We may also speculate on the diffusion path followed by the displaced protons. As a Na$^+$ ion enters the cavity closest to the surface, a proton on O10 is transferred to the water molecule of α-ZrP, which resides in the center of the cavity. This hydronium ion is in turn repelled by the Na$^+$ ion and moves toward the O7 nearest the surface whereupon the O7 atom gives up its proton to the outer solution. The [P1–O7]$^-$ group then accepts a proton from the hydronium ion. As the sodium ions diffuse further into the layer, a counter diffusion of protons along the O7 path must take place. Since the O7 atoms are one *b* length apart (or 5.35 Å) in the same layer, but about 3.5 Å apart in adjacent layers, the proton can be transferred by rotation of the hydronium ion followed by donation to cover the shorter distance. However, as the sodium ions diffuse inward, water follows to form a pentahydrate with an interlayer spacing of 11.8 Å[3]. Under these conditions the closest O7–O7 distance is *b* and some diffusion as well as rotation of the hydronium ion might occur to effect proton transfer.

In Figure 3 the dashed line indicates the *c* axis in terms of the original α–ZrP cavity. It is seen that the layers appear to be shifted along *a* to create a large β angle. In the fully exchanged ammonium ion form the β angle based on the original cavity is again small (102.7°).[10] The two ammonium ions are situated close to opposite sides of the cavity, one of them being surrounded by three O10 atoms and one O7 atom and the other one by three O7 atoms and one O10 atom. Thus, the layers realign themselves similar to their relative positions in α-ZrP.

It is perhaps fitting at this juncture to emphasize that the structural details emerging from these studies were made possible through the parallel development of ab initio methods of solving crystal structures from X-ray powder data. Our emphasis has been to use these techniques with ordinary diffractometer generated data on equipment that is readily available in every diffraction laboratory as opposed to using synchrotron radiation[32] or film methods.[33] Continuation of efforts in this direction, so as to obtain accurate data to higher 2θ values, should further improve the method and allow structure determinations to be carried out in a fairly routine manner for many situations where single crystals are unobtainable.

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Donor–Acceptor Properties of Ambient-Temperature Chloroaluminate Melts

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The donor–acceptor properties of room-temperature chloroaluminate ionic liquids composed of mixtures of $AlCl_3$ with either *N*-(1-butyl)pyridinium chloride or 1-ethyl-3-methylimidazolium chloride were studied. Gutmann donor and acceptor numbers were determined by using the Eu(III) reduction potential and the ^{31}P chemical shift of triethylphosphine oxide, respectively. Acidic melts are extremely poor donor and strong acceptor media. Basic melts are similar in basicity to DMF. No conclusions concerning the acceptor properties of the basic melt are drawn from this work since the strongly basic probe molecule, $Et_3P{=}O$, is leveled by the solvent. Conditions under which these parameters are potentially useful are outlined.

Introduction

The chemistry observed in ambient-temperature chloroaluminate ionic liquids composed of mixtures of $AlCl_3$ with either *N*–(1-butyl)pyridinium chloride (BuPyCl) or 1-ethyl-3-methylimidazolium chloride (ImCl), generally referred to as RCl, is strongly affected by melt composition.[1] The composition dependence of the chemistry of the ambient-temperature chloroaluminate melts is due to the change of the anionic makeup of the melt with composition. In basic melts, all aluminum chloride added is neutralized by reaction with chloride ion. Thus, only Cl^- and $AlCl_4^-$ ions are present in appreciable quantities in the basic melt. In acidic melts, all of the chloride is neutralized and the excess $AlCl_3$ present forms $Al_2Cl_7^-$. In this composition regime, $AlCl_4^-$ and $Al_2Cl_7^-$ are the principal anionic components of the melt. The character of the melts as solvents is determined by the presence of chloride ion in basic melts and heptachlorodialuminate ions in the acidic melt, as given by the equation

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad (1)$$

The most common descriptive construct for acid–base chemistry in molten salts is the anionotropic solvent system model.[2] The properties of solutes are described in terms of the transfer of characteristic anions. A base is a substance that liberates this anion, while an acid consumes it. This concept, a generalization of the Arrhenius acid concept, was first applied in the study of oxide-containing systems by Lux, Flood, and Førland.[3,4] When this concept is applied to chloroaluminates, basic solutes liberate chloride and acidic solutes are chloride acceptors. Melt acidity is defined in terms of the quantity –log [Cl$^-$], or pCl, of the melt. Unfortunately, this formalism provides no information not known from the equilibrium constant for the anion equilibrium. Furthermore, this description of acidity is entirely medium specific and no information concerning the properties of the melt relative to other solvents is available. Comparisons with other solvent media allow one to have some insight and predictive ability concerning the chemistry of solutes in the melt.

An alternative to the simple specification of melt composition or pCl for describing medium acid–base properties is the specification of suitable solvent parameters. The Gutmann donor[5,6] and acceptor[6,7] number parameters, DN and AN respectively, are simple and widely used solvent basicity and acidity parameters.

