

freedom, even at $-30\text{ }^{\circ}\text{C}$. The structural analogy of the two complexes allows one to compare their O-O stretching frequencies. Both are located in the superoxide region. A 19-cm^{-1} decrease is observed for $\nu_{\text{O-O}}$ when *N*-MeIm is replaced by $\text{C}_6\text{HF}_4\text{S}^-$. This is in agreement with the shift observed for the $\nu_{\text{C-O}}$ of the carbonyl adducts. This stresses again the influence of the σ -donor properties of the thiolate toward the trans ligand. The different RR activities shown by the Fe-O₂ and the O-O modes are difficult to rationalize in the absence of excitation profiles for these modes. In the case of MbO₂ (or HbO₂), where only the Fe-O₂ vibration is RR active, direct coupling of this mode to the porphyrin π - π^* transition is favored.²⁶ Since the same RR activity was observed for the

model complex Fe(TpivPP)(*N*-MeIm)(O₂), the same mechanism may be operative. It is quite possible that the enhancement of the O-O vibration as observed for Fe(TpivPP)(C₆HF₄S⁻)(O₂) originates in a different electronic process.

In conclusion, the RR spectrum of Fe(TpivPP)(C₆HF₄S⁻) is typical of high-spin ferrous complexes. No significant influence of the π -donor properties of the thiolate ligand is observed; however, the sensitivity of RR frequencies to π interactions, in the case of high-spin ferrous complexes, is not well documented. For the carbonyl and oxygen low-spin ferrous complexes, the porphyrin ring, CO, Fe-CO, and O-O vibrations also show a lack of sensitivity to the π -donor properties of the thiolate ligand. The concomitant decrease of the Fe-CO and CO frequencies is explained by the σ -donor character of the thiolate ligand.

Registry No. Fe^{II}(TpivPP)(C₆HF₄S⁻), 86161-44-6; Fe^{II}(TpivPP)(C₆HF₄O⁻), 93403-09-9; Fe^{II}(TpivPP)(OH), 93452-45-0; Fe^{II}(TpivPP)(Cl), 93452-46-1; Fe(TpivPP)(C₆HF₄S⁻)(CO), 86161-84-4; Fe(TpivPP)(C₆HF₄S⁻)(O₂), 86124-04-1; CO, 630-08-0; O₂, 7782-44-7.

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Spectrophotometric Studies of Iodine Complexes in an Aluminum Chloride-Butylpyridinium Chloride Ionic Liquid

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Iodine, iodine chloride, tetraethylammonium iodide, and tetraethylammonium triiodide solutions in aluminum chloride-*N*-1-butylpyridinium chloride ambient-temperature ionic liquids have been studied by UV-visible spectrophotometry. The different oxidation states of iodine show a distinct dependence on the solvent acidity. Iodine(1+) exists in the form of ICl in acidic melts and in the form of ICl₂⁻ in basic AlCl₃-BuPyCl mixtures. Molecular iodine does not form strong complexes in acidic or neutral solutions. Triiodide ion is stable in neutral butylpyridinium tetrachloroaluminate, but not in acidic melts. In solutions of iodine or triiodide in basic AlCl₃-BuPyCl ionic liquids equilibrium mixtures of I₂Cl⁻, I₃⁻, ICl₂⁻, and I⁻ are formed. The charge-transfer bands observed for iodide solutions in neutral and basic melts reveal the formation of iodide ion-butylpyridinium cation ion pairs. Similar bands in pure basic AlCl₃-BuPyCl mixtures indicate the association of chloride ion and butylpyridinium cation.

