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Determination of Nuclear Quadrupole Coupling Constants in 1:2 LiCl−Ethylaluminum Dichloride Solutions

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Introduction

The ^{27}Al NMR of neat $EtAlCl_2$ consists of a broad peak at 129 ppm relative to external standard $Al(H_2O)_6{}^{3+}$.[1,2] This peak is assigned to the dimer of $EtAlCl_2$, consistent with this species' ability to form C_{2H} dimers and the fact that other dimers of alkylaluminum compounds have similar chemical shifts.[1−7] In room-temperature melts containing 1-ethyl-3-methylimidazolium chloride (ImCl) and $EtAlCl_2$, a sharp (long T_2) peak is observed at 102 ppm in addition to the broad $(EtAlCl_2)_2$ peak centered at 129 ppm.[1,3] The sharp peak at 102 ppm is that of $EtAlCl_3{}^-$, as evidenced by its similarity to the ^{27}Al peak for $AlCl_4{}^-$ at 103 ppm,[3] in terms of both relaxation time and chemical shift (coordination number).[6]

NaCl is virtually insoluble in $EtAlCl_2$ whereas LiCl is soluble up to a mole ratio of 1:2 (LiCl−$EtAlCl_2$). The initial addition of LiCl to $EtAlCl_2$ is accompanied by a decrease (and eventual disappearance) of the broad 129 ppm peak and the appearance of a single sharp peak at 100.5 ppm.[2] This report contains ^{27}Al relaxation data obtained from the 100.5 ppm peak over the temperature range −12.5 to +65 °C. The quadrupolar relaxation rates ($R^Q = 1/T^Q$) of this peak (100.5 ppm) are used to determine correlation times. These correlation times are used to calculate a quadrupole coupling constant (QCC) for ^{27}Al in the ethylaluminum dichloride part of the complex. Finally, semiempirical calculations (MOPAC-PM3) using recently developed lithium parameters provide a structure for a 1:2 LiCl−$EtAlCl_2$ complex.

Experimental Section

^{27}Al NMR spectra were recorded at 78.15 MHz and temperatures calibrated against methanol or ethylene glycol. Pulse widths are typically 6−8 μs, and $T_1{}^Q$'s were measured by the inversion recovery method (180°−τ−90°−T) with $T > 10T_1$. At least 12 delay times (τ) were used, and relaxation times (in duplicate or triplicate) were obtained from a three-parameter exponential fit of magnetization as a function of τ. There was no evidence of any nonexponential behavior. Transverse (spin−spin) relaxation times, T_2, were determined from half-height peak widths ($=1/\pi{}^*T_2$, where $^*T_2 \approx T_2$). The relatively narrow ^{27}Al line widths made T_2 measurements less subject to signal acquisition problems as outlined elsewhere.[8] All chemical shift measurements are relative to $Al(H_2O)_6{}^{3+}$.

Calculation of Correlation Times

A very sensitive indication of molecular and/or ionic symmetry is the value of the nuclear quadrupole coupling constant (QCC), which approaches zero as cubic symmetry about the quadrupole nucleus is realized. Knowledge of nuclear quadrupole coupling constants in the liquid state can therefore provide much useful information concerning a particular nucleus and its surrounding ligands.[9] At present, the only simple approach for liquids involves using the dual spin probe (NMR relaxation) method,[10−12] in which a quadrupolar relaxing nucleus is adjacent to a dipolar relaxing nucleus such as ^{13}C. Assuming identical correlation times, isotropic motion, and the condition of extreme narrowing ($\omega^2\tau_c^2 \ll 1$, where $\omega = 2\pi\nu$ and τ_c = the effective correlation time), one can then relate the quadrupolar relaxation rate, $R_1{}^Q$ ($=1/T^Q$), to the dipolar relaxation rate, $R_1{}^{dipolar}$. This method has been used to obtain values for ^{23}Na and ^{27}Al quadrupole coupling constants in several cases including room-temperature melts.[10,11] While this approach is possible for nonviscous solutions, it appears questionable for particular room-temperature melts (acidic chloroaluminate melts) or other solutions of high viscosity where the condition of extreme narrowing ($\omega^2\tau_c^2 \ll 1$) is unlikely to be met. If this is the situation, then another method must be devised to determine the correlation time, τ_c, for highly viscous solutions. One alternative involves the use of subambient measurements such as those reported recently for melt systems based on ethylaluminum dichloride.[3] However, there is another possible solution to this problem as follows. To determine an accurate value for τ_c, one may combine the following classic equations[13] for $R_1{}^Q$ and $R_2{}^Q$ in order to solve for the correlation time, τ_c:

