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^{27}Al NMR relaxation studies of molten salts containing ethylaluminum dichloride

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Abstract

The microdynamics of room temperature molten salts containing $EtAlCl_2$ are examined by ^{27}Al NMR relaxation methods as a function of melt composition and temperature. The melts examined include neat $EtAlCl_2$ and mixtures of $EtAlCl_2$, 1-ethyl-3-methylimidazolium chloride (MEICl) and $AlCl_3$. Information obtained from this study indicates interactions between $EtAlCl_2$ containing species ($EtAlCl_3^-$ and $EtAlCl_2$ dimers) and MEICl or $AlCl_3$. Quadrupole coupling constants obtained for ^{27}Al using the extreme narrowing condition compare favorably with those obtained previously by the dual spin probe (DSP) method.

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]. They are ionic liquids whose interionic interactions affect their chemistry. These ionic liquids have considerable potential as battery electrolytes and various types of electrochemical agents [8–10].

The composition of a room temperature melt has a profound 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 of $AlCl_3 > 0.5$) are termed acidic with $AlCl_4^-$ and $Al_2Cl_7^-$ the predominant anions, while melts with excess MEICl are termed basic. The basic melts contain Cl^- and $AlCl_4^-$ as the predominant anions. At neutral composition (mole fraction of $AlCl_3 = 0.5$), electrochemical [11] and spectroscopic probes [2, 5] indicate that $AlCl_4^-$ is the only detectable anion. Wilkes and co-workers have shown that the addition of NaCl as a ternary component buffers the medium to Lewis neutrality, where $AlCl_4^-$ is the only anion in an $Na_{0.22}{}^+MEI_{0.78}{}^+AlCl_4^-$ melt. [12].

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 study [13], ^{13}C NMR relaxation measurements were used to investigate the motion and interaction of the MEI cation. The results indicate that $AlCl_4^-$ in an $Na_{0.22}{}^+MEI_{0.78}{}^+AlCl_4^-$ 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 [14, 15] in which the dual spin probe method [16] supported the existence of $MEI(AlCl_4)_n{}^{(n-1)-}$ complexes in neutral ($AlCl_3 =$ MEICl) and buffered melts (acidic melts buffered to neutrality with NaCl). ^{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 [14, 15].

Recently, a new chloroaluminate room temperature molten salt system has been studied using Raman spectroscopy [17]. This melt [17] is a mixture of ethylaluminum dichloride ($EtAlCl_2$) and 1-butyl-3-methylimidazolium chloride and is liquid over a wide range of temperature and melt compositions. A similar melt system containing 1-ethyl-3-methylimidazolium chloride (MEICl) and $EtAlCl_2$ has also been reported [18]. In this study, ^{17}Al NMR relaxation rates were obtained on room temperature melts containing 1-ethyl-3-methylimidazolium chloride (MEICl) and either $AlCl_3$, $EtAlCl_2$, or a combination thereof.

Experimental

Materials

The 1-ethyl-3-methylimidazolium chloride and chloroaluminate molten salts were prepared as previously

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described [13]. All materials were stored under anhydrous helium gas atmosphere in a dry box. All molten salt preparations and manipulations were performed in a dry box. Samples were loaded into 5 mm sample tubes, capped and sealed with parafilm. They were then removed from the dry box and sealed immediately with a torch.

NMR measurements

^{27}Al NMR spectra were recorded on a Varian XL-300 spectrometer at 78.15 MHz. Temperature measurements were calibrated against methanol or ethylene glycol and are accurate to within 0.5 °C. Pulse widths were typically 5–10 μs, and longitudinal relaxation times were measured by the inversion–recovery method (180°–τ–90°–T) with $T > 10T_1$. For all melt samples, at least 12 delay times (τ) were used and relaxation times (in duplicate) obtained from a three parameter exponential fit of magnetization as a function of τ. We failed to observed non-exponential behaviour for any of these melts. All ^{27}Al chemical shift (δ) values reported herein are relative to $Al(H_2O)_6^{3+}$ made from $AlCl_3$ [18].

