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A FUNDAMENTAL STUDY ON SOLUBILITY OF HEAVY METAL OXIDES IN AMMONIUM AND PHOSPHONIUM BASED DEEP EUTECTIC SOLVENTS

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Abstract

Water pollution has become increasingly prevalent in our daily lives and has caused a serious threat at a global level. Among the various pollutants that exist, heavy metal pollution has become an issue of great concern due to their high toxicity, greater bioaccumulation in human body and food chain, non-biodegradability nature, and carcinogenic effects to humans. This study aims to address the heavy metal ion contamination in wastewater by providing a low cost and efficient removal technique using DESs. In this investigation, the solubility of CuO and ZnO heavy metal oxide ions with concentration of 20g/L was studied in ammonium and phosphonium based DESs. The samples were left to stir at 250 rpm at 28, 45 and 65°C respectively for four hours in an incubator orbital shaker and the solubility of the heavy metal ions were analysed using Atomic Absorption Spectrometer (AAS) using serial dilution technique. Phosphonium based DES which contain Methyl Triphenyl Phosphonium Bromide (MTPB) showed higher solubility of CuO and ZnO ions. Based on the results obtained, DES 6 (MTPB: Glycerol) has the highest solubility of CuO, 0.197 mg/L at 65°C and the solubility of ZnO was found to be the highest in DES 7 (MTPB: Glycerol), 1.225 mg/L at 65°C. Higher solubility was observed in samples containing ZnO as they are more ionic compared to CuO.

Keywords: Heavy metals, Deep eutectic solvent, solubility, wastewater, removal.

Abbreviations

AAS	Atomic Absorption Spectrometer
ChCl	Choline Chloride
CuO	Copper (II) Oxide
DES	Deep Eutectic Solvent
DSC	Differential Scanning Calorimeter
HBD	Hydrogen Bond Donor
IL	Ionic Liquid
KFT	Karl Fischer Titration
MTPB	Methyl Triphenylphosphonium Bromide
RPM	Rotations per minute
ZnO	Zinc (II) Oxide

1. Introduction

Water covers almost 70% of the earth's surface and is an important resource to the people and environment. Today, water pollution has become increasingly prevalent in our daily lives and has caused a serious threat at a global level. Water pollution occurs when contaminants enters and dissolve in water bodies like oceans, rivers and lakes which result in the degradation of the water quality [1]. According to the Sick Water report by the United Nations Environmental Program (UNEP), up to 90 % of waste water in developing countries flow untreated into catchment areas and highly productive coastal zones, threatening the health food security and access to safe drinking and bathing water [2]. The Sick Water report also revealed that an estimated 245,000 kilometres squared of marine ecosystems are affected by hypoxia (Oxygen depletion caused by coastal eutrophication) and has brought a severe impact on fisheries and the livelihood of people. The number of people suffering from water related diseases have increased tremendously and around 2.2 million people die each year from diarrhoeal conditions in which 1.8 million of them are children under 5 years old [2].

Water pollution poses a serious challenge due to its impact on various types of economic activities [3]. Major pollutants can be classified into several categories such as anions and cations (nitrates, phosphate, sulphates, Ca^{+2}, Mg^{+2} and F^{-}), inorganic pollutants (acids, salts and toxic metals), pathogens (bacteria, viruses and protozoa) and water soluble radioactive substances [4]. Among these classified pollutants, heavy metal pollution has become a global issue due to their high toxicity level, high bioaccumulation in human body and food chain, non-biodegradable property and carcinogenic effects to humans [5]. The high concentration of transition metals like Cd, Cu, Pb and Zn in urban topsoil and dusts tend to washout from infrastructures and contaminate the water sources [1].

