Electrochemical and Spectroscopic Studies of Boron and Sulfur Species in Nonaqueous Media.

Jianzhong Liu
Louisiana State University and Agricultural & Mechanical College

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ELECTROCHEMICAL AND SPECTROSCOPIC STUDIES
OF BORON AND SULFUR SPECIES IN NONAQUEOUS MEDIA

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

By

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B.S., Hunan University, 1982
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August 1997
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are so considerate, understanding, and helpful in the adversities international students could meet in a new environment.
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ABSTRACT

Room temperature molten salts have been of interest because of their unique properties such as aprotic nature and excellent Lewis acid-base adjustability. They provide a novel medium for fundamental studies and constitute a promising electrolyte for metal plating and secondary batteries.

In the present study, the room temperature N-Butyl-pyridinium chloride (BPC)-boron trichloride (BCl₃) and mixed BCl₃-AlCl₃-BPC melts have been prepared and characterized using reaction stoichiometries, electrochemistry and secondary ion mass spectrometry (SIMS). At normal atmosphere and room temperature, even when excess BCl₃ was added, BCl₃-BPC melts have a constant composition of 52:48 mole ratio BCl₃:BPC. SIMS studies confirmed previous Raman results, that is, speciation of boron in the BCl₃-BPC melts is mainly involved in forming boron tetrachloride anion (BCl₄⁻). Polyboron species were not detected. The excess boron chloride in the melts is dissolved as molecular BCl₃. In the BCl₃ saturated chloroborate and mixed chloroborate-chloroaluminate melts, an irreversible wave has been assigned to the formation of a passive boron film. The mixed chloroborate-chloroaluminate melts cannot go beyond neutral melts since Al₂Cl₆ or acidic species such as Al₂Cl₇⁻ ion reacts with existing boron tetrachloride anion in the melt to form BCl₃ which is volatile at room temperature. Results from SIMS indicate that, aluminum chloride anions in BPC-based chloride melts are more surface active than boron chloride anions.

x

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Speciation of sulfur in nonaqueous media has been of interest for fundamental studies and secondary battery development. In an attempt to prepare organic sulfides, which could find applications for the development of room temperature organic molten salt battery electrolytes, it was found that in acetonitrile, sodium sulfide reacts very fast with BPC to form a dark brown solution. The reaction products were characterized by UV, HPLC, NMR, and GC-MS. A reaction mechanism was proposed with the initial step occurring via N-substituted pyridinyl radicals and monosulfur anion radicals. The monosulfur anion radical has not been characterized in liquid phases and this reaction provides a means for its generation and study.
CHAPTER 1
GENERAL INTRODUCTION

1.1. CONCEPT OF MOLTEN SALTS

What is a molten salt? As the name suggests, it is a salt which has been heated up and is kept at a molten state at elevated temperature. This suggestion leads to the popular conception that a molten salt is a medium very hot and, of course, very hard to handle. Indeed, most molten salt systems, especially those used in industry, are of high temperature. These high temperature molten salts are conventionally metal halides (particularly chlorides and fluorides), also nitrates, carbonates, and certain other salts with melting points between 150 and 1500°C and can be single-component (mostly of academic interest and not used in industry) or multicomponent, i.e., consist of mixtures of several salts. However, molten salts are not necessarily limited to these traditional high temperature inorganic systems. There are several classes of molten salts which are of low temperature, loosely termed “room temperature” (to be discussed later in this chapter). These molten salts have received vast interest in recent years.

A precise definition of molten salts is difficult. Traditionally, molten salts are defined as the liquid states of those substances that in the solid state possess ionic crystal lattice structures [1.1]. But this definition may exclude a very important and also popular class of molten salts which consist of alkali or
alkali-earth metal salts and AlCl₃, where the crystals are not considered to be ionic. Actually, the terminology "molten salts" has been broadened to encompass those molten phases that are neither derived from "salts", nor melt to form an ionized milieu [1.2].

It is to be noted that there are some other terms which are often alternately used to refer to molten salts. Among them, "fused" salts and "molten" salts can be considered as synonyms. Each of the rest may emphasize certain unique aspects of molten salts. "Ionic liquids" are, perhaps, used to distinguish molten salts from those molecular solvents such as water and organic solvents, but this term is also used to refer to slags which consist of metal oxides and nonmetal oxides with melting points between 1200 and 2500°C and are usually discussed separately. "Ionically conducting melts" may emphasize that the temptation to ascribe the high conductance of molten salts to conduction by electrons should be rejected. "Pure liquid electrolytes" may emphasize the limiting case of zero solvent, that is, no solvents are involved to obtain electrolyte medium. Because the most widely used solvent to dissociate electrolytes to obtain electrolyte media is water, molten salts are also known as a class of nonaqueous solvents. It is to be pointed out that there is a class of aqueous or hydrated molten salts that contain bound molecular solvent. Obviously, this class of molten salts are not "pure liquid electrolytes".

Unlike aqueous and organic media, in many cases, there is no obvious line of distinction among solutes, solvents and solutions in molten salts. For
example, Al$_2$O$_3$ in NaF-AlF$_3$-Al$_2$O$_3$ melt for electrochemical extraction of aluminum can be thought as a solute because the content of Al$_2$O$_3$ is about 8%, but in 45%LiCl-55%KCl molten salt for electrochemical extraction of lithium, it is not appropriate to distinguish the solvent from the solute. Usually, people simply use the term of system, or melt, or electrolyte, to refer to multi-components molten salts.

1.2. SCOPE OF MOLTEN SALTS

The wide-ranging scope of molten salts depends on their unique properties. First of all, many molten salts are of high temperature. The higher temperature of molten salt solvents can cause a very marked increase of reaction rate for both organic and inorganic reactions. Different molten salts have different stable temperature ranges and different capabilities of dissolution, which allows a wide variety of thermal reactions to proceed. Moreover, a very high temperature provides a condition to study interesting unusual chemistry of elements and compounds. Instead of the familiar oxidation numbers, for example, 3 for aluminum at low temperature, aluminum can occur in both 1 and 2 oxidation states at high temperature.

Another distinguishing property of molten salts is that they have high values of specific conductivity. For example, molten NaCl has a specific conductance that is some $10^8$ times as great as that of water and molten KCl at 800°C has a specific conductance about 22 times that of normal aqueous KCl.
solution at 20°C. These higher conductivities make the problem of iR greatly diminished. In conventional (not using microelectrodes) electrochemistry studies in aqueous or organic solutions, a Luggin capillary is needed to minimize iR drop and supporting electrolytes are added to decrease the effect of migration currents. Sometimes, selection of appropriate supporting electrolytes, especially in organic solutions, presents a problem. In industrial electrolytic processes, higher conductivities allow higher currents which in turn increase the rate of conversion of electrical energy into chemical change and vice versa. Higher conductivity can also indirectly improve other situations. For example, higher conductivity allows wider distance between the anode and the cathode in electrowinning of metals, which would decrease reoxidation of metals at the anode and hence increase current efficiency.

If a small class of hydrated molten salts are excluded, molten salts constitute a huge class of nonaqueous media. In many cases, the presence of water is a nuisance. In electrolytes of promising batteries of using sulfur as negative electrodes, homogeneous reaction between proton and sulfur species will deteriorate electrolytes by forming H₂S. In electrolytic processes, protons in aqueous solutions will compete in cathodic reaction with interested metals or alloys. For example, in electroplating Fe-Ni alloy films in aqueous solutions, the liberation of hydrogen not only decreases current efficiency but also alters film structures. Of course, some metals such as alkaline metals and aluminum cannot be electrowinning in aqueous solutions at all.
Another interested field of research that attempts to exploit the nonaqueous property of molten salts is that of the energy storage device for automobiles. It has been realized that the search for an alternative to the internal combustion engine is highly necessary because of the growing danger of pollution from automobile exhausts - they account for 70% of the carbon monoxide, 35% of the hydrocarbons, and 44% of the nitrogen oxides (NO$_x$) released in the USA [1.3], the increasing concentration of CO$_2$ (with the consequences of a warmup of the atmosphere, the so-called "green-house effect"), the limited reserves of fossil oil, etc. Nuclear reactors with their attendant shielding problems will always be too heavy for the relatively small power needed in road vehicles. Thus, advantages are very attractive if a fumeless, vibration-free electric power source is developed. However, the current widely used cheap electrochemical device - the lead-acid battery - has a low theoretical energy density, not allowing the electric energy which it stores to offer reasonable performance with convenient distance range between recharging. Electrochemical-energy storers available today, which do have a sufficiently high energy capacity per unit weight, offer difficulties because of their expense. Storage devices, which utilize the dissolution of lithium or other metals that have lighter equivalent weights, offer higher theoretical energy densities. Aqueous electrolytes are excluded because, in them, these metals react spontaneously with water rather than dissolve with useful power production. Therefore, one answer to the need for an electrochemically powered transport system is the
development of a nonaqueous, electrochemical-energy storage system incorporating lighter-equivalent-weight metal electrodes. Molten salts provide a better answer to this problem than organic media because of their high conductivity and solvent stability. There are several molten salt batteries which have been explored and seem promising [1.4], such as the lithium/sulfur-based and sodium/sulfur-based batteries.

A summary of the typical properties of molten salts is listed in Table 1.1 and some important industrial applications of molten salts are listed Table 1.2 [1.2]. Many such applications are detailed in Molten Salts Technology [1.5].

1.3. PROBLEMS OF HIGH TEMPERATURE MOLTEN SALTS

While the high temperatures of molten salts have positive aspects such as increasing reaction rates, the problems associated with them are obvious. First of all is safety. Fire, explosion, pyrophoricity, radioactivity, and toxicity have all been identified by Janz [1.6] as potential hazards when working with molten salts. Among them, explosion may be emphasized because incidently allowing any small amount of water, plastic, rust, or even foodstuff to fall into high temperature molten salts could cause an explosion, or at least splash hot and aggressive melts around. Because of aggressivity, high temperature molten salts frequently place exceptional requirements on the materials used to design apparatus either used in laboratories or in industrial processes and often add extraordinary
Table 1.1. Typical Properties of Common Molten Salts

<table>
<thead>
<tr>
<th>Physical</th>
<th>Chemical/electrochemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Thermal conductivity</td>
<td>Wide range of thermochemical stability</td>
</tr>
<tr>
<td>High thermal capacity</td>
<td>Good solvents</td>
</tr>
<tr>
<td>Low Density</td>
<td>High reaction rates</td>
</tr>
<tr>
<td>Moderate viscosity</td>
<td>Good electrochemical stability</td>
</tr>
<tr>
<td>Optically transparent (pure)</td>
<td>Low gas solubilities (except by chemical reactions)</td>
</tr>
<tr>
<td>High electrical conductivity</td>
<td></td>
</tr>
<tr>
<td>Mutual miscibility</td>
<td>Low dielectric constants</td>
</tr>
<tr>
<td>High surface energy, good wetting with low</td>
<td>Adjustable acid-base properties</td>
</tr>
<tr>
<td>contact angles</td>
<td></td>
</tr>
<tr>
<td>Newtonian fluids</td>
<td>Nonaqueous environment</td>
</tr>
<tr>
<td>Low vapor pressures</td>
<td>Standard potentials depend on system and differ from aqueous</td>
</tr>
<tr>
<td></td>
<td>scale</td>
</tr>
<tr>
<td></td>
<td>Corrosive and hygroscopic</td>
</tr>
</tbody>
</table>
## Table 1.2. Molten Salt Applications

<table>
<thead>
<tr>
<th>Process</th>
<th>Operational</th>
<th>Projected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals extraction</td>
<td>Al, Be, alkali metals, alkaline earth metals, lanthanides, refractory metals, transuranic elements</td>
<td>Transition metals, noble metals</td>
</tr>
<tr>
<td>Metals purification and recycling</td>
<td>Al, Be, Mg, lanthanides, actinides</td>
<td>Alkali metals, alkaline earth metals, noble metals, transition metals, coinage and white metals</td>
</tr>
<tr>
<td>Metals treatment</td>
<td>Annealing, quenching, cleaning, cementation, welding, brazing, soldering, electroslag refining and welding.</td>
<td>Metalliding electroplating, electroforming, anodizing, leaching, partitioning.</td>
</tr>
<tr>
<td>Nonmetals production</td>
<td>Fluorine, other halogens, glasses and ceramics</td>
<td>Carbon, silicon, phosphorus, sulfur, germanium, semiconductors.</td>
</tr>
<tr>
<td>Nonmetals/organics processing</td>
<td>Fuel cracking, catalysis, organics synthesis and modification, plastics curing, etching, recycling rubber, vulcanizing, waste disposal, pyrolysis, gasification, gas scrubbing</td>
<td>Extension and expansion in most areas</td>
</tr>
<tr>
<td>Power generation and storage</td>
<td>Thermal energy storage, batteries (reserve)</td>
<td>Heat transfer, fuel cells, batteries (load-leveling and traction), nuclear (fission and fusion), solar energy conversion (various routes)</td>
</tr>
</tbody>
</table>
amounts of nonessential experimental manipulation. Indeed, some very basic
data of molten salts such as density need a big effort experimentally.

From an economical point of view, maintaining a high temperature molten
salt needs extra energy. For those electrolytic molten salt processes, high
temperature leads to lower current efficiency. In the Hall-Heroult extraction of
aluminum, which consumes 6% of all electricity, for example, the current
efficiency increases by 1% by every 10°C lower temperature.

Finally, the high liquidus temperature associated with molten salts often
limits their utilization as solvents for compounds which possess limited thermal
stability and high vapor pressures at the elevated temperatures.

