Determination of Aluminium Electronegativity in New Ambient-temperature Acidic Molten Salts based on 3-Butyl-1-methylimidazolium Chloride and $AlEt_{3-x}Cl_x$ (x = 0–3) by ^1H Nuclear Magnetic Resonance Spectroscopy

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Aluminium electronegativity in molten salts based on 3-butyl-1-methylimidazolium chloride and $AlEtCl_2$, $AlEt_2Cl$, $AlEt_3$ and mixtures of $AlEtCl_2$ and $AlCl_3$ has been determined by the modified Dailey–Shoolery equation using ^1H NMR spectroscopy. For Al to 3-butyl-1-methylimidazolium chloride molar ratios between 1 : 1 and 3 : 1 there is a linear relationship between the aluminium electronegativity of the anionic species present in the melts and the molar composition.

The acid–base properties of room-temperature chloroaluminate melts composed of mixtures of aluminium trichloride with alkylpyridinium or alkylimidazolium chlorides are strongly dependent on the melt composition.[1,2] Basic melts are characterized by the presence of free chloride ions in appreciable concentration, whereas in acidic melts it has been demonstrated that aluminium trichloride in excess is present in the form of $[Al_2Cl_7]^-$ or $[Al_3Cl_{10}]^-$ anions; $[AlCl_4]^-$ is common to acidic and basic melts. However, relatively little research has been done on the quantitation of the acidic properties of these media.

Using ^{27}Al NMR spectroscopy, Gray and Maciel[3] found a dependence of the ^{27}Al linewidth on the composition of the salt. Later, it was shown by ^1H NMR spectroscopy that the chemical shifts of the protons of the imidazolium ring are strongly dependent on the $AlCl_3$ mole fraction, but as this method measures only long-distance effects (effect of the anions) the variations are important only in the basic domain.[4] Probe molecules sensitive to the Lewis basicity or acidity of the surrounding media have been used to determine the donor–acceptor properties of the molten salts. Thus, the UV spectral shift of Pb^{2+} ('optical basicity') has been used as an indicator for titration of the Cl^- base in $AlCl_3$–$NEtH_3Cl$ systems.[5] On the other hand IR and UV spectral shifts of organoiron complexes containing CO and CN ligands suggest a strong interaction of the donor atoms with $AlCl_3$ or Al_2Cl_6.[6] In a similar way, it has been demonstrated that there is a relationship between the ^{31}P NMR chemical shift of triethylphosphine oxide and the composition of the melt, but the method seems to be not very sensitive for low-acidity melts.[7] Lastly, the ^1H NMR resonance for the cyclopentadienyl (cp) protons in $[M(cp)Cl_2]$ (M = Ti, Zr or Hf) is shifted more downfield as the acidity of the melt is increased, indicative of removal of electron density from the complexes.[8]

Recently we have demonstrated[9,10] that, in a way similar to aluminium chloride, alkylaluminium dichloride ($AlRCl_2$) forms, in admixture with 3-butyl-1-methylimidazolium chloride (bmic) and some other quaternary ammonium or phosphonium chlorides, liquid salts at room temperature (and below) over a wide range of composition. As suspected previously[11] it has been shown by Raman spectroscopy that, in such salts, the ionic species are quite similar to those present in conventional aluminium halide-based molten salts.[9]

One advantage of alkylaluminium dichloride over aluminium trichloride-based molten salts is in that pure alkylaluminium dichloride is nearly liquid at room temperature, whereas aluminium trichloride melts at 195 °C. This enables the room-temperature liquid compositions to be extended over a wider range (from $AlRCl_2$: bmic = 0.5 : 1 to $AlRCl_2$ with a trace of bmic), making possible the investigation of the nature of the species present in the very-high-acidity domain. Another interesting property conferred by the alkyl group present on the aluminium atom is that the resulting salts can act both as solvents and alkylating agents for transition-metal complexes, which can be used as catalysts for various reactions.[10,12]

