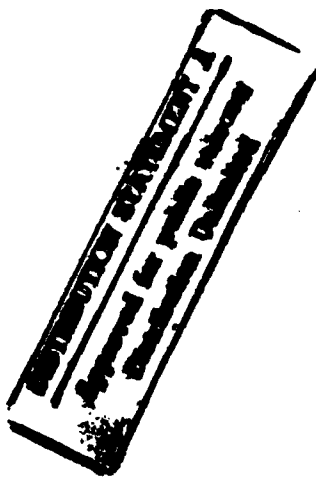


**Best  
Available  
Copy**



F55RL-JR-92-0017

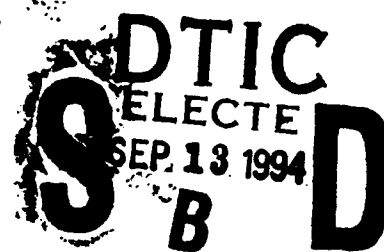
①



# NMR RELAXATION STUDIES OF MICRODYNAMICS IN CHLOROALUMINATE MELTS

Pamela A. Shaw, W. Robert Carper, Charles E. Keller  
and John S. Wilkes

Frank J. Seiler Research Laboratory, USAF Academy,  
CO 80840-6528, USA



## INTRODUCTION

Room temperature molten salts consisting of mixtures of  $\text{AlCl}_3$  and 1-ethyl-3-methylimidazolium chloride (MEICl), are of interest as aprotic solvents for studying a wide range of both organic and inorganic compounds [1-7]. These chloroaluminate molten salts possess considerable potential as battery electrolytes and various types of electrochemical agents [8-10].

The composition of a chloroaluminate melt has a considerable effect on its physical properties. The variations in physical properties of the melt are due to a combination of factors including ion-ion interactions [4], and Lewis acid-base properties. Chloroaluminate melts with  $\text{AlCl}_3$  present in excess (mole fraction,  $N$ , of  $\text{AlCl}_3 > 0.5$ ) are termed acidic with  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  the predominant anions.

The use of NMR relaxation methods provides useful information about the dynamics and structure of various chemical systems and chloroaluminate systems in particular. In a previous work [11],  $^{13}\text{C}$  NMR relaxation measurements were used to investigate the motion and interactions of the MEI cation. The results indicate that  $\text{AlCl}_4^-$  in a  $\text{Na}^+_{0.22}\text{MEI}^+_{0.78}\text{AlCl}_4^-$  melt forms a complex by interacting with the C-2, C-4 and C-5 hydrogens on the MEI<sup>+</sup> ring. This investigation was followed by studies [12,13] in which the Dual Spin Probe method [14] supported the existence of  $\text{MEI}(\text{AlCl}_4)_n^{(n-1)+}$  complexes in neutral ( $\text{AlCl}_3 = \text{MEICl}$ ) and NaCl-buffered melts.  $^{27}\text{Al}$ ,  $^{23}\text{Na}$  and  $^{13}\text{C}$  NMR relaxation results confirmed the presence of the chloroaluminate-MEI<sup>+</sup> complexes and yielded  $^{27}\text{Al}$  and  $^{23}\text{Na}$  liquid state quadrupole coupling constants [12,13].

Application of the Dual Spin Probe (DSP) relaxation

method typically requires knowledge of  $^{13}\text{C}$  dipolar relaxation rates which are defined by (1), the basic equation in which the  $^{13}\text{C}$  nucleus is relaxed by  $^1\text{H}$  [15]:

$$R_1^{\text{dd}} = N_H (\hbar \gamma_C \gamma_H)^2 r_{\text{CH}}^{-6} \tau_{\text{eff}} \quad (1)$$

where  $R_1^{\text{dd}} (= 1/T_1^{\text{dd}})$  is the dipolar relaxation rate,  $N_H$  is the number of hydrogens attached directly to the carbon atom,  $\gamma_C$  and  $\gamma_H$  are gyromagnetic ratios and  $r_{\text{CH}} = 1.09 \text{ \AA}$ .  $\tau_{\text{eff}}$  is the effective correlation time and varies exponentially with temperature. Equation (1) is operative while under the "extreme narrowing condition" ( $\omega \tau_{\text{eff}} < 1$ ) which is usually applicable for small molecules including the chloroaluminate melts [11].

