CHEMISTRY LETTERS, pp. 1651-1654, 1992.

The Effect of Cation on Kinetic Properties of Chloroaluminate Anions. ^{27}Al NMR in Dialkylimidazolium Chloride-$AlCl_3$ and LiCl-$AlCl_3$ Melts

Kazuhiko ICHIKAWA,* Mitsunori IZUMI, Takashi JIN,† and Toshiyuki MATSUMOTO
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060
†Section of Physiology, Research Institute of Applied Electricity, Hokkaido University, Sapporo 060

We have carried out the ^{27}Al NMR measurements of spectra and logitudinal magnetization recovery curves for 1-methyl-3-butylimidzolium chloride (DIMCl)-$AlCl_3$ at 65±1 mol% $AlCl_3$ and LiCl-$AlCl_3$ melt at 63±1 mol% $AlCl_3$. The lifetime of $Al_2Cl_7^-$, τ_A, increases with increasing the size of cations from Li^+, Py^+ (butylpyridinium cation) to DIM^+.

Room temperature chloroaluminate melts have been employed extensively for fundamental use of electrochemical, spectroscopic, and photo-chemical studies. They have been also formulated for practical use as aluminum electroplating baths. Their function is developed by the adjustable Lewis acid-base properties, which can be represented by the following equilibrium:

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

where $Al_2Cl_7^-$ is a Lewis acid and Cl^- is a Lewis base. This equilibrium is an autosolvolysis reaction which is analogous to water autoprotolysis: $Al_2Cl_7^-$ plays the role of H^+ in aqueous solution.[1,2] It is therefore significant to elucidate the effect of the size of cation on the kinetic properties of $Al_2Cl_7^-$, or its own lifetime τ_A.

This paper reports the effects of the size of cations on the fractional populations $X_{A,B}$ between $Al_2Cl_7^-$(A) and $AlCl_4^-$(B), and their chemical exchange lifetimes $\tau_{A,B}$ for the 1-methyl-3-butylimidazolium chloride (DIMCl)-$AlCl_3$ and LiCl-$AlCl_3$ melts. The spin-lattice relaxation rates $R^*_{1,A,B}$ have been also obtained on the basis of both experimental and theoretical studies on the ^{27}Al longitudinal magnetization recovery (lmr) curves.[3]

The DIMCl and LiCl, and their binary mixtures with $AlCl_3$ were prepared by the method described in the literature.[4] The manipulation of all materials was performed in an argon-filled glove box.

We carried out the ^{27}Al NMR measurements of molten DIMCl-$AlCl_3$ at 65±1 mol% between 20 and 100 °C and LiCl+$AlCl_3$ at 63±1 mol% at 160 °C. The ^{27}Al resonance frequencies and the time intervals t_d between the last 90° pulse and the onsets of data acquisition were ca. 52.1 MHz and 400 μs on a Varian XL-200, and ca. 26.1 MHz and 366 μs on a Bluker SXP4-100, respectively. The observed lmr curves have been obtained from the initial intensity, $M_Z(\tau)$, of the free-induction decays,by using the inversion recovery (or π-τ-π/2) method, until $M_Z(\tau)/M_Z°$ reaches ca. 0.7-0.9.

The ^{27}Al NMR spectra of molten DIMCl-$AlCl_3$ at 65±1 mol% $AlCl_3$ between 20°C and 100°C. and of molten LiCl-$AlCl_3$ at 63±1 mol% $AlCl_3$ and 160°C are shown in Figs. 1 and 2. The ^{27}Al resonance lineshape depends upon t_d for the DIMCl-$AlCl_3$ melt.[5-7] Since the large signal attributed to ^{27}Al in $Al_2Cl_7^-$(A) masked a much smaller contribution from $AlCl_4^-$(B), each of the spectra showed a single peak for t_d=30μs. For t_d=400 μs partially resolved peaks were observed [see Fig. 1], where the partially resolved lineshapes located at high and low fields can be assigned to B and A, respectively. Increasing the temperature gives rise to an increase in the intensity of the resonance line located at low-field (i.e., the concentration of $Al_2Cl_7^-$) [see Fig. 1]. The experimental points of the lmr curves are shown in Figs. 3 and 4. At the lower temperatures the non-linear logarithmic lmr curves were observed for molten DIMCl-$AlCl_3$.

