Journal of Fluorine Chemistry 165 (2014) 116–122

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

MAS NMR study of the solidified cryolite systems with FeO addition

František Šimko [a,*], Aydar Rakhmatullin [b], Catherine Bessada [b], Miroslav Boča [a]

[a] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia
[b] Conditions Extrêmes et Matériaux: Haute Température et Irradiation CNRS, 1D av. de la Recherche Scientifique, 450 71 Orléans, France

ARTICLE INFO

Article history:
Received 24 April 2014
Received in revised form 19 June 2014
Accepted 21 June 2014
Available online 28 June 2014

Keywords:
MAS NMR
Fluorido-oxido-aluminates
FeO
Cryolite
Chiolite

ABSTRACT

Unexpected results were obtained during investigation of the chemical processes between cryolite (Na_3AlF_6) and FeO by multinuclear ^{27}Al, ^{23}Na and ^{19}F MAS NMR spectroscopy in the system with different amount of FeO; $(1-x)Na_3AlF_6$–xFeO ($x = 0.00, 0.05, 0.10, 0.14$). Surprisingly, no reactions products are present in solidified fractions of samples after melting. NMR data of all the bulks proved the presence only of non-reacted cryolite and NaF, which is the product of known partial cryolite dissociation reaction. No FeO containing phases or other phases containing iron are present in the bulk of analyzed samples. On other hand all reaction products were identified in the condensed vapours that escape from the melts at reaction conditions. Two volatile (high temperature and low temperature) fractions were separated. In the high temperature condensate the presence of AlF_3, $Na_5Al_3F_{14}$, cryolite and Al_2O_3 was evidenced. The presence of AlF_3 and $Na_5Al_3F_{14}$ phases arises from decomposition of the vaporized $NaAlF_4$ phase. The presence of Na_3AlF_6 and Al_2O_3 in condensed high temperature vapours seems to be ground-breaking result. The presence of these two phases was explained by the sequence of processes when at the beginning FeO was dissolved in cryolite, then oxygen was bounded to aluminium forming some fluorido-oxido-aluminates that are volatiles and during condensation they decompose to Na_3AlF_6 and Al_2O_3. Phases with remaining iron were identified in the low temperature condensed vapours.

1. Introduction

Interactions of cryolite (Na_3AlF_6) with other phases are in the centre of interest many decades because of their essential role in aluminium production. Even many experimental and theoretical techniques were applied the exact mechanisms of these interactions are frequently still not satisfactory established. A significant part of published data deals with interaction of cryolite with alumina (Al_2O_3) and more or less successful proof of fluorido-oxido-aluminates (according to IUPAC nomenclature) existence (it should be noted that in older literature terms such as oxo-fluoro-, oxy-fluoro- or oxy-fluoride-aluminates can also be found) [1–15]. NMR experiments proved the ability to give a selective view on the alumina dissolution in molten cryolite by the direct signature of the fluoride-oxido-complexes using ^{17}O and ^{27}Al NMR. At least two different fluorido-oxido-aluminate species: $Al_2OF_6^{2-}$, at low alumina content, and $Al_2O_2F_4^{2-}$, that becomes the major species for higher amount of alumina were confirmed by the ^{17}O and ^{27}Al NMR signals evolution in good agreement with Raman data published by Gilbert et al. [14,15]. On cooling, these fluorido-oxido-aluminate species decomposed into a mixture of cryolite and alumina and cannot be stabilized at room temperature.

In aluminium electrolysis another important point to consider is the reaction of cryolite with impurities introduced in the system from different technical flows or operations. Iron compounds may influence the current efficiency and the metal quality, since they have lower decomposition potential than alumina [16]. A better understanding of FeO solubility in cryolite melts is of primary importance to understand also corrosion mechanisms [12,17–21]. The purpose of the present work is to describe the mechanism of dissolution of iron oxide in cryolite-based melts by ^{27}Al, ^{23}Na and ^{19}F solid state NMR study of Na_3AlF_6–FeO binary system. The combination of information obtained from NMR spectra of the different nuclei present in these high-temperature melts enables us to discuss previously proposed models and to give the first experimental evidence of the presence of new species originated from dissolution of FeO.

