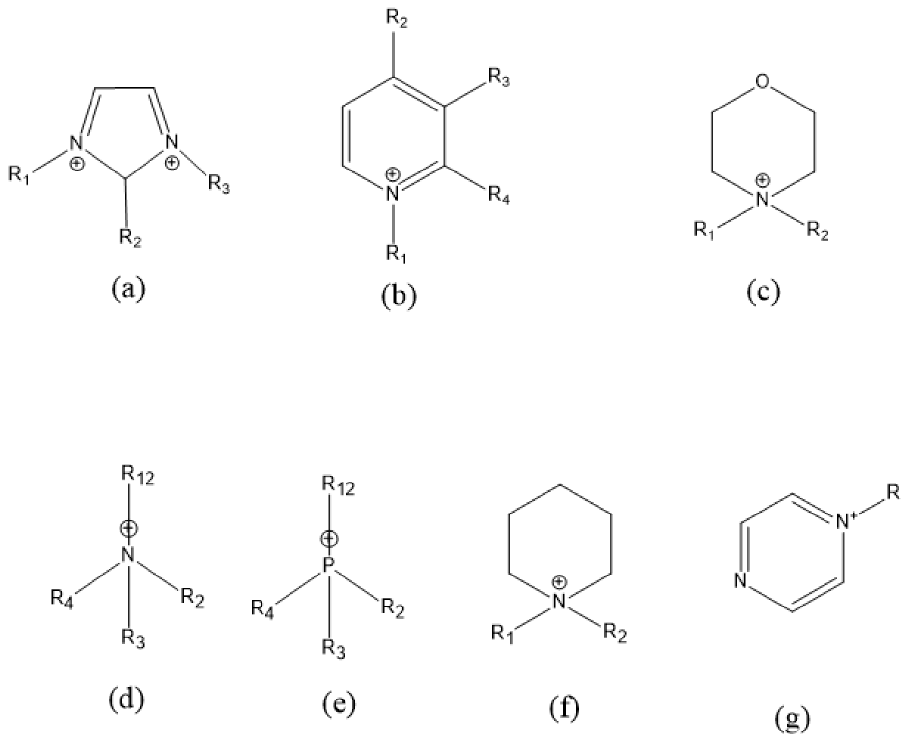


Figure 1.Common IL cations: (a) imidazolium, (b) pyridinium, (c) morpholinium, (d) ammonium, (e) phosphonium, (f) piperidinium and (g) pyrazinium.[11]

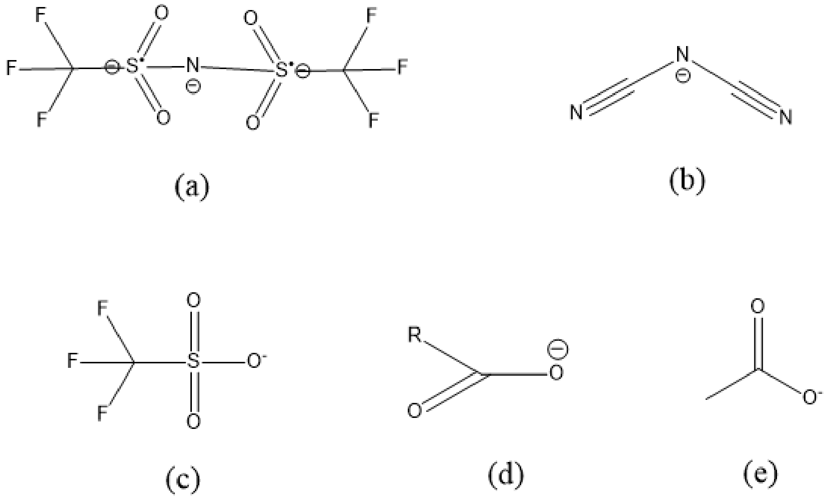


Figure 2. Common IL anions: (a) bis(trifluoromethanesulfonyl)imide, (b) dicyanamide, (c) trifluoromethanesulfonate, (d) carboxylate, (e) acetate.[11]

1.2 Deep eutectic solvents

1.2.1 Overview

Deep eutectic solvents (DES) are defined as a mixtures of two or more components. This eutectic mixture is often formed through the hydrogen bond interactions and have lower melting points than their individual components.[1,12]The formation process allows a wider range of compounds to be used as solvents (i.e. higher melting components) and so opens the possibility of using less toxic and more easily biodegradable components etc.. DESs generally are mixtures of halide salts and hydrogen bond donors (HBD). The decrease in the melting point has been proposed to arise from charge delocalization caused by hydrogen bonding between the halide salts and the HBD, nevertheless, this has been disputed and it has been suggested that the melting point reduction is an entropic effect arising from the multiple conformers possible due to those H-bonding interactions rather than an enthalpy effect from reduced charge density.[12,13] Figure 3 represents typical freezing point behavior of DESs.[12] The degree of the interaction between the two components and their size determines how much the freezing temperatures of the eutectic composition of a two-component system diverge from a linear relationship between the composition and freezing point. In other words, strong interaction will result in pronounced deviations from the ideal freezing temperature while weak interaction comparatively results in less deviations.[12] In addition, the preparation of DESs is convenient as the raw material needed is cheap, renewable and the synthetic method is simple and not energy intensive, which facilitates the creation of alternative solvents.

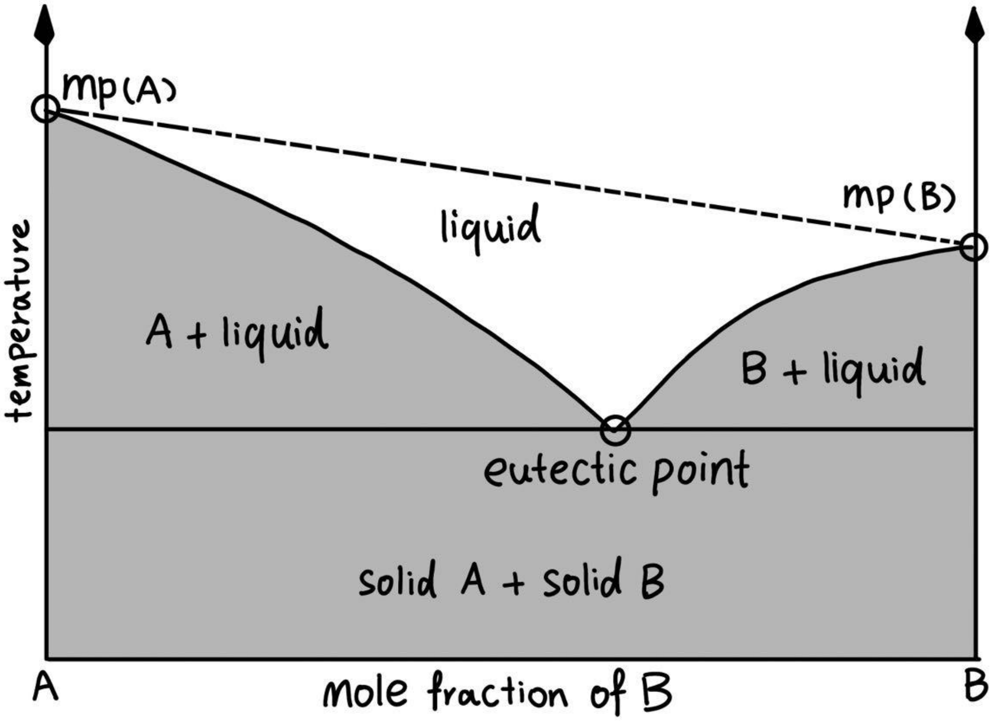


Figure 3. Eutectic point on a two-component phase diagram. Reproduced from Smith et al. under a CC BY license[12]

1.2.2 Classification of deep eutectic solvent (DESs)

DESs can be classified based on the composition of the hydrogen donor and acceptor. According to Smith et al. in 2014, the combination of DESs can be classified into four classes, with a fifth class of DESs being proposed in 2019.[12,14,15] Figure 4 below shows the classification of DESs.[16]

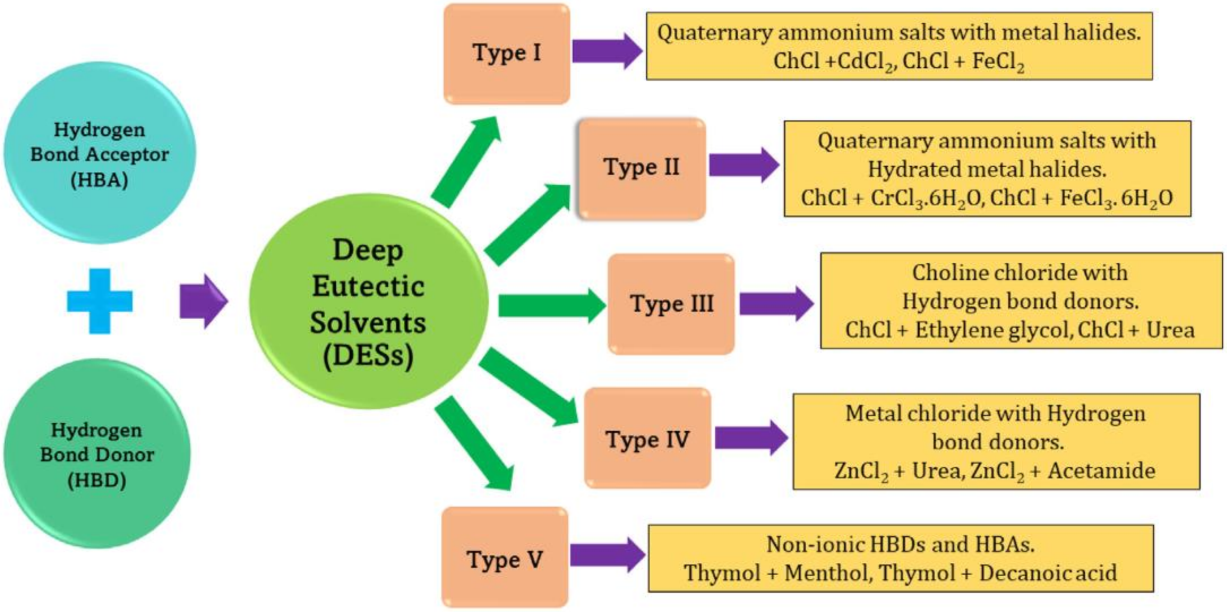


Figure 4. *Classification of Deep eutectic solvents. Reproduced from Prabhune and Dey et al. under CC BY license.*[16]

Type I includes the chloroaluminate/imidazolium salt melts combined with various metal halides such as $FeCl_2$, AgCl, CuCl, LiCl, $CdCl_2$, $CuCl_2$, $SnCl_2$, $ZnCl_2$, $LaCl_3$, YCl_3, and $SnCl_4$. However, the range of the non-hydrated metal halides which have a low melting point to form DESs is limited and hence, type II DES is developed.[12]

Type II includes hydrated metal halides and organic salts such as choline chloride. The relatively low cost of hydrated metal salts coupled with their inherent moisture insensitivity makes their use in large scale industrial processes viable.[12]

Type III includes only organic components, where one is salt. The general formula of this type is Cat^+X^-zY where Cat represents any ammonium, phosphonium, or sulfonium cation, and X is a Lewis base generally a halide anion. Y is either a Lewis or Bronsted base and Z is the number of Y molecules. Because of their ability to solvate a wide spectrum of transition metal species, including chlorides and oxides, type III eutectics, produced from choline chloride and hydrogen bond donors, have aroused the curiosity of researchers. To date, a variety of hydrogen bond donors have been investigated, with deep eutectic solvents generated from amides, carboxylic acids, and alcohols. These liquids are easy to make and relatively unreactive with water. Many DESs are biodegradable and inexpensive. Because of the variety of hydrogen bond donors available, this family of deep eutectic solvents is very versatile. A wide range of applications has been developed based on Type III DESs including the removal of glycerol from biodiesel, processing of metal oxides and the derivatization of cellulose.[12]

Type IV DESs involve a transition metal chloride and organic hydrogen bond donors. A variety of transition metals has been examined for their ability to be incorporated into ambient temperature eutectics, and $ZnCl_2$ has been shown to form eutectic mixture with urea, acetamide etc.[12]

Type V includes purely non-ionic organic compounds such as the recent discovered thymol-menthol in a molar ratio of 1:1. These types of phenolic component demonstrate that a salt is not required to enable the melting point depressions required for a DES.[15]

The figure 5 below represents the commonly used compounds for synthesis of DESs. With different types of DESs, a variety of applications has been explored.

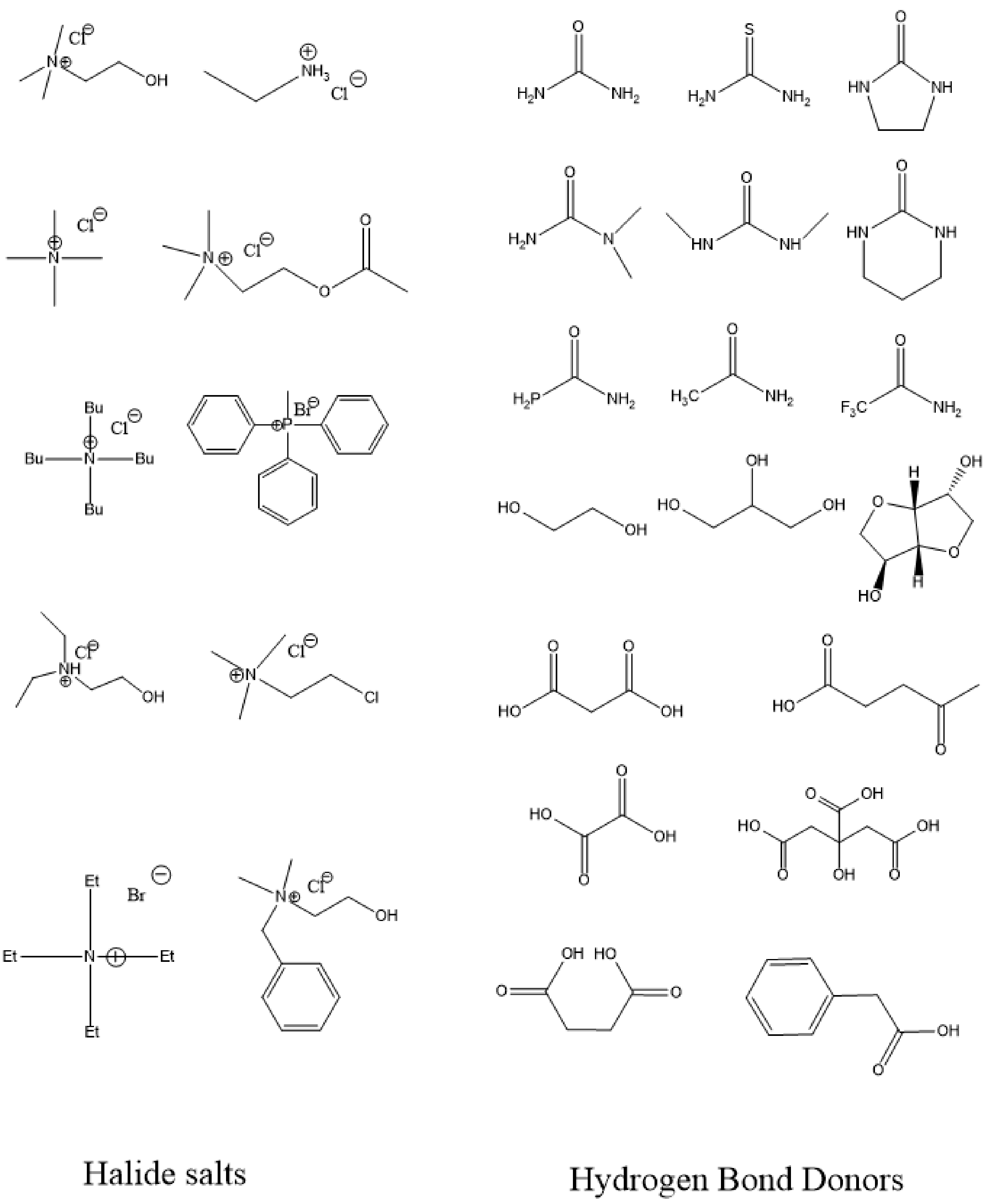
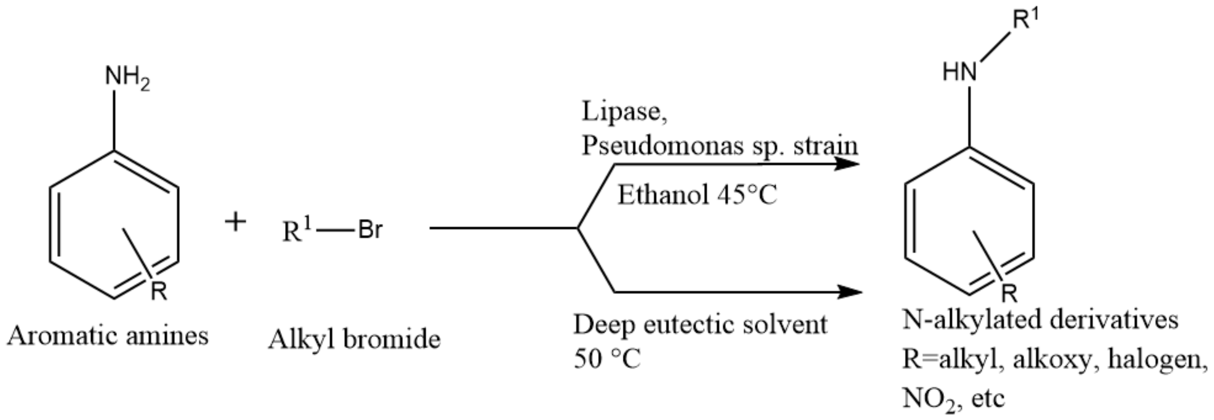


Figure 5. Structure of halide salts and HBD commonly used for synthesis of DES.[12]

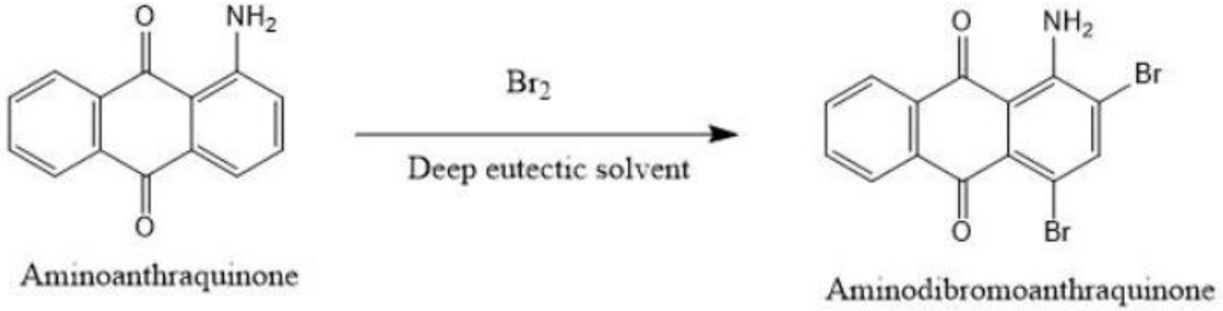
1.2.3 Applications

DESs have been widely investigated for applications such as organic synthesis, extraction media and metal processing etc.[12] One of the main focus areas for DESs has been metal processing including metal electrodeposition, metal extraction and metal electroplating. Metal extraction and electrodeposition will be discussed further in section 4, as they are the main aim of the research. Current electroplating approaches using aqueous acidic or basic solutions are limited by the electrochemical stability of the aqueous solution, leading to hydrogen embrittlement of the metal formed. In addition, passivation of the electrodes is another issue in aqueous solution systems, as the deposition of the metal will be inhibited due to the formation of insoluble oxides on the surface of the electrode.[12] Replacing aqueous solutions with DESs could potentially reduce the passivation effect due to their high solubility of metal oxides and hydroxides, preventing their precipitation on the electrode surface, this has been demonstrated for electroplating on chrome, aluminum, copper, nickel, zinc, and alloy plating. [12]

In terms of organic synthesis, DESs potentially play an important role but it has not been gaining as much attention as metal processing. DESs have been explored and used in a wide range of synthetic reactions including Diels-Alder reactions, Fischer indole annulations and polymerizations, which have been carried out using ChCl-$ZnCl_2$ solvents.[17] In Scheme 1, DESs have been utilized for selective N-alkylation of aromatic primary amines, reducing the complexity of producing multiple alkylations that could potentially be induced by polar organic solvents and high reaction temperatures.[18] In addition, Shankarlings' research has shown that, in order to avoid the use of volatile organic compounds (VOCs) or acids as solvents or catalysts in the bromination of 1-aminoanthra-9,10-quinone (Scheme 2). Instead, it was found that ChCl:Urea can act as a catalyst and reaction medium to significantly reduce the reaction time from 10-12 h in chloroform and methanol to 2-3 h, increasing the yield at the same time from 70-75% to 95%. The improvement in the product yield has proven that the DES can act as effective solvents for several reactions of organic synthesis.