Removal of pollutants in waste water is the fundamental goal of waste water treatment systems. Gupta and Ali (2013) summarised the different methods involved in wastewater treatments which include adsorption, centrifugation and filtration, micro and ultrafiltration, coagulation, crystallization, electro dialysis, electrolysis, evaporation and many more. Adsorption is an example of a heavy metal removal technique that has been commonly used and researched extensively [6]. The adsorption capacities of heavy metal ions that are commonly found in wastewater sources such as Zn^{2+}, Cu^{2+} and Cd^{2+} are compiled in Table 1. Among the adsorbents used, agricultural wastes were found to have high adsorption capacity of these ions.

Table 1. Adsorption capacities of heavy metals using different types of adsorbents.

Adsorbent	Adsorbent capacity (mg/g)					References
	Pb^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Ni^{2+}	
Zeolite, clinoptilolite	1.6	2.4	0.5	1.64	0.4	[7]
Clay/poly (methoxyethyl) acrylamide	81.02	-	20.6	29.8	80.9	[8]
Maize cope and husk	456	493.7	495.9	-	-	[9]
Pecan shells activated carbon	-	-	13.9	31.7	-	[10]
Bacillus-bacterial biomass	467	85.3	418	381	-	[11]

In general, physicochemical waste water treatments offer several benefits such as fast separation process and easy to operate. However, the advantages of these systems are often outweighed by a number of disadvantages. The main drawbacks identified from conventional physiochemical treatment systems requires a more proficient separation technique that is low in cost and easy to operate. Some of the main advantages and disadvantages of conventional wastewater treatment techniques are summarized in Table 2.The main drawbacks identified from conventional physiochemical treatment systems requires a more proficient separation technique that is low in cost and easy to operate. Some of the main advantages and disadvantages of conventional wastewater treatment techniques are summarized in Table 2.

Fuerhacker et al. (2012) performed an investigation on the application of ILs for the removal of heavy metals from waste water and activated sludge. The removal of heavy metals from activated sludge using quaternary ammonium and phosphonium ILs has proven to be more successful than conventional methods [12]. The removal rate of heavy metals by sorption to ILs was complex and could not be predicted using standard solutions. However, more than 90% of removal was successfully achieved for Cu, Ni and Zn by both ILs, [PR4][MTBA] and [PR4][TS] from the extraction of activated sludge [12]. The success in the removal of heavy metals using ILs has provided an opportunity to perform further research on other cheaper alternatives of ILs.

Unfortunately, in recent years the environmental aspects related to ILs have been strongly addressed, stating that many ILs commonly used cannot be regarded as ‘green derivatives’ [15]. It has been demonstrated that some ILs, based on imidazolium or pyridinium cations, turned out to be as toxic as conventional solvents, and caused adverse effects to microorganisms as well as the environment [16, 17]. In addition, the synthesis of ILs is far from being environmentally friendly as it typically requires a large amount of salts and solvents in order to completely exchange the anions [18].

Table 2. The main advantages and disadvantages of different physiochemical methods for treatment of heavy metal in wastewater.

Treatment Method	Advantages	Disadvantages	References
Adsorption using new adsorbents	• Easy operating conditions • Low cost of adsorbent • Wide range of pH • High metal binding capabilities	• Low selectivity • Cause production of waste products	[7]
Chemical precipitation	• Low capital cost • Simple operation	• Generation of sludge • Extra operational cost for sludge disposal	[13]
Electro dialysis	• High separation selectivity	• High operational cost due to energy consumption and membrane fouling	[14]
Membrane filtration	• Small space requirement • Low pressure • High reparation selectivity	• High operational cost due to membrane fouling	[13]

One of the key breakthroughs in the development of ionic liquids was identified when 1 mol equivalent N-ethylpyridinium bromide: 2 $AlCl_3$ was successfully synthesised by Hurley and Weir in 1951 which was a eutectic liquid at 20°C [19]. The term “deep eutectic solvent” was first invented a decade ago by Abbott, a notable pioneer in the field [20]. Abbott discovered the concept of mixing two solid organic materials to produce a free flowing fluid with a freezing temperature far below the individual components [20]. The fusing of the mixtures resulted in the formation of a eutectic mixture with a melting point lower than its original components which led to the mixture being called a DES [18, 21, 22]. DESs belong to a class of ionic liquids which are mixtures of a quaternary salt with either a hydrogen bond donor (HBD), metal halide (Lewis acid) or a hydrated salt [23]. The HBD can consist of an alcohol, amide or a carboxylic acid which act as a complexing agent [23].

