

Determination of the Stability of the AlO^+ Complex in Alkali Halide Melts*

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The solubilities of $\text{Al}_2^{18}\text{O}_3$ in LiCl-KCl eutectic mixtures containing dissolved AlCl_3 were measured using a sensitive proton activation technique. The results are consistent with the presence of an AlO^+ species at 4.7×10^{-5} mole fraction with AlCl_3 at 10^{-2} mole fraction. When combined with other thermodynamic data, these solubilities are used to deduce a formation constant for the AlO^+ species from Al^{3+} and O^{2-} ions of 1.94×10^{22} (in mole fraction units) and a specific bond free energy ("bond strength") of 300 kJ mol^{-1} .

Introduction

Formation of coulomb complexes between polyvalent ions and oxide or sulfide ions in molten salt solution has been discussed in recent papers [1, 2]. Coulomb complexing may be responsible for the solubilization of Al_2O_3 by AlCl_3 in LiCl-KCl eutectic melt observed in a preliminary study [2]. However, quantitative information concerning the dissolved oxide species could not be obtained in the previous study by visual observation because of the small solubility of Al_2O_3 at the specific temperature of the experiment. In order to study the degree of coulomb complexing quantitatively, it is essential to have a sensitive and reliable analytical method of measuring dissolved oxides in molten salts. The accurate determination of small amounts of dissolved oxides in hygroscopic halide melts is generally difficult because of the reactive nature of the solvent. Haupin measured the solubility of Al_2O_3 in LiCl- AlCl_3 melts by the $^{16}\text{O}(\text{n}, \text{p})^{16}\text{N}$ reaction utilizing a fast neutron source available at the Oak Ridge National Laboratory [3]. However, the blank in Haupin's study showed an average of 0.051% of ^{16}O indicating that a significant amount of moisture was inevitably involved in his experiments. This level of contamination would limit the detection of

dissolved oxide in the salt to approximately 10^{-3} mole fraction. We have recently used a proton activation process utilizing the $^{18}\text{O}(\text{p}, \text{n})^{18}\text{F}$ reaction to measure dissolved oxide in LiCl-KCl eutectic melt. Using ^{18}O labeled Al_2O_3 in our experiments, we were able to measure the dissolved ^{18}O in the melt at 10^{-5} mole fraction. The analytical technique and the formation of AlO^+ complex from the reaction of Al^{3+} and Al_2O_3 in LiCl-KCl eutectic melt are described in this note. In addition, we calculate the formation constant of AlO^+ species from solvated Al^{3+} and O^{2-} ions and use this to deduce a "specific bond free energy" for the AlO^+ complex.

Experimental

Polarographic grade LiCl-KCl (58 mol%-LiCl) eutectic and KAlCl_4 were obtained from Anderson Physics Laboratory, Inc. (Urbana, Illinois). These chemicals were supplied in sealed glass ampules under inert atmosphere, and were used without purification. ^{18}O labeled Al_2O_3 (enriched to 89.3% ^{18}O) was purchased from Stohler Chemicals Isotope. The labeled Al_2O_3 was heated in a vacuum oven at 450°C for six hours before the experiment. X-ray diffraction patterns of the heated oxide indicated that the major phases present were δ and γ alumina.

The experiments were carried out in a helium filled glove box with a furnace well attached to the bottom of the box. The glove box atmosphere was continuously circulated through a purifier, and the oxygen and water content were kept below 5 ppm. In each experiment, a 40 gram charge of anhydrous LiCl-KCl eutectic was melted in a quartz tube of

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one-inch ID and 18-inch in length heated at 450°C . About 100 mg of the labeled Al_2O_3 was added to the melt. A blank sample was taken after Al_2O_3 settled to the bottom. Less than 1 mole percent of KAlCl_4 was then added to the system and the melt was continuously stirred with a quartz rod. The system was heated at 450°C for at least 15 hours. Stirring was stopped about an hour before sampling to allow Al_2O_3 to settle to the bottom. Tests based on visual observation indicated that particulates in suspension had all settled to the bottom after this period of waiting. Bath samples were then taken with a quartz spoon for chemical analysis. The concentration of Al^{3+} in each sample was determined by inductively coupled plasma – atomic emission spectrometry.