Scheme 1. Selective N-alkylation of aromatic amines with alkyl bromide in lipase-catalyzed medium and deep eutectic solvent medium.[18]



Scheme 2. Bromination of 1-aminoanthra-9,10-quinone using choline chloride.[17,19]

Another application of DESs is the purification and manufacturing of biodiesel.[12] Biodiesel acts as an alternative to fossil fuel which can be synthesized from a natural product (e.g. from naturally occurring triglycerides) and produced pronounce fewer particulates than conventional diesel fuel with no sulfurous emissions. However, before biodiesel can be used, glycerol is an unavoidable byproduct due to the nature of the methylation reaction but that it has undesirable properties which requires that it is separated from the resultant biodiesel.[12] In order to address the issue, many research groups have developed new methods for extracting glycerol from biodiesel. One approach has been the use of DESs, for example glycerine from the transesterification biodiesel product was extracted using a 1:1 mixture of biodiesel:[Choline chloride:glycerine][20] Shahbaz et al have also used choline chloride and the HBD ethylene glycol or 2,2,2-trifluoracetamide to successfully extract glycerol from palm-oil-based biodiesel.[21–24] While the investigation into DESs has mainly focused on metal processing, DESs as alternative solvents are beginning to be explored for a wider range of applications. One major challenge, particularly for extraction/separations is the hydrophilicity of many DES which makes it hard to use them to separate compounds from aqueous solution.

1.2.4 Overview of Hydrophobic Deep Eutectic Solvents (HDES)

One approach has been developing hydrophobic DES to address the difficulty of separating components from aqueous stream. DESs can be categorized into hydrophilic and hydrophobic based on their affinity to water. They both pose the same characterization of low price, ease of handling, easy preparation, non-flammable, biodegradable and non-toxic.[25,26] The structure of some of the HBA and HBD used for the synthesis of HDESs in this research is shown in figure 6. The hydrophobic deep eutectic solvents were first presented by van Osch et al. in 2015 consisting of a fatty acid and a quaternary ammonium salt.[25] Decanoic acid was chosen as a HBD due to its pronounced hydrophobic behaviors in combination with its moderate ability to undergo hydrogen bonding interactions. Six quaternary ammonium salts were chosen as HBA combined with decanoic acid and were investigated for their water content following saturation with an aqueous solution. The results of this investigation showed that the good hydrophobicity can be concluded from the low water content after mixing with water and low leaching of the quaternary salt.[25]

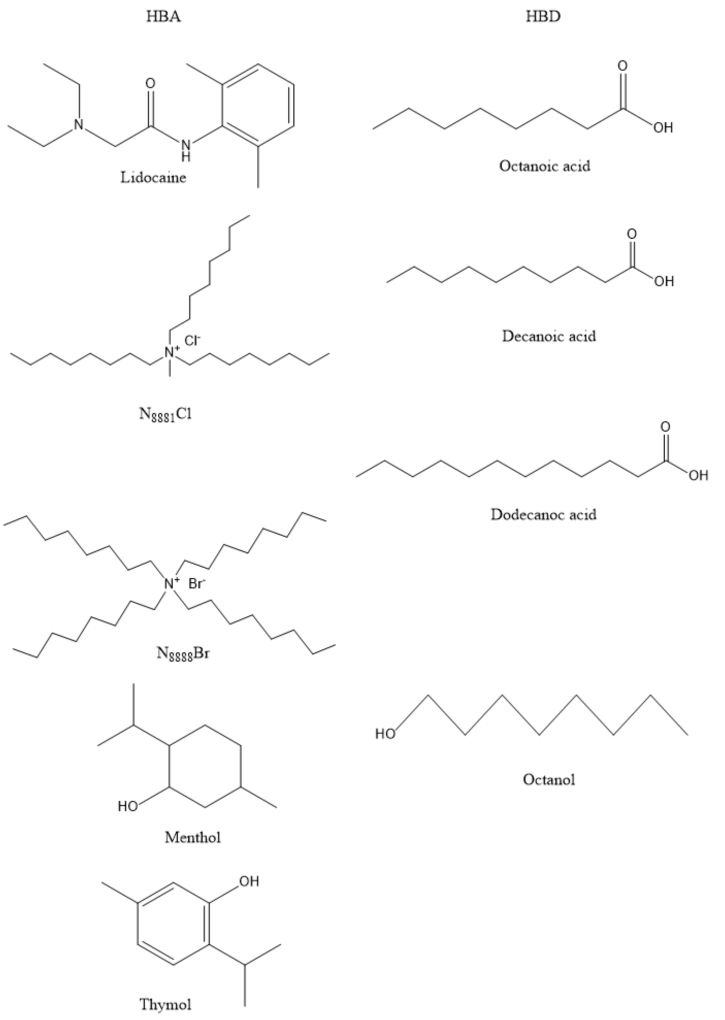


Figure 6. Structure of HBA and HBD used for HDESs.

HDESs holds advantages compared to hydrophilic eutectic mixture, as the HDESs can extract from aqueous environments easily. Applications of HDESs include the isolation of biomolecules, extraction of heavy metals, and removal of pesticides from agricultural runoffs.[27] For example, Naga Sai et al. has synthesized thymol and tetradecanol in a 2:1 molar ratio for the selective extraction of furfural[28]; Gonzalez et al. used menthol based HDESs in extraction of phenolic compounds from diluted aqueous solutions generated from biomass.[29] In addition, the increasing micropollutants from pesticides is harmful to living organisms, water, and soil due to bio-accumulative effects. Florido et al. have used DL-menthol and tetrabutylammonium chloride salts based HDES acts as HBD with various acid acts as HBA have been used in the extraction process of pesticides from water, resulting in 80% extraction efficiency for the pesticides with DL-menthol and acids HDESs.[30] With the applications of HDESs being explored in different areas, some of the HDESs' physicochemical properties are required to have further investigation.

1.2.5 Synthesis and Physicochemical properties of HDESs

A wide range of HDESs have been synthesized after Van Osch et al. introduced the first HDES, hence, their physicochemical properties is important to be explore. Table 2 summarizes the physicochemical properties of some synthesized HDESs.[31] HDESs can be categorized based on their HBA, with the major classes being tetra-alkyl-quaternary-ammonium based, terpene-based, and other types of HBA.[31] Tetraalkyl-quaternary-ammonium based HDESs were the first HDESs explored by van Osch et al. and typically involve a tetraalkylammonium salt combined with a long chain carboxylic acid. As those quaternary ammonium salts containing long carbon chains, they pose strong hydrophobicity compared to the short chain ammonium salts such as tetrabutylammonium (N4444), methyltrioctylammonium (N8881), and tetraheptylammonium (N7777).[31] One parameter for identifying the hydrophobicity of the solvent is the proportion of water included in the HDESs when saturated with water. It was found that the water solubility of the prepared HDESs in a water saturated environment was 1.8-6.9 wt%. After the previous water solubility investigation, a range of other long chain alcohols or fatty acid have also been examined under the same method, resulted in these HBD being able to form HDESs with tetra-alkylammonium salts.[32–36] In addition, a ternary HDESs composed of N8881-Cl, octanol, and octanoic acid at a 1:2:3 molar ratio has been reported by Cao et al.[37]. The viscosity of quaternary-ammonium based HDESs are relatively high, with a range from 228 to 1139 mPa s at 293.15 K. The coulombic charge interactions in the salt are responsible for the high viscosity, which is similar to ILs and other DESs. The melting point (T_ms) for the quaternary-ammonium based HDESs is little known, however, a literature review has reported that their melting point is sufficiently low.[38] The melting point of one HDES in this class has been determined. This HDES is N8881-Cl : decanoic acid (1:2) and the melting point was found to be -0.05°C.[25] In addition, the density of the HDESs in this type is also an important property that affects the extraction performance based on two liquid phases. This is because it decides whether the organic phase can be collected either from the top or bottom phase. In general, the hydrophilic DESs have higher density than water with a range between 1.01-1.63 g cm^{-3} as reported by Zhang et al.[39] In contrast, HDESs with quaternary-ammonium based HBA have a lower density than water. This concludes that when liquid-liquid extraction from water is performed, the analyte-enriched HDESs phase can be obtained from the upper liquid phase.

Another widely explored category of HDESs are those based on terpenes as HBAs, particularly menthol and thymol. Menthol can be extracted from Mentha which is cheap, natural, and abundant.[40] Ribeiro et al. synthesized a number of different HDESs that have menthol as HBA and combining with organic acid or long chain length of carboxylic acid acts as HBD.[40] Menthol based HDESs have relatively low viscosity compared to quaternary-ammonium based HDESs due to the absence of Coulombic interactions. The water solubility in these HDESs type was observed to lie in a range of 1.2-1.6%, much lower than the quaternary-ammonium based HDESs.

Thymol is another terpene used to create HDESs. Thymol can be extracted from thyme and can act as an HBA or HBD in HDESs. Thymol has been used as HBA in HDESs in several studies as an extractant.[15,41,42] In general, all the fatty acids that were used in the synthesis of menthol based HDESs, also are capable of forming DESs with thymol in different molar ratio. Furthermore, extraction is more effective in a low viscosity solvent, all else being equal, due to improved mass transport between phases, hence, terpene based HDESs are preferable as extractants compared to quaternary ammonium based HDESs as they have lower viscosity. One exception is menthol: lactic acid (1:2) that has a viscosity of 371 mPa s.[40] The density of terpene based HDESs is lower than water apart from menthol: lactic (1:2) acid and menthol: salol (1:1) that both have densities slightly higher than water.[43] The menthol based HDESs show slightly lower densities than the thymol based HDESs when the HBD compounds were the same.

Apart from the previous two types of HDES, there are other types of HDESs. Van Osch et al. has used lidocaine as HBA combined with decanoic acid as HDESs.[26] The reported HDESs have lower density than water and have water solubility from 7-20%. The viscosity of this types of HDESs was rather high (> 198 mPa s at 293.15K). The viscosity of the solvent was found to slightly decrease when saturated with water.[26] Moreover, dodecanoic acid has been examined with other fatty acids to form less viscous HDES, the water content of dodecanoic acid based DESs in a water saturated condition was measured to be 1.4 % or lower when the length of the carbon chain of carboxylic acid acts as HBD is increased.[44] With expectation of having longer chain fatty acids will result in lower water content, the HDESs composed of decanoic acid : dodecanoic acid (1:2) have water content at 0.5% in water saturated state compared to octanoic acid : dodecanoic acid that has 1.4 %. The density and viscosity of these solvents does not change with water content, owing to the low solubility of water in these solvents.

Farajzadeh et al. has reported a HDESs composed of 4-chlorophenol and choline chloride (2:1).[45–47] Choline chloride is commonly used in the synthesis of hydrophilic eutectic mixtures; however the solvent resulting from the combination with 4-chlorophenol was moderately hydrophobic and water immiscible. The prepared solvent has a density of 1.211 g cm^{-3} which is higher than water (1.0). In addition, phenol acts as HBD in incorporation with choline chloride in molar ratios of 1:1 and 1:4. Compared to 4-chlorophenol based solvent, the phenol based eutectic solvent appeared to have higher water solubility of up to around 7%. However, the high water solubility and the greenness of the phenol based eutectic mixture may not be considered as HDES.

Betaine and L-carnitine are also has been used as HBA and formed HDESs with hexafluoroisopropanol as a HBD in molar ratios of 1:2 and 1:3 respectively.[48] These types of HDESs exhibited the highest density of all HDESs reported by 2019. The viscosity of betaine based HDESs was much lower than the L-carnitine based HDESs. This is because an extra -OH group on L-carnitine resulted in stronger hydrogen bonding with hexafluoroisopropanol.

These other types of solvent reveal that a wide range of material has the potential to be explored and examined to become a new generation of HDESs.

***Table 2**. Physicochemical properties of commonly used HDES.*[31]

DES			Density (g cm^{-3})	Viscosity (mPa s)	T_m (°C)	Measure Temperature (K)
HBA	HBD	Molar ratio				
N4444-Cl	Decanoic acid	1:2	0.9199	368.54	-11.95	293.15
N7777-Cl		1:2	0.8996	227.96	-16.65	
N8881-Cl		1:2	0.8939	1138.73	-0.05	
N8881-Br		1:2	0.9456	814.53	8.95	
N8888-Cl		1:2	0.8921	654.18	1.95	
N8888-Br		1:2	0.9331	889.57	8.95	
Menthol	Pyruvic acid	1:2	0.999	44.637	-	293.15
	Acetic acid	1:1	0.9350	11.296	-	
	Lactic acid	1:2	1.0380	370.860	-	
	Dodecanoic acid	2:1	0.8970	33.058	-	
	Octanoic acid	3:2	0.8887	7.80	-	313.15
	Decanoic acid	1.5:1	0.8855	9.43	-	
	Dodecanoic acid	3:1	0.8823	12.40	-	
	Tetradecanoic acid	4:1	0.8812	14.21	-	

	Salol	1:1	1.07	-	22.28	Not specified
Thymol	Camphor	1:1	0.9873	25.8	-44.0	Room temperature
	Decanoic acid	1:1	0.9437	11.2	17.0	
	Dodecanoic acid	11:9	0.9107	7.01	-	318.15
	Tetradecanoic acid	3:1	0.9240	7.16	-	
	Hexadecanoic acid	4:1	0.9255	7.54	-	
	Octadecanoic acid	9:1	0.9357	6.88	-	
Betaine	Hexafluoroisopropanol	1:2	1.476	76	-39.4	Viscosity was measured at 298.15 with the other not specified.
		1:3	1.525	46	-34.7	
L-Carnitine		1:2	1.503	698	-18.7	
		1:3	1.505	149	-17.2	
Dodecanoic acid	Octanoic acid	1:3	0.9040	8.223	9.0	293.15
	Nonanoic acid	1:3	0.9010	10.115	9.0	
	Decanoic acid	1:2	0.8980	12.886	18.0	
Lidocaine	Decanoic acid	1:2	0.9624	352.5	-	293.15
		1:4	0.9461	197.5	-	

1.3 Metal extraction

1.3.1 Introduction to metal extraction from electronic waste (E-waste)

Electronic equipment is a major consumer of many critical metals, such as copper, tin, zinc, lead, and precious metals like gold and platinum.[49] As the demand for electronic products increases, more precious metals are needed to produce them. When the electronic products reach the end-of-life cycle, they turn into electronic waste and most of the treatment involves landfilling, with only a minor portion are going to chemically recycle.[50,51] With inappropriate processing of the e-waste, hazardous heavy metals may induce serious pollution to our living environment impacting marine and terrestrial environments as well as human health.[51–53] Incineration of e-waste is currently one of the traditional treatments with the aim at waste volume reduction but is also dangerous.[50,51] Dioxin, a toxic persistent pollutant that can cause cancer, reproductive and developmental problems, harmful our immune system, and interfere with hormones, can be produced by improper municipal waste incineration.[50] During the incineration, the copper involved in the e-waste acts as a catalyst for dioxin formation when the fire-retardants are burning.[50]

Hydrometallurgical processing is another treatment for the process of e-waste with the aim at metal recovery. The step of hydrometallurgical process generally consists of range of acid or corrosive leaches of solid waste such as cyanide, halide, thiourea, and thiosulfate.[50] Lixiviants containing toxic leaching reagents can heavily pollute water or soil if not properly contained or disposed of. Apart from the method discussed above, Wazeer et al. has reviewed and summarized the advantages and drawback of the current method used to extract heavy metals from wastewater, as presented in Table 3.[54] However, contamination of water containing high concentrations of heavy metal makes water undrinkable, hence, the process of e-waste has been taken into consideration not only by the government but also by the scientist.

