Inorg. Chem. **2005**, *44*, 6497−6499

Inorganic Chemistry
Communication

Selective Extraction of Metals from Mixed Oxide Matrixes Using Choline-Based Ionic Liquids

Andrew P. Abbott, Glen Capper, David L. Davies,* Raymond K. Rasheed, and Pragna Shikotra

Chemistry Department, University of Leicester, Leicester LE1 7RH, U.K.

Received April 8, 2005

The solubility of a range of metal oxides in a eutectic mixture of urea/choline chloride is quantified, and it is shown that the dissolved metals can be reclaimed from a mixed metal oxide matrix using electrodeposition.

Metal oxides are insoluble in most molecular solvents and are generally only soluble in aqueous acid or alkali. The dissolution of metal oxides is key to a range of important processes such as metal winning, corrosion remediation, and catalyst preparation. In this context, high-temperature molten salts have been used extensively for the recovery of refractory metals, such as titanium and aluminum, from their ores.[1,2] A limited number of studies have shown that ambient-temperature ionic liquids have potential as solvents for metal recovery. Whitehead et al. have shown that imidazolium-based ionic liquids can be used to extract gold and silver from a mineral matrix.[3] A patent has also been filed for the recovery of uranium and plutonium from spent nuclear fuel.[4] Some work has also been carried out on the electrowinning of metals, principally aluminum, from ionic liquids.[5,6] However, given the cost and sustainability of many imidazolium-based ionic liquids, cheaper alternatives are likely to be necessary for large-scale applications.

We have recently shown that substituted quaternary ammonium salts such as choline chloride form liquids at ambient temperatures when mixed with hydrogen bond donors such as amides[7] and carboxylic acids.[8] These liquids have properties similar to those of ionic liquids, viz., high conductivities, viscosities, and surface tensions. Some of the hydrogen bond donors used to date are common bulk commodity chemicals such as urea and oxalic acid, which are suitable for large-scale processes.

Analogous to high-temperature molten salts, low-temperature chloride eutectics demonstrate high solubilities for a wide range of solutes including metal oxides.[7] Table 1 shows the solubility of a variety of metal oxides in a 2:1 urea/choline chloride eutectic at 60 °C. Oxides such as ZnO, PbO_2, and Cu_2O exhibit appreciable solubility, whereas iron oxides and particularly Al_2O_3 are very poorly soluble. In high-temperature molten salts, it was shown that log metal oxide solubility is roughly inversely related to the melting point of the metal oxide and a similarly poor correlation is observed for the data in Table 1.[9]

Direct comparison with high-temperature molten salts is difficult because of the lack of comparable data. However, the solubilities reported in Table 1 for Cu_2O, NiO, and ZnO are higher than those reported for the NaCl−KCl system at 700 °C (1216, 2.3, and 27.6 ppm, respectively).[9] Of the oxides investigated, only CaO shows higher solubility in the high-temperature molten salt (369 ppm).

Table 1. Solubility of Metal Oxides in a 2:1 Urea/Choline Chloride Eutectic at 60 °C

metal oxide	mp/°C[10]	solubility/ppm[a]
Al_2O_3	2045	<1
CaO	2580	6
CuO	1326	470
Cu_2O	1235	8725
Fe_2O_3	1565	49
Fe_3O_4	1538	40
MnO_2	535	493
NiO	1990	325
PbO_2	888	9157
ZnO	1975	8466

[a] The metal solubility was determined using ICP-AES.

In high-temperature molten salts, the metal oxide dissolves to give predominantly the naked metal ion, i.e., $MO \rightarrow M^{2+} + O^{2-}$.[9] In our systems, O^{2-} is likely to be less stable. We propose that the high solubility of transition-metal oxides is in some cases due to their ability to complex with

---

* To whom correspondence should be addressed. E-mail: dld3@le.ac.uk. Tel: 44 116 252 2092. Fax: 44 116 252 3789.

(1) Fray, D. J.; Chen, G. Z. *Mater. Sci. Technol.* **2004**, *20*, 295.

(2) Cherginets, V. In *Handbook of Solvents*; Wypych, G., Ed.; ChemTec Publishing: Toronto, 2001; pp 1484−1496.

(3) Whitehead, J. A.; Lawrence, G. A.; McCluskey, A. *Green Chem.* **2004**, *6*, 313.

(4) Thied, R. C.; Seddon, K. R.; Pitner, W. R.; Rooney, D. WO 99/41752, 1999.

(5) Wu, B.; Reddy, R. G.; Rogers, R. D. U.S. Patent 0,070,122, 2002.

(6) McCluskey, A.; Lawrance, G. A.; Leitch, S. K.; Owen, M. P.; Hamilton, I. C. *ACS Symp. Ser.* **2002**, *818*, 199−212.

(7) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. *Chem. Commun.* **2003**, 70.

(8) Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. *J. Am. Chem. Soc.* **2004**, *126*, 9142.

