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Zinc Chloride as Acetamide based Deep Eutectic Solvent

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ABSTRACT

Solvents play a pivotal role in chemistry and other allied sciences. They find their use almost everywhere including chemical synthesis, drug delivery systems, extractions, purifications. However, most organic solvents available to us are highly volatile and their toxicity leads to skin, eye and respiratory tract irritation. In light of this, we have studied a newly emerging solvent system Deep Eutectic Solvents (DES). We synthesized a $ZnCl_2$-acetamide DES and evaluated its goodness as a solvent on the basis of three crucial parameters – its effectiveness in dissolving diverse solutes; its benignity to humans and environment and also the ease of its procurability at an undergraduate level. We found that DES could dissolve solutes from a wide range including metal oxides, inorganic salts, polar organics, aromatic acids and amino acids. The fact that DES is capable of dissolving various metal oxides, opens green avenues for the separation, selective recovery and recycling of metals from its solutions. Based on this, we performed the electrolysis of CuO dissolved in DES and found that copper metal could be obtained from it directly. The antimicrobial properties of DES were also explored. A culture of *E. coli* fostered on an agar plate was substantially inhibited, kindling the possibility of the use of DES as an antimicrobial solvent. The efficacy of the $ZnCl_2$-acetamide to absorb CO_2 was then studied qualitatively. The observations indicated that DES absorbs certain amounts of CO_2 indicating its probability as a greenhouse gas absorbent. DES promises to be a holistic solvent which is cheap to procure, very useful and also benign to the users and environment.

Keywords: Deep Eutectic Solvent, Ionic Liquid, Solvent, $ZnCl_2$-Acetamide

INTRODUCTION

Solvents are crucial for a number of processes. To do without a solvent is not impossible, but it is definitely not easy. There are some prerequisite viz. efficiency, non-toxicity, easy availability and safe handling that a solvent must satisfy before it can be brought in use in a process. However, the currently known solvents suffer from one or the other problem that restricts their widespread use across all processes of interest.

Concerns range from their poor efficacy, to their toxicity or volatility, to their non-biodegradable nature and high cost of procurement. Thus, the search for a new, benign, multipurpose solvent system is an area of persistent research.

Room **T**emperature **I**onic **L**iquids (**RTIL**s) for quite long were considered as wonderful solvents until there appeared reports of their toxicity and poor biodegradability (1)–(6). Purification of ionic liquids requires reagents like dichloromethane and acetonitrile which are known to be highly toxic and contaminating (7), (8). Moreover, the yield of RTILs during synthesis is not very heartening and in view of the high cost of the raw materials required for synthesis, the situation of they being readily used as solvents becomes contested.

In view of the limitations that ionic liquids pose, arises the need to explore another solvent system that is less toxic, readily available, cheap and equally efficient. In this regard, we studied a new class of solvent system called Deep Eutectic Solvents (DES). DES is a new family of ionic liquids which have been pursued with great interest recently as they have proven to have comparable efficiencies to ILs and in fact are better alternatives to it in view of their easy synthesis with cheaper raw materials, increased benignity, easy procurability, recyclability, biodegradability and non-flammability to name a few (9)-(11).

DES is a liquid generally composed of two or three safe and cheap components that are capable of self-association, often through H-bonding interactions to form a eutectic mixture (Figure I) (having uniform composition) with a melting point lower than 100°C. The resulting DES is characterized by a melting point lower than that of each individual component. These DESs exhibit similar physicochemical properties to the ionic liquids, while being more economical and environmentally benign.

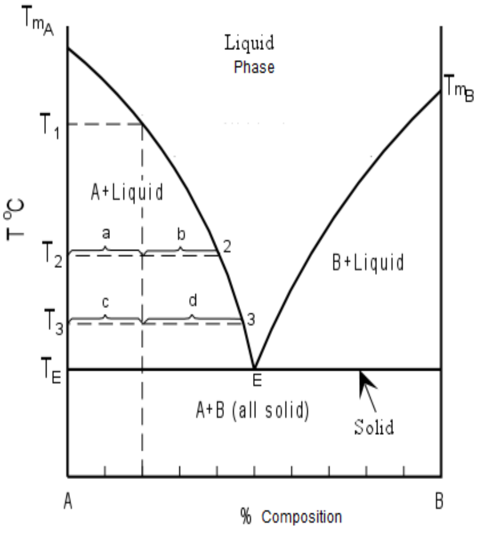

Figure - I Eutectic composition of individual components A and B at E. Till T_E, which is the eutectic temperature, the phase is liquid and only below it, the two solids start separating simultaneously

Abbott and co-workers defined DESs using the general formula $R_1R_2R_3R_4N^+X^-Y^-$ (12). General Classification of DES is as follows: TYPE I: DES Y= MCl_x, M=Zn, Sn, Al, Ga; TYPE II: DES Y =$MCl_x.yH_2O$, M=Cr, Cu, Ni, Fe and TYPE III: DES Y = R_5Z with Z= $-CONH_2$,-CONH,-OH.