Table 3. Advantages and disadvantages of the current methods applied to heavy metals extraction from wastewater.[54]

Method	Advantages	Drawbacks/limitation
Oxidation/Ion exchange	Fast kinetics, high removal efficiency, and effective in treating inorganic effluent.	Highly affected by the pH of the solution.
	No sludge disposal.	Fouling of metal ions.
	Low cost of material and less time-consuming process.	Suitable for low concentration of metals only.
		Higher capital and operational costs.
Chemical precipitation	Simple operation and low capital cost.	Further treatment is needed because of the production of a large amount of sludge
	Easily automated treatment method.	Slow metal precipitation and poor settling.
		Requires a large number of chemicals to reduce metals to an acceptable level for discharge.
Membrane treatment	Less energy consumption because of higher removal efficiency.	Production of concentrated sludge.
	Easy fabrication, environmentally friendly, and removes both organic and inorganic compounds	Membrane fouling.

	No additives and phase change involved.	Higher cost and lower permeate flux.
Flotation/Coagulation	Relatively economical and easy operation.	Production of sludge
		Incomplete removal of heavy metals.
Electrochemical technologies	Environmentally friendly and rapid process.	Higher electricity cost.
		Large capital investments.
		Formation of large particles.
Liquid-liquid extraction	Relatively low operational costs.	Use of large volume of organic solvents
	Easy operation.	Possible cross-contamination of the aqueous streams.
	Selectivity of exchangers for efficient removal of metals.	

1.3.2 Metal extraction by using HDESs

In order to address the pollution issue from e-waste stream, a novel green alternative solvent has been developed and widely investigated. HDESs enables the separation of metals from aqueous waste streams given their immiscibility with water, hence they have been explored for metal extraction. HDESs compared to conventional solvent are more environmentally friendly as the extraction process does not generate vast amount of hazardous substances, requires less heating energy, and low cost. In addition to the extraction method, solvent extraction was used and has advantages over other methods including the possibility to operate in a continuous mode, the use of easy operating equipment, less amount of extractant, and diversity of extractant choice.[26,55] Van Osch et al. revealed that the mechanism of the metal extraction is that the metal forms metal complexes with the deprotonated HBD (carboxy groups of organic acid), whereas negatively charged chloride interacts with the positively charged ammonium. A similar metal extraction mechanism has also been proposed by a different research group, which suggests a two-step process.[56–59] The first step involved the protonation of the hydrated metal oxide by the acidic HBD when the hydrogen atom of the functional groups in HBD reacted with the OH in the active sites of the hydrated metal oxide. The second step involves substitution of the carboxylate anion formed following the loss of water from the metal oxide surface. The second step reaction will be performed only when the metal-ligand complexes are more stable than the metal oxide complex. The mechanism is expressed as follows:

(1) Bulk = Metal-OH + HX $\leftrightarrow$ bulk = Metal-OH_2^+ …… X^{n-}

(2) Bulk = Metal-OH_2^+ …… X^{n-} $\leftrightarrow$ Metal-$X_{(DES)}^{n-}$ + H_2O

The number of investigation of HDESs for metal extraction rapidly increased after these original studies. Van Osch et al. have synthesized a HDES by using lidocaine as HBA and decanoic acid as HBD in different ratios which includes HBA:HBD (1:2; 1:3; 1:4) and explored an extraction of different metal chloride salts from water.[26] The table 4 below represents the result of metal extraction efficiency. The experiment with one metal salt, all obtained high extraction efficiency except for potassium because the decanoic acid prefers to bind with transition metals but not alkali metals. In experiment 5, lidocaine : decanoic acid in molar ratio from 1:2 to 1:4 has tested to extract varies of transition metals and alkali metals, and with rather low extraction efficiency on alkali metal ions and maintained promising result on Co, Ni, and Zn, moreover, the decreasing of extraction efficiency with increase of the decanoic acid potentially due to the hydrophobicity of the HDES.

Table 4. Distribution coefficients (D) of metal cations and chloride anions over the HDESs and aqueous phase.[26]

		Lidocaine:Decanoic acid (1:2)	Lidocaine:Decanoic acid (1:3)	Lidocaine:Deconoic acid (1:4)
Exp. 1	Co	>0.996 ± 0.001	>0.996 ± 0.001	0.983 ± 0.002
	Cl	>0.113 ± 0.113	0.078 ± 0.008	0.101 ± 0.059
Exp.2	Fe	>0.992 ± 0.001	>0.991 ± 0.001	>0.991 ± 0.001
	Cl	>0.197 ± 0.003	0.080 ± 0.001	0.113 ± 0.007
Exp.3	Mn	>0.992 ± 0.001	>0.991 ± 0.001	0.983 ± 0.004
	Cl	>0.086 ± 0.002	0.081 ± 0.027	0.065 ± 0.011
Exp.4	K	0.457 ± 0.001	0.397 ± 0.011	0.457 ± 0.001
	Cl	0.141 ± 0.001	0.078 ± 0.031	0.072 ± 0.001
Exp.5	Co	0.990 ± 0.001	0.946 ± 0.012	0.777 ± 0.008
	Ni	>0.996 ± 0.001	0.983 ± 0.001	0.880 ± 0.004
	Zn	>0.995 ± 0.001	>0.995 ± 0.001	>0.995 ± 0.001
	Cu	>0.996 ± 0.001	>0.996 ± 0.001	>0.996 ± 0.001
	Na	0.195 ± 0.001	0.140 ± 0.009	0.127 ± 0.040
	K	0.211 ± 0.028	0.161 ± 0.018	0.134 ± 0.005
	Li	0.266 ± 0.015	0.166 ± 0.001	0.128 ± 0.036

Tereshatov et al. in 2016 has also investigated the transfer of metallic species from aqueous solution into HDESs.[60] The metals explored is indium. The HDESs used for the extraction of indium consisted of either menthol and tetraheptylammonium chloride [$(C_7H_{15})_4NCl$] as HBA with HBDs consistent of lauric acid, decanoic acid, oleic acid, and ibuprofen. Tereshatov et al. research has drawn to the conclusion that three DESs consists of quaternary ammonium chloride and organic acid such as oleic acids, decanoic acid, and ibuprofen have promising metal extraction efficiency in the range of 0.001-10.2 M HCl and 1 x 10^{-7} – 8 x 10^{-1} M oxalic acid in the aqueous phase.

Terpene base HDESs have also been used for metal extraction. Schaeffer et al. in 2018 has conducted a study on using menthol or thymol as HBA of HDES with different alkyl chain length carboxylic acids used as HBDs to investigate their relationship to the metal extraction efficiency.[61] In figure 6, the highest extraction efficiency for Cu(II) and Fe(II) were observed for the thymol and capric acid as HBA and HBD after optimized the choice of HBA and the length of HBD.[61]

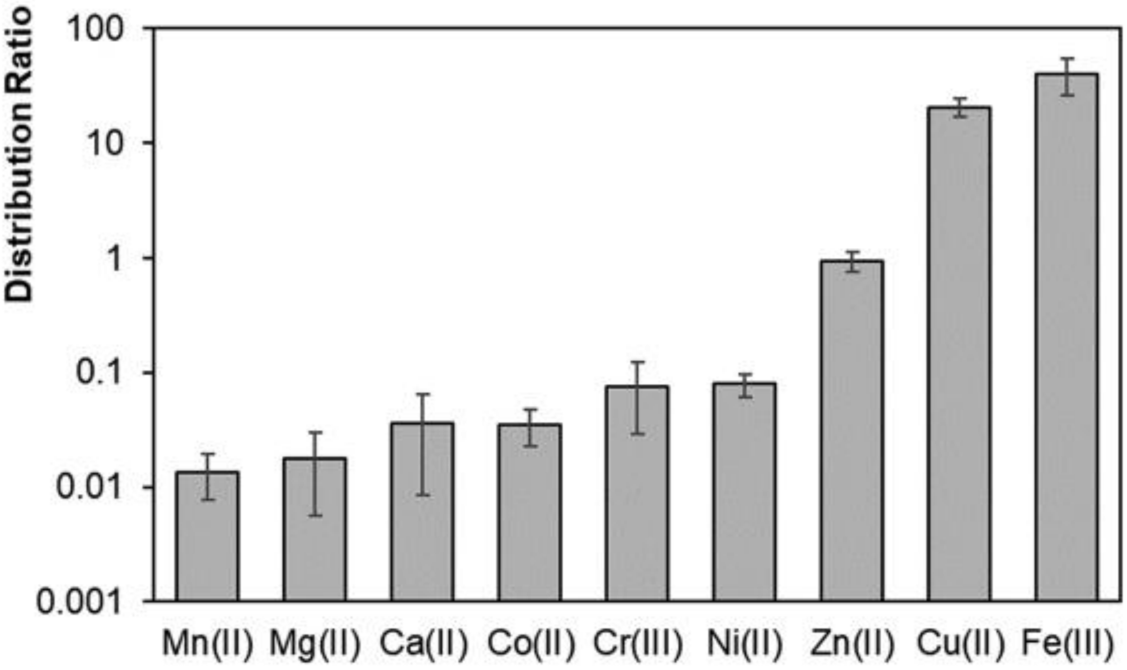


Figure 7. Distribution ratio for the extraction of 0.01 M transition metals in thymol: capric acid HDESs

While these studies demonstrate the feasibility of using HDESs on the extraction of metals, the application of these to lixiviant solutions from e-waste has not been investigated and only limited studies have explored the relationship between DES components and metal selectivity for these extractions.

1.4 Metal electrodeposition

1.4.1 Overview on metal electrodeposition

Metal electrodeposition also known as electroplating is an electrochemical process that causes the formation of metal solid on an electrode by its reduction in solution from a liquid electrolyte.[39] Metal electrodeposition is often used to enhance surfaces for corrosion-resistance, electrocatalysis, magnetic application, photoactive semiconductors electrotypes in the printing industry, hardening of steel for engineered components, and the production of printed circuit boards.[39] In general, the electrodeposition process composed of three-electrode electrochemical cell includes a reference electrode, cathode, and an anode as depicted in Figure 8.[39] The metal contained in the electrolyte will undergo reduction at an certain potential, and deposit on the cathode. Traditional electrodeposition is based on aqueous acidic or basic solutions, although organic solvents with an added electrolyte can also be used. The electrochemical window of the solvent here is an issue, this needs to be wide enough to enable electrodeposition with co-production of degradation products (particularly) hydrogen. Passivation in aqueous solutions is a common issue due to the formation of insoluble oxides and hydroxide on the surface of the electrode, inhibiting the deposition of the desired metal. The industry has proven proficient at working around the limits imposed by employing water as a solvent.[12]. The electroplating solutions ideally should have the properties of high solubility of metal salts, high conductivity, electrochemical stability, and low ohmic losses.[16] ILs have received attention and been used for metal electrodeposition. Although, ILs gained promising results on electrodeposition of metals, there are a number of drawbacks such as the syntheses of ILs, their sensitivity to water and potential degradation when exposed to oxygen. Therefore, DESs that possess similar properties to ILs have gained increasing interest for their possible use as an electrolyte.

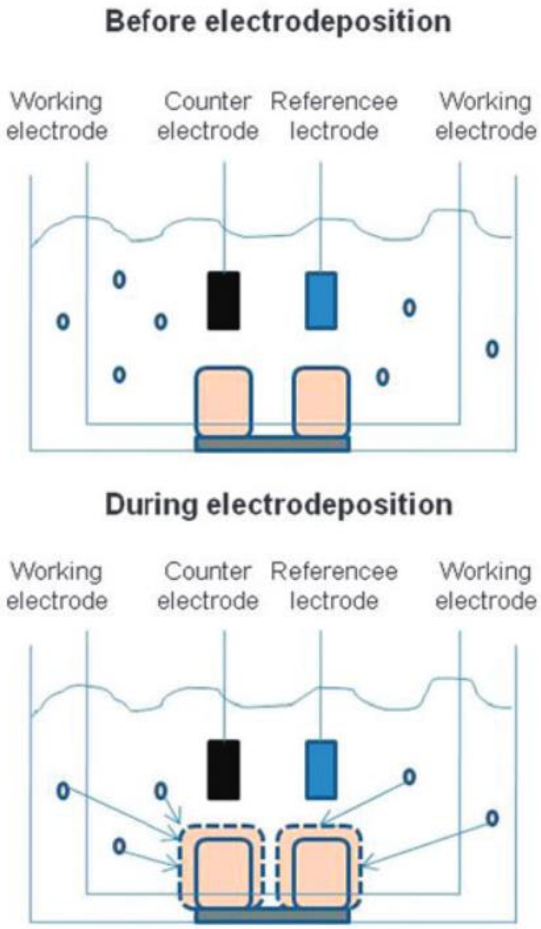


Figure 8. General process of electrodeposition of metals.[39]

1.4.2 Metal electrodeposition in deep eutectic solvent

DESs have higher water immiscibility than ILs and with their lower price and easier synthesis makes them more preferable over ILs for metal electrodeposition. A DES composed of choline chloride: Urea (1:2) has been used for electrodeposition of SmCo. Gomez et al. used this type of DES to deposit SmCo using cylindrical three electrode cell including vitreous carbon working electrode, platinum counter electrode, and Ag/AgCl reference electrode.[62] The redox potential window of the DES was in a range from -2.4 to 0.4 V with respect to Ag/AgCl electrode. Temperature was increased to 70°C to decrease the viscosity in order to manage the mass transfer problem. In addition, Dale et al. have conducted a metal electrodeposition of Gd over a Mo electrode in a reversible process with no interference of the solvent.[63] Other than Gd; CdS, CdSe, and Zn were also successfully electrodeposited using the same DES.[64] Moreover, nickel was also electrodeposited in the same types of DES using a copper microelectrode. The potential window of the ChCl: Urea is between -1.35 and 0.24 V.[65]

A DES composed of ChCl: ethylene glycol was also applied to metal electrodeposition. Bohlen et al. have reported using DES composed of choline chloride and ethylene glycol on indium deposition using copper, glassy carbon and platinum electrode.[66] Zn, Sn and Zn-Sn alloy electrodeposition were also been carried out by Abbott et al. using this DES. However, Cu electrodeposition is difficult in ChCl: ethylene glycol DES, progressive nucleation was observed for Cu electrodeposition which led to a bright nano-structure deposit. If the concentration of Cu in DES is lowered, a spontaneous nucleation of Cu will be observed, implied that a continuous metal layer will be forming during the electrodeposition process.[67] Also, Abbott et al. obtained a bright deposit when the concentration of copper is from 0.01 M and 0.1 M. The kinetic study of electron transfer of the Cu(I)/Cu(II) redox couple was performed by Llyod et al and have indicated that the electrodeposition was reversible and a large amount of free chloride was detected in the DES due to the dissociation of ChCl.[68] However, the electrodeposition of metal extracted from an aqueous stream has not been explored, thus, further investigation about using HDESs for extraction and subsequent electrodeposition of copper will be performed in this research.

2. Research aims

The aim of this project was to use of HDESs for liquid-liquid metal extraction to explore their potential for the isolation of metals from e-waste recycling waste streams. The research aims to understand the effect of HDESs selection on extraction efficacy through the use of a model copper sulphate solution alongside actual e-waste mixed metal solution. This will be achieved by a range of HDESs including quaternary-ammonium salts based and terpene-based acts as hydrogen bond acceptor (HBA) and carboxylic acid, terpene, and alcohol acts as hydrogen bond donor

Reaction conditions will be optimized by exploring the effect of temperature, reaction time, and the ratio of aqueous solution:HDESs volume, with the aim to achieve maximal copper extraction efficiency and selectivity.

The metal extraction will be monitored by different analytical techniques. The metal extraction efficiency is monitored by MP-AES and UV-Vis. The speciation of metals within the solution is explored using FTIR and mass spectrometry. These methods will provide insight into the metal extraction efficiency with the aim at copper extraction in the presence of different HDESs and reaction conditions.

The effect of the ratio of the HDESs components for the optimal HDES system on metal extraction will be explored by adjusting the ratio of the HDES components. The length of the carboxylic acid in HDESs effect will be explored by synthesizing a range of HDESs with several length of carboxylic acid and use in copper extraction. This will give an understanding of how, if any, the structure of the HDESs influences the outcome of the metal extraction.

The mechanism of liquid-liquid metal extraction in HDESs will be explored by investigating the ion exchange between the HDESs and copper during the extraction. This will be achieved by identifying the structure of the metal complex formed during extraction using techniques such MS and FTIR. The final aim is to explore a larger scale extraction of the system using an optimized HDES to investigate its recovery and recyclability. The copper extract will be recovered by electrodeposition using the HDES solution directly as the electrolyte, and the potential recyclability of the HDES system determined. This will indicate the feasibility of the HDES system developed for the recyclable separation of copper from mixed metal e-waste recycling waste stream.

3.Experimental procedure

3.1 General experimental procedure

All reagents used for the synthesis of HDESs were used as received: menthol, thymol, lidocaine, methyltrioctylammonium chloride, tetraoctylammonum bromide, octanoic acid, decanoic acid, dodecanoic acid, hexanoic acid, oleic acid, 1-hexanol, 1-octanol, and 1-dodecanol. Nitric acid was purchased in the highest purity available. Methanol, ethyl acetate, chloroform-D4 were used as purchase.

1H and 13C NMR spectra were obtained from a Bruker Avance 400 MHz spectrometer operating at 399.89 MHz for 1H and 100.55 MHz for 13C. Solvent evaporation was performed on a Rotavapor® R-100 rotary evaporator. Microwave digestion was performed on an Ethos Up high-performance microwave digestion system. MP-AES experiments were performed on an Agilent 4210. High resolution mass spectra were obtained on a Bruker MicrOToF-QII coupled with a Dionex HPLC system and Kd science Syringe pump using electrospray ionisation in positive mode. IR spectra was obtained on a Bruker Vertex 70v FT-IR Spectrometer. UV-visible absorption spectra were obtained using a Cary 300 UV-visible spectrometer equipped with a water recirculating Peltier temperature controller.

3.2 Preparation of HDESs

In a typical DES preparation, the two components were combined and stirred while being heated to 60 °C until a homogeneous liquid formed, usually 1-1.5 h. These liquids were used without further purification. The molar ratios of all prepared HDESs are shown in Table 5.

Table 5. HDESs and relative molar ratio used.

