ABSTRACT

Organochloroaluminate salts based on mixtures of (Ethyl)\textsubscript{n}AlCl\textsubscript{(3-n)} (n=1 to 3) with 1-methyl-3-butyl-imidazolium chloride (BMIC) are liquid near room temperature in a very large composition range. In the case of mixtures made with (Et\textsubscript{2}AlCl\textsubscript{2})\textsubscript{2} and (Et\textsubscript{3}Al)\textsubscript{2} demixion occurs above 0.75 mole fraction of the organoaluminium. The structural properties of all these mixtures have been studied by Raman spectroscopy and compared with the ones of classical chloroaluminate melts. They form mono and polynuclear anions and a whole new family of species has been identified. It was also found that the tendency to polymerize decreases with the increase of ethyl groups number. Because of the complexity of the spectra, the existence and the stoichiometry of the various species have been confirmed by a quantitative study of the bands intensity variation as a function of the composition.

INTRODUCTION

Mixtures of aluminium trichloride with organic chlorides have been shown to form liquids at room temperature over wide composition ranges (1-5). Recently, organic derivatives of aluminium trichloride have called the attention as presenting particularly interesting properties. For instance, ethylaluminium dichloride (EtAlCl\textsubscript{2}\textsubscript{2}) is a good reducing reagent capable of removing the proton impurities present in the room temperature chloroaluminate melts (6). Secondly, by mixing the organoaluminium chloride with an alkylpyridinium chloride or alkylimidazolium chloride, new molten salts are formed, also liquid at room temperature (7). These systems have been proved as very good solvents for the catalytic dimerization of propene into hexenes isomers by nickel complexes (8).

As it is the case for all chloroaluminate systems, the acid-base properties of the new mixtures are expected to be very depending on the composition, i.e. on the structure of the solvent. Initial structural studies have been made on the EtAlCl\textsubscript{2} - 1-butyl-3 methylimidazolium chloride (BMIC) mixtures. From Raman spectrometry, it was first proposed that monomer, dimer and trimer anions, analogous to those found in the usual chloroaluminates, are formed in the liquid (7). A recent study from \textsuperscript{27}Al NMR concluded...
also to the formation of anions but these anions are in equilibrium with an excess of EtAlCl₂ dimer, even in an equimolar composition mixture (9). This latter interpretation however is not in agreement with the Raman data neither with the recent measurements of the aluminium electronegativity by ¹H NMR (10).

Finally, these molten salts are good solvents for inorganic salts but do not dissolve hydrocarbons. They are consequently good candidates for a two-phase catalysis process where one can take advantage of the solubility of an organometallic catalyst and the insolubility of the products of the catalytic reaction. These products can then be extracted on a continuous basis. However, it has been known for a long time that contacting alkylaluminium chloride compounds with bases such as alkali metal halides (11) or ethers (12) results in disproportionation of the alkylaluminium into compounds containing more and less chloride. Similarly, due to the total miscibility of the chloroethylaluminium compounds and hydrocarbons, disproportionation could be expected when a molten salt based on dialkylimidazolium chloride and alkylaluminium chloride is contacted with an hydrocarbon. It is then very important to be able to characterize all the species involved in this process.

This paper describes the Raman spectra of mixtures made of (Ethyl)ₙAlCl₃.ₙ⁻ (n=0 to 3) mixed with BMIC as a function of their composition. The mixed salts formed with Al₂Cl₆ and (EtAlCl₂)₂ or (EtAlCl₂)₂ and (Et₂AlCl)₂ are also considered.

EXPERIMENTAL

All chemical manipulations were conducted in a glove box with a water and oxygen content below one ppm. The organic chlorides have been prepared as described previously (7). The 1-butyl-3-methylimidazolium chloride has been chosen instead of the more commonly used 1-ethyl-3-methylimidazolium chloride because its synthesis involves less hazard. The resulting solid is recrystallized from an acetonitrile-toluene mixture. Aluminium chloride was sublimed twice, first on aluminium powder and sodium chloride, then on sodium chloride. (EtAlCl₂)₂, (Et₂AlCl)₂ and (Et₃Al)₂ (Schering A.G.) were distilled in a vacuum tight apparatus before use.

The molten mixtures were prepared by weighing the required amounts of BMIC and the aluminium compound in a dry box. Upon mixing, the solids melt and a strongly exothermic reaction occurs. Only small amounts of melts were then prepared at one time (0.5-1 g) resulting in colorless solutions, stable for months.

