ELECTROCHEMICAL PROPERTIES OF THE SOLVENT
SbCl₃-AlCl₃-N-(1-BUTYL)PYRIDINIUM CHLORIDE AND ELECTROCHEMICAL AND
SPECTROELECTROCHEMICAL STUDIES OF THE SOLUTE 9,10-DIMETHYLANTHRACENE

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ABSTRACT

Physical and electrochemical properties were determined for ternary mixtures of SbCl₃, AlCl₃ and
N-(1-butyl)pyridinium chloride (BPCl) that are liquid at ambient temperatures. Specific conductivities of the com­
positions (mole %) 60:19:21 (basic) and 60:21:19 (acidic)
SbCl₃-AlCl₃-BPCl, measured over the temperature range
24 - 100°C, varied from 0.00395 to 0.02759 S cm⁻¹.
Viscosities of the 60:21:19 and 60:19:21 melts were
22.8±0.7 and 31.5±0.9 cp, respectively, at 25.1±0.5°C.
For a potentiometric titration between the compositions
60:18:22 and 60:22:18 with SbCl₃ fixed at 60 mol %, the
potential of the Sb(III)/Sb(0) couple increased by 0.43 V
at 27°C. Current-overvoltage curves for the oxidation of
antimony metal in a 60:21:19 melt at an Sb rod electrode
displayed Tafel behavior. The feasibility of performing
electrochemical studies in these media was demonstrated
using cyclic voltammetry, differential pulse polarography
and double potential-step chronocoulometry to elucidate the
electrochemical behavior of 9,10-dimethylanthracene (DMA)
in the 60:19:21 melt. The solute was reversibly oxidized
to its radical cation at an anodic peak potential of +0.50
V relative to the reference electrode SbCl₃-BPCl(α), sat.
SbCl₃/Sb at 27°C. Spectroelectrochemical experiments on
DMA using an optical multichannel spectrometer over the
range 479-984 nm are reported. The spectrum of the DMA
radical cation has four bands with the most intense at
678 nm.

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It has recently been shown (1) that certain SbCl₃-rich mixtures of SbCl₃, AlCl₃ and N-(1-butyl)pyridinium chloride (BPCl) are molten at room temperature and act as solvent-catalysts for hydrogen transfer reactions of anthracene, and that the 9H-anthracenium ion is stable in some of these media. These results suggest that low-melting SbCl₃-AlCl₃-BPCl mixtures may have chemical properties similar to those of higher-melting binary SbCl₃-AlCl₃ and SbCl₃-MCl systems (where MCl is a strong chloride ion donor such as KCl or [CH₃]₄NCI). These higher melting salts have been shown to have unique catalytic properties and to provide environments in which arene ions and arene radical cations are quite persistent and readily studied (2-9). The room temperature melts are more easily handled than the higher-melting mixtures, and carbocations may prove to be even more persistent at ambient temperatures than they are in the binary mixtures at elevated temperatures.

As a next step toward utilizing the ternary room temperature melts, we measured some of their physical and electrochemical properties, and studied the electrochemical oxidation of 9,10-dimethylanthracene (DMA). In studies of the higher-melting SbCl₃-rich mixtures, information on the potential of the Sb(III)/Sb(0) couple as a function of composition together with El/2 values for arene solutes proved to be of key importance in elucidating the chemistry of arenes in these media and we anticipate similar benefits from electrochemical studies of the ternary melts.

Materials. — Purification of the melt constituents has been described (1). 9,10-Dimethylanthracene (Aldrich, >99%) was used without further purification. Antimony metal (Bradley Mining Co., 99.99%) was vacuum cast into 3-mm diameter single crystal rods that were drilled and threaded to serve as electrodes.

Cells and Electrodes. — The spectroelectrochemical cell, electrodes and fittings have been described (9) except that tungsten (Alfa, 99.98%) was substituted for platinum wire as a working electrode material, and the reference electrode was fitted with a Pyrex screw joint, FETFE o-ring and teflon bushing (Ace Glass) for easy assembly. The electrolyte in the reference electrode was a binary SbCl₃-BPCl melt saturated with solid SbCl₃. This reference electrode is designated SbCl₃-BPCl(x), sat. SbCl₃/Sb. The indicator electrode for the EMF measurements was an Sb metal rod which was machined to expose a fresh surface and cleaned with methanol.
The acid-base titration (described below) was performed by pipetting a known volume of acidic melt into a known volume of basic melt.

