Electrochimica Acta 174 (2015) 721–727

Contents lists available at ScienceDirect

Electrochimica Acta

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

Analysis of the Ionic Conduction Behavior in a Few of Room Temperature Molten Fluorides

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ARTICLE INFO

Article history:
Received 7 March 2015
Received in revised form 1 June 2015
Accepted 1 June 2015
Available online 3 June 2015

Keywords:
Self-diffusion coefficients
transference number
ionicity
hydrogen fluoride
molten salt

ABSTRACT

The average self-diffusion coefficients of cations and anions increased with increasing the HF-concentration and temperature in $(CH_3)_3N{\cdot}m$HF, $(CH_3)_4NF{\cdot}m$HF, $(C_2H_5)_3N{\cdot}m$HF, and $(C_2H_5)_4NF{\cdot}m$HF melts. The behavior of the self-diffusion coefficients of cations and anions in every melt is in good agreement with an increase in ionic conductivity and a decrease in viscosity. The transference number of $(FH)_nF^-$ anions estimated from the values of self-diffusion coefficients for each ion in every melt was almost constant and their values were around 0.6 in the $(CH_3)_3N{\cdot}m$HF melt and around 0.7 in the $(CH_3)_4NF{\cdot}m$HF, the $(C_2H_5)_3N{\cdot}m$HF, and the $(C_2H_5)_4NF{\cdot}m$HF melts. The value of theoretical conductivity (σ_{NMR}) obtained from the average self-diffusion coefficients of cations and anions by using Nernst-Einstein equation was higher than the value of experimental ionic conductivity (σ). Therefore, it is concluded that the diffusion of $(FH)_nF^-$ anions is faster than that of each cation in every melt and that a part of both cation and anion in each melt may associate by interaction between both ions.

1. Introduction

Electrochemical fluorination is a useful process for production of perfluorinated organic compounds with functional group in starting materials [1,2]. Nitrogen trifluoride, NF_3, is widely used as dry etchant and cleaning gas for manufacturing semiconductor devices and liquid crystal display [3]. Perfluorotrimethylamine $(CF_3)_3N$ is a candidate for an etching gas for SiO_2 film on Si wafer used in the semi-conductor and electronics industries [4–6]. In addition, $(CF_3)_3N$ easily decomposes to release CF_3 radical or perfluoroalkyl group, which reacts with organic compounds and promotes those lipophilicity. Therefore, it is considered that $(CF_3)_3N$ is an important trifluoromethylating reagent for synthesis of fluorocompounds such as medicines and agricultural chemicals [7,8]. $(CF_3)_3N$ can be produced by electrolysis of $(CH_3)_3N{\cdot}m$HF or $(CH_3)_4NF{\cdot}m$HF melts [5,6]. These melts are called as a room temperature molten salt. In the previous study, ionic conductivities and viscosities of $(CH_3)_3N{\cdot}m$HF and $(CH_3)_4NF{\cdot}m$HF melts have been investigated [1,6,9]. Ionic conductivity of the $(CH_3)_3N{\cdot}m$HF and $(CH_3)_4NF{\cdot}m$HF melts increased with an increase in the *m* value and temperature, whereas the viscosity decreased with an increase in the *m* value and temperature. The behaviors of ionic conductivity and viscosity for the $(C_2H_5)_3N{\cdot}m$HF and the $(C_2H_5)_4NF{\cdot}m$HF melts are similar to those for the $(CH_3)_3N{\cdot}m$HF and the $(CH_3)_4NF{\cdot}m$HF melts [9–12]. The Walden plots [13] for every room temperature molten salt deviated considerably downward the ideal Walden line. [9,11] Infrared spectra were also measured for detecting the anionic species such as $(FH)_nF^-$ ($n = 1$, 2, and 3) and a molecular HF in these melts. The amount of molecular HF increased with increasing the *m* value [1,10]. These facts indicate that the non-ionic molecular HF makes the ionic conductivity lower. From the Walden plots, it is considered that a high degree of interaction in the motion of its cations and anions, i.e., the increase in ion pairs, is

