V. First, the Mn–O bond distance in **1** is 0.2–0.3 Å longer than in similar complexes of first-row transition metals. In addition, the structurally characterized high-spin ferric complex $[Fe(TMSO)_2TPP]^+ClO_4^-$, TMSO = tetramethylene sulfoxide, of Scheidt and Reed contains a trivalent first-row transition metal axially ligated to a neutral oxygen atom of hybridization similar to that of the oxygen of 2,6-lutidine *N*-oxide. The axial Fe–O distances in this complex are 2.069 (3) and 2.087 (3) Å, and although these distances are longer than other Fe^{III}–O bond distances, they are substantially shorter than the Mn^{III}–O bond distances in **1**. Most of this tetragonal elongation of the bonds to the axial oxygens in **1** can be attributed to a singly occupied axially antibonding d_{z^2} orbital and confirms a ground electronic state for the Mn^{III} atom of $(d_{xz}\pi,d_{yz}\pi)^2(d_{xy})^1(d_{z^2}\sigma)^1$. Second, the N–O bond lengths in the axial 2,6-lutidine *N*-oxide ligands of **1** are not greatly different from these bond lengths observed in the other complexes. Indeed, the entire range of N–O bond lengths for the complexes in Table V is 1.31 (1)–1.37 (2) Å with those of **1** being 1.330 (6) and 1.331 (7) Å. The conclusion from this coupled with the reasonable thermal stability of the isolated complex **1** is that the N–O bonds in **1** are not strongly activated electronically with respect to heterolytic cleavage to yield the formal oxomanganese(V) species and lutidine nor to homolytic cleavage to yield a formal oxomanganese(IV) species and lutidine cation radical, eq 1 and 2, respectively. The third and final feature worthy of comment is the angle defined by the metal atom and the oxygen and nitrogen atoms of the *N*-oxide ligands in the complexes enumerated in Table V. These angles, including those for 1, all fall within the narrow range of 117–128°. Since few of the aromatic *N*-oxide ligands are sterically encumbered by neighboring ligands or intermolecular solid-state interactions in these complexes, one might use the simple valence-bond formalism and attribute the M–O–N angles in part to M–O bonding involving orbitals residing primarily on oxygens that are largely sp^2 hybrid in nature.

$$[L(Por)Mn^{III}\leftarrow O{-}NR]^+ \rightarrow [L(Por)Mn^{V}{=}O]^+ + NR \qquad (1)$$

$$[L(Por)Mn^{III}\leftarrow O{-}NR]^+ \rightarrow L(Por)Mn^{IV}{=}O + NR^{+\cdot} \qquad (2)$$

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Registry No. $1\cdot C_7H_{16}$, 97073-98-8; **1**, 97073-97-7; $Mn^{III}TPP(ClO_4)$, 79408-54-1.

Supplementary Material Available: Crystallographic data for **1** including anisotropic temperature factors (Table SVI), hydrogen coordinates and temperature factors (Table SVII), observed and calculated structure factors (Table SVIII), nonbonded distances and torsion angles (Table SIX), nonessential bond distances and angles (Table SX), an ORTEP plot of **1**, and a stereoview of the crystal packing diagram for **1** (52 pages). Ordering information is given on any current masthead page.

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Optical and Thermodynamic Basicities: UV Spectra of Tl^+, Pb^{2+}, and Bi^{3+} in Molten Chloroaluminate Titrations

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Following a recent report on the strong environmental dependence of the $^3P_1 \leftarrow {}^1S_0$ transition of Pb^{2+} doped, in trace quantities, into thermodynamically characterized binary chloroaluminate molten-salt systems, we examined two other isoelectronic ions, Tl^+ and Bi^{3+}, in order to gain insight into the factors determining a spectral probe's sensitivity to chemical processes and into the limitations of the use of $d^{10}s^2$ ions as basicity probes. Major differences in the probe ion spectral responses ranging from full-range frequency shifts (Bi^{3+}) to no shift at all (Tl^+) were observed as their host solvent was titrated through a composition region where large thermodynamic changes are known to occur (equivalence point at the $AlCl_4^-$ stoichiometry). These differences are discussed in terms of differences in the polarizing power of the probe ions and the ions composing the solvent medium, and in terms of probe ion coordination symmetries and stoichiometries.

Introduction

The ultraviolet absorption spectrum of $d^{10}s^2$ ions doped, in trace quantities, into molten salts,[1-8] crystals,[9-10] and glasses[3-6,11-25] has been the subject of many publications. Interest has focused on the strong environmental dependence of the outer-orbital $^3P_1 \leftarrow {}^1S_0$ transition ("Rydberg") characteristic of $5d^{10}6s^2$ ions; in particular, the frequency dependence of this transition for Tl^+, Pb^{2+}, or Bi^{3+} on composition changes in the molten or glassy solvent has been of prime concern. For example, the spectrum of the dopant, or probe ion, exhibits progressive shifts to the lower energy region of the UV spectrum as the (Lewis) basicity of the solvent is increased, both by increasing the concentration of the more basic component within a single system (e.g., increasing the concentration of Na_2O in B_2O_3/Na_2O glass) and by going to stronger bases in a given solvent system (e.g., going from B_2O_3/Na_2O to B_2O_3/K_2O glasses[3]).

