There are many reasons for seeking liquid electrolytes that are free of molecular solvents for electrochemical applications. A leading one is the great reduction in fire hazard that such electrolytes usually offer. Another is the possibility of ionic conductivities competitive with those of the best salt-in-molecular solvent electrolytes. Wilkes and coworkers\(^1\)\(^,\)\(^2\) had long ago (1984) shown that liquid electrolytes based on the ethylmethylimidazolium (EMI) cation, with tetrachloroaluminate anions, had conductivities as high as 22 mS/cm at 25 °C and 81 mS/cm at 100 °C. These were a few% higher than the values reported some years earlier\(^3\) for the ρ-picolinum tetrachloroaluminate (61 mS/cm at 100 °C) and had the advantage of remaining liquid to ambient temperatures. Both exceeded the conductivities of the “standard” lithium cell electrolyte, (LiPF\(_6\) in the mixed cyclic-acyclic carbonate molecular solvents), 12 mS/cm at 25 °C for EC-DMC, 1:1.\(^4\)

Somewhat smaller values (9.1 mS/cm) can now be obtained with air- and water-stable ethylmethylimidazolium bis-triflamide \([\text{EMI}^{+}\text{[BF}_2(TFA)_2]^{-}}\) (or EMINTf\(_2\)) according to Pan et al.,\(^5\) who confirm the earlier values of Tokuda et al.,\(^6\) and Widegren et al.\(^7\) Slightly higher values (11 mS/cm) have recently been reported for \([\text{EMI}^{+}\text{[BF}_2\text{F}(\text{TFA})_2]^{-}}\) by Gores and coworkers in a wide-ranging and precise study of fluorborate-based anion systems.\(^8\)

Kim et al.\(^9\) have since found that solutions of LiNTf\(_2\) in EMINTf\(_2\) may have conductivities only slightly smaller than those of the EMINTf\(_2\) demonstrating that the pessimism concerning ion trapping of lithium in mixtures of lithium salts with ionic liquids expressed by Cooper and one of us, on the basis of early (1983) LiX-ILX (X = Cl, Br, I) solution studies,\(^10\) may have been premature. Evidently, the low basicity (related to polarizability) of the bis-triflamide can overcome much of the lithium ion trapping effect observed in the presence of polarizable anions, that Cooper had sought to overcome using tetrafluoroborate anions.\(^10\) Unfortunately the Li\(^+\) ion remains the least mobile species in these mixtures.\(^11\)\(^,\)\(^12\)

Nevertheless, in view of the low basicity of the AlCl\(_4^{-}\) anion, there seemed to be some prospect that these melts might provide a means of lowering the operating temperature, without too much sacrifice of conductivity, of cells of the ZEBRA (Na/NaCl\(_2\)) and sodium/sulfur types to the melting point of sodium - (or even to ambient temperature)\(^13\) if mixed alkali metal (Na-K) anodes could be used.

Contrary to this aspiration, however, was an observation reported by Wilkes\(^14\) in a 1994 internal (Frank J. Seiler Laboratory) report. Wilkes noted that there is a rapid decrease in conductivity when NaAlCl\(_4\) is added to \([\text{EMI}]^{+}\text{[AICl}_4^{-}\] “Surprisingly, as more sodium ion replaces the large imidazolium cation, the conductivity goes down”\(^14\) - see their Figure 9). The observation was interpreted\(^14\) in terms of the crystal structure of a 1:1 double salt forming in the binary system (melting point ~35°C), which revealed enclosure of the sodium ion within a network of tetrahedral anions that 6-coordinated the Na\(^+\) cations. This scenario would be consistent with the alkali cation trapping interpretation suggested earlier by Cooper.\(^10\)

Unfortunately, no conductivity isotherms were presented and the work was not published in the open literature. Similar observations were later made by Kim et al.,\(^15\) for the lower-conducting quaternary ammonium tetrachloroaluminate ionic liquid (three alkyls and a benzyl), who made important electrochemical observations (see later) but, again, a complete study to identify the location and depth of the conductivity minimum, was not made.

