Although many low-melting inorganic salts are known, and have been studied for various applications ranging from steel heat treatment quenching baths and molten carbonate fuel cells, to alkali metal batteries, the number of cases that are actually liquid below 100 °C is quite small. Mixtures of lithium haloaluminates can be molten at moderate temperatures (100–200 °C), though this problem can be overcome in systems running at intermediate temperatures (100–200 °C).

W wonder whether the use of similar chloride transfer salts might serve as well as the anions.

In electrochemical applications, mixtures of ammonium salts with melting points well below 100 °C, have been used as fuel cell electrolytes, thanks to the proton-carrying ability of the ammonium cation. To obtain single component inorganic liquid electrolytes is difficult. Some salts of the hydrazinium cation formed by proton transfer from acids to hydrazine, melt well below 100 °C and their mixtures with small amounts of water, have been used in the production of liquid propellants for use in artillery and rocketry. Derivatives of hydrazine that are low viscosity ionic liquids, have been used in producing hypergolic ionic liquids that ignite spontaneously on contact with appropriate oxidizing liquids.

Finally, batteries with open circuit voltages as high as 4.3 V have been constructed using the melt of the crystallizable salt [SCl$_2$]$^+$/[AlCl$_3$]$^-$ (dissolved in NaAlCl$_4$), as the active component in the catholyte. [Note: (It is reduced by electrons from Na in the anode compartment to yield elemental sulfur by a 4 electron reduction).]

A similar chloride transfer process was used to make “quasi-molten salts” with tetraethylaluminate anions for possible applications in lithium battery technology, because of the high conductivities that could be obtained in their solutions with LiAlCl$_4$.

The success experienced in the latter types of study lead us to wonder whether the use of similar chloride transfer salts might serve to replace the organic cations in ambient temperature electrolytes that have long been studied in the search for electrolytes that might be useful for low temperature sodium batteries. A recent study produced graphic examples of the loss of conductivity that can accompany the mixing of alkali salts with their organic cation counterparts. Although this problem can be overcome in systems running at intermediate temperatures (100–200 °C), the low conductivities at ambient temperature have severely restricted the use of ionic liquids with alkali cations in any applications that require high currents.

While the arguments advanced to explain the low conductivities of the mixed ionic liquids + alkali salt electrolytes would seem likely to apply to the inorganic chloride salt cases as well, we felt that the study of additional inorganic cation systems deserved some attention. Since AlBr$_3$ has been considered by many to be a more powerful Lewis acid than AlCl$_3$, (a view strongly supported by very recent work, both experimental and computational), and since PBr$_3$ is a more crowded species than SCl$_2$ or PCl$_3$, we have chosen the binary PBr$_3$ + AlBr$_3$, and its mixtures with an alkali metal analog, for an exploratory study. Such a study requires a characterization of the components of any mixture of interest, and it is perhaps in the components of the mixtures that the most interesting results of this work have been encountered.

Experimental

Materials.—AlBr$_3$, of stated purity 99.5%, was purchased in anhydrous form in ampoules from Aldrich. PBr$_3$ of 95% purity was purchased from Aldrich. NaCl was reagent grade from Sigma-Aldrich. All chemicals were stored under inert conditions before and after synthesis.

Synthesis.—All preparations were made in a low dewpoint, argon-filled drybox, using freshly opened ampoules of AlBr$_3$, PbBr$_3$, NaCl, and vacuum-dried NaCl. The glassware was freshly cleansed in a NaOH base bath, washed with deionized water, and oven-dried over a period of days. Stoichiometric amounts of the white powders were weighed inside the glove box, added to a glass weighing bottle and manually mixed with a stirring rod before capping. The samples were heated on a hotplate up to 160–190 °C for 3 hrs then allowed to cool back to room temperature overnight inside the glove box. For storage outside the glove box we used a rubber-sealed dessiccator containing Mg(ClO$_4$)$_2$ as drying agent. Samples were never exposed to the laboratory atmosphere. Glass sample bottles and vials were wrapped in Al foil as the bromoaluminates are apparently photosensitive.