HBA	**HBD**	**Molar Ratios**
Menthol	Octanoic acid	1.5:1
	Decanoic acid	1.5:1
	Dodecanoic acid	3:1
Thymol	Octanoic acid	1:1.4
	Decanoic acid	1:1
	Dodecanoic acid	1:2.5
TOAB	Decanoic acid	1:2
	Hexanoic acid	1:2
	Dodecanoic acid	1:2
	Octanoic acid	1:2
Lidocaine	Decanoic acid	1:2
	Dodecanoic acid	1:2
	Oleic acid	1:1
	Decanoic acid	1:1
	Dodecanoic acid	1:1
	Thymol	1:2
	Octanoic acid	1:2
	Menthol	1:1
Methyltrioctylammonium chloride (N8881Cl)	1-hexanol	1:1
	1-octanol	1:2

	1-dodecanol	1:2
	Hexanoic acid	1:2
	Octanoic acid	2:1
	Decanoic acid	2:1

3.3 Metal extraction

3.3.1 Metal extraction in copper stock solution

In a general procedure, the copper stock solution was prepared by dissolving $CuSO_4$.5H2O (0.08 M, 5.0144 g) and H_2SO_4 (0.25 M, 3.40 ml) and made up to 50 mL. 2 mL of HDES was combined with 2 mL of the copper stock solution and stirred at room temperature for 2 h. The solution was allowed to stand and the organic phase and aqueous phase separated. The concentration of copper in each phase was determined by MP-AES, with the concentration of copper in the aqueous phase also investigated using UV-Vis spectroscopy.

3.3.2 UV-Vis of Copper stock solution

The UV-Vis spectra were obtained from a Cary 300 UV-Visible spectrometer along with a water recirculating Peltier temperature monitor. The aqueous phase of the copper extraction was analyzed without further dilution by UV-Vis spectroscopy, using a spectral range of 500 to 900 nm at ambient temperature.

3.3.2 Metal extraction in lixiviant solution

The e-waste recycling mixed metal solution was provided by Mint Innovation. In a typical procedure, 2 mL of HDES was combined with 2 mL of the copper stock solution and stirred at room temperature for 2 h. The solution was then separated into the organic phase and aqueous phase. The concentration of metals was monitored by MP-MS.

3.3.1 Optimization of metal extraction

Optimization condition was generated using the Design of Expert version 7 (DoE) software and the detail will be shown in Table 7 in section 4.3.2. In a typical experiment, the desired amount of HDES was added to 2 mL of mixed metal solution and stirred for the required time at the specified temperature. At the end of the extraction time, the solution was allowed to settle at room temperature and the aqueous and organic phases separated and analyzed by MP-AES.

3.4 Microwave Digestion

The aqueous phase samples were prepared for analysis by diluting 0.5 mL of the aqueous sample with 4.5 mL of 5 Wt% nitric acid solution. After that, 1 ml of the solution was then further diluted with 24 ml diluted acid solution.

In an initial procedure, approximately 200 µg of the organic phase of the extraction was accurately weighed. To this sample was added 5 mL of concentrated nitric acid. The mixture was then heated using a microwave digestion system to 180 °C for 25 mins. The samples were cooled to room temperature, 45 mL of type I water was added, and the weight of the final sample recorded. As not all of the samples were completed digested using this procedure, the approximately 200 µg of organic/ aqueous mixtures was both heated to 180 °C for 40 mins for subsequent samples and then followed the same method above.

3.5 Microwave Plasma-Atomic Emission spectroscopy (MP-AES) analysis

Digested samples were analysed by MP-AES. These experiments were performed by Palak at Mint Innovations using a MP-AES Agilent 4210.

3.6 High resolution mass spectrometer (HRMS)

All samples prepared for mass spectrum were dissolved in methanol in a concentration of 1 mg/mL. These were analysed using Bruker MicrOToF-QII coupled with a Dionex HPLC system and Kd science Syringe pump via electrospray ionization in positive mode.

3.7 Recyclability of HDES

The scale up sample was prepared with 12 mL of HDES and mixed metal solution heating under 36 mins under 42°C. The organic phase and aqueous phase were then separated out and ready for electrodeposition. The re-extraction sample was prepared by mixing approximately 12 mL of organic sample and mixed metal solution. Heated under 42 °C for 36 mins and then separated into both organic and liquid phase.

3.8 Electrodeposition of Copper

Electrodeposition was performed in a CHI660D CH Instruments electrochemical workstation. The electrode used includes two platinum plates as working and counter electrode, silver wire as reference electrode. Copper electrodeposition is conducted under scan rate of 0.001 V/s, potential width from -2 to 1.2 V. The cleaning of the electrode platinum plate after electrodeposition is immersed the platinum electrode into 25% nitric solution for 2.5 h.

4. Result and discussion

The primary aim of this project is to explore the potential for HDES to selectively extract copper via liquid-liquid extraction from a mixed metal e-waste lixiviant. The first step in this project is to select an appropriate HDES system for this extraction. This was achieved by screening a selection of HDESs to explore their viability for copper extraction. These HDESs were based on tetraalkylammonium salts, lidocaine based and terpenes as HBAs as these HBAs have been shown to form HDESs that can extract copper previously although the relationship between HBD and HBA has not been widely explored.[26,39] The chosen HBDs for the HDESs are carboxylic acid or alcohol with different carbon chain length to investigate the relationship between the length of HBD carbon chain in addition to changes in its functionality on the metal extraction efficiency. The next step is to use an appropriate model solution to assess the inherent ability of these HDESs to extract copper under representative conditions with the complications of the mixed metal solution. The chosen HDESs system will be applied for the extraction of copper from the model solution and will be optimized further for extraction on the lixiviant solution.

4.1 Copper extraction from copper sulfate stock solution

A model copper solution involves 0.08M $CuSO_4$ and 0.25 M H_2SO_4, is prepared by dissolving copper sulfate pentahydrate into sulfuric acid with pH ~0 to replicate the conditions of the mixed metal solution. To screen the HDES, 2 mL of HDESs was stirred with 2 mL of the copper sulfate solution, under room temperature around 22 °C for 2 hours. These conditions are adapted from those that have been used previously for copper extraction.[26] Triplicate experiments were conducted for each HDESs used for copper extraction in order to be obtained high accuracy and consistent result. The concentration of the copper extracted through the reaction was then monitored by UV-Vis and MP-AES.

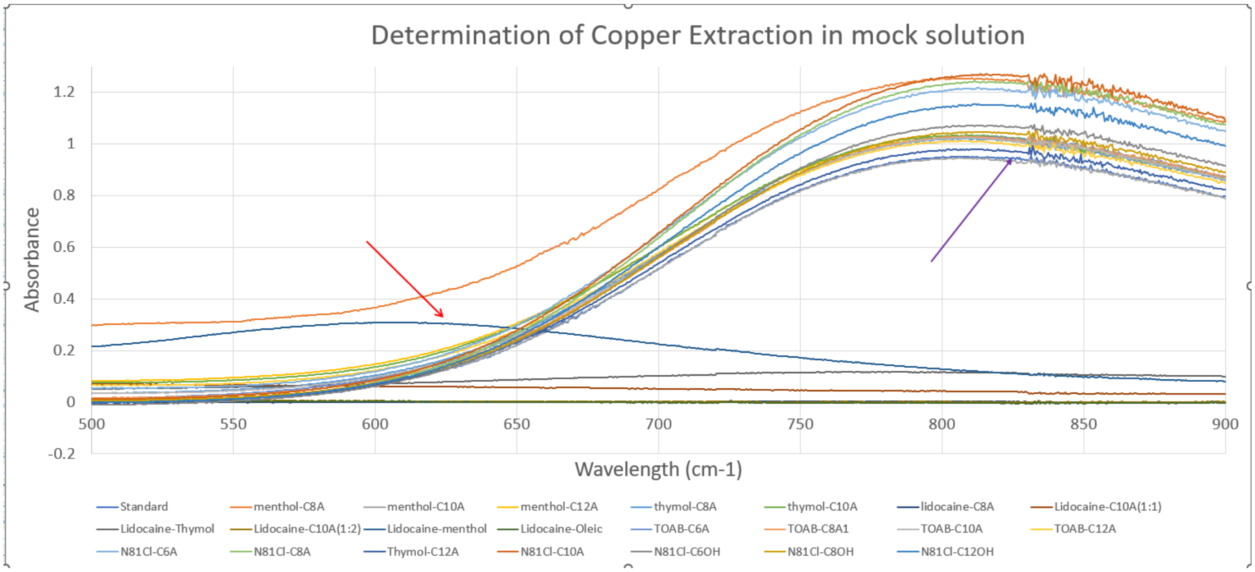


Figure 9. Representative UV-Vis spectra for the determination of copper concentration in the aqueous phase after extraction by the HDES.

Each aqueous phase from the samples after extraction was separated out and characterized by UV-Vis and compared to the UV-Vis of the original copper sulfate model solution which with copper absorbance at around 800 nm.[69] Figure 9 shows the UV-Vis spectra obtained, the line indicating an absorbance in ~0.8 at 850nm, pointed by the purple arrow, represents the standard sample. As this is the aqueous solution, a decreased in the copper extraction would be expected if copper had been successfully extracted . From Figure 9, it is apparent that all the aqueous phases obtained from lidocaine based HDESs have low absorbances compared to terpene and tetraalkylammonium based HDESs. The figure shows that some spectra display absorbances larger than the original copper is physically impossible, but this could indicate the possibility of water absorption by the HDES phase. In theory, the concentration of copper in the samples, after extraction, can only be lower or stay the same when compared to the raw copper sulfate mock solution. This leads to an assumption that samples with higher absorbance than the standard line, the water from the aqueous is potentially leaching into the organic phase. The water leaching would increase the concentration of copper in the solution even if the actual amount of copper remains unchanged which would account for the higher absorbance from copper than the original copper sulfate solution. In addition, the spectrum obtained from lidocaine : menthol HDES, depicted in the red arrow, shows an absorption at 600 nm rather than the typical absorption at

800 nm which may be due to the air bubble contained in the cuvette and reducing the amount of light reaching the detector and causing baseline fluctuations. Overall, it appears that the lidocaine based HDESs extracted most of the copper from the mock solution while the terpene and tetra-alkyl-ammonium based HDESs only extracted trace amounts of copper or did not extract any.

MP-AES enabled the analysis of both aqueous and organic phases to more precisely confirm the extraction of copper. Figures 10 and 11 show the copper concentration in organic and aqueous phase respectively, as determined by MP-AES. From Figure 10, the lidocaine based HDESs has extracted higher copper concentrations than terpene and tetraalkylammonium based HDESs, with exception of the lidocaine : menthol HDES. In all the lidocaine based HDESs used for the extraction, lidocaine : menthol, lidocaine : thymol HDES have extracted relatively low amount of copper. Thymol:HBD HDESs typically did not extract copper, with the exception of thymol:$C_{10}A$ which extracted in average of 516 ± 448 ppm cooper meaning that the result is not accurate. Methyl-trioctylammonium chloride and tetra-octylammonium bromide based HDESs both have extracted 0% of copper. N_{8881} Cl : C_8OH, N_{8881} Cl : $C_{10}A$, TOAB : $C_{12}A$, N_{8881} Cl : $C_{12}OH$, and N_{8881} Cl : C_8A have extracted trace amount of copper but with large error bar, this may explain with sampling error. The experimental errors observed for the organic phase are larger than those observed in the aqueous phase. This may be due to separation challenges due to the emulsification of the organic phase with the aqueous phase although despite the errors some notable trends were observed.

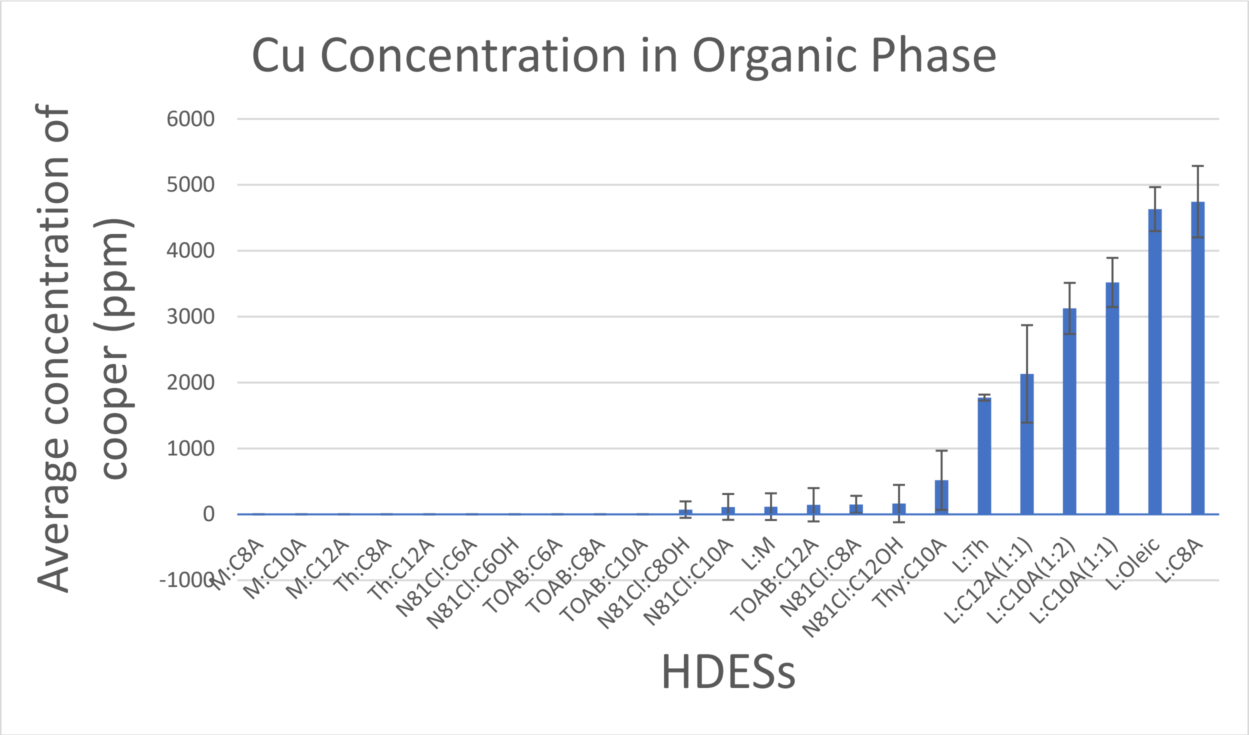


Figure 10. Concentration of copper in organic phase for each HDESs, as determined by MP-AES.

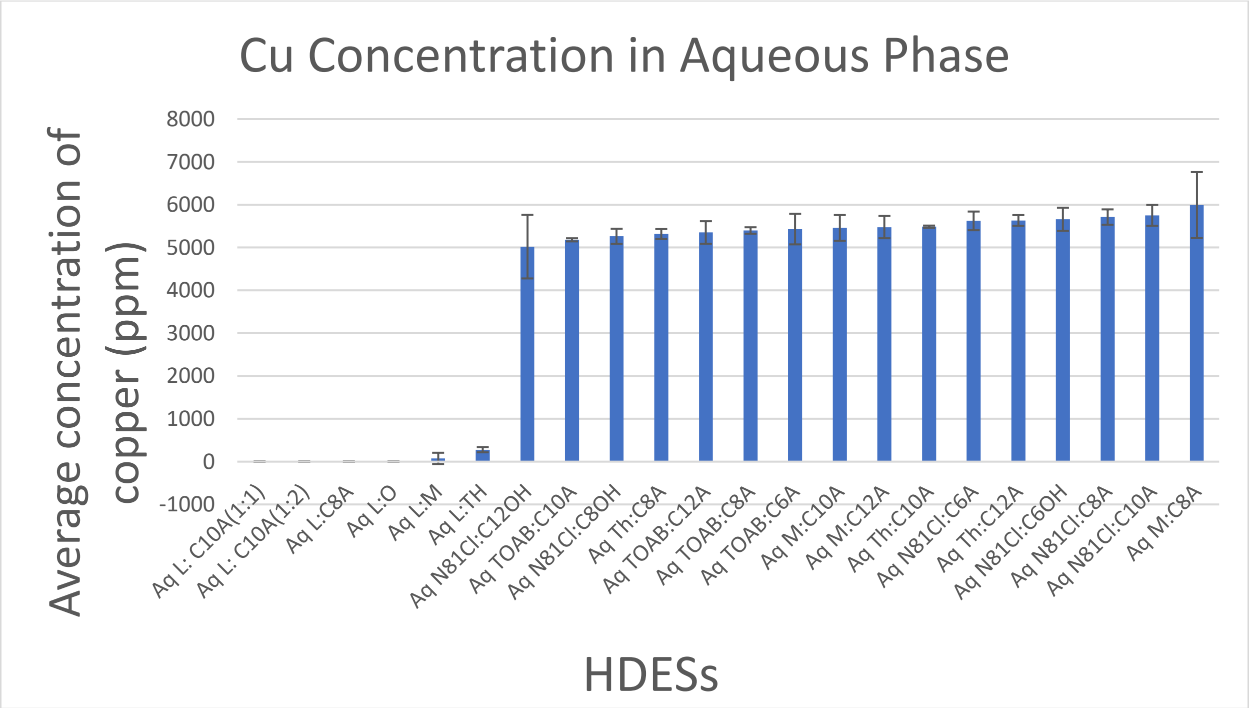


Figure 11. Concentration of copper in aqueous phase for each HDESs, as determined by MP-AES.

Figure 11 shows the copper concentration in the aqueous phase. The figure clearly indicates that the concentration of copper in aqueous phase for all HDESs, except for lidocaine based HDESs, remained at a high level compared to the original copper stock solution, which had an average Cu concentration of 4700 ppm. For lidocaine based HDESs, the aqueous phase of lidocaine : thymol has trace amounts of copper left while others have 0%. This suggests that copper has been fully extracted for lidocaine based HDESs but not extracted to a significant extent for terpene and tetra-alkylammonium based HDESs. An issue arose when comparing figure 10 and 11. The concentration of copper in the aqueous and organic phases should add to ~4700 ppm. However, some HDES system led to copper concentration significantly below this. It was observed that a precipitate formed in some of these samples which could explain the discrepancy in copper concentration. Figure 12 displays photographs of the samples of Lidocaine : $C_{12}A$ HDES after extraction and centrifugation. The precipitate formed over time during the extraction and could be easily separated by centrifugation. To prepare the samples for MP-AES, only the liquid phase is taken to run the microwave digestion. Therefore, the precipitate is not being characterized by AP-MES, causing the mirror image of both organic and aqueous phase to be not obtained.

