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Article

Measuring Self-Diffusion Coefficients up to 1500 K: A Powerful Tool to Investigate the Dynamics and the Local Structure of Inorganic Melts

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Self-diffusion is a fundamental property of liquid dynamics that also provides important structural information. To explore the dynamics in inorganic melts with high liquidus temperature, we propose a new setup based on pulsed field gradient NMR combined with laser heating that makes possible in situ self-diffusion coefficient measurements up to 1500 K. Applied to several corrosive molten fluorides in a wide range of compositions and temperature, we have evidenced the different key parameters of their motion along with their structural characteristics. In alkali fluorides, the self-diffusion coefficient of fluorine depends slightly on the composition compared to the temperature, displaying these systems as an ideal bath of polarizable hard spheres. In contrast, self-diffusion in rare earth and alkali fluorides mixtures presents a complicated balance between temperature and the network-forming process of the ionic long-lived units. These results open wide perspectives in the study of high temperature liquids.

Introduction

The study of dynamics is a prerequisite for a better understanding of liquids.[1] Among the dynamical parameters, the self-diffusion coefficient D is fundamental as it represents the ability of atoms or assembly of atoms to move inside their environment. In consequence, it is involved in every model describing dynamical systems.

Initially, D was measured by the capillary method.[2] Its demanding implementation and the requirement of radioactive tracers have limited its use. In room temperature liquids, diffusion processes have been widely studied thanks to the development of pulse field gradients (PFG) NMR[3] that allows one to rapidly obtain reliable values of D in a wide diffusion time range ($10^{-3}-10^{1}$ s). The other advantages of this method are the selectivity toward the isotope, the direct determination of D, and the possibility to perform in situ experiments with examples up to 700 K.[4]

The study of high temperature liquids is always a technical challenge that occurs in many fields of fundamental or applied industrial research such as geosciences (magma), metallurgy (metals and electrolytes), glasses, nuclear wastes recycling, and energy (battery, fuel cells, molten salt reactor). It often requires developing innovative experimental setups especially in the case of corrosive liquids. While thermophysical parameters (density, viscosity, conductivity, surface tension) or spectroscopic characterization (NMR,[5] infrared,[6] Raman,[7] X-rays,[8] and neutrons scattering[9]) have been already reported for molten materials up to more than 2500 K, there exist few studies of dynamical parameters by NMR relaxation time measurements[10] or inelastic X-ray scattering[11] in oxide melts.

When self-diffusion coefficients in molten salts are most commonly estimated through electrochemical experiments, they could be directly measured by PFG NMR experiments. We developed a specific high temperature experimental

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setup, based on the existing laser heated NMR device designed at CEMHTI-Orléans.[12] The main difficulty lies in the limited space available around the sample with the emission/detection coil located only at 2 mm from the hot sample (see the Supporting Information). The sample is contained in an inert boron nitride crucible acting as a small furnace, directly heated by two continuous CO_2 lasers (from top and bottom). The temperature homogeneity relies on the good thermal conductivity of boron nitride. With this new device, we are able to measure in situ self-diffusion coefficients at temperatures up to 1500 K in a few minutes and for a wide range of high temperature liquid compositions.

Molten salts (halides, oxides, nitrates, sulphates, carbonates, phosphates, ...) are of fundamental interest and used in various industrial applications ranging from electrolysis of metals, fuel cells, or nuclear energy. They constitute a particular class of liquids because of the predominance of short-range Coulomb forces[13] which tend to reduce the ionic mobility by preventing ions from escaping out of their counterion shell. The self-diffusion coefficient of the different species is a signature of the melt structure and the type of long-lived units involved.

Experimental Methods

Experimental details and comparative studies of NMR diffusion and capillary method measurements are available in another paper.[14] The fluoride salts (purity 99.99%) were purchased from Aldrich. 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 H_2O and O_2 contamination of the samples. The NMR cells are boron nitride AX05 grade (BN) crucibles (6 mm diameter, 10 mm height, 450 mg weight) tightly closed by a screw cap, purchased from MCSE (France). In order to prevent vaporization and recondensation of the salt during the experiment, the crucible is completely filled (the powder is pressed). The amount of salt in each crucible is ca. 50 mg. The in situ HT PFG NMR presented here is based on the CO_2 laser heating system developed for structural studies at CEMHTI-CNRS in Orléans (France).[15] The crucible is heated symmetrically by two CO_2 lasers (Coherent, 250 W). The power of the lasers, thus the temperature, is increased slowly in order to ascertain a stabilized and homogeneous temperature in the sample (around 15−20 min.). The heating rate is estimated to be 100 °C/min. The high temperature NMR (HT NMR) spectra were recorded using a Bruker Avance II WB 400 MHz spectrometer, operating at 9.40 T. The NMR probe specially built by Bruker company is based on a 10 mm axial liquid NMR probe equipped with a gradient coil (5.5 Gauss/(cm A)) coupled with gradient amplifier Great 10A (10 A). The thermal shielding of the radiofrequency and gradient coils is carried out by several ceramics barriers as shown in Figure 1. The crucible is inserted in a mullite support, surrounded by an alumina tube. An additional protection in silica glass is placed between the alumina tube and the coil. An argon flow at room temperature between the mullite cradle and the alumina tube allows one to cool the ceramics and to prevent the boron nitride crucible from oxidizing. The radiofrequency and gradient coils are also cooled down by an additional nitrogen stream.

