Articles

Study of NaF−AlF$_3$ Melts by High-Temperature ^{27}Al NMR Spectroscopy: Comparison with Results from Raman Spectroscopy

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The molten NaF−AlF$_3$ system has been studied by ^{27}Al NMR over the composition range $0.2 < X°(AlF_3) < 0.5$, using a high-temperature laser heating system. The experimental chemical shifts have been compared to the shifts calculated on the basis of a model obtained by the combination of Raman spectroscopy and thermodynamics results. This model involves three fluoroaluminate complexes (AlF_4^-, AlF_5^{2-}, AlF_6^{3-}). The agreement between experimental and calculated shifts strengthens the reliability of the suggested model.

Introduction

Because of their high industrial interest, cryolite-based melts have been studied for many years in order to obtain data for the aluminum electrolytic process.[1] However, a structural model consistent with all experimental data has proved to be very difficult to obtain and up to now, a full understanding of these melts has not yet been attained. Spectroscopic techniques are powerful tools to study the molten salts structure at the molecular level. In recent years, the use of Raman spectroscopy with a windowless cell allowed quantitative information to be obtained about the concentration of ionic complexes present in corrosive melts such as fluorides.[2−4] Recently, a reliable model was proposed, combining results from Raman spectroscopy and thermodynamic data.[5] This model involves three fluoroaluminate species (AlF_4^-, AlF_5^{2-}, AlF_6^{3-}) together with free fluoride ions F^-. These species are in equilibrium through the following reactions:

$$AlF_6^{3-} \rightleftharpoons AlF_5^{2-} + F^- \tag{1}$$

$$AlF_5^{2-} \rightleftharpoons AlF_4^{-} + F^- \tag{2}$$

The existence of major amounts of AlF_5^{2-} in this model seems to be a controversial issue. However, although several other possibilities were proposed, this model is the only one able to account for the Raman data in the MF−AlF$_3$ binary melts for the whole composition and temperature ranges.[5] In the KF−AlF$_3$ system, it gave very good results and even permitted the calculation of the liquidus line of the KF−K$_3$AlF$_6$ phase diagram.[6]

In solids and liquids, NMR spectroscopy can provide structural and dynamic information on the local atomic environment of the observed nucleus, through chemical shift and relaxation time.[7] In situ ^{27}Al NMR high-temperature experiments on liquid alumina bearing oxides concluded to the presence of several aluminum species,[8−11] in good agreement with MD simulations which indicated significant proportions of AlO$_5$ groups.

The ^{27}Al NMR spectrum observed for high-temperature liquid aluminates consists of a single narrow Lorentzian-shaped line due to motional averaging in the liquid. The observed ^{27}Al chemical shifts can be compared to the isotropic chemical shifts determined by ^{27}Al MAS NMR for different aluminum coordinations in crystalline and glassy phases[9]: AlO$_4$ [55−90 ppm], AlO$_5$ [30−40 ppm], and AlO$_6$ [−20 to 20 ppm]. The observation of a single Lorentzian line indicates that for a liquid consisting of aluminate polyhedra with different coordination numbers, chemical exchange between these species occurs at rates faster than the quadrupolar coupling constant (larger than several megahertz with the magnetic field used in this study). The observed peak maxima thus correspond to the average chemical shift of Al in the liquid.

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Stebbins et al.,[12] using a homemade high-temperature NMR probe combining boron nitride crucible and DC joule effect heating system, have reported ^{27}Al NMR results on cryolite-based melts but did not succeed in finding a satisfactory model. However, their fit, made on four different compositions only, was based on the assumption of an ideal mixture of the anions. We showed previously that this is not the case.[5] The authors themselves[12] emphasize that “^{27}Al NMR alone cannot be used to uniquely determine Al speciation in fully exchanging fluoride melts”.