With an interest in learning more about this unfortunate behavior, we decided to repeat the study with the aim of obtaining more detail on the trapping phenomenon and hopefully identifying some means of obviating it. Some encouragement to this end has been provided by the moderate success reported by Ui et al.\(^16\) in developing LiAlCl\(_4\)-\([\text{EMI}]^{+}\text{[AICl}_4^{-}\] electrolytes for “direct electrolyte” lithium battery technology.

It should be mentioned here that the electrochemical window offered by these electrolytes is highly dependent on the actual electrolyte composition, specifically the Cl\(^-\)/AlCl\(_3\) ratio. The acid-base reaction that forms the AlCl\(_4^{-}\) anion from the basic chloride of the EMICI and the Lewis acid AlCl\(_3\) is accompanied by a large free energy change. The free energy change accompanying this process was first evaluated for the alkali halide AlCl\(_3\) cases by the groups of Mamantov,\(^17\) Bjerrum,\(^18\) and Osteryoung,\(^19\) using thermodynamic studies of pCl\(_2\) and then supported by observations of the change in optical basicity\(^20\)\(^,\)\(^21\) (based originally on the \(P_{1}^{\text{h}}<<S_{0}^{\text{h}}\) UV spectral shift on crossing the AlCl\(_4^{-}\) stoichiometry) of indicator ions doped into the melt. The shift in UV absorption peak wavelength for probe ions Pb\(^{2+}\) ions observed by Bennett and Angell\(^22\) when the AlCl\(_4^{-}\) stoichiometry is crossed in the KCl-AlCl\(_3\) system, is extremely abrupt, and amounts to 40.1 nm. This translates to an (electronic) energy change \(h\Delta\nu = (h\nu(h)/\Delta\lambda)\) of 0.562 eV,\(^23\) which reflects very closely the thermodynamic change 2.303 RT/F(\(\Delta\nu(h)\)) = 0.57 eV - see also Figure 1 of Ref. 19 for the direct potentiometric titration in the NaCl-AlCl\(_3\) system. The much larger changes that occur when the EMI cation replaces the alkali cation can be appreciated by comparing titration curve of Ref. 23 with that from Hussey et al.\(^24\) for the EMICI + AlCl\(_3\) case, where the voltage step at AlCl\(_4^{-}\) stoichiometry rises to more than a full volt.
The widest electrochemical window in these systems is obtained when the pCl− is located at the neutral point of the titration, where the pCl− activity is pre-empted by formation of the soluble MgCl42− anion. CaCl2 will buffer at a slightly more basic chloride ion activity. Excess (solid) alkali chloride has long been known to buffer near the basic limit for inorganic buffers.

Our first objective in the present study is to quantify the phenomenon of alkali metal mobility depression, and the obvious first choice of system is one of the organic cation-based ionic liquids (e.g. EMICl-AlCl3). However to set the problem in perspective, it is desirable to consider the alternative possibilities. An alternative strategy employed for obtaining ambient temperature ionic liquids for electrolyte applications has involved the use of inorganic moieties. Inorganic salts with low melting points, such as hydrazinium nitrate, have been known for a long time.30 However they are not suitable for alkali battery purposes because of the labile protons typical of proton transfer salts. On the other hand, salts formed by halide transfer, rather than proton transfer, do not have this limitation.

Thus, highly conducting electrolytes have been prepared by using strong Lewis acids (AlCl3, BCl3) to extract halide ions from molecular species and thereby to create alternative tetrachloroaluminate liquids.25,32 These can be used as the corresponding salts of tetra-alkylammonium cations. An example of this type of solvent-free ionic liquid is [CH3N=PCl2][AlCl4−]. Samples (III) and (IV) are all-inorganic. (b) Conductivity isotherms in the binary system [M][AlCl4] + LiAlCl4 where M is trichlorophosphazosulfonyl chloride, Cl3PNSO2Cl (sample III in Figure 1a). The LiAlCl4 datum at 100 °C was obtained by extrapolation of higher temperature data. Sample identities: I: [CH3N=PCl2][AlCl4−], II: [CH3N=PCl2][AlCl4−], III: [Cl3P=NSO2]+[AlCl4−], IV: [Cl3P=NPOCl2]+[AlCl4−], V: [CH3N=PCl2]+[BCl4−].

