product was slowly consumed by reaction with the enolate ion nucleophile. A mixture of $PhPO(OEt)_2$ (0.023 M), biphenyl (0.011 M), and potassium pinacolone enolate (0.101 M) in 90 mL of ammonia was prepared and treated much as in our general procedure for competition experiments. Samples taken at various times showed the following percentages of the original $PhPO(OEt)_2$ to remain as such: 900 s, 99.7%; 1800 s, 79.6%; 3600 s, 65.0%; 8100 s, 26.1%. A byproduct of this experiment was a small amount of 2,2,7,7-tetramethyloctan-3,6-dione, recognized by its ^1H NMR spectrum matching that published by Komin and Wolfe,[26] as well as by its mass spectrum fragmentation pattern.

Aluminum-27 Nuclear Magnetic Resonance Study of the Room-Temperature Melt $AlCl_3$/*n*-Butylpyridinium Chloride

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Abstract: ^{27}Al NMR spectra were obtained on liquid samples consisting nominally of mixtures of $AlCl_3$ and *n*-butylpyridium chloride at various mole ratios and at various temps. Previous suggestions of the structure of the components of these melts have been supported, and the ^{27}Al NMR parameters of the $AlCl_4^-$ and $Al_2Cl_7^-$ ions in these melts have been determined. A chemical exchange rate has been estimated by spectral simulation. The species present in a solution obtained by adding $(CH_3)_4NI$ to a 1.4-to-1 melt ($AlCl_3$-to-BuPyCl) have been identified by ^{27}Al NMR.

Studies of molten salt systems involving mixtures of aluminum chloride and halide salts have been reported. For example, Boxall et al.[1] have investigated the important equilibria occurring in fused $NaCl/AlCl_3$ mixtures by electrochemical techniques. In the temperature range from 175 to 300 °C $NaCl/AlCl_3$ mixtures melt, and reaction 1 occurs essentially quantitatively. This system can be described by (1) and equilibria 2–5.[1] At 175 °C the following

$$\mathrm{Cl^- + AlCl_3 \overset{K_2}{\rightleftharpoons} AlCl_4^-} \tag{1}$$

$$\mathrm{Cl^- + Al_2Cl_3 \overset{K_1}{\rightleftharpoons} AlCl_4^- + AlCl_3} \tag{2}$$

$$\mathrm{2AlCl_3 \overset{K_3}{\rightleftharpoons} Al_2Cl_6} \tag{3}$$

$$\mathrm{AlCl_3 + AlCl_4^- \overset{K_4}{\rightleftharpoons} Al_2Cl_7^-} \tag{4}$$

$$\mathrm{2AlCl_4^- \overset{K_5}{\rightleftharpoons} Al_2Cl_7^- + Cl^-} \tag{5}$$

values of the equilibrium constants were determined by Osteryoung and co-workers: $K_3 = 2.86 \times 10^7$, $K_4 = 2.4 \times 10^4$, and $K_5 = 1.06 \times 10^{-7}$.

Osteryoung and co-workers have studied molten salt systems involving 1-*n*-butylpyridium chloride/$AlCl_3$ (BPC/$AlCl_3$) and 1-*n*-butylpyridium bromide/$AlCl_3$ by Raman spectroscopy,[2] by electrochemical methods,[3] and by ^1H and ^{13}C NMR.[4] For the BPC/$AlCl_3$ case Gale and Osteryoung[3] found that the equilibrium constant for (5) is less than 3.83×10^{-13} at 30 °C. Gale, Gilbert, and Osteryoung[2] concluded that $AlCl_4^-$ species have T_d symmetry and that $Al_2Cl_7^-$ species possibly have D_{3d} symmetry. However, X-ray diffraction studies of $Al_2Cl_7^-$ in a solid-state system indicate a nonlinear Al–Cl–Al bridge and the arrangement of Cl atoms about each Al atom approaching tetrahedral symmetry (the Al–Cl bond length in the bridge is only about 7% longer than the terminal Al–Cl bond length).[5]

To our knowledge no ^{27}Al NMR data have been reported on the "room-temperature" molten salt system BPC/$AlCl_3$. Anders and Plambeck[6] have reported ^{27}Al NMR data on the molten $NaCl/KCl/AlCl_3$ system at 170 °C. ^{27}Al NMR studies on the BPC/$AlCl_3$ system provide one the important opportunity of studying the anionic chemistry of $AlCl_4^-$ and $Al_2Cl_7^-$ in the molten state at lower temperature (near room temperature), where chemical exchange rates are expected to be lower than in the high-temperature melt.

