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Evidence of dynamical local scale distribution heterogeneities in CsF-AF (A=Li, Na, K and Rb) molten salts

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Highlights :

- Anomaly of the ^{133}Cs NMR chemical shift evolution versus composition in the CsF-AF series
- Liquid structure at nanoscale of molten CsF-LiF mixture differs from the series of other alkaline CsF-AF
- ^{133}Cs NMR chemical shift evidences dynamical local scale distribution heterogeneities

The local structure of molten CsF-AF (A=Li, Na, K and Rb) have been studied by high temperature Nuclear Magnetic Resonance (NMR) spectroscopy. The ^{19}F and ^{133}Cs chemical versus the molar fraction of CsF presents an anomaly in the series of the alkaline. The evolutions of ^{19}F and ^{133}Cs chemical shifts versus CsF-AF composition have been interpreted as a signature of dynamical local scale distribution heterogeneities.

Abstract

The local structure of molten CsF-AF (A=Li, Na, K and Rb) have been studied by high temperature Nuclear Magnetic Resonance (NMR) spectroscopy. The ^{19}F and ^{133}Cs chemical shifts have been measured as a function of the molar fraction of CsF. ^{19}F chemical shift varies linearly with composition while ^{133}Cs chemical shift present a break around the eutectics composition. Furthermore, in molten CsF-LiF at high CsF concentration, ^{133}Cs chemical shift is nearly constant. The evolutions of ^{19}F and ^{133}Cs chemical shifts versus CsF-AF composition have been interpreted as a signature of dynamical local scale distribution heterogeneities.

Keywords: molten alkali fluoride, molten salt, High temperature NMR, chemical shift

1. Introduction

Molten salts are unique solvent involved in many domains:¹ geoscience, energy (fuel cell,² nuclear energy,³ battery,^{4,5} solar technology^{6,7,8}...), wastes treatment, materials synthesis,^{9,10} metallurgy^{11,12}... Molten fluorides main applications under development concern the nuclear energy in many aspects,^{1,3} from the waste treatment^{13,14,15} up to the molten salt nuclear reactor (one of the six reactor concepts of the Generation IV initiative).^{16,17,18} Understanding and modelling their physical and chemical properties are crucial issues in such context.

The understanding of molten fluorides have achieved great advance during the past decade, thanks to theoretical and experimental improvements.¹⁹ An important factor in

these developments is the availability of high purity materials inert toward molten fluorides (boron nitride, pyrolytic boron nitride and glassy carbon) for the design of new sample containers. Nuclear magnetic resonance (NMR) spectroscopy,^{20,21} extended X-ray fine absorption spectroscopy,^{22,23} Raman spectroscopy,²⁴ electrochemistry,^{25,26} thermodynamics studies,^{27,28,29} etc. have thus benefited a new impulse. Nonetheless, the experimental study of molten fluorides still remains challenging. Numerical simulations have also reached a high level of accuracy.^{30,31} Another important reason in this advance is the combination of molecular dynamics simulations and experimental studies. The work of Pauvert et al. on molten ZrF_4 -AF illustrates this approach.³²

The very high charge density of molten fluorides induces a strong structuration of the liquids at short scale (very first coordination shells) along with long persistence length.^{19,33} Their structure span from simple bath of hard charged spheres to liquid network or liquid with free complexes.^{1,34,20} Indeed, it is well known that within the family of molten fluorides important modifications in the thermodynamic and transport properties occur when the nature of the cation is changed.^{35,36} One can distinguish acidic cations, which tend to form long-lived ionic bonds³⁷ with the fluoride anions from basic ones, which provide “free” fluoride anions to the melt, even though a proper scale of acidity remains to be built in these media³⁸. Molten rare earth/actinide (and analogous cations) fluorides typify acidic molten fluoride. Recent structural studies on rare earth/actinide (and analogous cations) alkali fluoride mixtures have shown that the liquid behaves like a labile network.^{39,40,41,42} On the reverse, molten alkali fluorides and their mixtures typify basic molten salts. Their viscosity is known to be of the same order of magnitude than liquid water, which means that these liquids are highly fluid.⁴³ The structure of alkali fluorides has been considered simple until

molecular dynamics simulation on LiF-KF 50-50 mixture predicted the existence of dynamical local heterogeneities, i.e. incomplete mixing at the nanoscopic scale.^{44,45}

The aim of this paper is to study the dynamical local heterogeneities in molten fluorides using NMR spectroscopy. We focused on the structural properties of CsF-AF (A=Li, Na, K and Rb) molten salts because one may expect stronger effect than in LiF-KF system. In addition, ¹³³Cs nucleus have better NMR properties than ³⁹K for such study. The chemical shifts of ¹⁹F and ¹³³Cs have been measured as function of the CsF molar fraction in the melt.

