Metal Oxide Solubility in Deep Eutectic Solvents – Applications in Decontamination in Decommissioning

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1. Introduction

Deep eutectic solvents (DES’s) are a new class of solvent, widely regarded as ionic liquid (IL) analogues [1]. The most commonly studied type of these liquids are composed of a quaternary ammonium salt (QAS), and a hydrogen bond donor (HBD). Most published works have focused on choline chloride as the QAS, mixed with either a carboxylic acid, amine or alcohol as the HBD (Fig. 1). Upon mixing the two components at the correct molar ratios, a clear eutectic liquid is formed.

These DES’s have many of the advantages of their analogous IL’s, such as low vapour pressure, wide liquid range, non-flammability and good conductivity. However, unlike IL’s they are made of inexpensive, common chemicals and are considered non-toxic. These advantageous properties have promoted interest in them in many areas, such as separations, waste recycling, catalysis, and batteries [2], [3].

DES’s have been shown to dissolve metal oxides such as CoO, NiO, ZnO and MnO₂ (among others) which are insoluble or barely soluble in most molecular solvents [1]–[3]. Solubilizing these in aqueous systems usually requires harsh conditions such as acid, alkali and high temperatures. In addition to this, aluminates and silicates compounds have been shown to be insoluble in DES’s [3]. This ability to dissolve such metal oxides under relatively benign conditions, whilst leaving silicates and aluminates alone may make them appropriate for the decontamination of wastes produced during nuclear decommissioning, such as concrete.

In this work a set of choline chloride based DES’s have been studied for their ability to dissolve metal oxides relevant to nuclear decommissioning processes. We have focused on NiO, CoO and lanthanide oxides as they are all present in nuclear wastes.

2. Methods

2.1 DES Production

DES were produced by stirring choline chloride and a hydrogen bond donor at the appropriate molar ratio (Table 1) on a heating mantle at 50°C overnight, whereupon a clear liquid was produced. The DES were stored in glass bottles until they were required for experiments.

Table 1. Ratio of choline chloride (QAS) to selected hydrogen bond donors (HBD) used in this work

<table>
<thead>
<tr>
<th>HBD</th>
<th>QAS : HBD</th>
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<tbody>
<tr>
<td>Ethylene glycol</td>
<td>1 : 2</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1 : 2</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>1 : 2</td>
</tr>
</tbody>
</table>

2.2 Metal Oxide Dissolution

Metal oxide (ca. 0.1 g) was added to a glass vial, followed by DES (ca. 4 g). Vials were left heating for at least 2 weeks at 50°C using a Daihan MaXtable HM dry heating block. Samples were then removed from the heating block and 3 samples of loaded DES (ca. 0.5 g) were taken from each. These samples were removed from the glovebox, dissolved in 10 mL of deionized water (> 18 MΩ) and filtered using a Whatman 0.45 μm filter. Aliquots of solution from these samples were then diluted with HNO₃ (10%) for ICP-OES analysis.
3. Results and Discussion

Metal oxide solubilities in three common DES’s are shown in Table 2. The general trend in solubility based on HBD is MA > EG > G. The higher solubility in the malonic acid DES is thought to be due to the presence of acidic protons acting as good oxygen acceptors and promoting dissolution. Increased solubility with the ethylene glycol HBD when compared to glycerol may be due to complexation stabilizing the dissolved metal cation. Ethylene glycol has been reported to bind to Ni$^{2+}$ in choline chloride based DES’s via its oxygen atoms [4]. It is unknown whether this happens with the other metals studied, but it is possible. Another factor may be differences in solvent polarity. However, quantification of this for DES’s has proved challenging, and both explicit and relative values remain unknown.

Table 2. Solubilities of metal oxides in DES (ChCl = choline chloride, MA = malonic acid, EG = ethylene glycol, G = glycerol). Errors are reported as one standard deviation

<table>
<thead>
<tr>
<th>Solubility / mg kg$^{-1}$</th>
<th>ChCl - MA</th>
<th>ChCl - EG</th>
<th>ChCl - G</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>814 ± 25.7</td>
<td>2.35 ± 0.305</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>CoO</td>
<td>23600 ± 1550</td>
<td>150 ± 8.76</td>
<td>59.9 ± 3.92</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>15.1 ± 0.787</td>
<td>1.16 ± 0.092</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td>1530 ± 355</td>
<td>101 ± 5.97</td>
<td>43.9 ± 9.15</td>
</tr>
<tr>
<td>Eu$_2$O$_3$</td>
<td>-</td>
<td>84.0 ± 5.68</td>
<td>39.4 ± 2.88</td>
</tr>
<tr>
<td>Dy$_2$O$_3$</td>
<td>4760 ± 119</td>
<td>26.6 ± 7.79</td>
<td>10.4 ± 1.07</td>
</tr>
</tbody>
</table>

CoO exhibits the highest solubility in all DES studied. Of particular interest is its much larger solubility than NiO. This has been observed previously in a choline chloride – malonic acid DES [2]. Though the explicit reasons for this are unclear, we believe that the affinity of the metal centre to Cl$^{-}$ ligands may be important. Co$^{2+}$ readily forms complexes with Cl$^{-}$ ([CoCl$_2$], [CoCl$_3$]$^-$, [CoCl$_4$]$^{2-}$), unlike Ni$^{2+}$. However, this is based on aqueous data, so this conclusion must be treated as tentative until further studies can be carried out.

In DES’s with an alcohol HBD, the observed solubility series for Ln oxides is Nd > Eu > Dy >> Ce. In aqueous systems, CeO$_2$ is only soluble in the presence of acid, whereby it is reduced to Ce(III). This reduction requirement may explain why it is more soluble in the acidic than alcoholic DES, and less soluble than the other trivalent Ln oxides tested.

4. Conclusions

Metal oxides are soluble in DES’s, but care must be taken when selecting the HBD as this can change solubility behavior. This brings in the idea of selecting a HBD to tailor the properties of the solvent to target processes. This could be especially useful in decommissioning.

The general trend for metal oxide solubility with changing HBD is MA > EG > G. It is hypothesized that this due to the presence of acidic protons and the ability of the HBD to coordinate with the metal ion.

With regards to decommissioning, if a carboxylic acid HBD is used then the solvent will degrade. This means it will need to be replaced more often than an alcohol HBD, having implications for process design and sustainability. Lower solubilities in alcohol DES’s may be combated through controlling redox potential, the addition of complex forming ligands, or continuous removal of the metal.

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REFERENCES