Experimental Section

Materials. 1-*n*-Butylpyridium chloride was prepared by the method outlined by Gale, Gilber, and Osteryoung.[2] The purified crystals had a melting point of 131–133 °C (lit.[2] 131.5 °C). $AlCl_3$ (Fluka) was reagent grade purity and was used without further purification. Tetramethylammonium iodide (Eastman) was also reagent grade and was dried under high vacuum at ambient temperature.

All materials were stored under an anhydrous nitrogen gas atmosphere in a dry box. All molten salt preparations and manipulations were performed in the dry box. Melts were generated by adding a weighed amount of $AlCl_3$ to a weighed amount of 1-*n*-butylpyridium chloride. Immediately following the addition, the mixtures become hot and fumes appeared, which created an uncertainty in the final melt composition. To minimize this uncertainty, we tightly capped the mixtures as soon as possible after the $AlCl_3$ addition.

NMR Measurements. Most aluminum-27 spectra were recorded on a Bruker HFX-90 spectrometer described elsewhere.[7] The receiver coil was tuned to optimize the detection of aluminum-27 resonances at 23.44 MHz. No provision was made to reference the observed aluminum-27 resonance frequencies, except by sample substitution. Unless otherwise stated, the NMR measurements were made at 36 °C. The spectra in Figure 2 were recorded on a Nicolet NT-150 spectrometer.

Viscosity Measurements. Measurements were made by using a Kimax 300 Ostwald viscometer in a constant temperature bath of 41.0 ± 0.1 °C. The interior of the viscometer and its contents were maintained under anhydrous nitrogen gas atmosphere. Plumb lines were used to maintain a vertical alignment of the viscometer. A calibration standard was prepared by using glycerol (Baker) and distilled H_2O. This mixture had a specific gravity of 1.203 (78.0% w/w glycerol) at 20 °C and a viscosity of 17.1 cP at 41.0 ± 0.1 °C.

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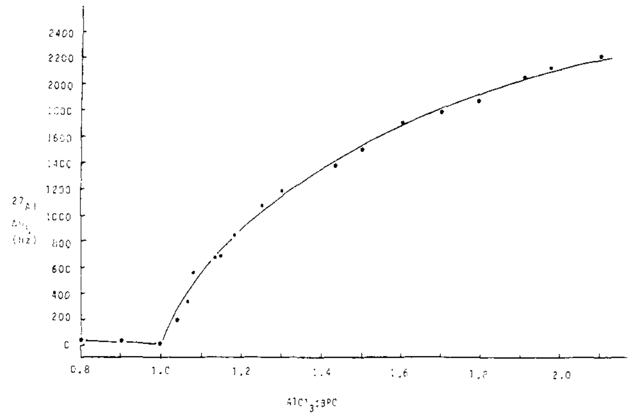

Figure 1. A plot of the ^{27}Al NMR line width, $\Delta\nu_{1/2}$, vs. the formal AlCl$_3$:BPC mole ratio. For all spectra the value of DE was 0.20 ms.

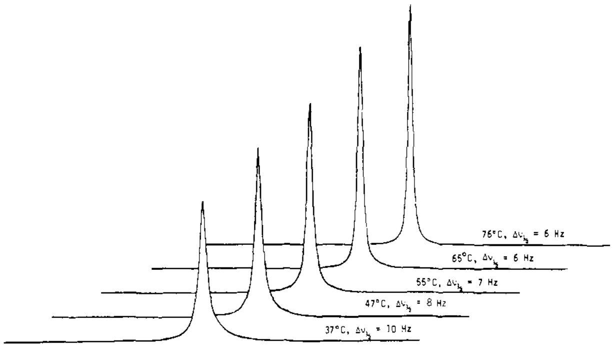

Figure 2. A series of ^{27}Al NMR spectra acquired at various temperatures, T, for a melt with a formal AlCl$_3$:BPC mole ratio of 1.0. The DE value was 0.10 ms, and the vertical and horizontal scaling parameters were the same for all spectra. For all spectra the bandwidth was ±5000 Hz; 32 transients were quadrature-phase detected with 16K data points and an acquistion time of 410 ms.

Results

NMR Data. Aluminum-27 NMR spectra were recorded for samples of the BPC/AlCl$_3$ molten salt system in which the formal AlCl$_3$:BPC mole ratio and the temperature were systematically varied. ^{1}H spectra were obtained whenever a magnet resolution check was necessary.