2. Results and discussion

The phase diagrams of CsF-AF (A=Li, Na, K and Rb) present different features depending on A.^{46,47} In CsF-LiF system, there are two eutectics at CsF molar fraction $x_{CsF} = 0.48$ (T=752 K) and $x_{CsF} = 0.60$ (T=766 K) and the incongruent melting of LiCsF₂ compound (T=767 K). In CsF-NaF and CsF-KF systems there is only one eutectic at $x_{CsF} = 0.76$ (T=883 K)^{48,49,50,51,52} and $x_{CsF} = 0.57$ (T=898 K)^{53,54}, respectively. In CsF-RbF system, there is neither an eutectic or particular point but there is a solid solution over the whole range of composition.⁵⁵

To investigate the local structure in molten CsF-AF mixtures, we have recorded the NMR spectra of ¹⁹F and ¹³³Cs in molten CsF-AF (A=Li, Na, K and Rb). The NMR chemical shift brings information on the local environment of the observed nucleus *i.e.* the first coordination shells. The measures were performed just above the melting temperature in order to prevent the evolution of composition during the experiment due to possible vaporization of one of the two compounds. The spectra of ¹⁹F and ¹³³Cs in molten CsF-NaF are presented in figures 1 and 2. Similar figures have been obtained for the other CsF-AF systems.

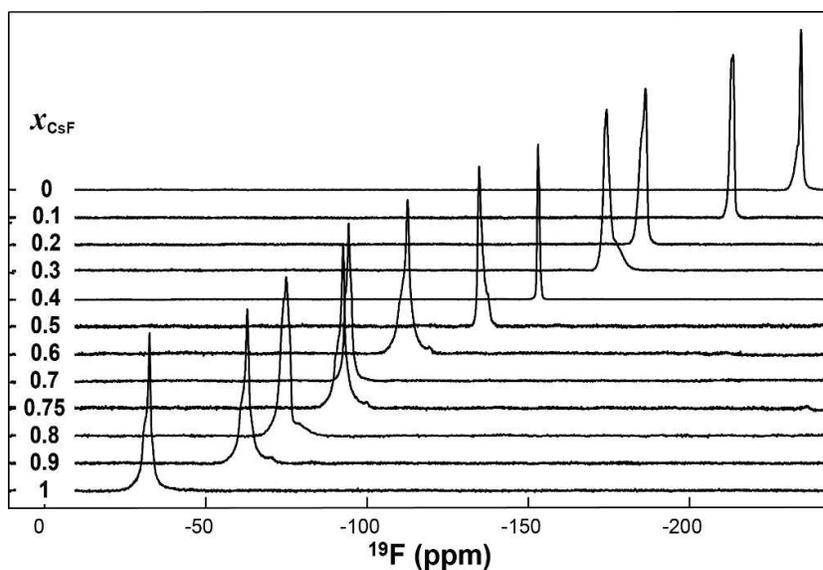


Figure 1: NMR spectra of ^{19}F (left) in molten CsF-NaF for various molar fraction of CsF