One observes the possibility, in Figure 1a, of systematically increasing the conductivity from the 1 mScm−1 of the all-inorganic case IV, by addition of LiAlCl4 (Figure 1b). If the LiAlCl4-LiAlI4 eutectic (Tf = 60 °C)35 were used as source of Li+ cations, the entire composition range would satisfy the ionic liquid criterion. These binary inorganic solutions also appear to have very wide electrochemical windows, and reductive stabilities sufficient to permit reversible deposition and stripping of lithium,32 hence presumably also of sodium.

Despite these favorable properties, the materials of Figure 1 are only referred to as “quasi-ionic” liquids,32 since reported low viscosities suggest that their ionitities might not be ideal. Ionity refers to the extent to which ions are free from association with species of the opposite charge. It is currently much discussed in the ionic liquids field,96-98 using such measures as (i) conformity to the classical Walden rule33 (assessed using a Walden plot)38 or (ii) accord with the Nernst-Einstein equation36 (see discussion section). Thus it was deemed preferable for the purposes of the present project to start our study with the organic cation salts since their liquid states are known to be of high ionity. Furthermore, while they are water and air-sensitive, they are not disadvantaged by toxicity issues. The wider electrochemical window in these systems is obtained when the pCl− is located at the neutral point of the titration, where the pCl− activity is pre-empted by formation of the soluble MgCl42− anion. CaCl2 will buffer at a slightly more basic chloride ion activity. Excess (solid) alkali chloride has long been known to buffer near the basic limit for inorganic buffers.

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Experimental

Materials.— Commercial grade NaAlCl4 and 99.5% NaCl were both purchased from Sigma-Aldrich. Anhydrous AlCl3 (99.9%) in sealed ampoules was obtained from Alfa Aesar. 1-ethyl-3-methyl imidazolium chloride (EMICl) was purchased from Arcos Organics. All materials except the NaCl were stored in a drybox, and only opened at the time of use.

Preparation of chloroaluminates.— The commercially obtained NaAlCl4, when fused, yielded a liquid that was not colorless nor fully transparent so was judged unsuitable for our purposes. By contrast the melt obtained my carefully premixing, and then fusing, pure NaCl and anhydrous AlCl3 (ampoules, see Materials) in a glove box, was of pleasing quality and was used for our further studies.

To obtain the corresponding ionic liquid for conductivity determinations, and for use in preparation of the binary chloroaluminate solutions of this study, the commercial EMICl powder was weighed out in stoichiometric proportions, in a glove box, and added to a pre-weighted amount of the anhydrous AlCl3, in a weighing bottle which was immediately capped. The components simultaneously reacted and fused to yield a clear ambient temperature liquid. Once in the form of the [EMI][AlCl4], the AlCl3 activity is greatly reduced and the need for great caution concerning exposure to atmospheric moisture is less urgent.

For binary tetrachloroaluminate solution preparations it was possible to add the preformed NaAlCl4, described above to weighed quantities of the liquid EMIAlicl4. However, it was mostly found more convenient to follow a procedure in which the EMICl and excess AlCl3 were first mixed, fusing spontaneously, and the stoichiometric mass of NaCl then added, using gentle warming as needed, to achieve the desired tetrachloroaluminate composition.

Conductivity measurements.— Demountable capillary cell.— Because of the high conductivities expected from previous measurements,1,39 the simple twin electrode dip-type cells that have been used in much of our recent work15,40 were deemed inadequate for the accuracy we sought, and a three part capillary cell suitable for use with highly water sensitive electrolytes, was designed. The cell consists of an upper electrode, with isolated thermocouple well, that mates, through a ground glass sleeve, with a capillary conducting path component, as illustrated in Figure 2a and 2b. The cell constant, determined completely by the choice of capillary length and bore, was chosen to be near 30 cm−1. These, together, then sleeve into an outer compartment that contains the lower electrode. The sample is added, and the cell assembled, inside the dry-box. Once assembled, all further actions can be safely taken outside the drybox.
To ensure that the liquid sample rises smoothly through the capillary to immerse the upper electrode, this segment contains a small hole, situated well above the upper electrode, which allows pressure to equalize as the sample rises up the capillary.

