Contribution from the Department of Chemistry,
Colorado State University, Fort Collins, Colorado 80523

Raman Spectra of Molten Aluminum Chloride: 1-Butylpyridinium Chloride Systems at Ambient Temperatures

R. J. GALE, B. GILBERT, and R. A. OSTERYOUNG*

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The Raman spectra of $AlCl_3$–1-butylpyridinium chloride liquids at ambient temperatures have been recorded for the 0.75:1.0 to 2.0:1.0 molar composition range, respectively. Four absorption bands each for $AlCl_4^-$ and for $Al_2Cl_7^-$ ionic species were assigned on the basis of higher temperature vibrational spectral results of $AlCl_3$–alkali metal chloride systems. The association equilibrium constant for $Al_2Cl_7^-$ ion formation, $2AlCl_4^- + Al_2Cl_6 \rightleftarrows Al_2Cl_7^-$, is significantly larger than that for the $AlCl_3$–MCl melts, where M represents an alkali metal cation.

Introduction

Aluminum halide–alkylpyridinium halide mixtures have relatively low liquidus temperatures which enables their use as aprotic molten salt media, of variable acidity, for studying the reactions of many organic or thermally unstable compounds at room or moderate temperatures.[1-4] The purpose of this investigation by Raman spectroscopy has been to study the aluminum species composition in the molten aluminum chloride–1-butylpyridinium chloride system for the 0.75:1.0 to 2.0:1.0 molar ratio range, respectively. Studies by proton magnetic resonance of species distribution in some 2:1 molar ratio $AlCl_3$–alkylpyridinium halide systems have been interpreted in terms of a major aluminum species of $Al_2X_7^-$ or Al_2X_6, but not AlX_4^-.[5]

Experimental Section

Raman spectra were recorded using a Spectra Physics Model 170 ion laser, argon 514.5-nm excitation, calibrated with a Fe-Ne lamp. Careful purification of the melt constituents was found to be necessary to minimize fluorescence from the fused-salt mixtures. To prepare 1-butylpyridinium chloride, 1-butyl chloride and pyridine (1:1 molar quantities) were refluxed for 48 h with a P_2O_5 tube vented to the atmosphere. The solid product was separated and purified by recrystallization from dry, redistilled ethyl acetate–acetonitrile mixtures. A decolorizing charcoal treatment was used in the first two recrystallizations and the product finally dried in vacuo (mp 131.5 °C). The highly hygroscopic crystals were protected from moisture and stored in a Vacuum Atmospheres Co. drybox under purified argon. Fluka AG aluminum chloride was purified by sublimation from aluminum chips in a sealed tube. The approximately 1-cm² cross sectional quartz cells used for spectroscopy were filled and sealed in the drybox.

Results

Figure 1 illustrates typical Raman spectra of the liquid $AlCl_3$–1-butylpyridinium chloride mixtures. As the acidity of the melts was increased by the addition of $AlCl_3$, the background quality of the spectra generally lessened. Table I summarizes the experimental frequency shifts (cm⁻¹) and the relative band intensities of the vibrational peaks. In order to characterize these spectra, the peak positions may be compared to the assignments which have been made for the $AlCl_4^-$ and $Al_2Cl_7^-$ ions in high-temperature molten salt media (Tables II and III). Bands due to any free Al_2Cl_6, higher order polynuclear aluminum ionic species such as $Al_3Cl_{10}^-$, and the 1-butylpyridinium cation also might be present in the spectra of these melts.

