

## SHORT COMMUNICATION

## *II. A potentiometric study of alumina solubility and the influence of complexing by fluoride ions in LiCl-KCl*

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### 1. Introduction

The work described in this short communication formed part of a preliminary study of the chemistry and electrochemistry of the compounds of the component elements of the mineral chromite in molten LiCl-KCl, which preceded the attempted model separation of the oxides corresponding to the main components of the mineral [1]. Chemical and electrochemical studies concerning chromium [2] and iron [3] have already been reported. After chromium and iron, aluminium is the third most important element in the spinel chromite. Thus a potentiometric technique has been used to study the solubility of  $\text{Al}_2\text{O}_3$  and the influence of the complexing of Al(III) by fluoride ions in LiCl-KCl.

### 2. Experimental

The apparatus and the procedure have been described in detail elsewhere [4]. Measurements were carried out in the temperature range  $400^\circ\text{C}$ – $500^\circ\text{C}$ .

### 3. Results and discussion

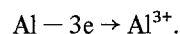
#### 3.1. Overall electrode process

Aluminium ions were introduced into the LiCl-KCl eutectic at  $500^\circ\text{C}$  by the anodic dissolution of an aluminium electrode at a current density of  $10^{-2}\text{ A cm}^{-2}$ . The equilibrium potentials of the

aluminium electrode were measured versus an Ag/Ag(I) ( $0.1\text{ mol l}^{-1}$ ) reference electrode as a function of the concentration of Al(III). The corresponding Nernst plot is shown in Fig. 1. The equation describing this plot is

$$E = -0.895 + 0.050 \log [\text{Al(III)}].$$

The slope ( $0.050\text{ V}$ ) corresponds to a mean ' $n$ ' value of 3.04. This is consistent with an anodic dissolution process



#### 3.2. Fluoro-complexes

Additions of fluoride ions to a melt containing  $2.019 \times 10^{-2}\text{ mol l}^{-1}$  of aluminium ions, led to large changes in the Al/Al(III) equilibrium potential (see Fig. 2) due to the strong complexing of aluminium ions by fluoride ions. This complexing may be quantified by  $\log F_0/\log [\text{F}^-]$  plots, the final limiting slopes (in this case the whole plot) of which should equal  $\bar{n}$ , the maximum coordination number for the fluoride ions. The actual plot (Fig. 3), in which the function  $F_0$  is defined as the ratio of the total (stoichiometric) aluminium ion concentration to the free (uncomplexed by fluoride ions, i.e. coordinated by chloride ions) aluminium ion concentration, is a straight line of slope 4.6. Therefore the most likely numbers of fluoride ions associated with aluminium ions (albeit probably along with one or two chloride ions) are four or five, corresponding

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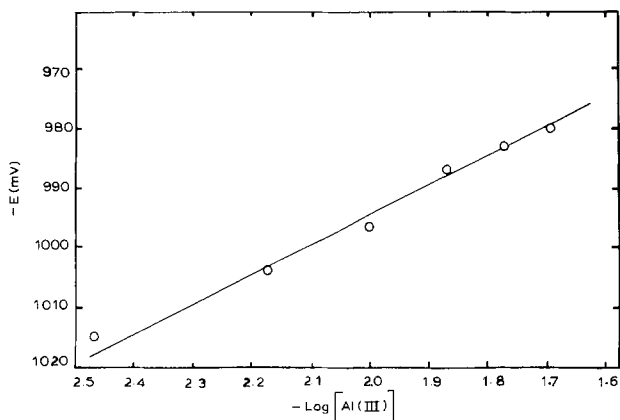


Fig. 1. Nernst plot for Al(III) ions in LiCl-KCl eutectic;  $[\text{Al(III)}]$  in  $\text{mol l}^{-1}$ ,  $E$  (mV) measured versus Ag/Ag(I) reference electrode.

to such species as, for example,  $\text{AlF}_4\text{Cl}_2^{3-}$  or  $\text{AlF}_5\text{Cl}^{3-}$ .