1.4. ROOM TEMPERATURE MOLTEN SALTS

While the problems with high temperature molten salts can be alleviated
with further investigations such as to find better materials for containers, and
have better experimental designs, or use additives into the molten salts to
decrease their melting temperatures, another approach is to find another class
of molten salts. One example is in extraction of aluminum, where a new
industrial process was invented and put into commercial operation (the so-called
Alcoa process) and uses a chloride system which has much lower operating
temperature than the traditional Hall-Heroult process which uses a fluoride
system.
In the last decade, considerable interest, especially in the USA and Japan, has arisen concerning a novel class of nonaqueous organic molten salts that are liquid proximate to room temperature (25°C). So far, only two types of these room temperature molten salts appear to have been studied in any detail. Table 1.3 lists the formulae for most of the known, suitable salt mixtures. It is to be noted that the two types of room temperature melts are classified as organic cation/metallohalide anion and organic cation/organometallic anion systems. Of those room temperature systems, the N-alkylpyridinium and substituted imidazolium chloroaluminate systems have been characterized most fully. Figures 1.1 and 1.2 [1.7] are illustrative phase diagrams of two example of these systems. Outlines of these two diagrams are similar and both exhibit eutectic points near the 1:2 and 2:1 molar ratio compositions. Why do these systems form liquids at room temperature? Even though there are no simple or clear answers, one common factor seems to be the presence of a large and asymmetric organic ion. For example, the stable liquidus range decreases for the molten salt series N-methyl- > N-(n-Propyl)- > N-ethyl- > N-(n-butyl)pyridinium chloride:AlCl₃, among which, the molten phases of aluminum chloride-N-(n-butyl)pyridinium chloride were liquid below 27°C over the composition range of 0.75:1 to 2:1 molar ratio aluminum chloride-N-(n-butyl)pyridinium chloride [1.8]. Thus far, two systems, the N-butylpyridinium chloride (briefly called BPC)-aluminum chloride and 1-methyl-3-ethylimidazolium chloride (MEIC) -aluminum
Table 1.3. Examples of Room Temperature Melts ($X^-$ = Halide)

**TYPE A:** Organic cation: metallohalide anion

1-Bu

[Chemical structure image]

$\text{N}^+$

$\text{Et}_3\text{NH}^+, \text{Et}_3\text{P Cl}^+$  

$\text{CuX}^-$

$\text{AlX}_4^-, \text{Al}_2\text{X}_7^-$

$\text{R}_4\text{N}^+$, $\text{R}_4\text{B}^-$

**TYPE B:** Organic cation: organoboride anion

$\text{R}_4\text{N}^+$  

$\text{R}_4\text{B}^-$  

(n $\text{FeX}_3^+$ $m\text{X}^-$)

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Figure 1.1. Phase diagram for the aluminum chloride-N-ethylpyridinium bromide molten salt system [1.7].
Figure 1.2. Phase diagram for the aluminum chloride-1-methyl-3-ethylimidazolium chloride molten salt system. Unfilled circles indicate transitions; the dotted line denotes extrapolated [1.7].
chloride mixture, are the most popularly used as solvents or electrolytes for fundamental and practical studies due to several researchers' pioneering work.

The emergence of BPC-aluminum chloride system may be attributed to Koch, Gale, Gilbert, Robinson and Osteryoung even though the similar concept (N-ethyl-pyridinium bromide instead of N-butyl-pyridinium chloride was used) was developed as early as 1948 [1.9-11]. In the nineteen eighties, they used improved procedures [1.12] to acquire a pure and clear room temperature BPC-Al\textsubscript{3} melt and used Raman spectroscopy [1.13] to reveal that in this system, acid-base character could be represented by the single ionic equilibrium reaction:

\[ 2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \]

Melts containing excess Al\textsubscript{2}Cl\textsubscript{7}\textsuperscript{-} are considered to be Lewis acidic (with molar ratio of AlCl\textsubscript{3}:BPC larger than 1:1) and those containing excess free Cl\textsuperscript{-} ion (with molar ratio of AlCl\textsubscript{3} smaller than 1:1) are considered as Lewis basic. The acidity or basicity can be easily adjusted by changing the molar composition of the melts. Potentiometric models [1.14, 1.16] of this system established that the equilibrium constant of this dissociation reaction is 3 \times 10^{-13}. It is to be noted that this constant is comparable to that of water (1 \times 10^{-14}) which provides a widely adjustable acidic-basic medium.
The initial work of MEIC-aluminum chloride should be credited to Wilkes and Hussey. They found this system [1.17] in an attempt to improve some properties of the BPC-aluminum chloride system, such as extending the electrochemical windows. It was found that the acidic-basic and some other properties of this system were similar to those of the BPC-aluminum chloride system except that the MEIC-aluminum chloride system had a wider electrochemical window and lower liquidus temperature. But preparation of this melt is a little harder because of the synthesis of MEIC.

Low liquidus temperature, low vapor pressure, aprotic nature and widely Lewis acid-base adjustable properties, and of course, the ionic nature of BPC or MEIC-aluminum room temperature molten salts have made them attractive media for fundamental electrochemical, spectroscopic, and photochemical studies for a variety of organic, organometallic, and inorganic solutes. These studies have been described in the reviews [1.18-20]. It is to be noted that these results invite comparison with those observed for conventional aqueous and nonaqueous solvent systems. For example, these systems can stabilize some unusual chemical species such as inorganic lower valent cations and organic radicals [1.18-1.21].

These molten salts have also been evaluated from a variety of prospective practical applications. Actually, at their inception, these molten salts were formulated as aluminum electroplating baths [1.10, 1.11]. It was also proposed that these melts could be used as reaction media for organics, organometallic
compounds, including polymerization reactions [1.22-25]. More inviting practical applications are perhaps to use these molten salts as electrolytes in molten salt batteries because of the reversible electrodeposition of aluminum metal in acidic melts, which provides an equivalent weight comparable with that of lithium. It was reported [1.4] that the energy density of some high temperature molten salt battery systems could be four to ten times that of the classic lead acid battery. However, these battery systems need to operate at temperatures from 200-400°C and therefore their use requires some power to maintain these temperatures in well-insulated enclosures. It is proposed that room temperature molten salts, as battery electrolytes, might provide a solution to this problem.

1.5. RESEARCH GOALS

Since the mixtures of BPC or MEIC with aluminum chloride are room temperature molten salts, it is also possible that the mixtures of BPC or MEIC with boron trichloride could also form low temperature molten salts because boron is located at the same column as aluminum in the periodic chart. If BPC or MEIC and boron trichloride can form low temperature melts, it is desired to know what their solvent, spectroscopic and electrochemical properties are in order that they might provide a new medium for fundamental studies or potential practical uses.
As mentioned above, the room temperature molten salts of BPC or MEIC with aluminum chloride could be used as electrolytes for high energy density molten salts batteries operating at room temperature. On one hand, the high energy density of molten salt batteries comes from lower equivalent weight of lithium, sodium and so on. On the other hand, lower density of electrolytes would also increase energy density. It would be of interest for battery electrolyte development to see if mixed chloroaluminate-chloroborate systems are useful for reversible Al deposition since boron compounds would decrease electrolyte density.

Koura and coworkers [1.26-1.28] have developed Al/FeS$_2$ secondary batteries using BPC-AlCl$_3$ or BPC-NaCl (or LiCl)-AlCl$_3$ electrolyte but no speciation of sulfide or polysulfide was evaluated, nor how the speciation may hinder or ameliorate the battery performance.

The goals of this research therefore have been:

1. To prepare chloroborate and mixed chloroborate and chloroaluminate room temperature melts. To investigate the electrochemistry of boron and aluminum species either in acidic or basic mixed chloroborate and chloroaluminate melts.

2. To investigate speciation of aluminum and boron in the melts using secondary ion mass spectrometry because a detailed understanding of their speciations is important for evaluation of solvents.
3. To investigate speciation of sulfide in room temperature BPC-AICl$_3$ molten salts by the controlled addition of sulfide into this type of molten salt.

1.6. REFERENCES


CHAPTER 2

CHLOROBORATE AND MIXED CHLOROBORATE / CHLOROALUMINATE ROOM TEMPERATURE MELTS

2.1. INTRODUCTION

Organic room temperature molten salts of an aprotic nature have received interest in recent years because of their unique properties and certain advantages over high temperature molten salts for several potential practical applications. Unfortunately, however, unlike traditional inorganic molten salts, the choices which these types of molten salts provide for molten salt chemists are limited since, so far, there are only several classes of them available. Two reviews, by Tissot [2.1] and Hussey [2.2], can be consulted for the details regarding their preparation, characterization, properties and applications. It has been desired and predicted that many new systems as such would appear, to provide more options for molten salt chemists.

Mamantov and coworkers [2.3] discovered a new type of organic room temperature molten salt system, which was derived from the combination of $\text{BCl}_3$ with the organic N-butylpyridinium chloride (BPC) or 1-methyl-3-ethyl-imidazolium chloride (MEIC). These types of melts are not only easy to prepare because of easy synthesis of the organic counterparts but also have lower melting points and lower densities than the corresponding chloroaluminate melts which come, it is believed, from the different anions. While these new systems could provide a
useful medium for fundamental studies and practical applications, which are yet to be investigated, it is of interest to see if mixed chloroauminate/chloroborate melts might also be useful media. It is well known that many inorganic systems can be modified by additives for improvement of certain properties and it could be so for organic room temperature molten salts. For example, if mixed chloroborate-chloroauminate melts permit the reversible electrodeposition of Al metal and have lower densities, they could provide another option for electrolyte development for room temperature molten salt batteries. Japanese scientists have reported BPC-based chloroauminates as battery electrolyte [2.4-6]. Since boron compounds would decrease electrolyte density, using the mixed melts as the electrolyte could increase the energy density.

The BPC and MEIC-based chloroborates have been characterized by Mamantov and coworkers mainly using Raman spectroscopy [2.3]. Additionally, they obtained some preliminary results of electrochemistry. In the present studies, BPC-based chloroborates and the corresponding mixed chloroborate-chloroauminate melts have been prepared and characterized by reaction stoichiometries and cyclic voltammetry in some detail.

2.2. EXPERIMENTAL

2.2.1. Maintenance of Inert Atmosphere

Most molten salts experiments need to be carried out in an inert atmosphere. The first reason is that many components constituting molten salts
are very hygroscopic and so are the resulting molten salts. A good example in this aspect is organic chloroaluminate systems which result from the mixture of highly hygroscopic aluminum trichloride and BPC or MEIC. Even though components of some molten salts are not hygroscopic themselves, for example sodium chloride and potassium chloride, the resulting molten salts are very reactive to water in ambient air at elevated temperature. The second reason to maintain an inert atmosphere is that in molten salts, dissolved oxygen from ambient air could greatly affect properties of molten salts, especially, the reduction-oxidation behavior of themselves or solutes. Some molten salts are even reactive to oxygen. For instance, oxygen is a strong oxidant in the fused hydroxide systems, with formation of superoxide ion from either oxide or water [2.7]. Thus, rather than a trivial task, it is imperative that well-controlled and inert atmospheres of molten salts be utilized with most molten salts.

Inert atmosphere maintenance in most traditional high temperature, inorganic molten salts is realized by the careful experimental design of furnaces and molten salt containers. For room temperature molten salts, an inert atmosphere can conveniently be maintained in a conventional glove box by taking advantage of the lower melting temperature of this type of molten salt. The glove box used in this work was constructed by the LSU machine shop. Figure 2.1 [2.8] shows a schematic of the glove box system that was employed. Argon was used for the inert gas for the glove box since argon is heavier than
Figure 2.1. Schematic of glove box apparatus
air and diffuses much slower than the alternative nitrogen and this provides greater protection against atmospheric contamination.

An open dish of P₂O₅ was always placed in the box to help remove as well as act as a visual check on moisture. The levels of trace oxygen and moisture were frequently monitored by continuously burning a 25-W light bulb that had a hole filed through the globe. It was reported [2.9, 2.10] that at a concentration of 1 ppm total oxygen and water vapor, the bulb would burn for 7 or more days, about 2 days at 5 ppm and 2-8 hours at 15 ppm. If the burning days were less than 2 days, leaking was checked and then, if necessary, the Cu-0803, T 1/8 copper catalyst (Harshaw) column was regenerated by a 10% hydrogen in nitrogen gas mixture. Generally, the frequency of regeneration is once in three months.

2.2.2. Synthesis of N-Butyl Pyridinium Chloride

Synthesis of N-butyl pyridinium chloride is based on the general organic neutralization reaction:

\[ RN + R'X = RR'N^+X^- \]  (2.1)

where RN is the aromatic amine and R'X the alkyl halide of interest. A detailed procedure of synthesizing BPC and its purification has been described and followed in this work [2.11]. Briefly, batches of equimolar pyridine and butyl
chloride were gently fluxed in the dark and free of moisture, followed by recrystallization using acetonitrile and ethyl acetate.

In our preparation, reagent grade chlorobutane and pyridine were used. Prior purification of these two reagents by distillation, followed by some researchers, is believed to be unnecessary since the crystalline product must be purified eventually anyway. Drying the reagents over 3 Å molecular sieves before use is recommended because commercial pyridine usually contains significant water, which can increase the difficulties of eventual product purification. HPLC grade acetonitrile and reagent ethyl acetate for recrystallization purposes were used without further purification but dried over 3 Å molecular sieves before use.

Refluxing time depends on the amounts of reagents and how gently to reflux. Long periods of refluxing are not a good practice since the formation of impurities by degradative side reactions increases the difficulties of purification, but 2-3 days of refluxing did not present problems. It should be pointed out that the reaction is not allowed to proceed completely because without pyridine and chlorobutane, heat will be built up to overheat the product, leading to thermal decomposition of BPC. This is perhaps the reason some researchers used 10% excess of chlorobutane. Since the refluxing period (depending on specific conditions) cannot be calculated accurately beforehand, the refluxing flask should be checked frequently to make sure that there are some reactants left. This can be easily achieved by checking the amounts of the two distinctive phases; BPC phase appears as solid crystals or as a brown oil (depending on the refluxing
temperature), both being the lower phase, while pyridine and chlorobutane appear as a colorless liquid layer on the top.

2.2.3. Purification of Aluminum Chloride

Commercial aluminum chloride usually contains impurities, mainly FeCl₃. Therefore, many lab techniques to purify aluminum chloride involve removing FeCl₃. These techniques include separation of the iron by d-c electrolysis [2.12], or the purification of aluminum chloride by vacuum sublimation from an NaAlCl₄ bath after the introduction of Al or Fe metallic chips, or the passage of reducing gases [2.13, 2.14]. In this work, vacuum sublimation was utilized to purify Fluka A.G. brand aluminum chloride. Al metallic chips were added as reducing metal and NaCl was added to form the lower phase to dissolve impurities. The detailed operating procedure described in the context [2.15] was followed in this work. What needs to be mentioned here is that almost every researcher has used Fluka brand aluminum chloride in this method. This brand aluminum chloride has been found to be least likely to cause an explosion during sublimation. In addition, the upper Al₂Cl₆ layers should be checked frequently to make sure that it is not sublimed completely. Otherwise, the sublimed aluminum chloride will be contaminated by sublimation from the lower layer of NaAl₂Cl₇.