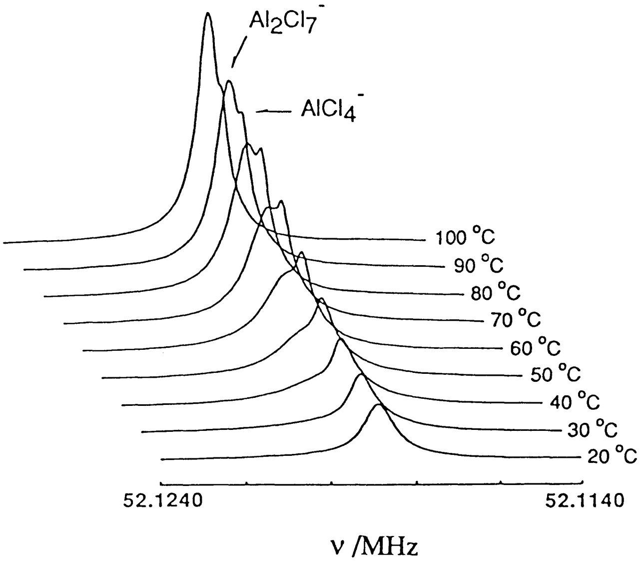

Fig. 1. ^{27}Al spectra for molten DIMCl-$AlCl_3$ at 65±1 mol% $AlCl_3$.

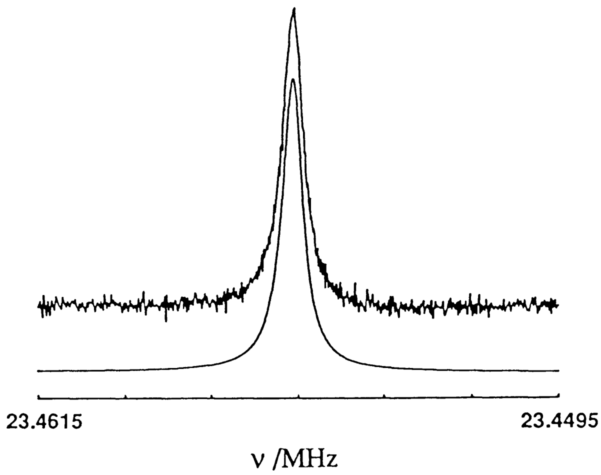

Fig. 2. ^{27}Al spectrum for molten LiCl-$AlCl_3$ at 63±1 mol% $AlCl_3$.

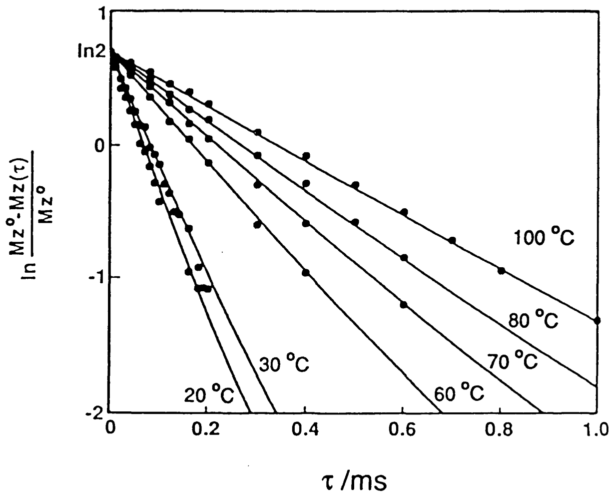

Fig. 3. ^{27}Al lmr curves for molten DIMCl-$AlCl_3$ at 65±1 mol% $AlCl_3$.

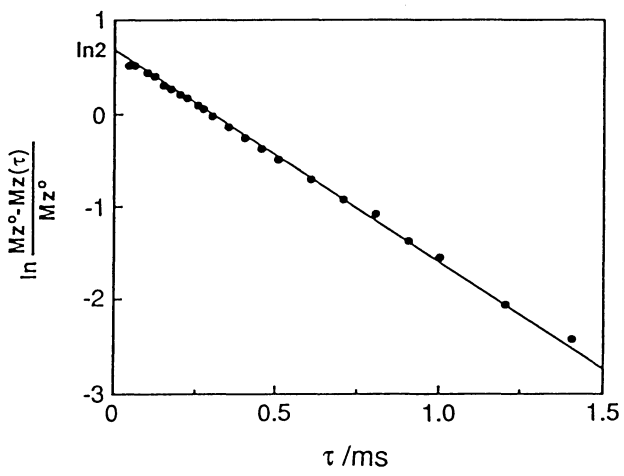

Fig. 4. ^{27}Al lmr curves for molten LiCl-$AlCl_3$ at 63±1 mol% $AlCl_3$.

Under the conditions of chemical exchange between the two sites $Al_2Cl_7^-$(A) and $AlCl_4^-$(B) the time evolution of the total longitudinal magnetization $M_Z(\tau)(=M_{Z,A}(\tau)+M_{Z,B}(\tau))$ is given by