These observations were interpreted in terms of the unusual sensitivity of the probe ions to the electron-donating propensity of their first nearest neighbors. The acid strength, or polarizing power, of the probe ion's second nearest neighbors determines the

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degree of polarization, and hence the ability to donate electrons, of its first nearest neighbors. That is, as the (Lewis) basicity of the solvent or host medium is increased, the electrons of the solvent molecules become more available for sharing and mix to a greater extent with the outer-orbital electrons of the probe ion. This causes an increased shielding of the probe ion's outer-orbital electrons, reducing the energy needed to bring about the "Rydberg" transition and leading to a shift in the absorption spectrum to lower energies.

This phenomenon is commonly known as the nephelauxetic effect and has been extensively evaluated by Jorgensen[26] for first-row transition-metal ions and by Reisfeld and Boehm[12-14] for $d^{10}s^2$ metal ions.

With these facts and observations as background, Duffy and Ingram[3] introduced the concept of optical basicity as a means of quantifying, for the first time, Lewis basicities. Their proposed optical basicity parameter, Λ, is a direct measure of the amount of negative charge that the anions or solvent molecules can donate to the probe ions, hence, it is seen as a reflection of the average state of polarization of the probe ion's first nearest neighbors. The implicit assumption is made that the basicity, or availability of electrons, of the probe ion's first nearest neighbors reflects the average basicity of the solvent.

The optical basicity parameter is empirically defined by eq 1,

$$\Lambda = (\nu_f - \nu)/(\nu_f - \nu_{min}) \tag{1}$$

where ν_f is the frequency of the $^3P_1 \leftarrow {}^1S_0$ transition of the "free" probe ion, ν is the observed transition frequency of the probe ion in the medium under study, and ν_{min} is the transition frequency of the probe ion in an ultimately basic environment. The free ion is a hypothetical species that would exist in a solvent incapable of donating negative charge to neighboring ions (i.e., the ultimate acid). ν_f is obtained by extrapolating to zero the Jorgensen "*h*" function;[26] the *h* function is a quantitative measure of a ligand's ability to donate negative charge. ν_{min} is an empirical quantity and is equal to the transition frequency for the given probe ion in a highly basic medium such as CaO for oxide glasses[3] and the LiCl–KCl eutectic for chloride molten salts.[2,3]

Duffy and Ingram also proposed a simple scheme, which incorporates the composition of the solvent system (concentration and charge of the "ions" composing the solvent) and a basicity moderating parameter, linearly related to Pauling electronegativity, to calculate[6,27] the optical basicity. This scheme has been applied in the interpretation of the chemistry, physics, and structure of oxide glasses and metallurgical slags.[6-8,18,20-25,27]

An examination of the relationship between transition frequency (related to optical basicity by eq 1) and thermodynamic basicity, first suggested by Duffy and Ingram[6] in their pioneering works, was the thrust of an earlier paper.[1] The transition frequency of Pb^{2+}, doped into thermodynamically characterized $AlCl_3$–alkali-metal chloride molten-salt solvents,[28-32] was studied as the composition of the solvent was changed through a well-defined equivalence point. Within the equivalence region (a region bracketing the 50 mol % $AlCl_3$–alkali-metal chloride by a nominal ±0.25 mol %), the alkali-metal chloride activity changes by some 4–6 orders of magnitude; the exact value of the alkali-metal chloride activity change depends on the basicity of the alkali-metal chloride used.

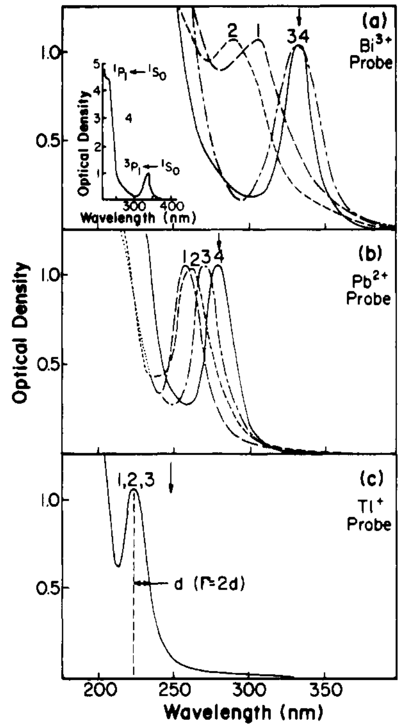

Figure 1. Absorption spectra for the $^3P_1 \leftarrow {}^1S_0$ transition for (a) Bi^{3+}, (b) Pb^{2+}, and (c) Tl^+ in selected melts: (1) pure $AlCl_3$; (2) NaCl-saturated $AlCl_3$–NaCl; (3) KCl-saturated $AlCl_3$–KCl; (4) pure EAHCl. The downward pointing arrow indicates the position of the band maximum in the LiCl–KCl eutectic reported by Smith et al.[2] The inset in part a shows the complete spectrum of Bi^{3+} in EAHCl and contains the higher energy band resulting from the fully allowed $^1P_1 \leftarrow {}^1S_0$ transition.