Introduction

Our electrochemical investigations of iodine in aluminum chloride-*N*-1-butylpyridinium chloride (BuPyCl) ambient-temperature molten salts^{1,2} showed that in this solvent iodine and its compounds are involved in extensive acid-base and redox equilibria. Variations in the AlCl₃:BuPyCl mole ratio lead to wide changes in Lewis acidity of the medium. Neutral equimolar mixture of AlCl₃ and BuPyCl can be made acidic by adding excess AlCl₃ or basic with excess BuPyCl. The present study was undertaken to obtain additional information on interactions of iodine in different oxidation states with the ionic solvent. The electrochemical experiments did not directly identify all the iodine species formed in basic AlCl₃-BuPyCl ionic liquid.² They did not indicate the formation of I₂⁺ ion in acidic ambient-temperature melts although this ion has been postulated on the basis of spectral results for mixtures of I₂ and Cl₂ dissolved in high-temperature AlCl₃-NaCl molten salts.³

It was also of interest to seek in this medium, containing a high concentration of butylpyridinium cation, charge-transfer bands for iodide and chloride ions. Charge transfer (CT)

transitions for alkylpyridinium iodides have been observed in many different solvents.⁴⁻⁷ CT bands have also been reported for myristylpyridinium chloride solutions in chloroform.⁶ It was assumed⁵⁻⁷ that these transitions occur for contact ion pairs; a possible contribution of solvent-separated ion pairs to ionic association equilibria in these systems was however unclear.⁶⁻⁸ Ionic association equilibria in AlCl₃-BuPyCl ionic liquids are different in this respect in that in this medium only contact ion pairs should be formed. Formation of this type of ionic association between butylpyridinium cation and iodide and chloride ions is indicated by charge-transfer bands reported herein.

Experimental Section

The procedures used for purification of AlCl₃ (Fluka), synthesis and purification of *N*-1-butylpyridinium chloride, and preparation

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Table I. Apparent Molar Absorptivity of (TEA)I Band at 330 nm in AlCl₃-BuPyCl Melt

melt composition, N _A :N _B ^a	10 ³ [(TEA)I], mol dm ⁻³	10 ⁻³ ε, dm ³ mol ⁻¹ cm ⁻¹
1:1	3.7	2.97
0.95:1	0.85	2.85
0.95:1	1.99	3.04
0.95:1	4.65	2.99
0.95:1	7.7	2.98
0.75:1	1.8	2.95
0.75:1	5.9	3.05

^a N_A = number of moles of AlCl₃; N_B = number of moles of BuPyCl.

Table II. Iodine Species at Different AlCl₃-BuPyCl Ionic Liquid Compositions

I oxidn state	melt composition		
	acidic	neutral	basic
+1	ICl	ICl	ICl ₂ ⁻
0	I ₂	I ₂	I ₂ Cl ⁻
-0.33		I ₃ ⁻	I ₃ ⁻
-1	AlCl ₃ I ⁻ , Al ₂ Cl ₆ I ⁻	I ⁻ (BuPy ⁺ ··· I ⁻)	I ⁻ (BuPy ⁺ ··· I ⁻)

of the melts were similar to those described previously.⁹ Iodine (Mallinckrodt AR), iodine chloride (Eastman Kodak), and tetraethylammonium iodide (TEAI) (Eastman Kodak) were used as received. Tetraethylammonium triiodide ((TEA)I₃) was prepared according to Chattaway and Hoyle¹⁰ and dried under vacuum.

