Aluminum-27 NMR Study of Some AlCl₃-MCl Molten Systems

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Aluminum-27 NMR was used to investigate AlCl₃-MCl (M = Li, Na, K, Butylpyridinium) molten mixtures. In AlCl₃ rich mixtures, the ²⁷Al resonance line was resolved into two components corresponding to the AlCl₅ and Al₂Cl₇ species, which were shown to undergo chemical exchange line broadening. This broadening was found to be cation and temperature dependent.

KEY WORDS: AlCl₃-MCl molten salts; aluminum-27 NMR; Dispa technique.

1. INTRODUCTION

Application of multinuclear NMR techniques to the studies of molten salts have been rather sparse. Initial studies⁽¹⁻⁵⁾ were exploratory in nature and were limited by the low sensitivity and resolution of the early NMR spectrometers. Nevertheless, these studies clearly showed the potential utility of the NMR technique for the elucidation of mechanisms of reactions in molten salt media and of the structures of dissolved species.

One of the main problems in the study of molten salts by the multinuclear NMR technique is the obvious fact that most salts melt at several hundred degrees Celcius and, at such temperatures, NMR measurements are difficult at best. Several years ago, however, Osteryoung and co-workers⁽⁶⁾ reported that mixtures of aluminum(III) chloride and n-butylpyridinium chloride (BPCl), which contain from 40-70 mol% of AlCl₃, are liquid at room temperature; Raman study of these mixtures showed the presence of the AlCl₅ and of Al₂Cl₇ ions with the concentration of the latter species increasing with increasing

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amount of AlCl$_3$ with the concomitant decrease in the concentration of the AlCl$_2^-$ anion.

While these room temperature melts are much more amenable to NMR studies than the more familiar molten salts, the number of such studies has not been excessive. Proton and carbon-13 NMR studies were carried out by Osteryoung et al.,$^7$ by Angell and Shuppert,$^8$ and by us.$^9$ Anders and Plambeck$^{10}$ reported $^{27}$Na, $^{27}$Al, and $^{35}$Cl NMR studies in KCl-NaCl-AlCl$_3$ mixtures at 170 $^\circ$C; only a single $^{27}$Al resonance line was reported. In a recent $^{27}$Al NMR study of the AlCl$_3$-BPCl system in the 28 to 76 $^\circ$C temperature range, Gray and Maciel$^{11}$ resolved the separate resonances for the AlCl$_2^-$ and Al$_2$Cl$_7^-$ species and determined the exchange rate between the two species.

The present work is part of a detailed study of MC1-AlCl$_3$ mixtures as solvent systems for the alkali cation complexation by macroryclic polyethers. The unusual character of these media lead us to investigate some of their properties; among these, the site exchange phenomenon detected by Gray and Maciel is important. Thus far, this phenomenon has not been observed in inorganic melts.

2. EXPERIMENTAL PART

2.1. Chemicals

Aluminum chloride was distilled, in the presence of metallic aluminum, into ampules which were sealed under vacuum; $n$-butylpyridinium chloride was prepared by a method described by Osteryoung et al.;$^6$ lithium, sodium, and potassium chlorides were of reagent grade and were not purified except for drying overnight at 200 $^\circ$C under vacuum; benzene-$_d_6$ (Aldrich) was used as received.

All of the molten salt mixtures and solutions were prepared by weight in a dry-box under inert atmosphere. The samples were placed in 5 mm NMR tubes and sealed under vacuum.

3. NMR MEASUREMENTS

Most of the $^{27}$Al NMR measurements were carried out using a WM-250 Bruker spectrometer operating at 58.72 kG and a resonance frequency of 65.18 MHz. A few spectra were obtained on a WM-400 Bruker spectrometer at 93.95 kG and 104.29 MHz. Below 100 $^\circ$C an aqueous solution, 1.0 $M$ in Al(NO$_3$)$_3$ and 1.0 $M$ in HNO$_3$, was used as the external reference. The variation of the chemical shift of the refer-