DESs have been considered an alternative to ILs as they are able to overcome some of the disadvantages of ILs. DESs have been regarded as an environmentally friendly solvent that is able to be synthesised at high purity and low cost compared to ILs [18, 22, 24]. DESs have been identified to overcome some of the principle disadvantages of ILS, as they are easy to synthesise in pure state, chemical inertness with water, non-toxic, biocompatible and biodegradable properties [18, 21, 22, 25]. The unique features of DESs have found its way into various applications such as electrochemical processes [26], production and purification of biodiesel [22, 27], biological catalysis [28], synthesis of solar cells [29], separation of aliphatic and aromatics [30] and many other potential applications.

In this study, different types of ammonium and phosphonium based DESs were synthesised and investigated for their ability to dissolve CuO and ZnO heavy metal oxide ions. CuO and ZnO will be used as the primary source of heavy metal oxide ions to determine their solubility level in the synthesised DESs. These ions were chosen as they can be easily found in urban topsoil and dusts that tend to washout from infrastructures [1]. Besides that, industries like battery manufacturing, electroplating and metal processing are highly responsible for the release of toxic metal ions into water sources [31]. Ammonium and phosphonium were selected as the source of quaternary salt ions in the synthesis of DESs as they are low cost and easy to synthesise at high purity [21, 22]. Various combination of ammonium and phosphonium based DESs were synthesised and their characteristics were analysed. A quantitative investigation was performed to identify a specific DES as a novel, efficient, safe, simple and most importantly cost effective solvent to dissolve heavy metal oxides. This research was dedicated to explore the efficiency of the synthesised DESs which is not reported in literature elsewhere. Findings from this research study can be useful in the application of DESs for the removal of heavy metal oxides from wastewater.

2. Experimental Methods

2.1. Chemicals

The materials required for this investigation consist of quaternary salts and HBDs for the synthesis of DESs and heavy metal oxides for the solubility experiment. Choline Chloride ($C_5H_{14}ClNO$) and Methyl Triphenyl Phosphonium Bromide ($C_{19}H_{18}PBr$) were selected as the source of quaternary salts for the synthesis of DESs. These chemicals were purchased from Sigma Aldrich with purity of >99%. Two different HBDs, glycerol ($C_3H_8O_3$) and triethylene glycol ($C_6H_{14}O_4$) were selected to bond with the quaternary salts for the synthesis of DESs. These HBDs were purchased from Merck Millipore and has purity of >99%. CuO and ZnO ions were selected as the source of heavy metals to be utilised in the solubility experiment. CuO was purchased from Labchem Sdn. Bhd. and ZnO was purchased from R&M Chemicals Sdn. Bhd. Both the heavy metal oxide ions has purity of >99%.

2.2. Synthesis of DES

In this study, 10 types of DESs based on ammonium and phosphonium based salts were synthesised to investigate the solubility of heavy metal oxides. ChCl and MTPB were selected as the source of quaternary salts for the synthesis of DESs. Two different HBDs, glycerol and TEG were selected to fuse with the quaternary salts for the synthesis of DESs. In order to increase the number of possible combinations, the DESs were prepared with different molar ratios of ChCl and MTPB salts to the HBDs. The preparation of DESs for this investigation was done according to the method used by Shahbaz et al. (2011).

To synthesise the DES, the mass of salt and the corresponding HBD were first weighed accurately using an electronic balance. Then, the weighed salt and HBD were carefully filled into 150ml Schott bottles and sealed with Para film to prevent any moisture from mixing with the contents. The Schott bottles were then allowed to heat at 70°C at 300 rpm until a homogenous and transparent liquid is formed Shahbaz et al. (2011). Table 3 shows the details of the DESs which were synthesised in this study. The synthesised DESs were given abbreviations.