### 3.3. Solubility of alumina and the influence of fluoride ions

In order to determine the solubility of alumina in melts containing fluoride ions, the stoichiometric quantities of oxide ions (as  $\text{Li}_2\text{O}$ ) to react with all the aluminium ions in solution to give  $\text{Al}_2\text{O}_3$ , were added. This procedure was repeated at four different concentrations of fluoride at a total Al(III) concentration of  $2.019 \times 10^{-2} \text{ mol l}^{-1}$ . The concentration of aluminium ions left in solution after the oxide addition was calculated from

the equation

$$E = \frac{2.303 RT}{nF} \log \frac{[\text{Al(III)}]_t}{[\text{Al(III)}]_f}$$

where  $\Delta E$  is the difference between the aluminium electrode potentials before and after an oxide addition at a determined fluoride ion concentration.  $[\text{Al(III)}]_t$  represents the total concentration of aluminium ion-containing species in solution before the addition of oxide ions and  $[\text{Al(III)}]_f$  represents the concentration of these species in solution after the addition of oxide ions. The alumina solubility was calculated as  $0.5 [\text{Al(III)}]_f$ , on the basis of the equilibrium

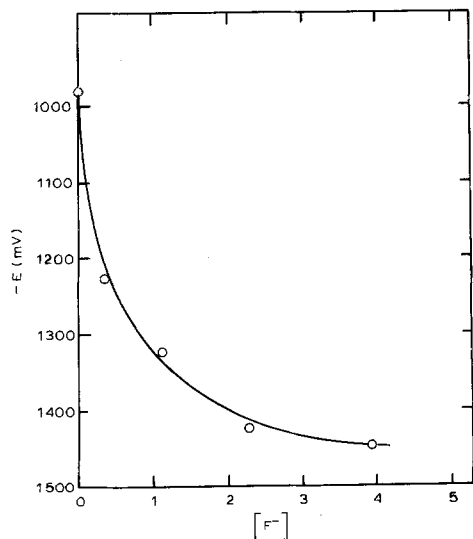
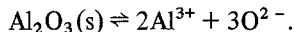


Fig. 2. Plot of electrode potential versus  $[\text{F}^-]$  for Al(III) ions in LiCl-KCl eutectic.  $[\text{Al(III)}] = 2.019 \times 10^{-2} \text{ mol l}^{-1}$ .

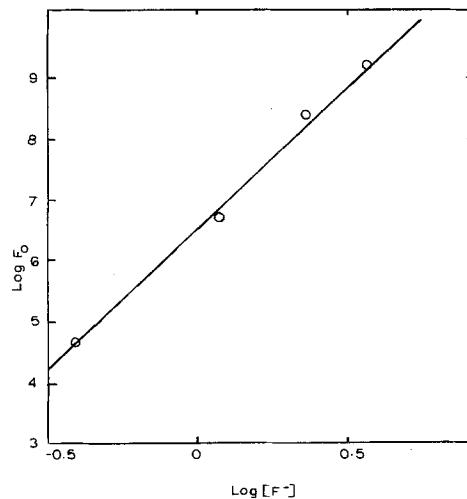


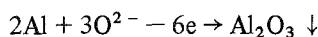
Fig. 3. Plot of  $\log F_0$  versus  $\log [\text{F}^-]$  for Al(III) ions in LiCl-KCl eutectic.  $[\text{F}^-]$  in  $\text{mol l}^{-1}$ .

Table 1. Solubility of alumina in LiCl–KCl eutectic at 500°C and 550°C where  $[Al(III)]_t = 2.019 \times 10^{-2} \text{ mol l}^{-1}$ . Concentration of  $O^{2-}$  ions =  $[Al(III)]_t \times 3/2$

$F^-$ concentration ( $\text{mol l}^{-1}$ )	500°C		550°C	
	$-E_{eq}^*$ (V)	$Al_2O_3$ solubility ( $\text{mol l}^{-1}$ )	$-E_{eq}^*$ (V)	$Al_2O_3$ solubility ( $\text{mol l}^{-1}$ )
0.39	1.228	$5.67 \times 10^{-5}$		
1.17	1.311	$1.25 \times 10^{-3}$		
2.32	1.423	$7.30 \times 10^{-3}$	1.378	$4.3 \times 10^{-3}$
3.86	1.465	$8.40 \times 10^{-3}$	1.440	$4.9 \times 10^{-3}$

\* Equilibrium potential Al(III)–Al(0) in the melt containing fluoride before the addition of  $Li_2O$ .