$$M_Z(\tau)=C_1 \exp(-R_{1,A}\tau) + C_2 \exp(-R_{1,B}\tau), \qquad (2)$$

where C_1 and C_2 are defined in Eqs. 13-17, and $R_{1,A,B}$ is given by $R^*_{1,\alpha}$ and τ_α in Eqs. 8-10 of Ref. 8. Here, we assume for simplification that no contributions from Al_2Cl_6 or higher polymers (e.g., $Al_3Cl_{10}^-$) appear in the NMR data of the chloroaluminate melts.[5-7] $R_{1,A,B}$ should be obtained from the simulation of the non-single-exponential decay of the observed lmr curves,[3] where $R_{1,A,B}$ is equal to $R^*_{1,A,B}$ for the very slow exchange or $R^*_{1,\alpha}\tau_\alpha \gg 1$. The reasonable simulation of the observed lmr curves and spectra for the DIMCl+$AlCl_3$ melt was carried out on the base of the Bloch equations modified by chemical-exchange effects[8,9] and under the condition that $R^*_{2,\alpha}$ (i.e., the spin-spin relaxation rates) = $R^*_{1,\alpha}$ for most liquids. Here, the fractions of nuclei $f_{A,B}$ for A and B should be replaced by $f_{A,B}$ in Eq.12 of Ref. 9 because of $R^*_{2,\alpha}\ t_d \approx 1$ for the case of $R^*_{2,\alpha} \approx 5\text{x}10^3 s^{-1}$ and $t_d \approx 5\text{x}10^2$ μs. The LiCl+$AlCl_3$ melt shows the rapid chemical exchange (i.e., $R^*_{1,A}\tau_A<0.5$) because of the pure Lorenzian lineshape and the single-exponential decay of the lmr curve [see Figs. 3 and 4]. For the rapid exchange limit the slope of the linear lmr plots should be equal to $\langle R_1\rangle$ $(=f_A^{app}\ R^*_{1,A} + f_B^{app}\ R^*_{1,B})$[8,10] because of $R^*_{1,A}\ t_d(=366\mu s) \approx 1$ and $f_A^{app} \neq f_A$. Since $R^*_{1,A}$ and $R^*_{1,B}$ are almost equal to 4000±20 s^{-1} and 100±10 s^{-1} at 160°C, $\langle R_1\rangle$ becomes equal to 2230 s^{-1}. On the other hand the slope of the observed line in Fig. 4 gives 2280±10 s^{-1}. From the above discussion it may be estimated as $R^*_{1,A}\ \tau_A<0.5$ and

$\tau_A < 10^{-4}$s.

Table shows the effect of the size of cations Li^+, butylpyridinium cation(Py^+) and ethyl-butylimidazolium cation (DIM^+) on the lifetime τ_A and the fractional population X_A of $Al_2Cl_7^-$. We can conclude that (1) X_A is almost given by the formal concentration of $AlCl_3$ and the contributions from the major species $Al_2Cl_7^-$(A) and $AlCl_4^-$(B), and (2) τ_A increases with increasing the size of cations. The above reaction (i.e., Eq. 1) of the exchange from $AlCl_4^-$ to $Al_2Cl_7^-$ is endothermic in the DIMCl-$AlCl_3$. The product $Al_2Cl_7^-$ is, however, more stable than the reactant $AlCl_4^-$ at the temperatures of interest because of the high entropy contribution.

Table 1. The Effect of the Size of Cation on the Lifetime of $Al_2Cl_7^-$ τ_A and Anion Fractions X_A

Cation	mol% $AlCl_3$	t/°C	τ_A/s	X_A
Li^+	63	160	$<10^{-4}$	
Py^+ 7)	66	50	2.8×10^{-1}	0.66
DIM^+	65	50	$>5 \times 10^{-1}$	0.66

We thank Dr. Y. Sato (Faculty of Engineering, Tohoku University) for the loan of the mixture of LiCl-$AlCl_3$ and Professor T. Ishikawa (Faculty of Engineering) for the loan of the crystalline $AlCl_3$. The NMR measurements were carrid out with a Varian XL-200 and a Bluker SXP4-100 in the NMR Laboratory of the Faculty of Engineering in Hokkaido University.

References

1) C. R. Boston, "Advances in Molten Salt Chemistry," ed by J. Braunstein et al., Plenum Press, New York (1971), Vol.1, p.219.
2) H. L. Chum and R. A. Osteryoung, "Ionic Liquids," ed by D. Inman and D. G. Lovering, Plenum Press, New York (1981), p.407.
3) T. Matsumoto and K. Ichikawa, J. Am. Chem. Soc., 106, 4316 (1984).
4) J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem., 21, 1263 (1982).
5) J. L. Gray and G. E. Maciel, J. Am. Chem. Soc., 103, 7147 (1981).
6) J. S. Wilkes, J. S. Frye, and F. Reynolds, Inorg. Chem., 22, 3870 (1983).
7) K. Ichikawa, T. Jin, and T. Matsumoto, J. Chem. Soc., Faraday Trans. 1, 85, 175 (1989).
8) K. Ichikawa, J. Chem. Soc., Faraday Trans. 2, 82, 1913 (1986).
9) K. Ichikawa and T. Matsumoto, J. Magn. Reson., 63, 445 (1985).
10) K. Ichikawa and T. Jin, Chem. Lett., 1987, 1179.

(Received May 25, 1992)