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RAMAN SPECTRA OF MOLTEN ALUMINIUM CHLORIDE: 1-BUTYL-PYRIDINIUM --ETC(U)
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RAMAN SPECTRA OF MOLTEN ALUMINIUM CHLORIDE: 1-BUTYL-
PYRIDINIUM CHLORIDE SYSTEMS AT AMBIENT TEMPERATURES.

by

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is significantly larger than that for the $AlCl_3:MCl$ melts, where M represents an alkali metal cation.

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PYRIDINIUM CHLORIDE SYSTEMS AT AMBIENT TEMPERATURES

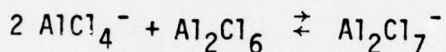
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ABSTRACT

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,



is significantly larger than that for the AlCl_3 : MCl melts, where M represents an alkali metal cation.

INTRODUCTION

Aluminium 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 aluminium species composition in the molten aluminium 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 aluminium species of Al_2X_7^- or Al_2X_6 , but not AlX_4^- ^[5].

EXPERIMENTAL

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 hours with a P_2O_5 tube 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 (m.p. found 131.5° C). The highly hygroscopic crystals were protected from moisture and stored in a Vacuum Atmospheres Co. drybox under purified argon. Fluka AG aluminium chloride was purified by sublimation from aluminium 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 AlCl₃: 1-butylpyridinium chloride mixtures. As the acidity of the melts was increased by the addition of AlCl₃, 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 AlCl₄⁻ and Al₂Cl₇⁻ ions in high temperature molten salt media (Tables II and III). Bands due to any free Al₂Cl₆, higher order polynuclear aluminium ionic species such as Al₃Cl₁₀⁻, 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 AlCl₄⁻ anion verifying T_d symmetry; 351, 126, 484 and 184 cm⁻¹. The results of Øye, Rytter *et al.*^[6] from

a spectral study of 1:1 $\text{AlCl}_3\text{:KCl}$ 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 in disagreement with the data for both solid and liquid $\text{AlCl}_3\text{:KCl}$ 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)*. The band due to the cation at 184 cm^{-1} probably overlaps the $\nu_4(\text{F}_2)$ 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 cm^{-1} and 774 cm^{-1} . None of the more intense Raman bands of liquid or gaseous aluminium chloride^[8] could be ascertained in the spectra of these ambient temperature melts.

A normal coordinate analysis of the dialuminium heptachloride ion has been made for a D_{3d} model with a linear Al-Cl-Al bridge^[6]. This analysis predicts 3 polarized (A_{1g}) at 469, 272 and 35 cm^{-1} and 3 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 4 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

*Footnote: low laser intensities ($\sim 60\text{ mW}$) were used to avoid thermal decomposition of samples. Bracketed figures denote relative intensities.

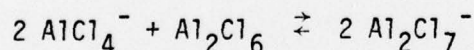
reported by Torsi, Mamantov and Bequn^[9] for the 2:1 $\text{AlCl}_3\text{:NaCl}$ melt.

Following Øye, 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 -

$$(I_{\text{Al}_2\text{Cl}_7^-}/I_{\text{AlCl}_4^-})_{1.5:1.0} = 1.20 \pm 0.05$$

$$(I_{\text{Al}_2\text{Cl}_7^-}/I_{\text{AlCl}_4^-})_{1.75:1.0} = 3.30 \pm 0.10$$

which indicates, together with the absence of the 351 cm^{-1} band in the 2.0:1.0 melt, that the molar excess of aluminium 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 predominate equilibrium reaction may be expressed as -



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 aluminium 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 chloride melts over that found in the higher temperature AlCl_3 :alkali metal chloride molten systems.

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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.