Briefly, the results of this previous study[1] showed a close correlation between $\Lambda(Pb)$ and the known thermodynamic basicity (i.e., $pCl = -\log a_{Cl^-} \sim -{}^1/_2 \log a_{MCl}$, where only a_{MCl} is well-defined) of the molten system. This correlation indicates that the Pb^{2+} ion can be used to indicate the thermodynamic basicity of its host solvent by way of its nephelauxetic effect. Also introduced in this earlier study was a novel low-temperature molten-salt system, $AlCl_3$ + ethylamine hydrochloride (EAHCl), in which evidence was presented for a second equivalence point, which occurs in the composition region between pure EAHCl and the 1:1 primary equivalence point.

The obvious question is how well the other $5d^{10}6s^2$ ions, namely Tl^+ and Bi^{3+}, behave as basicity probes. The present article reports a spectroscopic investigation of Tl^+ and Bi^{3+} in the same thermodynamically characterized molten-salt systems as previously studied for Pb^{2+}. The question of whether or not the probe ion actually generates sites within the solvent thereby reflecting local basicities rather than average basicities—and departing from a "basic" assumption of the optical basicity concept—is also discussed.

Experimental Section

All aspects of this study (e.g. materials purification and preparation, spectroscopic sample preparation and instrument arrangements, and titration procedures) were identical with those of the previous study[1] except that TlF and $BiCl_3$ were used as the source of the respective probe ions. Both Tl^+ and Bi^{3+} were present in the melts at concentrations of $\sim 10^{-4}$ M. Due to the low concentration of TlF, the F^- ion was considered not to interfere with the thermodynamics of the solvent melt.

Results

Bi^{3+} and Tl^+ Absorption Spectra. Figure 1 shows the absorption spectra for the $^3P_1 \leftarrow {}^1S_0$ transition for Bi^{3+}, Tl^+, and, for comparison purposes, Pb^{2+} in selected melts used in this study, viz., pure $AlCl_3$, pure EAHCl, and NaCl-saturated $NaAlCl_4$. The position of the absorption band maximum, λ_m, of the respective probe ion in LiCl–KCl eutectic melt (59 mol % LiCl), obtained

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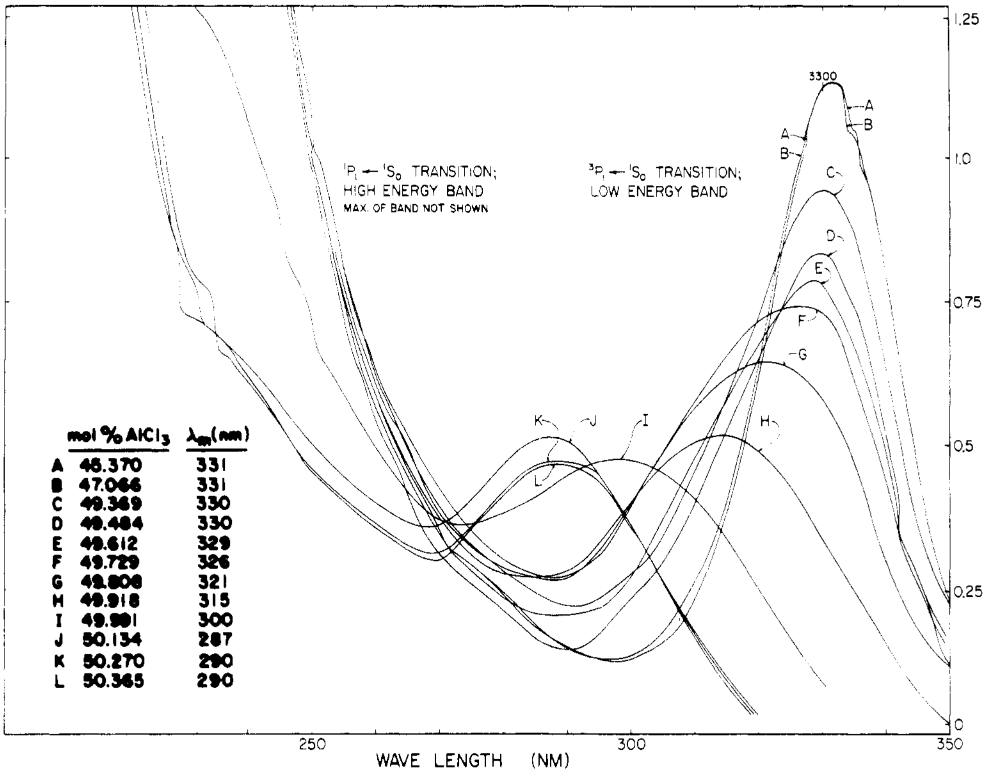

Figure 2. Family of Bi^{3+} spectra obtained in the equivalence region for the titration of EAHCl with $AlCl_3$ at 90 °C. The inset table identifies the melt composition and corresponding band position, λ_m, for each absorption spectrum.

by Smith et al.[2] is indicated by the arrow in Figure 1.

The inset in Figure 1a shows, for the case of Bi^{3+} in pure EAHCl in which the absorptions fall at relatively long wavelengths, a more complete spectrum for this spectral region. It contains a higher energy band due to the allowed transition $^1P_1 \leftarrow {}^1S_0$.[10,26,33] The relative oscillator strength, ~5:1, agrees with that observed and commented on by Smith et al.[2] For the more acidic melts there is considerable overlap of these two absorptions, leading to an apparent broadening and skewing of the $^3P_1 \leftarrow {}^1S_0$ band. Because of the problems involved in controlling the trace quantities of probe ion, and the notorious difficulty of obtaining reproducibly UV-transparent chloroaluminate melts, we have not attempted quantitative separations of these spectral components. Rather, we have recorded actual band maxima and recognized the distortion of the true absorption energy that this will sometimes cause.