We have recently published new ^{27}Al, ^{23}Na, and ^{19}F high-temperature NMR results on solid and molten cryolite (Na_3AlF_6) using a reliable high-temperature CO_2 laser heating system with boron nitride crucible.[13] At the melting point of cryolite (1010 °C), the increase of the ^{27}Al chemical shift from 4 to 19 ppm clearly indicates the decrease of aluminum coordination number. The ^{23}Na chemical shift (and thus the coordination number of sodium) remains constant ($\delta(^{23}\text{Na}) \approx -6$ ppm), and for fluorine a slight modification is observed through the jump of 10 ppm of its chemical shift.

Our ^{27}Al chemical value differs from the $\delta(^{27}\text{Al}) = 29$ ppm obtained by Stebbins et al.[12] This difference may be linked to the presence in their synthetic cryolite of an oxide impurity phase.

In this work, we report our ^{27}Al NMR results and compare them with the Raman data of Gilbert et al.[5]

Experimental Section

Preparation of the Samples. NaF (Merck, p.a.), cryolite (hand picked from Greenland) and AlF_3 (BDH, Fluortran) were dried under vacuum at 400 °C overnight. AlF_3 was purified by two sublimations at 1000 °C under vacuum in a graphite container. To avoid problems with oxide impurities, the mixtures were prepared in a drybox in which the water content was lower than 5 ppm. The required amounts of solids were first weighed and then crushed and mixed in an agate mortar. The powder was premelted under argon atmosphere in a glassy carbon crucible to ensure homogeneity.

NMR Spectra. For the high-temperature NMR experiments, 50−60 mg of powder was placed under argon in a high-purity boron nitride crucible (AX05 grade, Carborundum), whose airtightness was ensured by a screw cap. The compositions of the samples ranged between 20 and 50 mol % of AlF_3. The high-temperature NMR system has already been described elsewhere:[13,14] it consists of an axial probe modified to accept a boron nitride crucible (9 × 14 mm) that is irradiated by a continuous CO_2 laser ($\lambda = 10.6\ \mu$m). This CO_2 laser heating system allows us to record NMR spectra from room temperature up to 1500 °C. Experiments were carried out under argon atmosphere to avoid oxidation of the crucible. The copper radio frequency coil is protected from high temperature by a porous stabilized zirconia thermal shield. The electronics are cooled by an air flow at room temperature. As the temperature cannot be measured in situ during the NMR experiment, it has been calibrated in a separate experiment. Calibration is checked with the solid−liquid transition of the studied sample, clearly identified by NMR. The temperature accuracy can be estimated to ±10 °C.

All the ^{27}Al NMR spectra have been acquired with a Bruker DSX 300 (7T) NMR spectrometer ($\nu_0(^{27}\text{Al}) = 78.2$ MHz) and referenced to the ^{27}Al resonance in $Al(NO_3)_3$ (1 M) at room temperature. The peak positions accuracy is ±0.5 ppm. Each spectrum has been acquired using a single pulse sequence (pulse length of $\pi/16$, recycle delay of 1 s, spectral width of 40 kHz, and 32 scans). The spectra presented here have been acquired about 20 °C above the melting point of each sample.

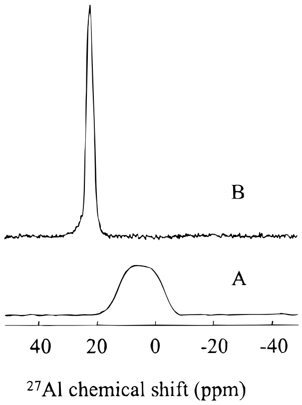

Figure 1. Temperature evolution of the ^{27}Al NMR spectrum for the cryolite (Na_3AlF_6) composition. (A) $T = 950$ °C; (B) $T = 1010$ °C.