The conductivity cells, instrumentation and experimental procedures were the same as described previously (10). Viscosity measurements were made at ambient temperature in a glove box using a Sargent-Welch Model S-83400D falling ball viscosimeter. Calibration of the viscosimeter (cell constant = 4.07±0.01 x 10⁻⁴ cm² s⁻¹) was accomplished as described in the literature (11).

Instrumentation. — The electrochemical instrumentation consisted of a Princeton Applied Research Model 174A Polarographic Analyzer, a Model 173 Potentiostat/Galvanostat equipped with a Model 179 Digital Coulometer, and a Model 175 Waveform Generator. Data were recorded with either a Hewlett-Packard Model 7045A X-Y recorder or a Nicolet Model 2090-III digital storage oscilloscope.

Absorption spectra for the spectroelectrochemical (SE) experiments were measured in the visible region with the following equipment. Radiation from a 10-W quartz/halogen lamp was filtered with neutral-density filters to control intensity and a 470-nm long-pass filter to eliminate second-order light. An image of the filament was focused on a square aperture to crop the edges, and a 4×4-mm image of the aperture was focused on the optical cell, which had a 1-mm path length. Light transmitted through the cell was focused on the entrance slit (0.025 mm) of a flat-field, 0.32-m spectrograph (Instruments SA, Inc. Model HR-320) equipped with a 152.5 grooves mm⁻¹ grating. Dispersed light was focused on the face of a linear silicon photodiode array detector (EG&G/PAR Model 1412). The detector array consisted of 1024 photodiodes and was thermoelectrically cooled to -20°C. Detector control and read-out were performed with an EG&G/PAR Model 1218 detector controller and Model 1215 system processor. Spectra were stored on 8-in. floppy disks, and hard copy was obtained with a Hewlett-Packard 9872B plotter and a Data Access Systems, Inc. Model 360 line printer. Wavelength calibration and resolution verification were performed with Hg, Ne, Ar, and Xe atomic lamps.

With the equipment described above a wavelength window 505 nm wide was spread over the 1024 photodiodes to give a maximum of 1024 optical channels at 0.5-nm resolution with a read-out time of 16.4 ms per spectrum. However, in the experiments described here neither such resolution nor such speed was required. By allowing the signal to accumulate and then reading the photodiodes in pairs, a 512-channel spectrum with high signal/noise ratio was obtained in ~0.2 s at a resolution of 1.0 nm. The spectra were corrected for dark current and a slight drift in lamp intensity. A Cary Model 219 spectrophotometer was used for non-SE optical measurements.

Experimental Procedures. — All material transfers were performed in an argon-filled glove box where O₂ and H₂O were
continuously monitored and kept below 1 ppm by circulation of the atmosphere through a purification train. Weighings were performed on an analytical balance in the glove box. Positive feedback circuitry was employed during voltammetric measurements to compensate for solution resistance. The SE experiment was computer controlled in such a way that a spectrum (intensity vs. wavelength) was measured every 60 s. The integration time per spectrum was 0.183 s, and the wavelength window was 479 - 984 nm. Absorbance was calculated by using a spectrum taken just prior to electrolysis as a reference. In order to remove gas bubbles trapped in the optically transmitting electrode (OTE), the SE cell was partially evacuated for a short period prior to the experiment and refilled with argon.

All temperatures (unless otherwise noted) were measured with copper/constantan thermocouples which were calibrated against a platinum resistance thermometer with a Minco RT 88078 bridge, the calibrations of which are traceable to NBS standards.

Results and Discussion

Reactions Among Components. — The SbCl$_3$-AlCl$_3$-BPCK mixtures considered here were restricted to the following formal compositions: 60 mol % SbCl$_3$, (20+$\alpha$) mol % AlCl$_3$ and (20-$\alpha$) mol % BPCK where -2<$\alpha$<+2. Aluminum trichloride is a strong chloride ion acceptor, SbCl$_3$ is a much weaker acceptor while BPCK is a chloride ion donor. Therefore, the dominant chloride-exchange reaction was

\[
\text{BPCK} + \text{AlCl}_3 + \text{BP}^+ + \text{AlCl}_4^- \quad (1)
\]