Four absorption bands in the 1:1 molar ratio melt spectra can be readily assigned to the $AlCl_4^-$ anion verifying T_d symmetry: 351, 126, 484, and 184 cm⁻¹. The results of Oye, Rytter, et al.[6] from a spectral study of 1:1 $AlCl_3$:KCl melts at 300 °C, assuming the $AlCl_4^-$ ion to be tetrahedral, were consistent with previous investigations of $AlCl_3$ mixtures with NaCl, NOCl, and PCl_5 but were in disagreement with the data for both solid and liquid $AlCl_3$–KCl of Balasubrahmanyam and Nanis.[7] A Raman spectrum of crystalline 1-butylpyridinium chloride revealed bands at 37 (1.6), 88–103 (3.8), 125 (6.4), 148 (1.3), 500 (1.3), 644 (3.6), 650 (1.4), 774 (1.8), and 1024 cm⁻¹ (10). [Low laser intensities (~60 mW) were used to avoid thermal decomposition of samples. Parenthesized figures denote relative intensities.] The band due to the cation at 184 cm⁻¹ probably overlaps the ν_4 (F_2) mode of the $AlCl_4^-$ ion (note intensities in Table I) but the 125- and 500-cm⁻¹ bands are not resolved for the acidic melt compositions of 1.75:1.0 and 2.0:1.0, in contrast to those bands at 650 and 774 cm⁻¹. None of the more intense Raman bands of liquid or gaseous aluminum chloride[8] could be ascertained in the spectra of these ambient temperature melts.

Table I. Summary of Experimental Raman Frequency Shifts (cm⁻¹) for Aluminum Chloride–1-Butylpyridinium Chloride Mixtures at Room Temperatures at Various $AlCl_3$:RCl Molar Ratios[a]

0.75:1.0	1.0:1.0	1.5:1.0	1.75:1.0	2.0:1.0
			−95 sh	−102 sh
−126 sh (0.9)	−127 sh (1.3)	−126 sh		
		−159 (1.2)	−163 (1.5)	−163 (2.3)
−186 (2.1)	−184 (2.0)	−183 (2.8)	−183 (1.6)	−182 (0.9)
−298 (0.9)	−295 (0.7)	−296 sh (1.4)	−295 sh (1.6)	−295 sh (1.1)
		−314 (8.8)	−316 (10.0)	−315 (10.0)
−351 (10.0)	−352 (10.0)	−351 (10.0)	−352 (5.0)	
−433 (0.1)	−433 (0.1)	−434 (2.7)	−433 (3.3)	−434 (2.2)
−485 (0.5)	−483 (0.4)			
−507 (0.6)	−504 (0.5)			
−653 (2.8)	−650 (2.4)	−651 (3.2)	−647 (4.7)	−651 (2.7)
−775 (0.7)	−770 (0.5)	−774 (0.2)	−772 (0.2)	−769 (1.0)
−786 (0.5)	−785 (0.3)			
−817 (0.7)	−828 (0.3)			
−891 (0.5)	−887 (0.4)		−887 (0.4)	
−912 (0.6)	−910 (0.4)		−907 (0.2)	

[a] Values in parentheses are relative intensities; sh = shoulder.

Table II. Raman Vibrational Frequencies (cm⁻¹) of the Aluminum Tetrachloride Ion

	Cation		
assignment	1-Bu(py)⁺ 30 °C	Na⁺ 225 °C[9]	K⁺ 300 °C[6]
ν_1 (A_1)	351 p	351	350
ν_2 (E)	126 d	121	122
ν_3 (F_2)	484 d	490	487
ν_4 (F_2)	184 d	186	182

Table III. Raman Vibrational Frequencies (cm⁻¹) of the Dialuminum Heptachloride Ion (2:1 Melt) with Various Cations

1-Bu(py)⁺ 30 °C	Na⁺ 225 °C[9]	K⁺ 170 °C[6]
102 sh, d	97 d	99 d
163 d	162 d	164 d
315 p	312 p	312 p
434 p	432 p	435 d

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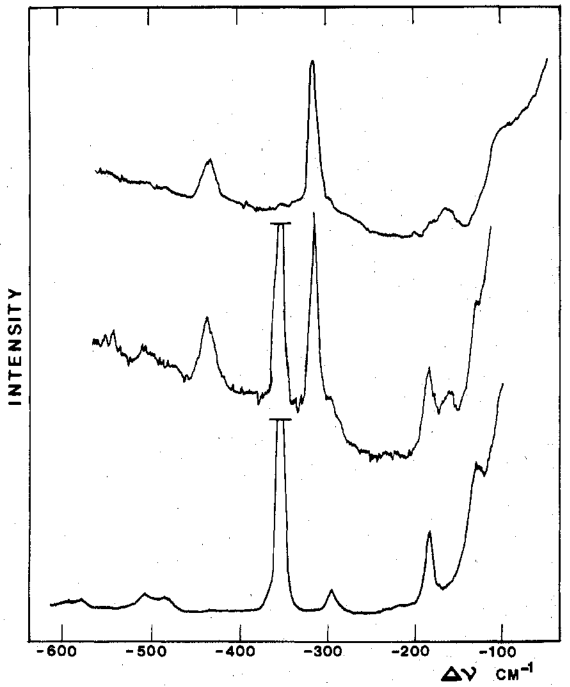