The wavelength λ_m, frequency ν_m at the band maximum, and bandwidth Γ (full width at half-height defined for overlapping bands as in Figure 1c) for selected melts of this and earlier studies are collected in Table I, along with the derived eq 1 optical basicities. Some features of Figure 1 and Table I are notable, and some are surprising and difficult to understand.

The bandwidth for Bi^{3+} in EAHCl is the narrowest yet observed for the $^3P_1 \leftarrow {}^1S_0$ absorption in melts, implying a very well-defined probe ion environment, presumably best described as a "complex ion" $BiCl_6^{3-}$. Comparably broad bands (when allowance is made for the higher sample temperature) and indistinguishable λ_m values are observed for KCl-saturated melts. The structural implications are the same.

In NaCl-saturated melts, however, despite the thermodynamic fact that the chloride ion activity has risen across the equivalence point by some 4 orders of magnitude, at 175 °C (see, for example, ref 31), the λ_m for Bi remains unshifted from the value exhibited on the acid side. Furthermore, this "tetrachloroaluminate spectrum" is as broad as, and even shorter in wavelength than, the spectrum in pure $AlCl_3$. the results was independent of the manner in which the NaCl-saturated melt was prepared. We will give this perplexing finding more consideration after examining both the Tl^+ spectra, and the Bi^{3+} spectroscopic titrations in the $AlCl_3$ + EAHCl system.

The Tl^+ ion absorption spectrum (the highest energy absorption of the three probes, Figure 1c) was found to be essentially identical in position [$\lambda_m(Tl^+)$ = 223 nm, $\nu_m(Tl^+)$ = 44850 cm^{-1}] and bandwidth (Γ = 4350 cm^{-1}) for pure $AlCl_3$ and all binary $AlCl_3$–MCl (M = Na, K) melts independent of temperature. The EAHCl-based melts were not investigated because of interference from $EtNH_3^+$ low-lying MO transitions. The position of the Tl^+ absorption band is shifted to lower energies in the basic LiCl–KCl eutectic melt [$\lambda_m(Tl^+)$ = 248 nm, $\nu_m(Tl^+)$ = 40 300 cm^{-1}] while the bandwidth, within experimental error, remains unchanged (Γ = 4360 cm^{-1}).[2] A shift to a similar position of λ = 245 nm, now as a shoulder, was observed when several mol % of NH_4Cl was added to a Tl^+-containing KCl-saturated $AlCl_3$–KCl solution. In view of the high vapor pressure of NH_4Cl and the lack of thermodynamic data for the $AlCl_3$–NH_4Cl system, systematic studies of Tl^+-based titrations were not pursued. λ_m and Γ for the Tl^+ ion absorption spectrum appear to be temperature independent for the chloroaluminate melts used in this study.

The Pb^{2+} spectra, which are generally more straightforward to interpret, were adequately described in our earlier paper.[1] For comparative purposes, though, we note here that in the Pb^{2+} case, the KCl-saturated melt spectrum was the *broadest*, Γ = 5200 cm^{-1}, and was not shifted as far toward the visible as in EAHCl, implying a poorly defined environment compared to that of Bi^{3+} in the same melt. The NaCl-saturated spectrum had indeed shifted with respect to its position immediately before the equivalence point but much less than in the KCl-saturated melts, presumably reflecting the presence of the same influences that cause the unexpected behavior of Bi^{3+} in NaCl-saturated melts.

Spectroscopic Titrations. Because of the rapidity with which additions of EAHCl dissolved in an existing $AlCl_3$–EAHCl melt, it was possible to carry out a detailed study of the spectroscopic behavior in the equivalence region. The family of Bi^{3+} spectra obtained at ~0.1 mol % EAHCl intervals across the equivalence point is displayed in Figure 2. Note the marked changes in bandwidth in this region and the extreme sensitivity in band position at 50.00 ± 0.1%. It is notable that, unlike the earlier case of Pb^{2+}, the Bi^{3+} probe is not thrown out of solution at the

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[33] J. A. Duffy and M. D. Ingram, *Phys. Chem. Glass*, **15**, 34 (1974).

Table I. Spectroscopic Characteristics of the $d^{10}s^2$ Ions Tl^+, Pb^{2+}, and Bi^{3+} in Chloride Melts of Different Basicities: The $^3P_1 \leftarrow {}^1S_0$ Transition

solvent	T, °C	λ_m, nm	ν_m, cm^{-1}	Λ	fwhh (Γ), cm^{-1}
		Tl^+			
$AlCl_3$	250	223	44 850	0.706	4350
EAHCl					
NaCl-satd	175	223	44 850	0.706	4350
KCl-satd	310	223	44 850	0.706	4350
KCl-satd NH_4Cl		245	40 820	0.978	
LiCl–KCl eutectic	440	248	40 300	1.00	4360
		Pb^{2+}			
$AlCl_3$	230	258	38 800	0.984	3710
EAHCl	133	280	35 700	1.02	2660
NaCl-satd	175	263	3 800	0.927	4125
KCl-satd	270	270	37 000	0.967	5200
LiCl–KCl eutectic	440	276	36 200	1.00	3870
		Bi^{3+}			
$AlCl_3$	255	304	32 900	0.895	5160
EAHCl	115	334	29 900	1.01	2170
NaCl-satd	175	290	34 500	0.833	5160
KCl-satd	275	331	30 200	1.00	2580
LiCl–KCl eutectic	440	331	30 200	1.00	3710