x_{CsF}

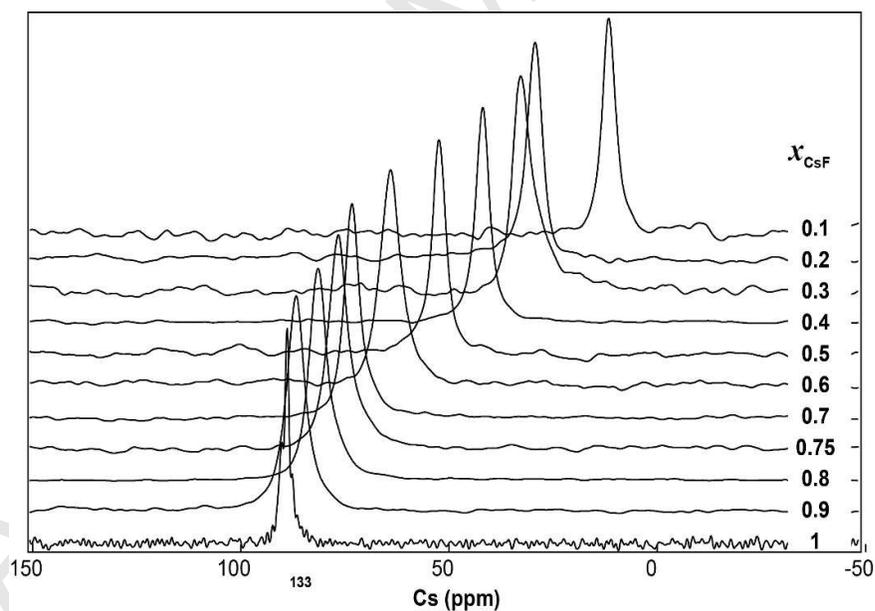


Figure 2: NMR spectra of ^{133}Cs (right) in molten CsF-NaF for various molar fraction of CsF

x_{CsF}

Only one peak is observed for each nucleus. For solid compounds, the NMR spectrum exhibits to as many peaks as there are different environments for the observed nucleus,

provided sufficient resolution. For molten salts, the nucleus experiences all the different environments during the measurement because NMR measurement characteristic time is much longer than the ion motions. In consequence, the NMR spectrum consists only in one sharp peak (provided no phase separation occurs in the system). Nevertheless, the peak position is the weighted average of all the individual peak positions that should be obtained if the measurement was faster than the ion motions.²⁰ Hence, the value of the measured chemical shift can be derived using:

$$\delta = \sum n_i x_i \delta_i$$

where n_i is the number of fluorine involved in the i^{th} complex, x_i the molar fraction and δ_i its chemical shift.

The positions of the ^{19}F and ^{133}Cs peaks are shifted toward negative values when AF amount increases in the mixtures (figure 1 and 2). These variations are better seen by plotting the chemical shifts values, versus the AF molar fraction x_{AF} . Figure 3 presents the variation of ^{19}F chemical shift $^{19}\text{F} \delta$, for each molten CsF-AF (A=Li, Na, K and Rb) system. A straight line is observed, whatever the alkali A, between $^{19}\text{F} \delta$ in pure CsF (-32 ppm) and in pure AF (-200, -235, -149 and -115 ppm for LiF, NaF, KF and RbF, respectively).