The assembled cell fits snugly down into a removable cylindrical block which itself inserts into a temperature-controlled, cartridge-heated, aluminum block (Figure 2c) sitting in a glass wool-insulated container, the upper volume of which is then filled with glass wool to ensure a uniform temperature over the whole cell. Temperature is controlled to ±0.1°C by a Barnant Co. Model 68900–11 temperature controller which permitted also the use of a continuous heating ramp.

**Frequency independent conductivity determinations.**—Measurements of the conductivity as a function of frequency, over the range 0.01–100 kHz, were usually performed in a continuous heating mode at a ramp rate of 1K/min. Data were acquired using a PAR VMP2 potentiostat (Princeton Applied Research) with a frequency range of 10 Hz to 1 MHz of which we used only the lowest four orders. After the heating run was complete, further measurements were made during cooling to confirm that the heating rate was slow enough for the data to be collected under effectively isothermal conditions (see Results section).

The dc conductivity was determined by the standard complex impedance method. Because of the high conductivity of our samples, most of the impedance measurements were made at frequencies below those at the $Z''$ minimum of the Nyquist plot ($Z''$ vs $Z'$), meaning that conductivity values would depend on an extrapolation to $Z'' = 0$. Concern with measurement precision required us to worry about the details of the Nyquist plot in the vicinity of the minimum, because, in the absence of a perfect conductivity vs frequency plateau, the dc conductivity value must be assessed using a single extrapolation.

Figure 3 shows a set of low temperature data for which the data extend into the domain of the complex impedance arc that is intrinsic to the conductivity relaxation. The complete form of this intrinsic conductivity arc is shown as a dashed curve in Figure 3. It would seem that the dc conductivity is easily and unambiguously defined from such a plot, however this is where problems can arise. The insert to Figure 3 shows a blow-up of the data in the highlighted zone of the main figure. It shows that close to the minimum there is a change of slope, which in some cases can be much more significant than in the case shown.

The blow-up shows that data in this “low slope” zone should be omitted from the extrapolation if a precise meeting (with the extrapolation of the intrinsic conductivity arc), is to be obtained on the $Z'' = 0$ axis (red and blue dashed lines in Figure 3). Otherwise uncertainties in excess of 1% in the conductivity measurement may be incurred. In the case shown, the two extrapolations agree within 0.5%.

**Results**

In Figure 4 are shown Arrhenius plots of several compositions in the binary system from the present measurements. Comparison is made with the data of Fannin et al. for the pure [EMI][AlCl₄], and the agreement is seen to be satisfactory in view of the sensitivity of conductivity to the precise composition in the vicinity of AlCl₄⁻ stoichiometry, and the fact that neither preparation was buffered at the midpoint pCl⁻. While there have been a number of electrochemical studies of this particular system concerned with electrodeposition, not much attention has been given to the conductivity itself since the detailed studies of Ref. 1.

The highest conductivity in the system is clearly that of the alkali chloroaluminate itself, though the temperature range is limited. The data in Figure 4 for NaAlCl₄ extend to well below the thermodynamic
In these cases the liquid conductivity goes through a sharp maximum at the 50 mol% composition. This is true also in the case of alkali metal halide system KCl + AlCl3 melts (studied at higher temperatures). In each of these cases, the next nearest neighbor cation to the univalent Na+ is an AlCl3 species and the second nearest neighbor cation is another sodium ion. The high charge density of AlCl3 polarizes the chloride ion electron density toward it, decreasing the coulomb energy of the system, making it less viscous, and leaving the univalent cation free to move. In the case of the lithium cation, the Li+ may even be superionic (see the Walden plot of Ref. 33 that is reproduced, with additional data, below). In fact, the simulations of Salanne et al.,44 suggest that all the alkali metals in their tetrachloroaluminate melts are weakly superionic with respect to the anion mobility (though Li+ is less free than the Na+).