Since the AlCl$_3$:BPCK mole ratio was close to unity for all melts, one can regard the liquid as consisting of the binary mixture SbCl$_3$-BPCK (75-25%) to which small amounts of TPCK or BPC1 were added. The acidic and basic species in these solutions have been discussed elsewhere (1) so that we shall do no more here than summarize the principal equilibria that have been proposed to occur among them, namely:

\[
\text{SbCl}_3 \rightleftharpoons \text{SbCl}_2^+(\text{solvated}) + \text{Cl}^-\text{(solvated)} \quad (2)
\]

\[
2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^-\text{(solvated)} \quad (3)
\]

\[
\text{SbCl}_2^+(\text{solvated}) + 2\text{AlCl}_4^- \rightleftharpoons \text{SbCl}_3 + \text{Al}_2\text{Cl}_7^- \quad (4)
\]

\[
\text{SbCl}_2^+(\text{solvated}) + \text{AlCl}_4^- \rightleftharpoons \text{SbCl}_2(\text{AlCl}_4) \quad (5)
\]

where SbCl$_2^+$ and Cl$^-$ are strongly solvated by SbCl$_3$ molecules. It is expected that equilibria (2), (3) and (4) are displaced strongly
to the left so that $\text{SbCl}_2^+$ (solvated), rather than $\text{Al}_2\text{Cl}_7^-$, is the
dominant Lewis acid in melts for which $\text{AlCl}_3:\text{BPCl} > 1$.

Physical Properties. — The viscosities of the 60:21:19 (acidic)
and 60:19:21 (basic) melts were determined at 25.1±0.5°C to be
22.8±0.7 and 31.5±0.9 cp, respectively. The viscosity of the acidic
melt is comparable to viscosities measured for $\text{AlCl}_3$-alkylypyridinium
chloride (AlkPC) melts with an $\text{AlCl}_3$:AlkPC mole ratio of 2:1 (12).

The electrical conductivities of the 60:19:21 and 60:21:19
melts were measured over the temperature range 24 to 100°C with
results that are shown in Fig. 1. The specific conductivities of
the two ternary mixtures are almost equal at ambient temperatures,
but at higher temperatures the basic melt becomes more conducting.
The conductivities are comparable to those reported for binary
$\text{AlCl}_3$:AlkPC (2:1) mixtures (12), but are about one order of
magnitude less than the conductivities reported for acidic alkali
metal chloroaluminate melts at slightly higher temperatures (13).

For comparison with $\text{SbCl}_3$-$\text{AlCl}_3$ melts, we have included in
Fig. 1 the conductivity of the binary melt whose composition most
closely resembles the $\text{SbCl}_3$:AlCl$_3$ ratio in the ternary melts (10).
As can be seen in Fig. 1, the conductivity vs. temperature function
for the ternary melts has a curvature (slope increasing with
temperature) opposite to that of the binary melt curve.

Current-Overvoltage Studies. — In an earlier investigation
(14) of the acid-base dependence of the potential of an Sb metal rod
immersed in $\text{SbCl}_3$-$\text{AlCl}_3$ (>90 mol % $\text{SbCl}_3$) an appreciable irrever-
sibility was observed. Furthermore, in a preliminary study using
cyclic voltammetric and chronocoulometric measurements of the
electroreduction of $\text{SbCl}_3$ at inert microelectrodes in acidic
$\text{AlCl}_3$-$\text{NaCl}$ melts, we found the process to be kinetically hindered.
Therefore, we investigated the electrochemical reversibility of the
Sb(III)/Sb(0) couple in an acidic 60:21:19 melt by means of current-
overvoltage curves.

In the absence of mass transfer effects the Butler-Volmer
equation (15) may be used to predict current-overvoltage behavior.
For large overpotentials ($\eta > 0.118/n$ mV) the equations
\[
\ln i = (-\alpha n\eta f \eta) + \ln I_0
\]
for cathodic currents, and
\[
\ln i = [(1 - \alpha) n f \eta] + \ln I_0
\]
for anodic currents should be valid (15). The data are plotted in
Fig. 2; the anodic branch displays Tafel behavior for $\eta > 40$ mV.
The apparent exchange current obtained from the intercept of this
curve is 13 μA cm$^{-2}$, and the transfer coefficient determined from the slope is 0.8. The cathodic branch is somewhat more complicated, and the electrode process may involve more than one fundamental step (16). The possible complications are not significant in potentiometry as long as the current densities are low, as is the case with the high-impedance circuits used in the present investigation. For potentiometric purposes (including the use of antimony as a reference electrode) the electrode was considered to behave reversibly.

Equilibrium Studies. — The overall reduction of SbCl$_3$ releases Cl$^-$ ions according to Eq. (8)

$$\frac{1}{3} \text{SbCl}_3 + e^- \rightarrow \frac{1}{3} \text{Sb} + \text{Cl}^- \quad (8)$$

Thus, the potential of the Sb(III)/Sb(0) couple is dependent on the chloride ion activity. An acidic medium will drive reaction (8) to the right, thereby increasing the "oxidizing power" of SbCl$_3$.