The melts were placed into 1 cm square glass tubing cells which were sealed or closed with vacuum-tight grease free fittings. If necessary, the spectra of the melts could be recorded at higher temperature with a furnace similar to the one already described (13) but provided with a much better temperature controller (± 0.2 °C). The spectra were recorded with a modified Cary 81 spectrometer interfaced to a computer allowing fast recording rates and full data treatment (13). Slit widths from 2 to 4 cm⁻¹ and a time constant of 0.1 sec. were used depending on the bands intensities. No smoothing was applied to any of the spectra.
RESULTS AND DISCUSSION

When a pyridinium or imidazolium chloride is mixed with AlCl₃, it has been shown that the well-known AlCl₄⁻ and Al₂Cl₇⁻ anions are formed in equilibrium and their relative proportion depends on the melt composition (3). The Raman spectra of such mixtures are quite difficult to obtain because of fluorescence originating from organic impurities. However, by improving the purification of the starting materials, it is now possible to record good quality spectra on such systems. Fig. 1 shows the Raman spectrum of Al₂Cl₇⁻ which has never been published in details. In this spectrum, eleven bands (noted by a capital letter) can be assigned to Al₂Cl₇⁻, the other belonging either to the organic cation or to some AlCl₄⁻. Because only six bands are expected for a linear molecule (of D₃d symmetry), this result confirms that the anion must be bent, as already suggested (14). However, a non-linear molecule (symmetry Cₛ) is expected to present 21 Raman active modes and ten lines are then too weak or hidden by others. This emphasizes the difficulty of deducing a symmetry for a molecule simply by counting the number of experimental bands with their polarization state.

During our study of EtAlCl₂-BMIC mixtures, we have shown that another technique can be applied to deduce the stoichiometry of species in equilibrium (7). It involves the quantitative measurement of the intensity ratios of two bands, each characteristic of one species, as a function of the mixture composition. In the present case, this ratio has been measured for the 349 cm⁻¹ band of AlCl₄⁻ and the 307 cm⁻¹ band of Al₂Cl₇⁻ at various melt compositions (Fig. 2). If the model is correct, this ratio should be proportional to the ratio of the amounts of concerned species:

\[ R = \frac{I_{307}}{I_{349}} = K \left[ \frac{\text{Al}_2\text{Cl}_7^-}{\text{AlCl}_4^-} \right] \]

The ratios [Al₂Cl₇⁻]/[AlCl₄⁻] is readily calculated from the assumed stoichiometry and mass balance consideration. Fig. 3 shows a plot of the measured intensity ratios versus the respective calculated concentration ratios. A straight line is observed indicating that the model is indeed correct. In addition, the slope of that line represents the ratio of the scattering efficiencies of the species of concern. Here, the experimental ratio is 0.87 ± 0.02, which means that the main vibration of Al₂Cl₇⁻ scatters less per mole than the corresponding one of AlCl₄⁻.

In the case of EtAlCl₂-BMIC mixtures, a straight line was also observed in similar conditions, indicating that the reaction EtAlCl₃⁻ + EtAlCl₂ → Et₂AlCl₅⁻ is quantitative, at least up to a composition of 0.66 (expressed in mole fraction N) (7). It should be noted that this latter result and the recent aluminium electronegativity measurements (10) do not agree with the work of Keller et al. (9) where it is proposed that EtAlCl₂ dimer exists as major species even in a 1:1 melt. From our measurements, a 1:1 or more basic mixture never showed any of the very characteristic (EtAlCl₂)₂ bands. Fig. 4 shows that these two spectra are clearly distinct.
Because of their possible interest in the two-phase catalysis, the Et₂AlCl-BMIC and Et₃Al-BMIC mixtures which are also liquid at room temperature have been investigated as well. The spectra of 1:1 mixtures were found totally different than the ones of corresponding pure ethylaluminium compound (Fig. 5 and 6). In addition, if the amount of BMIC is further increased, the main spectrum stays unchanged, only the intensity of the BMI⁺ cation bands increases. We have then assumed that the AlCl₄⁻ equivalent species are formed, i.e. Et₂AlCl₂⁻ and Et₃AlCl⁻ respectively. These species are characterized by their main band at 366 and 492 cm⁻¹ respectively.

When Et₂AlCl is added to a 1:1 Et₂AlCl-BMIC mixture, the bands assigned to Et₂AlCl₂⁻ are progressively replaced by another distinct spectrum which is not the one of Et₂AlCl (Fig. 7). By analogy to the behaviour of the other above systems, this new species has been assumed as (Et₂AlCl)₂Cl⁻; it exhibits one major band at 410 cm⁻¹ and a weaker one at 366. In this case, the 366 cm⁻¹ band of (Et₂AlCl)₂Cl⁻ overlaps with the intense band of Et₂AlCl₂⁻. However, because the spectrum of Et₂AlCl₂⁻ can be obtained alone, it can be easily quantitatively subtracted from each spectrum of Fig. 7. The intensity ratio of all the resulting bands stays constant at any composition up to N= 0.67, a proof of the existence of only one additional species. The same quantitative procedure described above for AlCl₄⁻ has then been applied to the intensity ratios of the 410 cm⁻¹ band of the hypothetical (Et₂AlCl)₂Cl⁻ over the 366 cm⁻¹ band of Et₂AlCl₂⁻. A straight line is obtained between these ratios and the calculated amounts of species showing that the following reaction should occur:

$$(\text{Et}_2\text{AlCl})\text{Cl}^- + \text{Et}_2\text{AlCl} \rightarrow (\text{Et}_2\text{AlCl})_2\text{Cl}^-$$