Figure 1. Raman spectra of liquid $AlCl_3$–1-butylpyridinium chloride mixtures with molar ratios 1.0:1.0 (lower), 1.5:1.0 (middle), and 2.0:1.0 (upper); room temperature.

A normal-coordinate analysis of the dialuminum heptachloride ion has been made for a D_{3d} model with a linear Al–Cl–Al bridge.[6] This analysis predicts three polarized (A_{1g}), at 469, 272, and 35 cm^{-1}, and three depolarized (E_g), at 470, 166, and 83 cm^{-1}, Raman-active fundamental frequencies. Unfortunately, the quality of the spectra in the acidic composition regions was such that only four bands could be ascribed to the $Al_2Cl_7^-$ ion; however, the frequencies do correspond well with previous experimental assignments in high-temperature systems (Table III). The band at 434 cm^{-1} was found to be polarizable, as reported by Torsi, Mamantov, and Begun[9] for the 2:1 $AlCl_3$:NaCl melt.

Following Oye, Rytter, et al.,[6] it is possible to assume that the mole fractions of the $AlCl_4^-$ and $Al_2Cl_7^-$ ionic species are proportional, approximately, to the intensity of the strongest bands for each species. Then the intensity ratios for the integrated peaks at 315 and 351 cm^{-1} for the two different melt compositions are

$$(I_{Al_2Cl_7^-}/I_{AlCl_4^-})_{1.5:1.0} = 1.20 \pm 0.05$$

$$(I_{Al_2Cl_7^-}/I_{AlCl_4^-})_{1.75:1.0} = 3.30 \pm 0.10$$

which indicates, together with the absence of the 351-cm^{-1} band in the 2.0:1.0 melt, that the molar excess of aluminum chloride is converted virtually completely to the $Al_2Cl_7^-$ ion. In addition, the most intense peak of the $Al_2Cl_7^-$ ion at 315 cm^{-1} is absent from the spectra for the two most basic melt compositions (Table I). Hence, for these media containing the 1-butylpyridinium cation, the predominant equilibrium reaction may be expressed as

$$2AlCl_4^- + Al_2Cl_6 \rightleftarrows 2Al_2Cl_7^-$$

on the basis of the Raman vibrational spectra.

Discussion

The absorption frequencies assigned to the $AlCl_4^-$ and $Al_2Cl_7^-$ anionic species show little change from those found in their other melt systems, an indication that the nature of the cation does not appreciably influence the structures. Similarly, the butylpyridinium cation in these melts, compared to that in solid, crystalline 1-butylpyridinium chloride, did not exhibit any bands with appreciable frequency shifts for the frequency range under investigation. Traces of molecular aluminum chloride could not be detected in these spectra but its relatively intense band at about 340 cm^{-1}[8] may be obscured by the 315- or 351-cm^{-1} bands of ionic $Al_2Cl_7^-$ and $AlCl_4^-$, respectively. Calculated frequencies based on D_{3d} symmetry for the $Al_2Cl_7^-$ ion structure are not particularly good compared to the experimental values[6] and refinement of the model probably must await additional experimental evidence. The most important conclusion to be made from this present Raman spectral study is that the formation of the $Al_2Cl_7^-$ ionic species is enhanced in $AlCl_3$–1-butylpyridinium choride melts over that found in the higher temperature $AlCl_3$–alkali metal chloride molten systems.

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Registry No. $AlCl_3$, 7446-70-0; 1-Bu(py)$^+$·Cl^-, 1124-64-7; 1-Bu(py)$^+$·$AlCl_4^-$, 67226-46-4; 1-Bu(py)$^+$·$Al_2Cl_7^-$, 67226-45-3.

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