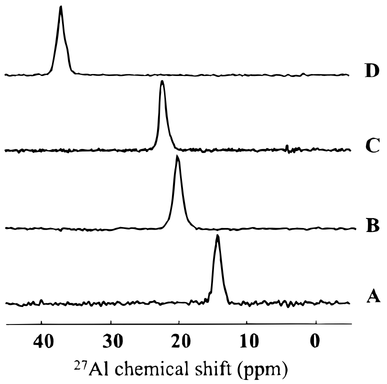

Figure 2. High-temperature ^{27}Al NMR spectra of different molten mixtures of NaF−AlF_3. (A) X°AlF_3 = 0.2, $T = 1000$ °C; (B) X°AlF_3 = 0.26, $T = 980$ °C; (C) X°AlF_3 = 0.33, $T = 960$ °C; (D) X°AlF_3 = 0.5, $T = 880$ °C.

Raman Spectra. The spectra have been recorded using the same procedure and experimental setup as reported earlier (2). An adjusted weight of the premelted material is introduced into a windowless graphite cell, which is contained in a quartz tube under argon atmosphere. The tube is then heated in a furnace specially designed for Raman measurements, allowing a temperature control and stability of ±5 °C. The graphite cells were degassed overnight under vacuum at 1000 °C before use. The spectra were recorded using a Spectra Physics model 2020 argon-ion laser (1 W 488.0 nm) and a modified Cary 81 spectrometer interfaced with a microcomputer, allowing fast recording rates. Slit width of 5 cm^{-1}, a time constant of 0.1 s, and a scan rate of 250 or 500 cm^{-1}/min were used for each spectrum.

Results and Discussion

Figure 1 shows the modification of the ^{27}Al NMR spectrum with temperature for the cryolite composition (Na_3AlF_6). The melting at 1010 °C is clearly marked by a strong decrease of the line width (from 1 kHz to ≈80 Hz) and a shift from 4 to 19 ppm for the chemical shift. In the liquid phase, the spectrum consists of a single, narrow, Lorentzian-shaped line because of the fast chemical exchange between the different species present in the melt.

Selected spectra obtained for different compositions are presented in Figure 2. Table 1 summarizes the compositions, chemical shifts, line widths, and recording temperatures for all the compositions investigated in this work. There is a clear shift of the line position from 14 ppm (at 20 mol % AlF_3) to 38 ppm (at 50 mol % AlF_3). For compositions between 25 and 40 mol % of AlF_3, the variations of the chemical shifts are rather small and the average value of this shift is ≈24 ppm. This composition range corresponds in the phase diagram of the NaF−AlF_3

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Table 1. Composition, Temperature, Experimental Chemical Shifts, and Line Width of ^{27}Al NMR Spectra in NaF−AlF$_3$ Melts

X°(AlF$_3$)	*T* (°C)	δ(^{27}Al) (ppm)	width (Hz)
0.5	880	37.8 ± 0.7	110
0.45	840	35 ± 0.4	60
0.4	790	27.6 ± 0.4	70
0.36	880	27.3 ± 0.4	70
0.33	960	22.1 ± 0.6	100
0.31	1000	21.3 ± 1.4	220
0.29	1000	20.8 ± 0.7	110
0.28	1000	21.2 ± 1.3	210
0.26	980	20.9 ± 0.8	120
0.25	1010	18.8 ± 1.1	180
0.22	1000	17.1 ± 0.8	130
0.2	1000	14.2 ± 0.6	100

binary,[15] to the region between the cryolite and the chiolite (Na$_3$Al$_5$F$_{14}$) compositions. The shift of line position toward higher values when increasing the amount of AlF$_3$ can be correlated with a lowering of the average coordination of Al with F. The stability of the ^{27}Al chemical shifts indicates that the *average* coordination of aluminum nuclei does not vary very much in these melts. The increase of chemical shifts observed for higher content of AlF$_3$ (>40 mol %) shows again a lowering of the average coordination.