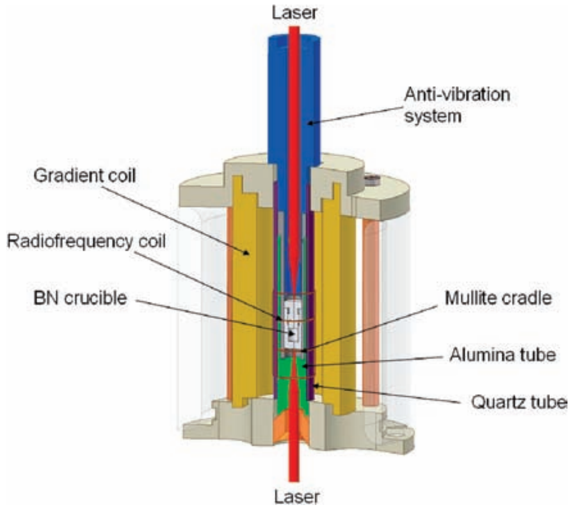

Figure 1. Schematic drawing of the high temperature PFG NMR probe head.

The pulsed-gradient spin−echo NMR method was used to measure $^{19}F^-$ self-diffusion coefficients. The pulses sequence was stimulated spin−echo sequence.[16] Self-diffusion coefficients were calculated by measuring the decrease in the NMR echo signal intensity through increasing magnetic field gradients (eight gradients). The $\pi/2$ pulse length was 13 μs, and recycle delay was 5 s (relaxation times about 1 s). The self-diffusion coefficients were obtained by nonlinear least-squares fitting of the echo attenuation. The gradient strength ranged from 0 to 50 G/cm, and all the measurements were performed for $\Delta = 50$ ms (diffusion time) and $1 < \delta < 3$ ms (gradient duration). The diffusion measurement takes about 10 min (16 scans per gradient strength). The evolution of the signal intensity does not follow the characteristic ones observed in the case of convection.[17] Moreover, the self-diffusion coefficients D were measured for different diffusion time Δ. If convection occurs, D depends on Δ. There is no dependence of D versus Δ in our measurements. This insures that the measured D are free from convection artifacts.

An estimation of the precision of this experimental setup can be given with the measurement of D_F in pure LiF that has been done ten times with different samples. The averaged value is 7.3×10^{-9} m^2/s, and the standard deviation is 0.3×10^{-9}. The accuracy is more difficult to estimate as there are very little published data to compare with. Despite the fact that the temperature control (see the Supporting Information) is the weaker point of this method and possibly induces little over estimating D values, the latter are in good agreement with the values obtained using the capillary method on molten NaF[18] and Na_3AlF_6[19] (discrepancy less than 10%).[14] We have evaluated the accuracy of these measurements at 10%. In addition, the sample stability is controlled during the experiment thanks to the chemical shift: no variation is observed between the first and the final gradient step. Moreover, successive measurements on the same sample give the same result confirming the sample stability.

Results and Discussion

Let us first consider the simple case of the LiF−KF system taken as a typical example of molten alkali fluorides. We have

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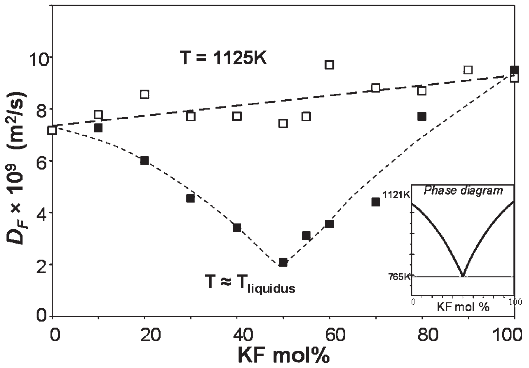

Figure 2. D_F in molten LiF−KF versus the KF concentration: about 10 K above the liquidus temperature (solid squares) and at 1125 K (open squares).

measured the self-diffusion coefficients of fluorine (D_F) over the whole range of compositions, about 10 K above the liquidus temperature. The values are plotted in Figure 2 as a function of LiF concentration.