The change in the potential of an antimony electrode resulting from changes in ternary melt composition was measured using the following concentration cell:

$$\text{Sb/SbCl}_3(\text{solid}), \text{SbCl}_3-\text{BPCL}(\text{liquid})/\text{frit}: \text{SbCl}_3-\text{AlCl}_3-\text{BPCL}(60:x:y \text{ mole %})/\text{Sb}$$

where $x:y$ varied from 22:18 to 18:22. The lack of information regarding the transference numbers of charge carriers prevented a calculation of the junction potential. No attempt was made to analyze the data for the purpose of establishing an acidity scale.

The EMF data are shown in Fig. 3 and demonstrate that the potential of the Sb(III)/Sb(0) couple may be tuned over a potential range of 0.43 V for the compositions indicated. For comparison, the Sb(III)/Sb(0) couple may be varied over a 0.44 V range by titrating SbCl$_3$-KCl (90:10) with AlCl$_3$ (14). These data provide information for estimating the extent to which a dissolved solute will be oxidized by a given solvent composition, provided that the half-wave potential of the solute is known.

Voltammetry and Chronocoulometry. — The available electrochemical window in the SbCl$_3$-AlCl$_3$-BPCL mixtures (Fig. 4) is somewhat larger than that reported for SbCl$_3$-CsCl and SbCl$_3$-AlCl$_3$ (>90 mole % SbCl$_3$) melts at 100°C (9). The potential span for both the 60:21:19 and 60:19:21 compositions is about 1.8 V, compared to 1.4 V for the binary melts. [The total potential span available in AlCl$_3$-BPCL binary mixtures between the cathodic limit of the 1:1 melt and the anodic limit of the 2:1 melt is roughly 3 V. (17)] The negative potential limit in the ternary melts is the reduction of Sb(III) to...
Sb metal. As can be seen in Fig. 4, overpotentials for the reduction process at an inert electrode exist for both ternary melts. The anodic limit for the liquids is the oxidation of Sb(III) to Sb(V).

DMA is soluble only to a limited extent in a 60:19:21 melt and the dissolution rate is slow. Solutions were prepared by adding DMA to the melt and heating to 80-100°C with stirring in a closed container for a period of about an hour.

A voltammogram obtained on a basic melt containing DMA at a glassy carbon electrode is shown in Fig. 5. The peak potentials ($E_p$) and half-peak potentials ($E_p/2$) for both waves are listed in Table I along with the difference in peak potentials ($\Delta E_p$). The experimental values of $\Delta E_p$ correspond well with the theoretical value for a one-electron Nernstian process of 60 mV (18). Also included in the Table are half-wave potentials ($E_{1/2}$) calculated from the expression (18)

$$E_{1/2} = E_p/2 + 1.09 \frac{RT}{nF}$$

and values of $n$ calculated from

$$E_p - E_p/2 = 2.2 \frac{RT}{nF}$$

Scan rates up to 20 V s$^{-1}$ revealed no significant shift in the anodic peak potential, and the half-wave potentials determined by differential pulse polarography (19) (average = 0.47 V) corresponded well to the values calculated from Eq. (7).

The integrated Cottrell equation (20) predicts that for diffusion controlled electrode reactions, a linear relationship holds between the charge ($Q$) and the square root of time ($t^{1/2}$). Fig. 6 shows a plot of $Q$ vs $t^{1/2}$ for times up to 20 s; it is clearly linear. The intercept of the plot yields a value of the apparent double-layer capacitance of approximately 5 $\mu$F cm$^{-2}$, while the slope (uncorrected for impurities) gives an upper limit on the diffusion coefficient of neutral DMA of $2.5 \times 10^{-7}$ cm$^2$ s$^{-1}$. Finally, the technique of double potential-step chronocoulometry (20) demonstrates that the charge consumed around a square potential cycle obeys theoretical predictions ($Q_{2T}/Q_T = 0.414$) (21) for 10 and 20 s pulse widths. Thus, there is no significant reaction of the DMA radical cation on a voltammetric time scale.

Spectroelectrochemical Studies. Measurements of absorption spectra at an OTE during electrolysis of ~1 mM DMA in a basic 60:19:21 melt and during subsequent open-circuit decay verify the formation of the DMA radical cation and demonstrate that it is very persistent under these conditions.
Fig. 7 shows spectra measured during electrolysis and Fig. 8 shows spectra measured during open-circuit decay. Bands assigned to the DMA radical cation are at 550, 600, 656 (sh) and 678 (max) nm. Weak, broad shoulders at about 620, 760 and 850 nm are attributed to other species, probably subsequent reaction products because they develop at a much slower rate during electrolysis and are more persistent under open-circuit conditions than those assigned to DMA. In a previous investigation (22) transient spectra of DMA radical cations were measured in benzonitrile solutions at a much lower optical resolution than reported here. To within experimental uncertainty, these spectra show the same profiles as those in Figs. 7 and 8.