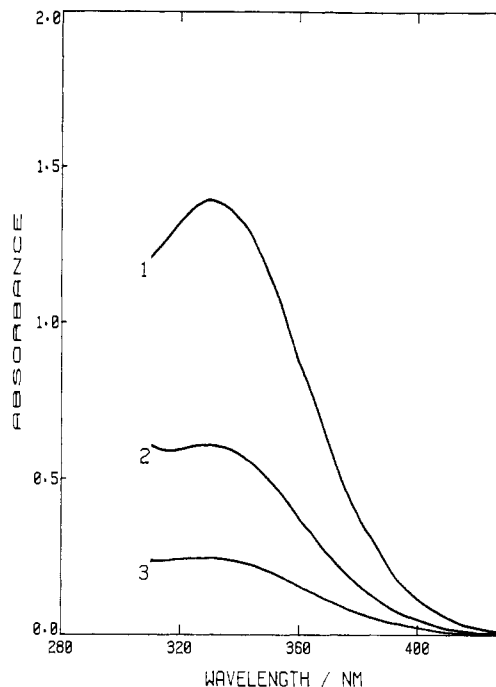
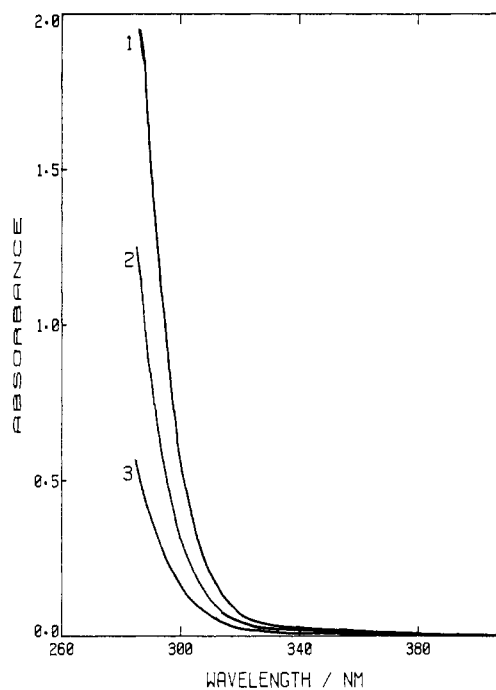
Absorption spectra were obtained with a Perkin-Elmer model Coleman 750 spectrometer using 0.1-cm matched quartz cells (Wilmad). Cells were filled and sealed under a purified argon atmosphere in a Vacuum Atmospheres drybox with an HE 493 Dri-Train.

Results

Iodide and Chloride Ions. Iodide ion, which in acidic melts does not exhibit any absorption in the accessible UV region,¹ shows a single absorption band with a maximum at ca. 330 nm in neutral and basic solutions (Figure 1). This band was found to obey Beer's law at iodide concentrations from 8 × 10⁻⁴ to 7 × 10⁻³ mol dm⁻³, and the apparent molar absorptivity at 330 nm was 3 × 10³ dm³ mol⁻¹ cm⁻¹ in the neutral as well as in basic 0.95:1 and 0.75:1 melts (Table I).

Visible or near-UV absorption bands observed for alkylpyridinium iodides in many different solvents⁴⁻⁷ have been assigned to charge-transfer transitions⁴⁻⁷ and taken as an evidence for contact ion pair formation.⁵⁻⁷ The observed independence of the apparent molar absorptivity on iodide concentration in butylpyridinium tetrachloroaluminates indicates full association of iodide ions with butylpyridinium cations. It is also interesting to note that the molar absorptivity in the ionic liquid is distinctly higher than in the other solvents where its value varied between 300 and 1600 dm³ mol⁻¹ cm⁻¹.⁴⁻⁷ Since in the ionic liquid only contact ion pairs are formed, the measured value can be regarded as the molar absorptivity of the contact BuPy⁺I⁻ ion pair. Lower values of apparent molar absorptivity observed in the other solvents⁴⁻⁷ suggest that solvent-separated ion pairs are a significant fraction of ionic associations formed there.

Spectra recorded for pure melts at different AlCl₃:BuPyCl mole ratios revealed a dependence of the short-wavelength "cutoff" on the melt composition. In acidic and neutral melts the "cutoffs" were essentially the same; an absorbance equal to 1 at 284 nm for 1.5:1 and at 285 nm for the neutral AlCl₃:BuPyCl mole ratio (1.0:1.0) melts (at 0.1-cm path lengths, the spectra recorded vs. air). For basic melt compositions these "cutoffs" shifted to 313 nm for 0.95:1, to 319

**Figure 1.** Absorption spectra of tetraethylammonium iodide solution in 0.95:1 AlCl₃:BuPyCl melt. C_{(TEA)I} = (1) 4.65, (2) 1.99, and (3) 0.85 mM.**Figure 2.** Absorption spectra of butylpyridinium chloride added to neutral butylpyridinium tetrachloroaluminate. The excess of BuPyCl is (1) 18, (2) 11, and (3) 5.4 mM.