On the other hand the presence of an ethyl group on aluminium opens up a new way for the determination of aluminium electronegativity, the subject of the present paper, then of the acidity of these media, which is an important parameter in catalytic reactions.[10,12]

In their pioneering work, Dailey and Shoolery[13] found that for ethyl halides an empirical linear relationship exists between the electronegativity χ of the four halogens, computed on the basis of Huggins assumptions,[14] and the difference Δ in the ^1H NMR chemical shifts of the CH_2 and the CH_3 of the ethyl groups. Later[15] a similar linear relationship was found for the ethyl derivatives of elements with low electronegativity such as Zn, Ge, Si, Pb and Al for which equation (1) was proposed. This

$$\chi = 0.62\Delta + 2.07 \qquad (1)$$

relationship was determined for neat compounds but dilution does not significantly affect the results.

The complexing of a base, such as an ether, to triethyl-gallium or -aluminium decreases the electron-withdrawing ability of the metals and their apparent electronegativity.[16] This has been applied to the measurement of the Lewis acidity of triethylaluminium[17] and of ethylaluminium halide complexes.[18] We thought that this method could be useful in quantitating the aluminium electronegativity and then the acidity of room-temperature molten salts having various compositions, without modifying the medium. This paper describes the results obtained using molten salts based on bmic and ethylaluminium dichloride, new molten salts formed with diethylaluminium chloride and triethylaluminium, and mixed salts formed with $AlEtCl_2$ and aluminium trichloride.

Experimental

The compound bmic was synthesised as previously described,[2] $AlEtCl_2$, $AlEt_2Cl$ and $AlEt_3$ (Schering) were distilled before use and aluminium trichloride (Aldrich) was sublimed twice, first on aluminium turnings and sodium chloride then on sodium

Table 1 Chemical shifts (δ) for Al–Et

N	CH_2	CH_3	N	CH_2	CH_3
$AlEtCl_2$–bmic			$AlEt_2Cl$–bmic		
0.351	−0.340	0.704	0.408	−0.384	0.805
0.421	−0.325	0.709	0.489	−0.322	0.858
0.500	−0.282	0.732	0.549	−0.242	0.897
0.580	−0.115	0.788	0.600	−0.144	0.936
0.621	−0.070	0.815	0.670	−0.057	0.967
0.647	−0.030	0.813	0.731	0.040	1.010
0.667	−0.019	0.825	0.754	0.084	1.031
0.737	0.109	0.865	1.000	0.433	1.253
0.764	0.132	0.854			
0.865	0.275	0.904			
0.900	0.309	0.904	$AlEt_3$–bmic		
0.980	0.371	0.950	0.433	−0.321	1.004
1.000	0.382	0.960	0.500	−0.321	1.002
			0.550	−0.238	1.043
			0.610	−0.145	1.091
			0.667	−0.077	1.129
			0.749	0.111	1.193
			1.000	0.663	1.388

$AlEtCl_2 + AlCl_3$–bmic

$AlEtCl_2:AlCl_3 = 1:9$			$N_g = 0.621$		
N_g	CH_2	CH_3	$AlEtCl_2:AlCl_3$	CH_2	CH_3
0.449	−0.365	0.679	1:0	−0.070	0.815
0.571	−0.047	0.701	3:1	−0.028	0.783
0.621	−0.021	0.699	1:3	−0.008	0.724
0.670	0.060	0.698	1:9	−0.021	0.699
			5:95	−0.034	0.684