Table 3. Compositions and abbreviations of the synthesised DES.

Salt	**Hydrogen Bond Donor (HBD)**	**Molar Ratio (Salt: HBD)**	**Abbreviation**
Choline Chloride (ChCl)	Glycerol	1:2	DES 1
	Glycerol	1:3	DES 2
	TEG	1:3	DES 3
	TEG	1:4	DES 4
	TEG	1:5	DES 5
Methyl triphenyl phosphonium bromide (MTBP)	Glycerol	1:2	DES 6
	Glycerol	1:3	DES 7
	TEG	1:3	DES 8
	TEG	1:4	DES 9
	TEG	1:5	DES 10

2.3. Heavy metal ion solubility in DES

Heavy metal ion solubility was determined by mixing 0.1 g of the metal oxide (CuO and ZnO with >99% purity) in 5 ml of the synthesised DES. Samples were prepared for 10 combinations of DESs with 2 combinations of heavy metal oxide ions separately. The samples were left to stir at 250 rpm at 28, 45 and 65°C respectively for four hours in an incubator orbital shaker. These temperatures were selected in order to study the solubility behaviour of the ions at low, medium and high temperature conditions. The stirred samples were then left overnight for settling before being analysed using the AAS.

2.3.1 Atomic Absorption Spectrometer (AAS) analysis

The samples containing DESs and heavy metal oxide ions was analysed for heavy metal ion content using the AAS equipment. The samples for AAS analysis were prepared by performing a serial dilution technique, in which 1 ml of DES containing heavy metal oxide is diluted in 9 ml of distilled water three times before being analysed. The specifications of the AAS equipment are shown in Table 4.

Table 4. AAS analytical conditions.

Atomic Absorption	
Oxidant	Air
Oxidant flow rate	10.0 L/min
Acetylene flow rate	2.5 L/min
Flame Emission	
Oxidant	Nitrogen oxide, N_2O
Oxidant flow rate	6.0 L/min
Acetylene flow rate	7.5 L/min
Replicates	3

3. Results and Discussion

3.1. Synthesis of DES

In this study, ChCl and MTPB were used to synthesis DESs by mixing these quaternary salts with two different HBDs, glycerol and triethylene glycol. The DESs were prepared with different molar rations to form ChCl based DESs (DES 1- DES 5) and MTPB based DESs (DES 6 - DES 10). The selection of molar ratios used to synthesise the DESs was done based on the research performed by Shahbaz et al. (2011). All 10 types of DESs that were synthesised formed colourless eutectic mixtures with no salt present inside the solvent. The DESs formed a clear homogenous solution and there were no undissolved salts left in the solvent. The freezing point and water content of the DESs was measured using a Differential Scanning Calorimeter (DSC) and Karl Fischer Titration (KF). All the synthesised DESs showed low water content (1 wt%) and the solvents formed have lower freezing points compared to their individual constituents. The formation of the eutectic mixtures is a result of hydrogen bonding between its constituents.

3.2. Solubility of heavy metal oxides in DESs

Based on this research investigation, all the synthesised DESs are capable in dissolving both CuO and ZnO heavy metal oxides at different temperatures. The analysis performed using AAS was successful and showed significant results in this study. There are several factors that influenced the solving ability of the DESs during this research. These factors include, effect of temperature, type of DES and type of heavy metal oxide ions. The details of each factor are explained in the following section of this paper.

3.2.1. Effect of temperature

In general, it is known that when a solvent is subjected to additional heating, the particles of the solute present in that solution tend to move more easily between the solid phase and the solution. The heavy metal oxides that are solid in room temperature and pressure tend to become more soluble when the temperature is increased. Heating the DESs with the heavy metal oxides at different temperatures makes it easier for the particles of solid to move between the DES solution and the solid phase. This can be proven based on the Second Law of Thermodynamics which predicts that the solutes will tend to shift to the more disordered and dispersed state resulting into the two components being in a solution form [32].