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The donicity of a solvent is defined as the enthalpy of formation of a 1:1 adduct of the solvent with $SbCl_5$ at infinite dilution in 1,2-dichloroethane (DCE). This parameter is based on the calorimetric work of Lindqvist and Zackrisson,[8] extended by Gutmann to define a quantitative basicity scale. The AN is determined from the ^{31}P chemical shift of triethylphosphine oxide dissolved in the solvent of interest.

The DN and AN parameters correlate well with a wide variety of solvent-dependent phenomena, including several other solvent parameters such as the Grunwald–Winstein Y value,[9] Kosower's Z value,[10] and the Dimroth–Reichert E_t parameter,[11] all of which are related to the AN parameter.

The acid–base characteristics of ambient-temperature chloroaluminate melts are, of course, implied in the chemistry observed for the wide variety of solutes studied in these systems.[1] However, relatively few studies have focused explicitly on the acid–base chemistry of the room-temperature chloroaluminates. The anion equilibrium (eq 1) has been studied by potentiometric and voltammetric techniques.[12-14]

Woodcock and Shriver[15] have studied the organometallic compounds $Fe(phen)_2CN_2$, $Cp_4Fe_4(CO)_4$, and $CpFe(CO)_2CN$ in $AlCl_3$–BuPyCl melts. These compounds are sensitive to the Lewis acidity of the surrounding media and were used as probes of the Lewis acidity in the melts. A qualitative discussion of the Lewis acid strength of $AlCl_3$ in the melt relative to that of group III halides in other media is given in their work.

In this work, we describe the determination of the Gutmann solvent parameters for room-temperature chloroaluminate melts as functions of composition. The AN values are determined directly, while the DN values are estimated by taking advantage of one of the many correlations between solvent acidity and easily measurable phenomena. Here we employ the correlation between solvent donicity and the formal potential of the Eu(III)/Eu(II) redox couple.

Experimental Section

The preparation and purification of BuPyCl and ImCl have been described elsewhere.[16] Melts were prepared by slowly adding the organic chloride to aluminum chloride (Fluka purissimo), which was sublimed prior to use. All melt preparation and handling were carried out in a drybox (Vacuum Atmospheres Co.) under an argon or helium atmosphere. Oxygen and water content were kept below 5 ppm each. Anhydrous $EuCl_3$ (Alfa Chemical) was used as obtained. Triethylphosphine oxide (Alfa Chemical) was dried in vacuo prior to use.

NMR samples, except for those used in susceptibility measurements (see below), were loaded into 10-mm tubes (Wilmad Glass Co.), which were then capped and sealed with Parafilm. Initially, some samples were fitted prior to sealing with a precision coaxial tube that was filled with a reference material. However, this method was found to yield results equivalent to those obtained by referencing by substitution. All values reported here were measured by using the latter method.

All ^{31}P chemical shift measurements were carried out under conditions of complete proton decoupling at 30 °C on a JEOL FX-270 NMR spectrometer operating at 109.15 MHz. Volume susceptibilities of melts were estimated by using Becconsal's method,[17] taking advantage of the different geometric factors for susceptibility corrections for samples oriented parallel and perpendicular to the field axis. A JEOL FX-90Q NMR spectrometer was used for this experiment in addition to the FX-270 instrument mentioned above. The inner coaxial tube was filled with neat benzene-d_6, and the annular region was filled with a sample of melt containing a small amount (roughly 5% by weight) of benzene-d_6. The susceptibility was then calculated from the differences with field axis orientation of the differences in the ^{13}C chemical shifts between benzene-d_6 in the inner and outer tubes.

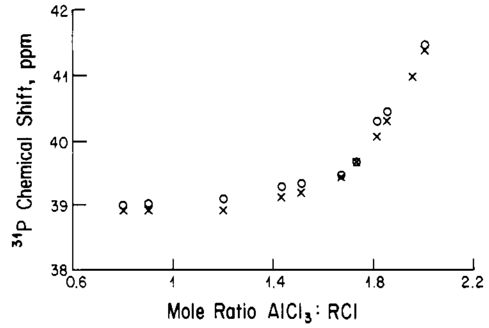

Figure 1. Plot of the ^{31}P chemical shifts of 0.2 M $Et_3P{=}O$ solutions in (×) $AlCl_3$–BuPyCl and (○) $AlCl_3$–ImCl melts versus the mole ratio of $AlCl_3$–RCl mixtures.

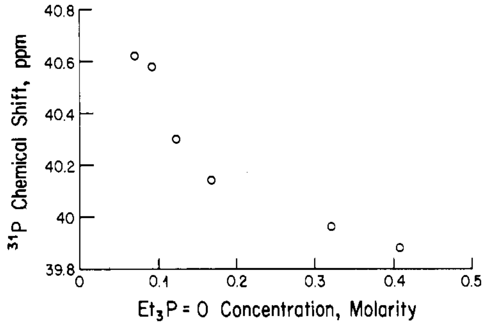

Figure 2. Plot of the ^{31}P chemical shifts of $Et_3P{=}O$ solutions in 1.8:1.0 $AlCl_3$–ImCl melts as a function of molarity of $Et_3P{=}O$.