The observed position of the peak is the average of the chemical shifts of all aluminum containing species present in the melts, weighted by their molar abundance:

$$\delta_{\mathrm{obs}} = \Sigma_i x_i\, \delta_i \tag{3}$$

x_i and δ_i are the ionic fraction and the chemical shift of the *i*th species:

$$x_i = \frac{n_i}{\Sigma n_i} \tag{4}$$

If we suppose, as suggested by Gilbert et al.,[5] the existence of the three aluminate coordinations in the liquid (IV, V, and VI) respectively referred to the subscripts 4, 5, and 6, the observed average chemical shift is thus expressed by:

$$\delta_{\mathrm{obs}} = x_4\delta_4 + x_5\delta_5 + x_6\delta_6 \tag{3$'$}$$

Unfortunately, little information is available on ^{27}Al chemical shifts for Al nuclei in fluoride environments, except for "AlF$_6$" groups in crystalline phases. The ^{27}Al chemical shifts range that we have measured in solid fluorine compounds (Al in octahedral sites) extends from 4 to −15 ppm. Herron *et al.*[16] measured a chemical shift of 49.2 ppm for Al in an organic cation salt of tetrafluoroaluminate, and attributed this shift to a tetrahedral AlF$_4^-$ species in solution.

To go further and to propose a more quantitative view of these melts, by mean of species distribution, we have to determine first, the ^{27}Al chemical shifts for the four- and five-coordinated Al sites.

^{27}Al Chemical Shift in AlF$_6^{3-}$. For the ^{27}Al chemical shift of AlF$_6^{3-}$, we chose the value measured in solid cryolite at 900 °C, where the coordination number of aluminum is 6: $\delta_6 = 4$ ppm.[13]

^{27}Al Chemical Shift in AlF$_4^-$. The Raman spectrum of an equimolar mixture of NaF and AlF$_3$ consists of four bands as predicted by group theory for a tetrahedral species. An extensive study of the different NaAlX$_4$ melts (X = F, Cl, Br) concluded that for this composition, AlX$_4^-$ is the only complex present in the liquid.[17] The Raman spectrum of NaAlF$_4$ is shown in Figure 3A. We have thus measured the ^{27}Al chemical shift of AlF$_4^-$ for the NaAlF$_4$ composition, X°(AlF$_3$) = 0.5, at 880 °C: δ_4 = 38 ppm.

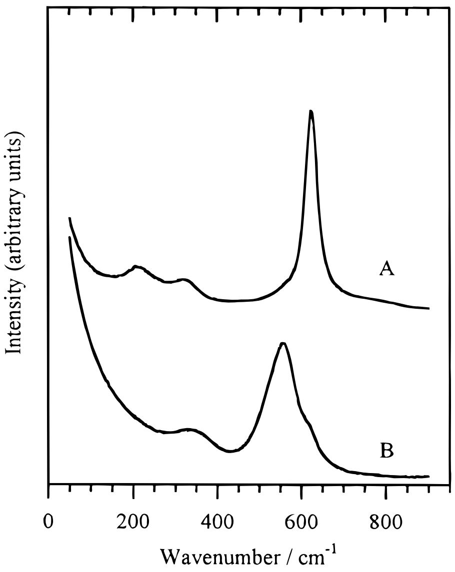

Figure 3. (A) Raman spectrum of molten NaAlF$_4$, *T* = 900 °C. (B) Raman spectrum of molten cryolite (Na$_3$AlF$_6$), *T* = 1020 °C.

^{27}Al Chemical Shift in AlF$_5^{2-}$. As it is done in oxide media,[11] we assume for the ^{27}Al chemical shift of AlF$_5^{2-}$(δ_5), an average value between δ_6 and δ_4, i.e., δ_5 = 21 ppm. This value is in good agreement with that proposed by Kohn *et al.*[18] in a jadeite glass doped with cryolite.

We have chosen to correlate the ^{27}Al experimental chemical shifts with those calculated from the distribution of the AlF$_4^-$, AlF$_5^{2-}$, and AlF$_6^{3-}$ complexes previously reported by Gilbert et al..[5] We used the values of the stoichiometric constants proposed before[5] for reactions 1 and 2 to calculate n(AlF$_4^-$), n(AlF$_5^{2-}$), and n(AlF$_6^{3-}$), where *n* is a number of moles.