The dependence of the ^{27}Al line width, $\Delta\nu_{1/2}$, on the formal AlCl$_3$:BPC mole ratio is shown in Figure 1, obtained by using a preacquisition delay value (DE) of 0.20 ms (milliseconds). These line widths (and all other line widths reported in this paper) are considered accurate to within about ±5%. All spectra consisted of a single peak. Within experimental error the center position of the ^{27}Al resonance did not vary on changing the formal AlCl$_3$:BPC mole ratio. Qualitatively, the $\Delta\nu_{1/2}$ variation in Figure 1 and the apparently constant center of resonance frequency are similar to the ^{27}Al NMR results on the NaCl/KCl/AlCl$_3$ system reported by Anders and Plambeck.[6]

The ^{27}Al $\Delta\nu_{1/2}$ was found to depend upon the DE value (the time interval between the observe pulse and the onset of data acquistion), when the formal AlCl$_3$:BPC mole ratio exceeded 1.0. For a melt with a formal AlCl$_3$:BPC mole ratio of 1.4 at 36 °C the $\Delta\nu_{1/2}$ was 1380 Hz at DE value of 0.20 ms; increasing the DE value to 0.40 ms produced a $\Delta\nu_{1/2}$ of 1100 Hz, and when the DE value was 2.0 ms, the $\Delta\nu_{1/2}$ was 370 Hz. Increasing the DE to values larger than2.0 ms had no effect on the $\Delta\nu_{1/2}$ value.

The results of a variable-temperature study on a melt with a formal AlCl$_3$:BPC mole ratio of 1.0 are shown in Figure 2, for which the DE value was 0.10 ms. Repeating this series of experiments at a DE value of 2.0 ms had no noticeable effect other than a uniform decrease in the intensity of each peak; i.e., a larger number of transient accumulations were necessary to reproduce the signal-to-noise ratio observed in Figure 2. The results of a similar temperature variation study on a melt with a formal

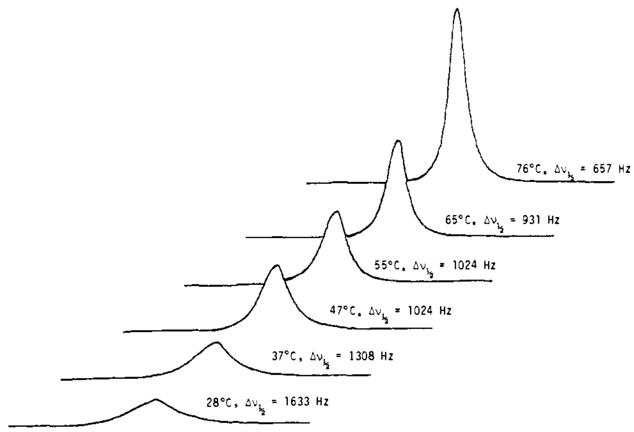

Figure 3. A series of ^{27}Al NMR spectra acquired at various temperatures, T, for a melt with a formal AlCl$_3$:BPC mole ratio of 1.4. The DE value was 0.30 ms, and the vertical and horizontal scaling factors for all spectra were the same. For all spectra the band width was 5151 Hz; 4000 transients were collected by using 1K data points and an acquistion time of 33 ms.

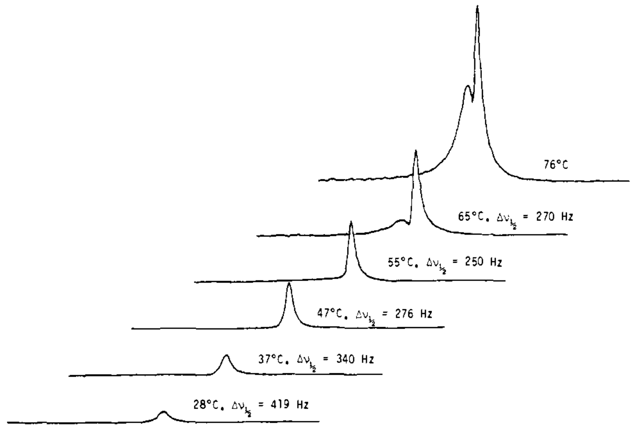

Figure 4. A series of ^{27}Al NMR spectra from the same melt as described in Figure 3. The vertical and horizontal scaling factors were the same for all spectra. All data acquistion parameters were the same as those used to collect the spectra in Figure 3, except the DE value was 2.0 ms; 20 000 transients were collected by using 1K of data points and a bandwidth of 15151 Hz. $\Delta\nu_{1/2}$ is the line width of the narrow peak in each spectrum.