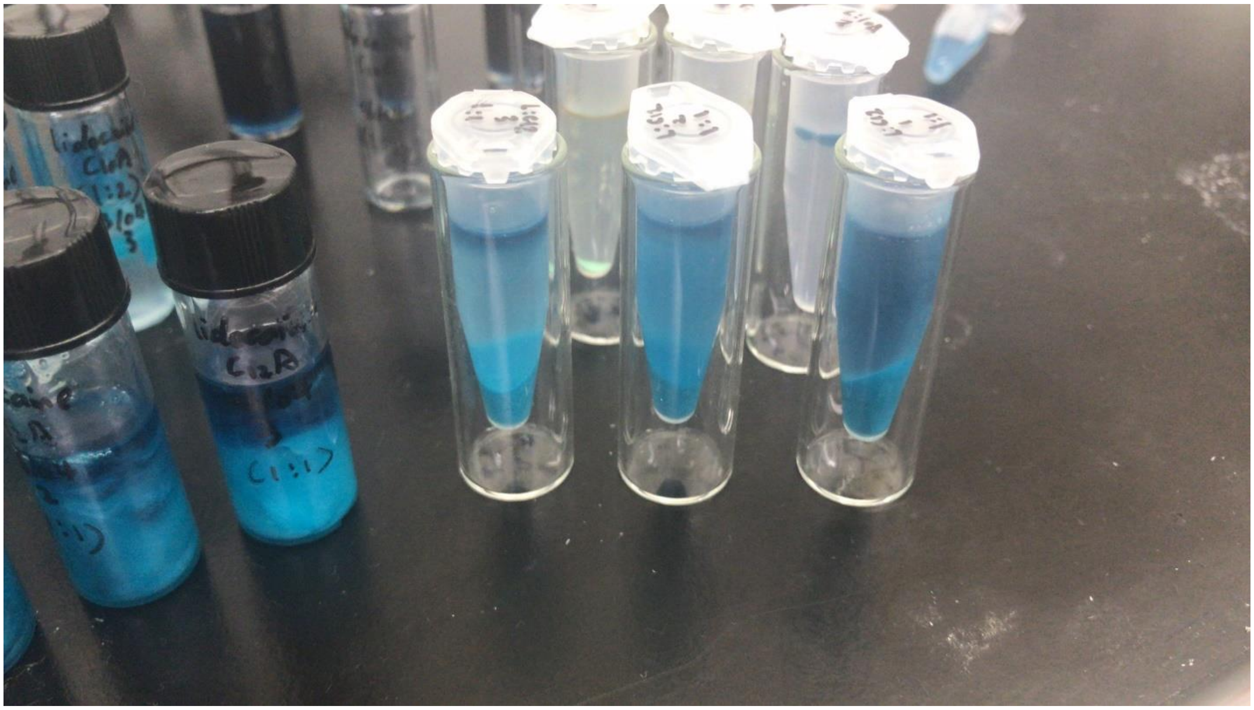


Figure 12. Samples of Lidocaine : $C_{12}A$ HDES after extraction are shown, with the original extraction sample on the left and the organic phase sample after centrifugation on the right.

Figure 13 is the copper extraction efficiency of HDESs from the copper sulfate solution. The calculation of the copper extraction efficiency is based on the proportion of the copper that has been reduced from the original stock solution following extraction by the HDES. Menthol : C_8A obtained -27 % of copper extraction efficiency, which is likely due to the inclusion of water in the organic phase. The formation of the precipitate meant that the copper extraction efficiency is solely on the aqueous phase since the precipitate can considered a method of separation for the copper. Overall, the initial screening of the HDESs in extraction of copper in the mock solution has drawn to the conclusion that lidocaine based HDESs combined with different HBD such as terpene compound and varies length of carboxylic acid obtained pronounced copper extraction efficiency, but with the terpene and tetra-alkyl-ammonium based HDESs obtained poor extraction efficiency.

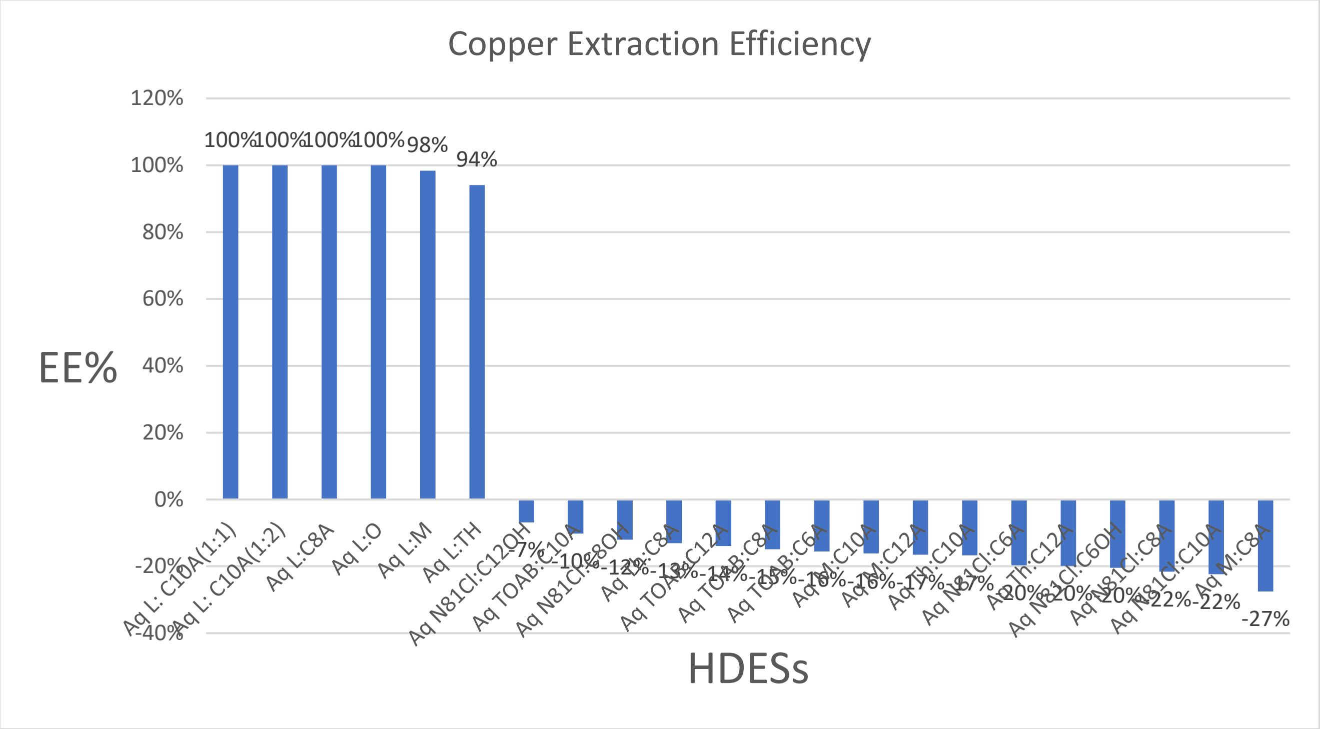


Figure 13. Extraction efficiency of copper in a mock solution.

4.1.1 Investigation of the precipitate

The precipitate formed during the extraction of copper is unexpected and was not reported in the literature, even for extractions using the same HDES.[26] MS and FTIR were used to investigate and characterize the structure of the precipitate. The lidocaine : $C_{12}A$ (1:1) HDES extraction sample was chosen to be used in this investigation as it form a similar precipitate to the others. Mass spectra were obtained of the precipitate. Figure 14 shows the mass spectrum of the precipitate formed after extraction and being filtered and washed by ethyl acetate. Peaks on the mass spectrum that were identified are at 186.22 m/z, 235.17 m/z, 353.18 m/z, 441.30 m/z, 637.46 m/z. Peaks at 123.05 m/z and 149.01 m/z could not be easily assigned to any known components. In Figure 14, 186.22 m/z and 235.17 m/z could be assigned to lidocaine and the HDES gives rise to the peaks at 441.30 m/z. The peaks at 353.18 m/z and 637.46 m/z are indicative of the formation of Cl-Cu-C_{12}A complex, corresponding to the fragment of the complex and the complex, respectively. Figure 15 shows the zoom-in spectrum around the peak at 637 m/z. Two adduct ions were found to be likely to match the peak at 637.46 m/z, and 659.47 m/z which are, 2M+acetonitrile+H, and 2M+acetonitrile+Na respectively (M = Cl-Cu-C_{12}A complex). Also, these two peaks show the characteristic isotope pattern of Cu (^{63}Cu and ^{65}Cu) respectively. The peak at 621.45 m/z has yet to be identified. Overall, the solid contains the HDES and appears to contain Cu; however, the specific MS identity could not be conclusively determined to confirm the formation of the Cl-Cu-C_{12}A complex.

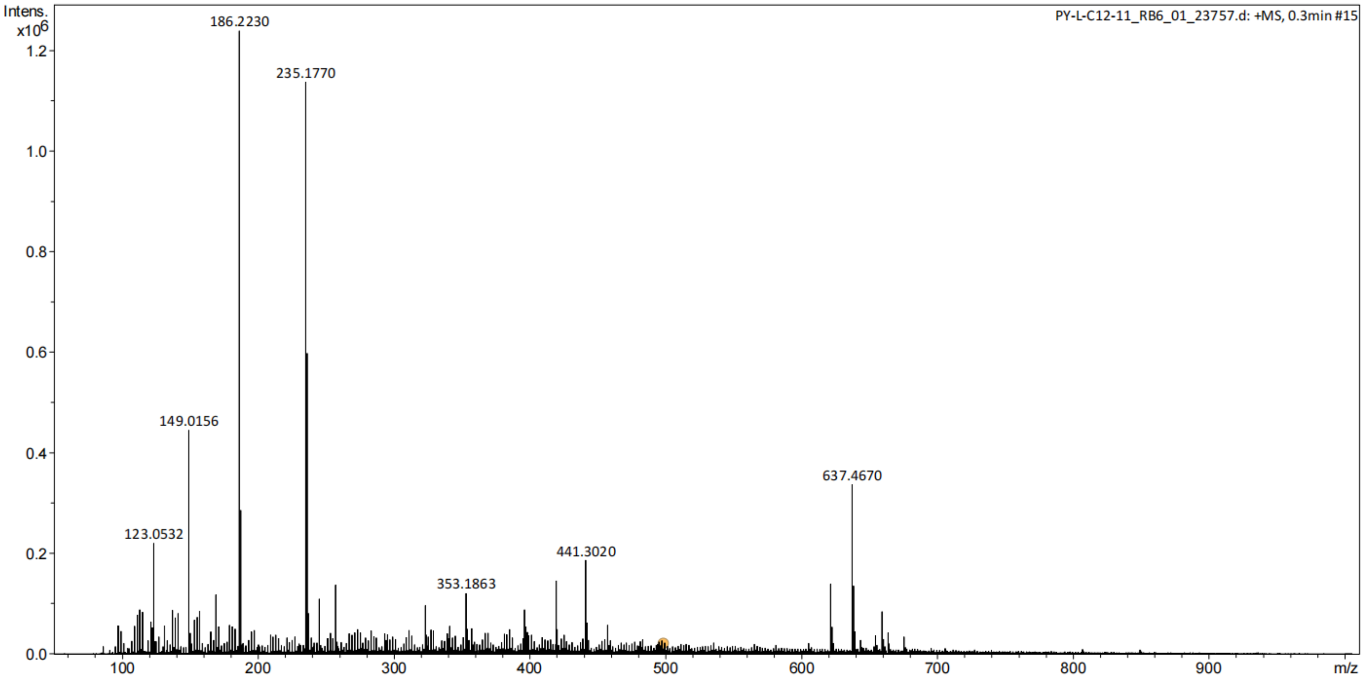


Figure 14. Mass spectrum of precipitate obtained from the extraction of copper using the lidocaine : C_{12}A HDES.

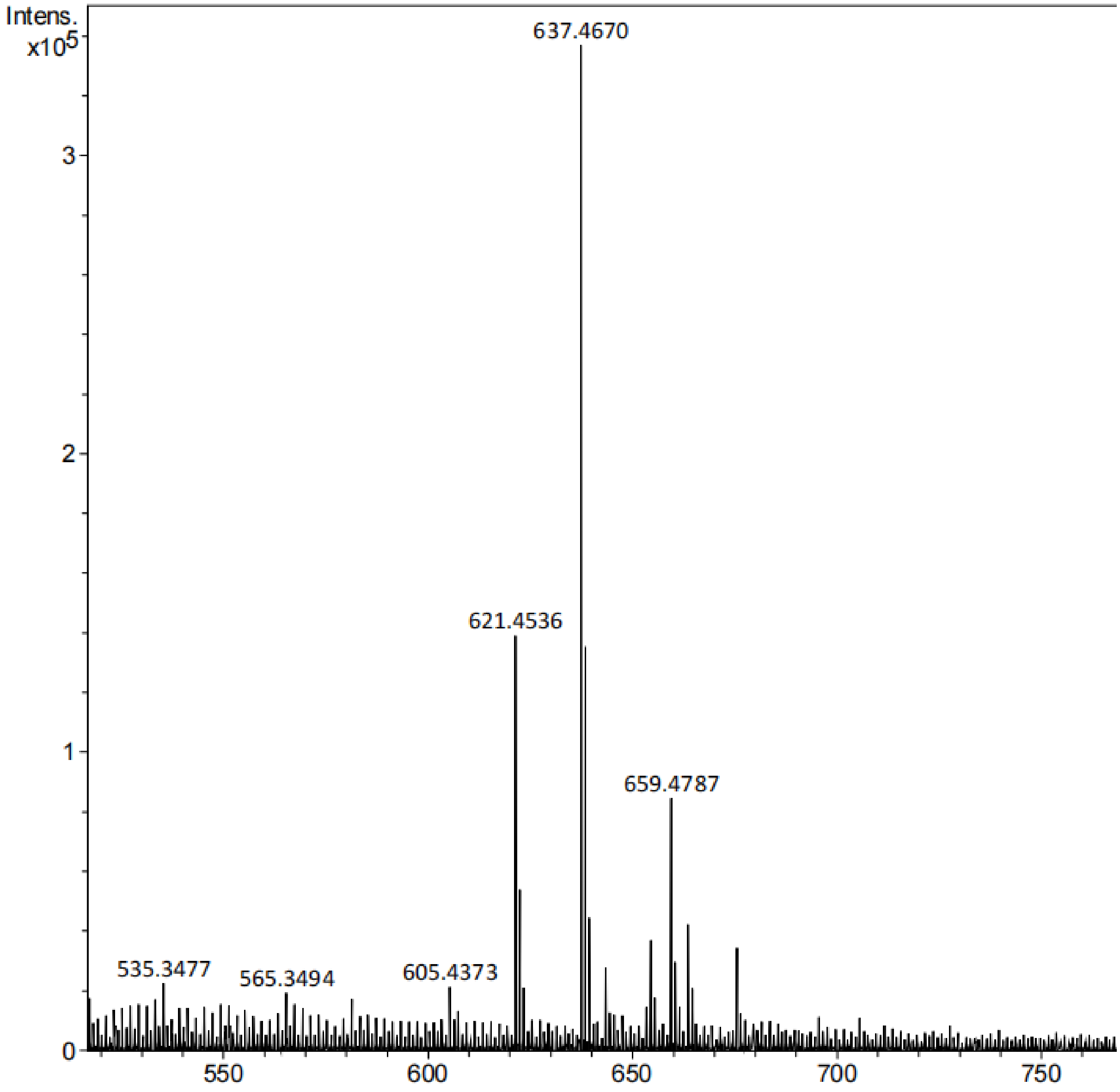


Figure 15. Zoom-in of the precipitate mass spectrum from 500-800 m/z.

FT-IR is also used to characterize the structure of the precipitate. Figure 16 shows the FT-IR spectra of the individual components of the lidocaine : $C_{12}A$ (1:1) HDES and the HDES itself and Figure 17 is the FT-IR spectrum comparing the precipitate and the lidocaine : $C_{12}A$ (1:1) HDES. The assignment of the peaks present in $C_{12}A$ and lidocaine is based on the literature.[70–72] From Figure 15, the NH stretching peak at around 3250 cm^{-1} of the lidocaine is reduced in intensity and has shifted in position compared to the HDES. Additionally, the OH bend peaks of $C_{12}A$ at around 930 cm^{-1} and 1420 cm^{-1} compared to the HDES has also been reduced in intensity which is indicative of ionization or strong H-bonding interactions. From Figure 17, the overall spectra of the precipitate have been shifted to lower wavenumber, this may be caused by the increase in the mass of a compound, lengthens the bond resulting in a shift to lower wave number. Cu-N stretches have characteristic weak bands at 456 cm^{-1} and[73] Cu-O bonds have been reported at wavenumbers below 400 cm^{-1}.[74–76] Peres et al. has proposed two absorption bands at 1445 cm^{-1} and 1586 cm^{-1} , which correspond to the interaction between copper ions with symmetric and asymmetric carboxylate respectively, but did not observed in figure 16.[77] As the range of wavenumbers obtained was from 400 – 4000 cm^{-1}, the possible formation peak of Cu-O bonds will not be observed, and Cu-N bonds have not shown a pronounced stretching peak in 456 cm^{-1} to indicate the existence of Cu-N bonds formation. Overall, MS suggested a possible structure of the precipitate formed during copper extraction, leading to a possible structure that the $C_{12}A$ is being ionized in the eutectic mixture and could bonds to the Cu-Cl to form copper complex, but with FTIR did not observe a clear peak correspond to the formation of Cu-carboxylate, indicates that further determination on the structure of the precipitation is required.

