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# Investigation on fluoroacidity of molten fluorides solutions in relation with mass transport

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## ABSTRACT

Equilibria between species in solution and its corresponding gaseous species were investigated in various molten fluorides mixtures. From the measurements of boron and silicon kinetic constant of gas release, a relative fluoroacidity scale of solvents was proposed. Due to very high kinetic rates of  $\text{SiF}_{4(g)}$  and  $\text{BF}_{3(g)}$  release for the most acidic melts, another approach to evaluate fluoroacidity based on mass transport was considered. Relationships between bridging fluorine atoms, viscosity and fluoroacidity was demonstrated. Diffusion coefficients of Si(IV) and B(III) ions were measured and correlated to the viscosity through the Schmidt number (Sc) defined as the ratio between solvent viscosity and solute diffusivity. These results confirmed the fluoroacidity scale previously obtained, validating the original approach developed on mass transport.

## 1. Introduction

Conditions for an effective control of any electrochemical process are the knowledge of the electrolyte structure and its physico-chemical properties (acidity, viscosity. . .), combined with the understanding of the electrochemical species behaviour in the electrolyte. The chemical equilibrium of a solute in a melt both depends on the salt composition and temperature. By analogy with aqueous media, in which the acid-base properties of the electrolyte are critical for the solute stability, fluoroacidity (pF) is based on free fluorides content in molten mixtures:

$$pF = -\log(a_{F^-}) \quad (1)$$

The basic form,  $F^-$  donors, and the acidic form,  $F^-$  acceptors, are in equilibrium as described in Eq.2:



The more a molten salt contains free fluorides (i.e. fluorodonor), the higher its basicity is.

In this paper, fluoride stands for  $F^-$  ion, and fluorine for F element.

Fluoroacidity needs to be studied for a better knowledge of the melt and species physico-chemical properties, as it plays an important role on the ions solvation and reaction processes. Since 40 years, authors worked on relationships between the nature and the composition of molten mixtures, as Toth *et al.* [1–3] who observed

by spectrometric methods that coordination numbers and dynamic equilibria of U(IV), Th(IV) and Zr(IV) are highly affected by the fluoride ion concentrations. More recently by nuclear magnetic resonance (NMR), Bessada *et al.* [4,5] and Rollet *et al.* [6] proposed the existence of three kinds of fluorides depending on the composition in  $\text{AlkF-LnF}_3$  mixtures (Alk = Li, Na, K, Rb and Ln = La, Ce, Sm, Th, Lu, Y):

- fluorides not involved in coordination, called free  $F^-$ ;
- fluorides involved in coordination of one complex;
- fluorides involved in coordination, forming bridges between complexes.

In pure  $\text{AlkF}$  media, free fluorines are stated to be the dissociated fluorines. With  $\text{LnF}_3$  addition, some fluorides participate to  $\text{LnF}_3$  complexes formation (non-bridging), and up to 25 mol%, fluoride ions start to be bridging by corner and/or edge sharing. A strong influence of the nature of the alkali was also observed: the more polarisable (i.e. the higher atomic number of the alkali), the less bridging fluorines and the less coordination number.

The chemical behaviour (coordination and bridging) influences the physico-chemical properties of the bath. Grande *et al.* [7] showed that the melt viscosity increases with the valency of the counter-cation with a constant ratio  $\text{Zr:F} = 1:5$  (i.e.:  $\text{NaF-ZrF}_4 < \text{BaF}_2\text{-2ZrF}_4$ ), and is linked to zirconium complexes formation. Moreover, change of composition significantly changes the fluid viscosity within a binary or ternary system. Dracopoulos *et al.* [8] studied molten  $\text{KF-ZrF}_4$  mixtures and suggested that an increase of the  $\text{ZrF}_4$  amount leads to the formation of octahedral species, and to an increase of the zirconium chain length ( $\text{ZrF}_6^{2-}$ ,  $\text{Zr}_2\text{F}_{10}^{2-}$ ,

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Zr<sub>3</sub>F<sub>14</sub><sup>2-</sup>...). C.F. Baes [9] worked on the relationship between viscosity and fluoroacidity in BeF<sub>2</sub> based molten salts, and observed that the viscosity decreases with the addition of basic fluoride due to the break of bridging fluorine bonds, leading to a decrease of the polymerization degree. Thus molten mixture was described as a network-like structure (Be<sub>2</sub>F<sub>7</sub><sup>3-</sup>, Be<sub>3</sub>F<sub>10</sub><sup>4-</sup>) [10,11].