$$R_1{}^Q = [(3\pi^2/100)(1 + \eta^2/3)][(2I + 3)/I^2(2I - 1)](QCC)^2[(2\tau_c/(1 + \omega^2\tau_c{}^2)) + (8\tau_c/(1 + 4\omega^2\tau_c{}^2))] \quad (1)$$

$$R_2{}^Q = [(3\pi^2/200)(1 + \eta^2/3)][(2I + 3)/I^2(2I - 1)](QCC)^2[6\tau_c + (10\tau_c/(1 + \omega^2\tau_c{}^2)) + (4\tau_c/(1 + 4\omega^2\tau_c{}^2))] \quad (2)$$

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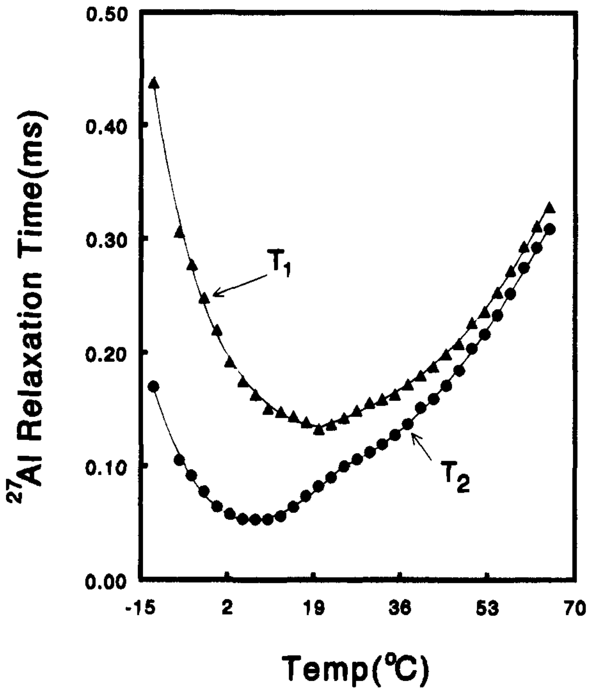

Figure 1. ^{27}Al spin–lattice (T_1) and spin–spin (T_2) relaxation times (ms) for LiCl·(EtAlCl$_2$ from −12.5 to +65 °C.

where η is an asymmetry parameter that accounts for deviation from axial symmetry ($\eta = 0$ for AlCl$_3$).[14]

In the case where one is outside the region of extreme narrowing, $R_2^Q > R_1^Q$, eqs 1 and 2 can be combined[15] to form

$$R_1^Q/2R_2^Q = [(1/(1 + \omega^2\tau_c^2)) + (4/(1 + 4\omega^2\tau_c^2))]/[3 + (5/(1 + \omega^2\tau_c 2)) + (2/(1 + 4\omega^2\tau_c^2))] \quad (3)$$

Solving eq 3 for $\omega\tau_c$, one obtains

$$\omega^4\tau_c^4 + [3.0833 - 0.6667(2R_2^Q/R_1^Q)]\omega^2\tau_c^2 - 0.4167(2R_2^Q/R_1^Q) + 0.8333 = 0 \quad (4)$$

The solutions of the above quartic include a single value for the effective correlation time when $R_2 > R_1$, whereas only complex roots are obtained when $R_2 < R_1$. A similar equation can be derived for other cases (^{13}C dipolar relaxation) if accurate correlation times are of significance to the investigator.