Figure 1 shows the solubility profile of CuO in DES 1(ChCl: Glycerol) and DES 6 (MTPB: Glycerol) at 28, 45 and 65°C. Both DES have the same molar ratio of salt to HBD, 1:2. Based on the graph, DES 1 and DES 6 exhibit an increasing trend in solubility with increase in temperature. DES 6 has the highest value of solubility at 65°C (0.197 mg/L) followed by DES 1 (0.098 mg/L).

The increase in solubility of CuO in the DESs is due to the increase in kinetic energy among the particles when subjected to higher temperature in which the solids move readily between the solution and the solid phase. It is apparent that both the DESs show increase in solubility with increase in temperature as mentioned in the second law of thermodynamics.

Figure 2 represents the results for the solubility of ZnO in DES 1 and DES 6 at 28, 45 and 65°C. It is observed that the solubility of ZnO exhibits an increasing trend in DES 6 but shows a decreasing trend in DES 1. ZnO is most soluble in DES 6 (0.575 mg/L) and least soluble in DES 1 (0.267 mg/L) at 65°C.

As mentioned earlier, the increase in heavy metal solubility in the DESs are due to the increase in kinetic energy among the particles at high temperatures. However, the trend observed with ZnO differs from the trend observed with CuO for DES 1 and DES 6. The difference in solubility can be due to the presence of different anion groups in the DES in which DES 1 has Chloride (Cl^-) ions whereas DES 6 has bromide (Br^-) ions. Since both DESs are comprised of the same HBD, glycerol, the solubility is also affected by the presence of three hydroxyl group in glycerol.

Similarly, Fig. 3 shows the solubility profile of CuO in DES 2 (ChCl: Glycerol) and DES 7 (MTPB: Glycerol). Both the DESs were synthesised with salt to HBD ratio of 1:3. Based on the figure, DES 7 shows an increasing trend in solubility with respect to temperature, however, the increasing trend in DES 2 experiences a decline in solubility at 65°C. The highest solubility was achieved by DES 7 (0.169 mg/L) whereas the lowest solubility was achieved by DES 2 (0.116 mg/L).

The variation in the trend of solubility depends on the increase in temperature. It can be observed that DES 2, which is the ChCl based DES experiences a decline after 45°C. This indicates that this type of DES does not exhibit good solving properties at high temperature. However, DES 7, which is a MTPB based DES showed better solving properties when subjected to higher temperature.

Based on the solubility of CuO and ZnO in all the synthesised DESs, it can be seen that the difference of solubility between each temperature show variation as small as 0.001 mg/L. Besides that, the range of temperature that was studied, 28, 45 and 65°C should be increased in order to understand the significance of temperature in the solubility of these metal oxides. This is because the incubator shaker equipment is also subjected to heat losses and may have caused slight deviation in the readings obtained. However, higher solubility readings at 45°C compared to 65°C in some DES combination requires further investigation to justify the sudden decline in solubility.

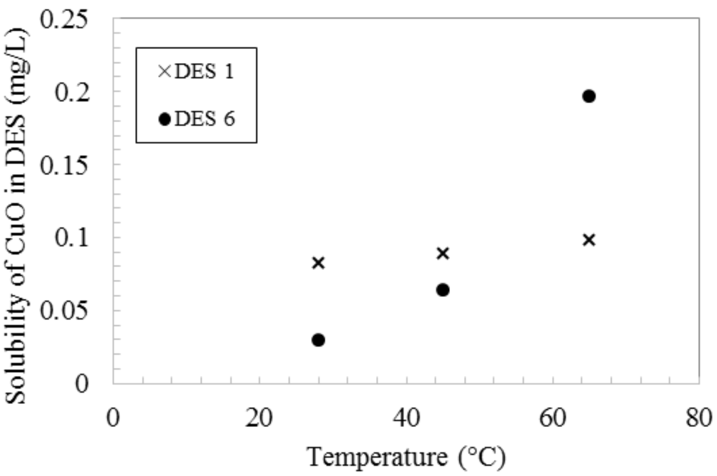

Fig. 1. Solubility profile of CuO in DES 1 (ChCl: Glycerol) and DES 6 (MTPB: Glycerol) as a function of temperature.