2.2.4. Preparation of Melts

Chloroaluminate melts were prepared by mixing accurately weighed quantities of aluminum chloride and BPC in the glove box. Since the reaction
between aluminum chloride and BPC is very exothermic, care must be taken to prevent overheating of the mixture. The correct procedure is to add gradually aluminum chloride to BPC (not vice versa) with a teflon-coated magnetic stir bar to help mixing. In this way, colorless melts can be obtained and no further purification is necessary. If an excessive reaction temperature during mixing led to dark-colored melts due to thermal decomposition, the melts were discarded since the purification of melts is difficult and cannot produce satisfactory results [2.16-18].

Chloroborate melts in reference [2.3] were prepared by distillation of a measured volume of BCl₃ onto a weighed amount of BPC, or MEIC, in a glass tube cooled with liquid nitrogen, followed by sealing and warming the tube. We used a simpler procedure, which is as follows:

1. Quantities of BPC were weighed accurately into a flask in the glove box; 2. The flask was fitted to a ground joint with a closed stopcock, and then brought out into a fume hood; 3. The teflon tubing connecting the flask and BCl₃ lecture bottle (Matheson) exposed to air was flushed fully with dry nitrogen before connection, and then BCl₃ was released to react with the BPC, under stirring of a teflon-coated stirbar, with cooling of iced water; 4. After two phases were observed to form (the upper phase is BCl₃ and the lower the melt), the flask was taken into the glove box and the extra pressure was released. By the weight increase, the compositions of the melts were calculated.
The experimental setup for preparing chloroborate melts is illustrated in figure 2.2. Mixed chloroaluminate-chloroborate melts were prepared by dissolving aluminum chloride, or adding chloroaluminate melts into chloroborate melts in the glove box.

2.2.5. Electrochemical Cell and Electrodes

**Electrochemical Cell**  The electrochemical cell used for electrochemical investigations was a conventional three-electrode system. Cell arrangements are illustrated in figure 2.3.

In traditional high temperature molten salts, Luggin capillaries of reference electrodes are seldom used not only because of the difficulty of experiments with high temperature, but also because of the high specific conductance, the iR drops are negligible. In room temperature molten salts, a reference electrode with a Luggin capillary was used [2.19]. In this work, for convenience, a tube with fine porosity glass frit was used as the reference electrode arrangement. The reference electrode was placed as close as one centimeter to the working electrode. For melts electrochemically investigated in this work, the minimum specific conductance was about 0.012 Ohm$^{-1}$ cm$^{-1}$. If the potential profile is considered linear and the currents are about 50 µA, the potential uncertainty due to iR drop will be of the order of 4 mV.

**Reference Electrode**  There are no reference electrodes commercially available for molten salts as for aqueous solutions. Molten salt reference electrodes are always "customer-made". It is known that only a few
Figure 2.2. Schematic view of the experimental setup for preparation of $\text{BCl}_3$-BPC melts.
Figure 2.3. Electrochemical cell arrangement.
reference electrodes can serve for most electrochemical investigations in aqueous solutions, but an appropriate reference electrode needs to be considered separately for each molten salt system, since each molten salt system has different chemical and physical properties. There is a wide range of molten salt systems, so it is usually a big task to choose a best reference electrode for electrochemical investigations of molten salts. Fortunately, a wide range of choices are available due to fast electrochemical processes (that is, large exchange currents) of many molten salt systems, which makes the choice of a reference electrode for molten salts not very hard in many cases.

For molten salts, since there is no common solvent frame like water in aqueous solutions and the melting points are different, there is no common zero reference electrode like the standard hydrogen electrode in aqueous solutions. Therefore, an emf series is meaningful for the specific solvent electrode system and standard reference electrode at a specific temperature only. Critically evaluating the literature of molten salt electrochemistry, Plambeck [2.20] described 14 electrolyte systems as being the most frequently used media in molten salt electrochemical studies and reported emf series of metal electrodes for each.

For BPC based chloroaluminates and chloroborates, a high purity, coiled Al wire immersed in a melt of 2:1 AlCl₃:BPC has been successfully used as a reference electrode. Robinson and Osteryoung [2.21] compared the electrochemical potentials for the ferrocene/ferrocinium couple and the oxidation
of 12 aromatic hydrocarbon in acetonitrile with those in the AlCl₃: BPC molten salt and it was found that the Al reference in the 2:1 melt lies approximately at +0.15 V vs. SCE (aqueous, 25°C).

In this work, an aluminum wire with diameter 1.0 mm was obtained from Aesar (99.999% purity). Before use, it was cleaned in a 30:30:40 volume mixture of concentrated sulfuric, nitric, and phosphoric acids, washed with distilled water and acetone and dried in the oven. The 2:1 melt was contained within glass fritted tubes with fine porosity glass frits. The level of the reference melt was always kept above the liquid level of the bulk melt to ensure that the reference melt diffused into the bulk melt and not vice versa. The liquid-junction potentials of this system were found negligible [2.21-23].

Working Electrode A hanging mercury drop has been easily and successfully used as a working (or indicator) electrode in room temperature chloroaluminates [2.24], which is one of advantages of room temperature molten salts. Vitreous carbon, tungsten, platinum and gold were used as solid working electrode materials and it was found that vitreous carbon and tungsten had the widest inert potential ranges [2.25].

In the present work, vitreous carbon electrodes were mainly used. Platinum electrodes were used only for investigation of electrochemical aluminum deposition. Vitreous carbon or platinum rods were sealed into Pyrex glass. Prior
to use, the electrodes were polished to a mirror like finish using fine alumina (Type B). Next, they were rinsed with distilled water, wiped dry and further buffed on a fine polishing cloth. Afterwards, they were again rinsed with distilled water, washed with acetone, dried and immediately transferred into the glove box.

Geometrical areas of carbon and platinum electrodes were 0.10 cm$^2$ and 0.05 cm$^2$, respectively. Compared to the volume of melts used in electrochemical investigations, these electrodes are considered as "microelectrodes" (small A/V conditions), that is, electrodes are small enough that the passage of current does not alter the bulk concentrations of the electroactive species. Putting quotation marks on microelectrodes is intended to distinguish them from the other concept of microelectrodes, in which, currents are so small that migration currents and iR drops can be negligible.

**Counter Electrode** As in aqueous solutions, the counter (or auxiliary) electrode used in molten salts must satisfy the criteria of long-term stability, relative large mass and area, and where possible, ease and cheapness of fabrication. In this work, a plate of glassy carbon was used as a counter electrode. It was constructed by wrapping nichrome wire around one end of a piece of glassy carbon and attached with silver epoxy. Because during electrochemical investigations, either chlorine (Cl$_2$), or aluminum, or boron, was
produced on the counter electrode, it was not separated from the working-electrode compartment.

2.2.6. Instrumentation

The potentiostat was a model RDE 3, Pine Instrument Company. An X-Y recorder was used to record the potential-current response.

2.3. RESULTS AND DISCUSSION

2.3.1. Chloroborate Melts

By following the procedures described in the experimental section, clear viscous chloroborate melts were obtained at room temperature and normal pressure. Table 2.1 contains the results for final stoichiometries of chloroborate melts in four separate experiments. The results show that at room temperature, the compositions of the melts are almost constant. The mole ratio of boron chloride and BPC is approximately equal to 52:48. Mamantov and coworkers studied the Raman spectra [2.3] of BPC and MEIC-based chloroborate melts and evidence for $\text{BCl}_4^-$ species was found in both neutral and acidic melts. Additionally, evidence for $\text{BCl}_3$ was found in acidic melts and in neutral MEIC-based melts but not much in neutral BPC-based melts. This is perhaps because the neutral melts they prepared were not really neutral because the composition of their melts was uncertain by about 15%. It is known that in chloroaluminates, there exist polyaluminumchloride species such as $\text{Al}_2\text{Cl}_7^-$, but in the acidic
### Table 2.1. Compositions of BCl$_3$-BPC Melts
(1 Atm and Room Temperature)

<table>
<thead>
<tr>
<th>#</th>
<th>BPC (g)</th>
<th>BCl$_3$ (g)</th>
<th>Mole Ratio BCl$_3$-BPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.09</td>
<td>14.87</td>
<td>52.05:47.95</td>
</tr>
<tr>
<td>2</td>
<td>20.56</td>
<td>15.41</td>
<td>52.33:47.66</td>
</tr>
<tr>
<td>3</td>
<td>21.04</td>
<td>15.19</td>
<td>51.40:48.60</td>
</tr>
<tr>
<td>4</td>
<td>21.00</td>
<td>15.22</td>
<td>51.50:48.50</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>15.22</strong></td>
<td><strong>51.50:48.50</strong></td>
<td><strong>51.82:48.18</strong></td>
</tr>
</tbody>
</table>

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chloroborate melts, evidence for polyboronchloride species such as $B_2Cl^-$ was not found. It seems that only the following reaction happened quantitatively:

$$BPCI + BCI_3 = BP^+ + BCl_4^-$$  \hspace{1cm} (2.2)

Excess boron chloride was dissolved in the melt in the form of $BCl_3$. Since at fixed temperature and pressure, $BCl_3$ will have a fixed solubility in the melt, the compositions of the melts are constant, which is about 52:48 $BCl_3$:BPC, corresponding to the solubility of $BCl_3$ of 0.25 m (molal).

Compared with BPC based chloroaluminate melts, BPC based chloroborate melts are aprotic and have comparable conductivities but lower freezing points and density [2.2, 2.3]. Moreover, they are easy to prepare and no problems of purification have been met. However, unlike chloroaluminates, polyboronchloride species were not detected in chloroborate melts, perhaps because boron chloride cannot form dimer $B_2Cl_6$ (but $B_2Cl_4$ does exist) like $Al_2Cl_6$. This property will limit their acid-base adjustability.

Utilizations of room temperature chloroborate melts as media in both fundamental studies and practical applications need to be explored and, without doubt, research in these aspects will be interesting. For example, sulfur has been a promising anode material in high energy density batteries and chloroaluminates have been proposed and studied as electrolytes for this type of battery. However, sulfur species involved in chloroaluminates are very
complicated because of formation of very large chloroaluminumsulfide species without definite composition, which leads to very complicated cathodic processes. Will there be a simpler sulfur species in chloroborate melts? Can BPC or MEIC based chloroborate melts be used as cathodic electrolytes in room temperature molten salt batteries? The answers to these questions may be very interesting and worthwhile.

2.3.2. Mixed Chloroborate/Chloroaluminate Melts

Mixed chloroborate/chloroaluminate melts were prepared in three ways; namely adding either slightly basic chloroaluminate, acidic chloroaluminate melts, or aluminum chloride into the 51.50:48.50 $\text{BCl}_3$-BPC melt. 1. When 0.95:1 mole ratio $\text{AlCl}_3$-BPC melt was added into the chloroborate melt, no visible experimental phenomena happened and no weight was lost. 2. When 2:1 $\text{AlCl}_3$-BPC melt was added into 51.50:48.50 $\text{BCl}_3$-BPC melt, bubbling was observed and weight was lost. The moles of $\text{BCl}_3$ lost were approximately equal to the moles of excess $\text{AlCl}_3$ in the 2:1 $\text{AlCl}_3$-BPC melt added. 3. When $\text{AlCl}_3$ was added into 51.50:48.50 $\text{BCl}_3$-BPC melt, bubbling was observed and weights were lost again. Weights lost are shown in Table 2.2. From Table 2.2, it can be seen that one mole of aluminum chloride displaced approximately one mole of boron chloride. The following displacement reactions might occur:

$$\text{BCl}_4^- + \text{AlCl}_3 = \text{AlCl}_4^- + \text{BCl}_3 \quad (2.3)$$

$$\text{BCl}_4^- + \text{Al}_2\text{Cl}_7^- = 2\text{AlCl}_4^- + \text{BCl}_3 \quad (2.4)$$

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Table 2.2. Evolved Weights of BCl$_3$ When Adding AlCl$_3$ into 11.08 g 51.50:48.50 BCl$_3$-BPC Melts

<table>
<thead>
<tr>
<th>AlCl$_3$ Added (g)</th>
<th>Weight Lost (g)</th>
<th>Mole Ratio AlCl$_3$:BCl$_3$</th>
<th>Mole Ratio AlCl$_3$:BPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>0.32</td>
<td>1:1.14</td>
<td>0.06:1</td>
</tr>
<tr>
<td>1.69</td>
<td>1.40</td>
<td>1:0.92</td>
<td>0.40:1</td>
</tr>
<tr>
<td>2.25</td>
<td>1.97</td>
<td>1:1.00</td>
<td>0.85:1</td>
</tr>
<tr>
<td>1.04</td>
<td>0.66</td>
<td>1:0.72</td>
<td>1.06:1</td>
</tr>
<tr>
<td>0.68</td>
<td>0.03</td>
<td>1:0.05</td>
<td>1.20:1</td>
</tr>
</tbody>
</table>
These two reactions indicate that chlorine bonds to aluminum more strongly than to boron, which suggests that aluminum chloride is a stronger Lewis acid than boron chloride. Since AlCl₃ and Al₂Cl₇− displace BCl₄⁺, acidic mixed chloroborate/chloroaluminate melts cannot be prepared.

By the total weight of BCl₃ lost, the weight of BCl₃ in the original chloroborate melt, the weight of BCl₃ remaining in the melt and the final weight of the melt, the solubility of BCl₃ in the mixed melt can be estimated to be 0.19 m, slightly lower than that found in the chloroborate melts.