Results and discussion

Quadrupole relaxation

^{27}Al NMR relaxation measurements are useful in that a nucleus of spin greater than 1/2 that relaxes primarily through a quadrupole mechanism can be used as a NMR 'probe' to monitor isotropic molecular tumbling [14, 16]. Quadrupolar relaxation results from time-dependent electric field gradients at the nucleus. A quadrupole will not interact with a constant electric field but with an electric field gradient in which the quadrupole will have an interaction energy that is dependent on the orientation of the quadrupole relative to the electric field gradient. The electric field gradient at a quadrupolar nucleus in a molecule or in a crystal lattice is in general a tensor quantity. This tensor may be transformed into diagonal form and the field gradient is now described by the three principal components, $\partial^2V/\partial x^2 = V_{xx}$, $\partial^2V/\partial y^2 = V_{yy}$ and $\partial^2V/\partial z^2 = V_{zz}$ where V is the electrostatic potential and the principal axes are x, y and z. As Laplace's equation requires that $V_{xx} + V_{yy} + V_{zz} = 0$, only two quantities are required to describe the field gradient tensor. One of these quantities is the maximum component of the field gradient tensor along the z axis, and therefore $eq = V_{zz}$. The asymmetry factor (z in eqn. (1)) is simply $(V_{xx} - V_{yy})/V_{zz}$, with the principal axes chosen such that z varies between 0 and 1. It is apparent that if the quadrupolar nucleus is located in a symmetrical (cubic or tetrahedral) environment, the field gradient is zero. If such is not the case, as in the room temperature melts, there is an electric field gradient, and one observes quadrupolar relaxation.

In a manner similar to dipolar mechanisms, a nucleus of spin greater than 1/2 that relaxes primarily through a quadrupolar mechanism also can be used as a NMR 'probe' to monitor isotropic molecular tumbling. If there is a distortion from cubic or tetrahedral symmetry (as indicated above), nuclei such as ^{27}Al will be under the influence of an electric field gradient which produces the quadrupole interaction. The quadrupole interaction is affected by the reorientation motion of the ^{17}Al containing molecule (complex ion in this case) and the quadrupolar relaxation rate in the 'extreme narrowing region' is given by [19, 20]:

$$R_1 = 1/T_1 = [3\pi^2(2I+3)/10I^2(2I-1)] \times [1 + (z^2/3)][e^2Qq/h]^2\tau_c \tag{1}$$

where $I = 5/2$ for ^{27}Al, eQ is the nuclear electric quadrupole moment, eq is the maximum component of the field gradient tensor, and z is the asymmetry parameter of the electric field gradient tensor. τ_c is the effective correlation time and varies exponentially with temperature. The quadrupole coupling constant, QCC, is given by:

$$QCC = e^2Qq/h \tag{2}$$

NMR spectra

The ^{27}Al NMR spectra of the equimolar MEICl–$AlCl_3$ [18] and $Na_{0.22}{}^+MEI_{0.78}{}^+AlCl_4{}^-$ melts at 60 °C contain a single line centered at 103 ppm (Table 1), consistent with $AlCl_4{}^-$ being the primary Al-containing species present in these melts [2, 5, 11, 12]. The ^{27}Al NMR spectrum of the 0/0.5/0.5 melt (molar amounts $AlCl_3$/MEICl/$EtAlCl_2$) contains a broad ($T_1 = 201$ μs) down-

TABLE 1. Spin-lattice relaxation times (T_1) and chemical shifts (δ in ppm)[a] of $EtAlCl_2$ melts at 60 °C and 78.15 MHz

