# Solubility of Metal Oxides in Deep Eutectic Solvents Based on Choline Chloride

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The solubility of 17 commonly available metal oxides in the elemental mass series Ti through Zn have been determined in three ionic liquids based on choline chloride. The hydrogen bond donors used were urea, malonic acid, and ethylene glycol. The results obtained are compared with aqueous solutions of HCl and NaCl. Some correlation is observed between the solubility in the deep eutectic solvents and that in aqueous solutions but some significant exceptions offer an opportunity for novel solvato-metallurgical processes.

## Introduction

Hydrometallurgy is the cornerstone of many metal extraction processes. Aqueous acids or alkalis are predominantly used to dissolve the metal oxides, sulfides, or silicates. Electrowinning and solvent extraction are frequently used to recover and concentrate the metals. A limited number of high-temperature molten salts have also been used extensively for the recovery of refractory metals, such as titanium and aluminum, from their ores.[1,2] Preliminary studies have shown that ambient temperature ionic liquids have potential as solvents for metal recovery, and the feasibility of these solvents has been demonstrated for the extraction of gold and silver from a mineral matrix[3] and 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.[5−7] However, given the cost and sustainability of many of these imidazolium-based ionic liquids, simpler alternatives will be necessary for large-scale applications.

An alternative approach has been to take simple quaternary ammonium salts and make a complex anion in situ by mixing it with a metal salt,[8] a hydrated metal salt,[9] or simple hydrogen bond donors such as amides[10] and carboxylic acids.[11] These mixtures form eutectics where the depression of freezing point can be up to 200 °C. The mixtures have been shown to have similar solvent properties to ionic liquids with discrete anions. To distinguish them, the term deep eutectic solvents (DESs) has been coined. These liquids have high conductivities, viscosities, and surface tensions. The fact that some of the hydrogen bond donors are common bulk commodity chemicals such as urea and oxalic acid gives them the potential for large-scale applications.

The chemistry of metal oxide complexes in low-temperature ionic liquids has received little attention. However, several authors have investigated uranium oxo species in chloroaluminate melts.[12−14] Dai et al. determined the solubility of $UO_3$ in imidalozium-based chloroaluminate melts to be ≤ 24.58 mmol at 65 °C.[12] Bell et al. have studied the dissolution of $V_2O_5$ in (Emim) chloroaluminate ionic liquids.[15] The oxide was found to be very soluble in the basic melt, 0.15 g in 1 g, but also soluble in the neutral melt. The authors report that $V_2O_5$ reacts with the acidic chloroaluminate melt forming a volatile $VOCl_3$ compound. A key finding in their report is the lack of any solubility of $V_2O_5$ in neutral ionic liquids such as $(Bmim)(BF_4)$ and $(Bmim)(CF_3SO_3)$.[15] This signifies the need for a suitably strong coordinating anion to be present for the complexation of the metal oxide to form a soluble species.

We have recently shown that low-temperature chloride eutectics demonstrate high solubilities for a wide range of solutes including metal oxides.[10,11] In this paper, we report a systematic study of the transition metal oxides of Period 4 in three different DESs and compare the solubility of the oxides with those found in aqueous solutions. The differences in solubilities are discussed in terms of the metal speciation.

## Experimental Section

Choline chloride ($HOC_2H_4N(CH_3)_3{}^+Cl^-$) (ChCl) (Aldrich 99 %) was recrystallized from absolute ethanol, filtered, and dried under vacuum. Urea and malonic acid (both Aldrich > 99 %) were dried under vacuum prior to use. Ethylene glycol (EG) (Aldrich 99+ %) was used as received. The eutectic mixtures were formed by stirring the two components together at 100 °C until a homogeneous, colorless liquid formed. The molar ratios for the eutectic compositions were found to be 2:1 for urea or ethylene glycol with choline chloride whereas for malonic acid it is a 1:1 mixture. Metal solubility was determined by placing 0.1 g of the metal oxide (various sources all > 98 %) in 5 mL of the DES for 2 days at 50 °C. The solution was filtered at 50 °C, diluted with 0.1 N HCl, and analyzed using a JY Ultima 2 inductively coupled plasma-atomic emission spectrometer (ICP-AES). Metal solubility measurements for the metal oxides in the aqueous solutions were carried out by stirring 0.1 g of the metal oxide in 5 mL each of 0.181 $mol \cdot dm^{-3}$ NaCl and 3.14 $mol \cdot dm^{-3}$ HCl for 2 days at 50 °C. For comparison, the acid concentrations in the malonic acid eutectics was 4.91 $mol \cdot dm^{-3}$.