2.3.3. Cyclic Voltammetry of Chloroborate and Mixed Chloroborate/Chloroaluminate Melts

Basic Chloroborate Melts  Basic chloroborates with BPC were prepared by adding BPC into the slightly acidic chloroborates. Figure 2.4a shows background cyclic voltamgrams of a basic melt on a vitreous carbon at room temperature with an aluminum wire immersed in a 2:1 AlCl₃:BPC melt as a reference electrode. At the positive limit (1.0 V), bubbles on the electrode were observed and this gaseous product is believed to be Cl₂ produced by oxidation of free Cl⁻ ion. The electroreduction of BP⁺ (not BCl₄⁺) appears to corresponds to the negative limit at -1.1 V. By scanning to -1.6 V, followed by reverse scanning, an oxidation peak at -0.24 V appeared. At the second cycle scanning, a blue color was found near the electrode and two reversible couples B/B' and C/C' appeared (figure 2.4b). The trace between -1.1 to -1.6 V is not shown in in figure 2.4b because the current was very large. The overall picture of this...
Figure 2.4. Cyclic voltammogram (CV) of 0.8:1 BCl₂:BPC melt on vitreous carbon electrode (0.10 cm²) at room temperature; scan rate: 100 mV/s; a: scanning into -1.1 V; b: scanning into -1.6 V.
The cathodic process corresponds to that in basic BPC based chloroaluminates described by Gale and Osteryoung [2.19]. The reduction product at -1.1 V was the formation of a pyridinyl radical species:

\[
\text{Bu-N} + e \rightarrow \text{Bu-N}
\]  

(2.5)

followed by a rapid dimerization to form 1,1'-dibutyl-4,4'-tetrahydrobipyridine (DBTBP).

\[
2 \text{Bu-N} \rightarrow \text{Bu-N}
\]  

(2.6)

The anodic current peak A at -0.24 V was the oxidation of DBTBP. DBTBP was not chemically stable in the melt and decomposed into 1,1'-dibutyl-4,4'-bipyridinium monocation radical (i), which is responsible for blue color and the corresponding dihydrobipyridine (ii). The two reversible couples B/B' and C/C' correspond to the following electrode process (2.7) and (2.8) respectively.

\[
\text{Bu-N} + e \rightarrow \text{Bu-N}
\]  

(2.7)

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It is noted that changing anion from AlCl\texttextsubscript{4} to BCl\texttextsubscript{4} does not alter the unstable nature of DBTBP in BPC based room temperature melts. It is know that DBTBP is stable in acetonitrile [2.26]. Oxygen in ambient air can transform DBTBP into violiogen compounds in acetonitrile. The mechanism was said to involve trace water in acetonitrile [2.26]. However, to our knowledge, the decomposition mechanism of DBTBP in the room temperature molten salts has not been determined.

A study of neutral melts was not attempted because genuine neutral melts are hard to prepare.

**Acidic Chloroborate Melt**

Here, we consider the chloroborates with a molar ratio of BCl\textsubscript{3} to BPC larger than one, as acidic-like, room temperature chloroaluminates. Strictly speaking, these melts may not be considered as acidic because, as discussed above, excess BCl\textsubscript{3} is dissolved as a neutral molecular species and it is not involved in the ionic acid-basic equilibrium, as occurs in the AlCl\textsubscript{3}:BPC melts.

BCl\textsubscript{3} saturated melts were directly used for electrochemical study without any modification. Figure 2.5 illustrates the cyclic voltammogram of a room temperature chloroborate melt (51.50:48.50 BCl\textsubscript{3}:BPC) at vitreous carbon.
Figure 2.5. CV of 51.50:48.50 BCl₂:BPC melt at room temperature; vitreous carbon electrode (0.10 cm²); scan rate: 150 mV/s (top), 100 mV/s (middle) and 50 mV/s (bottom).
electrode at room temperature. The positive limit of +1.8 V (not shown in the figure 2.5) is similar to that of acidic BPC-aluminum chloride melt and is believed to be oxidation of Cl⁻ ion. The extended positive limit compared with basic melts is due to smaller concentration of free Cl⁻ ion. The negative limit was defined by a broad irreversible reduction wave with the peak potential at -0.88 V before BP⁺ ion reduction. However, in the second scan, this wave almost disappeared. Additionally, BP⁺ reduction was shifted to a more negative potential. After cleaning the electrode, or scanning to positive limit, this irreversible reduction wave appeared again. This would happen if the reduction product was nonconductive and passivated the carbon electrode surface. The behavior of this irreversible reduction wave is very similar to that of oxygen in the basic chloroaluminate melts, reported by Hussey and Osteryoung [2.27]. Therefore, oxygen or other impurities in our system might be responsible for this reduction wave. However, addition of BPC to neutralize the excess boron chloride in the melt to a slightly basic melt, removed this irreversible reduction wave. When AlCl₃ was added, bubbling occurred (that is, the melt was saturated with BCl₃ again) and the reduction wave appeared again. This suggested that the reduction wave was caused by a boron species, likely, BCl₃, or some other species containing boron.

Electrochemical reduction of boron has been recently studied in high temperature alkali metal fluorides or chlorides with tetrafluoroborate complex anion (BF₄⁻) as an active component on platinum, carbon and silver electrodes.
[2.28-32] because of interest of electrochemical synthesis of titanium diboride which is considered to be a very promising material for inert cathodes in aluminum electrolysis [2.33, 2.34]. It was found that boron is reduced directly from BF$_4^-$ by a single step of 3-electron process. The earlier studies, however, indicated that the mechanism of the boron electrochemical reduction involved the indirect reduction of the boron species with reduced alkali metal [2.35, 2.36]. An attempt to reduce BCl$_3$ with the metal did not provide a route to pure boron and the possibility of aluminum boride formation has been suggested [2.37]. There was no sodium species nor aluminum species in our melts and it was impossible that the reduction mechanism involved the participation of a reduced aluminum intermediate or reduced alkali metals. Therefore, boron might be directly deposited electrochemically from room temperature chloroborate by a simple single step of 3-electron irreversible process.

Table 2.3 contains peak potentials $E_p$ and currents $i_p$ data as a function of scan rate for the cyclic voltammograms. The current peak at -0.88 V vs. an Al(0) 2:1 AlCl3:BPC reference shifted negatively with increasing scan rate, which is diagnostic of a slow charge-transfer reaction rate (electron irreversible behavior). The peak currents were not proportional to $v$, nor to $v^{1/2}$. This is the case if boron species was weakly adsorbed on the carbon electrode. The peak current due to weakly adsorbed boron species on the carbon electrode overlapped the peak current due to diffusion of boron species from bulk solution. Since adsorbed
Table 2.3. Peak Potentials ($E_p$) and Peak Currents ($i_p$) against Scan Rates ($v$) of Acidic BCl$_3$-BPC Melt.

<table>
<thead>
<tr>
<th>$v$ (mV/S)</th>
<th>$v^{1/2}$</th>
<th>$i_p$ (µA)</th>
<th>$E_p$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>7.07</td>
<td>20.0</td>
<td>-0.880</td>
</tr>
<tr>
<td>100</td>
<td>10.00</td>
<td>28.0</td>
<td>-0.960</td>
</tr>
<tr>
<td>150</td>
<td>12.25</td>
<td>40.0</td>
<td>-0.980</td>
</tr>
</tbody>
</table>
species contributed to the diffusion current, the peak current was not proportional to $v^{1/2}$ and had a positive deviation.

To further investigate boron species adsorption and electrochemistry, a small amount of acidic chloroborate melt (100 $\mu$l) was pipetted into an acidic AlCl: BPC melt. Before addition, the rest potential on a carbon electrode in a 1.2:1 AlCl: BPC melt was -0.21 V and after addition of chloroborates, the rest potential became 0.23 V. On a platinum electrode, before addition, the rest potential in a 1.5:1 AlCl: BPC melt was 0.83 V and after addition, the rest potential became 0.86 V. Figures 2.6 and 2.7 illustrate the cyclic voltamograms of acidic chloroaluminates on vitreous carbon and platinum electrodes before and after chloroborates addition, respectively. Aluminum deposition behaviors in the melts before additions are similar to those reported by Osteryoung et al.[2.38]. On both carbon and platinum electrodes, aluminum deposition had a nucleation overpotential as shown in figures 2.6 and 2.7, but on the platinum electrode, aluminum underwent an underpotential deposition. In figure 2.7, peak C was the stripping wave of underpotential deposition product, but like that reported by Osteryoung, the underpotential deposition process appeared as a slowly rising current prior to bulk deposition, rather than a distinct peak. After addition of acidic chloroborate melt, aluminum deposition moved to more negative potentials and aluminum stripping moved to more positive potentials on both carbon and platinum electrodes. Additionally, only one stripping peak on the platinum
Figure 2.6. CV of 1.2:1 AlCl₃:BPC melt on vitreous carbon electrode (0.10 cm²) at room temperature; scan rate: 100 mV/s; top: without addition of BCl₃:BPC; bottom: addition of 100 µl BCl₃:BPC melt.
Figure 2.7. CV of 1.5:1 AlCl₃:BPC melt on platinum electrode (0.05 cm²) at room temperature; scan rate: 100 mV/s; top: without addition of 100 µl chloroborate melt; bottom: addition of chloroborate melt.
electrode was found. Presumably, the underpotential stripping wave disappeared instead of being overlapped.

As discussed previously, acidic chloroaluminates or aluminum chloride can displace $\text{BCl}_4^-$ to produce $\text{BCl}_3$ which has a saturated solubility of about 0.19 m in acidic chloroaluminate melts. When slightly acidic chloroborate melt was added into acidic chloroaluminate melts, electroneutral $\text{BCl}_3$ produced by replacement reaction was perhaps more surface active than other species such as $\text{Al}_2\text{Cl}_7^-$ and $\text{AlCl}_4^-$ and preferentially adsorbed on the electrodes. This was perhaps why the underpotential aluminum deposition was not found after the acidic chloroborate was added. An adsorbed $\text{BCl}_3$ film acted as electroinactive species before its reduction (peak potential at -0.88 V). This adsorbed, electroinactive film perhaps inhibited aluminum deposition by blocking the electrode surface so that aluminum deposition might occur either at the filmed portion of the electrode, or by penetration of $\text{Al}_2\text{Cl}_7^-$, or transfer of electrons through the film. Any of these cases would increase the reaction activity energy of aluminum deposition, resulting in an overpotential.

As to potential practical applications of metal electrodeposition of metals from room temperature molten salts, two practical applications seems promising. One is batteries and the other is metal plating. It is not desirable to use room temperature molten salts to prepare solid metals by electrodeposition, either from economical or technical points of view. The overpotential due to $\text{BCl}_3$ adsorption is not desirable for battery application, but it may be of benefit to metal plating.
For electroplating, certain overpotentials are required in order to obtain smooth and fine films. In aqueous solutions, this can be easily achieved by adding appropriate complexing reagents, or adding surface active organics. One of the problems with molten salt electroplating is that electrochemical depositions of most metals have lower overpotentials than for aqueous systems. Therefore, molten salt electroplating is a challenging field. It would be interesting to use chloroborates as surface active additives for room temperature molten salt electroplating.

Mixed Melts When AlCl$_3$ was added into slightly acidic or basic chloroborate melts, an irreversible reduction wave similar to that in the chloroborate melt was observed. This irreversible reduction wave is believed to be caused by reduction of BCl$_3$, which either exists in the original melts or is produced by the replacement reaction between tetrachloroborate anions and AlCl$_3$. There is no evidence of aluminum reduction, which is expected since in the mixed melts, there is no Al$_2$Cl$_7$ species. Therefore, the original conception of using mixed melts as electrolytes to deposit reversibly aluminum is invalid. However, BPC-based chloroaluminate, modified by adding chloroborate could provide a new type of medium for some other processes, which could utilize advantages of both chloroaluminates and chloroborates. The ability to produce
passive monolayers of boron might have applications in surface science or microelectronics.

2.4. CONCLUSIONS

1. At normal atmosphere and room temperature, the BCl₃-BPC molten salts have a constant composition of 52:48 mole ratio BCl₃-BPC even when excess BCl₃ was added.

2. BCl₃ is displaced from BCl₄⁻ by Al₂Cl₆ or Al₂Cl₇⁻. Acidic mixed chloroaluminate/chloroborate melts could not be prepared, but neutral or basic mixed melts could be prepared. These melts need to be further evaluated for possible fundamental or practical studies.

3. Boron species are electroactive in acidic chloroborate melts and mixed chloroborate/chloroaluminate melts, but it passivates carbon electrodes. In acidic chloroaluminates, small amounts of boron chloride inhibit electrodeposition of aluminum.

4. Boron does not form B₂Cl₆ readily like Al₂Cl₆. It does form stable subvalent species like B₂Cl₄ and B₄Cl₄. There is no evidence of the B₂Cl₇⁻ ion. If B₂Cl₇⁻ exists, it readily dissociates into BCl₄⁻ + BCl₃ (volatile).

2.5. REFERENCES


2.13. French Patent 688,566(1930); CA 25,780.

2.14. Brit. Patent 342,208 (1930); German Patent 530,892 (1930); CA 26,263; French Patent 1,380,362 (1964); CA62, 15807d; French Patent 710,166(1931); CA26, 1400; U.S. Patent 1,901,486 (1933).


2.34. K. Billehaug and H.A. Øye, Aluminum, 56, 642 (1980).


3.1. INTRODUCTION

3.1.1. Techniques of Structural Studies of Molten Salts

Very few molten salt systems are composed of simple cations and anions like Na<sup>+</sup>, K<sup>+</sup> and Cl<sup>-</sup> as in NaCl or KCl or NaCl-KCl systems. Instead, most molten systems contain complex species, which could result from either solutes or molten salts themselves. Structural knowledge of these species is important since these species affect physical and chemical properties of molten salts and hence the performance of molten salts in practical uses. Therefore, elucidation of structural information of these species constitutes a major research activity in molten salts.

In early days and still effectively nowadays, structural information on complex species in molten salts was speculated from results of electrochemistry, especially, potentiometry, and from studies on physicochemical properties such as densities, freezing temperatures (phase diagrams), viscosities, surface tensions, vapor pressures, conductivity, etc. Many modern techniques have been applied with some success to high temperature molten salts as progress has been made in development of materials and design of experiments. These techniques include electronic spectroscopy, infrared (IR) and Raman
spectroscopies, X-ray and neutron diffraction [3.1, 3.2]. Of course, in the situation of room temperature molten salts, these techniques, including NMR and EXAFS, have been more readily used [3.3, 3.4]. Because of the ionic and nonvolatile nature of most molten salts, however, powerful structure-elucidating mass spectroscopy has been excluded in molten salt studies until the advent of liquid secondary ion mass spectrometry (LSIMS) and fast atom bombardment mass spectroscopy (FABMS), in which the materials under examination do not need to be presented to the ion source in a gas state through thermal volatilization.