Phase transitions from differential thermal analysis.—Small amounts of the prepared samples were pipetted into 5 mm od 3 mm id pyrex glass tubes, under an inert atmosphere. Another smaller diameter thin-walled capillary tube for the thermocouple was inserted into the sample ~0.5 cm from the bottom of the outer capillary wall. The sample tube with thermocouple capillary in place was wrapped with Teflon tape to exclude moisture and then inserted into a close fitting sample hole of a twin bore aluminum block. For reference sample we used dried Al$_2$O$_3$ packed and wrapped in the same manner as the test sample. Fine k-type thermocouples, connected in the usual way, were inserted to reach the bottoms of the inner capillary tube. The thermocouple wires lead to a NI detector where the total and differential signals were recorded on LabView. The aluminum block was heated at ~12 K/min with a heating cartridge seated in a 3rd borehole in the Al block, and powered by a 120 V Staco Energy transformer. Temperature ramping by a Barnett controller was an option.

Electrical conductivities.—The same aluminum temperature smoothing block used in the previous study was employed for the present work but, in view of the less conductive system, and also the less quantitative ambitions of the present study, twin platinum wire electrode dip cells were used in place of the capillary cell of the...
previous work (the capillary cell also being more difficult to clean and maintain). Cell constants, determined by calibration in N/100 KCl solution, ranged from 4.52 to 5.27.

The dip cell support structure used was an improved version of our earlier dip cells, in which the plastic cap of the earlier cell was replaced by a Teflon lid and seal held in place by a machined aluminum cap with Viton seal. (photo-graphic available from the authors). The aluminum cap and teflon/viton components were needed to tolerate the higher temperatures (up to 265°C) during the slow temperature ramp of 1 K/min of the present work. The glass vials containing the electrolytes under study were loaded under an inert atmosphere, then the twin electrode assembly immersed in the electrolyte, and the cell finally sealed.

The frequency-independent conductivity (hereafter called conductivity), was determined by Nyquist plot analysis of the complex impedance measured using a PAR VMP2 potentiostat (Princeton Applied Research) in the frequency range 10–100 kHz during slow heating from ambient to temperatures as high as 250°C, and back to ambient temperature. The system stability is established by the reproducibility of measurements made during heating, in the cooling half of the temperature cycle. Comparisons with the benchmark conductivity of ethylmethylimidazalium tetrachloroaluminate, [EMI]AlCl$_3$ from Wilkes et al. will be made below.

**Viscosity.**—Viscosities were measured using a Brookfield LV1 rotational viscometer. The prepared electrolytes were placed in a cylindrical stainless steel container specifically designed for rotating cylinder viscosity measurements with the LV1 viscometer. The container has, at its base, a locator lug to ensure its precise positioning, with respect to the rotating cylinder, within the controlled temperature zone of the viscometer heater block. Temperature was ramped up and stabilized using a Barnett temperature controller, and held steady for 90 min prior to measuring. The sample area was covered with a glass dome with a tube inlet for dry nitrogen and a close fitting inlet tube for the rotating cylinder suspension wire link. A slow flow of nitrogen provided an inert protective atmosphere over the exposed surface of the rotating cylinder, within the controlled temperature zone of the viscometer heater block. Temperature was ramped up and stabilized using a Barnett temperature controller, and held steady for 90 min prior to measuring. The sample area was covered with a glass dome with a tube inlet for dry nitrogen and a close fitting inlet tube for the rotating cylinder suspension wire link. A slow flow of nitrogen provided an inert protective atmosphere over the exposed surface of the rotating cylinder, within the controlled temperature zone of the viscometer heater block.

**Density.**—The density was measured utilizing a 1 ml pycnometer. The flask was heated to the chosen temperature and excess sample pipetted off until the meniscus fell at the 1 ml mark, upon which the flask was immediately weighed to obtain the density at that temperature. This was repeated with careful remeltings at increasing temperatures. The equivalent volume, $V_E$, vs temperature data were used to convert specific conductivities, $\sigma$, to equivalent conductivities, $\Lambda_E = \sigma V_E$, for the Walden plot (presented later).