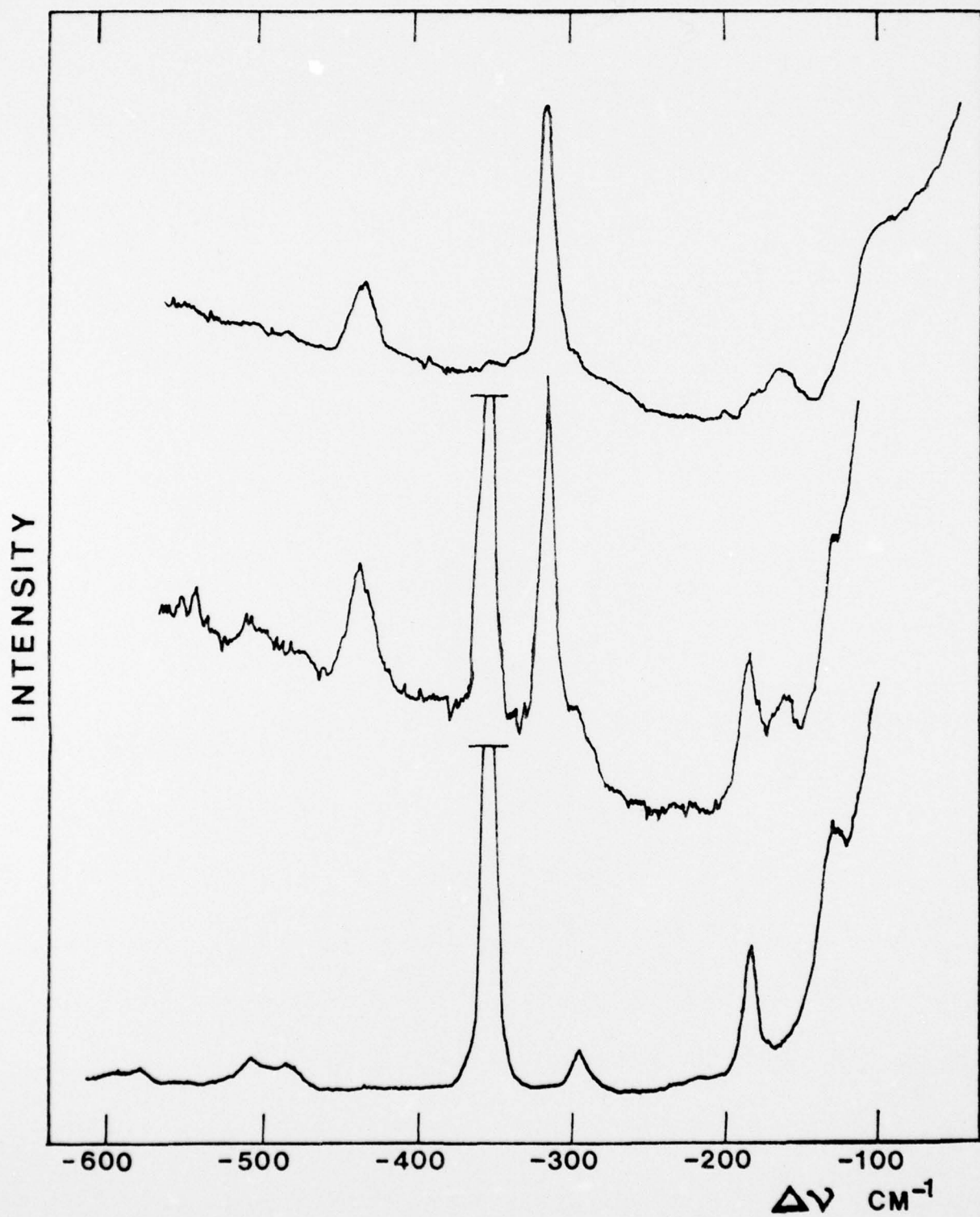


TABLE I

Summary of experimental Raman frequency shifts (cm^{-1}) for aluminium chloride:1-butylpyridinium chloride mixtures at room temperatures

Molar ratio $[\text{AlCl}_3]:[\text{RCl}]$				
0.75:1.0	1.0:1.0	1.5:1.0	1.75:1.0	2.0:1.0
-126 sh (0.9)	-127 sh (1.3)	-126 sh	-95 sh	-102 sh
-186 (2.1)	-184 (2.0)	-159 (1.2)	-163 (1.5)	-163 (2.3)
-298 (0.9)	-295 (0.7)	-183 (2.8)	-183 (1.6)	-182 (0.9)
		-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)	

() Relative intensities; sh-shoulder

TABLE II

Raman vibrational frequencies (cm^{-1}) of the aluminium tetrachloride ion.

Assignment	Cation		
	1-butylpyr. ⁺ 30°C	Na ⁺ 225°C[9]	K ⁺ 300°C[6]
ν_1 (A_1)	351P	351	350
ν_2 (E)	126D	121	122
ν_3 (F_2)	484D	490	487
ν_4 (F_2)	184D	186	182

TABLE III

Raman vibrational frequencies (cm^{-1}) of the
dialuminium heptachloride ion (2:1 melt).

Cation		
1-butylpyridinium ⁺ 30°C	Na ⁺ 225°C[9]	K ⁺ 170°C[6]
102 sh, D	97D	99D
163 D	162D	164D
315 P	312P	312P
434 P	432P	435D

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