In the mixtures of EMII and Na+ tetrachloroaluminates, the same considerations, but this time involving competition between the second nearest neighbor cations, lead to the opposite result - a strong decrease in conductivity in the mixtures. At 50 mol% NaAlCl4, the decrease in conductivity from its additive value amounts to a factor of 2 at 185°C and increases to more than an order of magnitude at ambient temperature (using extrapolated values for the pure NaAlCl4 conductivity from Figure 4). The maximum depression is found on the NaAlCl4-rich side of the 1:1 stoichiometry. Although the next nearest neighbor cation is still an AlCl3+, each alkali cation is now competing with a very weak-field second nearest neighbor for the AlCl3− complex anion taken as a whole. The alkali cation wins, and so creates a self-trap. Indeed, the partial phase diagram provided by Wilkes14 shows the presence of a mixed crystal with congruent melting point at the 50 mol% NaAlCl4 composition, the crystal structure of which they determined. It showed the Na+ ion enclosed in a cage of AlCl4− anions.

This is generally in line with expectations from the simple cation competition ion trapping, scenario advanced long ago for the corresponding phenomenon in mixed iodide ionic liquids.10 The line of thought actually has its roots in the early days of inorganic molten salt mixtures, when Kleppa and Hersh45 used the electrostatic argument to interpret enthalpy of mixing data in alkali metal nitrate binary solutions (later refined by a conformal solution theory argument46 for the same mixed alkali nitrates. An alternative anion polarization argument due to Lumsden47 lead to the same expectations. Since the arguments are quite general they should apply to all mixed monovalent cation systems, but be more severe for those systems with highly polarizable anions, thus more serious for alkali iodide +Li cation iodide systems than for the mixtures containing the less polarizable tetrafluoroborates. This was the reasoning that lead to the discovery in 1982 of the first water-soluble, air-stable, ambient temperature ionic liquid (methoxyethylidimethylammonium tetrafluoroborate, conductivity 1.7 × 10−3 S cm−1),10 which unfortunately was not promoted by its inventors at the time.

There are some problems with this model, however. The competitive electrostatics argument would lead to the expectation that Li+, with its highest charge/radius ratio, would be the most strongly trapped among the alkali metals while Cs+, with a much weaker field, would be the least affected. But this is not what is found in the laboratory. The limited data in the report by Wilkes14 shows that the decrease in conductivity on addition of MAIAlCl4 to [EMII][AlCl4] is most rapid when M is the largest alkali cation.

The explanation may lie in the kinetic factor associated with cation size. We know from previous studies of viscosity and conductivity in the case of LiAlCl4, that the Li+ motion is not strongly coupled to the motion of the anion except at high temperatures. This can be ascertained from a Walden plot containing data for LiAlCl4,43 reproduced below in Figure 6. The data for LiAlCl4, taken from Janz48 (and extrapolated from binary solution data where necessary), are for temperatures higher than those under discussion here (T < 150°C).
and so in supercooled states near ambient temperatures, the Li$^+$ ion would be at least a factor of 10 more mobile than the quasi-lattice in which it moves - and which determines the viscosity. Indeed decoupling indexes of 10$^9$ have been determined for LiAlCl$_4$ binary solutions at their glass transition temperature. Thus Li$^+$ can evidently escape quite easily from a tetrachloroaluminate environment.

On the other hand, using the viscosity data provided by Fannin et al., we can obtain an assessment of the degree of decoupling of conductivity from viscosity in the case of the single IL [EMI][AlCl$_4$]. The values are plotted in Figure 6, which contains also the data discussed for LiAlCl$_4$. Figure 6 shows, firstly, what was already assumed when the cations are mixed, a significant degree of coupling occurs. This can be interpreted as ion pairing or, more specifically, loss of alkali cation mobility due to trapping.

To better understand this observation we can turn to the detailed diffusivity studies of solutions of lithium salts in organic cation liquids that have been performed by Price and co-authors, and by Greenbaum and co-authors, for the cases of Li$^+$ in [EMI][BF$_4$]-LiBF$_4$ and in [PR$_3$][TFSI]-LiTFSI, respectively. In each case they found that the Li$^+$ cation is the least mobile species in the ionic liquid. Thus the "trapped alkali cation" model seems to retain some validity.