**Structural characterization.**—**NMR spectroscopy.**—To obtain structural information relevant to interpreting the interesting behavior of the liquid and crystal samples of this study, NMR chemical shifts for the nuclei $^{23}$Na, $^{27}$Al, and $^{31}$P were obtained, using a Bruker 400 MHz spectrometer. Spectra were taken in the range 25°C to 100°C on samples that had been flame-sealed under an inert atmosphere in standard NMR tubes. Because of intrinsic fast Na$^+$ motion, magic angle spinning was not necessary for any of the crystalline state spectra.

**X-ray diffraction for crystals.**—X-ray powder diffraction patterns were obtained using a Siemens D5000 diffractometer with Cu K-alpha radiation. The sample on a standard glass slide was covered with a transparent film to protect against atmospheric water. Background scattering from the glass slide and film were subtracted from the initial pattern. Unfortunately, an elevated temperature facility was not available to record the loss of structure on passing the phase transition at 62°C.

**Results**

**NaBr-AlBr$_3$ system.**—As in the NaCl-AlCl$_3$ system, there are two binary crystalline compounds, NaAlBr$_4$ and NaAl$_2$Br$_7$, the second of which is of special interest to us. The 25°C X-ray diffraction patterns for each, after background subtraction, are shown in Figure 1, and show many similarities doubtless related to the packing of AlBr$_4$ tetrahedra, isolated or linked as the case may be. It should be emphasized that a detailed structural analysis of the crystalline states of the compounds was not an objective of this study. The XRD’s were obtained only to show that the ambient temperature states of the system are crystalline and ordered.

According to the DTA thermograms, the crystal of NaAlBr$_4$ melts sharply at 196°C to a liquid of high conductivity, 300 mS/cm$^{-1}$. The conductivity and the DTA thermogram data for NaAlBr$_4$ from room temperature to above the melting point, are shown, superimposed, in Figure 2. We note that there is a high conductivity (approaching $10^{-3}$ S/cm$^{-1}$) in the solid state preceding the actual fusion, as is characteristic of all alkali chloroaluminates. Evidently the alkali cations move fairly freely in the crystalline lattice as the melting point is approached, even though the ambient temperature crystal structure shows little sign of disorder. There is additional pre-melting activity in both conductivity and calorimetry in the last 15°C, which could be due to disordering in the crystalline state on the one hand, or impurity pre-melting on the other.

This behavior takes a more striking form in the case of NaAl$_2$Br$_7$, for which the corresponding data are shown in Figure 3. It is clear that some dramatic structural change must take place at 63°C, which NMR data (shown below) will suggest is the onset of anion rotation. The high conductivity will then reflect the facilitation of the Na$^+$ motion, for which the corresponding data are shown in Figure 1. The system stability is established by the reproducibility of measurements made during heating, in the cooling half of the temperature cycle. Comparisons with the benchmark conductivity of ethylmethylimidazalium tetrachloroaluminate, [EMI]AlCl$_3$ from Wilkes et al. will be made below.
The NaAl composition is presented along with data for mixtures with this latter composition as [PBr$_4$] to clarify the presentation (as is common in the description of ionic liquids). We introduce the brackets to clarify the presentation. The conductivity of two ceramics are included as dashed lines in the figure.

The conductivity of NaAl$_2$Br$_7$ is in the mixed phase and comparable to that of the most NaAl$_2$Br$_7$-conductive solid phase known to date (the special NaSICON of Ceramatec). The data for the latter two ceramics are as dashed lines in the figure.

Figure 2. Superposition in temperature of the DTA thermogram and dc conductivity data for the composition NaAlBr$_7$. The conductivity is quite high in the crystalline state, but jumps another two orders of magnitude on melting. The conductivity of two ceramic separator materials, β-β’ alumina, and NaSICON from Ceramatec Co., are shown for comparison.

The PBr$_4$-AlBr$_3$ system. Two compounds form in this system. At the equimolar composition there is a well-defined compound with high melting point, that is not of interest to this study of the ionic conductivity. The conductivity of two ceramic separator materials, β-β’ alumina, and NaSICON from Ceramatec Co., are shown for comparison.