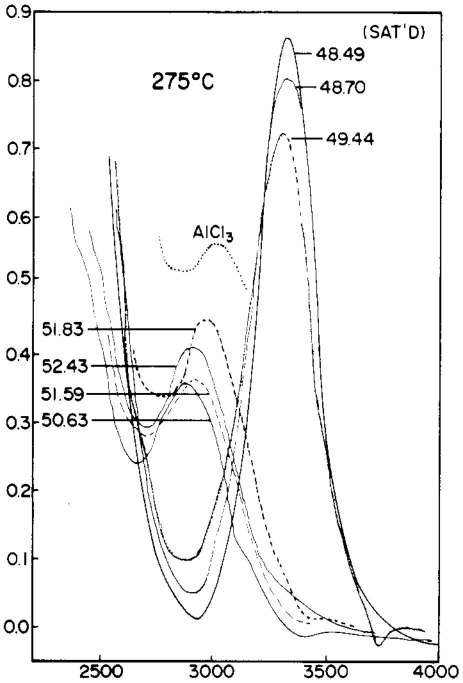

Figure 3. Family of Bi^{3+} spectra obtained in the equivalence region for the titration of KCl with $AlCl_3$ at 275 °C. Melt compositions, in mol % of $AlCl_3$, are indicated in the figure. Note the apparent shift to shorter wavelengths as the $AlCl_3$ composition decreases until the sudden spectral shift occurs between 50.63 and 49.44 mol % of $AlCl_3$.

equivalence point. A less complete but also interesting set is shown for the $AlCl_3$–KCl system in Figure 3.

Figure 4 summarizes the results for the composition dependence of λ_m(Bi) as both KCl and EAHCl are titrated with $AlCl_3$ at 275 and 90 °C, respectively. Since at 275 °C $AlCl_3$ becomes saturated with approximately 52 mol % KCl, the spectroscopic study is very limited on the basic side. In the case of EAHCl, however, the entire binary composition range can be explored. Also plotted in Figure 4 are λ_m(Bi) for pure EAHCl (115 °C), pure $AlCl_3$ (255 °C), the NaCl-saturated melt (175 °C), and LiCl–KCl eutectic (440 °C). Note that all systems on the acid side of the equivalence point give spectra more "acid" than in pure $AlCl_3$. The inset in Figure 4 shows the composition dependence of λ_m(Pb) for the $AlCl_3$-EAHCl system reported earlier.[1]

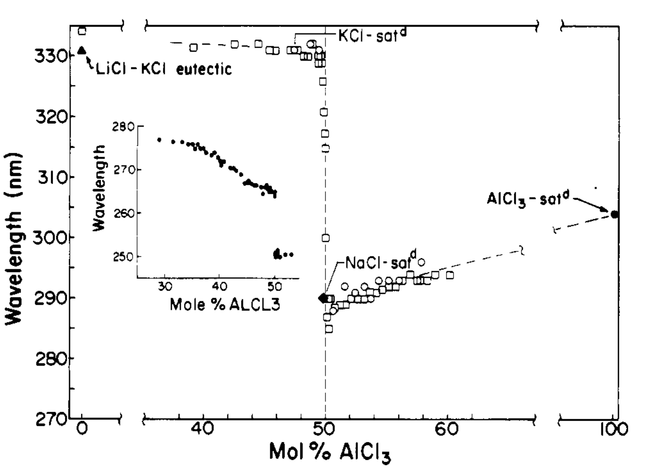

Figure 4. Composition dependence of absorption band maximum for Bi^{3+}, λ_m(Bi), in the systems $AlCl_3$ + KCl at 275 °C (○) and EAHCl at 90 °C (□). Also included for comparison are the spectral positions of Bi^{3+} in pure EAHCl at 115 °C (□), in pure $AlCl_3$ at 255 °C (●), in NaCl-saturated $AlCl_3$–NaCl at 175 °C (◆), and in the LiCl–KCl eutectic at 440 °C[2] (▲). The inset shows the composition dependence of λ_m(Pb) for the $AlCl_3$–EAHCl system. Note the response of Pb to the equilibrium centered at 33 mol % of $AlCl_3$, where Bi is unresponsive.

Within experimental error, the shapes of the two titration curves shown in Figure 4 are indistinguishable. Both can be described in terms of three distinct regions: the basic region (A), the equivalence region (B), and the acidic region (C). The basic region (A) is characterized by a relatively constant λ_m(Bi) extending from the composition of either pure EAHCl or KCl-saturated $KAlCl_4$ to the start of the equivalence region (B). Within region B, λ_m(Bi) undergoes a dramatic shift to higher energies, or shorter wavelengths, as EAHCl is stoichiometrically neutralized with $AlCl_3$. Region C shows an unexpected gradual increase in λ_m(Bi) with increasing $AlCl_3$ content beyond the equivalence region (B), which is seen most clearly in the $AlCl_3$–KCl case; see Figure 3. The similarity between the two titration curves is indeed surprising in view of the large temperature difference and the large difference in polarizing power of the cations (compare K^+ and EAH^+) of the two systems under study.