nm for 0.9:1, and to 325 nm for 0.75:1 AlCl₃:BuPyCl mole ratios. In acidic and neutral melts the "cutoffs" are due to butylpyridinium cation π-π* transitions.⁸ In aqueous solutions, maxima of alkylpyridinium cation absorption bands were observed at ca. 260 nm.⁵ The slight difference between 1.5:1 and 1:1 melts results from an increase in BuPy⁺ concentration, which is 3.5 mol dm⁻³ in 1.5:1 and 4.1 mol dm⁻³ in 1:1 melt. In basic melts, however, the BuPy⁺ concentration increase cannot account for the observed shift of the cutoff; BuPy⁺ concentration in the 0.75:1 melt is 4.45 mol dm⁻³. On the other hand, an absorbance edge observed between 285 and 310 nm increased when excess BuPyCl was added to the neutral bu-

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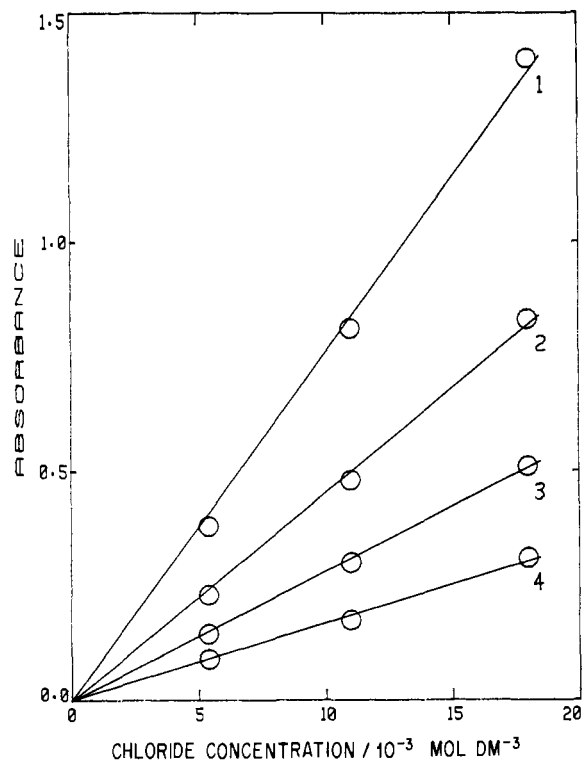


Figure 3. Absorbances at constant wavelength measured for spectra shown in Figure 2 plotted against chloride concentration at wavelengths (1) 290, (2) 295, (3) 300, and (4) 305 nm.

tylpyridinium tetrachloroaluminate (Figure 2). The absorbance at constant wavelength varied linearly with the concentration of "free" chloride (in excess over AlCl₃) (Figure 3). This shows that the absorption at these wavelengths is due to charge-transfer transitions for a butylpyridinium cation-chloride ion pair, similar to the BuPy⁺...I⁻ association. The proportionality between the absorbance and excess chloride concentration (at 305 nm Beer's law was obeyed in the chloride ion concentration range from 5×10^{-3} to 0.1 mol dm^{-3}) indicates full association of butylpyridinium cation and chloride ion under the conditions employed (large excess of BuPy⁺).

The charge-transfer band observed in the UV spectrum of AlCl₃-BuPyCl ionic liquid is a good indication of basic melt composition. It is especially useful at very low chloride concentrations, close to the neutral butylpyridinium tetrachloroaluminate. It was found that, at concentrations below $\sim 5 \times 10^{-3} \text{ mol dm}^{-3}$, neither chloride nor heptachloroaluminate ions effect the electrochemical window of the molten butylpyridinium tetrachloroaluminate,² which can be used as a criterion of the neutrality of the solvent.¹¹ However, in UV spectra analogous to those shown in Figure 2, $1 \times 10^{-3} \text{ mol dm}^{-3}$ excess chloride could be detected (at 290 nm the absorbance value corresponding to $1 \times 10^{-3} \text{ mol dm}^{-3}$ chloride was 0.043). This method did not require the preparation of an ideally equimolar neutral melt as the reference solution. Since, as discussed above, spectra of neutral and acidic melts were essentially the same, an acidic melt could be used as the reference.