$R_1^{\text{dd}}$  is obtained by measuring  $T_1$ , the Nuclear Overhauser Enhancement factor,  $\eta$  ( $\eta_{\text{max}} = \gamma_H/2\gamma_C$ ) and using eqn (2) [16]:

$$R_1^{\text{dd}} = \eta R_1 / 1.988 \quad (2)$$

The other part of the DSP method requires knowledge of quadrupolar relaxation rates for nuclei such as  $^{27}\text{Al}$  and  $^{23}\text{Na}$ . If there is a distortion from tetrahedral or cubic symmetry, nuclei such as  $^{27}\text{Al}$  and  $^{23}\text{Na}$  will be under the influence of an electric field gradient which produces the quadrupole interaction. The quadrupolar relaxation rate in the "extreme narrowing region" is given by (3) [15,17]:

$$R_1 = [3\pi^2(2I+3)/10I^2(2I-1)][1+(z^2/3)][e^2 Qq/\hbar]^2 \tau_c \quad (3)$$

where  $I = 3/2$  for  $^{23}\text{Na}$  and  $5/2$  for  $^{27}\text{Al}$ ,  $eQ$  is the nuclear quadrupole moment,  $eq$  is the maximum component of the electric field gradient tensor, and  $z$  is the asymmetry parameter of the electric field gradient tensor ( $z = 0$  for  $\text{AlCl}_3$ ).

94-29657



94 9 12 059

The quadrupole coupling constant, QCC, is given by:

$$QCC = [e^2 Q q / h] \quad (4)$$

The DSP method has been applied to chloroaluminate melts[12,13] and has provided evidence that the ring hydrogens of MEI<sup>+</sup> interact with the tetrachloroaluminate anion. The existence of these complexes has been supported by linear plots of <sup>13</sup>C dipolar relaxation rates( $R_1^{dip}$ ) vs. quadrupolar <sup>27</sup>Al relaxation rates( $R_1$ ) that pass through the origin as predicted by equation (5):

$$R_1^{dip}(^{13}\text{C})/N_H(\hbar\gamma_C\gamma_H)^2\tau_{CH}^6 = R_1(^{27}\text{Al})/\alpha\chi^2 \quad (5)$$

where  $\alpha = [3\pi^2/10][(2I + 3)/I^2(2I - 1)][1 + (z^2/3)]$ , and  $QCC = \chi$ .

In this study, the DSP method is applied to melts containing MEICl, AlCl<sub>3</sub>, and EtAlCl<sub>2</sub>. The inclusion of EtAlCl<sub>2</sub> provides a "baseline" as there is a covalent bond between the ethyl group and aluminum in EtAlCl<sub>2</sub>. The existence of covalent bonding(or complexation) between quadrupolar and dipolar nuclei in a molecule results in a linear plot of eqn. (5) that passes through the origin. In the MEICl-EtAlCl<sub>2</sub> melts reported herein, we observe a linear plot of eqn (5) that passes through the origin when applied to the terminal CH<sub>3</sub> carbon in EtAlCl<sub>2</sub> and one of the peaks in the <sup>27</sup>Al NMR of the melts.

## EXPERIMENTAL

### Materials

The 1-ethyl-3-methylimidazolium chloride (MEICl) and chloroaluminate molten salts were prepared as described previously [1]. Ethylaluminum dichloride (EtAlCl<sub>2</sub>) was obtained from Aldrich. All materials were stored under anhydrous helium gas atmosphere in a dry box. All molten salt preparations and manipulations were performed in the dry box. Samples were loaded into 5 mm sample tubes, capped in the dry box, removed, and sealed immediately with a torch.

### NMR Measurements

<sup>13</sup>C and <sup>27</sup>Al NMR spectra were recorded on a Varian XL-300 spectrometer at 75.43 or 78.15 MHz. Temperature measurements were calibrated against methanol or ethylene glycol and are accurate to within 0.5°C. Pulse widths(90°) were typically 8.6 (75.43 MHz) and 7.6(78.15 MHz) μs. Longitudinal relaxation times were measured by the the inversion-recovery method

(180°-τ-90°-T) with  $T > 10T_1$ . At least 12 delay times(τ) were used and the results fitted to a three parameter exponential. NOE measurements were made using the gated decoupler method[18]. It is likely that the error in the NOE measurements is in the 5-10% range[18].