Metal molar composition ($AlCl_3$/MEICl/$EtAlCl_2$)	Peak number					
	1		2		3	
	T_1 (μs)	δ	T_1 (ms)	δ	T_1 (ms)	δ
$EtAlCl_2$ (neat)	108	128.2		97		
0.5/0.5/0			111	103.0		
0/0.4/0.6	84	131.0	16.4	102.0		
0/0.45/0.55	85	130.0	37.0	102.0		
0/0.5/0.5	201	128.5	98.1	102.0		
0.25/0.4/0.35	68	130.8	7.1	102.6	3.8	96
0.3/0.4/0.3	68	130.2	5.7	102.6	3.3	96
0.35/0.4/0.25	49	127.0	1.7	102.5	1.8	96

[a] Chemical shifts relative to $Al(H_2O)_6^{3+}$.

field peak at 128.5 ppm which accounts for the majority (>90%) of the Al-containing species present in the melt. This peak has been identified as belonging to the dimer of $EtAlCl_2$ [21]. The sharp upfield peak at 102 ppm has a T_1 of 98 ms and represents less than 6% of the total Al-containing species in the melt. This latter peak has been identified as belonging to $EtAlCl_3^-$ [21]. If we decrease the molar ratio of MEICl to $EtAlCl_2$ from 0.5/0.5 to 0.45/0.55 and 0.4/0.6, we observe the growth of a small (<1% of total species concentration) narrow peak (shoulder) at approx. 96 ppm. This peak is attributed to $Et_2Al_2Cl_5^-$ [21] previously identified by Raman spectroscopy in melts consisting of 1-butyl-3-methylimidazolium chloride and $EtAlCl_2$ [22]. The $Al_2Cl_7^-$ species (not observed in this case) is known to have a chemical shift of 90 or 13 ppm upfield from $AlCl_4^-$ [22].

The NMR spectrum of neat $EtAlCl_2$ has a broad shoulder at 97 ppm ($EtAlCl_2$ monomer) which merges with the broad 128 ppm ^{27}Al NMR peak ($EtAlCl_2$ dimer) as the temperature is lowered from 80 to 35 °C [18, 21]. The narrow (T_1 in ms) peak at 96 ppm in the $AlCl_3$/MEICl/$EtAlCl_2$ melts does not merge onto the 129 ppm peak as the temperature is lowered from 80 to 35 °C, further supporting the assignment of this peak to the $Et_2Al_2Cl_5^-$ species. The $Et_2Al_2Cl_5^-$ peak is observed in the 0.25/0.4/0.35 melt and is reduced to a shoulder in the 0.35/0.4/0.25 melt where the ratio of $AlCl_3$ to $EtAlCl_2$ is greater than 1:1.

^{27}Al relaxation mechanisms

Figure 1 contains a plot of ln ^{27}Al R_1 (s^{-1}) for the dimer of $EtAlCl_2$ (peak 1: 127–131 ppm) versus 1000/K for neat $EtAlCl_2$ and the mixed 0/0.5/0.5, 0/0.4/0.6, 0.25/0.4/0.35 and 0.35/0.4/0.25 melts ($AlCl_3$/MEICl/$EtAlCl_2$). Table 2 contains E_a values over specified temperature ranges for each of the melts.

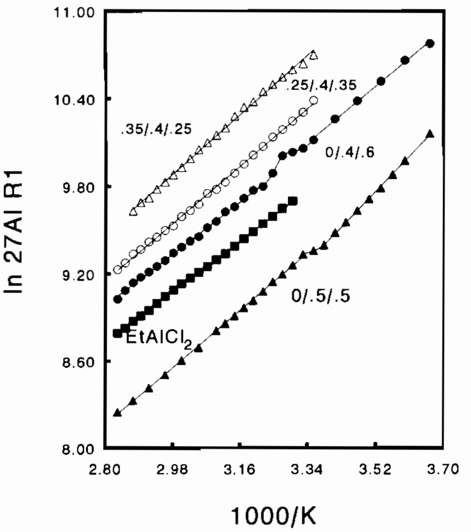

Fig. 1. ln ^{27}Al R_1 (s^{-1}) ($EtAlCl_2$ dimer peak) vs. 1000/K for $EtAlCl_2$ (■), and the 0.35/0.4/0.25 (△), 0.25/0.4/0.35 (○), 0/0.4/0.6 (●) and 0/0.5/0.5 (▲) melts.