---

* Corresponding author. Tel.: +421 2 59410495; fax: +421 2 59410444.
E-mail addresses: uachsim@savba.sk, Frantisek.Simko@savba.sk (F. Šimko).

http://dx.doi.org/10.1016/j.jfluchem.2014.06.018
0022-1139/© 2014 Elsevier B.V. All rights reserved.

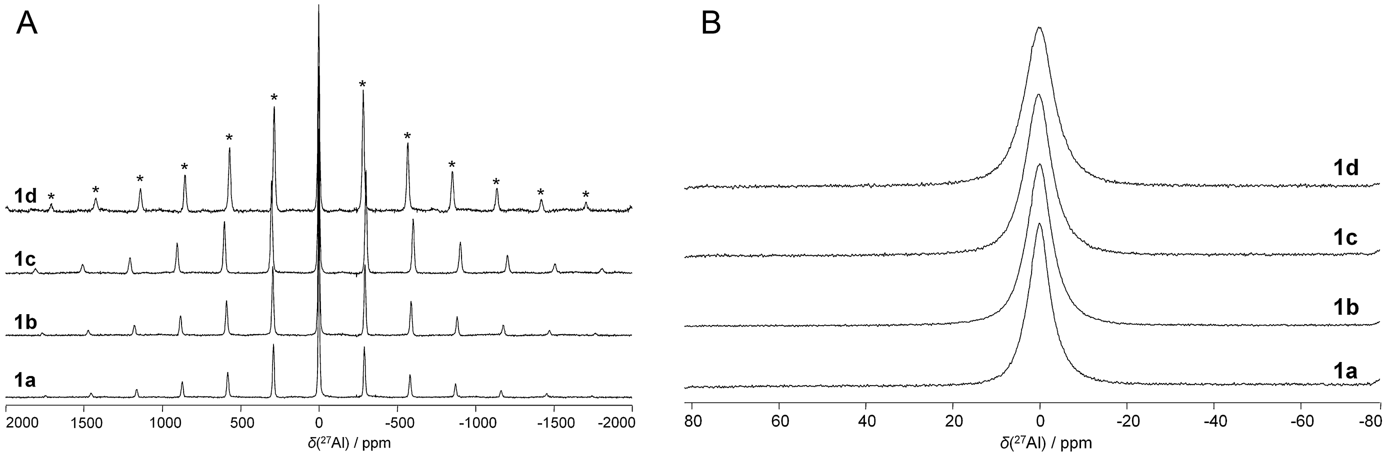

Fig. 1. ^{27}Al MAS spectra of solidified mixture of cryolite with various amount of FeO; (A-left) complete spectrum, (B-right) central part; (**1a**) 0 mol% FeO, (**1b**) 5 mol% FeO, (**1c**) 10 mol% FeO, (**1d**) 14 mol%; * – sidebands (indicated only for **1d** for clarity).

2. Results and discussion

This paper is continuation of previous experiments where the main intention was to characterize the melt of the system Na_3AlF_6–FeO and by high temperature NMR estimate the components formation [13,22]. After experiments the melts were rapidly solidified and then characterized by multinuclear (^{27}Al, ^{23}Na, and ^{19}F) high resolution solid state NMR spectroscopy. ^{27}Al MAS NMR spectra of solidified $(1-x)Na_3AlF_6$–xFeO compositions ($x = 0.00$, 0.05, 0.1, 0.14 – samples **1a**, **1b**, **1c** and **1d**, respectively) are shown in Fig. 1.

All spectra are composed of only one single narrow central peak with a set of sidebands due to magic angle spinning and corresponding to small quadrupolar interaction ($\nu_Q \approx 0.9 \pm 0.2$ MHz). The central line position is around $\delta(^{27}Al) \approx 0.0 \pm 0.7$ ppm for all the compositions (see Table 1). The chemical shift value can be attributed to six fold coordinated aluminium atoms in cryolite [23–27]. The intensity of spinning side bands increases correspondingly to the increase of the chemical shift anisotropy, with increasing amount of FeO in the initial mixture. Quadrupolar constant has slightly bigger to those in a literature report [13,25–27,31,35] values due to distortion of the local environment of the aluminium atoms. The quality and the resolution of obtained signals, whatever the FeO content, excludes the presence of paramagnetic species of high spin state iron in FeO. Low spin state can be excluded as this can be reached only after treatment at high pressure [28]. We can deduce from these observation that on melting FeO reacted with cryolite and Fe(II)-containing species evaporated from the melt. The evolution of the chemical shift anisotropy can be attributed to the presence of Fe(III)-containing species not volatile, resulting from Fe(II) oxidation. In previous paper, HT NMR ^{27}Al signal was detectable only after 14 min after 10 mol% of FeO was added to cryolite at 1000 °C. The signal initially perturbed by the paramagnetic Fe(II) containing species was then obtained in a few seconds [13].