The striking point is the resemblance between the variation of D_F and the liquidus temperature evolution over the whole phase diagram.[20] D_F strongly decreases from its value in pure LiF ($D_F = 7.2 \times 10^{-9}$ m^2/s, $T = 1125$ K) to a minimum ($D_F = 2.1 \times 10^{-9}$ m^2/s, $T = 775$ K) at the eutectic composition and then increases again up to its value in pure KF ($D_F = 9.5 \times 10^{-9}$ m^2/s, $T = 1125$ K). This feature suggests that the behavior is mainly ruled by the temperature. In order to confirm this hypothesis, D_F was measured for each composition at the same temperature, i.e. 1125 K. The values located on a straight line confirm this temperature influence. Both variations of D_F thus demonstrate that F^- anions are "free" in molten LiF−KF system as expected from previous spectroscopic measurements.[21]

These results also imply that the diffusion processes is governed by the very first coordination sphere. The slope of the linear regression for D_F at 1125 K (0.02×10^{-9} m^2/(s mol % KF)) is correlated to the difference of ionic potential between K^+ and Li^+. Indeed, the potential experienced by the fluorine ions is higher with Li^+ than with K^+. Hence, the barrier to get free from its first coordination sphere is higher with Li^+ than K^+. But as soon it goes over this barrier, F^- does not experience anymore the ionic potential because of the screening of the electrostatic forces. From D_F measurements, we confirm that the alkali fluorides AF systems can be seen as ideal charged sphere baths. Therefore the whole series LiF−AF (A = Na, K, Rb, and Cs) could be simply evaluated. The ionic potential of the alkali decreasing from Li to Cs, the self-diffusion coefficient of fluorine is expected to increase at a given temperature.

The study was extended to the system LiF−YF_3 representative of heavy rare earth and alkali fluorides mixtures that are of importance for nuclear waste recycling. D_F was measured about 10 K above the liquidus temperature for the whole range of composition. The values are plotted in Figure 3 (solid circles) as function of YF_3 concentration.

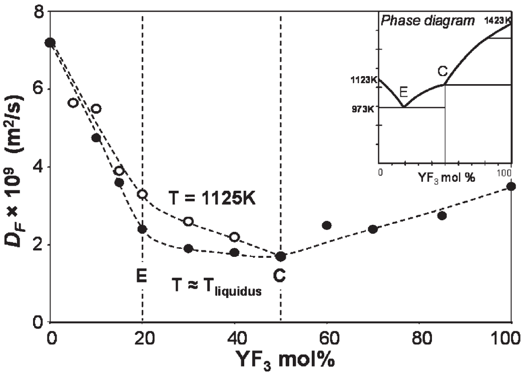

Figure 3. D_F in LiF−YF_3 molten mixtures versus the YF_3 concentration: 10 K above the liquidus temperature from 0 to 100 mol % YF_3 (solid circles); at 1125 K from 0 to 50 mol % YF_3 (open circles). E = eutectic composition; C = $LiYF_4$ compound.

The evolution of D_F versus the YF_3 concentration is quite different from the one observed in LiF−KF. D_F does not vary as the liquidus temperature does.[22] Nevertheless the inflection points of the evolution of D_F occur at particular compositions of the LiF−YF_3 system (20 mol % YF_3 = eutectic composition, 50 mol % YF_3 = $LiYF_4$). Such a feature with the phase diagram has not been noticed by the spectroscopy studies.[23] In particular, D_F rapidly decreases with T_{liquidus} from 0 to 20 mol % YF_3, it is stable while T_{liquidus} increases from 20 to 50 mol % YF_3, and it increases slowly as T_{liquidus} increases strongly above 50 mol % YF_3. This behavior clearly shows that the fluorine anions do not diffuse freely at a high temperature and should be associated in YF_x^{3-x} long-lived units. In order to highlight the fluorine "complexation", D_F was measured at 1125 K from 0 to 50 mol % YF_3. A significant decrease of D_F is observed up to 20 mol % YF_3 followed by a less marked decrease in the 20−50 mol % YF_3 domain. This inflection point near the eutectic composition is related to the formation of connections between these long-lived units by fluorine bridging. The nature of the long-lived units is still a matter of debate as spectroscopic studies suggest either YF_6^{3-} (Raman[24]) or YF_7^{4-} and YF_8^{5-} (NMR[25]) long-lived units. According to the Stokes−Einstein law[1] and by considering D_F for a free fluorine ion ($D_{F\text{-free}}$) as the value in pure LiF at 1125 K, one may attempt to calculate D_F for an isolated long-lived unit. It should be equal to $(R_{F\text{-free}}/R_{YFx})\cdot D_{F\text{-free}} \approx 2.9 \times 10^{-9}$ m^2/s (with R, the radius of the diffusing entity) by assuming the viscosity equality. This calculated value is higher than the values measured at 1125 K for compositions above 20 mol % YF_3 indicating that the averaged size of the diffusing entities is much bigger than that for the YF_x^{3-x} units. In other words, YF_x^{3-x} units are connected to each other, and above 20 mol %, these connections become predominant. Relating 20 mol % YF_3 to the number of fluorines embedded in YF_x^{3-x} units, we find that $x = 7$. Another interesting point is the plateau observed for the D_F values at the liquidus temperature in the 20−50 mol % YF_3 domain. It indicates that there is a balance between the temperature effect and the network formation. The increase in D_F from 50 to 100 mol % YF_3 shows that the