(9) Cherginets, V. L.; Khailova, E. G. *Electrochim. Acta* **1994**, *39*, 823.

10.1021/ic0505450 CCC: $30.25

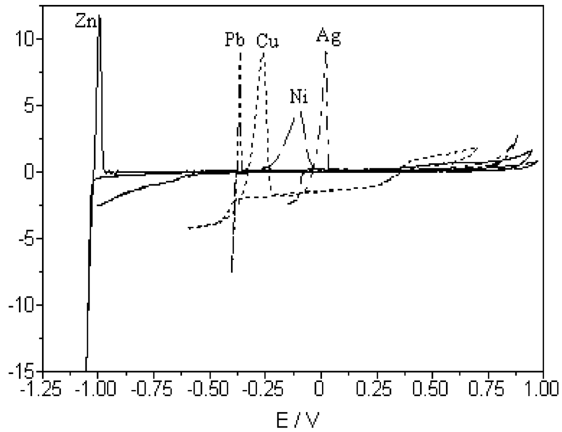

Figure 1. Cyclic voltammograms of ZnO, PbO_2, CuO, NiO, and Ag_2O in a 2:1 urea/choline chloride mixture on a Pt microelectrode at 60 °C.

urea, thus increasing their size and interaction with the solvent. Clearly, such an interaction is not present in the high-temperature molten salts. Our preliminary investigations to determine the form of the metal complex in the deep eutectic solvent are discussed below.

Electrospray mass spectrometry (MS) of ZnO dissolved in a 2:1 urea/acetylcholine chloride[11] eutectic shows a group of signals at *m*/*z* 174, 176, and 178 with an isotope pattern consistent with the formula $[\mathrm{ZnClO{\cdot}urea}]^-$. No other zinc-containing clusters are observed using this technique. MS experiments were also carried out by dissolving $ZnCl_2$ in a 2:1 urea/choline chloride eutectic, and in this case, $ZnCl_3^-$ and $Zn_2Cl_5^-$ were the predominant ions observed analogous to zinc chloride/choline chloride ionic liquids.[12] Hence, it can be concluded that when the ZnO dissolves in the deep eutectic solvent, the oxygen remains attached to the metal center and urea acts as a ligand. In agreement with this, UV−vis spectroscopy of CuO and $CuCl_2$ dissolved in a 2:1 urea/choline chloride eutectic mixture shows λ_{max} at 613 and 643, respectively, suggesting that, as for ZnO, the dissolution of CuO does not result in a homoleptic chlorometalate species.

Having shown that some metal oxides dissolve in these ionic liquids, it is important to demonstrate that they can also be efficiently extracted. Electrochemistry has been studied in some detail in ionic liquids, and the subject has been extensively reviewed in two recent papers.[13,14] The urea/ChCl mixtures have conductivities in the range 1−12 mS cm^{-1}; hence, it is possible to investigate the ability to electrowin the metals from solution.[7] Figure 1 shows a cyclic voltammogram of a Pt microelectrode immersed in solutions of various metal oxides dissolved in a 2:1 urea/choline chloride eutectic mixture. All of the metals show simple reduction to the metallic state with the exception of CuO, which is reduced via the Cu(I) state. All of the reduction steps are characteristic of metal deposition, and in all cases, the charge for deposition was effectively the same as that for stripping, demonstrating that the processes are reversible. Figure 1 also shows that most metal oxides dissolve with no change in the oxidation state of the metal. The one exception is PbO_2, which is found to be present as Pb(II). This was confirmed by the voltammetric response being the same as that for $PbCl_2$.

The potential window of the urea/choline chloride eutectic mixture is relatively small on a platinum electrode (−1.2 to +1.25 V vs Ag). However, metals can be deposited with high current efficiencies (see below) because the reduction kinetics of the eutectic are considerably slower on other metal surfaces; e.g., on Zn no significant decomposition of the eutectic occurs above −2 V.

With the exception of NiO, the reduction potentials are on the same order as the standard aqueous reduction potentials. Though not surprisingly, given that the metals are coordinated by some combination of oxide/hydroxide, chloride, and urea ligands, the differences between the reduction potentials are not the same as those between the standard aqueous reduction potentials; e.g., in the eutectic mixture, $E_{Ag^+/Ag} - E_{Zn^{2+}/Zn} = 1.00$ V compared to 1.56 V for the aqueous solutions. However, it is interesting that particular pairs or groups of metals demonstrate similar differences between their reduction potentials in the eutectic mixture and in aqueous solution; e.g., $E_{Ag^+/Ag} - E_{Cu^+/Cu} = 0.31$ V compared to 0.28 V between the standard aqueous reduction potentials and $E_{Pb^{2+}/Pb} - E_{Zn^{2+}/Zn} = 0.65$ V compared to 0.63 V in aqueous solutions. This suggests that Zn and Pb have a similar coordination environment in the deep eutectic solvent and removal of the ligands is energetically similar, while Ag and Cu have a similar ligation to each other, but the ligation is significantly different from that of Zn and Pb. This may be due to different ligands and/or different geometries for the different groups of metals.