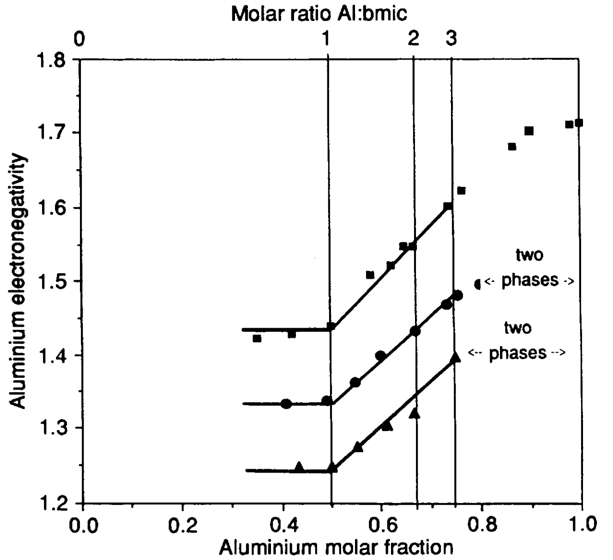

Fig. 1 Aluminium electronegativity as a function of aluminium molar ratio (N) in $AlEt_xCl_{3-x}$-bmic-based molten salts: x = 1 (■), 2 (●) and 3 (▲)

chloride. Molten salts were prepared in a glove-box filled with argon, by mixing the components at room temperature.

Proton NMR spectra were recorded with a Bruker Spectrospin AC200 spectrometer at room temperature or at 90 °C. Undiluted salts were introduced into a capillary tube (outside diameter 2 mm), which was placed inside a conventional 5 mm outside diameter tube containing a deuteriated compound (D_2O or CD_2Cl_2), thus avoiding any complexing effect of an added molecule. The chemical shifts of the ethyl group were measured at the centre line of the methyl triplet and the centre of the methylene quartet. The chemical shifts for the salts reported in Figs. 1–3 are given in Table 1. The points are experimental results without correction and the straight lines have been calculated by a linear combination of the chemical shifts of the two anionic species present for a given composition.

The composition of the melt is defined as the ratio, N, of the molar fraction of monomeric aluminium compounds introduced to the total number of molecules. In the case of mixtures (*e.g.* $AlCl_3 + AlEtCl_2$) this ratio will be written N_g.

Results and Discussion

Raman spectroscopic measurements[9] suggested that, in a similar way to aluminium trichloride-based molten salts, the dominant anionic species present in bmic–$AlEtCl_2$ melts are as follows: for $N < 0.5$, Cl^- and $[AlEtCl_3]^-$; $0.5 < N < 0.67$, $[AlEtCl_3]^-$ and $[Al_2Et_2Cl_5]^-$; $0.67 < N < 0.75$ $[Al_2Et_2Cl_5]^-$ and $[Al_3Et_3Cl_7]^-$. Whatever the composition of the melts may be, the ethyl groups display only two ^1H NMR resonances (a quartet for the CH_2, a triplet for the CH_3) the chemical shift of which depends on the composition.

In *basic melts* ($N < 0.5$), as expected, the chemical shifts are constant and do not depend on the excess of the quaternary salt (bmic). Thus the resonances can be assigned to the dominant species $[AlEtCl_3]^-$, the measured electronegativity of which is $\chi = 1.43$. In *acidic melts* ($N > 0.5$) the CH_2 resonance is shifted more upfield with increasing acidity, which corresponds to an expected increase in electron withdrawal. For $N = 0.67$ ($AlEtCl_2$: bmic = 2 : 1) and 0.75 (3 : 1) the chemical shifts can be assigned respectively to $[Al_2Et_2Cl_5]^-$ and $[Al_3Et_3Cl_7]^-$, the dominant anions. In the $0.5 < N < 0.75$ range of composition the chemical shifts are the average values of the chemical shifts of the two anionic species present for a given composition, owing to a rapid exchange (on the NMR time-scale). In this case, there is a linear relationship between the aluminium electronegativity and the melt composition (Fig. 1).

As the melts are made more acidic ($AlEtCl_2$: bmic > 3 : 1), Raman spectroscopy shows[19] that two main species are present in the melt, *i.e.* the $[Al_3Et_3Cl_7]^-$ anion and the $Al_2Et_2Cl_4$ molecular complex. When the molar fraction of $AlEtCl_2$ tends toward 1, the medium progressively loses its ionic nature, and as expected, the aluminium electronegativity of the mixture tends towards that of pure $AlEtCl_2$.