In the case of Tl^+, absorption spectra were observed in pure liquid $AlCl_3$, in an $AlCl_3$-rich alkali-metal chloride melt, and in both NaCl- and KCl-saturated melts. Since all gave the same spectrum, and since spectroscopic studies of Tl^+ ion in EAHCl- and NH_4Cl-containing melts were not practical, no value could be seen in further varying-composition studies with Tl^+ as the indicator ion.

An attempt was also made to follow the nephelauxetic effect of Tl^+ through the equivalence region in the low-temprature $AlCl_3$–EAHCl system by Tl^{207} NMR spectroscopy but was frustrated by the low solubility of TlCl. The solubility of TlCl was sufficiently high in acidic $AlCl_3$–EAHCl melts at 110 °C to give a chemical shift of approximately 20 ppm relative to that of aqueous TlF at 25 °C.[34]

Discussion

The ability of Pb^{2+} to follow the changes in chloride ion activity that occur at the equivalence point, and also to detect a secondary change on the basic side of the $AlCl_3$–EAHCl system (shown in inset in Figure 4), was described in our earlier paper.[1] Pb^{2+}, we concluded, would serve as a sensitive indicator for acid–base processes in these systems.

The present results show that the Bi^{3+} ion may also be an effective, though more limited, equivalence-point indicator. Figure 5 compares the composition dependence of Λ(Bi) with that of the thermodynamic activity of the basic chloride, plotted logarithmically, obtained from emf measurements by Torsi and Mamantov[29] and by Bjerrum et al.[32] However, where Pb^{2+} ion is able systematically to distinguish between (and perhaps ultimately quantify) the differences in absolute basicities of different bases,

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(34) P. D. Bennett and P. A. Budinger, unpublished results.

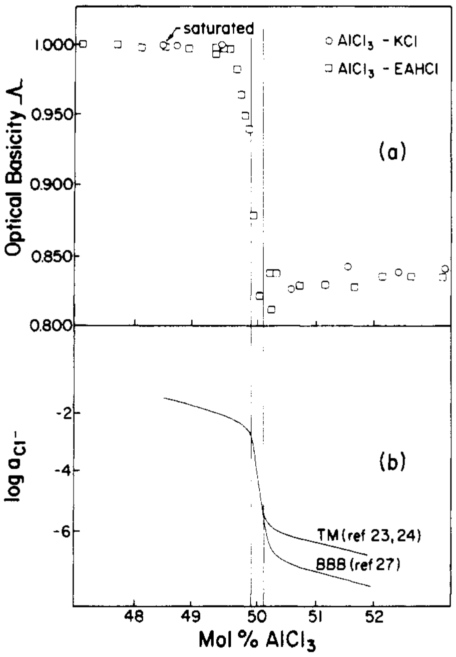

Figure 5. Comparison of the composition dependence of (a) Λ(Bi), from eq 1 for the systems $AlCl_3$–KCl at 275 °C (○) and $AlCl_3$–EAHCl at 90 °C (□), with that of (b) the thermodynamic activity of the basic chloride according to previous thermodynamic studies[24,27] in the $AlCl_3$–KCl system at 275 °C.

Bi^3 cannot. Furthermore, there is no evidence in Figure 4 for the second equilibrium centered at 33 mol % $AlCl_3$–67 mol % EAHCl, which was so apparent when Pb^{2+} ion was used as indicator (see inset).

These effects can be discussed in terms of the relative polarizing power of the indicator ions and of the ions composing the solvent medium; furthermore, environmental interactions between the indcator ion and its first and second nearest neighbors can be considered. On the basis of their charge-radius ratio, the relative polarizing power of the three $5d^{10}6s^2$ indicator ions is

$$Tl^+ < Pb^{2+} < Bi^{3+} \qquad (2)$$

while that of the cations in the solutions is

$$EAH^+ < Tl^+ \approx K^+ < Na^+ < Li^+ < Pb^{2+} < Bi^{3+} << Al^{3+} \qquad (3)$$

Consider first the case of the Tl^+ probe. Since the polarizing power of Tl^+ is much less than that of Al^{3+}, polarization of the Cl^- in the acidic $AlCl_3$-based melts is dominated by Al^{3+}, the interaction between Tl^+ ion and Cl^- ion is therefore weak. The same holds true for Tl^+ in basic $AlCl_3$–NaCl solutions, though to a lesser extent since the polarizing power of Na^+ (and Al^{3+}) is also greater than that of Tl^+. On the other hand, in basic $KAlCl_4$ the polarizing power of Tl^+ ion is about the same as that of K^+, and an equal competition between Tl^+ and K^+ for interaction with Cl^- should occur. This might have been expected to manifest itself in a spectral shift to the lower energy region of the spectrum. Since the Tl^+ absorption spectra are almost identical in all chloroaluminate melts studied, but are shifted to lower energies in the LiCl–KCl eutectic (at higher temperature), the absence of any shift in the present work must be attributed to a simple mass action effect of the excess tetrachloroaluminate anion (MCl saturation occurs at ~52 mol % KCl at the temperature for this study where only one Cl^- in 100 is "free" of Al^{3+} polarization). As noted earlier, when additional base is added as NH_4Cl, the absorption band moves to a position, 245 nm, close to that seen in the LiCl–KCl eutectic but is only observed as a shoulder. Since the shift only occurs for considerable excess base, however, we may conclude that Tl^+, as a spectroscopic indicator for the present acid–base titrations, is something of a failure.