For proton activation analysis of ^{18}O , samples were ground and homogenized with a mortar and pestle. The ground materials were made into pellets of 0.5-inch diameter and approximately 2 to 3 mm in thickness using a Parr pellet maker. The sample pellets were placed in aluminum discs of 0.51-inch ID and 0.25-inch depth and then sealed with aluminum foil of 10 mil thickness using a small amount of super glue. The sealed discs were transported from the dry box to a nearby cyclotron in a He filled container for proton irradiation. A 60-inch cyclotron which accelerated protons to an energy of about 10.5 MeV was used for sample irradiation. The actual energy of the protons bombarding the sample surface was reduced to about 8 MeV after penetrating through 0.01 inch of aluminum foil. At this energy, protons were totally absorbed by the sample pellet. Each sample was irradiated with a total charge of 300 microcoulomb from a proton beam of 0.5 microampere. After irradiation, samples were removed from the sealed discs and dissolved in 5 ml of 4 M HCl. the radioactive ^{18}F produced in the sample was precipitated in the form of LaF_3 by the addition of LaCl_3 and NH_4F -HF to the acid solution. The solubility of LaF_3 in the acid solution is extremely small at 25°C and, hence, ^{18}F can be separated from other positron emitters produced in the system [4]. The fluoride precipitate was separated from the solution by centrifugation and was counted with a $\text{Ge}(\text{Li})$ detector connected to a 4096 multi-channel analyzer. The 511 keV positron annihilation radiation from the decay of ^{18}F was used to measure ^{18}F activities in the precipitate.

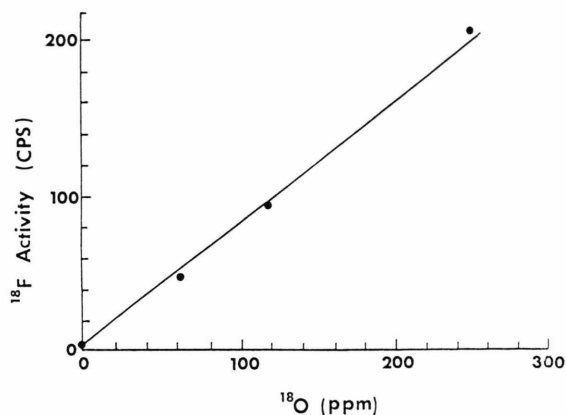


Fig. 1. Plot of ^{18}F activities (counts per second) in LaF_3 precipitate versus spiked ^{18}O concentrations in LiCl - KCl eutectic melt.

The concentration of ^{18}O was determined by comparing the activity of ^{18}F in a sample with a set of standards irradiated under the same conditions. Standards were prepared by mixing ^{18}O labeled Al_2O_3 in molten LiCl - KCl eutectic with vigorous stirring and samples were taken while Al_2O_3 was in suspension in the molten solution. A typical calibration curve obtained from standards with ^{18}O concentrations varying from 63 to 250 ppm is shown in Figure 1. A linear relationship was observed between the spiked ^{18}O concentrations and the ^{18}F activities found in the irradiated samples. The blank showed about 2.5 ppm of ^{18}O which is equivalent to a mole fraction of 7.7×10^{-6} . With this level of blank, the proton activation technique described in this note should be able to detect ^{18}O in LiCl - KCl eutectic melt at 10^{-5} mole fraction.

Results and Discussion

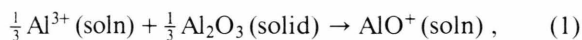
The solubility of AlCl_3 in LiCl - KCl eutectic melt at 450°C is about one mole percent, above which an immiscible phase begins to form [5]. Our study was carried out at 450°C with an AlCl_3 mole fraction of less than one percent so that this immiscible phase would not be involved in our experiments. Because the experiments were performed in open tubes, some AlCl_3 in the melt might be lost due to volatilization. Therefore, the actual mole fraction of Al^{3+} in the salt solution was determined by atomic emission spectroscopy as described in the experimental section. According to our experiments, the amount of dissolved ^{18}O in the salt solution

Table 1. Mole fraction of dissolved ^{18}O (X_{O}) as a function of X_{AlCl_3} in LiCl-KCl eutectic melt at 450°C .