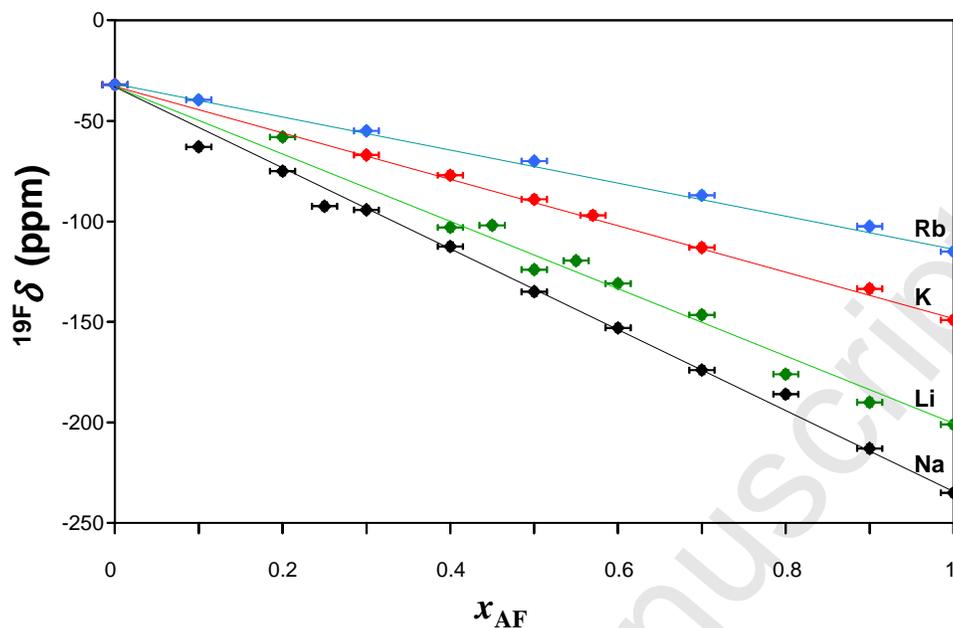


Figure 3: ^{19}F chemical shift $^{19}F \delta$ as function of AF molar fraction x_{AF} for CsF-LiF (green), CsF-NaF (black), CsF-KF (red), CsF-RbF (blue).

Linear variations have been also observed in other molten alkali fluoride mixtures: LiF-NaF and LiF-KF (figure 4).^{56,21} Nevertheless, the trend is different: $^{19}F \delta$ decreases with NaF addition whereas $^{19}F \delta$ increases with KF or CsF addition. The $^{19}F \delta$ values in pure solid⁵⁷ and molten AF⁵⁸ has been correlated to the polarizability of the anion-cation pairs α : $^{19}F \delta$ varies linearly with α . More precisely, it increases from -200 ppm ($\alpha = 0.927 \cdot 10^{-24} \text{ cm}^3$) for LiF to -32 ppm ($\alpha = 3.686 \cdot 10^{-24} \text{ cm}^3$) for CsF. However, an inversion between LiF and NaF positions has been observed for both solid and molten systems. The results presented in figure 4 are in agreement with those results.

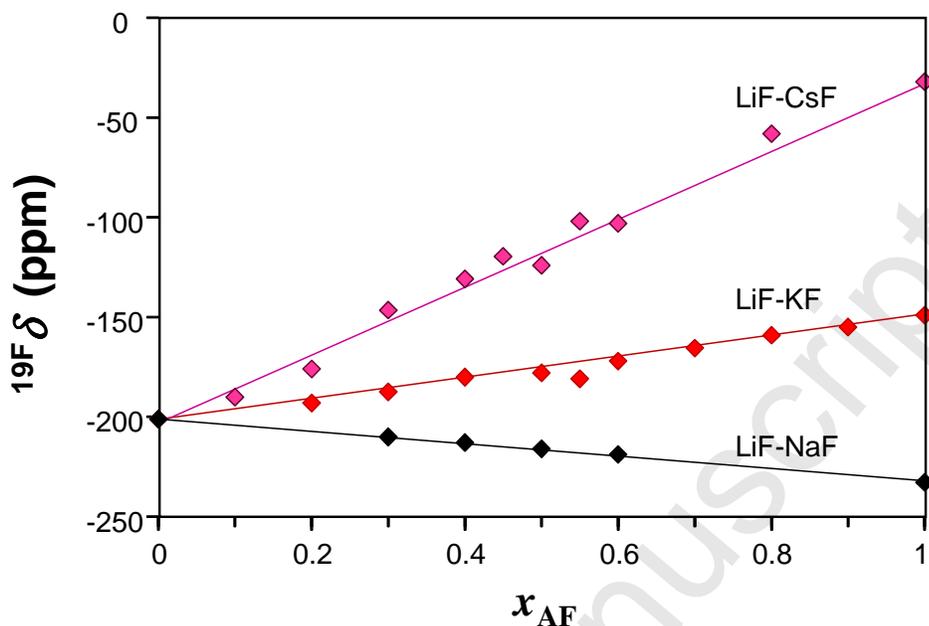


Figure 4: ^{19}F chemical shift $^{19}F\delta$ as function of AF molar fraction x_{AF} for CsF-LiF (pink), KF-LiF (red) and NaF-LiF (black).

