ELECTROCHEMICAL STUDIES IN A ROOM TEMPERATURE MOLTEN SALT

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ABSTRACT

A new, low temperature molten salt, N-(n-butyl-pyridinium) chloride (BPC) -aluminum chloride has been investigated as a solvent. The system, represented as $R^+\text{AlCl}_3^-$, has a dominant solvolysis, $2\text{AlCl}_3^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$, and the 1:1 $\text{AlCl}_3$:BPC is liquid at $27^\circ$C. The solvolysis constant has been determined as $3.8 \times 10^{-13}$ (mole fraction) at $30^\circ$C. Marked variation in acid-base properties results from addition of BPC or $\text{AlCl}_3$ to the 1:1 system. The oxidation of a number of polynuclear aromatic hydrocarbons has been studied. In a number of cases, the radical cation formed during the first oxidation step is stable to cyclic voltammetric measurements. Acid-base interactions of the hydrocarbons with the solvent, as indicated by reversible, melt composition-dependent color changes, are noted.

As part of our continuing investigation into the chemistry and electrochemistry of aluminum halide based molten salts (1,2) we had, several years ago, initiated work on the electrochemistry of certain organic compounds in the sodium chloride-aluminum chloride melt at $175^\circ$C. While we had demonstrated that certain compounds were both stable in these systems and possessed interesting electrochemistry, it was nevertheless not a tractable system for a great deal of organic electrochemistry which, at least in principle, might be carried out in such systems (3). In search for lower temperature melts, which would still be aluminum halide based, we found that Hurley and Wier, in the early 1950's, had carried out work in aluminum chloride-ethylpyridinium bromide (EPB) melts which, at a mole ratio of 2 $\text{AlCl}_3$ to 1 EPB was a liquid at room temperature and furthermore, could be employed as a solvent for a variety of inorganic ion reactions as well as for aluminum deposition (4). We have carried out a certain amount of electrochemical and photochemical studies in this melt, taking advantage of its anhydrous nature and low melting point (5,6,7). However, our main interest has been in investigations of solute chemistry in the aluminum halide based melts which show acid-base dependent behavior, and, for such behavior to manifest itself, it is necessary to work in an aluminum halide system where the ratio of $\text{AlX}_3$ to halide salt is variable about the 1:1 mole ratio.

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Aluminum chloride based melts, with a chloride salt, RCl, may be indicated as AlCl$_3$:RC1 (1:1 mole ratio) and may appropriately be represented as R$^+$AlCl$_6^-$ where R$^+$ may be an alkali metal cation or, as will be shown, an organic cation. The solvolysis equilibrium which dominates the acid-base chemistry of the solute, may be written as

$$2 \text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$$  \hspace{1cm} (1).

Most work in these systems to date has involved the NaCl:AlCl$_3$ system where, at 175°C, the equilibrium constant for the solvolysis reaction 1 is $1.06 \times 10^{-7}$ on the mole fraction scale. For this melt the equilibria of reaction 1 is not sufficient to describe the overall system behavior, as determined from the potential variation of an Al electrode in the melt with melt composition. ($0.98:1 < \text{AlCl}_3: \text{NaCl} < 2:1$). Equilibria such as

$$\text{AlCl}_4^- + \text{AlCl}_3 \rightleftharpoons \text{Al}_2\text{Cl}_7^-$$  \hspace{1cm} (2)

$$\text{Al}_2\text{Cl}_6 \rightleftharpoons 2 \text{AlCl}_3$$  \hspace{1cm} (3)

must be considered and, in addition, changes in the apparent activity coefficient of AlCl$_4^-$ were employed to "fit" the curve generated when the potential of an Al electrode in the melt was measured versus an arbitrary reference — usually an Al electrode in a NaCl saturated melt — as a function of melt acidity. A titration curve (E vs. mole ratio of AlCl$_3$:RC1) similar to that generated by a strong acid-strong base titration in aqueous solution results from such an experiment. The Al electrode may be considered to respond to Cl$^-$ activity in basic melt according to:

$$\text{AlCl}_4^- + 3 \text{e}^- \rightleftharpoons \text{Al} + 4 \text{Cl}^-$$  \hspace{1cm} (4)

which, when expressed as the potential of a concentration cell with negligible liquid junction may be written as

$$\Delta E = \frac{RT}{3F} \ln \left( \frac{[\text{AlCl}_4^-]_1}{[\text{AlCl}_4^-]_2} \right) + \frac{4RT}{3F} \ln \left( \frac{[\text{Cl}^-]_1}{[\text{Cl}^-]_2} \right)$$  \hspace{1cm} (5)

or, in acidic melt,

$$4 \text{Al}_2\text{Cl}_7^- + 3 \text{e}^- \rightleftharpoons 7 \text{Al} + 7 \text{AlCl}_4^-$$  \hspace{1cm} (6)

which leads to an analogous expression to (5):

$$E = \frac{4RT}{3F} \ln \left( \frac{[\text{Al}_2\text{Cl}_7^-]_1}{[\text{Al}_2\text{Cl}_7^-]_2} \right) + \frac{7RT}{3F} \ln \left( \frac{[\text{AlCl}_4^-]_1}{[\text{AlCl}_4^-]_2} \right)$$  \hspace{1cm} (7)

It is thus apparent that the 2 AlCl$_3$:1 EPB melt described above, although liquid at room temperature, did not possess the potential for varying the acidity of the system, since it was not liquid about the 1:1 mole ratio at low temperatures. Recently, however, we found that the system N-(n-butylpyridinium) chloride (BPC) - AlCl$_3$, at a mole ratio
of 1:1, was liquid at 27°C and, in fact, could readily be handled at 40°C over the range 1:1.33 < AlCl₃:BPC < 2:1 (8). BPC is readily prepared from the direct reaction of n-butyl chloride and pyridine; extensive purification is required to obtain a suitable salt for melt preparation (8).

Raman spectra on the AlCl₃:BPC melt at 40°C at various mole ratios of AlCl₃ to BPC revealed bands essentially identical to those found previously by other workers for both NaCl:AlCl₃ and KCl:AlCl₃ melts at various mole ratios, indicating the predominant species were as in these other, higher temperature melts (9,10,11). However, integrated intensities at two different mole ratios of AlCl₃ to BPC for the most intense bands assigned to AlCl₃⁻ and Al₂Cl₇⁻ suggested that reaction 2 above was markedly to the right compared to the NaCl:AlCl₃ system. This has since been verified by other work (12).

A number of polynuclear aromatics were studied in this melt as a function of melt acidity. Initially, the ferrocene-ferrocinium ion, which has seen extensive use as a probe species in nonaqueous systems, was examined (8). Cyclic voltammetry indicated a reversible, one electron transfer process, with no dependence on melt acidity being manifested by the oxidation potential, which was 0.24 V vs an Al reference in the 2:1 AlCl₃:BPC melt. The initial E𝐸₀/2 for the first oxidation step of the hydrocarbons studied is presented in Table I. Anthracene showed behavior rather similar to that presented in acetonitrile (13-16); two oxidation steps were observed, the first to the radical cation, the second to the dication which undergoes rapid followup chemistry. Cyclic voltammetric studies indicated the radical cation was much more stable in the molten salt than in acetonitrile. This is manifested by the appearance, at low sweep rates on the reverse scan, of the reduction of the radical cation formed during the first oxidation step. At scan rates of the order of 500 mV/sec, the reaction appears to be reversible. All potential values listed in Table I were independent of melt acidity at sweep rate up to 5 V/sec. The first six hydrocarbons listed in Table I showed evidence of significant radical cation stability, although benzo(e)pyrene and pyrene showed evidence of product adsorption at the glassy carbon electrode employed. No reduction of the radical cations of the last six aromatics listed in Table I was found at sweep rates up to 10 V/sec. If the E𝐸₀/2 values obtained were plotted against the ionization potential for the first electron removed, a linear plot was found, indicating minimal differences in the solvation energy between the parent hydrocarbon and the radical cation.