Another group of DES is composed of metal chlorides (eg. $ZnCl_2$) blended with different hydrogen donors such as urea, ethylene glycol, acetamide or hexanediol (Type IV).

One of the most widespread components used for the formation of DES is Choline chloride (ChCl). ChCl is an inexpensive, biodegradable and non-toxic quaternary ammonium salt ($HOC_2H_4N^+(CH_3)_3Cl^-$), which in combination with safe H-Bond donors such as urea, carboxylic acids (oxalic, succinnic, citric or amino acids) or renewable polyols (eg. glycerol, carbohydrates) is capable of rapidly forming a DES. Mixing the two solids *i.e* ChCl (m.p. = 302°C) and urea (m.p. = 133°C), a new liquid phase is generated, which is characterized by a lower value of freezing point (12°C) than that of individual constituents (13), (14). We, in our work, chose $ZnCl_2$: Acetamide (in 1:4 molar ratio) as they were readily available in the laboratory. Also the $ZnCl_2$: Acetamide DES (in 1:4 molar ratio) maintains its liquid form till temperatures as low as -16°C (11) thereby providing a broad range of temperature whereby it can be used as a solvent. The melting point of $ZnCl_2$ is 293°C, that of acetamide is 81°C, whereas the DES formed out of these in the salt:H-bond donor molar ratio of 1: 4 is as low as -16°C (11).

METHODOLOGY

A. Procedure for synthesis

DES was prepared by heating $ZnCl_2$: (acetamide) CH_3CONH_2 in a 1:4 molar ratio with constant stirring using a magnetic stirrer till the solids mix to form a clear homogenous liquid. The amounts of $ZnCl_2$ (0.125 moles = 17.0393 g) and acetamide (0.5 moles = 29.5350 g) were weighed and then transferred to a beaker. This beaker was placed in a preheated oil bath. The mixture was shaken on a magnetic stirrer maintaining a temperature range of about 80-100 °C. When a homogenous liquid formed, the stirring was stopped and the mixture was allowed to cool down. The apparatus set up for synthesizing DES is shown in Figure IIa whereas the DES synthesized is shown in Figure IIb.

Figure - II (a) Apparatus set-up for synthesizing $ZnCl_2$-Acetamide DES (b) Synthesized DES

B. Procedure for performing electrolysis of CuO dissolved in DES

Two pre-weighed copper electrodes were taken and dipped into the $ZnCl_2$-acetamide DES in which CuO was already dissolved. One electrode was connected to the positive terminal of the battery as anode while the other electrode was connected to the negative terminal, thus behaving as the cathode of the electrolytic cell. CuO dissolved in DES acted as the electrolyte. The set-up can be seen in Figure III.

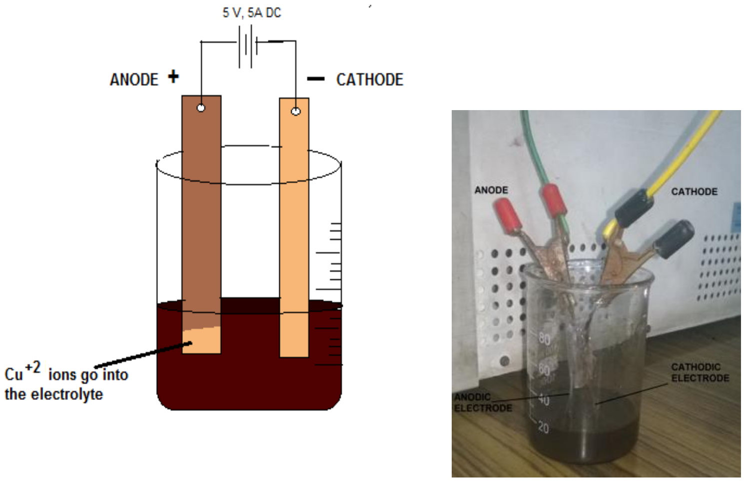

Figure - III Set up for Electrolysis

5 A DC current was passed through the setup for about 2 hours, out of which only about 0.1 A actually passed through. The electrodes were weighed before and after the electrolysis. A change in the mass of the electrodes was observed.

