^{27}Al NMR Spectra of the $RECl_3$–$AlCl_3$ (RE = Y, La) Glasses and Melts

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^{27}Al NMR spectra of pure crystalline and molten $AlCl_3$ and of $RECl_3$–$AlCl_3$ (RE = Y, La) glass forming binary mixtures have been obtained. Compositions corresponding mainly to $YCl_3/AlCl_3 = 1/3$ and $LaCl_3/AlCl_3 = 1/3.7$ have been studied from the glassy and crystalline state up to the melt. The ^{27}Al spectra can be unambiguously assigned to four-coordinated Al-species, such as Al_2Cl_6, '$AlCl_4$', and 'Al_2Cl_7'. The chemical shifts lie between 95 and 110 ppm, very well separated with the −1.6 ppm given by the '$AlCl_6$' coordination in solid $AlCl_3$. From the temperature evolution of the ^{27}Al NMR spectra, a description for the dynamic behaviour of these systems is proposed.

Key words: ^{27}Al MAS NMR; $RECl_3$–$AlCl_3$; Glass Forming Melts; Structure; Dynamics.

1. Introduction

The formation of viscous liquids and glasses in rare earth chloride-aluminum chloride ($RECl_3$–$AlCl_3$: RE = Y, La, Nd, Gd, Ho) binary systems has recently been established, and vibrational Raman spectroscopy has been used in order to examine the structural properties and determine the glass forming composition ranges of these systems [1–3]. In the proposed structural models the main participating units are '$AlCl_4$' and in part 'Al_2Cl_7' [1–3], which are linked to the RE so as to satisfy its preferential coordination, being 8 or 9. At high temperatures and in dilute in $RECl_3$ melts, Al_2Cl_6 (l) is also present. In the case of the $GdCl_3$–$3AlCl_3$ glass and supercooled liquid, a Gd L_{III}-edge EXAFS spectroscopic study has further elucidated the short-range structure concerning the first and second coordination sphere around Gd^{3+} ions [2, 4], while from a relaxational study by means of Photon Correlation spectroscopy [2, 3, 5], it was concluded to classify it as a relatively 'fragile' glass.

These viscous, non volatile melts are extremely hygroscopic, corrosive at high temperatures and very difficult to prepare with high purity, but are very important for developing industrial separation and extraction processes [4, 5].

We have recently reported preliminary ^{27}Al NMR data for the rare earth chloride aluminum chloride binaries [2, 3]. Now we present ^{27}Al NMR measurements on pure crystalline and molten $AlCl_3$ and on $RECl_3$–$AlCl_3$ (RE = Y, La) systems with compositions corresponding mainly to $YCl_3/AlCl_3 = 1/3$ and $LaCl_3/AlCl_3 = 1/3.7$ in the liquid, glassy and crystalline states, in the temperature range 10 to 285 °C.

NMR spectroscopy of molten salts can provide information on their structure and dynamics, even if much of the detailed information present in a high resolution solid state NMR spectrum may be lost due to the rapid exchange among the species in the melt [8]. The classical spectrum in the liquid consists in a single, narrow line, the position of which is quantitatively determined by the weighted average of the frequencies of the exchanging species [9–11]. The existence of $[AlCl_4]^-$ with tetrahedral symmetry has been evidenced in different studies on alkali or organic cation based systems, and the ^{27}Al chemical shift has been reported between 100 and 105 ppm [12–17]. This appears not so evident for $[Al_2Cl_7]^-$, the existence of which has been proposed from the NMR linewidth evolution with composition and not in terms of a well defined chemical shift [13, 17–20].

In the present study we give structural information on the system, including the description of the solid (crystalline or glassy) structure, by Magic Angle Spinning (MAS) NMR. From the temperature evolution of the ^{27}Al NMR spectra of the liquids we suggest traits of the dynamic behaviour of these systems.