Iodine, Iodine Chloride and Triiodide Ion. For solutions of iodine in neutral butylpyridinium tetrachloroaluminate a broad absorption band with a maximum at ca. 480 nm ($\epsilon_{I_2}^{480} = 800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), identical with one previously observed in acidic solutions containing iodine,¹ was found. A difference between the position of this band for iodine solution in liquid butylpyridinium tetrachloroaluminate and in CCl₄ ($\epsilon_{I_2}(\text{max})$

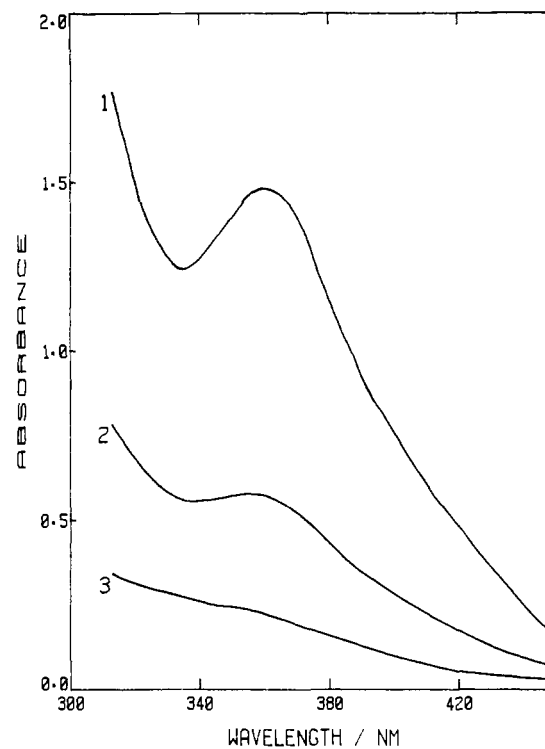
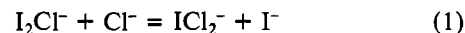


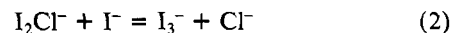
Figure 4. Absorption spectra of iodine in 0.95:1 AlCl₃-BuPyCl melt. C_I = (1) 3.5, (2) 1.68, and (3) 0.85 mM.

= 517 nm^{12}) reflects some weak intermolecular interactions between iodine molecules and solvent ions; nevertheless iodine in neutral as well as acidic AlCl₃-BuPyCl mixtures does not form strong complexes and is dissolved in the form of I₂ molecules.

Spectra obtained for iodine solutions in basic AlCl₃-BuPyCl ionic liquids (Figure 4) indicated the formation of polyhalogen ions; the uncomplexed iodine band at 480 nm was not observed. The dependence of the spectra on concentration of iodine and melt composition indicated equilibria involving chloride ion. The solvent "cutoff" did not allow a direct observation of polyhalogen ion absorption maxima at wavelengths shorter than 320 nm. Only the band at ca. 365 nm due to triiodide ion (vide infra) could be observed (Figure 4). Its formation in solutions of iodine dissolved in basic AlCl₃-BuPyCl melts shows that I₂ is involved in some redox reaction. Reversible changes of the spectra at varying melt compositions, an independence of the spectra on time, and the fact that more than 90% of the amount of iodine initially added to a basic melt could be observed by rotating-disk voltammetry after the melt was made acidic by AlCl₃ addition² showed that the possible reactions of iodine, reduction by chloride ion, and/or solvent impurities as well as the reaction with the organic cation could not account for the observed reaction. On the other hand, electrochemical experiments showed the presence of iodine(I+) as well as iodide in the solutions of iodine in basic melts,² thus indicating that the redox reaction involving iodine is the disproportionation equilibrium



Triiodide ion is formed in the consecutive equilibrium



Similar equilibria have been reported for I₂Cl⁻ solutions in acetonitrile¹³ and in water¹⁴ and recently for I₂⁻(CsCl-LiCl)

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melts.¹⁵ Since in the acidic melts the iodine disproportionation equilibrium is shifted far to the left,¹ the addition of AlCl_3 to the equilibrium mixture of polyhalogen ions existing in the solution of iodine in basic AlCl_3 -BuPyCl melt causes the formation of molecular iodine.