As a consequence, viscosity is strongly influenced by several parameters in molten fluorides, and a relationship between bridging fluorines, viscosity and fluoroacidity was envisaged [12].

To summarize, an increase of the fluoroacidity can be correlated with:

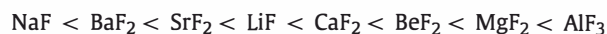
- a decrease of the free F<sup>-</sup>,
- an increase of the bridging fluorines,
- an increase of the viscosity.

Thus the fluoroacidity should impact the physico-chemistry of a medium and consequently, the transport of a species in the solution.

However, pF values are not available since the F<sup>-</sup> activity can't be measured, as no reference electrode is now valid in molten fluorides salts. Only relative fluoroacidity scales were established as proposed by Elwell [13]. He observed that the stability of dissolved Si(IV) ions and the release of silicon gaseous species was highly affected by the nature of molten mixtures, Si(IV) ions being more stabilised in the case of KF-based solvents than NaF-based solvents. Three media were thus sorted using their acidic character:



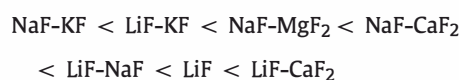
By comparing the acidic character of binary mixtures, the authors proposed the following ranking of fluoride salts from the lower to the higher acidity [14,15]:



In earlier works, Bieber *et al.* proposed an extended fluoroacidity scale based on Na<sub>2</sub>SiF<sub>6</sub> solute in equilibrium with SiF<sub>4(g)</sub> gaseous species [16–18]:



By definition, a fluorobasic bath (high [F<sup>-</sup>]<sub>free</sub>) stabilizes species in solution, while a fluoroacid bath (low [F<sup>-</sup>]<sub>free</sub>) promotes the reaction of gaseous species release. The study of the equilibrium SiF<sub>4+x</sub><sup>x-</sup>(bulk)/SiF<sub>4(g)</sub> moved by the free fluorides concentration, is an indicator of fluoroacidity. The release of SiF<sub>4(g)</sub> leads to a decrease of Si(IV) ions concentrations, controlled by in-situ electrochemical titrations. By calculating the kinetic constant of SiF<sub>4(g)</sub> release, the following ranking was established [16]:



Due to a too high rate constant and experimental difficulties for the most acidic media, comparison between divalent fluorides was difficult to perform. To complete this fluoroacidity scale two approaches were studied.

In a first part, the methodology developed by Bieber was reused, and two systems were studied in new solvent mixtures: SiF<sub>4</sub> and BF<sub>3</sub>. It is known that KBF<sub>4</sub> is decomposed at high temperatures to form BF<sub>3(g)</sub> [19,20] as:



As for silicon, the study of the equilibrium BF<sub>3+x</sub><sup>x-</sup>(bulk)/BF<sub>3(g)</sub> was performed by doing electrochemical titrations of B(III) ions versus time. Kinetics of SiF<sub>4(g)</sub> and BF<sub>3(g)</sub> releases were used to obtain an extended relative fluoroacidity scale.

In a second part, a new approach to evaluate the fluoroacidity based on mass transport was developed. Measurement of diffusion coefficients of Si(IV) and B(III) ions was performed by electrochemical methods. Results obtained were correlated with viscosity by the Schmidt number Sc, defined as the ratio of viscosity and solute diffusivity (Sc =  $\nu/D$ ). A relationship between Sc number and fluoroacidity was found.

## 2. Experimental

The cell consisted in a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled down by circulating water. The inner part of the walls was protected against fluoride vapours by a graphite liner. This cell has been described in previous work [21]. The experiments were performed under an inert argon atmosphere. The cell was heated using a programmable furnace and the temperatures were measured using a chromel-alumel thermocouple.

Several molten salts (Carlo Erba Reagents 99.99%) were used as electrolyte solvents (see Table 1).

All the solvent were initially dehydrated by heating under vacuum from ambient temperature up to their melting point during 4 days. Boron and silicon ions were introduced into the bath in the form of potassium tetrafluoroborate KBF<sub>4</sub> (Sigma Aldrich 99.99%) and sodium hexafluorosilicate Na<sub>2</sub>SiF<sub>6</sub> (Alfa Aesar 99.99%) powders.