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2. Experimental

2.1. Purification of the Chemicals and Sample Preparation

Aluminum Chloride (Fluka/Pure Inc. >99%) was purified by repeated slow sublimation using a temperature gradient in pyrex tubes sealed under vacuum. Yttrium chloride was obtained by dissolution of yttrium oxide (Y_2O_3, Cerac co, 99.9%) in a slight excess of dilute hydrochloric acid, followed by dehydration of the produced hydrate. Anhydrous YCl_3 and $LaCl_3$ (Cerac/Pure, 99.9%) were purified by dynamic sublimation under high vacuum (10^{-5} – 10^{-8} Pa) at 800 and 900 °C, respectively.

The samples were prepared as described in [1–3]. The chemical compounds were put into quartz ampules and sealed under vacuum. Glasses were obtained by rapid cooling of the liquids with compositions corresponding mainly to $YCl_3/3AlCl_3$ and $LaCl_3/3.7AlCl_3$. Devitrification of the $YCl_3/3AlCl_3$ glass (annealing at 100 °C for 48 hours) gave a crystalline compound, which was presumably YAl_3Cl_{12} [21].

For the MAS NMR measurements, the solids were ground into powder in an argon-filled glove box with a water vapor content of less than 1 ppm and transferred into the NMR rotors, which were then tightly closed with a boron nitride cup. The temperature evolution of the ^{27}Al spectra in the melts has been obtained in *static* experiments, for which we used directly the quartz cells with no other manipulations.

2.2. NMR Experiments

All NMR spectra were recorded on a Bruker DSX 400 (9 Teslas) operating at 104.2 MHz for ^{27}Al. The MAS NMR spectra were collected using a Bruker double bearing 4 mm MAS probe, with spinning rates of about 14 kHz for the high resolution spectra of crystalline samples at room temperature, and 10 kHz for the glasses at 10 °C. Cooling below the ambient temperature was found to be necessary in order to avoid crystallization. The spectra obtained in the melts and their evolution with temperature were obtained on a Bruker static probe using a variable temperature unit.

Each spectrum has been acquired using a single sequence: pulse length of $\pi/16$, recycle delay of 0.5 s, spectral width of 500 000 kHz. In order to improve the signal to noise ratio, 512 signals were typically accumulated before Fourier transformation, except for the MAS spectra for which we have increased the number of scans up to 5500. Chemical shifts are reported in ppm from an aqueous 1M solution of $Al(NO_3)_3$ at room temperature, and are accurate to ±0.5 ppm. Temperature was controlled to within ±5 °C.

The ^{27}Al MAS NMR spectra are characteristic of quadrupolar nuclei ($I = 5/2$). The MAS spectra of the glasses consist in an asymmetric broad line corresponding to the central $\langle -1/2 \leftrightarrow 1/2 \rangle$ transition and spinning side bands arising from the outer $\langle \pm 3/2 \leftrightarrow \pm 1/2 \rangle$ transitions, while the $\langle \pm 5/2 \leftrightarrow \pm 3/2 \rangle$ transitions are too wide to be detected. The isotropic chemical shift and the quadrupolar coupling constant ($C_Q = e^2 q\, Q/h$) are calculated according to previously discussed protocols [11, 22]. In the liquids, the spectra consist of a unique and sharp Lorentzian line. The isotropic chemical shift is directly determined by the position of the line (δ_{iso}, in ppm). The linewidth is given in Hz.

3. Results and Discussion

3.1. $AlCl_3$

$AlCl_3$ in the solid state is an ionic crystal and exhibits a layer structure with octahedrally coordinated aluminum atoms in a close packed chlorine lattice [23]. At room temperature (RT), the ^{27}Al MAS spectrum of pure crystalline $AlCl_3$, shown in Fig. 1, consists in one contribution at –1.6 ppm, with a set of spinning side bands indicating a low but significant quadrupolar coupling constant (C_Q ~ 500 kHz). This chemical shift is assigned to the '$AlCl_6$' coordination and is in accordance with the ^{27}Al MAS NMR signal at –2 ppm obtained by Reich et al. [24].