## RESULTS AND DISCUSSION

The ability of both AlCl<sub>3</sub> and EtAlCl<sub>2</sub> to form C<sub>2H</sub> dimers[19,20] led us to examine the <sup>27</sup>Al spectra of: (1) neat EtAlCl<sub>2</sub>, (2) mixtures of MEICl-EtAlCl<sub>2</sub> and (3) ternary melts ( $N = \text{AlCl}_3/\text{MEICl}/\text{EtAlCl}_2$  [21]. The neat EtAlCl<sub>2</sub> <sup>27</sup>Al NMR spectrum contains two peaks [21]. Peak 1 is a broad downfield peak that dominates the spectrum. The second peak (upfield) overlaps peak 1 and is only a fraction of peak 1 in total peak area. Peak 2 collapses into peak 1 as the temperature is lowered from 60 to 25°C. These two aluminum sites are consistent with the extent of monomer-dimer formation in liquid EtAlCl<sub>2</sub>[21].

The MEICl-EtAlCl<sub>2</sub> ( $N = 0.5/0.5$ ) melt <sup>27</sup>Al NMR spectrum also has two peaks. In this case, peak 1(downfield) is very broad while peak 2 is very sharp, and has a low peak area. Peak 2 increases slightly in area and peak 1 broadens as the temperature is lowered from 70 to 0°C. We have previously[21] made the tentative assignments of EtAlCl<sub>2</sub> for peak 1(downfield) and Et<sub>2</sub>Al<sub>2</sub>Cl<sub>3</sub> for peak 2.

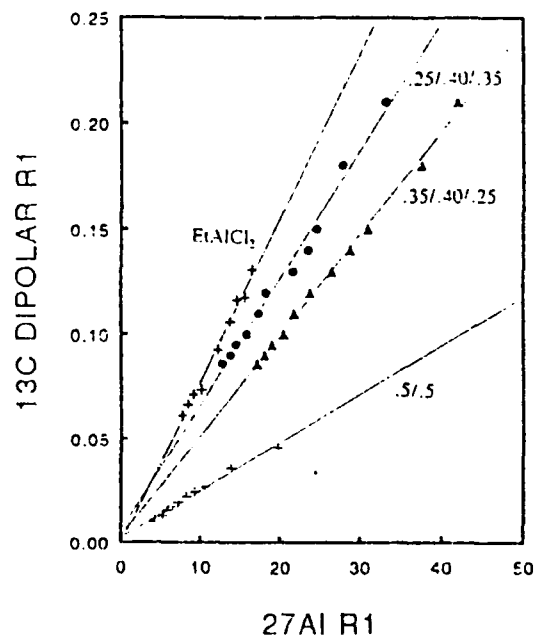


Fig. 1. <sup>13</sup>C Dipolar R1's vs <sup>27</sup>Al R1's(25 to 70°C) for Al peak 1 (127-131 ppm from Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>).

In this study, we first apply the DSP method to the  $\text{CH}_3$  carbon in  $\text{EtAlCl}_2$  and  $^{27}\text{Al}$  NMR peaks 1 and 2 from several melt combinations and neat  $\text{EtAlCl}_2$ . Fig. 1 contains the results for  $^{27}\text{Al}$  peak 1 (downfield) and Fig. 2 contains the results for  $^{27}\text{Al}$  peak 2. The fact that both plots are linear and pass through the origin, indicate that: (1) the DSP method is appropriate for these systems and (2) the species associated with each peak contains  $\text{EtAlCl}_2$ . Furthermore, the slopes of these lines can be used to

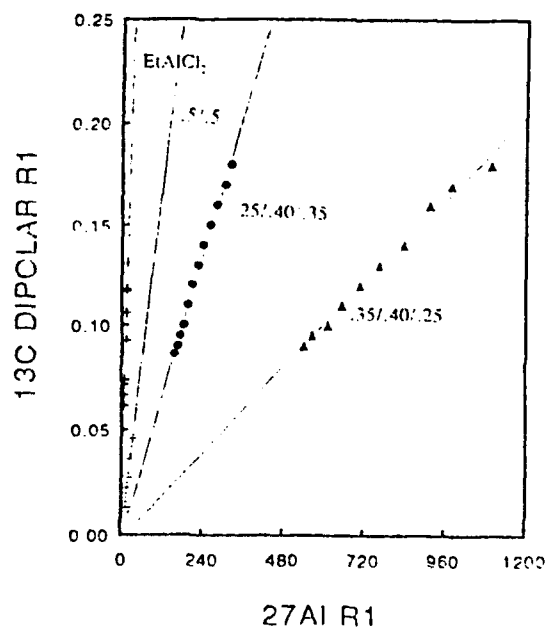


Fig. 2.  $^{13}\text{C}$  Dipolar R1's vs  $^{27}\text{Al}$  R1's (25 to  $70^\circ\text{C}$ ) for Al peak 2 (102.5-103.0 ppm from  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ).

