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Infrared Spectral Investigations of Room-Temperature Aluminum Chloride–1-Butylpyridinium Chloride Melts

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A simple, direct transmission infrared technique has been applied to obtain spectra of acidic and basic aluminum chloride–1-butylpyridinium chloride melts. Band assignments for the $AlCl_4^-$ ion show splitting of the ν_3 mode which confirms that tetrahedral distortion occurs in this melt environment. Comparison of the bands for the $Al_2Cl_7^-$ ion in solid $Te_4(Al_2Cl_7)_2$ and the anion species in the 2:1 mole ratio melt, in the 200–650-cm^{-1} region, supports the premise that the ion in the liquid phase has a bent Al–Cl–Al bridge. Detailed spectra also have been obtained of the 1-butylpyridinium cation, and the absence of extensive band broadening may indicate that the melt structure is quasi-crystalline.

Introduction

Structural investigations of the haloaluminate anionic species in molten salts by vibrational spectroscopic methods are hampered to varying extents by practical problems such as the high temperatures required or the reactivity of the melts with conventional cell window materials. For this reason, the experimentally more applicable Raman technique has generally been used,[1,2] although a Fourier-transform infrared system has been applied successfully to obtain emission spectra of $MAlCl_4$ melts at 160–250 °C (M = Li, K, Na).[3] As certain binary aluminum chloride–alkylpyridinium halide mixtures are ionic liquids at room temperatures, these systems are well suited for acid–base studies, as well as having interesting implicit properties. The primary objective of this study was to assess the extent to which vibrational information might be readily obtained for the $AlCl_4^-$ and $Al_2Cl_7^-$ anions in the room-temperature melts, taking advantage of the fact that the low liquidus characteristic of these melts facilitates experimental spectroscopic studies. Additionally, it is of interest to establish the infrared transparency of these melts as groundwork for future investigations of solute species.

Aluminum Tetrachloride Ion ($AlCl_4^-$). Figure 1B illustrates the IR absorption spectrum for a 1:1 mole ratio $AlCl_3$–1-BuPyCl liquid obtained by the transmission technique for the 200–650-cm spectral region, and the bands assignable to the $AlCl_4^-$ anion are reported in Table I. An extremely broad, intense peak is centered at 490 cm^{-1} with shoulders at 476 and 525 cm^{-1}. A weak band usually could be resolved at ~350 cm^{-1} despite a similarly intense band in the region due to the polyethylene windows.

Most Raman studies of the $AlCl_4^-$ anion in melts have been interpreted in terms of the ion possessing tetrahedral (T_d) symmetry,[2,4,5] although Balasubrahmanyam and Nanis[6] reported nine frequency shifts for each of the liquid and solid $AlCl_3$–KCl phases and proposed that the tetrahedral symmetry is distorted (C_{2v}). Their result is at variance with the more careful study of $AlCl_3$–KCl melts by Oye et al.[5] An undistorted tetrahedron possesses four Raman-active vibrations ($A_1 + E + 2\ F_2$) and two IR-active ($2\ F_2$) vibrations from point-group symmetry rules. In basic (chloride-rich) $AlCl_3$-1-BuPyCl, the Raman bands assigned to $AlCl_4^-$ are 351 $\nu_1(A_1)$, 126 $\nu_2(E)$, 484 $\nu_3(F_2)$ and 184 cm^{-1} $\nu_4(F_2)$.[2] Splitting of the weakly Raman-active ν_3 mode only can be used to determine whether or not the tetrahedral species is perturbed structurally if its band intensity permits. A better indication may be provided by splitting of the strongly IR-active ν_3 mode, when the normally inactive ν_1 and ν_2 modes may appear also. Smyrl, Mamantov, and McCurry[3] observed some additional band structure from IR emission spectra for ν_3 in the molten $AlCl_3$–LiCl, NaCl, and KCl spectra, but decomposition of the melts complicated the evaluation of anion perturbations by their emission technique. An IR study of the solid compounds Te_2AlCl_4, Te_3AlCl_4, Se_4AlCl_4, and $NaAlCl_4$ has found that their anionic ν_3 modes are split,[7] and a weak ν_1 mode at 347 cm^{-1} has been reported to occur in the spectrum of the $PCl_5 \cdot AlCl_3$ adduct $(PCl_4^+)(AlCl_4^-)$.[8] Raman studies of the $LiAlCl_4$ melt have revealed that the ν_3 mode splits at 473, 498, and 512 cm^{-1} and that the structural distortion decreases in the alkali metal series $Li^+ > K^+ > Cs^+$.[9]