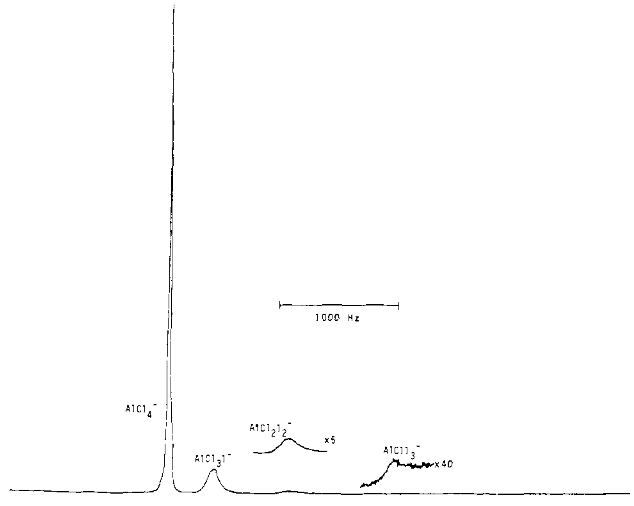

Figure 5. ^{27}Al NMR spectrum obtained from a melt with a formal AlCl$_3$:BPC mole ratio of 1.4 and saturated with (CH$_3$)$_4$NI. From left to right the resonances have chemical shifts of 0.0 ppm (line width of 16 Hz), −16.1 ppm (line width of 110 Hz), −44 ppm (linewidth of 190 ± 10 Hz), and −81 ppm (linewidth of 220 ± 10 Hz). Chemical shifts were calculated so that a positive value corresponds to lower shielding.

Table I. Summary of ^{27}Al Chemical Shift Data[a]

species	δ	δ_{KT}[b]
$AlCl_4^-$	0.0	0.0
$Al_2Cl_7^-$	13.1[c]	
$AlCl_3I^-$	−16.1 ± 0.2	−16.2 ± 0.3
$AlCl_2I_2^-$	−44 ± 1	−43.0 ± 0.3
$AlCl_3I^-$	−18 ± 2	−80.7 ± 0.4
AlI_4^-		−129.4 ± 0.2

[a] $\delta = (\nu_i - \nu_r)/(\nu_r \times 10^{-6})$, where ν_i is the frequency of the indicated species and ν_r is the reference frequency, with $AlCl_4^-$ taken as the reference. (Larger numbers correspond to lower shielding.) [b] Values reported by Kidd and Traux,[8] converted to our reference. [c] Computed by using frequency values obtained from a spectrum simulation at 76 °C (see text).

$AlCl_3$:BPC mole ratio of 1.4 at a DE value of 0.30 ms are shown in Figure 3. These experiments were repeated by using a 2.0-ms DE value, and the results are shown in Figure 4. Clearly two partially resolved peaks are seen in Figure 4 at 65 and 76 °C.

Figure 5 shows the ^{27}Al NMR spectrum of a melt with a formal $AlCl_3$:BPC mole ratio of 1.4, saturated with $(CH_3)_4NI$ (approximately 1 M in $(CH_3)_4NI$). From left to right in Figure 5 the peaks have $\Delta\nu_{1/2}$ values of 16, 110, 190, and 220 Hz. The assignments indicated in the figure are discussed below. The respective peaks have total integrated peak areas, relative to the $AlClI_3^-$ peak, of 178, 49, 8.9, and 1.0. A similar $(CH_3)_4NI$ saturation experiment was conducted by using a melt with a formal $AlCl_3$:BPC mole ratio of 1.0; only a single narrow resonance was observed in the spectra obtained just after preparation and 1 day later.

Table I summarizes the ^{27}Al chemical shift data obtained in this work, together with those reported by Kidd and Traux.[8] Our chemical shift assignments are described in the Discussion.

Viscosity Data. The results of viscosity measurements are summarized in Table II. The viscosity value at a formal $AlCl_3$:BPC mole ratio of 1.00 apparently agrees with a value of 20.9 cP reported by Robinson et al.[4] at 40 °C. The viscosity value for a formal $AlCl_3$:BPC mole ratio of 1.91 is within 10% of the viscosity value (13.7 cP) we calculated for a formal $AlCl_3$:BPC mole ratio of 2.0 by using the viscosity data reported by Carpio et al.[9]

Discussion

Gale and Osteryoung[3] concluded that at 30 °C equilibrium 4 has a large K value, whereas the equilibrium constant for (5) is very small for the BPC/$AlCl_3$ system. If equilibrium 1 consumes essentially all available Cl^- (requiring formal $AlCl_3$ contents greater than Cl^- contents), then for $AlCl_3$:BPC mole ratios greater than 1 equilibria 2–4 are the important equilibria needed to describe melt compositions. Thus, at a formal $AlCl_3$:BPC mole ratio of 1.5 there is approximately an equal number of the dominant aluminum species, $Al_2Cl_7^-$ and $AlCl_4^-$. We are assuming that the concentration of molecular $AlCl_3$ is small relative to $Al_2Cl_7^-$ and $AlCl_4^-$, because (1) significant concentrations of aluminum chloride are not indicated in the Raman spectra reported by Gale, Gilbert, and Osteryoung[2] and (2) Gale and Osteryoung[3] reported that condensation losses of Al_2Cl_6 are minimal from the BPC/$AlCl_3$ system at 175 °C.