All electrochemical experiments were carried out in the drybox with a three-electrode system with either a tungsten rotating-disk electrode (area 0.0784 cm^2, Pine Instrument) or a Pt-disk electrode (area 0.02 cm^2, Bioanalytical Systems) as the working electrode and Al wires immersed in 1.5:1.0 melts as the counter and reference electrodes. These last two electrodes were separated from the solution under study with fine-porosity glass frits. Voltammetric curves were recorded on a Houston Instruments Model 2000 x-y recorder with potentiostatic control maintained by an EG&G PARC Model 173 potentiostat connected to an EG&G PARC Model 175 universal programmer.

Results and Discussion

1. Acceptor Numbers. ^{31}P NMR spectra of pure solutions of triethylphosphine oxide in all melts studied generally consisted of a single line and did not change with time over the course of several days. The ^{31}P chemical shifts of 0.2 M solutions of $Et_3P{=}O$ in $AlCl_3$–BuPyCl and $AlCl_3$–ImCl melts as a function of the mole ratio of $AlCl_3$ to RCl are shown in Figure 1. In basic melts, the chemical shift is constant at 38.9 ppm. Comparison with the results of Gutmann et al.[7] reveals that this is a relatively large chemical shift for the triethylphosphine oxide molecule and thus that the medium is quite acidic.

In acidic melts, Figure 1 shows that the chemical shift increases through the range of compositions studied. Melts with mole ratio greater than 1.2:1.0 have larger chemical shifts, and thus higher functional acidity, than basic melts. The chemical shift varies similarly for both melts and are within 0.1 ppm of one another for equal melt compositions.

Figure 2 shows the concentration dependence of the ^{31}P chemical shifts of $Et_3P{=}O$ dissolved in a 1.8:1.0 $AlCl_3$–ImCl melt. In acidic melts, there is a downfield chemical shift with decreasing concentration of $Et_3P{=}O$. In the basic melt, there is no change of the shift value with concentration.

The acceptor number is normally calculated by extrapolation of the chemical shift to infinite dilution, correction for the volume susceptibility differences between the analyzed solvent and hexane, and division by the chemical shift observed for a 1:1 adduct of $Et_3P{=}O$ with $SbCl_5$ in 1,2-dichloroethane. The normalization is carried out to enable the calculation of enthalpies of interaction between solvents from the DN and AN values. If we define the susceptibility-corrected, infinite-dilution chemical shift of the probe molecule in a solvent (i) relative to that of the probe molecule

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Table I. Bulk Susceptibility Values for Ambient-Temperature Chloroaluminate Melts

melt composition	$10^6 \times$ susceptibility	melt composition	$10^6 \times$ susceptibility
1.8:1.0 $AlCl_3$–ImCl	−0.761	1.5:1.0 $AlCl_3$–BuPyCl	−0.766
1.2:1.0 $AlCl_3$–ImCl	−0.741		−0.761[a]
0.6:1.0 $AlCl_3$–ImCl	−0.716		

[a] Reference 18.

Table II. Chemical Shifts (and Concentration of $Et_3P{=}O$) Used To Calculate AN's as a Function of Melt Composition

melt composition	$[Et_3P{=}O]$, M	^{31}P chemical shift, ppm
0.8:1.0 $AlCl_3$–BuPyCl	0.064	38.87
0.8:1.0 $AlCl_3$–ImCl	0.057	38.87
1.2:1.0 $AlCl_3$–BuPyCl	0.080	39.75
1.2:1.0 $AlCl_3$–ImCl	0.081	39.88
1.5:1.0 $AlCl_3$–ImCl	0.053	40.60
1.6:1.0 $AlCl_3$–BuPyCl	0.059	40.81
2.0:1.0 $AlCl_3$–BuPyCl	0.074	41.62

Table III. Acceptor Numbers for Melts and Selected Solvents[a]

solvent	acceptor no.
hexane	0.0
1,2-dichloroethane	16.7
acetonitrile	18.9
water	54.8
0.8:1.0 $AlCl_3$–BuPyCl melt	98.2
0.8:1.0 $AlCl_3$–ImCl melt	98.2
1.2:1.0 $AlCl_3$–BuPyCl melt	98.3
1.2:1.0 $AlCl_3$–ImCl melt	98.6
$Et_3P{=}O$–$SbCl_5$ in 1,2-DCE	100.0
1.5:1.0 $AlCl_3$–ImCl belt	100.3
1.6:1.0 $AlCl_3$–BuPyCl melt	100.8
2.0:1.0 $AlCl_3$–BuPyCl melt	103.2
trifluoroacetic acid	105.3
methanesulfonic acid	126.3

[a] Data other than that for melts taken from ref 6.

in hexane as $\delta_{i,cor}$, the acceptor number is given by eq 2, taken from ref 6.

$$AN = 2.348\delta_{i,cor} \tag{2}$$

The susceptibility measurements were outlined above. Bulk susceptibility values for $AlCl_3$–BuPyCl and $AlCl_3$–ImCl melts are given in Table I. These results are similar to those reported, which were measured with a SQUID balance.[18] Corrections for this effect were small and did not vary strongly with composition.