At this point we need to ask if this problem can be fixed by replacing the organic cation by one of the inorganic, or mostly-inorganic cation, salts of Figure 1, or analog cases. After all, Figure 1b showed the opposite behavior from that seen in Figure 5. The answer is probably, no. This answer is based on the observation that the conductivity of the Figure 1a tetrachloroaluminates, are distinctly lower than that of [EMI][AlCl$_4$], probably due to low ionicity, though this remains to be established by appropriate methods. (For comparison of Nernst-Einstein equation method and Walden plot method, see Ref. 36 and references cited therein). Studies of this question using some novel halide transfer ionic liquids, are in progress.

How important is this depression of the ionic liquid conductivity in the sodium case, relative to the Li case? Figure 3 shows that even at the composition of maximum depression, the conductivity of the ionic liquid is still half a decade higher than the conductivity of any beta$^+$ alumina separator, so decreased conductivity itself should not be the rate-limiting factor in electrochemical device performance. However, when it comes to electrodes, the effect on electrodeposition rates might be more serious. Indeed Kim et al. reported that unlike Li$^+$, sodium is not electrodeposited from chloroaluminate ionic liquids, perhaps because the separation of the trapped Na$^+$ from the electrode surface makes the essential electron transfer step improbable. (The sodium trapping can apparently be partially relieved by addition of the volatile molecular liquid SO$_2$Cl$_2$).

Alternative approaches.— It is obvious from the above discussion, that there are serious impediments to the use of ambient temperature ionic liquids as the transporting medium for alkali cations in electrochemical systems. The problem is more severe for Na$^+$ and larger alkalis. The highest conductivities available are of the order of single mScm$^{-1}$ at ambient temperature, and the alkali species are the least mobile in the mixture. This turns attention back to the type of system in which the alkali cation is the most mobile, rather than the least - namely those in which the alkali metal is next nearest neighbor to a highly charged (Lewis acid) species, and in which there are no other low-charged cations in the system to encourage the sort of traps that have been discussed above. An apparent problem, here, would be the fact that such systems are invariably crystalline or glassy at ambient temperature, (assuming we have excluded molecular or aqueous solutions that engender a quite separate set of problems). But this problem is certainly not insuperable.

There are three classes of solid to be discussed. The first is the much-studied superionic crystal class of solid of which well-known Na$_x$-alumina and Nasicon ceramics are outstanding members. They have the disadvantage of brittleness but have already served well in hybrid alkali metal anode/aqueous cathode batteries, i.e., low temperature systems, as well as in the famous ZEBRA cells at higher temperatures.

The second is the glassy solid or glass-ceramic type of solid that is under intense study in the laboratories of Tatsumisago-Hayashi in Japan and Martin in the USA. A disadvantage is the dependency, so far, on sulphide anionic media for the highest conductivities. WO$_3$ and other spinel-like metal oxides obtained from sodium ions in sodium thio phosphate glass-ceramics, have been described. The single ion (Na$^+$) conductivity can be above 0.1 mScm$^{-1}$. Lithium ion equivalents have recently reached 17 mScm$^{-1}$, exceeding the best commercial molecular liquid solvent cases - and they are free of fire hazards and side reactions.

Finally, there is the alkali metal rotator solid class, the study of which is in its infancy - but could be transformative if successful. It depends on the generation of alkali salts of very large unpolarizable anions with relatively free rotational degrees of freedom at ambient temperature. Like the glasses, the mobile crystalline states are generally metastable with respect to ordered immobile solids, and kinetic preservation of the mobile state is a problem to be mastered. Examples of soft solids with lithium ion resonances only a few Hz broad implying high alkali ion mobility, are on record.

Concluding remarks.— The present conductivity study has confirmed and elucidated the presence of an alkali cation trapping phenomenon as a problem when the alkali cation is mixed with weaker field ionic liquid cations, even in a system with the least basic anions commonly available (tetrachloroaluminates). Physical models for the effect suggest it should be a general problem regardless of whether the large cations are organic, inorganic, or hybrid. Some alternatives that avoid the alkali cation trapping problem have been briefly considered.
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