The results shown in Figure 1 demonstrate the apparent $\Delta\nu_{1/2}$ dependence on the $AlCl_3$ content. In the region of formal $AlCl_3$:BPC mole ratios between 0.8 and 1.0 the only anionic species present in significant concentrations are assumed to be $AlCl_4^-$ and Cl^-, yet $\Delta\nu_{1/2}$ decreases from 40 Hz at an $AlCl_3$:BPC value of 0.8 to 10 Hz at an $AlCl_3$:BPC value of 1.0. The decreasing viscosity with increasing $AlCl_3$ content indicated in Table II can explain this $\Delta\nu_{1/2}$ behavior, since the quadrupolar relaxation rate depends upon the viscosity via the molecular reorientational correlation time.[10,11] At a formal $AlCl_3$:BPC mole ratio of 1.0 the $\Delta\nu_{1/2}$ value of 10 Hz indicates that the quadrupolar relaxation is slow compared with relaxation rates at all other formal $AlCl_3$:BPC mole ratios studied. This is consistent with the view that only the symmetric $AlCl_4^-$ species (T_d symmetry[2]) is present at a formal $AlCl_3$:BPC mole ratio of 1.0, as far as the available NMR sensitivity permitted us to determine. This conclusion agrees with the Raman data of Gale, Gilbert, and Osteryoung.[2] The sharp increase in $\Delta\nu_{1/2}$ as the $AlCl_3$:BPC value increases from 1 is due to the increased concentration of $Al_2Cl_7^-$ ions that are known to exist in these melts and are probably in chemical exchange with $AlCl_4^-$.

Table II. Variation in the Melt Viscosity with Chainging Formal $AlCl_3$:BPC Mole Ratios at 41.0 ± 0.1 °C

$AlCl_3$:BPC mole ratio	viscosity, cP	$AlCl_3$:BPC mole ratio	viscosity, cP
1.00	18.6 ± 0.2	1.62	13.9 ± 0.1
1.41	15.2 ± 0.1	1.91	12.4 ± 0.2

The large difference between the line widths of $AlCl_4^-$ and $Al_2Cl_7^-$ occurs because the ^{27}Al nuclei in the $Al_2Cl_7^-$ ion do not exist in an environment of cubic symmetry as in the $AlCl_4^-$ ion and because the $Al_2Cl_7^-$ ion has a larger volume than the $AlCl_4^-$ ion. In the D_{3d} structure for $Al_2Cl_7^-$ proposed by Gale, Gilbert, and Osteryoung (linear Al–Cl–Al)[3] the principle electric field gradient, *eq* in the notation of Abragam,[10] lies along the Al–Cl–Al bridge, and there is no symmetry restriction on the magnitude of *eq*. Thus, efficient quadrupolar relaxation is possible for the ^{27}Al nuclei in $Al_2Cl_7^-$. If the Al–Cl–Al bridge is bent, as suggested by solid-state X-ray diffraction studies,[5] then C_2 symmetry is likely for $Al_2Cl_7^-$ with no symmetry restriction on either *eq* or α, the asymmetry parameter,[10] and efficient quadrupolar relaxation is likely.

In either the bent or linear Al–Cl–Al bridge structure for $Al_2Cl_7^-$ each aluminum is bound to four chlorides. At the local atomic–electronic structure level this arrangement of chlorides in $Al_2Cl_7^-$ is somewhat similar to that found in $AlCl_4^-$. If the local atomic–electronic structure is largely responsible for the chemical shift values of $AlCl_4^-$ and $Al_2Cl_7^-$, then the Al–Cl–Al bridge structure, bent or linear, is consistent with the rather small chemical shift difference between $Al_2Cl_2^-$ and $AlCl_4^-$ implied by the apparent independence of the aluminum chemical shift with varying $AlCl_3$:BPC mole ratio, compared with a chemical shift range of about 200 ppm of aluminum in a variety of compounds.[12]