The equimolar MEICl–$EtAlCl_2$ melt has a small but measurable inflection in the ln ^{27}Al R_1 (s^{-1}) versus 1000/K plot between 20 and 30 °C. The 0/0.4/0.6 melt ($EtAlCl_2$ in excess) has a more pronounced inflection between 25 and 40 °C. The observed inflections are similar to those observed in phase changes [23–25], structural changes in metal ion–sugar complexes [26, 27] and for conformational changes in proteins [28–30]. The observed inflections suggest that one is observing: (a) a conformational change in the structure of the $EtAlCl_2$ dimer, (b) a change in overall dimer aggregation, or (c) a combination of both (a) and (b).

The $EtAlCl_2$ dimer activation energies for the 0/0.5/0.5 melt are 22.5 (0–20 °C) and 18.2 (30–80 °C) kJ. The value of 18.2 kJ for the higher temperature range is higher than that of neat $EtAlCl_2$ and very similar to those obtained for the other melts, as shown in Table 2. These and earlier results [18, 31] indicate similar weak $EtAlCl_2$ dimer interactions in these melts within specific temperature ranges. Furthermore, the $EtAlCl_2$ dimer interactions that occur between 0 and 20 °C in the equimolar MEICl–$EtAlCl_2$ melt are stronger than those present in any of the other melts over the temperature ranges investigated herein.

Figure 2 contains a plot of ln R_1 (^{27}Al) for $EtAlCl_3^-$ (upfield peak) versus reciprocal temperature for the 0/0.5/0.5 and 0/0.4/0.6 melts ($AlCl_3$/MEICl/$EtAlCl_2$). The equimolar MEICl–$EtAlCl_2$ melt exhibits a pronounced inflection between 20 and 30 °C, and a second change in relaxation mechanism at 60 °C. The 0/0.4/0.6 melt undergoes changes in its relaxation mechanisms at approx. 30 and 60 °C. Changes in relaxation mechanism for both of these melts were observed at similar temperatures (20–40 °C) for the $EtAlCl_2$ dimer in Fig. 1.

TABLE 2. Activation energies (kJ) for $EtAlCl_3^-$ and $EtAlCl_2$ dimers

Melt molar composition ($AlCl_3$/MEICl/$EtAlCl_2$)	$EtAlCl_3^-$		$EtAlCl_2$ dimer	
	Temp. (°C)	E_a	Temp. (°C)	E_a
$EtAlCl_2$(neat)			30–80	16.1
0/0.5/0.5	60–80	10.7	30–80	18.2
0/0.5/0.5	30–60	15.4	−10–20	22.5
0/0.5/0.5	−10–20	21.3		
0/0.4/0.6	60–80		40–80	16.5
0/0.4/0.6	30–60	6.2	25–40	
0/0.4/0.6	0–30	11.4	0–25	17.9
0.35/0.4/0.25	25–80	17.8	25–75	18.8
0.25/0.4/0.35	25–80		25–80	18.1

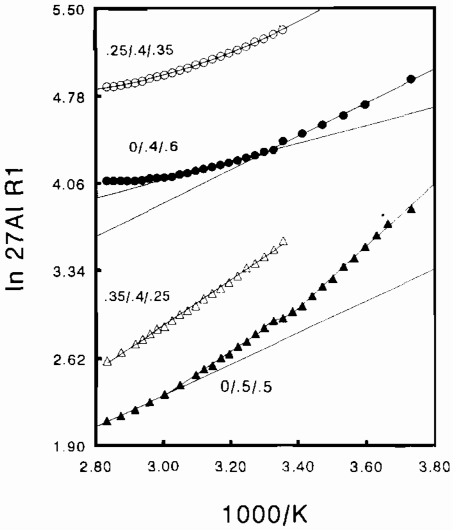

Fig. 2. ln ^{27}Al R_1 (s^{-1}) ($EtAlCl_3^-$ peak) vs. 1000/K for the 0.35/0.4/0.25 (△), 0.25/0.4/0.35 (○), 0/0.4/0.6 (●) and 0/0.5/0.5 (▲) melts. The ln R_1 values for the 0.35/0.4/0.25 melt have been reduced by 3.5.