## Results and Discussions

Table 1 shows that for most metal oxides the solubility is in the order HCl > malonic acid > urea > NaCl > ethylene glycol. Higher solubility is observed with the more ionic oxides such as ZnO in an analogous manner to that expected for aqueous acidic solutions. More covalent oxides such as $TiO_2$ exhibit negligible solubility. Table 1 also reports the data for the solubility of a limited number of metal oxides in ChCl:2 urea eutectic at 70 °C, and it can be seen that the trends in metal oxide solubility for the four metal oxides are in proportion to

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**Table 1. Solubility of Metal Oxides in Eutectic Mixtures of ChCl with Malonic Acid (1:1), Urea (1:2), and Ethylene Glycol (1:2) Compared to the Solubilities in Aqueous 0.181 mol·dm$^{-3}$ NaCl and 3.14 mol·dm$^{-3}$ HCl after 2 Days**[a]

| MO | malonic acid | urea | ethylene glycol | NaCl | HCl | urea |
|---|---|---|---|---|---|---|
| $TiO_2$ | 4 | 0.5 | 0.8 | 0.8 | 36 | |
| $V_2O_3$ | 365 | 148 | 142 | 3616 | 4686 | |
| $V_2O_5$ | 5809 | 4593 | 131 | 479 | 10995 | |
| $Cr_2O_3$ | 4 | 3 | 2 | 13 | 17 | |
| $CrO_3$ | 6415 | 10840 | 7 | 12069 | 2658 | |
| MnO | 6816 | 0 | 12 | 0 | 28124 | |
| $Mn_2O_3$ | 5380 | 0 | 7.5 | 0 | 25962 | |
| $MnO_2$ | 114 | 0.6 | 0.6 | 0 | 4445 | |
| FeO | 5010 | 0.3 | 2 | 2.8 | 27053 | |
| $Fe_2O_3$ | 376 | 0 | 0.7 | 11.7 | 10523 | 3.7 |
| $Fe_3O_4$ | 2314 | 6.7 | 15 | 4.5 | 22403 | |
| CoO | 3626 | 13.6 | 16 | 22 | 166260 | |
| $Co_3O_4$ | 5992 | 30 | 18.6 | 4.0 | 142865 | |
| NiO | 151 | 5 | 9.0 | 3.3 | 6109 | 21 |
| $Cu_2O$ | 18337 | 219 | 394 | 0.1 | 53942 | 22888 |
| CuO | 14008 | 4.8 | 4.6 | 0.1 | 52047 | 234 |
| ZnO | 16217 | 1894 | 469 | 5.9 | 63896 | 90019 |

[a] Solubilities/ppm were measured at 50 °C except for last column, which was obtained at 70 °C.

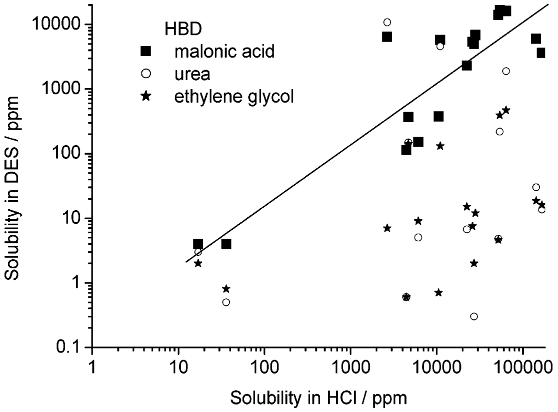

**Figure 1.** Correlation between the solubility of a variety of metal oxides in three deep eutectic solvents and the solubility in 3.14 mol·dm$^{-3}$ HCl(aq) after equilibration for 2 days at 50 °C.

those at 50 °C. It is also evident that the solubility exhibits strong temperature dependence particularly for $Cu_2O$ and ZnO.