Silver wires (1 mm diameter) were used as working electrode. The surface area of the working electrode was determined after each experiment by measuring the immersion depth in the bath. The auxiliary electrode was a vitreous carbon (V25) rod (3 mm diameter) with a large surface area (2.5 cm<sup>2</sup>). The potentials were referred to a platinum wire (0.5 mm diameter) acting as a quasi-reference electrode Pt/PtO<sub>x</sub>/O<sup>2-</sup> [22].

All the electrochemical studies were performed with an Autolab PGSTAT30 potentiostat/galvanostat controlled by a computer using the research software GPES 4.9.

## 3. Results and discussion

### 3.1. Determination of Si(IV) and B(III) diffusion coefficients and in-situ titration

Silicon reduction (added as Na<sub>2</sub>SiF<sub>6</sub>) was investigated by Bieber *et al.* in various molten fluorides mixtures on silver electrode [16]. The results showed that Si(IV) reduction occurred in a one step process exchanging 4 electrons under diffusion control in all molten fluorides mixtures. Diffusion coefficients were determined using Berzins-Delahay equation for a reversible soluble/insoluble system electrochemical response [23]:

$$j_p = -0.61nFC \left( \frac{nFD\nu}{RT} \right)^{1/2} \quad (5)$$

where  $j_p$  is the peak current density (A m<sup>-2</sup>),  $n$  the number of exchanged electrons,  $F$  the Faraday constant (C mol<sup>-1</sup>),  $C$  the solute concentration (mol m<sup>-3</sup>),  $D$  the diffusion coefficient (m<sup>2</sup> s<sup>-1</sup>),  $\nu$  the potential scan rate (V s<sup>-1</sup>),  $R$  the ideal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  as the solute temperature (K).

The reduction behaviour of B(III) ions was investigated in molten LiF-NaF (61-39 mol.%) in the 750-900 °C temperature range. As boron and silver are not miscible at operating temperature, silver wire was selected as working electrode [24]. Fig. 1 shows typical

**Table 1**  
Investigated molten fluorides mixtures.

KF-CsF	NaF-KF	LiF-NaF-KF	LiF-KF	LiF-NaF	LiF-BaF <sub>2</sub>	LiF-SrF <sub>2</sub>	LiF-MgF <sub>2</sub>	LiF-AlF <sub>3</sub>	LiF-AlF <sub>3</sub>
625	718	452	492	652	771	771	771	710	709
43-57	39.7-60.3	46.5-11.5-42	51-49	61-39	80.5-19.5	81.5-18.5	80.5-19.5	85-15	64.5-35.5

1<sup>st</sup> line: molten fluorides mixtures; 2<sup>nd</sup> line: melting point (°C); 3<sup>rd</sup> line: molar composition (all compositions are eutectics compositions, except for LiF-MgF<sub>2</sub> which has been selected in order to more easily compare divalent fluorides)

cyclic voltammograms of LiF-NaF-KBF<sub>4</sub> (0.1 mol kg<sup>-1</sup>) on silver at 750 °C and 100 mV s<sup>-1</sup>. Two reduction peaks at -0.9 V vs. Pt and -1.1 V vs. Pt, and their corresponding reoxidation peaks at -0.2 V vs. Pt and +0.2 V vs. Pt are observed. The first one is characteristic of an adsorption of the B(III) ions on the electrode as previously mentioned in references [25,26]. The second one is a 3 electron reduction of the B(III) ions to B(0) under diffusion control [27–29]. According to the voltammogram, it is clear that the electrochemical reduction process of B(III) is irreversible, the potential difference between reduction and reoxidation being greater than 1 V. The complex reoxidation process is currently under investigation.

According to characteristic equations of cyclic voltammetry for an irreversible soluble/insoluble system, the cathodic charge transfer coefficient  $\beta$  can be determined using the difference between the potential peak and the half peak potential [23]:

$$|E_p - E_{p/2}| = 1.857 \frac{RT}{\beta n F} \quad (6)$$

where  $E_p$  is the peak potential (V),  $E_{p/2}$  is the half peak potential (V), and  $\beta$  the cathodic charge transfer coefficient.