This variation can be compared to the one for other molten fluorides salts. In most cases $^{19}F\delta$ presents more complicated variations. For example in AF- AlF_3 , it describes a bell curve versus AlF_3 concentration corresponding to domains where different AlF_a^{3-a} units (with $x = 4, 5$ and 6) free F^- are in rapid exchange.^{59,60,61} In rare earth fluorides^{62,40} AF- LnF_3 ($Ln=La, Y, Ce, Lu$), actinides fluorides⁶³ AF- ThF_4 and transition metal fluoride⁴² AF- MF_x systems, the $^{19}F\delta$ variation is a parabola. In these cases, it has been demonstrated by several techniques that fluorines are in rapid exchange between at least three environments: free fluorine, fluorine embedded in MF_n^{z-n} unit (z the charge of the cation M and n the number of fluorine in this long-lived unit) and fluorine bridging at least two MF_n^{z-n} units.^{39,64,65,66} The proportion of these environments depends on the concentration of MF_x . For example, this number of fluorine n ranges mainly between 6 and 8 for rare earth.^{58,32,19} The residence times of the fluorine anions in the coordination shell of the alkaline cations is much shorter than in the

one of rare earth, actinide and transition metal cations.^{67,68} Therefore, in the case of alkali fluorides mixtures, only free fluorines are considered. However, the character “free” of fluorine in molten alkali has to be balanced according the alkaline.⁵⁸ Indeed its size and the polarizability are important factors to be considered. Dracopoulos et Papatheodorou have shown using Raman spectroscopy that $(\text{LiF})_x\text{A}$ units have longer life time in molten CsF-LiF (0.8ps) than in molten KF-LiF (0.3ps).⁶⁷ In addition, the accuracy of the molecular dynamics simulations necessitates taking account the ion polarizability.^{69,70,71}

In molten fluorides, the variations of the cations chemical shift have often provided crucial and more sensitive information to understand the local structure of the melt.^{58,40,72}

Figure 5 presents the variation of ^{133}Cs chemical shift $^{133}\text{Cs} \delta$ versus x_{AF} for each molten CsF-AF (A=Li, Na, K and Rb) system.

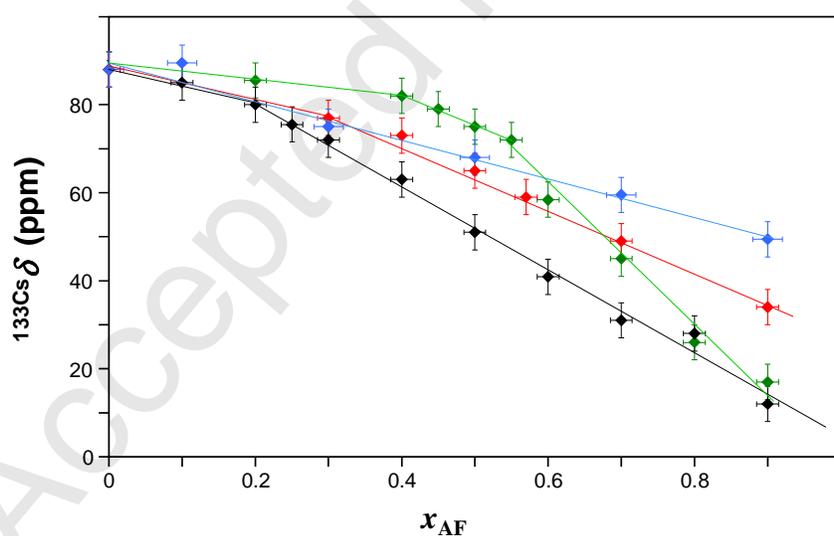


Figure 5: ^{133}Cs chemical shift $^{133}\text{Cs} \delta$ as a function of the AF molar fraction x_{AF} for CsF-LiF (green), CsF-NaF (black), CsF-KF (red), CsF-RbF (blue).

The ^{133}Cs chemical shift $^{133}\text{Cs} \delta$ variation is less simple than in the case of ^{19}F . In CsF-LiF, $^{133}\text{Cs} \delta$ varies linearly with two breaks in the slope around the eutectics of the system. In CsF-

NaF and CsF-KF, a similar feature is observed and the break occurs also around the eutectic. In CsF-RbF, a straight line is observed without any break (note that there is no eutectic in the CsF-RbF phase diagram). The most striking point is the $^{133\text{Cs}}\delta$ evolution in CsF-LiF at low x_{LiF} (<0.4) as compared with the other CsF-AF: a plateau is nearly observed for CsF-LiF while $^{133\text{Cs}}\delta$ decreases with AF content for the other CsF-AF. It can be also noticed that the $^{133\text{Cs}}\delta$ decrease is approximately equivalent for CsF-NaF, CsF-KF and CsF-RbF at low x_{AF} . It is also puzzling that the variation of $^{19\text{F}}\delta$ does not echo the $^{133\text{Cs}}\delta$ one.