Iodine chloride reacts with the acidic melt and is partly reduced to iodine,¹ so the spectra obtained for ICl solutions in acidic AlCl_3 -BuPyCl melts consisted of bands due to ICl as well as I_2 . Since the molar absorptivity of iodine is 5 times larger than the absorptivity of iodine chloride,¹⁶ and the two bands appear in the same wavelength range (the ICl band maximum was reported to be at 343–466 nm depending on solvent used¹⁶), only one very broad band was observed. The maximum of this band shifted from ca. 450 to 490 nm (in 2:1 AlCl_3 :BuPyCl melt) over a period of 24 h, reflecting the progress of the reaction



The spectra recorded for ICl solutions in acidic AlCl_3 -BuPyCl mixtures were different from the spectrum reported for an equimolar mixture of iodine and chlorine dissolved in the 2:1 AlCl_3 -NaCl melt.³ No band in the 600–800-nm region was observed; thus there was no evidence for the I_2^+ ion formation under the employed conditions. For ICl_2^- ion two absorption bands were reported,^{12–15} the main one at ca. 230 nm ($\epsilon_{\text{ICl}_2^-} = \text{ca. } 5.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and the second, much less intense band at ca. 340 nm ($\epsilon_{\text{ICl}_2^-} = \text{ca. } 300 \text{ cm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The spectra obtained for iodine chloride solutions in basic AlCl_3 -BuPyCl melts indicated the formation of ICl_2^- ; however, only the less intense band at 338 nm could be observed. Additionally, for the latter solutions a small maximum at ca. 420 nm was evident. This band decreased at higher chloride concentrations; it probably reflected the presence of the small equilibrium concentrations of molecular ICl in the solution.

The spectra obtained for $(\text{TEA})\text{I}_3$ solutions at melt compositions close to the neutral (as judged by the electrochemical window of the solvent¹¹) were qualitatively similar to the spectra recorded in acetonitrile, with two absorption maxima at 295 and 365 nm. However, apparent molar absorptivities were found to be very sensitive to small additions of AlCl_3 and BuPyCl to the solution. These variations reflect changes in the conditional stability of I_3^- ion, which result from acid–base interactions of iodide with AlCl_3 ¹ or iodine with chloride ion (vide supra). Even at concentrations of Cl^- or Al_2Cl_7^- ions below $5 \times 10^{-3} \text{ mol dm}^{-3}$, which did not affect the electrochemical window of the solvent, the apparent molar absorptivity of I_3^- distinctly changed. When the melt composition was adjusted to a true “neutral” state, however, the molar absorptivity of I_3^- in neutral butylpyridinium tetrachloroaluminate ($\epsilon_{\text{I}_3^-} = 2.25 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) agreed well with literature data.^{5,13} The value of the I_3^- ion molar absorptivity in neutral butylpyridinium tetrachloroaluminate confirmed the high stability of I_3^- ion observed in electrochemical experiments.²

Shapes of the spectra recorded for $(\text{TEA})\text{I}_3$ solutions in basic solvent compositions were dependent on triiodide and/or chloride ion concentrations (Figure 5). These variations were consistent with the reaction described by equilibrium 2. Thus reactions 1 and 2 lead to the formation of the equilibrium mixtures of all the ions: I_2Cl^- , ICl_2^- , I_3^- , I^- , and Cl^- in basic AlCl_3 -BuPyCl ionic liquids. In triiodide solutions reaction 2 is followed by reaction 1 (the presence of ICl_2^- and I^- ions in triiodide solutions in basic AlCl_3 -BuPyCl melts was observed in electrochemical experiments²). On the other hand, in iodine solutions iodide ion formed in reaction 1 reacts with