In the present work, this difference was found to be  $71 \pm 5$  mV, corresponding to a value of  $\beta n = 2.4 \pm 0.2$ . Therefore the boron cathodic charge transfer coefficient in LiF-NaF on silver is  $\beta = 0.80 \pm 0.07$  ( $n = 3$ ).

Additions of KBF<sub>4</sub> were performed and a linear relationship between reduction peak current density at -1.1 V vs. Pt and B(III) concentration was obtained:

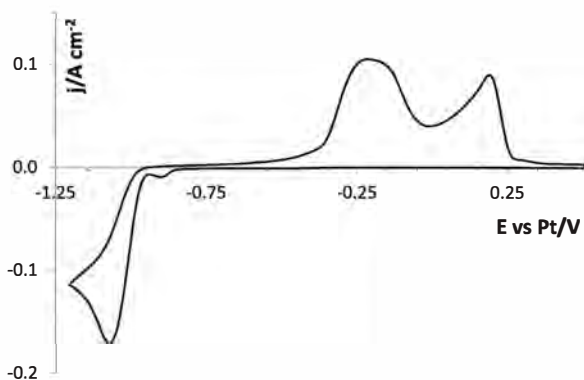
$$j_p / A cm^{-2} = -(1.72 \pm 0.09) [B(III)] / mol kg^{-1} \quad (7)$$

Diffusion coefficients were determined using the equation for an irreversible electrochemical response [23]:

$$j_p = -0.4958 n F C \left( \frac{\beta n F D \nu}{RT} \right)^{1/2} \quad (8)$$

At 750 °C, a value of  $(1.16 \pm 0.08) \times 10^{-9} m^2 s^{-1}$  for D was found.

The same methodology was applied to all other molten media to determine the diffusion coefficient and to correlate the peak current density with the concentration.



**Fig. 1.** Cyclic voltammogram of LiF-NaF-KBF<sub>4</sub> (0.1 mol kg<sup>-1</sup>) at 100 mV s<sup>-1</sup> and T = 750 °C. Working EL.: Ag; Auxiliary EL.: vitreous carbon; Reference EL.: Pt

### 3.2. Fluoroacidity evaluation by kinetics of gaseous compounds release

#### 3.2.1. Methodology overview

Relationships between reduction peaks current densities and concentrations of solutes in the bath allow the kinetic rates of gaseous species release to be calculated for a first order kinetics:

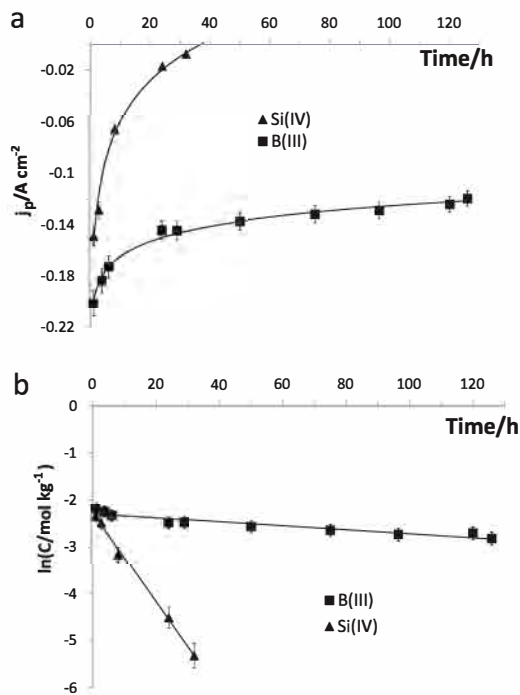
$$r = -dC/dt = kC \quad (10)$$

$$\ln C = -kt + \text{constant} \quad (11)$$

where  $r$  is the reaction rate (mol kg<sup>-1</sup> s<sup>-1</sup>),  $k$  is the kinetic constant (s<sup>-1</sup>),  $C$  is the dissolved concentration (mol kg<sup>-1</sup>) of boron (or silicon).

Variations of Si(IV) or B(III) reduction peaks current densities and logarithm of the concentrations were plotted versus time on Fig. 2a and Fig. 2b respectively, after an addition of 0.097 mol kg<sup>-1</sup> Na<sub>2</sub>SiF<sub>6</sub> and 0.12 mol kg<sup>-1</sup> KBF<sub>4</sub> in LiF-NaF at 750 °C.