Turning to Bi^{3+}, we note that in basic melts the probe ion competes only with the cation of the basic chloride (i.e. K^+ or EAH^+) for polarization of Cl^- ion. Since Bi^{3+} is much more polarizing than either K^+ or EAH^+, polarization of Cl^- ion is almost totally dominated by Bi^{3+} and well-defined chlorobismuthate ions are formed. The outer-shell electrons of Bi^{3+} are therefore unaffected by the weak polarization of Cl^- ion by its next nearest neighbor, K^+ or EAH^+. Hence, the observed Λ(Bi) values are, within experimental error, idential for all basic melts including pure EAHCl. As a result, neither the differences in basicity between the basic $AlCl_3$–KCl and $AlCl_3$–EAHCl systems nor the $AlCl_3$–EAHCl system's secondary equilibrium (at 33 mol % $AlCl_3$) is detected by Bi^{3+} ion.

The same argument applies to acidic melts where Bi^{3+} ion must compete with Al^{3+} ion for chloride interaction. In this case chloride polarization is dominated by Al^{3+}. Bi^{3+} therefore is surrounded by highly polarized chloride ions, and one would expect constant (i.e. composition *independent*) Λ(Bi) values for all acidic tetrachloroaluminate systems. This is only approximately true, however. Although at a given composition Λ(Bi) does not vary from system to system, it is composition *dependent and in an unexpected sense when compared with its behavior in oxide* glasses: Λ is increasing with $AlCl_3$ content (Figures 2 and 4) in a region in which thermodynamic basicity is decreasing. As Figure 3 shows most clearly, this is a real effect rather than a band-overlap artifact and it evidently involves both the $^3P_1 \leftarrow {}^1S_0$ and the stronger $^1P_1 \leftarrow {}^1S_0$ transitions. The band for the composition closest to the equivalence point that appears the most acidic also has the lowest oscillator strength. [A satisfying explanation of this effect is not currently at hand though it is possibly associated with the symmetry of the Bi^{3+} environment when all species by which it is coordinated ($AlCl_4^-$) are the same.]

These findings contrast sharply with those for Pb^{2+} in acidic tetrachloroaluminate melts[1] where composition-*independent* Λ(Pb) values are observed. Also significant is the fact that on the acid side of the equivalence point the Λ(Pb) values for the system containing the more basic chloride, EAHCl, are lower, indicating a *more acidic* melt, than for the systems containing the less basic chlorides, NaCl and KCl. We feel that this is a true indication of the relative acidic nature of the various melts and is a manifestation of the increased integrity of the $Al_2Cl_7^-$ ion in acidic EAHCl-containing melts. Osteryoung et al.,[35–37] in a spectroscopic study of the related room-temperature molten-salt system, $AlCl_3$–*n*-butylpyridinium chloride, showed that in the 66.6 mol % $AlCl_3$ melt *only* $Al_2Cl_7^-$ anion is present, compared with mixtures of $Al_2Cl_7^-$ and $AlCl_4^-$ in melts containing only alkali-metal cation. This suggests that the (acidic) *n*-butylpyridinium chloride-containing melt is more acidic than the high-temperature analogues containing, e.g., NaCl and KCl. In light of these observations the unexpected spectroscopic behavior of Bi^{3+} in acidic $AlCl_3$–EAHCl and –KCl melts, discussed above, cannot readily be interpreted as an indication of genuine increased basicity as the system departs from unit $AlCl_4^-$ anion fraction, and some other explanation of the spectral displacements must be found.

The failure of the Bi^{3+} spectrum to reflect the passing of the equivalence point in the $AlCl_3$–NaCl system, see Figures 1 and 4, is also striking and perplexing. The "end point" was clearly seen by the Pb^{2+} ion in our earlier reported study,[1] and the Bi^{3+} species should be more competitive for "free" Cl^- than is Pb^{2+}. The only explanation we can offer is that the greater chloride ion content of $BiCl_6^{3-}$ over $PbCl_4^{2-}$ leads to a greater excess chloride requirement than is present at NaCl-saturation to drive the neighbor change.

Finally, a set of spectra very similar to those of Figure 2 have been described for Bi^{3+} in an aqueous solution of variable-chloride low activity.[38,39] Stepwise equilibria were used to describe the various $BiCl_j^{3-j}$ species ($0 \le j \le 6$) in solvation, and equilibrium

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constants were calculated.[38] Analogous equilibria are believed to exist in the molten-salt systems studied here, where $AlCl_4^-$, $Al_2Cl_7^-$ and possibly $Al_3Cl_{10}^-$ assist in the solution process; we consider, however, the spectral precision achievable in the present difficult system to be inadequate for equilibrium quantification. The breadth of the bands G-I in Figure 2 must reflect the presence of multiple species of very different donor strengths if only two species are present.