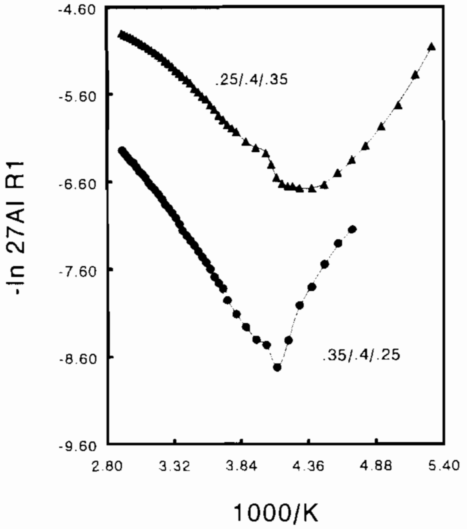

Fig. 3. $-\ln$ ^{27}Al R_1 (s^{-1}) ($EtAlCl_3^-$ peak) vs. 1000/K for the 0.25/0.4/0.35 (▲) and 0.35/0.4/0.25 (●) melts.

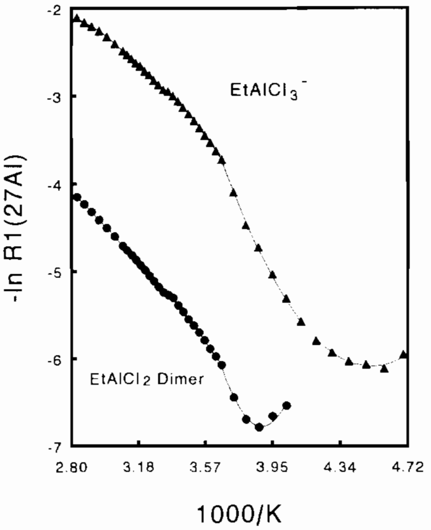

Fig. 4. $-\ln$ ^{27}Al R_1 (s^{-1}) vs. 1000/K for the 0/0.5/0.5 melt. $EtAlCl_2$ dimer (●) and $EtAlCl_3^-$ (▲) peaks are both included (4.0 has been added to the $-\ln$ ^{27}Al R_1 (s^{-1}) $EtAlCl_2$ dimer results).

The $EtAlCl_3^-$ activation energies for the 0/0.5/0.5 melt are 21.3 (−10 to 20 °C), 15.4 (30–60 °C) and 10.7 (60–80 °C) kJ. The $EtAlCl_3^-$ activation energies for the 0/0.4/0.6 melt are 11.4 (0–30 °C) and 6.2 (30–60 °C) kJ. Comparison of these activation energies with those obtained for the $EtAlCl_2$ dimer (downfield peak, 129 to 131 ppm) indicate that stronger forces exist for maintaining dimer interaction than exist for molecular interactions involving $EtAlCl_3^-$ in these melts.

In mixed melts, the 103 ppm ^{27}Al NMR peak is representative of both $EtAlCl_3^-$ and $AlCl_4^-$. Consequently, any relaxation measurements contain a contribution for each of these anions. The mixed melt (0.35/0.4/0.25) with $AlCl_3$ in excess of $EtAlCl_2$ has a single activations energy of 17.8 kJ over the temperature range 25–80 °C whereas a non-linear result is obtained for the melt (0.25/0.4/0.35) containing more $EtAlCl_2$ than $AlCl_3$. It is apparent that structural changes occur more frequently for $EtAlCl_2$-containing species than occur for $AlCl_4^-$ over this temperature range.

