

NMR RELAXATION STUDIES OF MICRODYNAMICS IN CHLOROALUMINATE MELTS

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INTRODUCTION

Room temperature molten salts consisting of mixtures of 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 AlCl_3 present in excess (mole fraction, N , of $\text{AlCl}_3 > 0.5$) are termed acidic with AlCl_4^- and Al_2Cl_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}C NMR relaxation measurements were used to investigate the motion and interactions of the MEI cation. The results indicate that 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⁺ 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}Al , ^{23}Na and ^{13}C NMR relaxation results confirmed the presence of the chloroaluminate-MEI⁺ complexes and yielded ^{27}Al and ^{23}Na liquid state quadrupole coupling constants [12,13].

Application of the Dual Spin Probe (DSP) relaxation

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

$$R_1^{\text{dd}} = N_{\text{H}}(\hbar\gamma_{\text{C}}\gamma_{\text{H}})^2 r_{\text{CH}}^{-6} \tau_{\text{eff}} \quad (1)$$

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

R_1^{dd} is obtained by measuring T_1 , the Nuclear Overhauser Enhancement factor, η ($\eta_{\text{max}} = \gamma_{\text{H}}/2\gamma_{\text{C}}$) 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}Al and ^{23}Na . If there is a distortion from tetrahedral or cubic symmetry, nuclei such as ^{27}Al and ^{23}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]:

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

where $I = 3/2$ for ^{23}Na and $5/2$ for ^{27}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 AlCl_3).

The quadrupole coupling constant, QCC, is given by:

$$\text{QCC} = [e^2Qq/h] \quad (4)$$

The DSP method has been applied to chloroaluminate melts[12,13] and has provided evidence that the ring hydrogens of MEI⁺ interact with the tetrachloroaluminate anion. The existence of these complexes has been supported by linear plots of ¹³C dipolar relaxation rates(R_1^{d4}) vs. quadrupolar ²⁷Al relaxation rates(R_1) that pass through the origin as predicted by equation (5):

$$R_1^{d4}(^{13}\text{C})/N_{\text{H}}(\hbar\gamma_{\text{C}}\gamma_{\text{H}})^2r_{\text{CH}}^{-6} = R_1(^{27}\text{Al})/\alpha\chi^2 \quad (5)$$

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

In this study, the DSP method is applied to melts containing MEICl, AlCl₃ and EtAlCl₂. The inclusion of EtAlCl₂ provides a "baseline" as there is a covalent bond between the ethyl group and aluminum in EtAlCl₂. 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-EtAlCl₂ melts reported herein, we observe a linear plot of eqn (5) that passes through the origin when applied to the terminal CH₃ carbon in EtAlCl₂ and one of the peaks in the ²⁷Al 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 (EtAlCl₂) 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

¹³C and ²⁷Al NMR spectra were recorded on a Varian A-300 spectrometer at 75.43 or 78.15 MHz. Temperature measurements were calibrated against methanol or ethylene glycol and are accurate to within 1°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 > 10T₁. 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 AlCl₃ and EtAlCl₂ to form C_{2H} dimers[19,20] led us to examine the ²⁷Al spectra of: (1) neat EtAlCl₂, (2) mixtures of MEICl-EtAlCl₂ and (3) ternary melts (N = AlCl₃/MEICl/EtAlCl₂)[21]. The neat EtAlCl₂ ²⁷Al 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 EtAlCl₂[21].

The MEICl-EtAlCl₂ (N = 0.5/0.5) melt ²⁷Al 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 EtAlCl₃ for peak 1(downfield) and Et₂Al₂Cl₅ for peak 2.

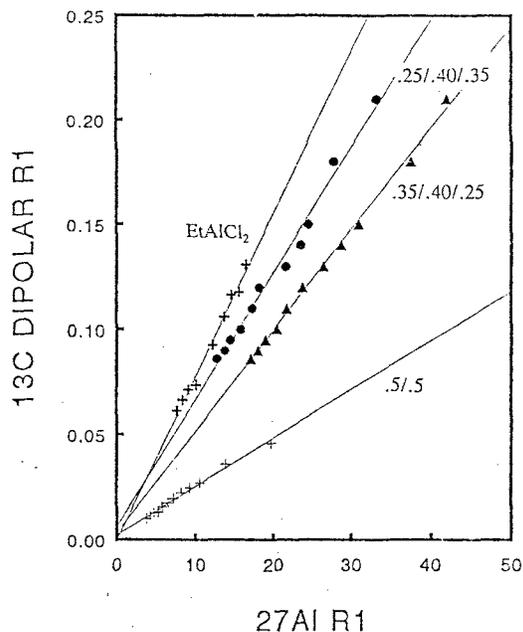


Fig. 1. ¹³C Dipolar R1's vs ²⁷Al R1's(25 to 70°C) for Al peak 1 (127-131 ppm from Al(H₂O)₆³⁺).