The decrease in the $\Delta\nu_{1/2}$ observed with increasing DE values suggests that the intensity of a broad line was being suppressed at large DE values, whereas the intensity of a second, smaller line width component was preferentially observed. (For example, focus on the spectra at 37 °C in Figures 3 and 4.) The ability to isolate the narrow peak by means of accumulation of the free induction decay (FID) at large DE values (time resolution) requires the lifetimes of $AlCl_4^-$ and $Al_2Cl_7^-$ in the chemical exchange process to be at least as long as the NMR time scale, which for this case is defined as the tranverse relaxation time for the smaller line width species and by the chemical shift difference between the peaks in the absence of chemical exchange. The 340-Hz $\Delta\nu_{1/2}$ value obtained for the narrow-line species whose NMR signal survives a 2.0-ms DE value (see Figure 4 at 37 °C) we assign to $AlCl_4^-$; this is considerably larger than the 10-Hz value observed for a formal $AlCl_2$:BPC mole ratio of 1.0. Incomplete isolation of the narrow line could result in a larger $\Delta\nu_{1/2}$ value for $AlCl_4^-$. However, using DE values greater than 2.0 ms produced no further reduction in $\Delta\nu_{1/2}$ which indicates that isolation is indeed complete at a 2.0-ms DE value. Two factors that might account for the $\Delta\nu_{1/2}$ enhancement of the $AlCl_4^-$ peak at a formal $AlCl_3$:BPC mole ratio of 1.4 are (1) increased quadrupole relaxation rate and/or (2) chemical exchange.

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(9) Carpio, R. A.; King, L. A.; Lindstrom, R. E.; Nardi, J. C.; Hussey, C. L. *J. Electrochem. Soc.* **1979**, *126*, 1644–1650.

(10) Abragam, R. "The Principles of Nuclear Magnetism"; Oxford University Press: London, 1961; p 314.

(11) To a first approximation the Stokes–Einstein equation can apply to the correlation time dependence on viscosity, molecular volume, and temperature, as given by $\tau_c = \eta V/kT$, where η is the viscosity, V the volume, and k Boltzmann's constant.

(12) Akitt, J. W. *Annu. Rep. NMR Spectrosc.* **1968**, *5A*, 465.

Enhanced quadrupolar relaxation can arise from larger electric field gradients at the aluminum-27 nucleus in $AlCl_4^-$ or by an increased correlation time for $AlCl_4^-$. The Raman results of Gale, Gilbert, and Osteryoung[2] do not indicate any major structural changes in the $AlCl_4^-$ anion as the $AlCl_3$ content of the melt increased. Thus, major structural changes necessary to create larger electric field gradients probably do not occur. If there are no structural changes occurring in the $AlCl_4^-$ ion, then an increase in the correlation time could arise only in conjunction with an increase in the bulk viscosity of the melt. However, the viscosity of the melts decrease as the $AlCl_3$ content increases, as shown in Table II. Therefore, by elimination, chemical exchange is the probable source for the broadening of the $AlCl_4^-$ resonance at a formal $AlCl_3$:BPC mole ratio of 1.4 (relative to the line width at a formal $AlCl_3$:BUPyCl mole ratio of one, where chemical exchange is for all practical purposes not important).

The spectra in Figure 2 for a melt with a formal $AlCl_3$:BPC mole ratio of one represents an experimental control. Only the single $AlCl_4^-$ resonance is observed in Figure 2, and, with the exception of a few hertz decrease in the line widths with increasing temperature, the spectra are virtually the same. The spectra were unaffected by increasing DE at the various temperatures, except for the expected reduction in the signal-to-noise ratio.

The spectra shown in Figures 3 and 4 demonstrate the affect of time resolution where, at the lower temperature (28–55 °C), only resonance is apparent in both figures. The non-Lorentzian shapes in Figure 3 suggest two overlapping resonances. In Figure 4 the isolated single resonances of $AlCl_4^-$ are observed at temperatures of 55 °C and below. At 65 and 76 °C two resolved peaks are apparent in Figure 4, with the broader resonance assigned to $Al_2Cl_7^-$ and the smaller line width peak to $AlCl_4^-$, corresponding to the chemical shift assignments given in Table I. The direct detection of the broad line at 65 °C in Figure 4 probably occurs because of a decrease in the correlation time, resulting from the increased temperature, which reduces the line width.[11] At these elevated temperatures DE is apparently no longer large compared with the transverse relaxation time of the $Al_2Cl_7^-$ species, and consequently magnetization of the broad-line component remains in the transverse plane for a DE value as large as 2.0 ms.