Figure 1 shows the correlation between the solubility of a variety of metal oxides in the three deep eutectic solvents and the solubility in 3.14 mol·dm$^{-3}$ HCl after equilibration of the oxide for 2 days at 50 °C. The concentration of aqueous acid was chosen to have a similar $H^+$ concentration as that in the malonic acid eutectic although it is clearly recognized that the activity of $H^+$ is different in the two liquids. The solubility of the oxides in the ChCl:malonic acid eutectic correlate well with those in aqueous HCl. The solubility of the oxides does not however correlate with those in aqueous NaCl solution (not shown), indicating that it is not related purely to the presence of $Cl^-$. The higher solubility of the oxides in HCl and the malonic acid eutectic compared to the other liquids is presumably because the protons act as an oxygen acceptor and change the complex formed.

We have previously shown that in the case of ZnO dissolving in the ChCl:2urea eutectic, the complex $[ZnClO.(urea)]^-$ forms (i.e., the oxygen remains bound to the metal).[16] FAB-MS was carried out on the eutectic samples shown in Table 1. It was only in cases where the metal oxides exhibited high solubility that complexes could be identified; hence, none were identified in the glycol-based liquid. No metal-containing cationic species were identified, and the anionic species that were identified are listed in Table 2. In the malonic acid-based eutectics CuO, $Cu_2O$, MnO, and ZnO gave predominantly chlorometalate species of the form $MCl_x^-$. This supports the idea that the protons act as an oxygen acceptor. The metals that exhibit higher solubilities tend to have less oxygen attached to the metal center; therefore, it is assumed that the oxygens are more basic in these complexes. Most of the complexes identified in Table 2 have incomplete coordination shells, and it is unlikely that this would be the case in a liquid containing strong ligands such as urea. Signals from the acids, amides, and alcohols coordinated to the metals are rarely detected using FAB-MS. It is only with zinc that evidence of amide binding has been observed. In aqueous solutions, water molecules will act as good ligands for the metal centers and will certainly contribute to the high solubility shown in Table 1.

**Table 2. Complex Anions Detected Using FAB-MS**

| hydrogen bond donor | metal oxide | complex anion |
|---|---|---|
| urea | $V_2O_5$ | $VO_2Cl_2$ |
| | $CrO_3$ | $CrO_2Cl_3$ |
| | ZnO | ZnOCl·urea |
| malonic acid | $CrO_3$ | $CrO_2Cl_3$ |
| | MnO | $MnCl_3$ |
| | $Cu_2O$ | $CuCl_2$ |
| | CuO | $CuCl_3$ |
| | ZnO | $ZnCl_3$ |

Very few studies have attempted to model the solubility of metal oxides due in part to the issue of speciation. Shin et al.[17] used modified solution theory to predict the solubility of a range of inorganic compounds in supercritical water. It was shown that the solubility of a solid solute is described by the expression

$$\ln \gamma = \frac{\Delta H_2^{\mathrm{m}}}{RT}\left(\frac{T}{T_2^{\mathrm{m}}} - 1\right) - \frac{\upsilon_2}{RT}(\delta_1 - \delta_2)\left(1 + \frac{\upsilon_2}{\upsilon_1}\right)\ln\frac{\upsilon_2}{\upsilon_1} \qquad (1)$$

where $\Delta H_2^m$ and $T^m$ are the heats of fusion and the melting points of the solute, and $\upsilon$ and $\delta$ represent the molar volume and solubility parameters. Subscripts 1 and 2 signify the properties of the solvent and solute, respectively. With the difficulty in identifying all the solute species, prediction of $\upsilon_2$ is complicated particularly because FAB-MS rarely detects the presence of the hydrogen bond donor in the complex. Solubility parameter data are also unknown in these types of solvents or for these solutes. However, to a first approximation, we will assume that the solutions behave ideally since the molar volume of the solute could be assumed to be constant; hence, eq 1 can be expressed as

$$\ln \gamma = \frac{\Delta H_2^{\mathrm{m}}}{RT}\left(\left(\frac{T}{T_2^{\mathrm{m}}}\right) - 1\right) + \text{constant} \qquad (2)$$

This is clearly an oversimplification; however, a plot of eq 2 for the data in Table 1 (where $\Delta H_2^{\mathrm{m}}$ is known) (Figure 2) shows that sufficient correlation is still obtained for the malonic acid eutectic and the HCl solution such that it can be predicted whether the metal oxide will exhibit significant or negligible solubility.