3.1.2. A Brief Review of SIMS and FABMS

SIMS and FABMS belong to a family of desorption ionization mass spectrometry techniques, a general term describing those methods in which energy in various forms is introduced into the condensed samples in such a way as to cause direct formation of gaseous ions. Included in this mass spectrometry classification are also plasma desorption mass spectrometry (PDMA) (produced by spontaneous fission of $^{252}$Cf), laser desorption mass spectrometry (LDMS), field desorption (FD), and electrohydrodynamic ionization (EHMS). Despite their difference in forms of initial energy, these desorption ionization techniques tend to produce very similar spectra, which give predominantly even-electron ions from large molecules, often with a limited degree of fragmentation. In 1970-80's, they were developed to analyze nonvolatile and thermally labile, large biological and biomedical compounds. Among these techniques, FABMAS and SIMS were
most successful and today have become routine analytical methods for many large polar and thermally labile compounds whose analyses were considered intractable by conventional mass spectrometry.

There are some controversies and confusion about the terminology of FABMS and SIMS in the literature. It will be helpful in the following discussion that a brief review is given below.

SIMS and FABMS have many similarities. Physically, both techniques utilize the phenomenon of sputtering. If a solid is bombarded by high-velocity charged or neutral particles, typically of Kev energy, then material will be removed into the gas phase where some will be in the form of positively or negatively charged ions. Experimentally, the basic designs of ion sources are similar and both atom and ion guns can be easily fitted on most modern mass spectrometers. However, the SIMS method is significantly ahead of FABMS in its development. It has been an established, highly-sensitive technique for the elemental analysis of metals, semiconductors and simple inorganic salts, capable of microscopic resolution and depth profiling [3.5]. Since interest in these analyses is element determination, it is known as an "atomic SIMS" or "inorganic SIMS". On the other hand, for high sensitivity and for the purpose of depth profiling, atomic SIMS usually uses a relatively high primary ion beam flux and therefore, this version of the technique is also termed "dynamic SIMS".

Organic, or more generally, molecular SIMS, where the interest of analysis is organic molecules, did not evolve until after the introduction of the concept of
"static SIMS" by Benninghoven [3.6]. The key innovation in static SIMS was the use of a sufficiently low primary ion current density to make the probability negligible that any surface will twice suffer ion impact during an experiment and therefore to minimize fragmentation and reaction of organic molecules at the surface (so-called sample thermal damage). In 1976, Benninghoven and co-workers reported the SIMS of a number of amino acids obtained by bombarding the solid sample with argon ions [3.7]. Similar results for a variety of organic compounds have been reported by a number of other researchers [3.8, 3.9]. Despite these initial successes, these earlier molecule SIMS, wherein interested organic samples were deposited from solutions into a solid film on a metal support which were bombarded with a primary ion beam, generally gave low intensity secondary ion beam and transient signals. These methods did not reach the potential to be a routine analytical method until Barber and co-workers' revolutionary work.

In the early 1980’s, Barber and co-workers [3.10] introduced a new method which they termed fast atom bombardment mass spectrometry (FABMS), where they dissolved or suspended samples in a low vapor pressure, viscous solvent, usually glycerol, and placed the sample solutions on a probe tip, bombarded by a beam of fast, neutral atoms. The liquid nature of samples keeps the sample surface fresh by delivering a constant supply of analyte to the interface through diffusion, minimizing sample damage problems, which in turn provides for spectra a longer life time and higher sensitivity because a higher flux of impacting.
particles is allowed. This innovation of sample preparation is so significant that it led to the immediate commercialization of FABMS instruments and quickly made FABMS a routine analytical method for polar and thermally labile substances whose analyses were considered intractable by conventional mass spectrometers.

The need for a neutral primary beam was originally promoted by the observation that charged primary beams resulted in surface charging of the sample and subsequent loss of the secondary ion beam. In addition, the difficulty of steering a charged primary beam into the high-voltage ion source region of modern sector instrument and a limited mass range capability were also cited as reasons for using a neutral atom primary beam. However, these claims were brought into question [3.11-13].

For the purpose of comparison with FABMS, in 1982, Aberth and co-workers [3.12] employed a Cs\(^+\) primary beam to bombard a wide variety of bioorganic compounds dissolved or suspended in glycerol. The results obtained established that for particles of similar kinetic energy mass (e.g., Xe\(^0\) vs. Cs\(^+\)), the charge or neutrality of the incident beam has no significant effect on mass spectra. The surface charging phenomenon has neither been observed to affect either the intensity or lifetime of the secondary ion mass spectra obtained. In light of these results and considering the similarities in the physical processes and the experimental arrangements of using charged or neutral particles sputtering, some people [3.11, 3.12] long time working on the SIMS
questioned why a different name FABMS was used. Indeed, using liquid matrices is just an extension of molecular SIMS and actually, solid matrices [3.14] have been used in molecular SIMS. Aberth suggested, if any different name be used, a name of liquid secondary ion mass spectrometry (LSIMS) for molecular SIMS using liquid matrices, no matter whether charged or neutral impacting particles are used. He considered it better to stick to well established and traditional terminology that the molecular SIMS people have used for years.

In contrast, other researchers [3.15] refer to molecular SIMS using liquid matrices as FABMS, whether charged or neutral particles are used, perhaps because they think that the contribution of using liquid matrices is largely responsible in making desorption ionization mass spectrometry a routine analytical technique today. On the other hand, there are cases where some "FABMS" researchers tended to consider some of their work to be original discoveries which are simply common sense already recognized for a long time in SIMS studies [3.16].

There are several authors [3.17] who termed SIMS as fast ion bombardment (FIB) since they thought that FIB makes more sense because it is systematically in line with the terminology like EI, CI, FAB, etc., which are descriptive of the methods themselves, whereas SIMS is the only term descriptive of the consequence of ionization in the field of mass spectrometry.

In our work, FABMS and SIMS will be distinguished terminologically not only because many researchers are so-doing but because fast atoms have been
used to bombard solid samples [3.18, 3.19], and gas samples [3.20, 3.21]. It was found that there was indeed some difference in SIMS and FABMS in the case of solid insulators [3.22].

It is generally accepted that three distinct types of molecular ions can be produced by SIMS or FABMS: (i) ions resulting from direct desorption of precharged compounds (salts), so-called intact ions, (ii) even-electron ions formed by cationization and anionization viz., clustering of the analyte with available inorganic ions, so-called pseudo- or quasi-molecular ions, and (iii) radical cations or anions. In addition to these different forms of molecular ions, fragmentation ions are also observed.

The mechanisms of how these ions are produced have been intriguing the SIMS and FABMS community since the invention of these techniques. There has been quite an effort dedicated to this problem [3.21, 3.23-26], but statements like "mechanisms are not at all well understood" still appear in the literature frequently. Nevertheless, the concept of "selvedge" [3.27], a plasma formed at and immediately above the surface during sputtering, which was often used in speculating mechanisms, has been recognized without much controversy.

Among the above-mentioned three molecular ions, precharged materials can be very efficiently desorbed. A simple explanation is that energy is needed only for desorption and not for the additional energy-consuming ionization step. Indeed, it is now common to manipulate the sample so as to generate precharged ions in situ, a "reverse derivatization" process (the term contrasts with
the derivatization of polar and nonvolatile compounds into volatile compounds in traditional mass spectrometry). The usual explanation for formation of even-electron cationization or anionization ions is that ion-molecule reaction occur in the selvedge region produced by sputtering. However, adducts can also be formed in condensed phases and subsequently emitted intactly from surfaces. Generation of odd-electron molecular ions in SIMS is relatively uncommon and is usually observed only for compounds known to exhibit great stability as radical ions. The fragmentation could attribute to unimolecular dissociation of molecular ions in the free vacuum, a process well documented in gas phase mass spectrometry, and direct decomposition of molecules at the sputtering site.

3.1.3. SIMS and FABMS as Techniques for Studies on Molten Salts

Molten salts seem to be perfect systems to subject to SIMS or FABMS analyses. First of all, molten salts are nonvolatile and viscous liquids and hence no viscous and nonvolatile matrices are needed. Secondly, molten salts are made of ionic species, which can be analyzed most effectively by FABMS or SIMS. Finally, the ability of molten salts to conduct charge away from the bombarded surface easily prevents the surface charging. In addition to their suitable characterization by FABMS or SIMS, molten salts could be used as matrices for nonpolar molecules which are insoluble in glycerol because molten salts uniquely dissolve nonpolar molecules in spite of their ionic nature. For
example, room temperature molten salts of AlCl$_3$/BPC are miscible with benzene and dissolve many nonpolar organic compounds [3.3].

The first application of FABMS in molten salt systems was performed by Todd and co-workers in 1984 [3.28]. The purpose of their study was to evaluate the performance of molten SbCl$_3$ as a SIMS matrix for pyrene, by comparison of the intensity of secondary emission of pyrene molecular ions from pyrene/SbCl$_3$ and pyrene/glycerol mixtures, as well as the secondary emission of the same ions from neat pyrene samples dispersed on a solid metal probe tip. In 1987 [3.29], Doyle designed a high-temperature FABMS sample holder to analyze molten B$_2$O$_3$, which provided some clues to analyze high temperature molten salts by FABMS or SIMS. The first FABMS analysis of room temperature molten salts was performed by Ackermann and co-workers in 1985 [3.30]. They tried to use positive mode FABMS to characterize the room temperature AlCl$_3$/BPC melts. The experiments were very successful but assessment of the anions which are of the greatest interest could not be well achieved. Conversely, Franzen et al. [3.31] successfully used negative mode SIMS for the first time to identify the major anionic species in 1986. In 1988 [3.32], Wicelinski and co-workers used fast xenon atoms to study the MEIC or BPC/AlCl$_3$ and MEIC or BPC/GaCl$_3$ systems in the negative mode. In 1993 [3.33], Welton et al. used both negative and positive mode FABMS to study MEIC/AlCl$_3$ systems. Wicelinski, Welton and Franzen's results were similar with the only difference being content of contamination because of the difference of sample handling.
Their results unequivocally confirmed the previous information about species, especially, anions speculated by other methods such as Raman and NMR. The studies of solute species in room temperature molten salts by FABMS, reported by Welton and co-workers in 1992, were also successful [3.34].

3.1.4. Objectives of This Study

In this study, both positive and negative mode SIMS will be used to characterize chloroborates and mixed chloroaluminates/chloroborates. Direct structural information on various species will be elucidated by mass, the isotopic pattern and fragmentation to confirm previous results obtained by other methods.

3.2. EXPERIMENTAL

Preparation of batches of melts and information of chemicals were detailed in Chapter 2. Melt samples for mass spectrometry were first drawn into glass syringes which were placed in a desiccator in a glovebox filled with an argon atmosphere for transfer. Then each sample (1-2 μL) was injected under an argon blanket onto a stainless probe tip which was placed immediately into the insertion of the mass spectrometer. SIMS studies were performed with a Finnigan-MAT TSQ70 triple quadrupole mass spectrometer. An Antek Cesium Ion Source gun was used for SIMS. Ion detection in the mass spectrometer was performed with the cesium gun at 4.1 KeV and a constant current of 130 mA with 1 scan/sec. Data acquisition and processing were done with Finnigan Mat ICIS.
(version 8.1). Calibration was done with glycerol at m/z 93. A total of 240 scans were acquired over a four minute run in all cases.

3.3. RESULTS AND DISCUSSION

3.3.1. Relative Abundances of Isotopic Peaks

Conventionally, when a single molecular species appears as a group of isotopic peaks, the m/z value is referred to the lowest one. For convenience (the mass spectrometer assigns the mass number to the highest peak in a group of isotopic peaks), in the following discussion, the m/z value in a group of isotopic peaks is referred to the highest peak. In the case of the BCl₄⁻ ion, the relative abundance of isotopic peaks can be calculated by the product of two binomial expansions: \((A_{35} + A_{37})^4 \times (A_{10} + A_{11})\), where \(A_{35}/A_{37}\) and \(A_{10}/A_{11}\) stand for the relative abundances of \(^{35}\text{Cl}/^{37}\text{Cl}\) and \(^{10}\text{B}/^{11}\text{B}\), respectively. Table 3.1 shows the results of masses, types of combination and relative abundances of isotopic peaks. The highest peak in the isotopic peaks of BCl₄⁻ turns out to be at 153 \([^{11}\text{B}^{35}\text{Cl}_3^{37}\text{Cl}]\). It is to be noted that the relative abundances of \(^{10}\text{B}\) chlorides vs. \(^{11}\text{B}\) chlorides are 1:4.