The values of kinetic constant for gas release were  $k_B = (1.00 \pm 0.05) \times 10^{-6} s^{-1}$  for BF<sub>3(g)</sub> and  $k_{Si} = (7.9 \pm 0.4) \times 10^{-6} s^{-1}$  for SiF<sub>4(g)</sub>. B(III) ions are more stable in solution than Si(IV) ions, and thus due to the very high kinetic rates of SiF<sub>4(g)</sub> release for the most acidic melts, boron system was preferred.



**Fig. 2.** (a) Variation of silicon and boron reduction peak current density vs. time after an addition of Na<sub>2</sub>SiF<sub>6</sub> and KBF<sub>4</sub> in LiF-NaF at  $t = 0$ ,  $T = 750$  °C. Working EL.: Ag; Auxiliary EL.: vitreous carbon; Reference EL.: Pt. (b) Linear relationship of the logarithm of Si(IV) and B(III) concentration in LiF-NaF vs. time at  $T = 750$  °C

**Table 2**  
Rate constant of SiF<sub>4(g)</sub> release (k<sub>Si</sub>) for different fluoride media at various temperature.

10 <sup>7</sup> k <sub>Si</sub> (s <sup>-1</sup> ) T (°C)	KF-CsF	LiF-NaF-KF	LiF-BaF <sub>2</sub>	LiF-SrF <sub>2</sub>	LiF-MgF <sub>2</sub>	LiF-AlF <sub>3</sub>
Molar comp.	43-57	46.5-11.5-42	80.5-19.5	81.5-18.5	80.5-19.5	85-15
660	0.7	7.4				
700		10.3				
750		13				
800		15				2020
820		17.8				
850		22.2	641		917	
900			769	1156	3570	
950			1342			

### 3.2.2. Fluoroacidity scale

Tables 2 and 3 show kinetic constants of SiF<sub>4(g)</sub> and BF<sub>3(g)</sub> release in different media, where no change in their electrochemical behaviour was observed.

Selected molten mixtures to extend the fluoroacidity scale previously established by Bieber *et al.* [16] are sorted from the more fluorobasic to the left, to the more acid to the right, according to the kinetic constants.

The relative fluoroacidity scale of molten fluorides was completed by coupling our own results with those published by Bieber *et al.* (Figs. 3a and 3b), and are in agreement with the literature [14,15].

The fluoroacidity scale of single alkali fluoride compounds is in good accordance with molecular dynamics calculations aiming to determine the polarizability of a species (i.e. the tendency of an electron cloud to be distorted from its normal shape by an electric field) [30,31]. More polarizable is the alkali (i.e. in the order Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup> < Rb<sup>+</sup> < Cs<sup>+</sup>), more the fluorine is available and more fluorodonor is this element (i.e. fluorobasic). The valency of the counter ion seems also to play an important role as fluoroacidity increases with it, except for BaF<sub>2</sub>. Compared to previous observations, MgF<sub>2</sub> was found to be more basic than CaF<sub>2</sub> [13–15]. Unfortunately, to confront this result obtained with silicon, no experiments could be performed with the boron system, due to its immiscibility in CaF<sub>2</sub>-based solvents [32,33].

This method for evaluating fluoroacidity has nevertheless some limitations:

- the solute has to be chosen more acidic than the solvent to capture fluorides (i.e. fluoroacceptor),
- the solute must be in equilibrium with a gaseous species,
- the solute should not react with the solvent.

### 3.3. Fluoroacidity: mass transport approach

#### 3.3.1. Effect of composition on mass transport

To avoid the limitations previously cited, another approach based on the influence of fluoroacidity on mass transport was studied.

To compare the effect of fluoroacidity on mass transport, two LiF-AlF<sub>3</sub> eutectic mixtures have been chosen (15mol% and 35.5mol%

**Table 3**  
Rate constant of BF<sub>3(g)</sub> release (k<sub>B</sub>) for different fluoride media at different temperature.

10 <sup>7</sup> k <sub>B</sub> (s <sup>-1</sup> ) T (°C)	LiF-NaF-KF	LiF-NaF	LiF-AlF <sub>3</sub>	LiF-AlF <sub>3</sub>
Molar comp.	46.5-11.5-42	61-39	85-15	64.5-35.5
700	5.1			
750	8.3	10		
800	14	19	29	115
850	22	26	74	155
900	31	62	173	203

AlF<sub>3</sub>). Having a similar melting point, the fluoroacidity should only be influenced by the solvent composition.