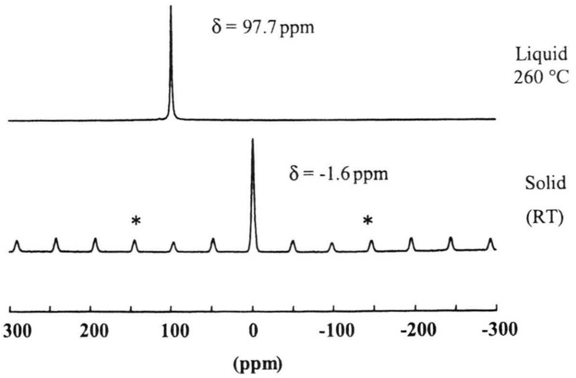

Fig. 1. ^{27}Al MAS NMR spectra of pure crystalline and molten aluminum trichloride. *: spinning side bands.

The ^{27}Al spectrum of molten aluminum trichloride at 260 °C (Fig. 1) consists of a signal Lorentzian line at 97.7 ppm, with a linewidth of 180 Hz. Similar spectra are obtained in the temperature range from 220 °C, a few degrees above the melting point (= 192.4 °C), up to 260 °C, and no change in the chemical shift or in the linewidth has been observed. The melt is composed by Al_2Cl_6 dimers having D_{2h} symmetry, in which two '$AlCl_4$' tetrahedra are connected via Cl–Cl edges, i.e. they share two common Cl atoms. The comparison of the two spectra in Fig. 1 shows the drastic structural changes occurring upon melting the $AlCl_3$ crystal to form the molecular liquid, and we can readily correlate the sharp line at 97.7 ppm with the four-coordinated Al in the Al_2Cl_6 dimers.

3.3. The YCl_3–$3AlCl_3$ and $LaCl_3$–$3.7AlCl_3$ Binary Systems

The ^{27}Al NMR spectra obtained for the binaries are much more complicated. Figure 2 shows the high resolution ^{27}Al MAS NMR spectra of the YCl_3–$3AlCl_3$ glass at 10 °C, the partially crystallized glass and the corresponding crystal at 25 °C, as well as the line obtained for the melt at 270°C.

The spectrum of the crystal (c), can be modeled with at least two contributions, distinguished mainly by their very different quadrupolar lineshapes. The more *visible* contribution is fitted with a chemical shift at 99.5 ppm and a quadrupolar coupling constant of 4.7 MHz, while a very broad second signal, corresponds to a C_Q of about 11 MHz and a chemical shift of 110 ppm. Because of the strong overlapping of the two contributions it is difficult to determine the isotropic chemical shift with high accuracy. In order to improve that determination, we have planned to perform more sophisticated NMR 2D experiments, such as MQMAS that is known to separate more easily such overlapped quadrupolar signals [25].

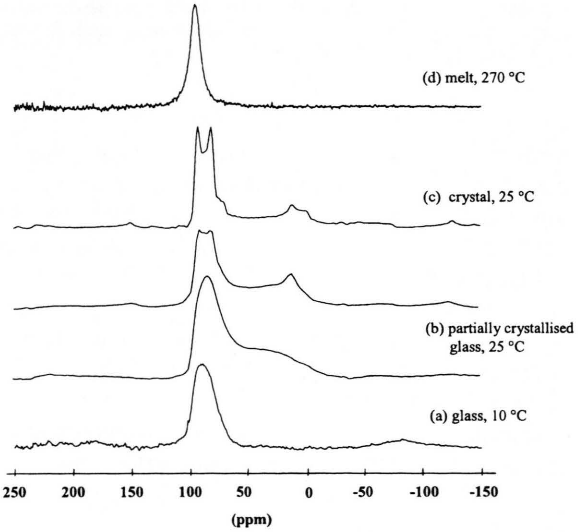

Fig. 2. ^{27}Al MAS NMR spectra obtained for the YCl_3–$3AlCl_3$ system.

YAl_3Cl_{12} crystal has a trigonal symmetry, space group: $P3_112$, $Z = 3$ [21], in which yttrium is surrounded by eight chlorines to form a square antiprism, edged linked with four '$AlCl_4$' tetrahedra, two of which are linked to the next 'YCl_8' polyhedron. Thus, the ^{27}Al MAS NMR signals can be attributed to the two kinds of '$AlCl_4$' tetrahedra ('terminal' and 'bridged') that exist in the crystal. As the terminal Al–Cl distances are much shorter than the bridging ones [21], we can assign the NMR contribution with the highest quadrupolar coupling constant, at 110 ppm, to the 'terminal'-type '$AlCl_4$' units which have two Cl bridged to Y, and two terminal.

