Ionic Liquids
Metal extraction from regolith

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Summary

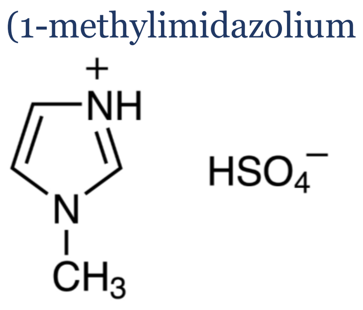
Ionic liquids are organic salts which are liquids at room temperature. They have several properties that make them useful, as a result of being entirely composed of ions: high electrochemical/thermal stability, low vapour pressure, and high ionic conductivity.
Task specific ionic liquids can be prepared as their chemical structure can be readily modified through simple chemical processes.

Regolith is a blanket of unconsolidated, loose, heterogeneous superficial deposits covering solid rock. Martian and Lunar regolith contains valuable elements which can be used in: cement (Mg, Ca, Si, O), additive Manufacturing (Mg, Fe, Al), solar cells (Si), and life support and propulsion (O)

Ionic liquids are a promising new class materials that allow for the development of ISRU (In Situ Resource Utilisation) technologies, which are vital to reduce the cost of future human space exploration missions. They also allow for technologies that may benefit companies such as NASA in exploration. Our group will be investigating the effectiveness of ionic liquids and how they can be used in the extraction of valuable materials from regolith.

Research aims

- Synthesise an ionic liquid (1-methylimidazolium hydrogensulfate)



- Prepare samples of metal oxides (models of regolith)
- Investigate the metal oxide dissolution with the 1-methylimidazolium hydrogensulfate as an alternative to the more expensive 1-ethyl-3-methylimidazolium hydrogensulfate
- Describe why certain metal oxides react

Experimental method

Synthesis of 1-methylimidazolium hydrogensulfate: concentrated sulfuric acid (4.905 g, 0.0501 mol, 1 eq) was added to 1-methylimidazole (4.105 g, 0.0501 mol, 1 eq) at 0°C with stirring. After 1 h, the temperature was allowed to rise to room temperature, and the reaction was stirred for a further 24 h.

Dissolution of copper (II) oxide: copper (II) oxide (1.04 g, 0.0130 mol, 1 eq) was added to a mixture of 1-methylimidazolium hydrogensulfate (4.70 g, 0.0261 mol, 2 eq) and water (26 cm³). The resulting mixture was stirred at room temperature for 48 h. Electrolysis was then used to revert the copper ions back to their original state, which is covered in the results section.

Dissolution of manganese (IV) dioxide: manganese (IV) dioxide (0.5 g, 0.00575 mol, 4 eq) was added to a mixture of 1-methylimidazolium hydrogensulfate (4.14 g, 0.0230 mol, 4 eq) and water (23 cm³). The resulting mixture was stirred at room temperature for 48 h.

Dissolution of iron (III) oxide: iron (III) oxide (1.04 g, 0.00653mol, 1eq) was added to a mixture of 1-methylimidazolium hydrogensulfate (7.06 g, 0.0392mol, 6 eq) and water (39 cm³). The resulting mixture was stirred at room temperature for 48 h. The mixture was then heated at 80 °C for 2 h.

Dissolution of zinc (II) oxide: zinc (II) oxide (0.73 g, 0.009mol, 1 eq) was added to a mixture of 1-methylimidazolium hydrogensulfate (3.25 g, 0.018mol, 2 eq) and water (13 cm³). The resulting mixture was stirred at room temperature for 48 hours.

Background Information

Ionic liquids can be used in a 3-step process to digest regolith and recover high purity metals.[1] Firstly, an acidic IL is used to digest the metal oxide, producing a solution of dissolved metal in depleted IL and water as a byproduct.

$$M_xO_y + 2yHSO_4^- \longrightarrow xM^{n+} + 2ySO_4^{2-} + yH_2O$$

The water produced here is electrolysed and the hydrogen produced is stored and used in the next step, where the dissolved metals are electrochemically plated out of solution while the depleted IL is regenerated to its original state.

$$2SO_4^{2-} + H_2 \longrightarrow 2HSO_4^- + 2e^-$$

$$M^{n+} + ne^- \longrightarrow M$$

1. Karr, L.J., Curreri, P.A., Thornton, G.S., Depew, K.E., Vankeuren, J.M., Regelman, M., Fox, E.T., Marone, M.J., Donovan, D.N., Paley, M.S., 2018. Ionic liquid facilitated recovery of metals and oxygen from regolith. In: 2018 AIAA SPACE and Astronautics Forum and Exposition. American Institute of Aeronautics and Astronautics Inc, AIAA.

Results

The dissolution of copper (II) oxide and zinc (II) oxide was successful. The formation of a blue solution with the former a clear indication of the presence of copper (II) ions. Leaving the manganese (IV) mixture for a week did not result in dissolution, with a suspension still being present. The separation of iron oxide was also unsuccessful, despite heating mixture at reflux.


Figure 1

Figure 1 shows a solution of copper (II) ions derived from IL extraction of CuO. You can see the blue colour associated with copper ions. On the right, a mixture of MnO2 and the IL. The IL was unable to disassociate the ionic compound. You can see this from the separated clear IL and MnO2 particles

Following this, we conducted an experiment to see if the metal ions could be converted to the elemental metal using electrolysis. For this we used one of our successful dissolutions. We were able to reduce copper (II) ions to copper metal.


Figure 2

Figure 2 shows the graphite rods before being inserted into the solution containing copper ions, which is about to undergo electrolysis.


Figure 3

Figure 3 shows the graphite rods after the solution had undergone electrolysis. As you can see, the rod on the left contains some copper particles coating the surface.

Analysis & conclusions

If an ionic compound has a high lattice enthalpy, ionic bonds between the ions are very strong and will need a higher amount of energy to overcome. If the lattice enthalpy is low, the ionic bonds are weaker, and a smaller amount of energy will be required to break apart the lattice. Lattice enthalpies can give us a good indication of dissolution, so we believe that compounds with lower lattice enthalpies will have a higher chance of success in extracting metal ions from regolith compared to compounds with higher lattice enthalpies. CuO has a lattice energy of dissociation of 4050 kJ mol-1 and when tested we found that it dissolved, and we were then able to extract the copper metal using electrolysis. Similar dissolution was observed with ZnO (LE = 3971 kJ mol-1). We also conducted tests using Fe2O3 and MnO2, with lattice enthalpies of 14774 and 13115 kJ mol-1 respectively. They proved to be unsuccessful as the lattice enthalpy was too high.
Having had some success with the chosen metal oxides in extracting the metal ion and reducing it, ionic liquids offer a way to produce metals in-situ in space rather than transporting them from Earth.

Next steps and Acknowledgements

Following on from this research, our next steps are to experiment using a wider variety of metal oxides to further solidify our conclusions, as well as making use of different examples of ionic liquids to experiment with and observe their effects.

"Quas dederis solas semper habebis opes", it is what you give that you will keep as eternal riches. In the spirit of our school motto, we would like to give huge thanks to Dr Pilkington for his constant support, management and dedication to ensuring that not only we understand the process of metal extraction, but also have fun doing so. Additionally, our gratitude also extends to our school's chemistry technician Mrs Stone, who helped procure different metal oxides alongside the instruments needed to conduct the whole research process. Lastly, thank you to IRIS for allowing us to present our research.

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