In light of the nonlinear dependence of the observed chemical shift on concentration, the extrapolation to infinite dilution was not carried out in estimating the AN values. Instead, the chemical shifts of the ^{31}P line obtained for dilute solutions of $Et_3P{=}O$ in melts were used to estimate the acceptor numbers. Since the changes in chemical shifts with concentration were not drastic and the AN is primarily used qualitatively, this method is deemed sufficient for our purposes. The actual chemical shifts used to calculate the acceptor numbers for the melt and the concentrations of $Et_3P{=}O$ used are shown in Table II.

Acceptor numbers obtained for several melt compositions are listed in Table III along with values for a few other solvents included as points of reference.

The range of acidity, as indicated by the measured AN's across the composition range studied, is small. The acceptor behavior of basic melts, which behave as strongly acidic media, is somewhat surprising. This is not in accord with the known chemistry of the basic melts. However, $Et_3P{=}O$ is a very basic molecule. This suggests that the AN estimated for basic melts is artificially high due to solvent leveling of the probe molecule by reaction with $AlCl_4^-$ to form an $Et_3P{=}O{\cdot}AlCl_3$ adduct and liberate chloride. No information concerning the interaction of the melt toward bases weaker than $Et_3P{=}O$ is obtained.

Table IV. Neutral Melt Titration of $Et_3P{=}O$ in a BuPyCl–$AlCl_3$ Melt

current,[a] μA	[BuPyCl],[b] mM	$[Et_3P{=}O)$,[b] mM
−22		
83	18.8	
140	36.2	
160	36.2	6.7
186	36.2	14.7

change in current per 1 mM of BuPyCl added: 3.25 μA
change in current per 1 mM of $Et_3P{=}O$ added: 3.12 μA

[a] RDE limiting current measured for Cl^- oxidation wave at a tungsten electrode; area 0.0784 cm^2; rotation rate 900 rpm; scan rate 20 mV/s, T = 40 °C. [b] Total concentration added to solution at each point in the experiment.

In order to test this hypothesis, we carried out a neutral melt amperometric titration as described by Lipsztajn and Osteryoung.[19] In this experiment either the Cl^- oxidation wave in a "slightly basic" melt or the $Al_2Cl_7^-$ wave in a "slightly acidic" melt is monitored as a solute is added to the melt. The change in the diffusion-limited voltammetric wave height as the solute concentration is increased indicates the stoichiometry of any complexation reaction that takes place. Data obtained from such an experiment carried out at the tungsten rotating-disk electrode (RDE) are summarized in Table IV. In this case, BuPyCl is added to a very slightly basic melt and an RDE voltammogram for chloride ion oxidation is measured. The data reported in Table IV are limiting current values for this voltammetric wave. First, BuPyCl was added to the melt. One chloride per molecule of salt added is released into the melt, and the voltammetric wave height increases accordingly. The current increase resulting from the addition of $Et_3P{=}O$ is compared to that resulting from addition of BuPyCl. The changes are approximately the same; i.e., the current per millimole of BuPyCl added results in approximately the same current increase as an equivalent number of millimoles of $Et_3P{=}O$, and thus one Cl^- is liberated per $Et_3P{=}O$ added. This confirms the formation of an $Et_3P{=}O{\cdot}AlCl_3$ adduct according to the reaction

$$AlCl_4^- + Et_3P{=}O \rightarrow Et_3P{=}O{\cdot}AlCl_3 + Cl^- \tag{3}$$

and further indicates that $Et_3P{=}O$ is a stonger base than Cl^- and is leveled by the solvent.

Since the chemical shifts for the probe molecule increase throughout the acidic composition regime, some further interaction must take place. The simplest such interaction is the addition of a second $AlCl_3$ to form a diadduct. As the melts are made more acidic, the concentration of $Al_2Cl_7^-$ increases, shifting reaction 4 to the right. This reaction also explains the observed concentration dependence of the ^{31}P shift in acidic melts. Decreasing the concentration of $Et_3P{=}O$ increases the ratio of $Al_2Cl_7^-$ to $Et_3P{=}O$, and the medium behaves as if it were more acidic, resulting in a downfield shift.

$$Et_3P{=}O{\cdot}AlCl_3 + Al_2Cl_7^- = Et_3P{=}O{\cdot}2AlCl_3 + AlCl_4^- \tag{4}$$