The MAS spectrum of the YCl_3–$3AlCl_3$ glass at 10 °C (a) evidences a typical symmetric contribution at 101 ppm with a moderate quadrupolar coupling constant, $C_Q = 5.2$ MHz. This can be assigned unambiguously to aluminum tetrahedrally coordinated to chlorines.

We show on spectrum (b) the progressive crystallization of the glass at room temperature. The rotation of the sample at very high spinning rates in MAS conditions is responsible for a small temperature increase [26], sufficient to overheat the samples above the glass transition temperature, which seems to be close to 25 °C. We can observe first the emergence of a broad signal close to the principal peak. Then the quadrupolar line shapes become more precise and can be compared easily with those observed in the crystal.

In the melt at 270 °C (spectrum (c)), a single Lorentzian type line is obtained at 95.5 ppm, with a line width of 1100 Hz.

Decreasing temperature causes an increase in both chemical shift and linewidth. We have observed the melting of the crystalline compound at 230°. On cooling below this temperature the spectra of the supercooled liquid state have been recorded. At 190 °C, the chemical shift moves to 99.3 ppm and the line width becomes 5300 Hz.

On going from the crystal to the glass and liquid, the chemical shifts lie between 110 and 95 ppm. Since no drastic changes are noticed, it may be concluded that the 4-fold coordination of Al in the crystal is preserved in the amorphous phases.

The spectrum of the $LaCl_3$–$3.7AlCl_3$ glass is too noisy to be exploited. In the melt, a single Lorentzian-type line is also found. In the high temperature melt at 285 °C, the position of the peak is observed at 98.4 ppm with a line width of 2300 Hz, while at 215 °C, the chemical shift is observed at ≈ 103 ppm and the linewidth is ≈ 7900 Hz. The chemical shifts lie in the same range as for the YCl_3–$3AlCl_3$ system and can be assigned to aluminum tetrahedrally coordinated to chlorines.

The observed ^{27}Al NMR chemical shift and linewidth evolution with temperature for the YCl_3–$3AlCl_3$ and $LaCl_3$–$3.7AlCl_3$ melts during the heating and cooling process are presented in Figure 3. The same trend is noticed for the two systems.

We can see a linear evolution of the chemical shift with decreasing temperature in the high temperature range (continuous lines), and a clear increase at lower temperatures, when the points start to become quite dispersed. The linear fits of the high temperature range are extrapolated (dashed lines) to 10 °C towards the isotropic chemical shift measured for the tetrahedrally coordinated aluminum sites in the glass (at 101 ppm) for the YCl_3–$3AlCl_3$ system, and towards 107 ppm for the $LaCl_3$–$3.7AlCl_3$ system.

For pure Al_2Cl_6 (l) we haven't observed any change of the chemical shift with temperature. In that case, where no structural modification occurs in the melt, the contribution of pure thermal expansion can be supposed to be negligible. The negative slope $d\delta/dT \approx -2$ ppm/ 100 °C, calculated from the temperature evolution in the YCl_3–$3AlCl_3$ liquid, can be more probably due to a continuous structural evolution of the high temperature melt towards the frozen state in the glass. In the lanthanum system, the change with temperature is even sharper ($d\delta/dT \approx -3$ ppm/ 100 °C).

The line width evolution shows a continuous increase upon cooling, that can be associated to a higher viscosity. In the whole temperature range studied, the linewidths are large, much larger than the one found in pure Al_2Cl_6 (l). In addition, the ^{27}Al NMR signals obtained for the lanthanum system at various temperatures are much broader compared to the corresponding signals of the yttrium system. A possible explanation for this could be the difference in the chemical environment around aluminum for the two binary systems studied. The ^{27}Al spectra are assigned to four-coordinated Al-species. In the literature, the existence of 'Al_2Cl_7' species has already been confirmed by the NMR linewidth enlargement [13, 18–21]. From our data we can propose that the 'Al_2Cl_7' species are more abundant in the $LaCl_3$–$3.7AlCl_3$ system than in the YCl_3–$3AlCl_3$ system.