C. Procedure adopted for studying antimicrobial and antifungal behaviour of the solvent

To study the antibacterial behavior of the prepared solvent, a culture of *Escherichia coli* was fostered on an agar-plate. This acts as the control plate. On another agar-plate, a well was bored into which around 1µL of DES was placed using a dropper. The *E. coli* culture was grown on the latter plate also. To establish the antifungal behaviour of the solvent, similar plates (control-plate & study-plate) were prepared wherein fungi were allowed to propagate for 3-4 days.

D. Procedure for studying CO_2 absorption by DES

Choline chloride based DES were reported to absorb CO_2 (11). In our own small way, we checked the efficacy of the zinc chloride-acetamide DES we synthesized in the laboratory to absorb CO_2. For this, we generated CO_2 *in situ* in DES by making use of the chemical reaction between sodium hydrogen carbonate and conc. hydrochloric acid. The evolution of brisk effervescence indicates the production of CO_2 gas in the reaction. The reaction may be represented as:

$$\boxed{NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2}$$

In a boiling tube, about 20 mL of DES was taken. To it $NaHCO_3$(s) was added gradually in small lots (0.2g), adding conc. HCl synchronously. It was ensured that the setup be as airtight as possible manually to avoid the possible escape of CO_2 produced into atmospheric air. This boiling tube containing DES (where *in-situ* CO_2 was being generated) was then connected to another boiling tube containing freshly prepared lime water via bent glass tubing. Additions of $NaHCO_3$ were continued till about 2.5-3 g of it was added looking for appearance of turbidity in lime water. The set up for this is depicted in Figure IV.

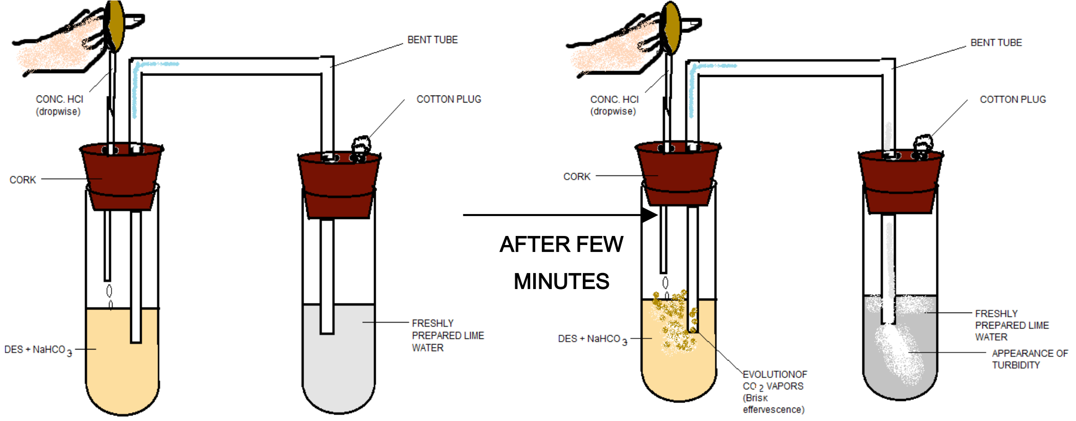

Figure - IV Set-up to study CO_2 absorption

RESULTS

We hereby report the observations made in our study. To start with, we analysed a few preliminary properties of the DES synthesized, which are reported hereunder.

A. Properties evaluated

We studied several physico-chemical properties of the synthesized DES. (a) Flammability: Little amount of the DES solution was taken on one edge of a glass rod and introduced to flame. It was found to be non-flammable in nature. (b) Density: The density of the DES that we synthesized was found to be 1.45 g/mL which was close to the its literature value *i.e* 1.36g/mL (11). Most DESs exhibit higher densities than water which may be attributed to the molecular organization or packing of DES. (c) Viscosity: DES appears to be a highly viscous liquid which is attributed to the extensive H-bond network between each component which results in the lower mobility of free species within the DES. DESs of low viscosity are desired and in general, viscosities of eutectic mixtures are mainly affected by the nature of the DES components. (d) Litmus blue test: About 1ml of DES solution was taken in a test tube to which two to three drops of litmus blue solution was added. The solution turned faintly red indicating that DES was weakly acidic in nature (Figure V).