calculate the relative quadrupole coupling constants for the  $\text{EtAlCl}_2$ -containing species in solution. The QCC values obtained from Fig. 1 (Al peak 1) are 171, 119, 106 and 93 MHz for the (.5/.5), (.35/.40/.25), (.25/.40/.35) melts and neat  $\text{EtAlCl}_2$ , respectively. The QCC values obtained from Fig. 2 (Al peak 2) are 6.9, 20, 11 and 93 MHz for the (.5/.5), (.35/.40/.25), (.25/.40/.35) melts and neat  $\text{EtAlCl}_2$  (repeated).

Results of the Dual Spin Probe method (eqn. [5]) applied to the (.5/.5), (.35/.40/.25) and (.25/.40/.35) melts indicate interactions between the Al-containing species in peak 2 (102.5-103.0 ppm relative to  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ) and both the  $\text{NCH}_3$  and ethyl terminal  $\text{CH}_3$  groups of MEI'. Fig. 3 contains the plots for the  $\text{NCH}_3$  group in each melt and Fig. 4 contains data for the terminal  $\text{CH}_3$  on the MEI ethyl group.

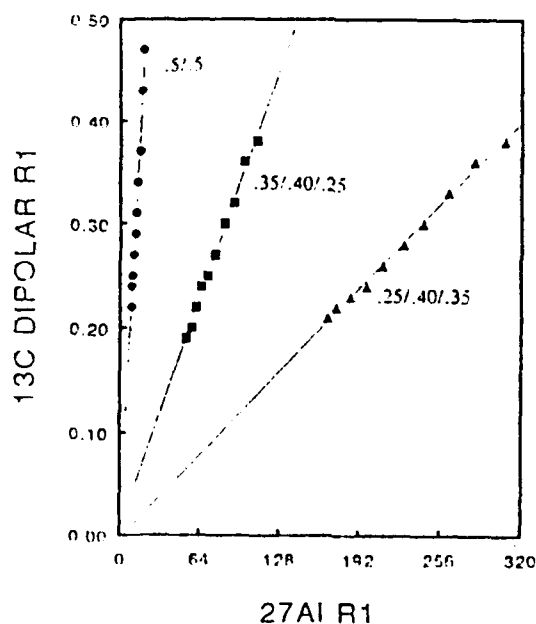


Fig. 3.  $^{13}\text{C}$  Dipolar R1's vs.  $^{27}\text{Al}$  R1's (25 -  $70^\circ\text{C}$ ) for  $\text{NCH}_3$  carbon vs Al peak 2 (25 -  $70^\circ\text{C}$ ).

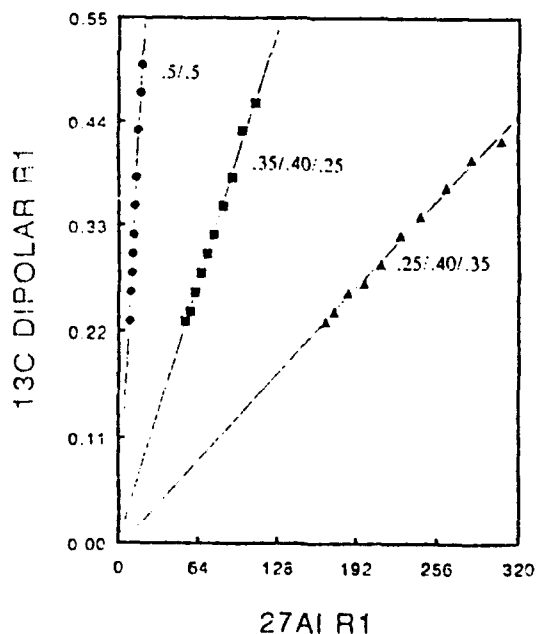


Fig. 4.  $^{13}\text{C}$  Dipolar R1's for ethyl  $\text{CH}_3$  carbon vs  $^{27}\text{Al}$  R1's (25 -  $70^\circ\text{C}$ ) for Al peak 2.