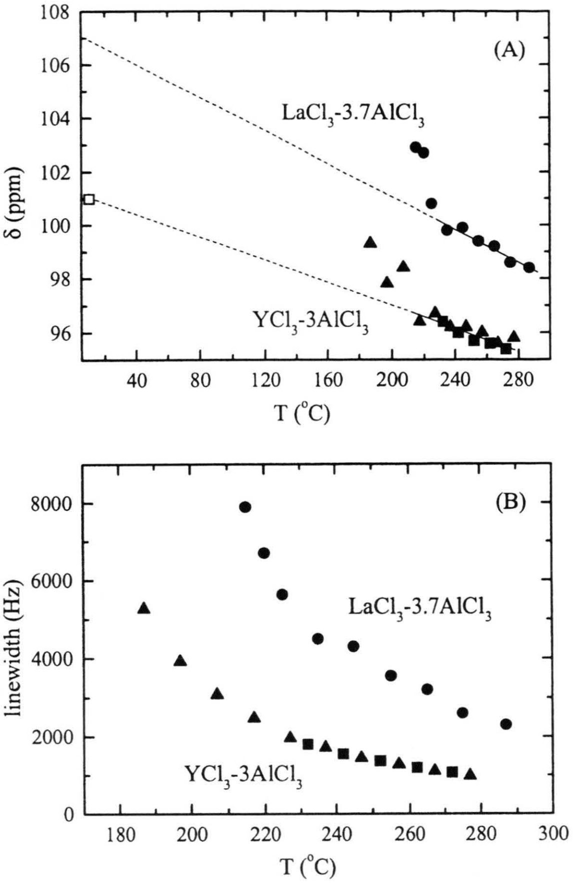

Fig. 3. ^{27}Al NMR chemical shift (A) and linewidth (B) evolution with temperature for the YCl_3–$3AlCl_3$ liquid while heating (■) and cooling (▲) and for the $LaCl_3$–$3.7AlCl_3$ liquid during cooling (●). □: chemical shift measured for the YCl_3–$3AlCl_3$ glass at 10 °C.

Raman spectra [2, 3] have shown that this is really the case. The data let propose that the '$AlCl_4$' species are the main participating units for both systems studied, while the 'Al_2Cl_7' Raman bands are more intense for the $LaCl_3$–$3.7AlCl_3$ binary.

Raman data also show that temperature-induced structural changes take place in the melts. This could probably further explain the ^{27}Al NMR spectral evolution with temperature.

We have started to measure the spin-lattice (T_1) and spin-spin (T_2) relaxation times at different temperatures.

In the high temperature range, the expression $1/\Delta\nu_{1/2} \approx T_1 \approx T_2$ is approached within experimental error bars for the liquids. Given also the Lorentzian shape of the resonance lines, we can conclude that the systems start to approach at high temperatures the fast exchange regime, where the ^{27}Al NMR linewidth gives the relaxation time of the ^{27}Al spin system [11].

We could thus extract two types of information from the NMR experiments: Average structural local information from the position of the line, δ_{iso}, as well as dynamic information from the relaxation time measurements. The experiments are planned to be extended to higher temperatures in order to estimate the NMR relaxation correlation times for the liquids [11].

4. Conclusions

Taking into account the similarities between the liquid, glassy and crystalline states, the evolution of the spectra with temperature, the differences between the systems studied, as well as literature data, we have assigned the ^{27}Al NMR MAS spectra of $RECl_3$–$AlCl_3$ (RE = Y, La) molten mixtures and glasses to different four-coordinated Al-species, such as '$AlCl_4$', '$AlCl_7$', and Al_2Cl_6, in consistency with the results of Raman spectroscopy.

The temperature dependence of the position and linewidth of the observed Lorentzian-shaped line in the liquids is correlated to the local structure evolution and the dynamics of the aluminum species in these melts. Further studies are in progress to extend the composition and temperature range in order to further elucidate the melt properties and the liquid/glass transition in these systems.

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