Figure 3. Superposition of dc conductivity data and DTA thermogram for the case of the composition NaAl$_2$Br$_7$. Here the higher temperature (weak) transition at 94°C is the (apparently congruent) melting transition, and the major transition at 62°C occurs in the solid state. The conductivity of this crystalline solid increases by four orders of magnitude to a remarkable 10 mS/cm$^{-1}$ at 65°C, higher than that of the well known Na$^+$ ββ’ alumina mixed phase and comparable to that of the most Na$^+$-conductive solid phase known to date (the special NaSICON of Ceramatec). The data for the latter two ceramics are as dashed lines in the figure.

The ionicity of this liquid is one of the questions to be addressed in our Discussion section.

The mixed cation system NaAl$_2$Br$_7$ + [PBr$_4$][[Al$_2$Br$_7$]$.—In this section we see the results for the intended inorganic cation equivalent of the mixed cation system studied in the recent paper that stimulated the undertaking of the present project. We refer to the study of the mixed tetrachloroaluminate system ethylmethylimidazolium tetrachloroaluminate + sodium tetrachloroaluminate, written more simply as [EMI$^+$][AlCl$_4$]$^-$ + NaAlCl$_4$. We were obliged to choose the [Al$_2$Br$_7$]$^-$ stoichiometry because of the high melting points of the tetrabromoaluminate compounds. Conductivity data for a binary cut across the ternary system NaBr-PBr$_3$-AlBr$_3$ at constant AlBr$_3$ content are shown in Figure 4.

The rotator phase of NaAl$_2$Br$_7$.—The conductivity of NaAl$_2$Br$_7$ between the first order transition temperature at 60°C and the melting point at 94°C, is among the highest conductivities ever measured for sodium ions in a solid state material. As Figure 3 makes clear, the sodium ion is almost as mobile in the plastic crystal state as it is in the liquid. A recent review of sodium ion-conducting systems (B) does not report any previous examples of such high sodium ion conductivity in simple inorganic compounds.

Discussion

The rotator phase of NaAl$_2$Br$_7$. The conductivity of NaAl$_2$Br$_7$ between the first order transition temperature at 60°C and the melting point at 94°C, is among the highest conductivities ever measured for sodium ions in a solid state material. As Figure 3 makes clear, the sodium ion is almost as mobile in the plastic crystal state as it is in the liquid. A recent review of sodium ion-conducting systems (B) does not report any previous examples of such high sodium ion conductivity in simple inorganic compounds.
The progression from low temperature ordered phase, to plastic crystal, to liquid, is well characterized by NMR spectroscopy, particularly for the $^{27}$Al nucleus. Spectra are shown in Figure 6a for $^{27}$Al and in Figure 6b for $^{23}$Na. The considerable structure in the $^{27}$Al spectrum for temperatures below that of the phase transition, is unexpected for a compound in which the Al is 4-coordinated. However, it is reproduced for two temperatures 30°C apart, and it is the main resonance at ~90 ppm that survives in the higher temperature phases.

The structure on the downfield side of this resonance is reminiscent of the effects of tilting the (AlO$_6$) building blocks in the structure of the $^{27}$Al NMR spectra of MOF crystals reported in the last segment of the review by Taulelle and co-authors. There the effect of tilting connectivity can generate additional resonances as much as 90 ppm downfield from the standard six coordinate $^{27}$AlO$_6$ resonance. The larger effect in the case of the AlBr$_4$ building blocks may be a reflection of the strong quadrupole on the bromide anion coupling with the quadrupole of $^{27}$Al.

What is not seen in the $^{27}$Al spectra, is any indication of how much of this freedom of alkali cation motion remains above the melting point, when the crystal lattice provided by the anions has collapsed. The answer is hinted at by the viscosity data for this liquid seen in Figure 5, but is only clearly seen when the data are presented in the combined form of the Walden plot presented in the next section.

The mixed cation system NaAl$_2$Br$_7$ + [PBr$_4$]$/[Al_2Br_7^-]$.—The first observation to be made in discussing the results for the present mixed inorganic cation system is that the form of the binary conductivity isotherms is different from that of the previously studied system containing the organic cation [EMI$^+$][AlCl$_4^-$] + NaAlCl$_4$. At first sight this might indicate the banishing of the alkali cation trap that frustrated the realization of high conductivities in the mixed alkali + organic cation system. Unfortunately it seems that the reason for the smoothly increasing conductivity with alkali content, is a more complicated one related to the intrinsically lower conductivity of the inorganic cation liquid.