Diffusion coefficients of B(III) ions were determined using equation 8. Kinematic viscosity  $\nu$  (in m<sup>2</sup> s<sup>-1</sup>), which is defined as the ratio of the dynamic viscosity  $\mu$  (in kg m<sup>-1</sup> s<sup>-1</sup>) and the density of the fluid  $\rho$  (in kg m<sup>-3</sup>), was calculated from tabulated values in the Molten Salts Handbook [34].

Results are presented in Table 4, where LiF-AlF<sub>3</sub> eutectics are sorted from the more basic to the left. Whatever the temperature, the diffusion coefficients decrease with acidity.

Akdeniz *et al.* [35] showed, by Raman spectroscopy in NaF-AlF<sub>3</sub> mixtures, that bridging fluorines increase with the AlF<sub>3</sub> content, and leads to a viscosity increase, as observed in Table 4. It is known that the viscosity increase implies a more difficult (i.e. slower) mass transport.

It was also observed that variations of diffusion coefficient are more sensitive than variations of kinematic viscosity: at a given temperature, viscosity increases slightly with the acidity, while diffusion coefficient decreases more rapidly.

As the viscosity is an intrinsic property of the solvent and the diffusion coefficient depends on the solute, the adimensional Schmidt number combining these two properties ( $Sc = \nu/D$ ) was used to characterize the molten solutions. Thus, it allows to compare the mass transport of species in molten systems, taking into account the effect of the viscosity of these systems.

At a given temperature, the results showed that  $Sc$  increases with the fluoroacidity of the molten mixtures. Table 4 shows that  $Sc$  variations with both temperature and composition are greater compared to  $D$  and  $\nu$ ; that is due to the opposite direction of change of these two properties.

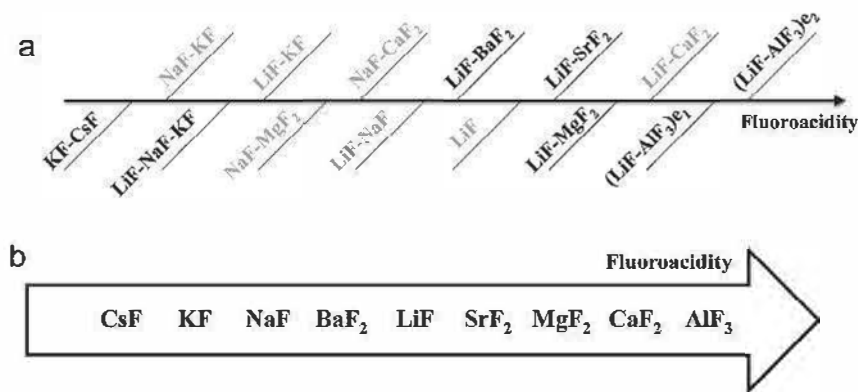
#### 3.3.2. Effect of fluoroacidity on mass transport

Table 5 presents results of Si(IV) and B(III) diffusion coefficients, determined with equations 5 and 8 respectively, in various molten fluorides at different temperatures (sorting from the more basic to the left, to the more acid to the right).

**Table 4**  
Diffusion coefficient ( $D$ ), kinematic viscosity ( $\nu$ ) and Schmidt number ( $Sc$ ) of B(III) ions for two LiF-AlF<sub>3</sub> eutectic mixtures at different temperature.

T (°C)	LiF-AlF <sub>3</sub>	LiF-AlF <sub>3</sub>
Molar comp.	85-15	64.5-35.5
10 <sup>9</sup> D (m <sup>2</sup> s <sup>-1</sup> )		
800	1.58	0.34
850	1.75	0.74
900	1.93	1.08
10 <sup>7</sup> $\nu$ (m <sup>2</sup> s <sup>-1</sup> )		
800	14.8	17.7
850	12.9	14.6
900	11.4	12.3
Sc = $\nu/D$		
800	936	5122
850	738	1964
900	592	1139





**Fig. 3.** (a) Qualitative fluoroacidity scale of various eutectic mixtures (in light grey results published by Bieber *et al.* [16]) (b) Qualitative fluoroacidity scale of different fluoride compounds

**Table 5**  
Diffusion coefficient (D), kinematic viscosity ( $\nu$ ) and Schmidt number (Sc) of Si(IV) and B(III) ions for different fluoride media at different temperature.