Pursuing our investigations in melts containing Al–Et bonds, we treated bmic with $AlEt_2Cl$ or $AlEt_3$. As for aluminium trichloride and $AlEtCl_2$, the reactions are exothermic and homogeneous stable clear liquids are obtained at room temperature in the range investigated (0.5 < Al : bmic < 3 : 1). Preliminary results of Raman spectroscopy[19] of $AlEt_2Cl$-based melts suggest that in the range of 1 < $AlEt_2Cl$: bmic < 2 : 1 the two main anionic species present are $[AlEt_2Cl_2]^-$ and $[Al_2Et_4Cl_3]^-$. As for the $AlEtCl_2$-based salts, we again observe, either for the $AlEt_2Cl$- or the $AlEt_3$-based melts, only two ^1H NMR resonances respectively for the CH_2 and the CH_3 group. The relationship between the aluminium electronegativity measured and the melt composition is linear (Fig. 1). Thus a similar behaviour can be inferred among $AlEtCl_2$-, $AlEt_2Cl$- and $AlEt_3$-based melts.

However, when the $AlEt_2Cl$: bmic and $AlEt_3$: bmic molar ratios are increased further (Al : bmic > 3 : 1) by adding the corresponding aluminium derivative, in both cases we observe the formation of a clear liquid upper phase which separates from the melts. These upper phases prove to be, respectively, pure $AlEt_2Cl$ and pure $AlEt_3$.[19] If a sufficient amount of bmic is added to the two-phase systems the upper phase disappears. Diethylaluminium chloride and $AlEt_3$, unlike $AlEtCl_2$, are little or not soluble in their corresponding polar phases. Molten salts are the first solvents to make a difference in solubility among the three alkylaluminium derivatives.

Although the modified Dailey–Shoolery relationship is obviously not suitable for the determination of the aluminium electronegativity of aluminium trichloride-based molten salts, it might be interesting to study the effect of the addition of

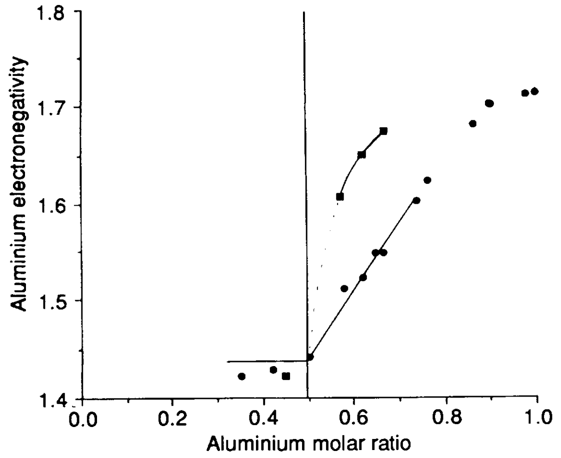

Fig. 2 Aluminium electronegativity as a function of aluminium molar ratio (N) in AlEtCl$_2$–bmic (●) and (AlEtCl$_2$ + AlCl$_3$)–bmic (■, AlEtCl$_2$: AlCl$_3$ = 1 : 9) based molten salts

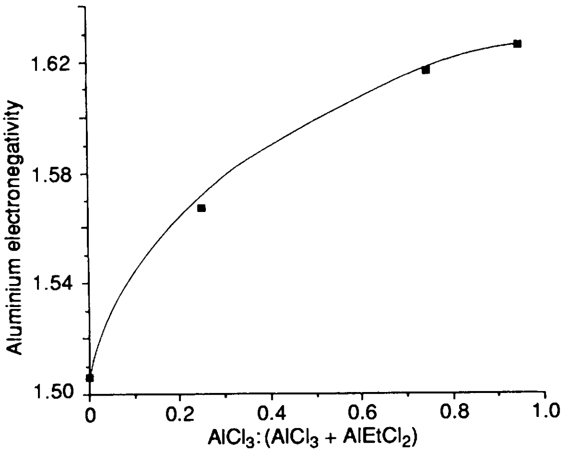

Fig. 3 Aluminium electronegativity as a function of AlCl$_3$: (AlCl$_3$ + AlEtCl$_2$) molar ratio in (AlEtCl$_2$ + AlCl$_3$) : bmic-based molten salts (N_g = 0.62)