For reasons at this time unknown, those hydrocarbons with E𝐸₀/2 of less than 1.4V were spontaneously oxidized in the most acidic melts. The mechanism, or oxidant, is not known. In melts of mole ratios AlCl₃:BPC less than 1.2:1, no oxidation was observed.
TABLE I

| Compounds                  | Ep/2 volts vs Al |
|----------------------------|-----------------|
| Benzo(a)pyrene             | 1.03            |
| 9,10 Diphenylanthracene    | 1.02            |
| Pyrene                     | 1.09            |
| Anthracene                 | 1.16            |
| Benzo(e)pyrene             | 1.20            |
| Hexamethylbenzene          | 1.36            |
| Pentamethylbenzene         | 1.53            |
| Naphthalene                | 1.58            |
| Phenanthrene               | 1.59            |
| Durene                     | 1.59            |
| Biphenyl                   | 1.73            |
| Mesitylene                 | 1.75            |

It was observed, however, that even in melts where no oxidation was found, color changes were noted when the hydrocarbons were added to acid melts in which no spontaneous oxidation took place. These changes were reversible upon making the melt basic. While the absorption spectra of a number of melts containing the hydrocarbons were recorded, no quantitative work in terms of the determination of extinction coefficients was performed. The reversibility of the color changes with melt composition strongly suggests an acid-base dependent equilibrium between the acid species in the melt and the hydrocarbon. While somewhat speculative, it is our view that these represent the formation of \( \sigma \)-complexes, \((17,18)\) which are formed by an equilibrium of the sort given in reaction 8.

\[
\text{acid} + \text{Al}_2\text{Cl}_7^- \rightleftharpoons \text{base} + \text{H}^+(\text{AlCl}_3)^- \quad (8)
\]

Comparison between the \( \lambda_{\text{max}} \) values for the spectrum of the colored species formed in the \( \text{melt} \) with those reported for the related aromatic carboxonium ion in HF and HF-BF\(_3\) leads to reasonable agreement except for phenanthrene and biphenyl \((19)\). Even here an argument may be advanced that the lack of agreement indicates a steric hindrance related to the size of the acid moiety, written in reaction 8 above as \( \text{AlCl}_3 \), compared to the proton.

The solvolysis equilibrium, reaction 1 above, has been determined from potentiometric titration and has a value of \( 3.8 \times 10^{-13} \) at 30°C \((12)\). The data for the titration curve may be fit completely by the equilibrium represented by equation 1, and does not require the additional equilibria, reactions 2 and 3, as is the case in the \( \text{NaCl: AlCl}_3 \) system. Further support to the evidence cited above from Raman...
for the increase in reaction 2 to the right is found in the fact that, at 175°C, the 2:1 AlCl₃:BPC melt — which is marginally stable at this temperature — does not appear to have anywhere near the vapor pressure of AlCl₃ above it compared to the 2:1 AlCl₃:NaCl melt at the same temperature.

This leads us to suspect that the chemistry of a variety of solutes, particularly organics, may in fact be drastically different than in the NaCl:AlCl₃ system, where the Al₂Cl₆ (or AlCl₃) activity is considerably greater. Preliminary experiments have already verified this expectation (20).

Various properties of these, and related systems have been measured, and ¹H and ¹³C NMR have been performed on the solvent (21,22). In addition, metal ion redox couples have been studied by King, Hussey and co-workers, and the behavior of Ni(II) in the melt has been investigated (23,24,25).

These solvents appear to represent unique and unexplored systems in which it is anticipated much new, novel and hopefully useful chemistry and electrochemistry can be carried out.

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