Results and Discussion

We have obtained ^{27}Al relaxation data on the room-temperature melt LiCl–ethylaluminum dichloride (1:2 mole ratio, fp ≈ 178 K).[2] In this melt, the broad (short T^Q) ^{27}Al peak at 129 ppm (EtAlCl$_2$ dimer) has been completely replaced by a single narrow (long T^Q) peak at 100.5 ppm[2], similar to those narrow peaks observed for AlCl$_4^-$ (103 ppm) and EtAlCl$_3^-$ (102 ppm).[9] The quadrupolar relaxation times ($T^Q = 1/R^Q$)[13] of this peak (100.5 ppm) between +65 and −12.5 °C are given in Figure 1 The T_1 and T_2 values approach each other at a temperature well above 65 °C. All of the data in Figure 1 are outside the extreme narrowing condition ($\omega\tau_c > 1$) and can be used to solve eq 4. Plots of ln R vs reciprocal temperature are linear at higher temperatures and give E_a values of 5.4 (42.5–65 °C) and 6.2 (35–65 °C) kcal for R_1 and R_2, respectively (correlation coefficients 0.998 and 0.999).

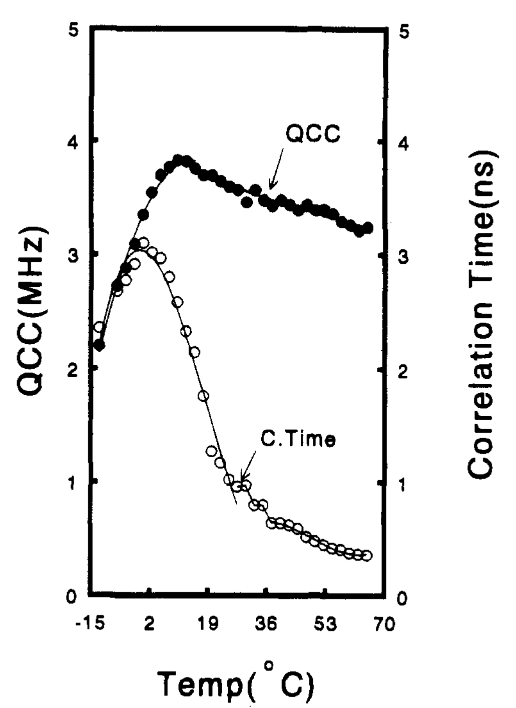

Figure 2. Nuclear quadrupole coupling constants, QCC's, (MHz), and effective correlation times, τ_c's (ns), for 1:2 LiCl–EtAlCl$_2$ from eq 4 vs temperature (°C).

The unequal T_1 and T_2 values (unlike those of EtAlCl$_2$, whose ^{27}Al T_1's and T_2's are identical at 78.15 MHz over the same temperature range) are used (eq 4) to determine correlation times from −12.5 to +65 °C as shown in Figure 2. The correlation times are (theoretically) the times required for the nuclei in question to rotate through a distance of one radian. Thus the faster the rotation, the shorter the correlation time. The existence of a correlation time maximum well above the freezing point of this melt suggests that the melt is going through a particular type of liquid structural change (phase transition etc.). Additional support for this concept follows from the calculated values of the ^{27}Al nuclear quadrupole coupling constants (QCC's).

As a numerical check, the existence of a T_1 minimum at 20 °C (Figure 1) allows the exact solution of eq 1 at the T_1 minimum where $\omega\tau_c = 0.6157$. In this case, one obtains a value of 3.70 MHz for (QCC)$(1 + \eta^2/3)^{1/2}$ or QCC when $\eta = 0$. Assuming that $\eta = 0$ introduces an error of 4% when $\eta = 0.5$ and an error of 15% when η is at its maximum of 1 ($\eta = 0$ for solid AlCl$_3$[14]). The resulting QCC of 3.71 MHz agrees with the value of 3.70 MHz calculated from eq 4. The R_1 maximum (T_1 minimum) at 20 °C is considerably above this solution's freezing point (≈178 K) and is similar to glasslike transition regions observed for other melts.[3]

The ^{27}Al correlation times for the ethylaluminum dichloride in Figure 2 are used to calculate QCC values using eq 1 (assuming that $\eta = 0$, similar to that of solid AlCl$_3$[14]). These QCC values are also shown in Figure 2 and indicate a gradual increase from 3.20 to 3.83 MHz between 65 and 10 °C. From +10 to −12.5 °C, there is a steady decrease in the QCC values. These two observations are consistent with a complex structure that (1) changes only slightly at the higher temperatures (one would expect a small increase in ^{27}Al QCC as the temperature rises due to increased mobility of the ethyl groups at the higher temperatures) and (2) approaches a structure of increased symmetry (C_{2v}, in this case) as the temperature is lowered. There is no particular physical or mathematical requirement that correlation times and QCC values have a maximum at the exact