Figure - V: *On the left,* blue litmus solution. *On the right,* blue litmus solution turned red in presence of DES.

B. Solubility of metal oxides

We tried dissolving a number of metal oxides available in our laboratory in the DES we prepared and the following results were obtained.

Table - I Observations on solubility of metal oxides

Oxide	**Solubility Status**	**Remarks**
ZnO	Dissolves completely in DES	On heating, its solubility increases
MnO_2	Dissolves completely in DES	Solubility increases with temperature
CrO_3	Dissolved completely in DES	-
PbO_2	Lead oxide dissolves in DES	-
CuO	Cupric oxide dissolves completely in DES	-
Al_2O_3	Not soluble in DES at room temperature	On strong heating, solubility increased minimally giving a white suspension
Fe_3O_4, NiO	Do not dissolve	Not even on strong heating

We tried dissolving many other compounds into $ZnCl_2$-acetamide DES ranging from *inorganic salts* (KCl) to *polar organics* (CH_3COOH), *aromatic acids* (benzoic acids), *amino acids* (aspartic acid, glycine), *enzymes* (alpha-amylase), *grease* to name a few. The results obtained were interesting. Most of these including KCl, $CuSO_4$, acetic acid, glycine, aspartic acid, benzoic acid could be easily solubilized. Grease was also found to be soluble in DES. Water doesn't dissolve greases; however its solubility in DES is a major advantage. The solubility of metal oxides and others can be seen in the Figure VI.

C. Electrolysis Results

The results of the electrolysis of CuO dissolved in DES are as follows. The electrodes before and after electrolysis are shown in Figure 7. The part of the anode that was dipped in the electrolyte can be distinctly seen to be *clearer* than the rest of the anode (Figure VII a) indicating that copper from its surface oxidized in solution. On the other hand, a black coating, absent before, appeared on the cathode indicating some copper deposition into it (Figure VII b). This can also be affirmed from the change in the masses of the two electrodes.

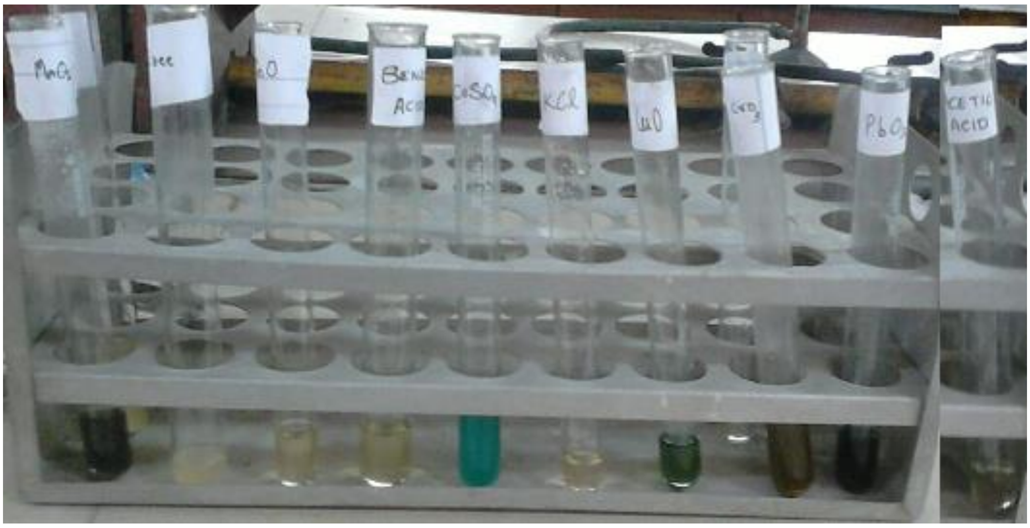

Figure - VI Solubility of different substrates in DES

The mass of anode, before and after electrolysis was 1.3622 g and 1.3528 g, respectively. Similariy, the mass of cathode, before and after electrolysis was 1.4151 g and 1.4192 g. While the anode lost a mass of 0.0094 g, cathode accumulated 0.0041 g of Cu.