When elements with isotopes in one species increase, for example, \([\text{BCl}_4^- \text{BP}^+\text{BCl}_4^-]\); the calculations will become increasingly complex. Computer programs [3.35] have been written for calculation of the exact masses of various combinations. For organic molecules, however, the mass numbers of the isotopes of a given component element generally cover only a small numerical

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Table 3.1. Calculated Isotopic Peaks of BCl₄⁻

<table>
<thead>
<tr>
<th>Combinations (Mass)</th>
<th>Relative Abundances</th>
<th>Combinations (Mass)</th>
<th>Relative Abundances</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹⁰B³⁵Cl₄</td>
<td>75</td>
<td>¹¹B³⁵Cl₄</td>
<td>75</td>
</tr>
<tr>
<td>(150)</td>
<td></td>
<td>(151)</td>
<td></td>
</tr>
<tr>
<td>¹⁰B³⁵Cl₃³⁷Cl</td>
<td>100</td>
<td>¹¹B³⁵Cl₃³⁷Cl</td>
<td>100</td>
</tr>
<tr>
<td>(152)</td>
<td></td>
<td>(153)</td>
<td></td>
</tr>
<tr>
<td>¹⁰B³⁵Cl₂³⁷Cl₂</td>
<td>50</td>
<td>¹¹B³⁵Cl₂³⁷Cl₂</td>
<td>50</td>
</tr>
<tr>
<td>(154)</td>
<td></td>
<td>(155)</td>
<td></td>
</tr>
<tr>
<td>¹⁰B³⁵Cl³³⁷Cl₃</td>
<td>11</td>
<td>¹¹B³⁵Cl³³⁷Cl₃</td>
<td>11</td>
</tr>
<tr>
<td>(156)</td>
<td></td>
<td>(157)</td>
<td></td>
</tr>
<tr>
<td>¹⁰B³⁷Cl₄</td>
<td>0.9</td>
<td>¹¹B³⁷Cl₄</td>
<td>0.9</td>
</tr>
<tr>
<td>(158)</td>
<td></td>
<td>(159)</td>
<td></td>
</tr>
</tbody>
</table>

Relative abundances of ¹⁰B chloride species vs. ¹¹B chloride species are 1:4.
range, and for many of the constituent elements one isotope will be predominant (for instance, $^{12}$C 98.89%, $^1$H 99.98%, $^{14}$N 99.63%) one isotopic combination will also be predominant. There will thus be a major peak accompanied by a number of minor peaks within a narrow mass range and usually, relative abundances of peaks larger than M+2 are very small. In the case of BP$^+$ (C$_6$H$_{14}$N), M (136): 100%; M+1 (137): 10.33%; M+2 (138): 0.48% [3.36]. BP$^+$ ion can be approximately treated as a single element with isotopes of 136 and 137. Relative abundances can be calculated by the equation or simply found by looking up the table [3.36]. Thus, approximately relative abundances of isotopic peaks of (BCl$_4^-$ BP$^+$ BCl$_4^-$)$^-$ can be calculated according to $(A_{35} + A_{37})^8 \times (A_{10} + A_{11})^2 \times (A_{136} + A_{137})$, where $A_{136}$ and $A_{137}$ are relative abundances of the BP$^+$ ions at 136 and 137 respectively. The highest peak in the isotopic peaks of the cluster triple (BCl$_4^-$ BP$^+$ BCl$_4^-$)$^-$ turns out to be 442 ($^{11}$B + 6 $^{35}$Cl + 2 $^{37}$Cl + BP). Similarly, the highest peaks of isotopic clusters (BP$^+$Cl$^-$BP$^+$)$^+$ and (Cl$^-$BP$^+$BCl$_4^{-}$)$^-$ are 307 and 324 ($^{11}$B + 4 $^{35}$Cl + $^{37}$Cl + BP), respectively.

3.3.2. Chloroborate Melts

Figure 3.1 illustrates a positive-mode SIMS mass spectrum of a slightly acidic chloroborate melt with BPC (51:49 BCl$_3$:BPC). As expected, the base peak (most intense) was at m/z 136 corresponding to the intact, even electron butylpyridinium cation, BP$^+$. In addition to this major peak, the spectrum shows less intense peaks at m/z 134, 106, 93, 80, 79, and 41. These peaks were also observed in positive mode FABMS of AlCl$_3$-BPC melts by Ackermann and...
Figure 3.1. Positive mode SIMS of a slightly acidic chloroborate melt (51:49 BCl$_3$:BPC).
coworkers [3.30], which implies that charged or neutral bombarding particles make no difference in spectra in the situation of molten salts. Since the counter anions are different (boron chloride vs. aluminum chloride anions) in these two melts, above the fragmentation ions were probably not the results of ion interactions in the selvedge but of free vacuum unimolecular dissociation of some \( \text{BP}^+ \) with high internal excitation. Proposed dissociation pathways are illustrated in figure 3.2.

In the positive FABMS of \( \text{BPC}/\text{AlCl}_3 \) [3.30] and \( \text{MEIC}/\text{AlCl}_3 \) [3.33] melts reported before, ion clusters \([ \text{BP}^+ \text{Cl}^- ]^+ \) or \([ \text{MEI}^+ \text{Cl}^- ]^+ \) and \([ \text{BP}^+ \text{AlCl}_4^- ]^+ \) or \([ \text{MEI}^+ \text{AlCl}_4^- ]^+ \) were identified. The relative intensities of \([ \text{BP}^+ \text{Cl}^- ]^+ \) vs \([ \text{BP}^+ \text{AlCl}_4^- ]^+ \) and \([ \text{MEI}^+ \text{Cl}^- ]^+ \) vs \([ \text{MEI}^+ \text{AlCl}_4^- ]^+ \) were related to melt compositions. Acidic melts had more intense \([ \text{BP}^+ \text{AlCl}_4^- ]^+ \) or \([ \text{MEI}^+ \text{AlCl}_4^- ]^+ \) peaks and basic melts had more intense \([ \text{BP}^+ \text{Cl}^- ]^+ \) or \([ \text{MEI}^+ \text{Cl}^- ]^+ \). In our positive SIMS of chloroborate, however, only the ion cluster \([ \text{BP}^+ \text{Cl}^- ]^+ \) at m/z value 307 was found. Perhaps, the peak of \([ \text{BP}^+ \text{BCl}_4^- ]^+ \) is too small to be seen because the melt is not acidic. It is well known that formation of ion clusters is very common in FABMS and SIMS. Three mechanisms [3.11, 3.37] were speculated: combination of sputtered ions in the selvedge; sputtering intact clusters from the condensed phase; mixed processes (hybrid mechanism) involving both intact ejection and recombination. Ion pairs such as \( \text{BP}^+ \text{Cl}^- \) and \( \text{BP}^+ \text{AlCl}_4^- \) in the condensed phase were suggested by proton and \(^{13}\text{C}\) NMR measurements [3.38, 3.39]. Therefore, these clusters most likely may be formed.
Figure 3.2. Proposed pathway of unimolecular dissociation of $\text{BP}^+$ sputtered by SIMS.
through a hybrid mechanism, that is, reactions between sputtered cation BP⁺ or MEI⁺ and intact ion pair BP⁺/MEI⁺AlCl₄⁻ or BP⁺/MEI⁺Cl⁻ in the selvedge.

It is known that molecular BCl₃ exists in the chloroborate melts [3.40], but Figure 3.1 does not display the radical ion BCl₃⁺ at m/z 116 and others related to its fragmentation species such as BCl₂⁺ and BCl⁺. It is a common observation that radical ions in FABMS or SIMS are very rare and only some organic compounds with low ionization energy have been observed, producing odd electron radical ions [3.41]. In the selvedge, anionization of sputtered neutral BCl₃ with sputtered Cl⁻ to form BCl₄⁻ is probably dominant over electron transfer to produce the radical ion BCl₃⁺.

Figure 3.3 shows a negative-mode SIMS mass spectrum of a butylpyridinium chloroborate melt. One major peak at m/z 153 was found. This cluster was amplified in width and reduced in height and is shown on the inset of Figure 3.3. There are two patterns of isotopic distribution. The larger patterns correspond to isotopic clusters resulting from combination of four chlorine with ¹¹B, while the smaller one with the less abundance isotope ¹⁰B (refer to table 3.1). Therefore, the cluster at 153 is unambiguously assigned to the BCl₄⁻ ion.

In addition to this major peak, there are four other small peaks at m/z 35, 70, 324 and 442. They are assigned to Cl⁻, [Cl₂]⁻, and ion clusters [Cl⁻BP⁺BCl₄⁻]⁺ and [BCl₄⁻BP⁺BCl₄⁻]⁺, respectively. Cl⁻ is a preformed ion directly sputtered from the melts as expected. The unexpected finding is its larger relative intensity compared with that of BCl₄⁻ because free Cl⁻ concentration in melts is considered...
Figure 3.3. Negative mode SIMS of a slightly acidic chloroborate melts.
to be low [3.3]. While unimolecular dissociation of chlorine species could be responsible for this, as discussed by Franzen and co-workers [3.31], collision reactions of various species in the selvedge may also be a reason. Ion clusters, as discussed above in the situations of positive clusters, are probably products of reactions in the selvedge between sputtered ions $\text{BCl}_4^-$ or $\text{Cl}^-$ and neutral ion pairs existing in melts. $\text{Cl}_2^-$ might result from complicated processes involving charge transfer and ion combinations in the selvedge.

The previous studies indicated that the oxy- or hydroxy- chloroaluminate and chlorogallate species are easily formed in the butylpyridinium chloroaluminate and chlorogallate melts [3.32]. The SIMS mass spectrum of the chloroborate melt, however, did not show these species even when the melt was deliberately exposed to air for several minutes. This perhaps means that $\text{BCl}_4^-$ or $\text{BCl}_3$ completely hydrolyzed to form neutral $\text{B(OH)}_3$.

\[
\text{BPBCl}_4 \leftrightarrow \text{BCl}_3 + \text{BPCl} \quad [3.1]
\]

\[
\text{BCl}_3 + 3\text{H}_2\text{O} = \text{B(OH)}_3 + 3\text{HCl} \quad [3.2]
\]

$\text{B(OH)}_3$ is either sputtered as neutral species which could not be detected by the mass spectrometer, or is less surface active than charge species and stays in bulk melts. Boron oxides and hydrolyzed oxide ions had been reported by Doyle [3.29] and therefore most probably, hydroxy products were staying in the bulk melts.
The polyatomic species $\text{B}_2\text{Cl}_7^-$ analogous to $\text{Al}_2\text{Cl}_7^-$ or $\text{Ga}_2\text{Cl}_7^-$ [3.32] has not been found. It is known that aluminum and gallium form dimer $\text{Al}_2\text{Cl}_6$ and $\text{Ga}_2\text{Cl}_6$ even in the gas phase but boron does not form $\text{B}_2\text{Cl}_6$ [3.42]. The steric repulsion may be a possible reason. Table 3.2 lists ion crystal radii and the intensity ratios of $\text{M}_2\text{Cl}_7^-$ and $\text{MCl}_4^+$ (M=B, Al and Ga). It can be seen from the table that with the increase of ion crystal radii from B through Ga, the ratios increase.

### 3.3.3. Mixed Chloroborate/Chloroaluminate Melts

Positive mode SIMS mass spectra of mixed chloroborate and chloroaluminate melts are similar to those of chloroborate melts. A typical negative mode SIMS mass spectrum of a mixed melt is shown in Figure 3.4. Two major peaks at m/z 153 and 169 are found and they correspond to $\text{BCl}_4^-$ and $\text{AlCl}_4^-$ ions, respectively. Small peaks correspond to $\text{Cl}^-$, $\text{Cl}_2^-$, and $\text{Al}_2\text{Cl}_7^-$ ions. No mixed species like $\text{AIBC}_{17}^-$ have been identified. It is also to be noted that this spectrum with significant content of $\text{BCl}_4^-$ are pretty clean of oxy- and hydroxy-species of aluminum chloride. Spectra resulting from melts with much less content of $\text{BCl}_4^-$ ions as shown in figure 3.5, display significant oxy- and hydroxy-species related aluminum chloride. This perhaps means that when a significant content of $\text{BCl}_4^-$ is present in solution, reactions 3.1 and 3.2 of $\text{BCl}_3$ and $\text{BCl}_4^-$ are preferred over hydroxidation of aluminum chloride species.

Table 3.3 lists the relation between the intensity ratios of $\text{BCl}_4^-/\text{AlCl}_4^-$ and the melt composition. The data show that even a low concentration of $\text{AlCl}_3$ displays a higher intensity of $\text{AlCl}_4^-$. It is also to be noted that in Fig 3.5,
<table>
<thead>
<tr>
<th>$\text{M}^{3+}$</th>
<th>Ionic Crystal Radii (Å) [3.43]</th>
<th>$\text{M}_2\text{Cl}_7/\text{MCl}_4^-$ Intensity Ratios</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.23</td>
<td>0.00</td>
<td>this work</td>
</tr>
<tr>
<td>Al</td>
<td>0.51</td>
<td>0.03</td>
<td>1.5:1 $\text{AlCl}_3/\text{MEIC}$ [3.32]</td>
</tr>
<tr>
<td>Ga</td>
<td>0.62</td>
<td>0.59</td>
<td>1.38:1 $\text{GaCl}_3/\text{MEIC}$ [3.32]</td>
</tr>
</tbody>
</table>
Figure 3.4. Negative mode SIMS of a mixed melt (3.27:1 BCl₃:AlCl₃).
Figure 3.5. Negative mode SIMS of a mixed melt (0.25:1.0 BC\textsubscript{3}:AlCl\textsubscript{3}).
Table 3.3. The Intensity Ratios of \( \text{BCl}_4^+ / \text{AlCl}_4^- \) in the Mixed Chloroborate/Chloroaluminate Melts with BPC.

<table>
<thead>
<tr>
<th>Mole Ratios of ( \text{BCl}_3 / \text{AlCl}_3 )</th>
<th>Intensity Ratios of ( \text{BCl}_4^+ / \text{AlCl}_4^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.26:1</td>
<td>77/100</td>
</tr>
<tr>
<td>3.27:1</td>
<td>23/100</td>
</tr>
<tr>
<td>1.14:1</td>
<td>4/100</td>
</tr>
</tbody>
</table>

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significant intensity of $\text{Al}_2\text{Cl}_7^-$ was illustrated. In basic melts or neutral melts, the concentration of $\text{Al}_2\text{Cl}_7^-$ should be very low [3.3]. It is well known that the relative intensities of species in glycerol frequently do not reflect the bulk composition. There are many explanations for this. One popular explanation is relative surface activity because SIMS reflects the melt surface compositions to a far great extent than their homogeneous (average) compositions. The relative surface activity may apply here. In Wicelinski and co-workers' FABMS studies of the mixed melts of chloroa aluminate and chlorogallate [3.32], 0.04 mole ratio of $\text{GaCl}_3/\text{AlCl}_3$ in a basic melt with MEIC produced an 0.65 intensity ratio of $\text{GaCl}_3/\text{AlCl}_3^-$. It seems that larger species (like longer chain organic compounds in glycerol) are more surface active. Therefore, the surface active order of group IIIA tetrachloride species in the room temperature molten salts is $\text{GaCl}_4^- > \text{AlCl}_4^- > \text{BCl}_4^-$. Species $\text{Al}_2\text{Cl}_7^-$ is more surface active than $\text{AlCl}_4^-$. 

3.4. CONCLUSIONS

Both positive and negative mode SIMS have proven to be effective techniques to obtain unambiguous structural information of species in the butylpyridinium chloroborate and mixed chloroborate/chloroa aluminate melts. Positive mode results are very similar to those earlier reported by FABMS. This means that whether impacting particles are neutral or charged does not make a difference in spectra in the situation of molten salts.
Unlike the chloroaluminate or chlorogallate melts, chloroborate melts do not appear to form polyatomic species like $\text{B}_2\text{Cl}_7^-$ or $\text{B}_3\text{Cl}_{10}^-$. In the mixed melts, only individual chloride species related to boron and aluminum were found and no mixed dinuclear Al-B chloro-species were found.