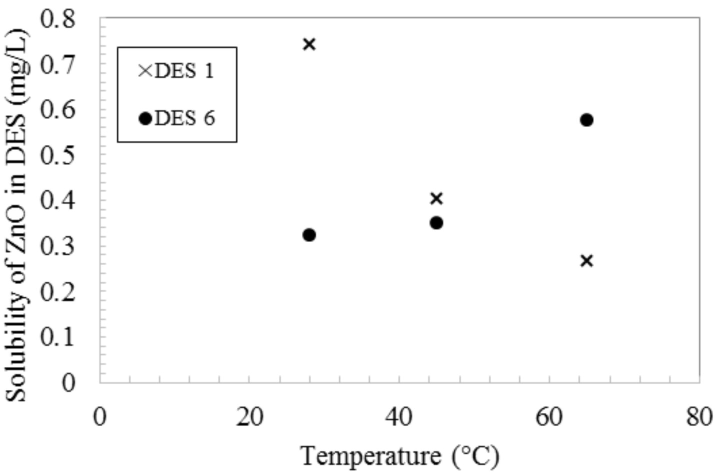

Fig. 2. Solubility profile of ZnO in DES 1 (ChCl: Glycerol) and DES 6 (MTPB: Glycerol) as a function of temperature.

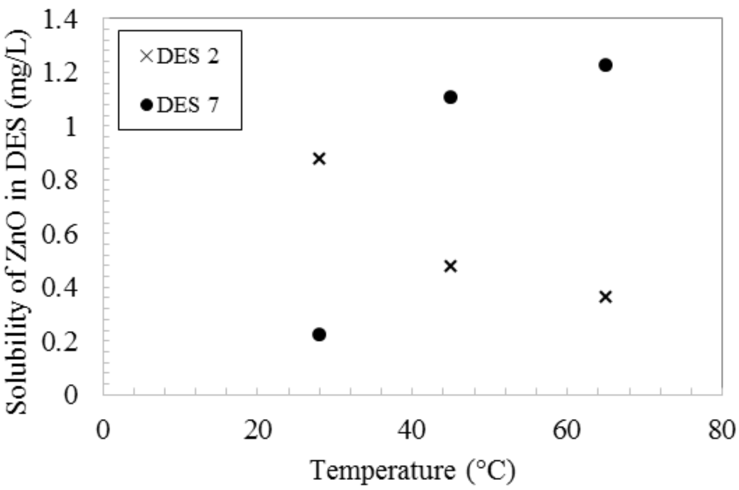

Fig. 3. Solubility profile of CuO in DES 2 (ChCl: Glycerol) and DES 7 (MTPB: Glycerol) as a function of temperature.

3.2.2. Effect of type of DES

The 10 types of DESs which were synthesised in this research study each have a unique combination of salt to HBD molar ratio. Figure 4 illustrates the solubility profile of CuO in DES 3, 4 and 5 with salt to HBD ratio of 1:3, 1:4 and 1:5 respectively. These DESs are made up of ChCl and TEG. The solubility profile shows an increasing trend as the temperature increases from 28 to 45°C, but experiences a decline at 65°C. DES 5 which has the highest HBD content compared to DES 3 and 4 exhibits the highest solubility at 45°C (0.0602 mg/L) followed by DES 3 (0.0503 mg/L) and DES 4 (0.0325 mg/L).

The increase in the amount of HBD in a particular DES plays a significant role in affecting the solubility properties of the solvent. In this case, DES 5 which has the highest amount of TEG content exhibits the highest solubility at 45°C. The presence of two hydroxyl functional groups in TEG affects the solubility of CuO. The higher number of hydroxyl group present in the DES increases the strength of the intermolecular forces formed between the heavy metal oxides and DES.