In viewing Figure 4, one should keep in mind that the conditions of the experiments represented discriminate dramatically against the broad-line component, giving a greatly enhanced appearance of the importance of the narrow-line component in the resulting spectrum. For a system with individual components with 10- and 650-Hz line widths, a predetection hiatus of 2.0 ms will eliminate more than 98% of the signal intensity of the broad-line component and only about 6% of the intensity of the narrow-line component. By comparison, a 0.30-ms predetection hiatus eliminates only 46% of the broad-line component's intensity and about 1% of the narrow-line component's intensity.

Evidence that some exchange coalescence is occurring at 65 and 76 °C is seen in Figure 4. At 65 °C the separation between the peaks is 417 Hz (17.8 ppm), whereas at 76 °C the separation is 300 Hz (12.8 ppm). The decrease in peak separation with increasing temperature can be accounted for by chemical exchange and the approach toward coalescence.

In Figure 3 the spectra at 28, 37, 47, an 55 °C all have distinct deviations from purely Lorentzian line shape. This observation is consistent with the existence of $AlCl_4^-$ and $Al_2Cl_2^-$ peaks that overlap. At the higher temperatures, 65 and 76 °C, spectra are still broad but apparently have nearly Lorentzian line shapes. This observation suggests that the predominant aluminum ions are $Al_2Cl_7^-$ in the melt at 65 and 76 °C. Thus, one might suspect that a significant shift in the equilibrium populations of $AlCl_4^-$ and $Al_2Cl_7^-$ occurs with changing temperature; i.e., the $Al_2C_7^-$ ions are favored at high temperature. A similar equilibrium shift was observed in the NaCl/$AlCl_3$ system studied by Boxall et al.[1]

In order to estimate the composition and $AlCl_4^-/Al_2Cl_7^-$ exchange rates in a melt and to test the qualitative ideas presented above to account for the line shapes observed in Figure 3 and 4, we carried out a spectrum simulation for the spectra obtained at 76 °C in terms of chemical exchange between two sites, as in reaction 5. A computer program (NTCXCH from Nicolet) was used that handles two-site exchange between components that may be present in different concentrations. The program computes a line shape from the following input parameters: values of the fractions of each component present, an "exchange lifetime" τ (with $\tau^{-1} = \tau_f^{-1} + \tau_r^{-1}$, where τ_f^{-1} and τ_r^{-1} are rate constants for the forward and reverse exchange processes), the chemical shifts of the individual components, and the line widths of the individual components in the absence of exchange. A computed spectrum was then Fourier transformed into the time domain to obtain a free induction decay (FID), which was then pretruncated by either 0.30 or 2.0 ms to correspond to the DE value used in the experiment. The resulting pretruncated FID was then Fourier transformed back into the frequency domain to provide simulated spectra for direct comparison with the corresponding experimental results.

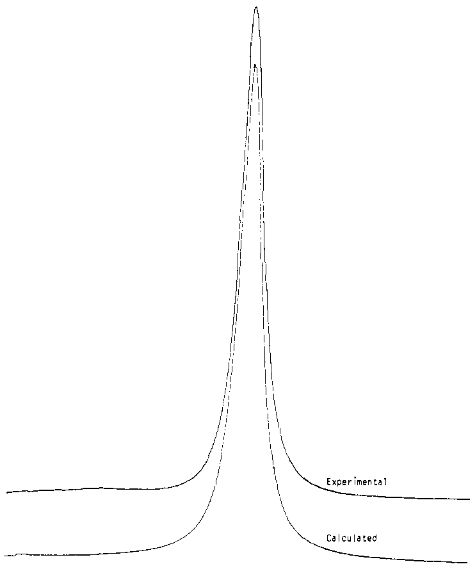

Figure 6. The upper curve represents the experimental ^{27}Al NMR spectrum of a melt with a formal $AlCl_3$:BPC mole ratio of 1.4 at 76 °C and at a DE value of 0.30 ms. The lower curve is a two-site chemical exchange simulation of the experimental spectrum.

Many combinations of parameters were tried in the simulations, and only a limited range of combinations was found to provide reasonable agreement. With use of a fraction of 0.0013 for the narrow-line component (0.9987 for the broad-line component), a τ value of 0.001 65 s, an internal chemical shift difference of 305 Hz (13.1 ppm, see Table I), and line widths of 10 and 650 Hz, excellent simulations were obtained. The simulated spectra are compared directly with the experimental spectra in Figures 6 and 7. While there may be other combinations of the simulation parameters that provide equally good or even better simulations, we have not found any. Hence, we believe the parameters represented in the simulations shown in Figures 6 and 7 constitute strong qualitative support for the ideas presented above and strongly indicate a major shift in the equilibrium composition of the melt from $AlCl_4^-$ to $Al_2Cl_7^-$ as the temperature is increased.