Determination of QCC for ^{27}Al

In previous reports [14, 15] we have used the dual spin probe (DSP) method to determine *QCC* values for ^{27}Al and ^{23}Na in neutral (0.5/0.5/0) and neutral-buffered ($Na_{0.22}{}^+MEI_{0.78}{}^+AlCl_3$) melts. An alternative method is to identify the temperature at which the extreme narrowing condition no longer applies (i.e. $\omega\tau_c \approx 1$ and solve for τ_c. At this temperature, eqn. (1) may be solved for *QCC* using the values for R_1 (quadrupolar) and τ_c ($= 1/2\pi \times 78.15$ MHz). Figure 3 contains Arrhenius plots of $-\ln$ ^{27}Al R_1 (s^{-1}) versus 1000/K for the 0.25/0.4/0.35 and 0.35/0.4/0.25 melts. In Fig. 4, similar plots are given for the $EtAlCl_3^-$ and $EtAlCl_2$ dimer peaks in the 0/0.5/0.5 melt. The plots in Figs. 3 and 4 exhibit apparent non-exponential relaxation processes close to their various glass transition regions. These complex relationships are due to either a hierarchy of relaxation processes or a superposition of relaxation exponentials indicating various parallel relaxation pathways. In all cases, the temperature at which T_1 reaches a minimum value is well above the freezing point of the melt and we observe glass transitions in these melts similar to those reported elsewhere [24, 32]. The approx. freezing points for these melts are −80 (0.25/0.4/0.35), −75 (0.35, 0.4/0.25), −65 (0/0.5/0.5) and −60 (0/0.4/0.6) °C respectively.

TABLE 3. ^{27}Al quadrupole coupling constants (*QCC*), R_1 and τ_c values for $EtAlCl_2$, $AlCl_4^-$ and $EtAlCl_3^-$

Melt molar composition ($AlCl_3$/MEICl/$EtAlCl_2$)	Temp. (°C)	R_1 (s^{-1})	τ_c (ns)	*QCC* (MHz)
0/0.5/0.5 [$EtAlCl_3^-$]	−50	454	2.04	0.486
	60	10.2	0.046	
0.25/0.4/0.35 [$EtAlCl_3^- + AlCl_4^-$]	−40	1121	2.04	0.762
	60	178	0.209	
0.35/0.4/0.25 [$EtAlCl_3^- + AlCl_4^-$]	−30	4484	2.04	1.52
	60	590	0.267	
0/0.5/0.5 $EtAlCl_2$ dimer	−15	48545	2.04	5.01
	60	4964	0.209	
0.5/0.5/0 [$AlCl_4^-$]	60	8.82	0.0022	0.821

The R_1 values at the temperature minima and the calculated values for *QCC* of ^{27}Al are contained in Table 3. These results may be compared with values of 0.82 and 2.10 MHz obtained for the 0.5/0.5/0 and $Na_{0.22}{}^{+}MEI_{0.78}{}^{+}AlCl_3$ melts using the DSP method [14, 15]. The observed decrease in *QCC* values from 2.10 to 0.82 MHz between the $Na_{0.22}{}^{+}MEI_{0.78}{}^{+}AlCl_3$ and 0.5/0.5/0 melts has been attributed to the distortion of tetrahedral symmetry ($AlCl_4^-$) caused by interaction between sodium ions and tetrachloroaluminate ions [15]. A similar decrease in *QCC* from 0.821 to 0.486 MHz between $AlCl_4^-$ and $EtAlCl_3^-$ suggests that the strong interactions between MEI^+ and $AlCl_4^-$ [13–15] do not exist between MEI^+ and $AlCl_3^-$.