Figure 5 shows the solubility profile of CuO in DES 8, 9 and 10 which comprise of MTPB and TEG with salt to HBD ratio of 1:3, 1:4 and 1:5 respectively. DES 8 exhibits the highest solubility among the rest at 45°C (0.0105 mg/L). However, CuO showed the lowest solubility in all three DESs at 65°C where DES 10 has the lowest solubility (0.017 mg/L) compared to DES 9 (0.021 mg/L) followed by DES 8 (0.030 mg/L).

The solubility of CuO in ChCl based DESs (DES 3- 5) and MTPB based DESs (DES 8- 10) showed a similar trend in which the solubility was the highest at 45°C compared to 28 and 65°C. Based on the solubility profile shown in Fig. 5, DES with TEG combination has two advantages, an increased solubility of heavy metal oxides ions and a decreased temperature of application. However, the solubility readings for MTPB based DESs were slightly higher compared the ChCl based DESs.

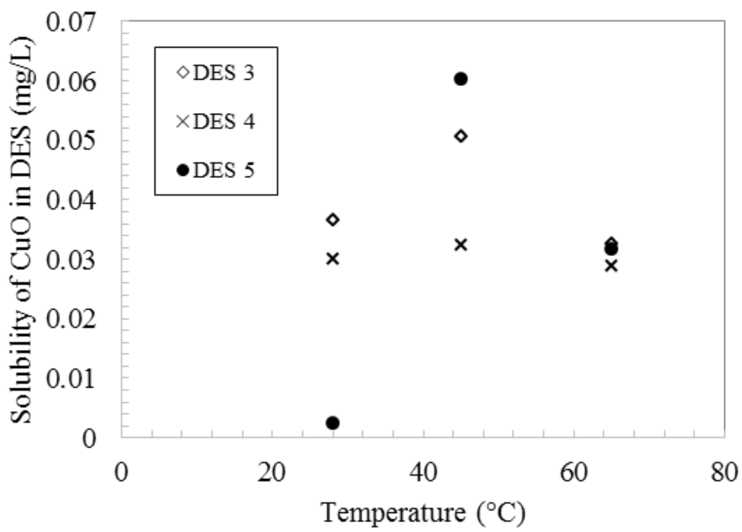

Fig. 4. Solubility profiles of CuO in DES 3- DES 5 (ChCl: Triethylene Glycol) as a function of temperature.

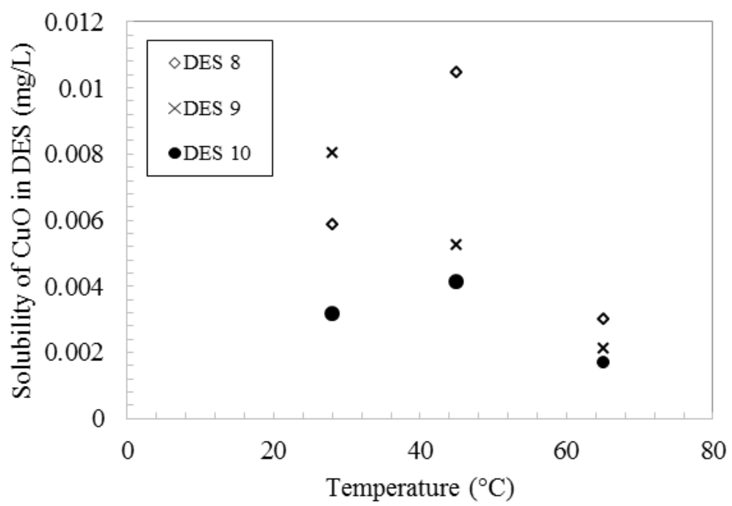

Fig. 5. Solubility profiles of CuO in DES 8- DES 10 (MTPB: Triethylene Glycol) as a function of temperature.