2. Donor Numbers. The Gutmann DN is the infinite-dilution enthalpy of formation of a 1:1 adduct of the donor solvent with $SbCl_5$ in 1,2-DCE. However, this measurement can provide a misleading estimate of the true solvent basicity for liquids that are structured, such as water, since the solvent–solvent interactions characteristic of the donor solvent are minimized at infinite dilution. An approach used to obtain a DN estimate in such cases is to employ an indirect means to determine the parameter, by using a spectroscopic or electrochemical probe that is known to correlate with the donicity of a number of solvents.[6]

The redox potentials of lanthanide(III/II) couples are known to vary linearly with solvent basicity as expressed by the Gutmann DN parameter.[20] Gilbert et al.[21,22] have studied the redox be-

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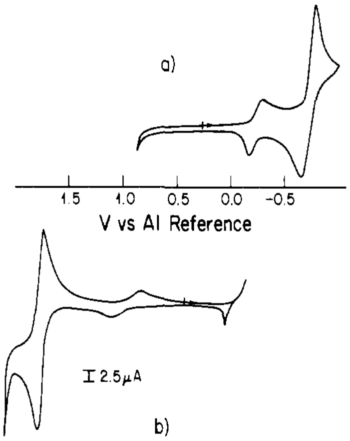

Figure 3. Cyclic voltammograms of 7 mM $EuCl_3$ in solutions of (a) 0.4:1.0 and (b) 1.1:1.0 $AlCl_3$–BuPyCl melts (5 mV/s scan rate; Pt electrode). Waves at −0.2 V (a) and +1.0 V (b) arise from proton impurity.

havior of several lanthanide ions in BuPyCl melts. Though reduction waves were observed in acidic melts, these workers found no reduction waves for Yb(III) or Sm(III) in basic melts. No attempt to observe the electrochemistry of Eu(III) in basic melts was reported in this work, though Eu(III) was studied in very acidic melts. Since the reduction potential of Eu(III) is considerably more positive than that of the other lanthanides studied, and a good linear correlation of the reduction potential of this species with donicity has been observed,[20] the potential of the Eu(III)/Eu(II) couple was measured as an indirect indicator of melt donicity.

Cyclic voltammograms of Eu(III) solutions in 0.4:1.0 and 1.1:1.0 BuPyCl melts are shown in Figure 3; the small waves in the figure are due to the reduction of protonic impurity. These cyclic voltammograms were recorded at slow scan rates in order to ensure that the curves obtained would be nearly reversible and, thus, that the formal potential of the couple could be reasonably estimated from the voltammetric peak potentials. The separation between anodic and cathodic peaks was 63–65 mV. Under these conditions, the system was essentially reversible and the formal potential was calculated as the average of the anodic and cathodic peak potentials.

The estimation of the donor number from the Eu(III)/Eu(II) potential requires that the potential of the reference electrode used be known with respect to the solvent-independent redox couple used in the original correlation, bis(biphenyl)chromium (BBCr). The potentials obtained from the experiment were corrected by utilizing the known potential of the ferrocene/ferrocenium couple,[23] another solvent-independent reference couple, relative to our reference electrode and relative to the BBCr reference. The donor number was then calculated by using the slope of the line from the plot of the Eu(III)/Eu(II) potential vs donicity.[6] The potential of $Fe(Cp)_2/Fe(Cp)_2^+$ is +0.4 V vs the Al–Al(III) 1.5:1.0 melt reference electrode and +1.12 V vs the BBCr reference. Thus, a correction factor of +0.72 V is added to the measured Eu(III)/Eu(II) potential in these calculations. The corrected potential is then used in the following equation to calculate a DN:

$$\mathrm{DN} = 15.1 - 16.33[E(\mathrm{vs\ BBCR}) - 0.8] \qquad (5)$$

Since the donor number of propylene dicarbonate (PDC) lies directly on the best fit line for the Eu(II)/Eu(III)–Donicity correlation, we chose this point as a convenient reference in the development of eq 5. The DN of PDC is 15.1, the Eu(III)/Eu(II) potential versus BBCr in PDC is +0.8 V, and the slope of the Eu(III)/Eu(II) potential vs DN[6] is −16.33 DN/V. The experimental results and the DN's obtained as indicated above are shown in Table V.

Table V. Donicities of Melts and Other Solvents[a]

solvent	donor no.	potential,[b] V
1,2-dichloroethane	0.0	
nitromethane	2.7	
acetonitrile	14.1	
diethyl ether	19.2	
dimethylformamide	26.6	
dimethyl sulfoxide	29.8	
0.4:1.0 $AlCl_3$–ImCl melt	29.8	−0.81
0.8:1.0 $AlCl_3$–ImCl melt	28.6	−0.76
0.9:1.0 $AlCl_3$–ImCl melt	27.2	−0.72
0.9:1.0 $AlCl_3$–BuPyCl melt	27.2	−0.72
1.1:1.0 $AlCl_3$–ImCl melt	−14.5	+1.85
2.0:1.0 $AlCl_3$–ImCl melt	−14.6	+1.86
2.0:1.0 $AlCl_3$–BuPyCl melt	−15.0	+1.88

[a] DN data other than that for melts taken from ref 6. [c] Potential of Eu(III)/Eu(II) couple vs Al/Al(III) reference; melts only.