For NiO, the potential for the onset of metal deposition is 0.24 V below the potential for metal stripping. This is common for other metals that routinely form octahedral complexes, e.g., Fe(III) and Co(II) (both not shown), and probably indicative of the difficulty in resolvating an octahedral complex from the electrode surface upon oxidation. Notwithstanding, these differences (results are in Figure 1) demonstrate that a range of metals can be electrowon from the eutectic mixture.

The different solubilities and reduction potentials provide a strategy for separating particular metal oxides. To demonstrate the viability of this approach, a sample of waste, which is commonly discarded, produced by the steel industry from the electric arc furnace was used. Analysis of the sample showed an approximate composition of Fe (38 wt %), Zn (33), Al (12), Mn (4.5), Si (4), Pb (4), Mg (2), V (1), and Cu (<1), with oxides being major constituents. This material was suspended in a 2:1 urea/choline chloride eutectic at 60 °C for 2 days. After filtration, the solution was found to contain only Zn and Pb in the ratio 6:1. This shows that ZnO can be effectively separated from Fe_2O_3 and Al_2O_3.

---

(10) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 55th ed.; CRC Press: Boca Raton, FL, 1974.

(11) Acetylcholine chloride was used in place of choline chloride because the signal for $[\text{choline} + 2\text{Cl}]^-$ would mask the peak for the zinc complex.

(12) Abbott, A. P.; Capper, G.; Davies, D. L.; Munro, H. L.; Rasheed, R. K.; Tambyrajah, V. *Chem. Commun*. **2001**, 2010.

(13) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *ChemPhysChem* **2004**, *5*, 1106.

(14) Endres, F. *ChemPhysChem* **2002**, *3*, 144.

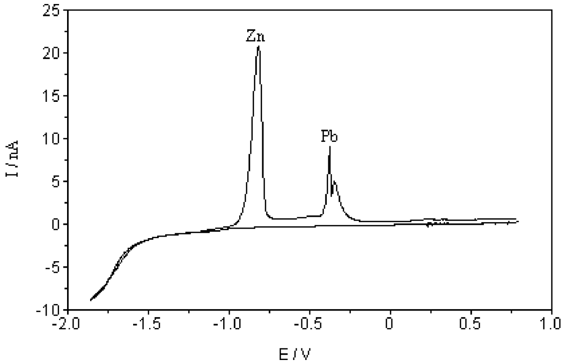

Figure 2. Cyclic voltammograms of a mixed metal oxide matrix dissolved in a 2:1 urea/choline chloride mixture on a Pt microelectrode at 60 °C.

Figure 2 shows the cyclic voltammogram of the eutectic mixture following the dissolution of the mixed metal oxide matrix. The deposition characteristics are different from those of the pure metal oxides, suggesting that some alloy formation occurs. This is corroborated by the appearance of a third peak on the anodic sweep (cf. Zn and Pb data in Figure 1), which is presumed to be due to the stripping of the alloy. The eutectic solution was electrolyzed for 1 h at a current density of 10 mA cm^{-2}. A dull gray metallic deposit was obtained and was found to contain principally zinc with a small amount of lead and traces of chloride by energy-dispersive X-ray analysis. The current efficiency of the electrowinning process was extremely high ($>95\%$), considerably better than that from aqueous solutions because unlike water there is no electrolysis of the deep eutectic solvent at these potentials. This demonstrates that metals can be effectively recovered from a mixed metal oxide matrix.

Experimental Procedure. Choline chloride ($HOC_2H_4N(CH_3)_3^+\ Cl^-$, ChCl; Aldrich, 99%) was recrystallized from absolute ethanol, filtered, and dried under vacuum. Urea (Aldrich, $>99\%$) was dried under vacuum prior to use. The eutectic mixtures were formed by stirring the two components together at 100 °C until a homogeneous, colorless liquid formed. No trace metal impurities were detectable, and the water content of the liquids was typically less than 500 ppm. The metal solubility was determined by placing an excess of the metal oxide in the solvent for 2 days at 60 °C. The solution was filtered, diluted with 0.1 N HCl, and analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES). Voltammetry was carried out using an Autolab PGSTAT12 potentiostat controlled with GPES software. A three-electrode system consisting of a platinum microelectrode (area $= 7.9 \times 10^{-7}$ cm^2), a platinum counter electrode, and a silver wire pseudoreference electrode was used. The working electrode was polished with 0.3-μm alumina paste, rinsed, and dried prior to all measurements. All voltammograms were performed at 60 °C with a scan rate of 20 mV s^{-1}.

Acknowledgment. The authors acknowledge Scionix Ltd. and the DTI for funding this work.

IC0505450