X_{Al}	$(X_{\text{Al}})^{1/3}$	X_{O}^a
1.25×10^{-3}	0.108	2.0×10^{-5}
3.32×10^{-3}	0.149	2.7×10^{-5}
7.70×10^{-3}	0.197	4.2×10^{-5}

^a After subtraction of blank.

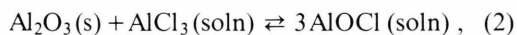
increases with the mole fraction of AlCl_3 present in the system as can be seen from the data in Table 1. If Al^{3+} reacts with Al_2O_3 to form an AlO^+ complex according to the equation



then the concentration of the complex should increase linearly with the cube root of the concentration of Al^{3+} in the solution if the AlO^+ species obeys Henry's law. A plot of the mole fraction of dissolved ^{18}O versus the cube root of the concentration (in mole fraction units) of Al^{3+} in the solution is shown in Figure 2. A linear relationship is observed indicating that the experimental data are consistent with the formation of an AlO^+ complex in the system. The mole fraction of dissolved oxide extrapolated to one mole percent of AlCl_3 in solution is about 4.7×10^{-5} , according to Figure 3. This concentration of dissolved oxide in LiCl-KCl eutectic melt is probably too low for spectroscopic studies and is considerably smaller than a preliminary value reported earlier [2].

Calculation of the Formation Constant of AlO^+

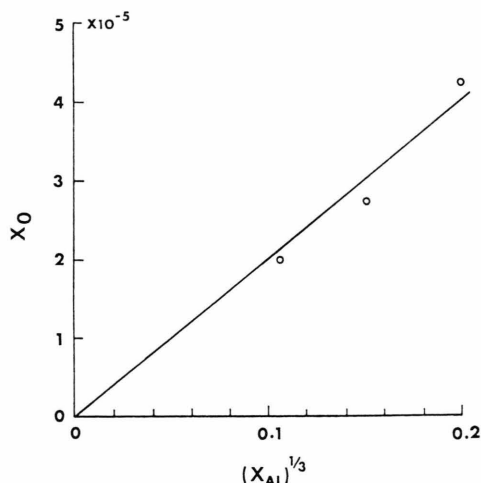
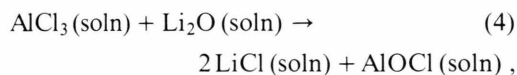
In order to deduce the formation constant of the AlO^+ species from Al^{3+} and O^{2-} ions, we first deduce the standard free energy of formation of AlOCl in solution from the equilibrium constant, K , for reaction (1) rewritten in terms of



(which is 1.04×10^{-11} in mole fraction units) and the standard free energies of formation of solid Al_2O_3 [6] and AlCl_3 in solution [7]. The AlO^+ formation reaction from the constituent ions in solution can be written in two equivalent representations:



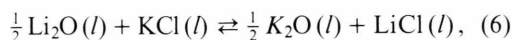
and

Fig. 2. Plot of mole fraction of dissolved ^{18}O versus cube root of mole fractions of Al^{3+} in LiCl-KCl eutectic at 450°C .

where reaction (4) is equivalent to reaction (3) when the AlCl_3 , Li_2O and AlOCl are dilute and obey Henry's law. To calculate the equilibrium constant for reaction (4), we require a knowledge of the "standard" free energies of formation of LiCl and Li_2O in solution in the LiCl-KCl eutectic melt. For LiCl, this quantity is given by $\mu_{\text{LiCl}}^0 + RT \ln X_{\text{LiCl}} \gamma_{\text{LiCl}}$ where μ_{LiCl}^0 is the standard free energy of formation of liquid LiCl [6], X_{LiCl} is 0.582 and γ_{LiCl} can be calculated from data given by Lumsden [8]. For Li_2O this quantity is given by $\mu_{\text{Li}_2\text{O}}^0 + RT \ln X_{\text{Li}_2\text{O}}^2 \gamma_{\text{Li}_2\text{O}}$ where $\mu_{\text{Li}_2\text{O}}^0$ is the standard free energy of formation of liquid Li_2O and $\ln \gamma_{\text{Li}_2\text{O}}$ can be calculated from the equation [9]