The potential of the aluminium electrode used as the indicating electrode tends to go more anodic with increasing time at low concentrations of fluoride ions, probably because of electrochemical oxidation, namely



balanced by some conjugate cathodic reaction. (The potential of the aluminium electrode will be more positive in this case.)

The (more negative) potentials become steadier at higher fluoride ion concentrations. For these

reasons, very low fluoride ion concentrations were avoided and at the lower concentrations studied ( $0.39 \text{ mol l}^{-1}$ ), the electrode potential was determined during a short immersion of the indicating electrode in the melt. This was not necessary at the higher concentrations. Table 1 shows the values found for the solubility of alumina at different fluoride ion concentrations and at different temperatures.

These results show clearly that the solubility of alumina is increased by the addition of fluoride ions. From a plot of the logarithm of the solubility of alumina versus the concentration of fluoride ions (Fig. 4), extrapolated to 0, the solubility of alumina in pure LiCl–KCl at 500°C is estimated to be around  $3 \times 10^{-6} \text{ mol l}^{-1}$ . This result is somewhat higher than that of Arthur [5] ( $0.7 \times 10^{-6} \text{ mol l}^{-1}$ ) for the same melt at the same temperature. The latter employed an indicating electrode of the second kind (responsive to oxide ions), but only in the pure chloride melt.

Table 1 also shows that the solubility of alumina decreases with increase in temperature. This effect is to be expected if the complexing of Al(III) ions by fluoride is the main factor controlling the solubility of alumina. The fluoro-complexes of aluminium found in solution become less stable as the temperature increases and the Al(III) ions are thus more available to form  $Al_2O_3$ .

Another effect observed was that the complexing by fluoride ions tended to reach a limit as their concentration was increased, as shown by the equilibrium potential measurements (Fig. 2). As a consequence of this, the solubility of alumina also seemed to reach a limit with increasing

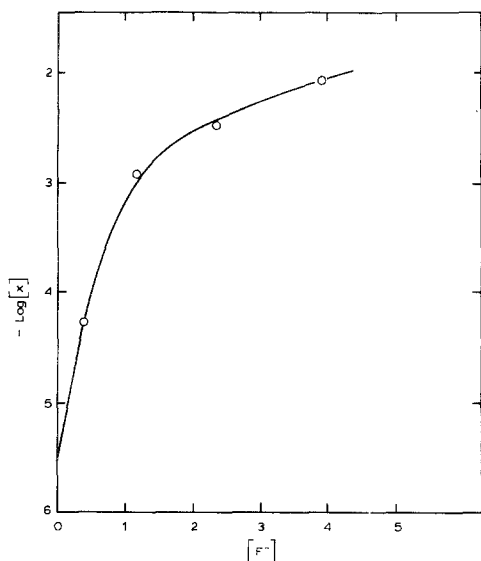


Fig. 4. Solubility of alumina in LiCl–KCl eutectic containing fluoride ions;  $[x]$  = solubility in  $\text{mol l}^{-1}$ ,  $[F^-]$  in  $\text{mol l}^{-1}$ .

fluoride ion concentrations (Fig. 4). A similar effect was found by Jordan and Milner [6], who studied the removal of oxide films from aluminium in LiCl–KCl–NaCl mixtures containing different concentrations of NaF. They showed that the equilibrium potential of aluminium in the system studied changed as the fluoride concentration was increased up to approximately 12% wt% NaF (approximately  $4.5 \text{ mol l}^{-1}$  of  $\text{F}^-$ ) after which it remained constant.

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## References

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