From the values of $E_{1/2}$ for DMA and the formal potential of the Sb(III)/Sb(0) couple in the 60:21:19 melt at 25°C, it is estimated that DMA should be partially oxidized with the simultaneous reduction of Sb(III) in this medium. The optical spectrum of DMA in the acidic melt revealed weak absorption bands due to DMA$^{+*}$, but the lack of accurate values for the molar extinction coefficients of the optical transitions prevented a quantitative determination of the concentration. Nevertheless, it is significant to note that solutes with $E_{1/2}$ values more negative than that of DMA will be appreciably oxidized in acidic melts.

Conclusion

The electrochemical properties of novel ternary molten salts as media in which reactive intermediates may be readily studied are reported in this paper. The principal advantages of these ternary melts as compared to SbCl$_3$-KCl and SbCl$_3$-AlCl$_3$ mixtures are ease of handling and a wider electrochemical window. The melts possess tunable redox and Lewis acid-base functions which may be exploited to initiate or suppress reactions in which Sb(III) serves as an oxidant.

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Table I. Electrochemical parameters determined from a 1.2 mM solution of DMA in a 60:19:21 melt at 27°C. Glassy carbon working electrode area = 0.071 cm².

| v (mV/s) | E_p(V) | E_c(V) | ΔE_p(mV)^2 | E_p/2a(V) | E_1/2a(V)^3 | n^4 |
|----------|--------|--------|-------------|-----------|-------------|-----|
| 10       | 0.505  | 0.440  | 65          | 0.445     | 0.473       | 0.95 |
| 20       | 0.500  | 0.440  | 60          | 0.443     | 0.471       | 0.95 |
| 50       | 0.503  | 0.440  | 63          | 0.443     | 0.471       | 1.0  |
| 100      | 0.503  | 0.443  | 60          | 0.445     | 0.473       | 0.98 |
| 200      | 0.505  | 0.445  | 60          | 0.447     | 0.477       | 0.98 |

1All potentials relative to liq. SbCl₃-BPCl (x), sat. SbCl₃/Sb
2Theory = 60 mV (18)
3Calculated from E_1/2 = E_p/2 + 1.09 RT/nF (18)
4Calculated from |E_p - E_p/2| = 2.2 RT/nF (18)

Fig. 1. Specific conductivities of
(a) SbCl₃-AlCl₃-BPCl (60:21:19);
(b) SbCl₃-AlCl₃-BPCl (60:19:21);
(c) SbCl₃-AlCl₃ (3:1) (Ref. 10).

Fig. 2. Tafel plot for the Sb(III)/Sb(0) couple in a SbCl₃-AlCl₃-BPCl (60:21:19) melt at 27°C. Sb metal working electrode, area = 1.51 cm².
(a) cathodic branch; (b) anodic branch.
Fig. 3. EMF of Sb(III)/Sb(0) couple at 27°C for ternary melts. Sb metal working electrode.

Fig. 4. Background cyclic voltammograms of (a) SbCl₃-AlCl₃-BPC₁ (60:21:19); (b) SbCl₃-AlCl₃-BPC₁ (60:19:21). Glassy carbon electrode, area = 0.071 cm². Sweep rate = 100 mV/s, temp. = 20°C.

Fig. 5. Voltammogram of DMA (saturated solution) in SbCl₃-AlCl₃-BPC₁ = 60:19:21. Glassy carbon electrode, area = 0.071 cm². Sweep rate = 500 mV/s, temp. = 27°C.
Fig. 6. Charge-time$^{1/2}$ plot for a 1.4 mM solution of DMA in SbCl$_3$-AlCl$_3$-BPCl (60:19:21). Potential step: +0.35 V to +0.65 V. Glassy carbon electrode area = 0.071 cm$^2$. Temp. = 27°C.

Fig. 7. Spectra measured every 60 s during 20-min electrolysis at 0.65 V of 1.2 mM DMA in a 60:19:21 melt. Pre-electrolysis spectrum used as reference. Pt-screen OTE and 1.0-mm pathlength.
Fig. 8. Spectra measured every 180 s during 57-min open-circuit decay following electrolysis in Fig. 7. Reference same as in Fig. 7.