Using these Raman-based values, NMR chemical shifts have been calculated using relation 3′, with δ_4 = 38 ppm, δ_5 = 21 ppm, and δ_6 = 4 ppm. The calculated and experimental chemical shifts are reported in Figure 4. The agreement between the two sets of data is very good. It validates the concentrations of the three species proposed from the Raman spectra, and also the coherence of this model.

A Remark about the (AlF$_4^-$, AlF$_6^{3-}$) Model. In this model, only the two species AlF$_4^-$ and AlF$_6^{3-}$ are supposed to be present in the melts. Then, the relation 3 would be expressed by

$$\delta = x_4\delta_4 + x_6\delta_6 \tag{3$''$}$$

with δ_4 = 38 ppm and δ_6 = 4 ppm.

The aluminum conservation implies

$$x_4 + x_6 = 1 \tag{5}$$

From the ^{27}Al chemical shift, we can thus calculate the abundance of AlF$_4^-$ and AlF$_6^{3-}$. As a consequence, the chemical shift observed for molten cryolite (19 ppm) would imply that,

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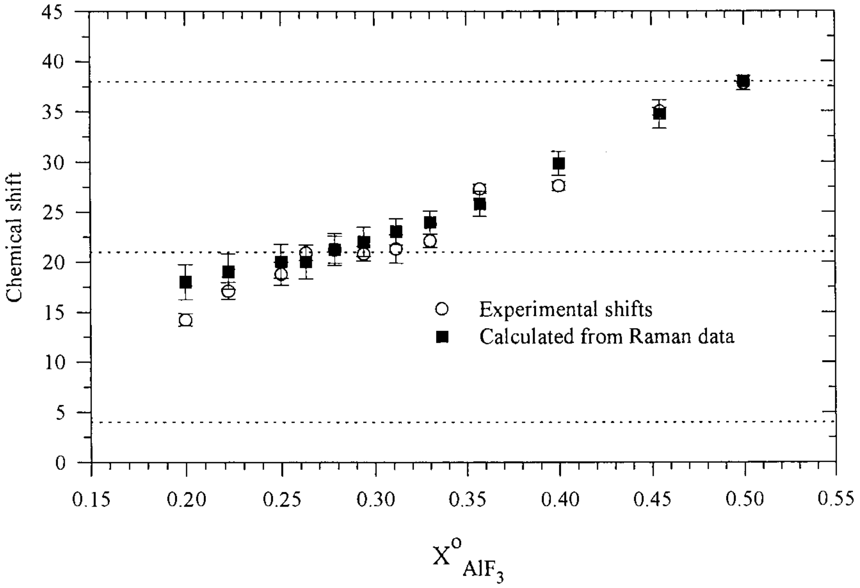

Figure 4. Comparison between the ^{27}Al chemical shifts measured and calculated from the Raman model.

at this composition, $x_4 = 0.47$ and $x_6 = 0.53$. It is obvious from the Raman spectrum of molten cryolite (Figure 3B), that the amount of AlF_4^- is small relative to the other species, whatever they are. Moreover, among the different models proposed through the years,[1,19] none proposed such a huge dissociation of AlF_6^{3-} into AlF_4^-. For the AlF_4^-−AlF_6^{3-} models, the generally accepted dissociation coefficient for the AlF_6^{3-} ion is around 0.3 (i.e., $x_4 = 0.3$ and $x_6 = 0.7$). The experimental ^{27}Al chemical shift measured in molten cryolite *does not account* for the concentrations proposed in such two-species models.

Conclusion

The model that gives the best results in the interpretation of NMR results over the whole composition range, while staying consistent with other type of measurements (i.e., thermodynamic methods), is the three-species model proposed by Gilbert et al.[5]

This study illustrates once more, that the combination of several techniques enables us to get reliable structural information. Using only one technique can be misleading, especially in these very complicated fluoride media. The results obtained here strengthen the reliability of the three species Raman model (AlF_4^-, AlF_5^{2-}, and AlF_6^{3-}) and its ability to describe the different properties of fluoroaluminate melts.

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