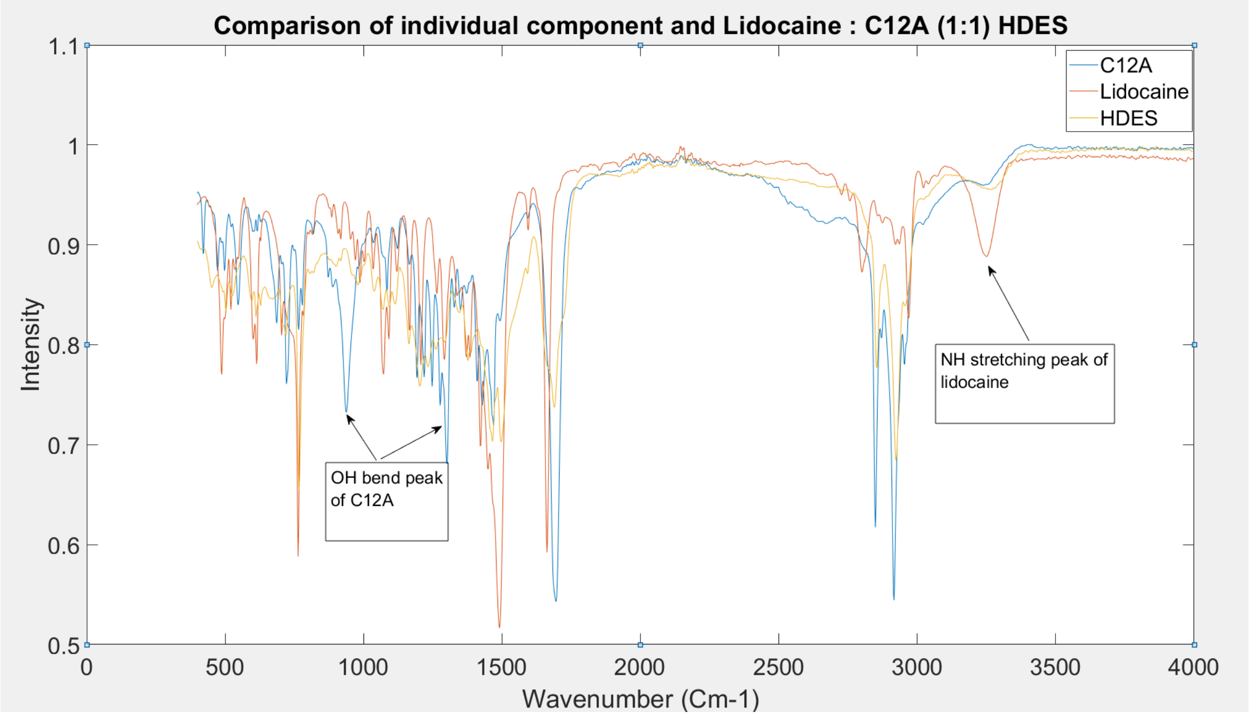


Figure 16. Comparison of C12A, lidocaine and lidocaine : C12A (1:1) HDES.

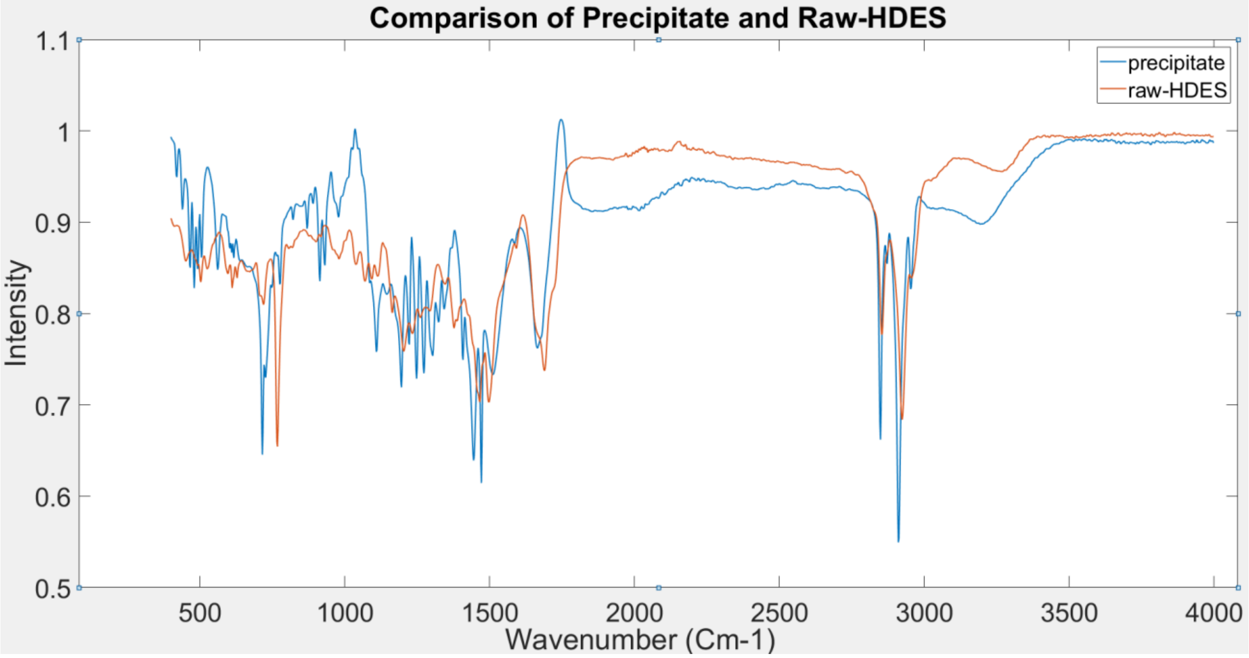


Figure 17. FT-IR spectrum of precipitate and the HDES.

4.2 Metal extraction on the mixed metal solution

4.2.1 Optimization of HDES selection

The initial screening of copper extraction for all HDESs in the copper sulfate stock solution was reported in section 4.1. These results indicated that lidocaine based HDESs have the greatest copper extraction efficiency among these HDESs, although can lead to the formation of copper-containing precipitates due to complexation of the acid and lidocaine. To investigate the potential to selectively isolate copper from realistic mixed metal e-waste lixiviant solution, Mint Innovation company has provided a commercial post-treatment of metal leaching solutions that contained varies of metal such as Al^{3+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} Sn^{2+}, and Pb^{2+} in a sulfuric acid solution with pH = 0. In the composition of the e-waste stream containing ~5000 ppm of Cu^{2+} and Fe^{2+}, 4000 ppm of Sn^{2+}, ~2000 ppm of Al^{3+}, Zn^{2+}, ~1400 ppm of H^{+}, ~500 ppm of Ni^{2+}, and 50 ppm of Pb^{2+} dissolved in the H_2SO_4.

Table 6. The chosen HDESs in copper extraction of mixed metal solution.

HBA	HBD	Molar Ratios
Menthol	Dodecanoic acid	3:1
Thymol	Dodecanoic acid	1:2.5
TOAB	Dodecanoic acid	1:2
Lidocaine	Decanoic acid	1:2
	Dodecanoic acid	1:2
	Oleic acid	1:1
	Decanoic acid	1:1
	Dodecanoic acid	1:1
	Thymol	1:2
	Octanoic acid	1:2
	Menthol	1:1
$N_{8881}Cl$	Dodecanol	1:2
	Decanoic acid	2:1

Table 6 shows the HDESs used in copper extraction of the mixed metal solution. Table 6 was chosen based on the results of the original copper sulphate extraction. Given the results of the copper extraction from the copper sulfate solution, lidocaine based HDESs were taken to further investigate in the mixed metal solution system. Although HDESs based another types of HBAs resulted in low extraction efficiency, they were chosen to perform copper extraction from the mixed metal solution in order to give insight of the effect of different HDESs on the selectivity as well as capacity of the metal extraction. A smaller range of HBDs were explored compared to the original copper screening, with a focus on the more hydrophobic dodecanoic acid HBD rather than shorter chained acids or alcohol.

4.2.2 Screening of HDESs in mixed metal solution

The initial extraction conditions for the mixed metal solution extraction was the same as those used for the stock solution; specifically, 2 mL of HDES and 2 mL of mixed metal solution stirred for 2 h at room temperature. The organic phase and aqueous phase are separated and centrifuged after extraction for preparation of MP-AES. Due to the number of different metals involved, UV-Vis was not used, and only MP-AES analysis was performed. Figure 18 shows the concentration of copper found in the organic phase after extraction by each HDESs. From Figure 18, it is evident that the lidocaine : C_8A HDES extracted the most amount of copper. Although the result of lidocaine : C_8A obtained large error bar, the lower quarter of the error bar is still higher than the higher quarter of $N_{8881}Cl$: $C_{10}A$ error bar. Lidocaine : Oleic acid and $N_{8881}Cl$: $C_{10}A$ both obtained similar results within experimental error which is really unexpected for $N_{8881}Cl$: $C_{10}A$ given the initial copper solution results. The copper extraction efficiency of TOAB : $C_{12}A$ and $N_{8881}Cl$: $C_{12}OH$ have obtained similar concentration of copper into the range of lidocaine based HDESs that has copper from 250-920 ppm, demonstrating that these HDESs have comparable copper concentration extracted from the organic phase. Thymol and menthol based HDES results show they both are incapable of extracting copper, with the exception of lidocaine: thymol which leads to a small but measurable copper concentration. The HDES lidocaine : C_8A obtained the highest copper concentration in organic phase. However, the copper extraction efficiency in the organic phase for lidocaine based HDESs did not show a trend where a larger carbon chain length of carboxylic acid acting as HBD, results in higher extraction efficiency.

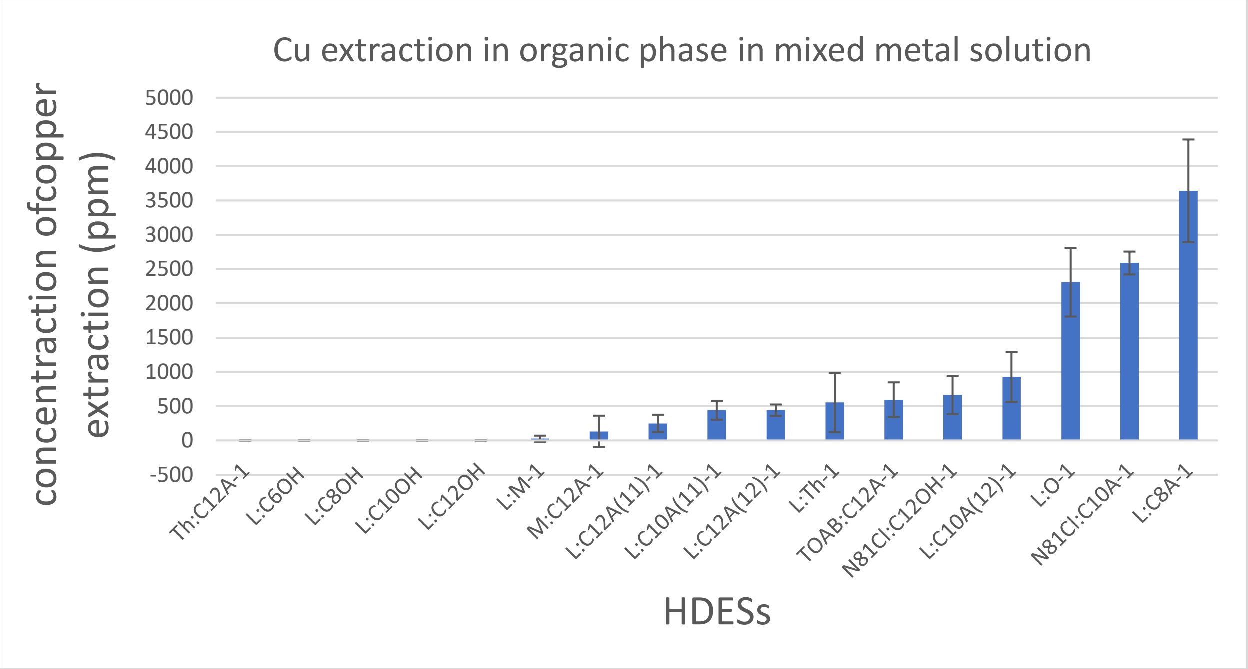


Figure 18. Copper concentration in the organic phase after HDES extraction of the mixed metal solution, as determined by MP-AES.

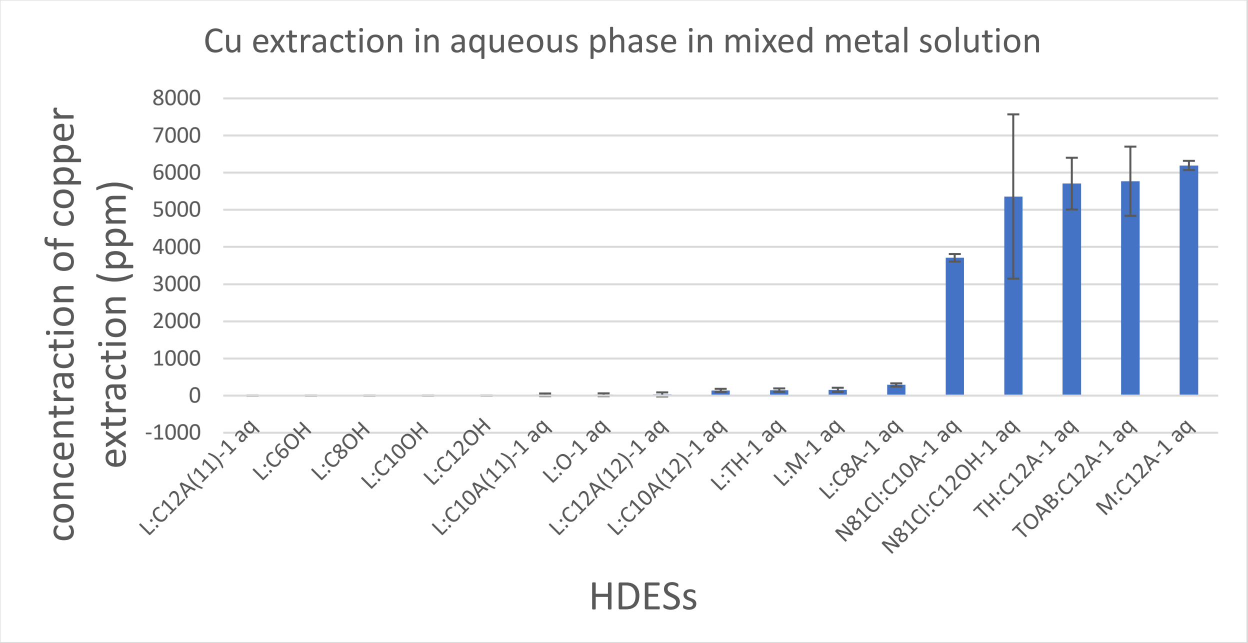


Figure 19. Copper extraction in aqueous phase in mixed metal solution.

Figure 19 shows the amount of copper observed in the aqueous phase after the extraction. Lidocaine based HDESs resulted in nearly complete copper extraction from the aqueous phase after 2 h. The aqueous phase of $N_{8881}Cl$: C10A has approximately 50% of copper removed. The copper concentration of the aqueous phase following extraction by terpene based HDESs and tetra-octylammonium bromide based HDES after extraction remained constant. $N_{8881}Cl$: $C_{12}OH$ has similar result with terpene based HDES but has larger error which may be due to the phases emulsification. As previously mentioned, the concentration of copper in both phase should add up to the total copper concentration given the volumes used are the same. Some of the lidocaine based HDES such as lidocaine : $C_{12}A$ and lidocaine : $C_{10}A$ contain unexpectedly low concentration of copper in both organic and aqueous phase. As was observed for the copper stock solution, these samples formed a precipitate which could account for the missing copper. This can be clearly seen in Figure 20 which shows the samples for lidocaine : $C_{10}A$ and lidocaine : $C_{12}A$ with precipitate clearly observed through the vial. The precipitate contains multiple colours indicating there is more than one type of metal being precipitated. The precipitate appears to act as a sorbent as the volume of the organic phase is significantly decreased, and the aqueous phase is hardly observed after precipitation has occurred. Hence, to analysis the copper concentration remaining in the aqueous phase, approximately 1 ml of water is added and rinsed through the precipitation then sampled to underwent MP-AES. Comparing the precipitation of lidocaine based HDESs in copper extraction in mock solution and mixed metal solution, the precipitation formed after extraction is potentially increased in mixed metal solution system based on visual observation. This may be due to the higher overall metal concentration in the mixed metal solution, reacting with the HDESs and forming an insoluble metal-containing solid. The structure of the precipitate forming in mixed metal solution was not further characterized due to the limited time on the investigation and the likely complex mixture formed is lidocaine : dodecanoic acid complex given the findings of the copper system.

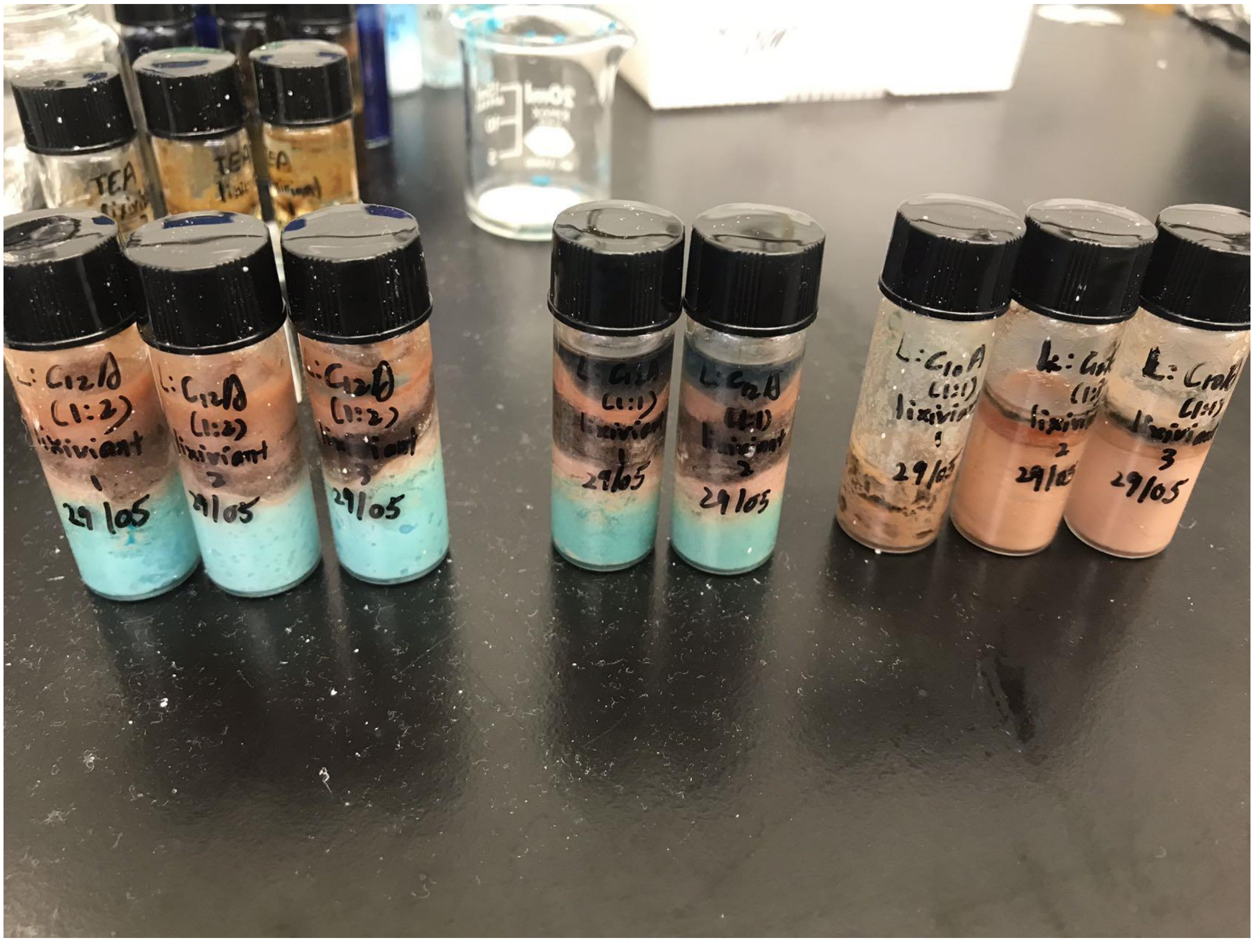


Figure 20. Observation of precipitate from lidocaine : C$_{12}$A (1:2) on the left, lidocaine : C$_{12}$A (1:1) in the middle and lidocaine : C$_{10}$A (1:1) on the right.