3.2.3. Effect of type of heavy metal oxides

The solving ability of the DESs is influenced by the type of heavy metal ion present in the solution. The heavy metal oxides, CuO and ZnO belong in the transition elements group in the periodic table. The ions that constitute the metal oxides. Cu^{2+} and Zn^{2+} are metal cations which are also known as Lewis acids. These metal cations act as electron pair acceptors when mixed with the DES.

Figure 6 shows the comparison between the solubility of CuO and ZnO in the synthesised DESs at 28°C. Based on the figure, it is apparent that the solubility of ZnO is significantly higher compared to CuO in all the DESs. The solubility of ZnO was found to be the highest in DES 2 (0.879 mg/L) followed by DES 1 (0.744 mg/L). In contrast, the solubility of CuO was found to be the highest in DES 1 (0.089 mg/L) followed by DES 2 (0.082 mg/L).

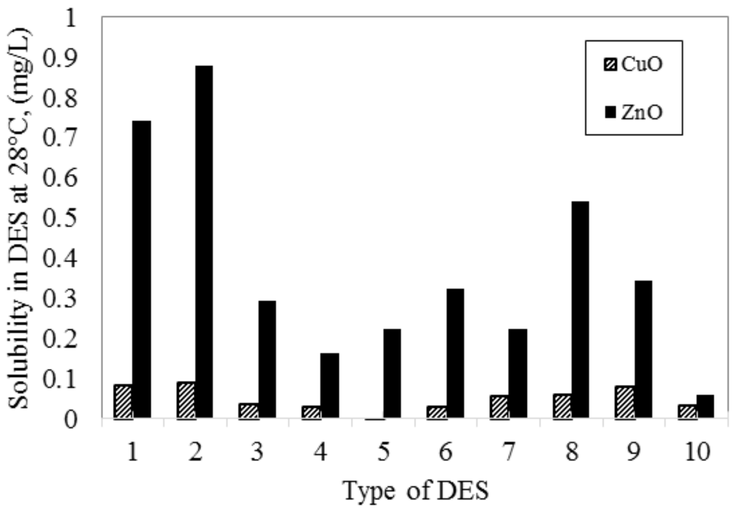

Fig. 6. Solubility of CuO and ZnO in DESs at 28°C.

Based on the results obtained, ZnO was found to be more soluble in the DES when compared to CuO. Higher solubility is observed in samples containing ZnO as they are more ionic compared to CuO [33]. Both CuO and ZnO ions exhibit strong temperature dependence when dissolved in DESs. However, further studies have to be performed in order to understand the complexation of the heavy metal oxides to form a soluble compound in the synthesised DESs.

4. Conclusion

The solubility of heavy metal oxides, CuO and ZnO in ChCl and MTPB based DESs with different salt to HBD combinations was investigated and analysed using AAS. It was found that CuO has the highest solubility in MTPB-Glycerol (1:2) with 0.197 mg/L at 65°C and the lowest solubility in MTPB-TEG (1:5) with 0.017 mg/L. ZnO was found to have the highest solubility in MTPB-Glycerol (1:3) with 1.225 mg/L and the lowest solubility in MTPB-TEG (1:5) with 0.017 mg/L. The findings obtained from this research study can be enhanced in future work in order to identify a particular DES that exhibit the highest heavy metal oxide solving property since the analysed ions was soluble in all the synthesized DES. Firstly, additional analytical techniques can be applied to understand the behaviour of heavy metal oxide ions in DESs at different temperature conditions. FAB-MS analysis can be employed to understand the binding of DESs with the metal ions during the solubility experiment [33]. The measurement of pH must also be performed as it is a crucial analysis for wastewater treatment procedures.

Besides that, further study can be done to identify a suitable separation method after DESs are used to dissolve heavy metal ions. The recovery of the spent DESs after allowing the solvent to dissolve the ions is crucial to ensure that the proposed method is suitable to the environment.

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