In this study, we first apply the DSP method to the CH_3 carbon in EtAlCl_2 and ^{27}Al NMR peaks 1 and 2 from several melt combinations and neat EtAlCl_2 . Fig. 1 contains the results for ^{27}Al peak 1 (downfield) and Fig. 2 contains the results for ^{27}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 EtAlCl_2 . Furthermore, the slopes of these lines can be used to

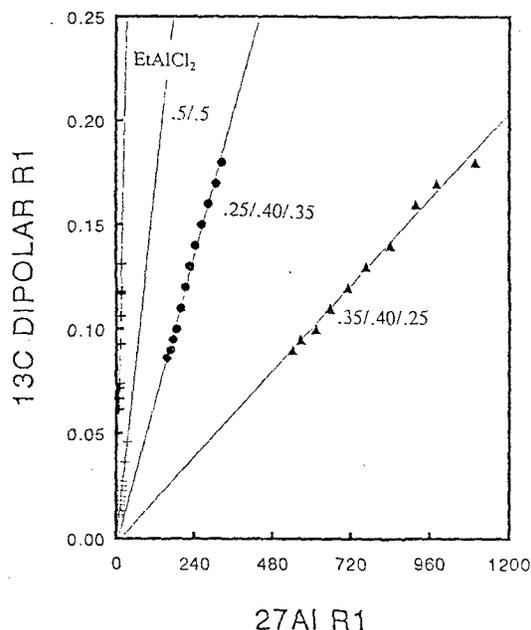


Fig. 2. ^{13}C Dipolar R1's vs ^{27}Al R1's (25 to 70°C) for Al peak 2 (102.5-103.0 ppm from $\text{Al}(\text{H}_2\text{O})_6^{3+}$).

calculate the relative quadrupole coupling constants for the 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 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 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 NCH_3 and ethyl terminal CH_3 groups of MEI^+ . Fig. 3 contains the plots for the NCH_3 group in each melt and Fig. 4 contains data for the terminal CH_3 on the MEI ethyl group.

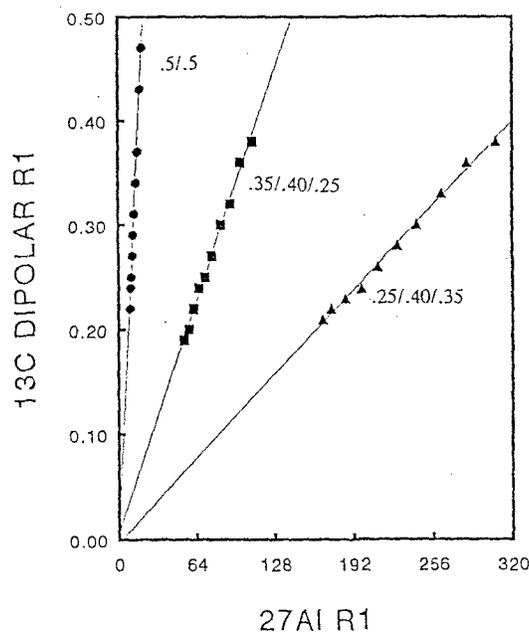


Fig. 3. ^{13}C Dipolar R1's vs. ^{27}Al R1's (25 - 70°C) for NCH_3 carbon vs Al peak 2 (25 - 70°C).

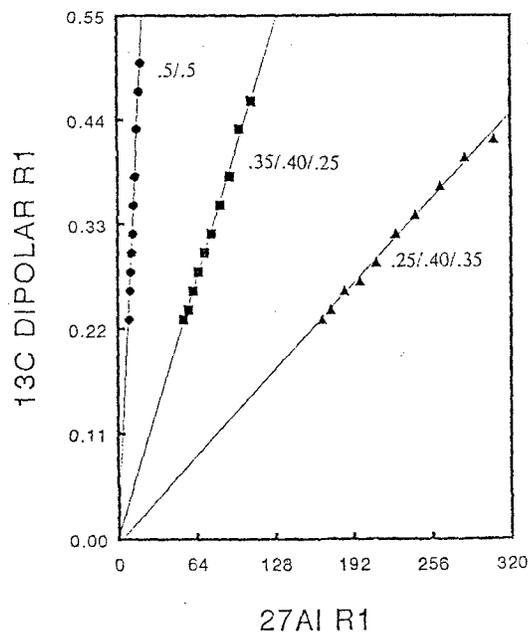


Fig. 4. ^{13}C Dipolar R1's for ethyl CH_3 carbon vs ^{27}Al R1's (25 - 70°C) for Al peak 2.

The QCC's obtained from the slopes in Fig. 3 (MEI 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 CH₃ 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 ²⁷Al peak R₁'s. This result is directly opposite to that found in MEI-Cl-AlCl₃ 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 MEI⁺ and any of these aluminum containing species. These and previous results [21] suggest that the formation of various charged dimers containing EtAlCl₂ takes precedence over the formation of complexes between EtAlCl₂⁻ and the MEI⁺ ring hydrogens. However, there is evidence of interaction between the various Al-containing species and the CH₃ groups (NCH₃ and terminal CH₃ in the ethyl group) of MEI⁺ in these melts.

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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. Kovang 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).