The effect of saturating a melt having a formal $AlCl_3$:BPC mole ratio of 1.4 with $(CH_3)_4NI$ is given in Figure 5, showing the appearance of three aluminum-containing species other than $AlCl_4^-$ or $Al_2Cl_7^-$. The peak assignments in Figure 5 are based on a chemical shift correlation to the ^{27}Al NMR results of Kidd and Traux (see Table I) on the $Al_2I_6/CH_2Cl_2/(n\text{-}C_3H_7)_4NI$ system.[8] Kidd and Traux based their original peak assignments on known chemical shift values for $AlCl_4^-$ and AlI_4^- and on electric field gradient arguments for the line widths of the mixed chloroiodoaluminate ions. We did not observe any indication of a AlI_4^- in the spectrum in Figure 5.

A melt with a formal $AlCl_3$:BPC mole ratio of 1.0, saturated with $(CH_3)_4NI$, produced no indication of iodide substitution for chloride in spectra recorded just after preparation and 1 day later. This indicates that direct I^- substitution for Cl^- is not rapid with

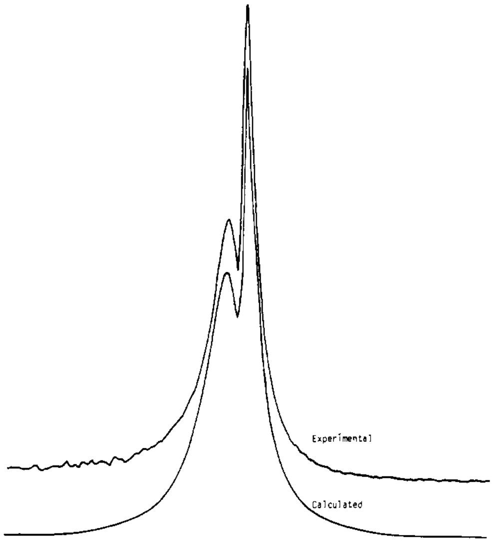

Figure 7. The upper curve represents the experimental ^{27}Al NMR spectrum of a melt with a formal $AlCl_3$:BPC mole ratio of 1.4 at 76 °C and at a DE value of 2.0 ms. The lower curve is a simulation of the experimental spectrum.

$AlCl_4^-$. In Figure 5 the line width of the $AlCl_4^-$ peak is 16 Hz, which indicates very little $Al_2Cl_7^-$ present. The small concentration of $Al_2Cl_7^-$ and the observation of the mixed tetrahaloaluminate ions leads to the postulation of the equilibria.

$$AlCl_4^- + I^- \overset{K_a}{\rightleftharpoons} AlCl_3I^- + Cl^-$$

$$AlCl_3I^- + I^- \overset{K_b}{\rightleftharpoons} AlCl_2I_2^- + Cl^-$$

$$AlCl_2I_2^- + I^- \overset{K_c}{\rightleftharpoons} AlClI_3^- + Cl^-$$

$$AlClI_3 + I^- \overset{K_d}{\rightleftharpoons} AlI_4^- + Cl^-$$

The last equilibrium is included for completeness, although there is no indication of an AlI_4^- peak in the spectrum in Figure 5. Perhaps if higher ^{27}Al NMR sensitivity had been available, such a peak would have been detected. Using observed values for the total-integrated peak area and noting that this quantity is proportional to concentration, one can show that the magnitude of the equilibrium constants have the order $K_a > K_b > K_c$ K_d.

The shielding of the aluminum-27 nucleus depends in these mixed chloriodo complexes, as one would expect, upon the number of coordinated iodide ligands. However, as one sees from Table I, the chemical shift variation is not linear with changing iodide coordination numbers. That is, the ^{27}Al chemical shift does not have a simple, additive contribution arising from iodide substitution for chloride.

The effects of halide substitution for H_2O on the chemical shift of Cd(II) and Zn(II) have been studied by ^{113}Cd and ^{67}Zn NMR by Maciel and co-workers.[13] For the halide complexes of these two transition-metal ions, the effect of halide substitution on the metal ion shielding does not always follow a simple additive pattern. Maciel et al.[13] argue that an important factor governing the shielding of the transition-metal ions is the symmetry and detailed electronic distribution of the complexes, which may account for the nonadditive nature of the shielding variation with halide substitution of solvent. In view of those arguments, it is not surprising that the aluminum-27 chemical shift variation with the iodide coordination number is not linear.

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