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 $SiF_{4(g)}$ and $BF_{3(g)}$ 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.

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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:

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

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

$$\text{fluorobase} \rightleftharpoons \text{fluoroacid} + nF^- \qquad (2)$$

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 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 AlkF media, free fluorines are stated to be the dissociated fluorines. With LnF$_3$ addition, some fluorides participate to 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 Zr:F = 1:5 (i.e.: NaF-ZrF$_4$ < BaF$_2$-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 KF-ZrF$_4$ mixtures and suggested that an increase of the ZrF$_4$ amount leads to the formation of octahedral species, and to an increase of the zirconium chain length (ZrF_6^{2-}, $Zr_2F_{10}^{2-}$,

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$Zr_3F_{14}{}^{2-}\ldots$). C.F. Baes [9] worked on the relationship between viscosity and fluoroacidity in BeF_2 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 ($Be_2F_7{}^{3-}$, $Be_3F_{10}{}^{4-}$) [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^-,
- 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^- 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:

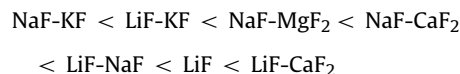$$KF\text{-}BaF_2 < KF\text{-}CaF_2 < KF\text{-}MgF_2$$
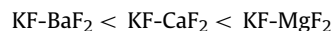
By comparing the acidic character of binary mixtures, the authors proposed the following ranking of fluoride salts from the lower to the higher acidity [14,15]:

$$NaF < BaF_2 < SrF_2 < LiF < CaF_2 < BeF_2 < MgF_2 < AlF_3$$
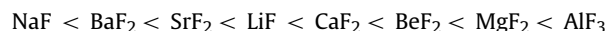
In earlier works, Bieber *et al.* proposed an extended fluoroacidity scale based on Na_2SiF_6 solute in equilibrium with $SiF_{4(g)}$ gaseous species [16–18]:

$$SiF_{4+x}{}^{x-}{}_{(bulk)} \rightleftharpoons SiF_{4(g)} + xF^- \tag{3}$$

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

$$NaF\text{-}KF < LiF\text{-}KF < NaF\text{-}MgF_2 < NaF\text{-}CaF_2$$

$$< LiF\text{-}NaF < LiF < LiF\text{-}CaF_2$$

$$KF < NaF < LiF < CaF_2$$

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_4 and BF_3. It is known that KBF_4 is decomposed at high temperatures to form $BF_{3(g)}$ [19,20] as:

$$BF_{3+x}{}^{x-}{}_{(bulk)} \rightleftharpoons BF_{3(g)} + xF^- \tag{4}$$

As for silicon, the study of the equilibrium $BF_{3+x}{}^{x-}{}_{(bulk)}/BF_{3(g)}$ was performed by doing electrochemical titrations of B(III) ions versus time. Kinetics of $SiF_{4(g)}$ and $BF_{3(g)}$ 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 = υ/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_4 (Sigma Aldrich 99.99%) and sodium hexafluorosilicate Na_2SiF_6 (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^2). The potentials were referred to a platinum wire (0.5 mm diameter) acting as a quasi-reference electrode $Pt/PtO_x/O^{2-}$ [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_2SiF_6) was investigated by Bieber *et al.* in various molten fluorides mixtures on silver electrode [16]. The results showed that Si(IV) reduction occured 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]:

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

where j_p is the peak current density (A m^{-2}), n the number of exchanged electrons, F the Faraday constant (C mol^{-1}), C the solute concentration (mol m^{-3}), D the diffusion coefficient (m^2 s^{-1}), υ the potential scan rate (V s^{-1}), R the ideal gas constant (8.314 J mol^{-1} K^{-1}), 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