An alternative empirical approach is to assume that the stability of the metal oxide and, hence, its reticence to dissolve is related to the charge density of the metal. Figure 3 shows a plot of solubility of the metal oxides in the malonic acid eutectic versus $z/r^3$ where $z$ is the charge on the metal and $\mathbf{r}$ is the crystal ionic radius. Relatively good correlation is observed ($R = -0.601$) with two significant exceptions: $V_2O_5$ and $CrO_3$. These

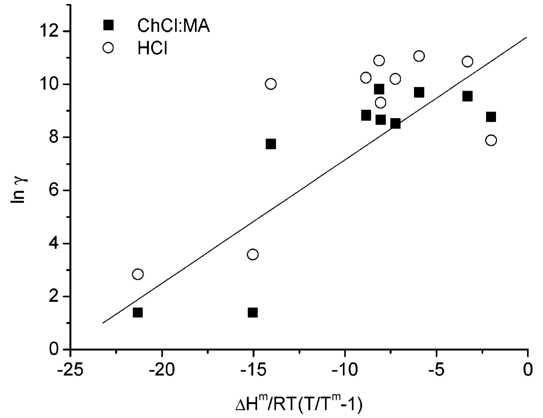

**Figure 2.** Fit of data in Table 1 to eq 2 for the solubility of a variety of metal oxides in the malonic acid deep eutectic solvent and the solubility in 3.14 mol·dm$^{-3}$ HCl(aq). $\Delta H_2^m$ and $T^m$ data obtained from ref 18.

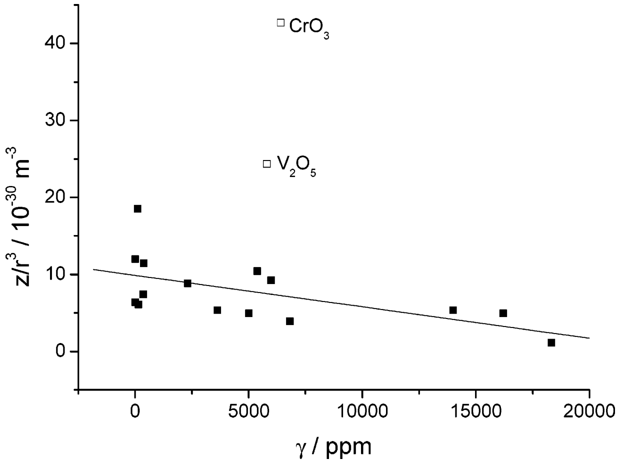

**Figure 3.** Correlation between the solubility of a variety of metal oxides in the malonic acid deep eutectic solvent and the charge density on the metal. *r* data obtained from ref 18.

two metals are strong oxidizing agents and could be reduced in the dissolution process; however, this is not likely as the colors of the two solutions are characteristic of the metals in their V and VI oxidation states, respectively. The FAB-MS data show some signals that could arise from species with these oxidation states.

Almost no correlation is observed for the data obtained with the urea and ethylene glycol based eutectics. It is assumed that the major contributory factor is the difference in speciation caused by the protons acting as good oxygen acceptors. Hence for metals with lower oxidation states (I and II), dissolution of the metal oxides tend to produce halo-metalate anions in malonic acid based eutectics. We assume the same will be true of other DESs using carboxylic acid based hydrogen bond donors.[11] However, preliminary results using ZnO, CuO, and $Fe_3O_4$ in malonic acid, oxalic acid, and phenylpropionic acid showed[11] that the solubility of the oxides could be varied significantly using different carboxylic acids. This could be achieved to such an extent that the relative solubility ratios could be inverted (e.g., using oxalic acid $\gamma(ZnO)/\gamma(Fe_2O_3) = 0.21$ whereas using phenylpropionic acid $\gamma(ZnO)/\gamma(Fe_2O_3) = 33.8$). This suggests that the hydrogen bond donor does play a significant part in solvation of the complex, although this cannot be observed using FAB-MS alone.

## Conclusions

Malonic acid based DESs exhibit higher solubility than the corresponding liquids based on urea and ethylene glycol. This is thought to originate from the protons acting as good oxygen acceptors and leading to chlorometalate species. Good correlation is observed between the solubility of metal oxides in the malonic acid based eutectics and aqueous HCl solutions.

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