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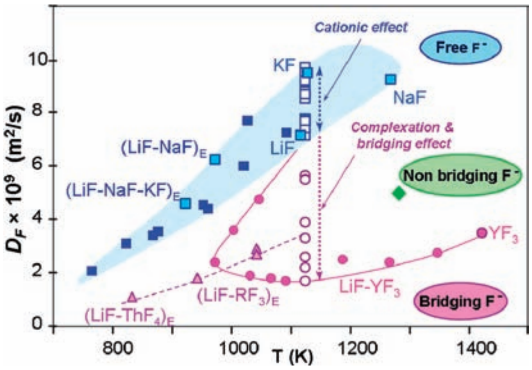

Figure 4. D_F versus temperature measured in different systems: AF = LiF, NaF, KF, and their mixtures (squares); cryolite (Na_3AlF_6) (green diamond); rare earth and alkali fluoride mixtures (LiF$-$YF$_3$ full circles at $T_{Liquidus}$ and open circles at 1125 K; LiF$-$LaF$_3$, LiF$-$LuF$_3$ at $T_{Liquidus}$ mauve triangles); LiF$-$ThF$_4$ (mauve triangle). The values for rare earth are given in the Supporting Information. The subscript E indicates the eutectic composition.

temperature effect is stronger than the enhancement of the liquid network.

To go further in the investigation on the dynamics of molten salts, we have measured and plotted in Figure 4 the D_F of a large assortment of molten fluorides as a function of the temperature. The alkali fluorides (AF = LiF, NaF, KF) and their mixtures are the simplest solvent in the molten fluorides series. Cryolite (Na_3AlF_6) has been widely studied because of its use in aluminum production. Rare earth and alkali fluorides mixtures are an important issue in nuclear waste recycling and LiF$-$ThF$_4$ is proposed to be the fuel in the molten salt nuclear reactor. In this figure, $D_F(T)$ gives a valuable insight of the different structural classes of molten fluorides. AF and their mixtures can be described as a bath of polarizable charged hard spheres with free fluorine ions. The temperature is the predominant factor compared to the ionic potential of cations. In fact, D_F can be defined inside a narrow domain from which one can reliably estimate the self-diffusion coefficients of AF mixtures.

The case of cryolite is also interesting as $D_{F\text{-cryolite}}$ is far below the domain corresponding to the free fluorine ions. Indeed, this feature is in agreement with the fact that the fluorine ions are involved in non connected anionic long-lived units.[26] The size of the diffusive species is therefore larger. For the rare earth and actinide fluorides mixed with LiF, the low D_F values obtained for the eutectic composition evidence the formation of anionic long-lived units RF_x^{3-x} probably connected by fluorine bridging.[27] The dashed line linking all the $(RF_3{-}LiF)_E$ at different temperature suggests that all the eutectic melts present similar structure.

Conclusions

Self-diffusion coefficients in high temperature liquids (770$-$1420 K) were measured for the first time thanks to the pulsed field gradients NMR technique. The self-diffusion coefficients of fluorine measured in different molten fluorides at temperatures ranging from 770 to 1420 K allows us to bring to light the key parameters of the ionic transport. In addition, it is evidence of the local structure in agreement with recent studies of spectroscopy[27] and numerical simulations.[28] This technique opens wide prospects for studying the dynamics of high temperature liquids.

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Supporting Information Available: Temperature calibration and supplementary data. This material is available free of charge via the Internet at http://pubs.acs.org.

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