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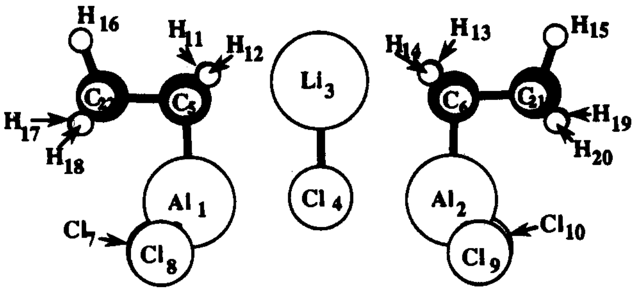

Figure 3. PM3-optimized structure for the LiCl·2EtAlCl$_2$ complex.

same temperature. This may be explained in terms of several dynamic processes being involved in the structural changes of EtAlCl$_2$ as it approaches a glassy or crystalline state.

It is useful to compare the ^{27}Al QCC results, which have a maximum of 3.83 MHz and a minimum (at −12.5 °C) of 2.20 MHz, with those for other similar aluminum-containing compounds. Other ^{27}Al QCC values include 0.471 MHz for solid AlCl$_3$,[14] 0.909 MHz for EtAlCl$_3^-$,[3,16] 0.821 MHz for AlCl$_4^-$,[3] and 9.39 MHz for the EtAlCl$_2$ dimer.[3,16]

Semiempirical (MOPAC−PM3) calculations[17] with recently obtained parameters for lithium[18] were used to calculate a structure for a 1:2 LiCl−EtAlCl$_2$ complex. This complex contains LiCl in its center with two ethylaluminum dichloride molecules located on opposite sides as shown in Figure 3. The heat of formation of this adduct (complex) is −307.2390 kcal. Table 1 contains bond distances and bond angles for the complex. In the PM3[17] version of this complex, each aluminum may be considered as being in the center of a distorted tetrahedron. The change in structure about each aluminum from planar (C_{2H})[4] to distorted tetrahedral (PM3) as the EtAlCl$_2$ dimer is converted to a lithium adduct (Figure 3) would result in a lowering of the ^{27}Al QCC value as we observe in this report (Figure 2).

Table 1. Optimized Geometry for the 1:2 LiCl−EtAlCl$_2$ Complex

atoms[a]	interatomic dist (Å)	atoms[a]	bond angle (deg)
Li(3)−Cl(4)	2.1915	Cl(4)−Al(1)−Cl(8)	105.6
Li(3)−H(11)	2.2762	Cl(7)−Al(1)−Cl(8)	118.2
Li(3)−H(12)	2.2663	Cl(4)−Al(1)−Cl(7)	105.6
Li(3)−H(13)	2.2735	Cl(4)−Al(2)−Cl(10)	105.4
Li(3)−H(14)	2.2714	Cl(4)−Al(2)−Cl(9)	105.6
Li(3)−C(5)	2.5376	Cl(9)−Al(2)−Cl(10)	118.2
Li(3)−C(6)	2.5370	C(5)−Al(1)−Cl(4)	90.8
Al(1)−Cl(7)	2.0855	C(5)−Al(1)−Cl(7)	115.8
Al(1)−Cl(8)	2.0856	C(5)−Al(1)−Cl(8)	115.8
Al(1)−Cl(4)	2.4384	Al(1)−C(5)−C(22)	95.3
Al(2)−Cl(4)	2.4380	Al(2)−C(6)−C(21)	95.3
Al(2)−Cl(9)	2.0841	C(6)−Al(2)−Cl(4)	91.0
Al(2)−Cl(10)	2.0890	C(6)−Al(2)−Cl(9)	115.8
Al(2)−C(6)	1.9314	C(6)−Al(2)−Cl(10)	115.6
Al(1)−C(5)	1.9316	H(11)−C(5)−H(12)	109.6
C(5)−C(22)	1.4994	H(13)−C(6)−H(14)	109.6
C(6)−C(21)	1.4995		

[a] Atoms numbered as in Figure 3.

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