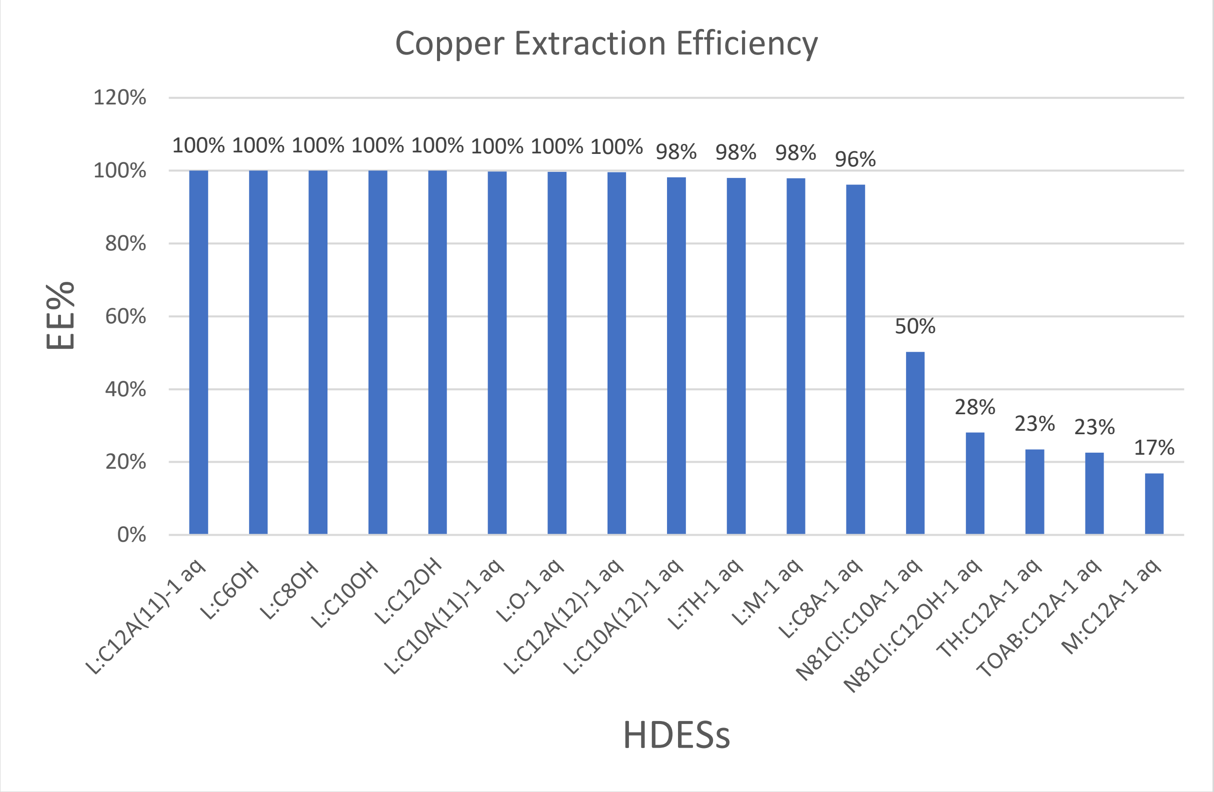


Figure 21. Copper extraction efficiency based on aqueous phase of the HDESs used for mixed metal extraction.

The calculation of the copper extraction efficiency in Figure 21 is based on the data presented in Figure 19, that is the copper concentration remaining in the aqueous phase. Due to the unwanted precipitation forming during the copper extraction, the copper extraction efficiency only demonstrates the copper removed from the aqueous phase but not necessarily the copper extracted into the organic phase. The formation of the precipitation revealed that the copper is not conveniently being separated out from other metals, limiting the further investigation on recycling the copper. To examine the recycling of copper from HDESs, it is preferable to avoid any precipitation forming during or after the copper extraction due to the possible issue may occur such as loss of metal and process complexity. From Figure 21, $N_{8881}Cl$: $C_{10}A$ HDES has a copper extraction efficiency of 50%. More importantly, the $N_{8881}Cl$: $C_{10}A$ HDES extraction sample did not form any precipitation after the extraction. $N_{8881}Cl$: $C_{12}OH$ HDES extraction sample although have 28% of copper extraction efficiency, slightly higher than terpene based and tetra-octyl ammonium bromide based HDESs, did lead to a visible amount of precipitation shown in Figure 22. Terpene based and tetra-octylammonium bromide based HDES did not form a precipitate but have lower copper extraction efficiency. Overall, in order to efficiently investigate further in copper recycling and re-extraction, $N_{8881}Cl$: $C_{10}A$ HDES is chosen to be further explored.

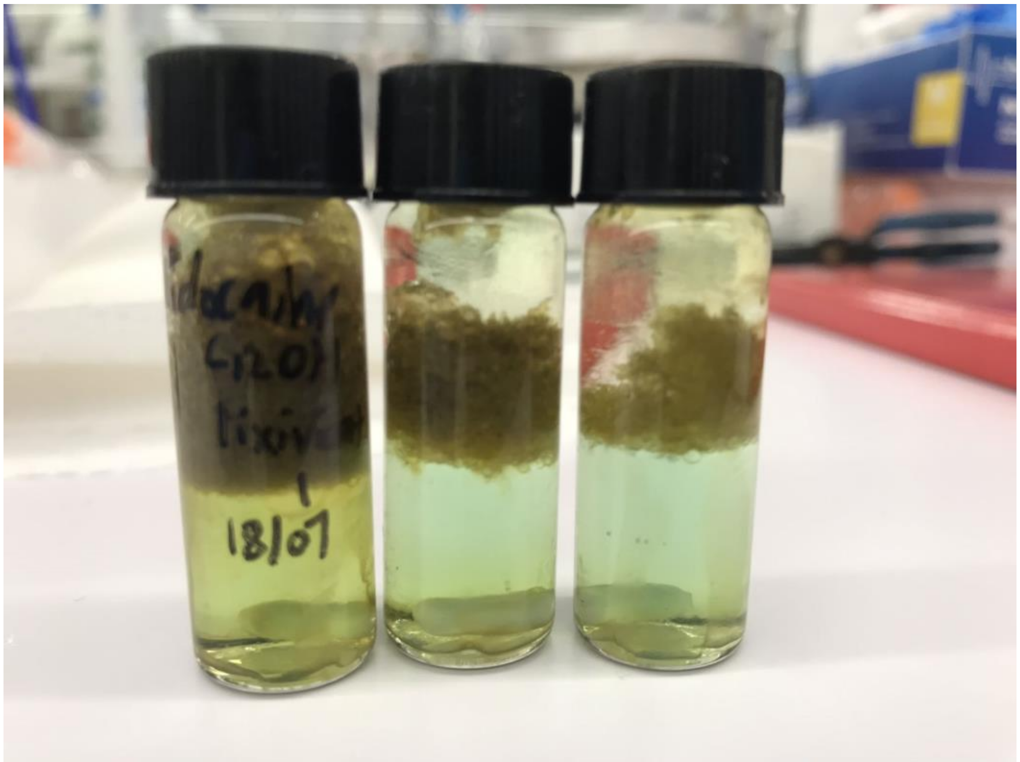


Figure 22. Precipitation formed from copper extraction in lidocaine : $C_{12}OH$.

4.3 $N_{81}Cl$: $C_{10}A$ HDES optimisation study

Comparing the copper extraction efficiency of $N_{81}Cl$: $C_{10}A$ between the copper only stock solution and the mixed metal solution, indicates very different results. Almost no copper extraction is observed in the copper stock solution but this suddenly increases to approximately 50 % of copper extraction efficiency in the mixed metal solution. The pronounced extraction efficiency changes on the mixed metal solution system may be contributed by the addition of other types of metal, enhanced the solubility of copper being extracted into the organic phase.. The exploration of $N_{81}Cl$: $C_{10}A$ HDES in extraction of copper is divided into two parts. The first part will involve the study of the effect on different molar ratio of HBA/HBD on copper extraction efficiency. The second part will involve an optimisation of extraction conditions and its effect on the copper extraction efficiency.

4.3.1 Exploration on the effect of $N_{81}Cl$: $C_{10}A$ Ratio

The impact of the HBA/HBD ratio of $N_{8881}Cl$: $C_{10}A$ HDES was studied to give insight into how the individual components of the HDES affects the extraction efficiency. This includes the use of the individual components of the $N_{8881}Cl$: $C_{10}A$ HDES themselves, although octanoic acid (C_8A) was used instead of $C_{10}A$ as C_8A is a room temperature liquid. It was assumed that the extraction capacity of C_8A is similar result to $C_{10}A$. The reaction condition for this experiment is used in the same conditions as the initial screening.

The copper extraction efficiency in section 4.3 has been calculated differently. Since the precipitate is no longer forming in these HDES extraction samples, the copper extraction efficiency can be calculated based on the concentration of copper in organic phase divided by the total amount of copper in an individual sample.

Figure 23 shows the concentration of copper in the organic layer of the HDES against the ratio of the two components. From Figure 23, it is apparent that the samples containing only the C_8A or $N_{8881}Cl$ do not effectively extract copper, with C_8A not having any copper in the organic phase and $N_{8881}Cl$ has copper at 0.1 % ± 0.1 % ppm. These results suggest a synergistic relationship between the HDES component. This is suggesting that potentially the $C_{10}A$ in the HDES is facilitating the copper being solubilized into the organic phase and the chloride anion in the $N_{8881}Cl$ will undergo ion exchange with copper to form CuCl. Figure 23 also shows the copper extraction efficiency is decreasing as the ratio of $C_{10}A$ involved in the HDES is increasing, so long as at least some $C_{10}A$ is present. The $N_{8881}Cl$: $C_{10}A$ HDES with ratio in 1:2 led to the extraction of less than 200 ppm copper, The poor reproducibility of this value may be due to difficulty separating the aqueous and organic phases. Overall, the effect of the ratio of HBA:HBD indicates that each component plays an independent but necessary role and that while the acid is required for copper extraction, increasing its concentration does not lead to any further increase in extraction yield. A suggestion for this trend is the importance of coordination of the Cu by decanoate to enable its phase transfer, with additional Cl acting as a supporting ligand. Increasing decanoic acid concentration potentially increases the pKa of the acid due to the less polar and ionic solvent environment reducing both the solubility of the metal complex but also the efficacy of the decanoic acid as a ligand. Also, the more decanoic acid that is present the less polar the organic phase becomes which could explain the reason of lower ratios did not give good extraction efficiencies.

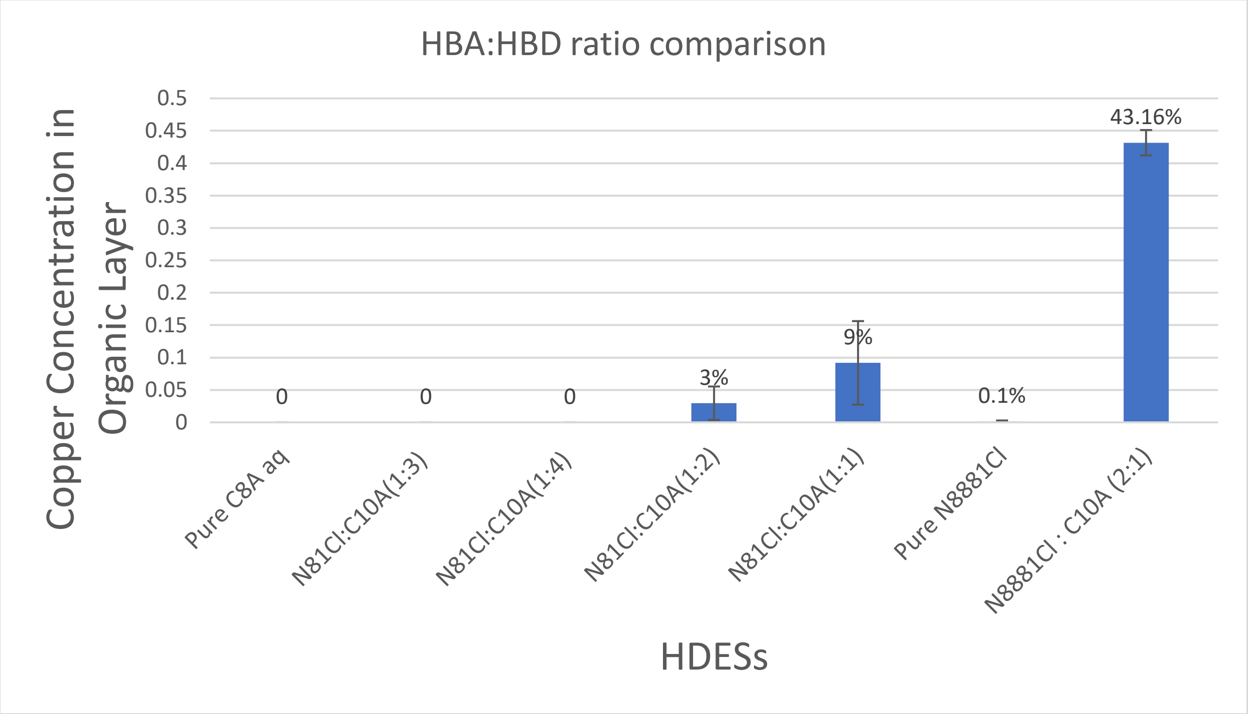


Figure 23. Copper extraction efficiency with different HBD molar ratio of $N_{8881}Cl$: $C_{10}A$. Pure C_8A was used instead of $C_{10}A$ as it was a room temperature liquid.

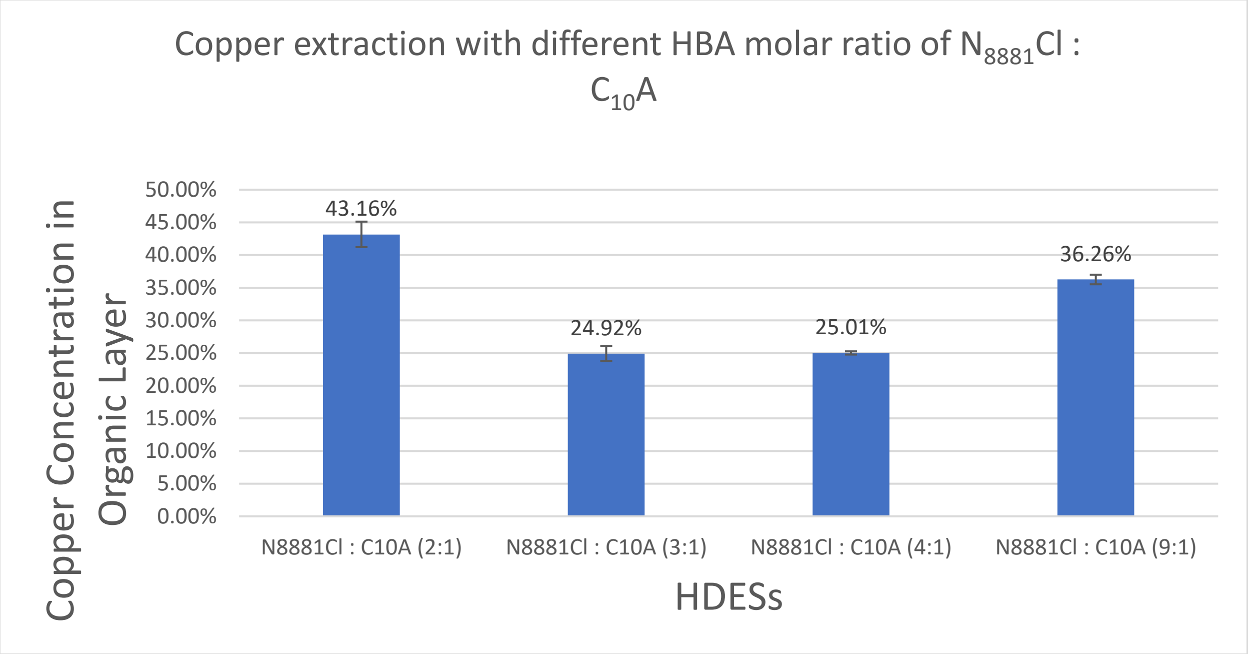


Figure 24. Copper extraction efficiency with HBA:HBD molar ratio of $N_{8881}Cl$: $C_{10}A$ from 2:1 to 9:1.

After exploring the effect of molar ratio of HBD in $N_{8881}Cl$: $C_{10}A$ HDES, the influence on the molar ratio of HBA in $N_{8881}Cl$: $C_{10}A$ HDES was also investigated to provide a wider insight into how the molar ratio of HDES can influence the metal extraction efficiency. Figure 24 shows the copper extraction efficiency with increasing the molar ratio of HBA in $N_{8881}Cl$: $C_{10}A$ HDES. With increasing the molar ratio of HBA which is the $N_{8881}Cl$, the copper extraction efficiency did not increase in a monotonic way. The sample of $N_{8881}Cl$ came from a different supplier, so to ensure consistency with other experiments in the series, the 2:1 experiment was performed again.