aluminium chloride to AlEtCl$_2$-based melts. For this purpose we conducted two series of experiments. In the first the AlEtCl$_2$: AlCl$_3$ molar ratio was kept constant (and low enough, 0.1 : 1, to ensure the highest interaction between AlEtCl$_2$ and AlCl$_3$) and the AlEtCl$_2$ + AlCl$_3$: bmic molar ratio was varied. Conversely, in the second series of experiments the AlEtCl$_2$ + AlCl$_3$: bmic molar ratio was kept constant and the AlEtCl$_2$: AlCl$_3$ molar ratio was varied. The results are given in Figs. 2 and 3.

In basic melts the aluminium electronegativity of the mixed salts is constant and corresponds to the, already determined, aluminium electronegativity of [AlEtCl$_3$]$^-$. This confirms that even a large excess of [AlCl$_4$]$^-$ does not interact with [AlEtCl$_3$]$^-$. On the contrary, in acidic melts, the aluminium electronegativity of the mixed salts is always higher than that of the corresponding pure AlEtCl$_2$-based salt (for the same Al : bmic molar ratio). However, in this case, the relationship between aluminium electronegativity and mixed salt composition is no longer linear.

It is clear that some species more electronegative than the components present in the acidic AlEtCl$_2$-based melts, *i.e.* [Al$_2$Et$_2$Cl$_5$]$^-$ and [Al$_3$Et$_3$Cl$_7$]$^-$, were formed and that all these species are in equilibrium. We tentatively suggest the following formulas: [Al$_2$EtCl$_6$]$^-$ for $0.5 < N_g < 0.67$ salts and [Al$_3$EtCl$_9$]$^-$ or/and [Al$_3$Et$_2$Cl$_8$]$^-$ for $0.67 < N_g < 0.75$ salts. Thus for $0.5 < N_g < 0.67$ salts the aluminium electronegativity might result from an equilibrium (2) (see below) and an exchange (again only two single ^{1}H NMR resonances are displayed for the CH$_2$ and the CH$_3$ groups) among the three species, *i.e.* [AlEtCl$_3$]$^-$, [Al$_2$EtCl$_6$]$^-$ and [Al$_2$Et$_2$Cl$_5$]$^-$. For the mixed salts the limit seems to be the aluminium electronegativity of Al$_2$Et$_2$Cl$_4$, which is the most acidic species containing an Et group.

For an AlCl$_3$ + AlEtCl$_2$: bmic constant molar ratio (Fig. 3), the aluminium electronegativity of the mixed salts is all the higher as the AlCl$_3$: AlEtCl$_2$ molar ratio increases. This could be ascribed to the suspected equilibrium (2).

$$[\mathrm{Al_2Et_2Cl_5}]^- + [\mathrm{Al_2Cl_7}]^- \rightleftharpoons 2[\mathrm{Al_2EtCl_6}]^- \quad (2)$$

For these new salts, as for AlCl$_3$-based melts, the chemical shifts of the protons of the imidazolium ring are strongly dependent on the composition of the salts, but once more only in basic melts.

Conclusion

Proton NMR chemical shifts prove to be a valuable tool for the determination of the aluminium electronegativity of molten salts containing aluminium–ethyl bonds, at least in the acidic domain. Thus this method can be applied for the determination of the global Lewis acidity of alkylaluminium chloride-based salts.

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