Upon addition of Et₃Al to a 1:1 Et₃Al-BMIC mixture, the shape of the Et₃AlCl⁻ spectrum does not change very much except that the main 493 cm⁻¹ band intensity seems to increase. In order to solve this problem, we have added to each investigated mixture an internal intensity standard. This standard must be miscible, inert and should not exhibit any band in the region of interest. We then chose to refer all intensity measurements to the intensity of the 992 cm⁻¹ band of C₆H₆ whose concentration was kept constant in each mixture. Examples of such spectra are shown in Fig. 8 where it can be seen that the 493 cm⁻¹ band intensity increases regularly with the Et₃Al addition. We then proposed that this band is made of two components: one is the Et₃AlCl⁻ which decreases progressively and is replaced by the bridged (Et₃Al)₂Cl⁻. Again, the intensity ratios of the two components, obtained by computer, were found directly proportional to the expected amounts calculated from the reaction:

$$(\text{Et}_3\text{Al})\text{Cl}^- + \text{Et}_3\text{Al} \rightarrow (\text{Et}_3\text{Al})_2\text{Cl}^-$$

The above considerations are valid for compositions up to N=0.66. Above 0.66, it has been shown that the AlCl₃ based mixtures contain, in addition to AlCl₄⁻ and Al₂Cl₇⁻, Al₃Cl₁₀⁻ trimers. The composition range where the mixture stays liquid is however very limited (15-17). In the EtAlCl₂-BMIC mixtures, trimers are also formed but they are rapidly replaced by (EtAlCl₂)₂ which is miscible all the way up to pure (EtAlCl₂)₂ (7).
For the Et₂AlCl-BMIC and Et₃Al-BMIC mixtures where N>0.66, the spectra can be interpreted respectively as mixtures of (Et₂AlCl)₂Cl⁻ or (Et₃Al)₂Cl⁻ with (Et₂AlCl)₂ or (Et₃Al)₂. No trimer was found and demixion occurs at N=0.8 (Et₂AlCl) or N=0.75 (Et₃Al). The demixed phase is made of the corresponding pure ethylaluminium.

All these experiments have allowed to measure the scattering efficiencies within each couple (Ethyl)ₙAlCl⁻(3-n)Cl⁻ / ((Ethyl)ₙAlCl⁻(3-n)₂Cl⁻ (n=0 to 3). In order to determine the concentration of any such species involved in a reaction, it is necessary to measure the scattering efficiencies of the various couples versus each other. In this purpose, we have prepared mixed salts formed from Al₂Cl₆ and (EtAlCl₂)₂ or (EtAlCl₂)₂ and (Et₂AlCl)₂. Fig.9 shows the spectrum obtained by mixing a 0.5:0.5:1 AlCl₃-EtAlCl₂-BMIC mixture (spectrum A). This spectrum exhibits only the characteristic bands of AlCl₄⁻ and EtAlCl₃⁻ and no other species is observed. Consequently, the number of mole of each species must be the same and the ratio of scattering coefficients is simply the ratio of the heights of the respective ν₁ major bands. A similar experiment has been made with a 0.5:0.5:1 EtAlCl₂-Et₂AlCl-BMIC mixture to measure the relative scattering coefficients between EtAlCl₃⁻ and Et₂AlCl₂⁻. Finally, all the scattering coefficients have been expressed versus a common reference, the ν₁ AlCl₄⁻ band.

To complete this study, we have recorded the spectra of mixed acidic systems. First, an equimolar EtAlCl₂ and Et₂AlCl mixture of global Lewis acid composition N=0.66 exhibits a spectrum of its own (characterized by a main band at 366 cm⁻¹, Fig.10 A) which corresponds most probably to the mixed dimer (EtAlCl₂)(Et₂AlCl)Cl⁻. If this spectrum resembles the one of Et₂AlCl₂⁻, the confusion is not possible because several strong bands are present which do not belong to any known species up to now. Secondly, the equivalent mixture made from AlCl₃ and EtAlCl₂ is more complex (Fig. 10 B). From a detailed analysis of this figure, one can indeed recognize the main bands of Al₂Cl₇⁻ (307 cm⁻¹) and of (EtAlCl₂)₂⁻ (349 cm⁻¹). By subtracting these two spectra from the original, a third spectrum is left (main band at 333 cm⁻¹) which belongs to the mixed dimer (AlCl₃)(EtAlCl₂)Cl⁻. Hence, this dimer is not totally stable and dissociates through the following reaction:

\[ 2 \text{(AlCl₃)(EtAlCl₂)Cl⁻} \rightarrow \text{Al₂Cl₇⁻} + \text{(EtAlCl₂)₂⁻} \]

which also means that the association of EtAlCl₂ with AlCl₃ is not as strong as with Et₂AlCl.