The absence of any other signal/s of ^{27}Al seems to be surprising. Based on the investigation reports of the cryolite–M_xO_y ($M = Al^{3+}$, Fe^{3+}, Ni^{2+}, Fe^{2+}, etc.) [9,12,14,29,30] systems, it is expected that when oxygen containing compound is mixed with cryolite, melted and cooled the result will be the stable solid-state mixture that contains aluminium atoms surrounded by oxygen atoms in some way in any case. It is probably due to strong affinity of aluminium to oxygen. The dissolution of Fe_2O_3 in cryolite suggested that dissolved oxygen ions ("O^{2-}") seem to form stable $Na_2Al_2OF_6$, $Na_6Al_2OF_{10}$ and $Na_2Al_2O_2F_4$ compounds [9]. The investigation of the solubility of M(II) (M = Fe, Ni) indicated that MO dissolve into the melt provide Al_2O_3 and MF_2 species. These fluoride species may be associated with sodium fluoride in the form $Na_xMF_{(2+x)}$ [29]. In the well-known system Na_3AlF_6–Al_2O_3, MAS NMR spectra of solidified mixtures showed always more than one aluminium signal. These are at $\delta(^{27}Al) = 14$ ppm and at $\delta(^{27}Al) = 50$–70 ppm, they correspond to $\{AlO_6\}$ and $\{AlO_4\}$ environments in the solid

Table 1
^{27}Al, ^{23}Na, and ^{19}F chemical shifts (±0.2 ppm), quadrupolar constants ($\nu_Q \approx 0.1$ MHz) and line widths (full width at half-maximum: fwhm) at room temperature for samples **1a**, **1b**, **1c** and **1d**.

Sample	Compound	^{27}Al			^{23}Na			^{19}F		
		Site	δ_{iso} (ppm)	ν_Q (MHz)	Site	δ_{iso} (ppm)	ν_Q (MHz)	Site	δ_{iso} (ppm)	fwhm (kHz)
1a	Na_3AlF_6	$\{AlF_6\}$	−0.5	0.8	$\{NaF_6\}$	1.4	0.3	$\{AlF_6\}$	−190.4	1.7
	Na_3AlF_6				$\{NaF_8\}$	−10.4	0.7			
	NaF				$\{NaF_6\}$	7.2	0.3	$\{NaF_6\}$	−224.1	1.5
1b	Na_3AlF_6	$\{AlF_6\}$	−0.1	0.9	$\{NaF_6\}$	1.8	0.4	$\{AlF_6\}$	−189.7	1.9
	Na_3AlF_6				$\{NaF_8\}$	−10.4	0.8			
	NaF				$\{NaF_6\}$	7.5	0.5	$\{NaF_6\}$	−224.8	1.5
1c	Na_3AlF_6	$\{AlF_6\}$	0.5	1.0	$\{NaF_6\}$	2.5	0.5	$\{AlF_6\}$	−189.1	2.3
	Na_3AlF_6				$\{NaF_8\}$	−10.9	0.8			
	NaF				$\{NaF_6\}$	7.2	0.8	$\{NaF_6\}$	−224.6	1.6
1d	Na_3AlF_6	$\{AlF_6\}$	0.7	1.1	$\{NaF_6\}$	2.7	0.5	$\{AlF_6\}$	−189.3	2.3
	Na_3AlF_6				$\{NaF_8\}$	−10.9	0.9			
	NaF				$\{NaF_6\}$	7.5	0.8	$\{NaF_6\}$	−224.6	1.6