In Figure 7 we compare the results for the two systems. It is seen that at 25°C the non-alkali end member is more than two orders of magnitude less conductive when the cation is the inorganic [PBr$_4$]$^+$. To show that this is not due only to reduced ionicity, we turn to the Walden plot, Figure 8 below, which examines the conductivity per mole of ions, (assuming full conversion, by chloride transfer, to form ions [PBr$_4$]$^+$ and [Al$_2$Br$_7^-$] which do not form ion pairs or other associates) as a function of the liquid fluidity (reciprocal of the viscosity for which data were displayed in Figure 5.) To see the
almost ideal behavior of low-melting mixtures of pure alkali metal tetrachloroaluminates with tetrabromoaluminates, all except one (solid symbol) of the data points are obtained by extrapolation of higher temperature data.

We see that the points for [PBr₄⁺][AlₓBr₇⁻], while further below the ideal line than in the ideal EMIIAlCl₄ case, are still deviating from it by only about a factor of two. Indeed, except for the behavior of sodium dialuminum heptabromide, the deviations from the ideal Walden line found for the solutions of this study are not much greater than those seen for a typical collection of ionic liquids in the literature. The largest negative deviation in Figure 8 is found for the 1:1 mixture indicating that the alkali cation trapping phenomenon is more important in this system than it is in the mixed tetrachloroaluminates.

NaAlₓBr_{7−x}, on the other hand, shows a greater positive deviation than has been seen for any ionic liquid except the silver ion conducting system AgCl₀.₃₅ AgI₀.₄₅CsCl₀.₂₀. While the possibility of overestimates in the viscosity data mentioned earlier for this difficult composition cannot be discounted, they seem unlikely to be the explanation. A ²³Na pulsed field gradient NMR diffusivity comparison with ³¹P diffusivity in this system would be able to confirm that the extreme decoupling seen in the plastic crystal state of this compound is indeed carried over to the liquid state.

The ³¹P NMR spectra.—For the molecular cation salt, [PBr₄⁺][AlₓBr₇⁻], the high ionics suggested by the Walden plot are supported by the ³¹P resonances observed in this system. These are extraordinarily diverse in frequency, see Figure 9, but are dominated by a resonance that can be attributed to the PBr₄⁺ cation as argued below. The ³¹P NMR spectrum has features that cover the range from 230 to −82 ppm. Since the areas under the resonance spectra are quantitatively related to the number of participating nuclei, they are revealing in the information they give about speciation in the liquid. There are three resonances in evidence, of which the one at +227 ppm, which we attribute to the reduced molecular species PBr₃, accounts for only 3% of the ³¹P nuclei in the system. The resonances are so separated in frequency that exchange of bromides between species is probably not obscuring the quantitative aspects of the speciation. The main peak in our ³¹P spectrum (with 87% of the ³¹P nuclei) lies at −82 ppm and we attribute it to PBr₄⁺ on the basis of the MAS NMR study of Dillon et al. for PX₄⁺ cations in crystal structures (X is one or more halogens). In that study the resonance for PBr₄⁺ was placed in the range −66 to −80 ppm, referenced to the standard 85% H₃PO₄ solution. Even more precisely, Aubauer et al. plotted δ³¹P in relation to P-Br bond length in PBr₄⁺ for a series of counter anions of decreasing basicity, and for

Figure 8. Walden plot showing the equivalent conductivity as a function of the inverse viscosity. The diagonal is the ‘ideal’ behavior in which the ionic mobility is strictly controlled by the fluidity of the medium in which the ions are moving. PBr₄⁺AlₓBr₇⁻ is a quite good ionic liquid by this criterion. For the sodium bromoaluminate, the conductivity is found to be much higher than predicted from the viscosity which implies almost free sodium ion motion, as in the high temperature crystal. Such behavior has only been seen previously in the case of the silver halide glassformer, AgCl₀.₃₅ AgI₀.₄₅CsCl₀.₂₀, where a comparable decoupling of conductivity from viscosity was displayed by comparison of the conductivity and shear viscosity relaxation times.