Concluding Remarks

(1) The relative efficacies of the spectroscopic probes Tl^+, Pb^{2+}, and Bi^{3+} for detecting changes in the thermodynamic state of these chloroaluminate acid–base systems seem consistent with experience with conventional protonic acid–base indicators; viz., the best indicator for a process is the one with a basicity midway between the extremes. Here the extremes of basicity are determined by the polarization resulting from monovalent cations at one extreme and trivalent Al^{3+} at the other. Thus Pb^{2+}, with an intermediate field strength is best, while Tl^+ is unconscious of the equivalence point. To probe less pronounced basicity changes in a system such as $ZnCl_2 + AlCl_3$ (in which Co^{2+} coordination changes have been induced by composition variations[40]) it is probable that Pb^{2+} would be insensitive but Bi^{3+} would serve well as a probe.

(2) The magnitude of the electronic energy change from acidic to basic conditions is of interest. Changing the chloride ions with which the probes interact from Al^{3+}-polarized to Li/K-polarized in the LiCl–KCl eutectic results in changes in the photon energy needed to promote the $^3P_1 \leftarrow {}^1S_0$ transition amounting to 0.333, 0.313, and 0.562 eV for the Bi^{3+}, Pb^{2+}, and Tl^+ ions, respectively. Since it is the same change in electronic polarization state that provides the free-energy driving force for the acid–base process, e.g. in $AlCl_3 + KCl$, it is perhaps not surprising to observe that the free-energy change determined by electrochemical or other means at the equivalence point is of the same order $\Delta G = 2.303(RT/F)[\Delta(\mathrm{pCl})] = 0.57$ eV for the case $AlCl_3 + KCl$. For the case of Bi^{3+} in $AlCl_3 + KCl$, see Figure 4, the change in excitation energy across the 50% equivalence point, 4720 cm^{-1}, is in fact 0.59 eV.

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Phonons in Mixed-Valency and Mixed-Metal Salts $A_2M_{0.5}Sb_{0.5}Cl_6$ (A = Rb, Cs; M = Sb, Bi, Tl): An Inelastic Neutron Scattering Study

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Incoherent inelastic neutron scattering has been used to measure the phonon density of states (dos) of the mixed-valency and mixed-metal salts $A_2M_{0.5}Sb_{0.5}Cl_6$ (A = Rb, Cs; M = Sb, Bi, Tl) from 0 to 360 cm^{-1}, i.e. up to and including the intramolecular stretching modes. Similar measurements were also made on the cubic model compound Cs_2SnCl_6 and mixed-valency $Rb_{2.67}SbCl_6$. To assign the peaks in the frequency-dependent dos, a rigid-ion model was used to fit zone-center phonon frequencies previously available from infrared and Raman spectroscopy to a set of force constants and ionic charges. The latter were used to calculate phonon dispersion relations and a model dos for each compound. Above 110 cm^{-1} the measured dos are dominated by zone-center intramolecule modes of MCl_6^{3-} and $SbCl_6^-$ while in the region of the lattice modes the dos of all the salts are very similar. Consistent with the strong electron localization in the ground state, there are no features in the phonon dos of Cs_2SbCl_6 specifically assignable to mixed valency. The relevance of the phonon dos data to the quantitative interpretation of the intervalence absorption band shape is briefly discussed.

Introduction

The hexahalogenoantimonate(III,V) salts have long been recognized as prototypes of Robin–Day[1] class II mixed-valency behavior. Their structural simplicity makes them ideal starting models for an understanding of the dynamics of intervalence electron transfer in weak interaction mixed-valency systems. A detailed study of the temperature dependence of the shape[2] of the Franck–Condon optical charge-transfer profile in $(CH_3NH_3)_2Sb^{III}{}_{x/2}Sb^{V}{}_{x/2}Sn^{IV}{}_{1-x}Cl_6$ and its low-energy tail[3] in $Rb_{2.67}SbCl_6$ indicates that both lattice and intramolecular vibrational modes are involved in varying the lattice potential energy around the two Sb sites, and thus coupling to the electron transfer from Sb(III) to Sb(V). Consistent with this analysis are the resonance Raman results on Cs_2SbCl_6,[4] indicating the resonance enhancement of a lattice mode, and on $Cs_2Sb_xSn_{1-x}Cl_6$,[5] whence some $Sn^{IV}Cl_6^{2-}$ vibrations are similarly resonance enhanced. Furthermore, the gain in elastic energy associated with the strong electron–phonon coupling in these systems is responsible for overcoming the unfavorable repulsion of the two electrons occupying the same orbital.

Information about the phonon modes in mixed-valency compounds has come so far from infrared and Raman spectroscopy,[4,6,7] but these are confined by the selection rules to modes close to the Brillouin zone center, whereas information about the complete phonon density of states (dos) across the Brillouin zone is required in order to estimate the lattice elastic and Coulomb energy. The most suitable experimental method for such a study is inelastic neutron scattering (INS). Unfortunately the hexahalogenoantimonates(III,V) cannot be grown into large single crystals so INS experiments must be restricted to incoherent scattering (IINS). Given that hydrogen has an incoherent cross section ca. 20 times larger than any other element, IINS has mostly been used in studies of hydrogenous materials.[8] However, high-flux reactors and high-resolution spectrometers have recently made it possible to enlarge the range of possible experiments on weak or moderate incoherent neutron scatterers.

We have undertaken a detailed study of the phonon spectra of the mixed-valency $Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ and mixed-metal $Cs_2Bi^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, $Cs_2Tl^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$, $Rb_2Tl^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ salts by IINS. Due to superlattice ordering,[9] the primitive unit cell in these

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