Table I. Infrared Vibrational Frequencies (cm^{-1}) of Chloroaluminate Ions in Basic and Acidic Aluminum Chloride–1-Butylpyridinium Chloride Melts (Room Temperature) and Solid $Te_4(Al_2Cl_7)_2$[a]

$AlCl_4^-$ (1:1 melt)		$Al_2Cl_7^-$ (2:1 melt)		$Te_4(Al_2Cl_7)_2$
Raman[2]	IR	Raman[2]	IR	IR
		102		
126				
		163		
184				
		315	315 m, sh	318 m, sh
			328 s, sh	334 m, sh
			334 s	338 m
351	353 w		378 s, sh	375 s, sh
			386 s	384 s
		434	434 m	
	476 s, sh			430 m
484	490 s		500 s, sh	485 s, sh
	525 s, sh		~545 vs, br	535 s, br
	550 w, sh			
			585 m, sh	

[a] Key: w = weak, m = medium, s = strong, sh = shoulder, br = broad.

Dialuminum Heptachloride Ion ($Al_2Cl_7^-$). A typical IR spectrum of the 2:1 molar ratio $AlCl_3$-1-BuPyCl melt is shown in Figure 1C for the 200–650-cm^{-1} region, and the bands attributable to the $Al_2Cl_7^-$ ion are listed in Table I. There is relatively little IR data available for comparison but two IR peaks at 530 and 480 cm^{-1}, present in the spectrum of acetyl heptachlorodialuminate, have been assigned to Al–Cl modes of the $Al_3Cl_7^-$ anion.[10] Previous attempts to correlate Raman

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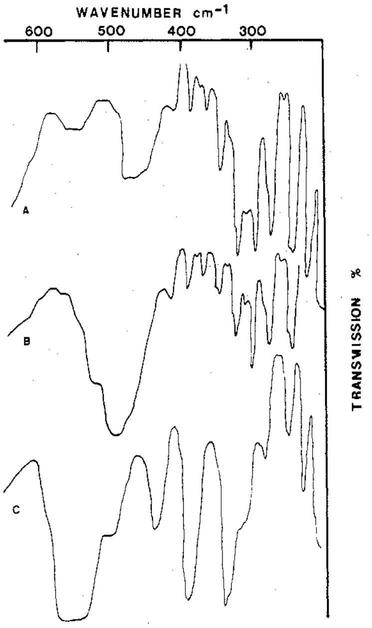

Figure 1. Infrared transmission spectra of (A) the empty polyethylene cell, (B) the 1:1 molar ratio $AlCl_3$–1-BuPyCl melt, and (C) the 2:1 molar ratio $AlCl_3$–1-BuPyCl melt at room temperature.

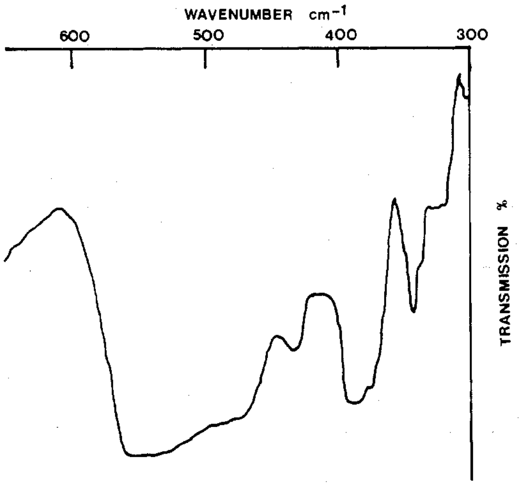

Figure 2. Infrared transmission spectrum of solid $Te_4(Al_2Cl_7)_2$.