Figure 9. NMR spectra of ³¹P in the liquid states of the inorganic liquid, supporting the representation of the conducting liquid of Figure 4, lower curve, by the formula [PBr₄⁺][AlₓBr₇⁻]. At ambient temperature, 87% of the ³¹P nuclei are in the structure with resonance at −82 ppm, which is attributed to the PBr₄⁺ species (see text) Only 9% are found in the structure with resonance at −62 ppm which is of uncertain origin. The faint resonance at +227 ppm is due to the reduced P⁶⁺ state in the molecule PBr₃.
the case of AlBr$_4^-$ anion show the value $-75$ ppm. The decreased anion basicity associated with the change from AlBr$_4^-$ to AlBr$_7^-$ in our system, would indeed move the resonance downfield towards the value $-82$ ppm that we observe.

The narrower peak at $-62$ ppm, that grows with increasing temperature, is not easily accounted for. A decoupled fast-spinning molecular PB$_3$ formed by reversal of the halide transfer process (which increases the entropy as demanded by temperature increase) should have a resonance well downfield of PbBr$_4^+$, though it is possible that a tight ion pair PbBr$_3^+$Br$^-$, such as is seen in the crystal state of PB$_2$, could explain it.

Halogen transfer salts of much higher conductivity than that observed in Figure 4 are known, e.g., the liquid [CH$_3$Cl = O]$^+$$[AlCl_4]^-$ which has a 25 °C conductivity$^{11}$ equal to that of [EMI$^+$][AlCl$_4^-$], i.e., well over 10 mScm$^{-1}$. However, the cation in this case is not inorganic so the conducting liquid is not an inorganic ionic liquid. The inorganic case of [SCl$^+$][AlCl$_4^-$] mentioned in the introduction is too high-melting to be considered an “liquid” in the current understanding. On the other hand, in preliminary work for a conference presentation$^{28}$ we did obtain a mixed bromide chloride analog [SCIBr$_2^+$][Al$_2$Br$_7^-$] that was liquid at ambient temperature. It had a conductivity that was intermediate between that of the present [PB$_3^+$][Al$_2$Br$_7^-$] and that of [CH$_3$Cl = O]$^+$$[AlCl_4]^-$ and will be included in a future publication.

The PB$_3^+$ cation is a large and heavy species, and it is perhaps not surprising that its liquid with the Al$_2$Br$_7^-$ anion should have a lower conductivity than that of the liquid [EMI$^+$][AlCl$_4^-$] with which comparison is made in Figures 4 and 7. It is noted that the conductivity in the binary system [PB$_3^+$][Al$_2$Br$_7^-$] + NaAl$_2$Br$_7^-$, although lacking the pronounced minimum of the system with EMI$^+$ cations, still has a large negative deviation from linearity, and a large negative deviation from the ideal line in the Walden plot (Figure 8). This is no doubt due to the same alkali cation trapping phenomenon that was identified in our earlier study, the results of which are included in Figure 7. It is implied that near the NaAl$_2$Br$_7^-$ composition there must be a dramatic crossover from subionic to superionic alkali cation behavior, which might prove interesting to investigate in future studies.

Concluding remarks.—This project has revealed some interesting phenomenology concerning the possible degrees of freedom of motion of sodium ions in inorganic ionic liquids and their crystalline phases, though it has evidently missed its original objective of providing a simple inorganic cation that is competitive with the widely used EMI cation of our earlier alkali cation trapping study. In this case it would seem that small, covalently-bonded inorganic molecular cations such as NO$_2^+$, NSF$^+$ and the borenium cations [BCL$_2^-$] L, a ligand (whose ionic liquids have been described recently$^{29}$), could provide a better choice for increased conductivity and ionicity. Unfortunately, the number of small singly charged molecular cations available for testing is not large.

Noting the success of the Na/Na $\beta$Al$_2$O$_3$/[SCl$^+$][Al$_2$Cl$_6$] − 4 volt rechargeable cell mentioned in our introduction, it is a matter of interest whether a PB$_3^+$ analog, based on the observations of the present paper, might also be feasible. The 5-electron reduction would lead to a high charge storage capacity. It might be expected that it would encounter many of the same sealing and solid electrolyte problems that have delayed commercialization of the Na/sulfur(IV) cell, but the lower temperature of operation could provide important advantages.

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