Chloroborates or mixed chloroaluminates with significant content of chloroborates are clean of oxy- and hydroxy- species. This could mean that boron chloride species may react more preferentially with trace water in air to form less surface active species.

There was no evidence of the ionization of neutral $\text{BCl}_3$, but this does not mean that room temperature molten salts could not be used as an alternative matrix for some compounds. Anionization with Cl$^-$ ion could be a useful ionization process for certain samples dissolved in the molten salts.

Finally, as in glycerol, surface activities play an important role in SIMS or FABMS of molten salts. The surface active order of group IIIA tetrachloride species in the melts is, perhaps, $\text{GaCl}_4^- > \text{AlCl}_4^- > \text{BCl}_4^-$, and $\text{Al}_2\text{Cl}_{7}^-$ is more surface active than $\text{AlCl}_4^-$. Therefore, caution should be taken when SIMS or FABMS results are used to try to characterize the composition of molten salts.

3.5. REFERENCES


CHAPTER 4
ONE ELECTRON OXIDATION OF
SULFIDE ION IN NONAQUEOUS MEDIA

4.1. INTRODUCTION

Speciation of sulfur and its reduced or oxidized forms in various solvents is very complicated but of great interest from the point of view of the nature of "blue" sulfur to sulfur related batteries. However, very little was known of this speciation till Kummer and Weber of Ford Motor Company in 1967 developed the concept of the sodium-sulfur battery which operated at 300-350°C using a solid electrolyte, β-alumina. A need for a better understanding of speciation of sulfur in polysulfide melts for the development of this battery stimulated many fundamental studies of the Na-S system, such as phase diagrams, Raman spectrometry, and various electrochemical/physicochemical studies of the Na-S system [4.1].

Even though the sodium-sulfur battery was of some success, its discharge is not allowed to go beyond Na₂S₃, which makes the available energy density only one-half of the theoretical value for Na₂S and also materials and safety constraints associated with high temperature, corrosion, thermal cycling, and cell fabrication have slowed its development.

Much effort has been made to minimize those problems by developing modified sulfur-based battery systems which include using liquid electrolytes,
other anode materials and different forms of sulfides as positive electrodes. One example is using aluminum as the positive electrode, liquid chloroaluminates as the electrolytes and iron sulfide or disulfide as the positive electrode. Chloroaluminates could be made of alkali metal chlorides or organic chlorides (MEIC or BPC) with aluminum chloride. This type of battery has been mainly developed by Koura et al. in Japan [4.2-4.3] and the Bjerrum group in Denmark [4.4].

Speciations of sulfur and its reduced and oxidized forms in MCl-AlCl$_3$ (M=alkali metals) molten salts were mainly characterized by electrochemistry and Raman spectrometry. Sulfur is dissolved in the melts in the form of S$_8$ and can be oxidized to S$_2^{2+}$, existing as S$_2$Cl$^+$ in basic melts and to S$^{4+}$, existing as SCl$_3^+$ in acidic melts [4.5-4.7]. Sulfur can also be reduced to sulfide in NaCl-AlCl$_3$ melt and sulfide is involved in an acid-base equilibrium with the solvent acting as a tribase in acidic melts and as a dibase in basic melts, according to the following two equations [4.8, 4.9]

\[
S^{2+} + 3\text{Al}_2\text{Cl}_7^- \rightleftharpoons \text{AlSCl} + 5\text{AlCl}_4^-
\]

\[
S^{2+} + 2\text{Al}_2\text{Cl}_7^- \rightleftharpoons \text{AlSCl}_2^+ + 3\text{AlCl}_4^-
\]

where AlSCl and AlSCl$_2^+$ were speculated to be solvated as Al$_2$S$\text{Cl}_6^-$ and Al$_2$S$\text{Cl}_6^{2-}$. Berg et al. [4.10] have presented Raman evidence for the chain species
[AlSCI₂]ₙ⁻ in some melt systems such as the basic AlCl₃-CsCl melt. The formation and dissociation of such species may be responsible for the observed irreversibility of the sulfur-sulfide couple.

Studies of speciation of sulfur in the room temperature BPC/MEIC-AlCl₃ molten salts were relatively few. Mamantov and coworkers [4.11] investigated the electrochemistry of sulfur in AlCl₃-BPC melts. They found that sodium sulfide was not soluble and sulfur was only slightly soluble in this type of melt. In acidic melts, it is possible to oxidize sulfur to sulfur(IV) in two steps with the formation of an intermediate sulfur(I) species, but the sulfur(IV) is reduced to sulfur(I) through a reaction with the melt. Sulfur can be reduced to sulfide through an irreversible, two-electron process in basic melt. They speculated that sulfide probably exists in the form of ALSCI-like species. Therefore, we proposed to use FABMS to investigate this sulfo-aluminum chloride species, such as may form when sulfide ion resulting discharge of Al/FeS(or FeS₂) batteries interacts with chloroaluminate anions. Because sodium sulfide is not soluble in BPC-AlCl₃, we attempted to prepare pyridinium sulfide and then add this organic sulfide into BPC-AlCl₃ melts with the conception that organic sulfides might be soluble in BPC-AlCl₃ melts.

We tried to obtain pyridinium sulfide through the reaction between BPC and anhydrous sodium sulfide in dried acetonitrile. To our surprise, however, BPC reacted very fast with sodium sulfide to produce a dark-brown color solution. Several possibilities could account for this phenomenon. Sulfide anion could
form a charge-transfer $\pi$ complex with pyridinium cation or sulfide as a nucleophilic reagent would attack pyridine ring to form an addition $\sigma$ complex. Another possibility is that sulfide anion in acetonitrile is capable of reduction of the butylpyridinium cation, $R^+$,

$$R^+ + S^{2-} \rightarrow R^+ + S^-$$

This would mean that the standard potential for one electron sulfide oxidation would be negative of about -1.28 V against SCE in acetonitrile [4.12]. This reaction is of considerable interest since it affords a simple and convenient means of generating the sulfur monoanion radical intermediate, $S^-$ ion, in nonaqueous media and thus we decided to focus some studies on this. Since pyridinyl radical forms dimers and also $S^-$ could dimerize to form $S_2^{2-}$, we tried to obtain some indirect evidence for $S^-$ through the characterization of reaction products between BPC and sodium sulfide.

4.2. EXPERIMENTAL

4.2.1. Chemicals

Anhydrous sodium sulfide (Strem Chemicals, Inc., 95%) was used without further purification. Sulfur (J.T. Baker Chemicals Co.) was recrystallized twice in toluene. HPLC grade acetonitrile was used without further purification but dried
over 3 Å molecular sieves before use. The UV spectrum of the dried acetonitrile was transparent down to 200 nm.

4.2.2. Preparation of Na$_2$S$_2$

The Na$_2$S$_2$ was prepared from a 1:1 mixture of Na$_2$S and sulfur [4.13]. The mixture of 1.20 g sulfur and 2.92 g Na$_2$S was ground and put into a quartz tube in the glove box. After it was evacuated, the tube was sealed and rolled to insure mixing. The mixture was reacted at 250° C (solid state) for 15 to 20 hours and then at 574° C (liquid state) for 1 hour. The tube, containing the final product, was then returned to the glove box for handling and storing.

4.2.3. Synthesis of 1,1'-Dibutyl-4,4'-Tetra-hydrobipyridine (DBTBP)

DBTBP was synthesized by one electron reduction of BPC with Na-Hg alloy (Na 0.6% wt.) to a pyridinyl radical species, followed by a rapid dimerization in aqueous solution. The product was extracted by ether and the ether was removed by vacuum to leave a yellow/brown oily residue, which was used without further purification. DBTBP is stable in acetonitrile.

4.2.4. Spectroscopic Techniques

UV-visible spectra were recorded using an AVIV 14DS system. HPLC was run on a Rabbit HP with an ISO r* Absorbance detector and a 15 cm microsorb Si-C18 column. Proton NMR spectra were recorded using a 400 MHz Bruker system. GC-mass spectra were obtained using a HP 5890 series II GC coupled
to a HP 5971A Mass Selective Detector with injector port temperature of 200°C and interface temperature of 280°C.

4.3. RESULTS

4.3.1. UV Spectroscopy

BPC is soluble in acetonitrile and its maximum UV-visible absorbance is at 259 nm. The relation between absorbance and concentration follows Beer's law well at the 259 nm peak with an extinction coefficient of 5,000 M⁻¹ cm⁻¹. Sodium sulfide is not soluble in acetonitrile. The reaction between sodium sulfide and BPC is actually heterogeneous. The reaction was made to proceed by adding sodium sulfide into BPC solution under stirring in the glove box.

Figure 4.1 illustrates UV spectra of reaction mixtures against reaction time. The spectroscopy was obtained by the following procedure: dissolve 2.00 g BPC in 40 ml acetonitrile, and then add 1.09 g sodium sulfide (mole ratio of BPC and Na₂S: 1:1) into the solution under stirring; at the designed increments of time, pipet 18 µl of the solution to 25 ml acetonitrile (this dilution was supposed to stop the reaction) and then the solution was transferred into a capped quartz cuvette for UV-visible measurements.

The reaction was very fast. The major absorbance at 357 nm actually did not change after five minutes. Considering that the reaction is heterogeneous, the reaction is perhaps complete in several seconds. This could be the case of an electron transfer reaction between BP⁺ and sulfide S²⁻.
Figure 4.1. The UV spectrum of reaction mixture vs. reaction time in CH$_2$CN (1:1 BPC:Na$_2$S)
It is well known that pyridinium cations and certain anions can form charge-transfer complexes which absorb UV-visible around this peak [4.14, 4.15]. Disulfide $S_2^{2-}$ also absorbs UV-visible around this peak in DMF and NaOH melts [4.16, 4.17]. However, the extinction coefficients of the bands around 360 nm of those charge-transfer complexes are smaller than those of the corresponding pyridinium cation maximum absorbance around 260 nm. The extinction coefficient of disulfide is around 800. Cursory examination of figure 4.1 illustrates that the coefficient of the major peak at 357 nm is about 10,000 compared with the peak at 259 nm of pure BPC even if BPC is completely transformed into the compound that absorbs at 357 nm. Therefore, the peak at 357 nm probably is not due to charge-transfer complexes, nor to disulfide $S_2^{2-}$ ion. Figure 4.2 shows the UV-visible spectrum of saturated Na$_2$S$_2$ in acetonitrile. It seems that Na$_2$S$_2$ is not soluble in acetonitrile since there is no absorbance peak around 357 nm. The peak at 617 nm may be assigned to the radical $S_3^{2-}$, probably resulting from disproportionation of $S_2^{2-}$. There was no reaction found between Na$_2$S$_2$ and BPC in acetonitrile.

N-substituted alkyl thiopyridones usually have a strong absorption peak around 357 nm. For example, 1-methyl-2(1H)-pyridinethione and 1-methyl-4(1H)-pyridinethione have maximum absorbances at 341 nm ($\log \varepsilon: 3.91$) and 333 nm ($\log \varepsilon: 4.37$), respectively [4.18]. However, the high energy fragment, hydride, cannot leave without the help of oxidants and heating and thus pyridinethiones.
Figure 4.2. The UV spectrum Na$_2$S$_2$ saturated in acetonitrile.
could not be formed in our case. Analogous σ complexes, (I) and (II), are probably responsible for this peak.

\[ \text{S-Na}^+ \]

Another observation about the peak at 357 nm was that after the diluted acetonitrile solution of the reaction products were exposed to light for several days, the peak at 357 nm disappeared and another peak at 259 nm (BPC peak) appeared.

The UV spectrum of pure DBTBP in acetonitrile is illustrated in figure 4.3 and its maximum absorbance is at 229 nm with an extinction coefficient of 10400. UV data of 2,2'(III) and 2,4'(IV) isomers of DBTBP are lacking. Several peaks in addition to 229 nm below 300 nm in the reaction products are probably due to isomers (III) and (IV).
Figure 4.3. The UV spectrum of pure DBTBP in acetonitrile.
The reaction stoichiometry between Na\textsubscript{2}S and BPC was studied by adding different amounts of BPC to a fixed amount of Na\textsubscript{2}S in acetonitrile and measuring the absorbances at 357 nm of the resulting reaction mixtures. Figure 4.4 illustrates the relation between the absorbance at 357 and the molar ratio of BPC:Na\textsubscript{2}S. It can be seen that the absorbance does not change after the molar ratio of BPC:Na\textsubscript{2}S is over 1.8. This means that one mole Na\textsubscript{2}S can react 1.8 moles of BPC. Therefore, in the following spectroscopic studies, a 1:1 mole ratio of BPC and Na\textsubscript{2}S was used to guarantee that BPC reacts completely with Na\textsubscript{2}S in order to minimize complications resulting from excess BPC.

4.3.2. HPLC RESULTS

HPLCs of pure DBTBP and the reaction products were run at several wavelengths. When the UV detector was set at 357 nm, that is, the wavelength of the maximum absorbance of the reaction products, there were no peaks observed even up to 10 minutes and with the detector set to high sensitivity. The same occurred with a pure BPC solution of acetonitrile when the detector was set at 259 nm, the wavelength of the BPC maximum absorbance. Since BPC in acetonitrile is ionic, probably the species with the maximum absorbance at 357 is also ionic.

Figures 4.5a and b are HPLC chromatograms of the pure DBTBP and the reaction products at 229 nm, the wavelength of the DBTBP maximum absorbance, respectively. Comparing two chromatograms illustrates that in the reaction products, in addition to DBTBP, there are two other species, probably
Figure 4.4. Absorbance of the reaction mixtures in acetonitrile at 357 nm vs. molar ratio of BPC:Na$_2$S; reaction time: 30 min.; Na$_2$S was kept constant.
Figure 4.5. HPLC chromatogram of the pure DBTBP (a) and the reaction products (b); wavelength: 229 nm; flow rate: 1.0 ml/min.; 25°C.
isomers (IV) and (V). It is to be noted that relative quantities of isomers cannot be deduced from heights or areas since the spectrogram was obtained at the wavelength of the DBTBP maximum absorbance.