Let first discuss the general decrease of $^{133\text{Cs}}\delta$ with x_{AF} . As explained at the beginning of the discussion, the NMR chemical shift is sensitive to the first shells of neighbours i.e. their nature, coordination number and distance. In order to estimate the coordination number N_+ (number of fluorine anions around cation) in molten salts using NMR spectroscopy, it is often convenient to build an empirical scale of chemical shifts versus coordination number. For this purpose, the chemical shift is measured for several crystalline compounds which structure is perfectly defined.^{73,59} Unfortunately, crystalline compounds containing cesium and fluorine ions are scarce. In addition to pure CsF, two other compounds CsLiF₂ (C 1 2/c 1)⁷⁴ and Cs₃SiF₇ (P 4/m b m)⁷⁵ are good candidates but were not available for this study. In addition, LaCs₃F₆ has been reported but its structure has not yet been elucidated.⁷⁶ CsF crystallizes in P m -3 m space group and Cs is surrounded by 6 F.⁷⁷ In solid CsF, the $^{133\text{Cs}}$ chemical shift has been determined using MAS NMR and is equal to +175ppm.^{78,79} In pure molten CsF, $^{133\text{Cs}}\delta = +88\text{ppm}$ and the coordination number N_+ has been estimated to 5.6.⁸⁰ Though it may be rather tricky to define a coordination number in these systems and to compare directly results of simulations and NMR data¹⁹: a slight decrease of N_+ around cesium seems thus to induce a decrease of $^{133\text{Cs}}\delta$. In molten CsF-AF, the decrease of $^{133\text{Cs}}\delta$ with x_{AF} may indicate a slight decrease of N_+ with x_{AF} . Change of N_+ may be correlated to

the change of melt fluoroacidity. By analogy with the pH scale in aqueous solutions, the fluoroacidity ($pF = -\log a_F$) is based on the “free” fluorine ions content in molten mixtures. The more fluoro-donor, the higher basicity. Recently, a new electrochemical method to build the first fluoroacidity scale has been proposed. It is based on the measurement of the equilibrium between gaseous SiF_4 or BF_3 and dissolved species in molten fluorides.^{81,82} The authors have shown that the fluoroacidity follows the sequence $\text{LiF} > \text{NaF} > \text{KF} > \text{CsF}$. This fluoroacidity scale is in good agreement with the ^{133}Cs δ variation observed in molten CsF-AF.

The second important feature seen in figure 5 is the quasi-plateau at low x_{LiF} (<0.4) for the CsF-LiF system. Surprisingly, ^{133}Cs ion seems to be not affected by the presence of lithium ion in the melt. Few years ago, numerical simulations on molten LiF-KF have obtained unexpected results on the medium range structure of these molten salts.^{44,45} The partial structure factors revealed the existence of local heterogeneities in ionic distribution. More precisely, clustering of Li^+ and of part of the F^- ions in the KF matrix was observed, evidencing an incomplete mixing of LiF and KF at the nanoscopic scale. The authors expected to find also clustering of K^+ but the absence of low- k features in the like-like partial structure factor of K^+ shows that its distribution was homogeneous (k being the scattering vector). The emerging picture was a homogeneous but disordered (i.e. non-network-like) matrix consisting of K^+ and F^- ions in which clusters of Li^+ ions are formed.⁴⁵ Furthermore, these effects do not affect the first solvation shell because they correspond to the formation of medium range order. An enhancement of these effects is expected in the CsF-LiF system. Indeed, the difference in the properties (size, polarizability) between cesium and lithium ions is much greater than the one between potassium and lithium ions.^{83,69} Furthermore, the evidence of these effects must be higher at low x_{LiF} . The direct consequence of the existence of local clustering of Li^+ in the molten CsF-LiF on the ^{133}Cs chemical shift ^{133}Cs δ would be the

absence of variation with x_{LiF} . This is what is observed in figure 5. This phenomenon is expected to be sensitive to the temperature. Thus, the experiments have been also performed for some CsF-LiF at higher temperature, 80° above the liquidus temperature. The values of $^{19F} \delta$ are almost the same as at the liquidus temperature whereas the $^{133Cs} \delta$ values are strongly modified. The $^{133Cs} \delta$ variation with x_{LiF} resembles now more to the CsF-RbF one (see supplementary materials) where no clustering was suspected.