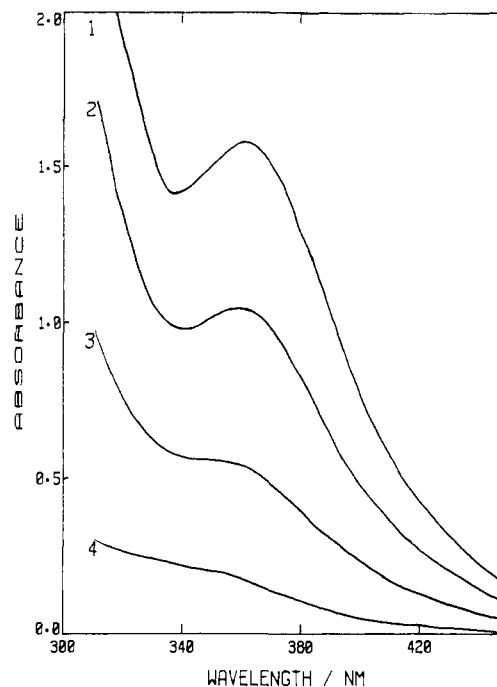


Figure 5. Absorption spectra of tetraethylammonium triiodide in 0.95:1 AlCl_3 -BuPyCl melt. $C_{(\text{TEA})\text{I}_3} = (1) 1.89, (2) 1.42, (3) 0.85, \text{ and } (4) 0.35 \text{ mM}$.

I_2Cl^- ion according to equilibrium 2.

Discussion

UV–visible spectrophotometric studies characterized the species formed by iodine in different oxidation states at widely varied acidities of the AlCl_3 -BuPyCl ionic liquid. The summary of these results, which are in agreement with electrochemical experiments,^{1,2} is shown in Table I. The variety of species formed at different solvent acidities reflects characteristic features of the acid–base interactions in chloroaluminate molten salts. The ionic nature of the solvent promotes strong interactions between Lewis acids and chloride ion in basic melt compositions and between Lewis bases and heptachloroaluminate ion present in acidic melts. At the same time the high stability of triiodide ion in neutral butylpyridinium tetrachloroaluminate indicates relatively weak intermolecular interactions in this solvent.

Charge-transfer transitions observed for butylpyridinium cation–iodide and butylpyridinium cation–chloride ion pairs indicate a high degree of association between these ions in basic AlCl_3 -BuPyCl ionic liquids. The results obtained in the solutions containing a large excess of BuPy⁺ over Cl^- and I^- did not allow a quantitative analysis of the association equilibria. Qualitatively, however, the results observed for basic AlCl_3 -BuPyCl mixtures agreed with the conclusions drawn from the analysis of the conductivity measurements for ambient-temperature chloroaluminate ionic liquids.¹⁸ The proportionality between the absorbance at 305 nm and chloride ion concentration observed up to 0.1 mol dm^{-3} indicates that, at formal concentrations of butylpyridinium cation up to 4 mol dm^{-3} , at least 90% of the chloride is involved in the charge-transfer transition and thus is associated with BuPy⁺ cation (accuracy of the measurements was arbitrarily assumed to be $\pm 10\%$). This gave an estimated value for the association constant $K = [\text{BuPy}^+\text{Cl}^-]/([\text{BuPy}^+][\text{Cl}^-]) > 2.3$, which favorably compares with the value of the association constant for a similar low-temperature chloroaluminate system, aluminum chloride–imidazolium chloride, which was estimated

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as 2.¹⁸ The ionic association of butylpyridinium cation with chloride ion has been indicated by NMR¹⁹⁻²¹ and FTIR²² studies of AlCl₃:BuPyCl melts.