Table VI. Calculation of DN from H^+/H_2 Potential

melt composition[a]	E_f, V vs Al(III)	E_f, V vs $Fe(Cp)_2$	DN(H)
0.8	−0.40	−0.65	+26.5
1.2	+0.80	+0.55	+2.5
1.4	+0.85	+0.60	+1.5
1.6	+0.90	+0.65	+0.5
2.0	+1.05	+0.80	−2.5

[a] $AlCl_3$–BuPyCl mole ratio.

For basic melts, the donicity is similar to that of DMF. There is a large change in potential, and thus donicity, between basic and acidic melts. The donicity of the acidic melt is negative, reflecting the extremely poor solvating characteristics of the acidic melts toward other acidic species. Thus, acidic species should be quite reactive in acidic melts. An interesting case in point is that of H^+, which is a strong oxidant in acidic melts.[24] The precise value presented for the acidic melt donicity should be viewed with some skepticism since the estimation of these numbers required an extrapolation of the linear plot obtained by Gutmann et al.[20] and there is no assurance of the validity of a linear extrapolation. However, the acidic melts clearly have exceedingly weak basic character.

The results are qualitatively in accord with our expectations on the basis of previously known chemistry in the melts. Many metal ions and organic bases are known to exhibit large changes in potential as the composition is changed from acidic to basic.[1] Also, the dominant chemistry of acidic solutes in basic melts is chloro-complexation chemistry. Note also that the difference between the donicities of the $AlCl_3$–ImCl- and $AlCl_3$–BuPyCl-based melts of similar composition is not large, corresponding to a difference of about 20 mV in the potentials measured for Eu(III/II) in the two melts. The potential difference is small enough to be within the range of experimental error for the method used to estimate the formal potential.

Additionally, the results agree with donicities estimated for the melts from other known correlations with donicity or from the behavior, in other solvents of known donicity,[6] of the anions present in the melt. The donicity of the chloride ion has been estimated to be roughly 26, in good agreement with our results.[6] The $AlCl_4^-$ ion, which is the most basic species present in the acidic melt, is less basic than nitromethane since $HAlCl_4$ dissociates in nitromethane[25] (i.e. the solvation of H^+ by nitromethane is sufficiently strong that solvation is preferred to ion pairing). Thus, the donicity must be less than that of nitromethane, in agreement with the results reported here.

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The potential of the proton reduction at platinum in various solvents is known to correlate with donicity.[25] This correlation can also be used to estimate the donicity of the melt. The potential of the H^+/H_2 couple in the melt can be estimated from the data of Sahami and Osteryoung.[24] These values are then corrected to the $Fe(Cp)_2/Fe(Cp)_2^+$ potential scale, and the DN is calculated from eq 6, taken from ref 25. E_H is the formal potential for the

$$DN = 20E_H - 13.5 \qquad (6)$$

H^+/H_2 couple estimated by averaging the values of cathodic and anodic peak potentials shown in ref 24. The numbers used in this calculation for various melt compositions are given in Table VI. The donicity of the basic melt estimated in this way agrees surprisingly well with that estimated from the Eu(III/II) correlation. For the acidic melts, the DN near zero may be a more reasonable estimate than the very low value obtained from the Eu(III/II) correlation because no extrapolation is necessary. The donicity of the acidic melts is in either case very low.

Since we now have indications of both the acidity and basicity of the melts, it is germane to consider melt reactivity in terms of donor–acceptor concepts. Application of the DN/AN approach to melt chemistry is likely to yield at least qualitatively correct conclusions in certain cases. Promising cases include consideration of the chemistry of cosolvents or solutes with known donor or acceptor properties added to the melt and the redox behavior of those coupled whose redox behavior in other solvents is well correlated with solvent donicity or AN. Cases unlikely to be adequately described by donor–acceptor considerations include those of "soft" donors or acceptors and those where reaction with the melt involves more than simple adduct formation.

The chemistry of cosolvents aded to melts has been of interest from the time of the initial investigations carried out in ambient-temperature chloroaluminates.[26] Dilution of the $AlCl_3$–BuPyCl melts with benzene served to decrease the melt viscosity and increase its conductivity.[26] Benzene does not undergo any specific interaction with the melt, as evidenced by the constant benzene ^{13}C chemical shift,[26] regardless of changes in benzene concentration and in melt composition. Further interest in cosolvents has been sparked by the goal of creating conditions under which Al(III) can be reduced in basic melts.

A simple method, based on DN/AN considerations, for predicting the chemistry of basic cosolvents in melts of various compositions is to consider all melt reactions with cosolvents as leveling reactions. Thus, cosolvents more basic than melts of a given composition will be leveled by the melt. This allows us to divide potential cosolvents into three categories according to donicity (not according to experimentally observed reactivity): (1) those that are leveled in both basic and acidic melts, (2) those that are leveled in acidic melts but not in basic melts, and (3) those that react with neither basic nor acidic melts. Very roughly, category 1 includes all solvents (or solutes) of donicity above about 25, category 2 includes materials with DN values between about 0 and 25, and category 3 should include all materials with DN values below that of the melt.