4.3.3. PROTON NMR

Figures 4.6 and 4.7 illustrate NMR of BPC and DBTBP in deuterated acetonitrile CD$_3$CN, respectively. Hydrogen assignments are shown in the figures. Figure 4.8 illustrates the NMR of the reaction products in deuterated acetonitrile. Confirmatory conclusions made from this spectrum is that NMR signals from BPC are completely gone and the aromaticity of the pyridine ring is disrupted (the highest chemical shifts of pyridine and BPC are 8.6 and 9.6 ppm, respectively). Charge-transfer $\pi$ complexes of the pyridinium cation with some anions indeed do show a move of NMR signal of the pyridinium cation to higher fields because of part neutralization of the positive charge in the pyridine ring, but the shifts are not very much and their NMR spectra are more like those of the oxidized form of pyridine, that is, pyridinium [4.19]. Therefore, compounds of a reduced pyridine ring are formed and these compounds are perhaps DBTBP, its isomers, and the pyridine sulfur compounds (I) and (II), but conclusive hydrogen assignments are difficult from this very complicated NMR spectrum of reaction mixture. Nevertheless, tentative assignments are attempted through analogue with the literature as follows.

Chemical shifts $\delta$ (ppm) of N-D-2-Butyl-1,2-dihydropyridine [4.20]: 2H (3.84); 3H (4.77); 4H (5.61); 5H (4.35); 6H (5.94). There is lack of NMR spectra
Figure 4.7. NMR of pure DBTBP in CD$_3$CN, 400 Mhz.
of N-substituted 2(1H)-pyridinethiones and N-substituted 4(1H)-pyridinethiones in the literature, but the NMR spectra of 2-mercaptopyridine and 4-mercaptopyridine are available [4.21, 4.22]. It is well known that 2-mercaptopyridine and 4-mercaptopyridine exist predominantly as 2(1H)-pyridinethione and 4(1H)-pyridinethione [4.23]. NMR spectra of 2 (or 4)-mercaptopyridine will be similar to those of N-substituted -2 or 4 (1H)-pyridinethiones. Chemical shifts of 2(1H)-pyridinethione: 3H (7.56); 4H (6.84); 5H (7.44); 6H (7.71). There is only one peak in the NMR spectrum of 4(1H)-pyridinethione, that is, 7.4 ppm. Therefore, two peaks around 7.3 ppm in the reaction products are tentatively assigned to compounds (I) and (II), and the other peaks to DBTBP, (III) and (IV).

4.3.4. GC-MS of Pure DBTBP and the Reaction Products in Acetonitrile

Figures 4.9A-E are the GC-MS spectra of DBTBP in acetonitrile. The compound that elutes at 4.2 minutes is pyridine and its mass spectrum is shown in figure 4.9B. The mass spectrum of the compound which elutes at 8.8 minutes and its proposed pathway of unimolecular dissociation are shown in figures 4.9C and 4.9c, respectively. The fragmentation pattern is in agreement with those reported in the literature [4.24, 4.25]. Major fragmentations are the loss of a hydrogen radical and a N-substituted group to form stable pyridinium ions.
Figure 4.9A. GC of pure DBTBP in acetonitrile.
Figure 4.9B. The mass spectrum of the compound that elutes at 4.2 minutes in figure 4.9A.

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Figure 4.9C. The mass spectrum of the compound that elutes at 8.8 minutes in figure 4.9A.
Figure 4.9c. The proposed pathway of unimolecular dissociation of the compound that elutes at 8.8 minutes in figure 4.9 A.
Figure 4.9D. The mass spectrum of the compound that elutes at 11.1 minutes in figure 4.9A.
Figure 4.9E. The mass spectrum of the compound that elutes at 11.4 minutes in figure 4.9A.
The mass spectra of the compounds which elute at 11.1 minutes and 11.4 minutes are similar. They have the same molecular mass and both lose a hydrogen or a butyl radical to form stable pyridinium ions at the masses of 192 and 136. They are probably isomers of dihydropyridines. Two choices are N-butyl-2-butyl-1,2-dihydropyridine and N-butyl-4-butyl-1,4-dihydropyridine. It is to be noted that the compound which elutes at 11.1 minutes has lower intensity at mass 192 than the other compound does. The former compound is probably 1,2 isomer because the steric factor in the 1,2 isomer could make the butyl group leave easier, which competes with losing hydrogen radical and makes the relative intensity of 192 lower. Another reason is that the 1,2 isomer should have a lower boiling point than the 1,4 isomer and elute first. It is not clear why the compound, which elutes at 11.4 minutes and presumably is the 1,4 isomer, has a lower intensity at peak mass 80. Perhaps, the internal energy of the species at 136 of the 1,4 isomer is relatively lower.

The thermal decomposition products of tetra-hydrobipyridine were reported as follows [4.26]:

\[
\begin{align*}
\text{(VI)} & \quad \xrightarrow{\Delta} \quad 2R \text{N} \text{R} + \text{N} \\
\end{align*}
\]
The above process explained part of our products, that is, the presence of pyridine and N-butyl-4-butyl-1,4-dihydropyridine.

One paper [4.27] reported that the thermal decomposition of the above tetrahydrobipyridine (VI) produced 3% N-R-1,4-dihydropyridine which corresponds to the compound that elutes at 8.8 minutes, but the mechanism was not available.

The thermal decomposition of DBTBP in this GC-MS experiment could involve the following mechanisms.

\[
\text{Bu-} \quad \text{Bu} \quad \triangle \quad 2 \quad \text{Bu-} \\
\rightarrow \quad \text{Bu} \quad \text{N-Bu} + \quad \text{Bu-N} \quad \text{N} \\
\]

\( (4.5) \)

\[
2 \quad \text{Bu-} \quad \text{N} \rightarrow \quad \text{Bu} \quad \text{H} + \quad \text{CH}_2=\text{CHCH}_2\text{CH}_3 + \quad \text{N} \\
\]

\( (4.6) \)

\[
2 \quad \text{Bu-} \quad \text{N} \rightarrow \text{CH}_2\text{CN} \quad 2 \quad \text{Bu-} \quad \text{N} + \quad \text{NCCH}_2\text{CH}_2\text{CN} \\
\]

\( (4.7) \)

Figures 4.10A-E are the GC-MS spectra of the reaction products between 1:1 molar ratio BPC:Na\textsubscript{2}S. There are four compounds but no pyridine. The
Figure 4.10A. GC of the reaction products between 1:1BPC:Na₂S in acetonitrile.
Figure 4.10B. The mass spectrum of the compound that elutes at 8.8 minutes in figure 4.10A.
Figure 4.10C. The mass spectrum of the compound that elutes at 12.0 minutes in figure 4.10A.
Figure 4.10c. The proposed pathway of unimolecular dissociation of the compound that elutes at 12.0 minutes in figure 4.10A.
Figure 4.10D. The mass spectrum of the compound that elutes at 13.3 minutes in figure 4.10A.
Figure 4.10d. The proposed pathway of unimolecular dissociation of the compound that elutes at 13.3 minutes in figure 4.10A.
Figure 4.10E. The mass spectrum of the compound that elutes at 16.4 minutes in figure 4.10A.
Figure 4.10e. The proposed pathway of unimolecular dissociation of the compound that elutes at 16.4 minutes in figure 4.10A.
elution time and fragmentation pattern of the first one are exactly the same as those of N-butyl 1,4 dihydropyridine in the GC-MS spectra of DBTBP, but N-butyl 1,2 dihydropyridine could not be excluded because mass spectrometry of these two isomers (unsubstituted on the pyridine ring carbons) are not distinguishable [4.28]. The unimolecular dissociation pathway of the second compound is shown in figure 4.10c. While one of the above proposed thermal decomposition mechanisms of DBTBP could partly be responsible for the compound that elutes at 8.8 minutes, a new mechanism must be proposed to explain the compound that elutes at 12 minutes.

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Since there is no detectable pyridine in the GC-MS spectra of the reaction products, the 2, 2' isomer could be the major tetrahydrobipyridine in the reaction products.

The pathway of unimolecular dissociation of the third compound which elutes at 13.3 minutes is proposed in figure 4.10d, where fragmentations are very similar to those for N-propyl-2-pyridinethione [4.29]. The pathway of unimolecular dissociation of the fourth compound which elutes at 16.4 minutes is proposed in figure 4.10e. It is to be noted that the big difference between figure 4.10d and 4.10e is that there is no fragmentation species at 78 in figure 4.10e. This behavior could be used to distinguish N-butyl-2-pyridinethione from N-butyl-4-pyridinethione. Therefore, the compound which elutes at 13.3 minutes is assigned to N-butyl-2-pyridinethione and the compound which elutes at 16.4 minutes to N-butyl-4-pyridinethione. It should be noted that in figure 4.10A, the peak at 13.3 minutes are larger than the peak at 16.4 minutes. This means that N-butyl-2-pyridinethione is the major product of the two pyridinethiones.

4.4. DISCUSSION

Interest in dihydropyridines has been multiple. It was found that "hydrogen-transferring coenzyme" is a dihydropyridine derivative and this discovery stimulated many studies on model dihydropyridines, generally N-substituted dihydronicotinamides. The substitution reactions of pyridine and its derivatives often proceed via an addition-elimination mechanism with
dihydropyridines as intermediates (σ-complexes). Dihydropyridines are also involved in the chemistry of viologens. Viologens are considered as related to some herbicides. The reversible one electron transfer behavior of viologens makes them the ideal reference standards for dosimetry and actinometry purposes in radiation chemistry and photochemistry. Therefore, characterization of dihydropyridines, especially pyridine ring substituted dihydropyridines, by spectroscopic techniques such as UV, NMR, MS and electrochemical methods is well documented.

Unlike benzene, pyridine is more likely subject to nucleophilic attack rather than electrophilic attack. N-substituted pyridinium cations undergo nucleophilic reaction with much ease. Nucleophiles attack pyridine at the 2 (6) or 4 positions. If steric effect is not a factor, major products will be the 2 addition or substitution products. There is no preferential position in radical reactions from theoretical calculation, but it has been found that nucleophilic radicals prefer to attack the 2 position [4.30].

Elimination of hydride from dihydropyridine intermediates, so called σ-complexes, is not favorable since the hydride ion is a high energy fragment but with the help of oxidants or heating, the process can occur. Actually, Ziegler-Zeiser reaction, that is, addition of organometallic reagents to pyridine with subsequent elimination of metal hydride under heating to give pyridine ring substituted products, has been a general method to synthesize alkyl pyridines.
When N-alkylpyridinium cations react with nucleophiles to form dihydropyridines through nucleophilic addition, in several cases, viologen radicals have been detected and this means that one electron processes have been involved [4.31, 4.32].

Monosulfur anion radicals, \( S^- \), have been reported in solid states [4.33, 4.34] but never in liquid phases. From our analysis of the reaction products between sodium sulfide and BPC, it seems that monosulfur anion radical was involved in the reaction. A stop flow experiment using DMF as solvent was attempted to detect radicals but unsuccessful, perhaps because the life times of radicals are too short. Free N-alkyl pyridinyl radical (ring carbon-unsubstituted) has never been detected.

The mechanism of the reaction between anhydrous sodium sulfide and BPC in acetonitrile is proposed in figure 4.11. This reaction might prove to be a convenient means to produce the \( S^- \) ion radical for future chemical or biochemical studies.

4.5. REFERENCES


Figure 4.11. The proposed mechanism of the reaction between Na₂S and BPC in acetonitrile.


CHAPTER 5
SUMMARY

Molten salt chemistry has and does play an essential role in active metal extraction, especially, aluminum. Because of their unique properties such as high conductivities and nonaqueous nature, molten salts also constitute good electrolytes for secondary batteries. Room temperature molten salts are desired because problems with high temperature would be relieved. Sulfur as the secondary battery cathode is promising because of its availability and low cost. Therefore, this study was oriented for studies of sulfur chemistry in room temperature molten salts for the purpose of battery development. During these studies, some interesting homogeneous redox chemistry was found.

The mixtures of BPC with BCl₃ or with BCl₃ and AlCl₃ are ionic liquids at room temperature but the chloroborate melts cannot go far beyond neutral melts, nor the mixed chloroboroate-chloroaluminate melts since Al₂Cl₆, or acidic species such as Al₂Cl₇, reacts with existing boron tetrachloride anion in the melt to form BCl₃ which is volatile at room temperature. Therefore aluminum could not be electrochemically deposited from this melt. As a new type of room temperature melt, this system could be useful for other fundamental or practical studies.

Secondary ion mass spectroscopy has proven to be a powerful technique to characterize both cations and anions in room temperature melts. In addition, it can also provide some information about the interaction between ions, that is,
ion pairing. Because room temperature molten salts have properties good for SIMS analyses and are capable of dissolving many organic compounds, it would be interesting to use room temperature molten salts as matrixes for some organic compounds.

Some evidence for monosulfur anion radicals have been reported in solid phases but never in liquid phases. In this study, some results from GC-MS, NMR, UV, HPLC have provided some indirect evidence for monosulfur anion radical in acetonitrile. Better NMR could be obtained if a method to separate the reaction products, such as using appropriate solvents to extract different compounds, is found. Because some of the reaction products are thermally unstable, HPLC-MS could provide better results. Of course, some experiments to provide direct evidence such as ESR need to be designed and performed. Finally, applications of monosulfur anion radicals in chemical and biochemical studies could be very informative.
Jianzhong Liu was born on April 10, 1958, in a remote village, Hunan province, the People's Republic of China. After finishing high school, he had been a farmer for four years until March, 1978, when the Chinese government resumed the national entrance examination, which was mainly used to admit college students. He went to Hunan University, majoring in analytical chemistry. After working in the First Automobile Works in Changchun as an analytical chemist for one year and a half, in 1983, he went to Changchun Institute of Applied Chemistry for graduate study in inorganic chemistry towards a Master's degree. Before joining Dr. Robert J. Gale's group at Louisiana State University in 1989, he had been a research chemist in the Changchun Institute of Applied Chemistry for three years, mainly working on using high temperature chloride and fluoride molten salts to prepare rare earth metals and their alloys electrochemically or through thermal reduction. He has been an environmental specialist in the Louisiana Department of Environmental Quality since 1995.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Jianzhong Liu

Major Field: Chemistry

Title of Dissertation: Electrochemical and Spectroscopic Studies of Boron and Sulfur Species in Nonaqueous Media

Approved:

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Dean of the Graduate School

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