vibrational data of melts to a model structure have not been particularly successful[5,9] and Oye and co-workers have been reluctant to propose a bent Al–Cl–Cl bridge because of the excessive number of vibrations predicted for such a structure over those found experimentally. Methods other than vibrational spectroscopy used to investigate the structures of dialuminum heptahalide ions, for example, X-ray crystallography of the solids KAl_2Br_7,[11] $Pd_2(C_6H_6)_2(Al_2Cl_7)_2$,[12] and $Te_4(Al_2Cl_7)_2$,[13] confirm the presence of a bent bridge. In addition, applications of the NQR double-resonance technique to solid KAl_2Br_7 have produced results consistent with the crystallographic findings (ref 14 and references therein). As a first-order approximation, it is of interest to attempt to correlate the far-IR spectrum of $Te_4(Al_2Cl_7)_2$ to that of the 2:1 $AlCl_3$–1-BuPyCl melt. Figure 2 contains the spectrum of $Te_4(Al_2Cl_7)_2$ and it is apparent that the overall profile in the 300–650-cm^{-1} region corresponds closely to that of the 2:1 $AlCl_3$–1-BuPyCl spectrum (Figure 1C). The frequencies and intensities of the major bands for $Al_2Cl_7^-$ ion in solid $Te_4(Al_2Cl_7)_2$, at 535 (s, br), 485 (s, sh), 430 (m), 384 (s), 375 (s, sh), 338 (m), 334 (m, sh), and 318 cm^{-1} (m, sh), are very similar to those for the bands found for $Al_2Cl_7^-$ ion in the molten salt (cf. Table I). Spectra of molecules fixed in a crystal lattice are affected by symmetry rules determined by the lattice symmetry constraints as well as the molecular point-group symmetry. Nevertheless, it seems most probable that the $Al_2Cl_7^-$ anion in these melts has a bent Al–Cl–Al bridge and that the small number of vibrational modes detected previously in the Raman results is due to the experimental difficulties of attaining detailed spectral resolution.

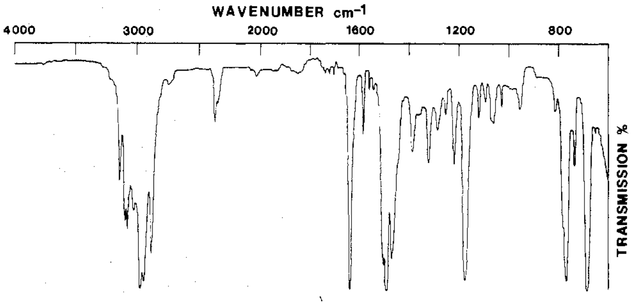

Figure 3. Infrared transmission spectrum of the 1:1 $AlCl_3$–1-BuPyCl melt at room temperature.

1-Butylpyridinium Cation ($C_9H_{14}N^+$). The IR spectrum of the cation measured in a basic 0.8:1 molar ratio liquid is illustrated in Figure 3. In view of the relatively weak peak intensities in the regions 800–1150, 1200–1450, 1510–1620, 1650–2800, and >3100 cm^{-1}, it should be relatively easy in many instances to identify organic solutes in these melts. The use of differential liquid cells or background subtraction methods might also be applied advantageously to obtain vibrational information of solutes. Spinner[15] has made a detailed analysis of the vibrational spectrum of 1-methylpyridinium cation and tentative band assignments might be possible on the basis of these data. A few differences occurred in the spectrum of an acidic 2:1 melt compared to the basic melt spectrum shown in Figure 3; a shoulder appeared instead of the weak band at 1256 cm^{-1}, a medium band replaced the shoulder at 1360 cm^{-1}, and the pattern of bands at ca. 1450–1500 cm^{-1} modified in intensity. Far more differences in the 600–1600-cm^{-1} region were found in the spectrum of solid 1-butylpyridinium chloride in a Nujol mull and only two sharp peaks (503 and 580 cm^{-1}) were resolved in the 200–600-cm^{-1} region.

Discussion

In the $LiAlCl_4$ melt, splitting of the ν_3 band by symmetry lowering has been explained by the tendency of the small Li^+ cation to form partly covalent Li–Cl bonds with the $AlCl_4^-$ anion and this tendency decreases in the alkali metal series $Li^+ > K^+ > Cs^+$.[9] It is improbable that the splitting effect manifested in the $AlCl_3$–1-BuPyCl system arises from the same direct cationic polarizability behavior in view of the large soft cation. Assuming the absence of specific non-Coulombic forces, screening by the pyridinium π system and the alkyl group may decrease the effective dielectric constant of the solvent. The result of lowering secondary interionic attractive and repulsive forces would thus promote contact anion–cation pair formation. It is difficult, however, to assess the relative magnitude of the splitting effect with respect to those found in the alkali metal systems, without comparative IR data.