Figure – VII (a) Electrodes before electrolysis (b) Electrodes after electrolysis

D. Antibacterial and antifungal behavior

After incubating the control plate and study plate containing bacterial culture for 24 hours, it was observed that bacterial growth was sufficiently inhibited in a circular region around the DES spot whereas there were lawns of bacteria all over the rest of the plate (Figure VIII a). It was enriching to observe such exceptional bacterial inhibition behaviour exhibited by $ZnCl_2$ – acetamide DES. After incubating the fungal culture plates for 4 days, we observed that the fungal growth was also well inhibited around the well containing DES (Figure VIII b).

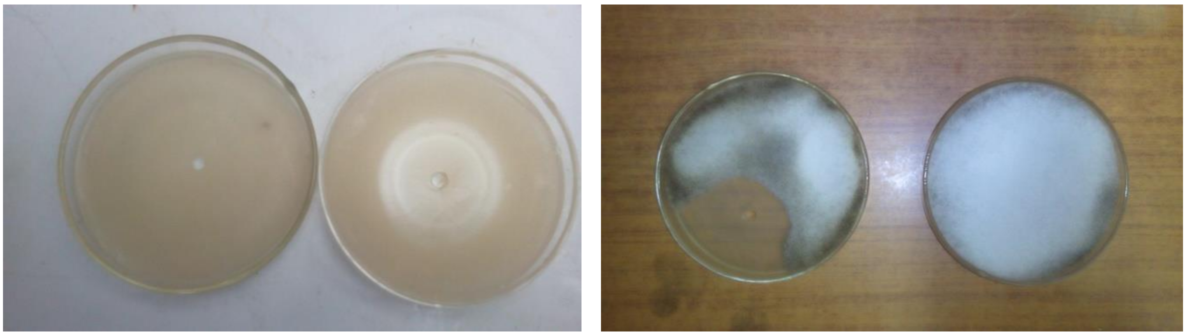

Figure - VIII (a) *On the left* is the control agar-plate where colonies of *E. coli* can be seen all over. *On the right* is the agar-plate in which no bacterial growth is seen in a circular region around the central well where DES was placed. (b) Inhibited fungal growth can be seen (on the left) against the right control plate.

E. CO_2 solubility in DES

Even after addition of 3g of $NaHCO_3$ in around 30 mL of DES followed with subsequent additions of HCl, the lime water did not turn milky indicating possible absorption of the CO_2 gas by DES. After this, when a bulk amount of $NaHCO_3$ was added, it was observed that there was rapid and fervent bubbling into the lime water solution placed at the other end, rendering it largely milky in little time. This could be possibly because of the DES achieving saturation and being unable to absorb further CO_2 gas into itself.

This test aims a qualitative evaluation of the CO_2 absorption capability of DES. It can be inferred that since the CO_2 gas was produced *in-situ* and no milkiness appeared till around addition of 3g of sodium bicarbonate, we estimate that the gas would have been absorbed by the DES as it had nowhere else to go. This indicates that CO_2 indeed absorbs certain amounts of CO_2.

DISCUSSION

From our studies, we made some key observations. DES is found capable of dissolving a wide array of substrates including metal oxides whose dissolution had till now been a challenge. This opens green avenues for separation, selective recovery and recycling of metals directly from its solutions in DES. The solutions of metal oxides in DES can be electrolysed to directly obtain metal as cathode depositions. Our studies of microbial inhibition in presence of DES led to the conclusion that DES systems portray a substantial degree of antifungal and antimicrobial activity kindling the possibility of further research on their usage as antifungal and antibacterial agents.

The set-up we used to study the absorption of CO_2 in DES is a crude one and is not quantified, nevertheless it does stress on the fact that DES can absorb CO_2 opening scope for further exploration. CO_2 absorption has a great potential for a variety of chemical processes such as separation and purification of gases, chemical fixation of CO_2 and catalysis, among many. We can also utilize this property to purify the air or improvise its quality. A possible approach could be its use in chemistry laboratories in particular to absorb the carbon dioxide present in the air there, thus keeping a check on the quality of air.

CONCLUSIONS

Our project aimed at assessing solvent systems on the basis of three crucial parameters – utility, benignity to human and environment, and ease of procurability. We explored a newly emerging solvent system Deep Eutectic Solvent (DES). We realized that DES holds immense potential and satisfies (i) the condition of being benign in all respects and low toxicity to humans and environment, (ii) convenient synthesis, (iii) easily affordable since most of DESs can be prepared from readily accessible and cheaper chemicals. Not only this, DES also promises some wonderful applications that can be further investigated. DES is only a decade old in research and a lot about it still needs to be explored and explained opening doors for numerous new opportunities.

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