$N_{8881}Cl$: $C_{10}A$ (2:1) has obtained copper extraction efficiency around 43%, higher than other samples in different molar ratios. The relatively small error bars observed for all four samples indicates that these results are reliable. From molar ratios in 3:1 to 9:1, it shows an increasing trend in copper extraction efficiency although the trend is reversed for 2:1. An explanation of such trend may arise from consideration of the solvent eutectic point and Cl^- anions availability. A significant drop of copper extraction efficiency in $N_{8881}Cl$: $C_{10}A$ HDES molar ratio from 2:1 to 3:1

may be caused by the excess of the Cl^- anions bonding to the copper to form the water soluble $CuCl_2$ which remains in the aqueous phase, whereas the molar ratio in 2:1 is reaching the eutectic point and thus, minimum concentration of the free Cl^- anions is contain in the organic phase. Apart from the Cl^-, decanoic acid plays a role in terms of the result. One article has elaborated that the formation of carboxylate ions is more stabilized in an ionic environment compared to their pure carboxylic acid form.[78] The finding of the literature suggests that as the concentration of Cl^- anions increases, the concentration of decanoate ion may potentially increase with reducing the concentration of decanoic acid. Since copper extraction requires the bonding to decanoate ions and Cl^-, the copper extraction efficiency could be increased even with increasing the molar ratio of HBA in $N_{8881}Cl$: $C_{10}A$ (2:1) HDES.

4.3.2 Optimization of extraction conditions

To investigate the relationship between the extraction conditions and the copper extraction efficiency; the effect of the temperature, aqueous phase : organic phase volume ratio, and extraction time were explored. Design of experiment (DoE) software was used to generate an optimisation reaction condition table to minimize the number of independent experiments required. Each of the factors was explored at 3 levels. Table 7 shows the DoE optimization extraction conditions and the corresponding copper extraction efficiency. In the three factors explored, the extraction time varies from 30 mins to 120 mins, heating temperature varies from 20 °C to 60 °C, and the volume of mixed metal solution : HDESs ratio varies from 1:1 to 10 : 1. Each arrangement of the experiment standard (std) is generated under full factorial Box-Behnken design and then advise a predicted optimization extraction condition that gives the highest copper extraction efficiency.

Table 7. Optimization extraction conditions and outcome of 2:1 $N_{8881}Cl$: $C_{10}A$ HDES extraction experiments.

Std	Run	Factor 1 A: time Min	Factor 2 B:Temperature	Factor 3 C:Lixiviant:HDES ratio	EE%
1	6	30	20	5.5	2.40%
2	10	120	20	5.5	4.06%
3	11	30	60	5.5	6.86%
4	15	120	60	5.5	4.58%
5	7	30	40	1	14.05%
6	14	120	40	1	32.96%
7	13	30	40	10	1.29%
8	9	120	40	10	3.74%
9	3	75	20	1	24.54%
10	1	75	60	1	41.05%
11	5	75	20	10	1.42%
12	8	75	60	10	2.65%

13	2	75	40	5.5	5.68%
14	4	75	40	5.5	5.82%
15	12	75	40	5.5	6.65%

From Table 7, the result of copper extraction efficiency for each individual experiment are presented. Std 10 gives the highest copper extraction efficiency of 41.05 %, followed by the second highest copper extraction efficiency 32.96% in std 6. Std 9 and Std 5 also obtained relatively high copper extraction efficiency, with 24.54 % and 14.05% respectively. The rest of the std samples obtained comparably low extraction efficiency from range of 1.29 % to 6.86 %. Comparing std 1 and std 2 that has copper extraction efficiency of 2.40 % and 4.06 % respectively, which have the factor 2 and 3 remained unchanged, the increased extraction time (factor 1) from 30 minutes to 120 minutes did not give a significant enhancement on the copper extraction efficiency. Also, std 3, 4 and std 7, 8 have the same temperature and volume ratio with different extraction time gave similar outcome which all have low copper extraction efficiency. This situation further suggests that the extraction time is less important. When comparing std 1, 3, std 2, 4, and std 11, 12, they have both the extraction time and volume ratio the same, with increased temperature from 20 °C to 60 °C also did not give a pronounced enhancement on the copper extraction efficiency, suggested that the temperature is less important. Comparing std 6, 8 and std 5, 7, with they both have the same on the extraction time and the temperature, the difference on the volume ratio gave significant increased on the copper extraction efficiency from 3.74 % to 32.96 %, and 1.29 % to 14.05 %, suggested that increasing the volume of HDES in extraction will improve the copper extraction efficiency. However, the increased on the extraction time in std 5, 6 and increased temperature in std 9, 10 all gave increased on the copper extraction efficiency. This may mislead the conclusion that factor A and B are important parameters in copper extraction, because all four std sample have volume ratio at 1:1. Std 13-15 have similar extraction efficiency from 5.68 % to 6.65% with all factors on the same value representing a control and reliable optimization design.

Table 8. Anova analysis for Quadratic model.

Source	Sum of squares	df	Mean square	*F* value	*P*-value prob ☐ *F*	Remarks
Model	0.75	9	0.083	50.37	0.0002	significant
A-time	0.065	1	0.065	39.52	0.0015	significant
B-Temerature	0.054	1	0.054	32.88	0.0023	significant
C-Lixiviant:DES	0.51	1	0.51	311.21	< 0.0001	significant
AB	9.262E-003	1	9.262E-003	5.63	0.0637	Not significant
AC	0.043	1	0.043	26.10	0.0037	significant
BC	0.024	1	0.024	14.85	0.0120	significant
A^2	5.756E-003	1	5.756E-003	3.50	0.1202	Not significant
B^2	2.704E-003	1	2.704E-003	1.64	0.2559	Not significant
C^2	0.033	1	0.033	20.11	0.0065	Not significant
Residual	8.219E-003	5	1.644E-003			
Lack of Fit	8.219E-003	3	2.740E-003			
Pure Error	0.000	2	0.000			

The optimization of the extraction conditions is determined using a quadratic model generated from the DoE software. Due to the ratio of maximum to minimum of the extraction efficiency being greater than 10 (31.82), it was suggested that an inverse transformation model was used to reduce the impact of the few large values on the fitted model. Following the inverse transformation, a model was created with the model statistic depicted in Table 8. The model F-value of 50.37 suggests that the model is significant, and the p-value, which less than 0.05 implies the model is significant. From table 8, the term A (time), B (temperature), C (lixiviant :HDES), BC, and AC are marked as significant terms, suggesting that the analysis on table 8 implies that the extraction efficiency relies on the significant term.

Table 9. Experimental and predicted results at optimal condition.

A: time (minutes)	B: Temperature (°C)	C: Mixed metal solution : HDESs ratio	Response: 1/Extraction efficiency (%)		
			Predicted	Measured	Error (%)
97.96	34.98	1.15	0.022		
69.67	56.50	1.58	0.020		
36.59	41.84	1.04	0.022	0.043	6

The calculated optimum reaction condition on Table 9 are based on the DoE model. The predicted extraction efficiency is based on a minimisation of the predicted value due to the inverse transformation of 1/extraction efficiency. Comparing these three methods, the last one is preferable as it has higher predicted extraction efficiency and less extraction time. The copper extraction efficiency of the last method is 23.1 % which is 0.043 in inverse space. The 6 % error from the result of predicted copper extraction efficiency represents the data is moderately reliable. However, the measured copper extraction efficiency of 23.1 % is significantly lower than the predicted copper extraction efficiency which is 45 % calculated by 0.022 in inverse space. The approximately two times lower than the predicted copper extraction efficiency indicates that the model is fairly unreliable and may arise from the inverse transformation which may in fact understate the optimised values. Also, the variation of the copper extraction efficiency may contribute to the fact that there is overfitting of the model as there were some insignificant parameters.

4.4 Electrodeposition of copper

After demonstrating that the HDES N_{8881}Cl : C_{10}A (2:1) is viable for the extraction of copper, it was of interest to explore the isolation of the extracted copper. The electrodeposition of copper in HDES N_{8881}Cl : C_{10}A (2:1) is has not been previous explored in the literature but has been explored in choline chloride based DES.[79] Prior to the electrodeposition, a 12 mL scale of copper extraction was performed in order to collect sufficient organic phase to conduct the electrodeposition. A three electrode system was used, in which two platinum plates acted as working and counter electrodes and silver wire acted as a reference electrode, in a setup that has been used for related electrodeposition processes.[79] The electrodeposition was conducted in a potential window from 1.2 - -2 V at a scan rate of 1 mV/s. Figure 25 is the voltammogram of the process. In Figure 25, two arrow depicted the two possible reduction peaks from Cu (II) to Cu(I) and Cu(I) to Cu at approximately 0.4 V and -0.4 V respectively. This assignment is based on previous reports of copper electrodeposition in DESs.[79] The difference of reduction peak may vary from different control parameters such as heating time, scan rate, and types of DES, therefore, the copper reduction peak in figure 25 may be different compared to the literature reported.[79]

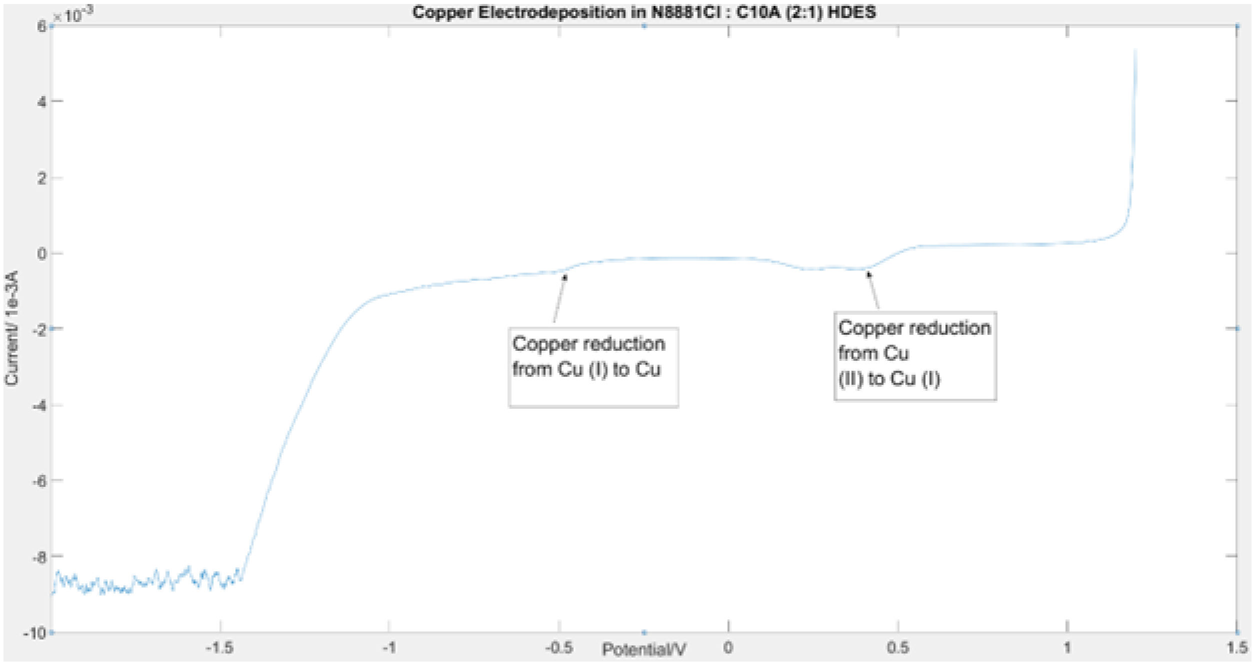


Figure 25. Voltammogram of copper electrodeposition from N8881Cl : C10A (2:1) HDES with three electrode system.

The color of the platinum went black after the electrodeposition process. The platinum plate was immersed in a dilute nitric acid for around 2 h to remove any metal deposited on the surface. Figure 25 shows a comparison of the platinum plate before and after washing. It is clear there is decomposition of the solvent from both the CV and the colour of the electrode. This may mask the presence of any electrodeposited metal and so the platinum was washed. To examine the accuracy of the conclusion made from the observations, the concentration of the metal in the HDESI was tested before and after electrodeposition. The results are shown in Table 9.

Table 10 shows there is roughly 360 ppm of Cu being electrodeposited. Iron has around 50 ppm variation before and after the electrodeposition and aluminum has nearly all been removed. The dark color on the platinum plate may be contributed by the degradation of the HDES as Figure 25 shows a strong reduction occurring below -1.5 V, thus, avoiding the solvent degradation is potentially critical to getting decent electrodeposition.

From observations in figure 26, the platinum plate on the right is clear which suggests that the removal of any metal deposited on it. Thus, the metal composition of the used diluted nitric solution was explored using MP-AES and the result is shown in Table 11. Trace amounts of aluminium are being removed. The amount of copper and iron being removed are close to each other. This may be caused by the similar potential window of Al and Fe. However, the amount of copper being electrodeposited does not match the concentration of copper being removed from the platinum plate as well as the Cu recovered which will mention in next section. The difference in metal concentration suggests that the removal of copper from the platinum plate is not complete and could potentially be affected by the absorption of the Cu onto other surfaces in the electrodeposition apparatus. Due to limited time, the copper electrodeposition experiment could not be reproduced and hence, optimisation of the electrodeposition conditions and further study of the electrochemistry in $N_{8881}Cl$: $C_{10}A$ (2:1) HDES was not able to be achieved.

Figure 26. Comparison of platinum plate before and after washing.

Table 10. Comparison of metal concentration in the HDES before and after the electrodeposition process.

	Al	Cu	Fe
Before electrodeposition (ppm)	62.26	2486.25	1209.6
After electrodeposition (ppm)	0.63	2127.99	1162.69

Table 11. Composition of metals in used diluted nitric solution.

	Al	Cu	Fe
Concentration (ppm)	8.23	23.09	18.27

4.4.1 Recycling of electrodeposited HDES

The extraction of copper by the HDES $N_{8881}Cl$: $C_{10}A$ (2:1) after electrodeposition was explored to investigate the recyclability of the HDES. The extraction conditions of the 12 mL scale copper extraction followed the last optimum condition in Table 8 and the result is shown in Table 12. The initial 12 mL scale copper extraction efficiency has obtained 30.7 %, slightly higher than the copper re-extraction efficiency after electrodeposition which has 25.6 % . As the difference is 5% without replicates, the variability of the result is unknown. Given that most of the copper still remains in the HDES, it suggests that the HDES is simply saturated with copper rather than any factor of electrodeposition. The other potential effect is that the decomposition observed due to the electrodeposition might play a role in the reduction of extraction efficiency, but the extent of the decomposition is too small to be that important.

Table 12. Copper extraction efficiency of HDES $N_{8881}Cl$: C10A (2:1) before and after electrodeposition.

	Copper extraction efficiency (%)
Initial HDES extraction	30.7%
Recycled HDES extraction	25.6%

5. Conclusion

The aim of this project was to explore the use of HDESs for the extraction of copper from an aqueous e-waste lixiviant stream. This was modelled using a mock copper sulfate solution prior to the use of the e-waste stream. HDESs prepared from quaternary ammonium based and terpene based as HBA and carboxylic acid, terpene, and alcohol as HBD were used to identify their efficacy for the separation of copper.

In the mock solution system, the lidocaine based HDESs displayed the greatest copper extraction efficiency compared to terpene based, tetra-octyl ammonium based, and methyl-trioctylammonium based HDESs. However, in many cases a precipitate was observed. The precipitate was explored using MS and FT-IR which indicated that the precipitate is likely a copper complex containing Cl^- from lidocaine and the dodecanoate as ligands.

In the mixed metal solution system, the lidocaine based HDESs still obtained the highest copper extraction efficiency compared to other types of HDESs. Terpene based and tetra-octylammonium bromide based HDESs has shown the viability of extracting copper even with extremely low copper extraction efficiency. The key finding in the selected HDESs screening in copper extraction in mixed metal solution is that the methyl-trioctyl ammonium chloride based HDESs, particularly $N_{8881}Cl$: $C_{10}A$ HDES, could successfully extract 50% of the copper without forming a precipitate, this was in contrast with the performance in the copper stock solution.

The effect of the molar ratio of components on the extraction efficiency of the $N_{8881}Cl$: $C_{10}A$ HDES was investigated. The molar ratio of the HBA:HBD of 2:1 was identified to be the optimal HBA:HBD molar ratio for the extraction of copper from the mixed metal solution. In the molar ratio of HBA:HBD investigation, the result has shown that a higher molar ratio of $N_{8881}Cl$ is more effective than higher molar ratio of $C_{10}A$ in copper extraction from a mixed metal solution and that neither component on its own is capable of extracting copper. The result of the optimization on the reaction condition showed that the solubility of copper is the limiting factor for its extraction.

On the copper electrodeposition, the electrodeposition was attempted and shows a relatively limited electrochemical window of the solvent but there was some evidence that Cu reduction took place. This needs to be optimized to identify the viability of Cu electrodeposition from this solution. In the exploration of recyclability of the $N_{8881}Cl$: $C_{10}A$ HDES, the results show that the $N_{8881}Cl$: $C_{10}A$ HDES is able to be recycled for copper extraction after electrodeposition with reduction in the copper extraction efficiency.

Overall, the HDESs system has gained a promising performance on metal extraction in both metal solution as well as in electrodeposition, also, the dependence on the ratio of components highlights the importance of understanding these interactions to tailor more selective extraction system. Further investigation of varies HDESs system and their mechanism in metal extraction will help approach on other extraction system study.

6.Future work

Based on the overall outcome of this research project, there are a few areas of the future work that can be explored:

- Synthesis and used of different types of HDESs system such as ether-based and alkylamine-based on exploration of metal extraction in mock solution system and mixed metal solution as it will provide more insight on whether other types of HDESs can extract copper or other metal.
- As the outcome of copper extraction efficiency in the mock solution and mixed metal solution cannot be explained comprehensively, a control experiment can be conducted involving the focus on the change in the pH and adding iron in the mock solution as the $N_{8881}Cl$: $C_{10}A$ HDESs on copper extraction only works for the mixed metal solution. This will provide inclusive understanding of the mechanism on metal extraction and will also explore whether the addition of metal will facilitate the copper extraction.
- Investigation of the unexpected precipitate formed during metal extraction in both mock solution and mixed metal solution to confirm the structure and mechanism for the complex metal formation.
- Investigation on varying the molar ratio of other types of HDESs on metal extraction can further understand whether the solvent eutectic point and Cl^- availability have significant effect on the metal extraction efficiency.
- The measurement of recyclability of all the HDESs that has extracted copper to examine the viability of the HDESs for reuse in metal extraction.
- Exploration on the metal selectivity in different HDESs system by controlling temperature, extraction time, and volume ratio of aqueous : organic. This will provide an understanding of the significance of different factors during metal extraction.
- Optimization condition on copper electrodeposition such as longer electrodeposition time, different electrode, and understanding of the solvent potential window to achieve higher recovery of copper.

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