T (°C)	Si(IV)			B(III)	
	NaF-KF	LiF-NaF-KF	LiF-KF	LiF-NaF-KF	LiF-NaF
Molar comp.	39.7-60.3	46.5-11.5-42	51-49	46.5-11.5-42	61-39
$10^9 D$ (m <sup>2</sup> s <sup>-1</sup> )					
700		0.45	0.28	2.18 (2.06 [29])	
750	1.29	0.93	0.39	2.72	1.16
800	1.97	1.34	0.53	2.88	1.86
850	2.9	1.82	0.71	3.13	2.16
900	4.1	2.85	0.91	3.52	2.67
$10^7 \nu$ (m <sup>2</sup> s <sup>-1</sup> )					
700		12.5	12.3	12.5	
750	11.3	10.2	10.5	10.2	13.9
800	9.8	8.4	9.1	8.4	12.1
850	8.7	7.1	8.0	7.1	10.8
900	7.8	6.1	7.1	6.1	9.7
Sc = $\nu/D$					
700		2786	4395	575	
750	873	1094	2691	374	1220
800	499	629	1720	293	651
850	300	391	1132	228	499
900	191	214	785	174	362

As previously demonstrated for each temperature and for both species (silicon in Table 5, and boron in Tables 4 and 5), the diffusion coefficients decrease with the fluoroacidity. It was also noticed that the kinematic viscosity increases with fluoroacidity at a given temperature, except for NaF-KF. Its viscosity is higher than LiF-NaF-KF and LiF-KF, which are more fluoroacid.

Diffusion coefficients may also be affected by the solute ionic radius of  $\text{SiF}_{4+x}^{x-}$  and  $\text{BF}_{3+x}^{x-}$ . Indeed, Pauvert *et al.* [36] demonstrated that the coordination number increases with fluoroacidity. An increase of the solute complex radius slows down the mass transport.

The Schmidt number was calculated for silicon and boron, and the fluoroacidity ranking was the same as the one obtained with kinetic rates of gas release: Sc increases with fluoroacidity and allows sorting melts.

The diffusion coefficient is thus directly affected by a cumulative effect of the viscosity and the solute complex radius, the latter can be modified by the environmental structure and the property of the solvent to be more or less fluoroacceptor or fluorodonor.

Due to relationships between bridging fluorines, viscosity, and consequently mass transport in solution, new ways to evaluate fluoroacidity are either to measure diffusion coefficient in the molten mixtures, or for more sensitivity to calculate the Schmidt number.

#### 4. Conclusion

Dissolved species in equilibrium with gaseous compounds allow an evaluation of the melt fluoroacidity, thanks to kinetic rates of gas release. A significantly extended fluoroacidity scale was proposed, for more fluorobasic and fluoroacid compounds (divalent and trivalent species).

It was observed for alkalis that fluoroacidity decreases with polarizability. The valence of the cation is important as fluoroacidity increases with it, except for  $\text{BaF}_2$  which was found more fluorobasic than LiF. However this method has limitations as the solute:

- has to form a gaseous species and to be in equilibrium with the gas phase,
- must not react with the solvent,
- and has to be more acid (i.e. fluoroacceptor) than the solvent.

Moreover, rankings of very acid melts are difficult to perform due to the very high kinetic rates of  $\text{SiF}_{4(g)}$  and  $\text{BF}_{3(g)}$  release.

Another method to evaluate fluoroacidity was proposed in this work and was extended to systems that do not form gaseous species. This approach was found to be more suitable than the evaluation by kinetics of gas release.

It consists in measuring a mass transport property of a solute, the diffusion coefficient, which decreases with acidity. Indeed an increase of the fluoroacidity promotes bridging between units and a viscosity increase: diffusion coefficient decreases as the viscosity or the complex ionic radius increase.

As viscosity is an intrinsic property of the solvent and diffusion coefficient concerns the solute, the Schmidt number ( $Sc$ ) was proposed to compare the mass transport by taking into account the effect of the viscosity in various molten systems. Results showed that  $Sc$  increases with acidity and is a very sensitive indicator of fluoroacidity. This new approach could be envisaged to extend the fluoroacidity scale to more fluoroacid melts, as tetravalent fluorides.

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