Conclusions

In a previous study of the equimolar MEICl–$AlCl_3$ melt system [15] we observed a change in the ^{27}Al relaxation mechanism for the $AlCl_4^-$ peak at approx. 25–30 °C. The activation energies for the equimolar MEICl–$AlCl_3$ melt [15] are comparable to the equimolar MEICl–$EtAlCl_2$ melt, as they vary from 18.4 (0–40 °C) to 12.6 (40–70 °C) kJ. In view of the fact that only a single species is present at 103 ppm ($AlCl_4^-$ in ref. 15 or $EtAlCl_3^-$ in this study) in both equimolar melts, it is likely that the changes in relaxation mechanism indicate structural changes in the various complexes present in these two equimolar melts. Finally, we provide supporting evidence that the DSP method can be used (under appropriate conditions) to obtain reasonable values for quadrupolar coupling constants in the liquid state.

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References

1 J.S. Wilkes, J.A. Levisky, R.A. Wilson and C.L. Hussey, *Inorg. Chem., 21* (1982) 1263.
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. Am. 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. Auborn, *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 M. Lipsztajn and R.A. Osteryoung, *J. Electrochem. Soc., 13* (1983) 1968.
12 T.J. Metlon, J. Joyce, J.T. Maloy, J.A. Boon and J.S. Wilkes, *J. Electrochem. Soc., 137* (1990) 3865.
13 W.R. Carper, J.P. Pflug, A.M. Elias and J.S. Wilkes, *J. Phys. Chem., 96* (1992) 3828.
14 W.R. Carper, J.L. Pflug and J.S. Wilkes, *Inorg. Chim. Acta, 193* (1992) 201.
15 W.R. Carper, J.L. Pflug and J.S. Wilkes, *Inorg. Chim. Acta, 202* (1992) 89.
16 J.J. Dechter and U. Henriksson, *J. Magn. Reson., 48* (1982) 503.
17 B. Gilbert, Y. Chauvin and I. Guibard, *Vib. Spectrosc., 1* (1991) 299.
18 W.R. Carper, C.E. Keller, P.A. Shaw, M. Parrish and J.S. Wilkes, in *Eighth International Symposium on Molten Salts,* The Electrochemical Society, New York, 1992, p. 336.
19 A. Abragam, *Principles of Nuclear Magnetism,* Oxford University Press, Oxford, 1961, Ch. 8.
20 B. Lindman and S. Forsen, in P. Diehl and E. Fluck (eds.), *NMR Basic Principle and Progress,* Vol. 12, Springer, New York, 1976, p. 22.
21 C.E. Keller, W.R. Carper and B.J. Piersma, *Inorg. Chim. Acta, 209* (1993) 239.

22 J.L. Gray and G.E.J. Maciel, *Am. Chem. Soc., 103* (1981) 7147.

23 E.W. Lang, W. Fink, H. Radkowitsch and D. Girlich, *Ber. Bunsenges., Phys. Chem., 94* (1990) 342.

24 C.A. Angell, E.J. Sare, J. Donnella and D.R. MacFarlane, *J. Phys. Chem., 85* (1981) 1461.

25 I.M. Hodge, C.A. Angell, in D. Inman and D.G. Lovering (eds.), *Ionic Liquids,* Plenum, New York, 1981, p. 15.

26 D.B. Coffin and W.R. Carper, *Magn. Reson. Chem., 26* (1988) 591.

27 W.R. Carper and D.B. Coffin, *Inorg. Chim. Acta, 167* (1990) 261.

28 D.J. Birkett, R.A. Dwek, G.K. Radda, R.E. Richards and A.G. Salmon, *Eur. J. Biochem., 20* (1971) 494.

29 R.A. Dwek, G.K. Radda, R.E. Richards and A.G. Salmon, *Eur. J. Biochem., 29* (1972) 509.

30 B. Blicharska and A. Bula, *Z. Phys. Chem., N.F., 153* (1987) 565.

31 P.A. Shaw, W.R. Carper, C.E. Keller and J.S. Wilkes, *Bull. Magn. Reson., 14* (1992) 92.

32 C.L. Hussey, in G. Mamantov (ed.), *Advances in Molten Salt Chemistry,* Vol. 5, Elsevier, New York, 1983, p. 185.