The QCC's obtained from the slopes in Fig. 3 (MEI  $\text{NCH}_3$ ) are 1.7, 2.3 and 4.4 MHz for the (.5/.5), (.35/.40/.25) and (.25/.40/.35) melts. The QCC's from

Fig. 4 (terminal  $\text{CH}_3$  on the MEI ethyl group) are 1.6, 6.9 and 1.3 MHz for the (.5/.5), (.35/.40/.25) and (.25/.40/.35) melts.

Finally, there is no correlation between the ring hydrogen dipolar R1's and any of the  $^{27}\text{Al}$  peak R1's. This result is directly opposite to that found in  $\text{MEI}^+\text{-AlCl}_3$  systems [11,12].

## CONCLUSIONS

Application of the DSP probe method to these mixed melt systems indicates a lack of complexation between the ring hydrogens of  $\text{MEI}^+$  and any of these aluminum containing species. These and previous results [21] suggest that the formation of various charged dimers containing  $\text{EtAlCl}_2$  takes precedence over the formation of complexes between  $\text{EtAlCl}_2$  and the  $\text{MEI}^+$  ring hydrogens. However, there is evidence of interaction between the various Al-containing species and the  $\text{CH}_3$  groups ( $\text{NCH}_3$  and terminal  $\text{CH}_3$  in the ethyl group) of  $\text{MEI}^+$  in these melts.

## ACKNOWLEDGMENTS

This work was partially supported by a National Research Council and Summer Faculty Research Associateship to W. R. C. and a summer Graduate Fellowship to P. A. S.

## REFERENCES

- [1] J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, **21** 1263 (1982).
- [2] J. S. Wilkes, J. S. Frye and G. F. Reynolds, *Inorg. Chem.*, **22** (1983) 3870.
- [3] A. A. Fannin, L. A. King, J. A. Levisky and J. S. Wilkes, *J. Phys. Chem.*, **88** (1984) 2609.
- [4] A. A. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes and J. L. Williams, *J. Phys. Chem.*, **88** (1984) 2614.
- [5] K. M. Dieter, C. J. Dymek, N. E. Heimer, J. W. Rovang and J. S. Wilkes, *J. Amer. Chem. Soc.*, **110** (1988) 2722.
- [6] C. J. Dymek and J. J. P. Stewart, *Inorg. Chem.*, **28** (1989) 1472.
- [7] J. A. Boon, J. A. Levisky, J. L. Pflug and J. S. Wilkes, *J. Org. Chem.*, **51** (1986) 480.
- [8] C. J. Dymek, J. L. Williams, D. J. Groeger and J. J. Auburn, *J. Electrochem. Soc.*, **131** (1989) 2887.
- [9] C. J. Dymek and L. A. King, *J. Electrochem. Soc.*, **132** (1985) 1375.
- [10] C. L. Hussey, T. B. Scheffler, J. S. Wilkes and A. A. Fannin, *J. Electrochem. Soc.*, **133** (1986) 1389.
- [11] W. R. Carper, J. L. Pflug, A. M. Elias and J. S. Wilkes, *J. Phys. Chem.* **96** (1992) 3828.
- [12] W. R. Carper, J. L. Pflug and J. S. Wilkes, *Inorganica Chimica Acta* **193** (1992) 201.
- [13] W. R. Carper, J. L. Pflug and J. S. Wilkes, *Inorganica Chimica Acta* (in press).
- [14] J. J. Dechter and U. Henriksson, *J. Magn. Res.*, **48** (1982) 503.
- [15] A. Abragam, "Principles of Nuclear Magnetism", Oxford University Press, Oxford (1961).
- [16] K. F. Kuhlmann and D. M. Grant, *J. Amer. Chem. Soc.*, **90** (1968) 7355.
- [17] B. Lindman and S. Forsen, in "NMR Basic Principles and Progress," P. Diehl, E. Fluck and R. Kosfeld, Editors, Vol. 12, p. 22, Springer-Verlag, New York (1976).
- [18] D. Neuhaus and M. Williamson, "The Nuclear Overhauser Effect in Structural and Conformational Analysis", VCH Publishers, New York (1989).
- [19] J. Weidlein, *J. Organomet. Chem.*, **17** (1969) 213.
- [20] B. Gilbert, Y. Chauvin and I. Guibard, *Vib. Spectros.*, **1** (1991) 299.
- [21] W. R. Carper, C. E. Keller, P. A. Shaw, M. P. and J. S. Wilkes, in "Eighth International Symposium on Molten Salts", Electrochem. Soc., New York (in press).

Library Codes

Call and/or

Special

A-1/20