$$\begin{aligned} RT \ln \gamma_{\text{Li}_2\text{O}} = 2X_{\text{K}} \Delta G^0 + 2X_{\text{K}}(X_{\text{K}} - X_{\text{Li}}) \lambda_{\text{Cl}} \\ + 2X_{\text{K}} X_{\text{Li}} \lambda_{\text{O}} + 2X_{\text{Li}} \lambda_{\text{Li}} \\ + 2X_{\text{K}} \lambda_{\text{K}} + 2X_{\text{K}} X_{\text{Li}} A, \end{aligned} \quad (5)$$

where ΔG^0 is the standard free energy change for the metathetical reaction



λ_i is the binary interaction parameter for a binary molten salt solution in which the two components each contain the ion i , $A = -(\Delta G^0)^2 / 2z RT$ and $z = 6$. ΔG^0 was calculated from data in the JANAF tables [6] using a value of $3.4 \text{ kcal mol}^{-1}$ for the free

energy of fusion of K_2O at 723 K. The value of λ_{Cl} was taken from Lumsden [8] and the value of λ_{O} , which is unknown, was assumed to be the same as λ_{Cl} . Since deviations from ideality of binary mixtures of two salts with a common cation are generally small, λ_{Li} and λ_{K} were assumed to be zero. The calculated value of $\ln \gamma_{\text{Li}_2\text{O}}$ is 6.399. The resultant equilibrium constant for reactions (3) and (4) is 1.94×10^{22} . This very large value reflects the strength of the bonding of the AlO^+ species. A measure of the strength of the bond can be deduced by calculating a "specific bond free energy", ΔA deduced from the statistical mechanical equation [10]

$$K = Z[\exp(-\Delta A/RT) - 1], \quad (7)$$

where Z is a coordination number. For $Z = 4$, ΔA is $-71.74 \text{ kcal mol}^{-1}$ ($300.15 \text{ kJ mol}^{-1}$), and for $Z = 6$, $\Delta A = -71.16 \text{ kcal mol}^{-1}$ ($297.72 \text{ kJ mol}^{-1}$). The bonding is very strong, albeit not quite as strong as indicated by our preliminary data (when ΔA was calculated as -390 kJ mol^{-1}). As we noted earlier [2], our results indicate that the bonding is less strong than deduced from a very simple coulomb calculation we discussed. This can be due to several unknown factors, including shielding by the solvent ions and quantum mechanical effects which cannot be described by the overly simple ionic pair potentials and model we used. Quantum mechanical calculations have been performed of the energetics of forming an Al-O bond in vapor molecules [11] which helps to clarify this point. It is our hope that a combination of measured values (such as is presented here) with theoretical calculations will ultimately help to deduce simple models for predicting the bond strengths of coulomb complexes.

Conclusions

We have developed a proton activation technique for the precise determination of the solubilities of

oxides in molten salts. From measurements of the solubility of Al_2O_3 , we have deduced the specific bond free energy (bond strength) of the AlO^+ species in the molten LiCl-KCl eutectic mixture (300 kJ mol^{-1} for the likely coordination number of Al^{3+} of 4). The formation constant of AlO^+ is much larger and the bond is much stronger than the same quantities for the AlS^+ species. Although this trend is consistent with the predictions of a naive version of the concept of coulomb complexing [1, 2], the magnitudes are much smaller. It is probable that effects such as charge compensation and quantum mechanical effects [1, 2] are major factors in decreasing the bond strength. Quantum mechanical studies have been performed on vapor molecules [11] and molecular dynamics calculations are planned with the aim of quantifying the means for making predictions of the strength of coulomb complexes.

This study has provided experimental evidence to support the formation of the AlO^+ complex in LiCl-KCl eutectic melts. The proton activation technique described in this note can be applied to both chloride and fluoride melts and appears to be a suitable technique for studying coulomb complexing in various solvents. Further studies in this direction are in progress.

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