In practice, such a rough method works quite well to discriminate between categories 1 and 2, but the discrimination between categories 2 and 3 (the latter of which appears to be empty) is not perfect. Of course, this is because we are considering the donor behavior of an acceptor medium. The relevant quantity to discriminate between categories 2 and 3 is the medium acidity. Table VII lists many solvents and their donicities, divided among the classes described.

Categories 1 and 2 above, identified on the basis of predicted behavior of these solvents in the melt, also contain groups of solvents that exhibit distinctly different behavior toward $AlCl_3$ or $AlCl_4^-$ dissolved in the solvent. Solvents in category 1 displace chloride from both $AlCl_3$ and $AlCl_4^-$ added to solution since these solvents are more basic than chloride (DMF falls into a gray area—more basic than chloride ion on the basis of the apparent donicity of Cl^-, but with a slightly lower donicity than that of a basic melt). Solutions of $AlCl_3$ and $AlCl_4^-$ in these solvents form solvated ions,[27] such as $Al(DMF)_6^{3+}$ or $Al(H_2O)^{3+}$. We have recently found that DMF displaces chlorides from $SOCl_2$, as expected from the differences in donicity.[28]

Table VII. Donicity "Categories" (DN)

Category 1: DMF (26.6), DMSO (29.8), diethylformamide (30.9), pyridine (33.1), HMPA (38.8), tetramethylurea (31), hydrazine (44), piperidine (51), ethylenediamine (55), ethylamine (55), ammonia (59), triethylamine (61)

Category 2: acetyl chloride (0.7), thionyl chloride (0.4), nitrobenzene (4.4), acetonitrile (14.1), dioxane (14.8), ethylene sulfite (15.3), benzophenone (16.6), dimethoxyethane (20), acetone (17), ethyl acetate (12.1), THF (20)

Category 3: none

Solvents belonging to category 2 exhibit different behavior toward $AlCl_3$ than toward $AlCl_4^-$. $AlCl_4^-$ is stable in these solvents, while $AlCl_3$ tends to disproportionate to form $AlCl_4^-$ and solvated ions that may or may not contain chloride. Examples include the case of acetonitrile, in which $AlCl_4^-$ and $Al(CH_3CN)_6^{3+}$ are the principal ions formed (see ref 29 for more detail) and THF, in which $AlCl_3$ disproportionates[30] to form $AlCl_4^-$ and $AlCl_2(THF)_2^+$.

Few melt–cosolvent systems have been investigated in detail. Donahue et al.[31] have carried out studies of melt–acetonitrile mixtures. Acetonitrile does indeed solvate Al(III) in acidic melts but is unreactive toward basic melts, in accord with our expectations.

Of course, basic cosolvents are just special cases of basic solutes dissolved in the melt. Thus, similar considerations should apply for the chemistry of any solute in the melt. The chemistry of pyrrole in the melt, which we have recently described,[32] is readily rationalized by using the DN of the melt and that of pyrrole. The donicity of pyrrole was estimated by using the known correlation between donicity and the ^{23}Na chemical shift of $Na(B(C_6H_5)_4)$ or $NaClO_4$ salts in dilute solution in a solvent.[33,34] The ^{23}Na chemical shift of $Na(B(C_6H_5)_4)$ in pyrrole is −13 ppm relative to NaCl in water. The DN of pyrrole estimated from this chemical shift value is about 6. This leads to the prediction that pyrrole will not form an adduct in the basic melt (DN = 27–29) but will react with acidic melt (negative DN), as is observed.[32]

Many correlations of redox properties of metal ions or metal ion complexes with medium donicity exist. Of course, one such correlation, that between Eu(III)/Eu(II) potential and DN, was exploited to estimate the melt donicities. Examples of metal ions or complexes whose reduction potential in various solvents correlate with donicity include[6] Tl^+, Zn^{2+}, Cd^{2+}, Sm^{3+}, Yb^{3+}, $Fe(CN)_6^{3-}$, and $Co(en)_3^{3+}$.

The oxidation of $Fe(CN)_6^{4-}$ in acidic melts has recently been shown to occur at roughly +2.35 V vs the Al–Al(III) 1.5:1 melt reference.[35] When the correlation of $Fe(CN)_6^{3-}$ reduction potential with AN, as shown in ref 6 (the high-AN portion of this curve is roughly linear with a slope of 37 mV/AN), is used, this potential is corrected to the BBCr reference, and the measured AN's for the melt are used, estimates of the oxidation–reduction potential for the ferro/ferricyanide couple ranging from +1.84 V, in a 1.2:1.0 melt, to +2.02 V, in a 2.0:1.0 melt, both vs the

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Al/Al(III) 1.5:1 melt reference, can be made. Though these potentials are somewhat less positive than that observed experimentally, the estimates are qualitatively reasonable.