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The spectral differences between basic and acidic melts at cation frequencies could reflect a difference in the cation–anion interactions or simply be a result of packing constraints. The importance to physical properties of the nature of the anion can be considerable and the acidic ($Al_2Cl_7^-$ containing) system is liquid at far lower temperatures than the basic melts. For $C_5D_5N^+CH_3$, the asymmetric CH_3 bending band at 1452 cm^{-1} broadens in aqueous solution, thereby satisfying the criterion for a low barrier to alkyl-group rotation.[15] In general, the spectra of the melts seem to be more similar to that of the solid chloride salt and the rotational freedom may be restricted by a quasi-crystalline lattice type of solvent structure. Detailed IR studies, which include band assignments from isotropic studies, could aid in answering questions as to how the rotational and molecular entropy factors are related to the low liquidus temperatures of these melt systems.

Additional applications of infrared studies on solutes in these systems will be forthcoming.[16]

Experimental Section

Preparation of chemicals and melts have been described previously.[2] Liquid IR cells were filled and sealed with Teflon stoppers in a drybox containing a purified argon atmosphere. Spectra in the 200–650-cm^{-1} regions for the 2:1 and 1:1 melts were recorded on a Beckman IR 12 spectrometer with 0.045-in. polyethylene windows and a 0.003-in. Teflon spacer. Although an attempt was made to eliminate the polyethylene spectra by matching cells in the double-beam mode, this approach was not particularly successful. Cancellation of the window contribution to the spectra by digitalization of the data and computer subtraction methods might be more fruitful. The window material showed no visible sign of interaction with these molten salts. A conventional NaCl liquid cell (Fisher Scientific) was used for the 4000–650-cm^{-1} experiments.

The purple solid $Te_4(Al_2Cl_7)_2$ compound was prepared according the the procedure of Couch et al.[13] and its IR spectrum obtained in a Nujol mull between polythylene plates. An attempt to record its Raman spectrum was unsuccessful.

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Registry No. $AlCl_3$, 7446-70-0; 1-BuPyCl, 1124-64-7; 1-$BuPy^+$-$AlCl^{4-}$, 67226-46-4; 1-$BuPy^+Al_2Cl_7^-$, 67226-45-3; $Te_4(Al_2Cl_7)_2$, 36645-21-3.

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Stability and Species Spectra of Cobalt(II) Halide Complexes in Molten Eutectic (K,Li)NO_3 at 160 °C

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The stepwise formation of halide complexes of Co(II) in molten eutectic (K,Li)NO_3 at 160 °C has been followed by a spectrophotometric technique. Stability constants for $CoCl_j^{2-j}$ and $CoBr_j^{2-j}$ ($0 \leq j \leq 4$) and the corresponding resolved species spectra for all complexes are reported. In particular, it is shown that a spectrum of only CoX_4^{2-} is experimentally unobtainable in (K,Li)NO_3 in this temperature region. No definite conclusions on the coordination geometry of intermediate species between dodecahedral $Co(NO_3)_4^{2-}$ and tetrahedral CoX_4^{2-} can be drawn from the resolved spectra. No fluoride complexes can be detected. The order of decreasing complex stability is $Cl^- > Br^- \gg F^-$, which is in sharp contrast to the sequence $F^- > Cl^- > Br^-$ for aqueous solution. This shift in F^- position is an obvious consequence of the presence of high-field Li^+ cations in the solvent.

Introduction

A typical a–a association in molecular solvents is thought of as being energetically favored mainly by a large gain in configurational entropy due to desolvation of donor and acceptor ions, whereas the predominantly electrostatic donor–acceptor bonds yield small negative or even positive enthalpy contributions to the free energy of complexation.[1] Such arguments are unlikely to hold in ionic melts. In typical ionic liquids with an inherent short-range order, complex association is generally considered to be due to nonionic interaction between central ion and ligand. Therefore, it is of great interest to obtain a more detailed knowledge of the coordination chemistry of potential class a acceptors in ionic model solvents of rather "hard" character, such as alkali nitrate melts.

From the sequence of stability of halide complexes in aqueous solution, F > Cl > Br,[2–4] Co(II) may be classified as a class a acceptor.[5] The ability of Co(II) to form halide complexes in nitrate melts is well-known from several studies,[6–10] predominantly on chloride systems. It appears, however, that attempts of quantitative characterization of the stepwise complex formation have yielded largely conflicting and incomplete results.

The moderate tendency for precipitation of Co_3O_4 from halide-containing nitrate melts below 200 °C[11] makes such systems accessible to investigation by visible spectrophotometry. Gruen and co-workers[12,13] and later Tananaev and

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