As general conclusion, if our interpretations are correct, the ethylaluminium derivatives mixed with an organic chloride form a new class of ionic mixtures with a behaviour very similar to the one of regular chloroaluminates. All the identified species have been collected in table I as a function of the composition. In addition, it is now possible by Raman spectroscopy to identify and quantify any of the reaction products involved in an industrial process based on these melts. Because of the overlap of some of the major bands, this identification and quantification can be made safely by considering the full spectrum of one given species and not the main bands only.
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Table I: Species identified from the Raman spectra

| EADC = EtAlCl₂; DEAC = Et₂AlCl; TEA= Et₃Al |
|------------------------------------------|
| **Cl⁻**                                    | **AlCl₄⁻**                           | **Al₂Cl₇⁻**                           | **Al₃Cl₁₀⁻**                          | **Cl⁻**                                    |
| (EADC)Cl⁻                                   | (EADC₂)Cl⁻                           | (EADC₃)Cl⁻                           | (EADC₄)Cl⁻                            | (EADC)Cl⁻                                   |
| (DEAC)Cl⁻                                   | (DEAC₂)Cl⁻                           | (DEAC₃)Cl⁻                           | (DEAC₄)Cl⁻                            | (DEAC)Cl⁻                                   |
| (TEA)Cl⁻                                    | (TEA₂)Cl⁻                            | (TEA₃)Cl⁻                            | (TEA₄)Cl⁻                            | (TEA)Cl⁻                                    |

**MIXED SPECIES**

| (AlCl₃)(EADC)Cl⁻                           | (EADC)(DEAC)Cl⁻                       | (EADC)(DEAC)                           |

| Mole fraction of (Ethyl)ₙAlCl₃-(n) (n=0 to 3) |

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Fig. 1: Raman spectrum of the $\text{Al}_2\text{Cl}_7^-$ anion; capital letters: $\text{Al}_2\text{Cl}_7^-$; lowercase letters: organic cation (butyl pyridinium); greek letters: $\text{AlCl}_4^-$ and $\text{Al}_3\text{Cl}_{10}^-$. 

![Raman spectrum of the Al2Cl7- anion](image)

Fig. 2: Raman spectra of $\text{AlCl}_3$-BMIC mixtures at various compositions

N = respectively A: 0.475; B: 0.56; C: 0.582; D: 0.617; E: 0.639

![Raman spectra of AlCl3-BMIC mixtures](image)

Fig. 3: Plot of the $I_{367}/I_{349}$ ratio as a function of the $\text{Al}_2\text{Cl}_7/\text{AlCl}_4^-$ calculated ratio.

![Plot of the I367/I349 ratio](image)
Fig. 4: Raman spectra of A: pure \((\text{EtAlCl}_2)_2\)  
B: \(\text{EtAlCl}_2\)-BMIC 1:1 mixture

Fig. 5: Raman spectra of A: pure \((\text{Et}_2\text{AlCl})_2\)  
B: \(\text{Et}_2\text{AlCl}\)-BMIC 1:1 mixture

Fig. 6: Raman spectra of A: pure \((\text{Et}_3\text{Al})_2\)  
B: \(\text{Et}_3\text{Al}\)-BMIC 1:1 mixture

Fig. 7: Raman spectra of \(\text{Et}_2\text{AlCl}\)-BMIC mixtures at various compositions  
\(N = \) respectively: A: 0.495; B: 0.572; C: 0.631; D: 0.675
Fig. 8: Raman spectra of Et$_3$Al-BMIC mixtures with C$_6$H$_6$ as internal intensity standard:
N =: A: 0.5; B: 0.588; C: 0.649; D: 0.708
From 800 cm$^{-1}$, the sensitivity is reduced 5 times

Fig. 9: Raman spectra of:
A: AlCl$_3$-EtAlCl$_2$-BMIC 0.5:0.5:1
B: EtAlCl$_2$-BMIC 1:1
C: AlCl$_3$-BMIC 1:1

Fig. 10: Raman spectra of:
A: EtAlCl$_2$-Et$_2$AlCl-BMIC 1:1:1 mixture
B: AlCl$_3$-EtAlCl$_2$-BMIC 1:1:1 mixture