Two questions arise about 19F NMR results: why there is a single peak in the 19F spectrum instead of two at -200ppm (pure LiF) and -32ppm (pure CsF) and why there is no evidence in the evolution of the $^{19F} \delta$ versus x_{LiF} ? The answer comes from the lifetime of these clusters. Ribeiro has estimated it to a few picoseconds,⁴⁴ much shorter than the NMR characteristic time. In consequence, one observe only the average structure, ergo a single peak in the spectrum. Furthermore, as underlined by Salanne et al.⁴⁵ the first solvation shell is not affected. Hence, the fluorine is in rapid exchange between two environments: surrounded by lithium and surrounded by cesium (note that a fluorine anion surrounded by a Cs and b A gives a contribution to $^{19F} \delta$ equal to $(a/a+b) ^{19F} \delta_{CsF} + (b/a+b) ^{19F} \delta_{AF}$ as explained at the beginning of the discussion). This means that the evolution of $^{19F} \delta$ versus x_{LiF} is a straight line as observed in figures 3 and 4.

During the past ten years, the existence of dynamical local scale distribution heterogeneities has been evidenced in various simple liquid mixtures, *i.e.* without surfactants or long chains molecules: water – room temperature ionic liquids,^{84,85} water – ethanol and water – methanol,^{86,87,88} molten glasses,⁸⁹ metallic melts.⁹⁰ It is the first time that such phenomenon is experimentally evidenced in molten salts. The knowledge of such distribution heterogeneities are important to deeply understand the solubility and miscibility of species.

3. Experimental and Method

The fluoride salts (purity 99.99%) were purchased from Alfa Aesar. The appropriate quantities of binary mixtures were weighted and then filled into NMR cells in a gloves box under dried argon in order to avoid H₂O and O₂ contamination of the samples. The CsF salt being very hygroscopic, the NMR cells are based on double confinements: a small crucible made in pyrolytic boron nitride is put in wider crucible in HIP (hot isostatically pressed) boron nitride. The latter crucible is tightly closed by a screw cap. The amount of salt in each NMR cell is ca. 70 mg.

The High Temperature NMR (HT NMR) spectra were recorded using a Bruker Avance WB 400MHz spectrometer, operating at 9.40 T. *In situ* HT NMR spectra were obtained by using the CO₂ laser heating system developed at CEMHTI-CNRS in Orléans (France) and previously described.^{91,92} The samples were heated directly up to melts and the spectra were collected about 10 to 20K above respective liquidus temperature for each composition.

The HT NMR spectra were acquired using a single pulse sequence with a 1s recycle delay and 8 to 128 accumulations. The pulses were $\pi/2$ pulses for ¹⁹F and with $\pi/4$ pulses for ¹³³Cs. The chemical shifts were referred to CCl₃F for ¹⁹F, CsNO₃ 0.1M solution for ¹³³Cs. NMR spectra were treated using DMFIT software.⁹³

Conclusion

The ¹⁹F and ¹³³Cs chemical shifts in CsF-AF (A=Li, Na, K and Rb) have been measured as a function of the molar fraction of CsF using HT NMR. The ¹⁹F chemical shift varies linearly with

composition while ^{133}Cs chemical shift present a break around the eutectics composition. The ^{133}Cs chemical shift does not follow the same feature in CsF-LiF than in the other CsF-AF. In particular at low x_{LiF} , no ^{133}Cs chemical shift variation is observed with x_{LiF} . This evolution is interpreted as evidence of dynamical local scale distribution heterogeneities i.e. existence of local clustering of Li^+ in the molten CsF-LiF.

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