In addition to redox potentials, IR stretching frequencies, NMR chemical shifts, and enthalpies of solvation or transfer of various complexes and ions are correlated with donicity.[6] By direct comparison or by analogy, this body of work can be drawn upon in considering the chemistry of various compounds in the melt.

Unfortunately, the DN/AN approach is not universally applicable in the simple way outlined above. An interesting class of cases in which donicity considerations are unlikely to adequately describe chemistry in the melts is that of "soft" ions or compounds intereacting with the melt. Since most solvents have hard reactive sites, donor and acceptor numbers do not adequately reflect the reactivity of soft sites. (Of course, this also means that the consideration of solvent "softness" is not important in many cases.)

No work done to date in ambient-temperature chloroaluminates has specifically considered the influence of softness of ions studied on their chemistry. A situation in which this type of interaction could be important is the solvation of ions such as Cu(I) or Ag(I), which are known to be quite soft. Indeed, it may be possible to observe some preferential solvation effects for these ions in solutions of melts with cosolvents or with soft bases present. Ag(I) is known to be strongly solvated by acetonitrile. Perhaps I^- present in melts would also provide additional stabilization for soft metal ions.

Another type of reaction that is not completely predictable on the basis of DN/AN comparisons is that in which further rearrangement takes place after initial adduct formation. The further rearrangement can provide an additional energetic driving force to the reaction. Consider the case of an alcohol added to the melt. The oxygen on the alcohol will behave as a donor toward Al(III) to form an adduct.[36] This initial step can be followed by loss of a proton into the melt, which solvates the proton. This solvation step can provide an additional driving force.

The scope of the reactions described that are not likely to be readily explicable by DN/AN considerations certainly limits the power of the donor–acceptor approach. However, this approach, for all its crudeness, still can provide at least qualitative information on the reactivity of these melts toward a wide variety of solutes. Furthermore, the determination of the AN and DN values described above represents a first attempt to systematically compare chemistry in a molten salt system with that in typical organic solvents. From this point of view, we know that toward solutes which are not very basic, a basic melt will behave like DMF. On the other hand, acidic melts are similar in acidity to trifluoroacetic acid. This information provides at least a starting point for the interpretation of chemistry observed in the melt and for speculation on the suitability of the melt as a solvent for classes of chemical reactions.

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Crystal Structures of Three Brilliantly Triboluminescent Centrosymmetric Lanthanide Complexes: Piperidinium Tetrakis(benzoylacetonato)europate, Hexakis(antipyrine)terbium Triiodide, and Hexaaquadichloroterbium Chloride

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The crystal structures of three brilliantly triboluminescent lanthanide complexes are found to be centrosymmetric, contrary to the expectation that triboluminescent activity derives from bulk polar charge distributions (i.e., by piezoelectrification). Crystal data for piperidinium tetrakis(benzoylacetonato)europate (**2**): monoclinic, $P2_1/n$, $a = 11.910$ (4) Å, $b = 19.667$ (8) Å, $c = 18.520$ (9) Å, $\beta = 106.07$ (3)°, $V = 4169$ Å^3, $Z = 4$, $R(F) = 3.85\%$. Crystal data for hexakis(antipyrine)terbium triiodide (**3**): rhombohedral, $R\bar{3}$, $a = 13.897$ (3) Å, $c = 31.980$ (8) Å, $V = 5349$ (2) Å^3, $Z = 3$, $R(F) = 4.47\%$. Crystal data for hexaaquadichloroterbium chloride (**4**): monoclinic, $P2/n$, $a = 7.8926$ (12) Å, $b = 6.5091$ (12) Å, $c = 9.6167$ (12) Å, $\beta = 93.751$ (12)°, $V = 493.0$ (1) Å^3, $Z = 2$, $R(F) = 2.81\%$. The structures of **2** and **4** reveal eight-coordinate, tetragonal-antiprismatic metal ion geometries, and the structure of **3** shows an octahedral environment. No single factor can account for the unexpected triboluminescence of these complexes other than the presence of easily deformable, weakly bonded interactions between ions or between ions and molecules in the lattices. On application of pressure, these weak interactions may deform to create polar domains. None of the structures displays significant disorder.

Introduction

Attempts to correlate solid-state structures with triboluminescent activity in crystalline materials are not entirely successful due primarily to their failure to account for the presence of activity in centric materials.[1] It is generally asserted that crystal cleavage resulting in light emission represents the visible evidence for the discharge of nascent charged surfaces.[2] The ability of a crystalline material to readily form charged surfaces on cleavage is a property intuitively associated with acentric, polar structures by analogy to the properties of piezoelectric materials.[3] Although numerous examples of triboluminescent activity in centric structures have been discovered in the last decade,[4] it is generally found that in groups of chemically related triboluminescent materials containing both acentric and centric members, the centric members are much less active. In fact, Zink estimates that the correlation of triboluminescence activity with noncentrosymmetric space groups is greater than 95%.[5]

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