For solutions of iodine and (TEA)I₃ in basic AlCl₃-BuPyCl ionic liquids the spectrophotometric studies confirmed polyhalogen equilibria deduced from the electrochemical results.² In particular, the formation of I₃⁻ in iodine solution, expected from the values of equilibrium constant for reactions 1 and 2 estimated in the electrochemical studies,² was directly observed. Attempts to obtain more accurate estimates of the equilibrium constants for reaction 1 and 2 from the spectral data were unfortunately unsuccessful. Spectra recorded for I₂ and

(TEA)I₃ solutions in basic AlCl₃-BuPyCl mixtures were limited to a narrow range of wavelengths and consisted of overlapping bands of all ions involved in the polyhalogen equation, i.e., ICl₂⁻, I₂Cl⁻, I₃⁻, and I⁻. Additionally, a spectrum of I₂Cl⁻ ion could not be obtained separately; thus molar absorptivity values for this ion were uncertain. However, the spectra obtained for iodine and triiodide solutions at low chloride concentration (Figures 4 and 5) confirmed the approximate values of the equilibrium constants for reactions 1 and 2. Concentrations of I₃⁻ ions calculated from these equilibria agreed reasonably well with the I₃⁻ concentrations estimated from the absorbance measured at 365 nm.

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Registry No. AlCl₃, 7446-70-0; BuPyCl, 1124-64-7; ICl, 7790-99-0; ICl₂⁻, 14522-79-3; I₂, 7553-56-2; I₂Cl⁻, 17705-05-4; AlCl₃I⁻, 23606-63-5; Al₂Cl₆I⁻, 93426-73-4.

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Proton Exchange of Co(NH₃)₆³⁺ Ion with Cosolvent Water in Me₂SO Solutions: A ⁵⁹Co NMR Study

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⁵⁹Co NMR spectra are reported for the hexaamminecobalt(III) ion in dimethyl sulfoxide solutions containing small amounts of deuterium oxide and triethylamine. The spectra show the time dependence of the isotopomer distribution which requires that the base-catalyzed exchange process proceed by two paths: one involves a single hydrogen-exchange event while the other requires equilibration of the complex with the isotopic composition of the proton-exchangeable solvent at each activation event by the base.

Introduction

Conjugate base formation may be an important step in reactions of transition-metal amine complexes leading to racemization and ligand substitution.^{1,2} Several groups have examined conjugate base participation by following the base-catalyzed proton-exchange reactions in complexes of cobalt(III),^{3,4} platinum(II),^{5,6} and platinum(IV)⁷ using proton NMR spectroscopy. In contrast to the proton NMR spectra, the cobalt-59 NMR spectrum permits observation of each H/D isotopomer. There is a 5.6 ppm isotope shift experienced at the cobalt nucleus for every deuterium atom substituted for a proton at the nitrogen in the hexaamminecobalt(III) ion.⁸⁻¹⁰ Similar shifts are found with the tris(ethylenediamine)cobalt(III) ion.⁹ The ⁵⁹Co NMR spectrum thus provides an efficient means for following the H/D exchange reactions in detail as it approaches equilibrium: The final isotopomer distribution will be dependent on the number of exchangeable positions in the metal complex and the H/D ratio in the solvent.

Figure 1 shows representative spectra for hexaamminecobalt(III) chloride recorded as a function of time in an aqueous solution containing 75% deuterium oxide at pH 4.00. A plot of the H₁₈ isotopomer resonance amplitude against time gives a linear plot with a pseudo-first-order rate constant of 2.1 × 10⁻³ min⁻¹ for the decrease in the H₁₈ isotopomer concentration. The mechanism expected,^{1,2} involving base catalysis

with a rate law first order in cobalt(III) and in hydroxide ion, is consistent with our data. An ion-pair mechanism for proton exchange has also been proposed,¹¹ but questioned.^{12,13} Block and Gold¹⁴ maintain that the acidity of the hexaamminecobalt(III) complex is consistent with a rapid hydroxide association process, conjugate base formation, rapid proton interchange, and regeneration of the hydroxide ion. The cobalt NMR spectrum provides a sensitive method for probing such reaction mechanisms further because the spectral resolution provides the isotopomer distribution as a function of time. We report here results for proton exchange in a nonaqueous solvent that was partly motivated by applications to analytical methodologies.⁹ These data also provide a striking example of the detailed mechanistic information sometimes available from high-field multinuclear NMR spectrometers.

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