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http://dx.doi.org/10.1016/j.electacta.2015.06.002
0013-4686/

the reason for the poor conductivity at a given viscosity [9–11]. In order to confirm the validity of our consideration, we applied Watanabe approach [14,15] to estimate the ionic conductivity basically neglecting the interaction between cations and anions. Generally, the Stokes-Einstein equation is clearly valid at infinite dilution of charge carriers. However, the Stokes radius (r) of each ion estimated by Stokes-Einstein equation will provide the apparent average diffusion radius including the ionic pairs. Also, the Nernst-Einstein equation has the same rule, which is exactly valid for the electrolyte solutions at infinite dilution state [16]. But, the comparison of the real experimental ionic conductivities σ by AC impedance with the theoretical ionic conductivities (σ_{NMR}) obtained from molar concentration (c) and the average self-diffusion coefficients of cations and anions by using the Nernst-Einstein equation will supply useful information about the apparent degree of dissociation for the molten salts, i.e. ionicity.

In this study, we measured the average self-diffusion coefficients of cations and anions in the $(CH_3)_3N$·mHF, $(CH_3)_4NF$·mHF, $(C_2H_5)_3N$·mHF, and $(C_2H_5)_4NF$·mHF melts by the pulsed-field gradient spin-echo nuclear magnetic resonance (PFG-NMR) methods [17]. The Stokes radius (r) and transference numbers of cations and anions were estimated by Stokes-Einstein equation and from the obtained self-diffusion coefficients of ions, respectively. In addition, the theoretical conductivities (σ_{NMR}) were compared with the experimental ionic conductivities (σ) of $(CH_3)_3N$·mHF and $(CH_3)_4NF$·mHF melts at room temperature, respectively, in order to evaluate the ionicity of molten salts. The same comparison of σ_{NMR} with σ was also discussed for $(C_2H_5)_3N$·mHF and $(C_2H_5)_4NF$·mHF melts at room temperature.

2. Experimental

2.1. Preparation of room temperature molten fluorides of $(CH_3)_3N$·m*HF*, $(CH_3)_4NF$·m*HF*, $(C_2H_5)_3N$·m*HF*, and $(C_2H_5)_4NF$·m*HF*

$(CH_3)_3N$·mHF (m = 3.0, 3.5, 4.0, 4.5, and 5.0), $(CH_3)_4NF$·mHF (m = 3.5, 4.0, 4.5, and 5.0), $(C_2H_5)_3N$·mHF (m = 3.0, 3.5, 4.0, 4.5, and 5.0), and $(C_2H_5)_4NF$·mHF (m = 3.5, 4.0, 4.5, and 5.0) melts were prepared by feeding gaseous anhydrous HF (Morita Chemical Industries Co., Ltd.) through $(CH_3)_3N$·3.0HF, $(CH_3)_4NF$·3.5HF, $(C_2H_5)_3N$·3.0HF, $(C_2H_5)_4NF$·3.5HF (Morita Chemical Industries Co., Ltd.), respectively, in a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA) vessel placed in a glovebox purged with a dry nitrogen.

2.2. Measurement of the self-diffusion coefficients by PFG-NMR methods

^{1}H NMR measurements were conducted with JNM-ECA500 spectrometer (500 MHz, JEOL) using deuterium water (Sigma–Aldrich Corp.) as an external standard. The melts for NMR measurements mentioned above were sealed in a PFA tube in order to avoid reaction between samples and reference material, which was placed in an NMR sample tube with outer diameter of 5.0 mm (Optima USA, Inc.) filled with the deuterated solvent.

After observing presence of a peak by ^{1}H-NMR, the PFG-NMR methods were performed on JNM-ECA500 (500 MHz, JEOL) spectrometer in order to determine the average self-diffusion coefficients of cations and anions in room temperature molten

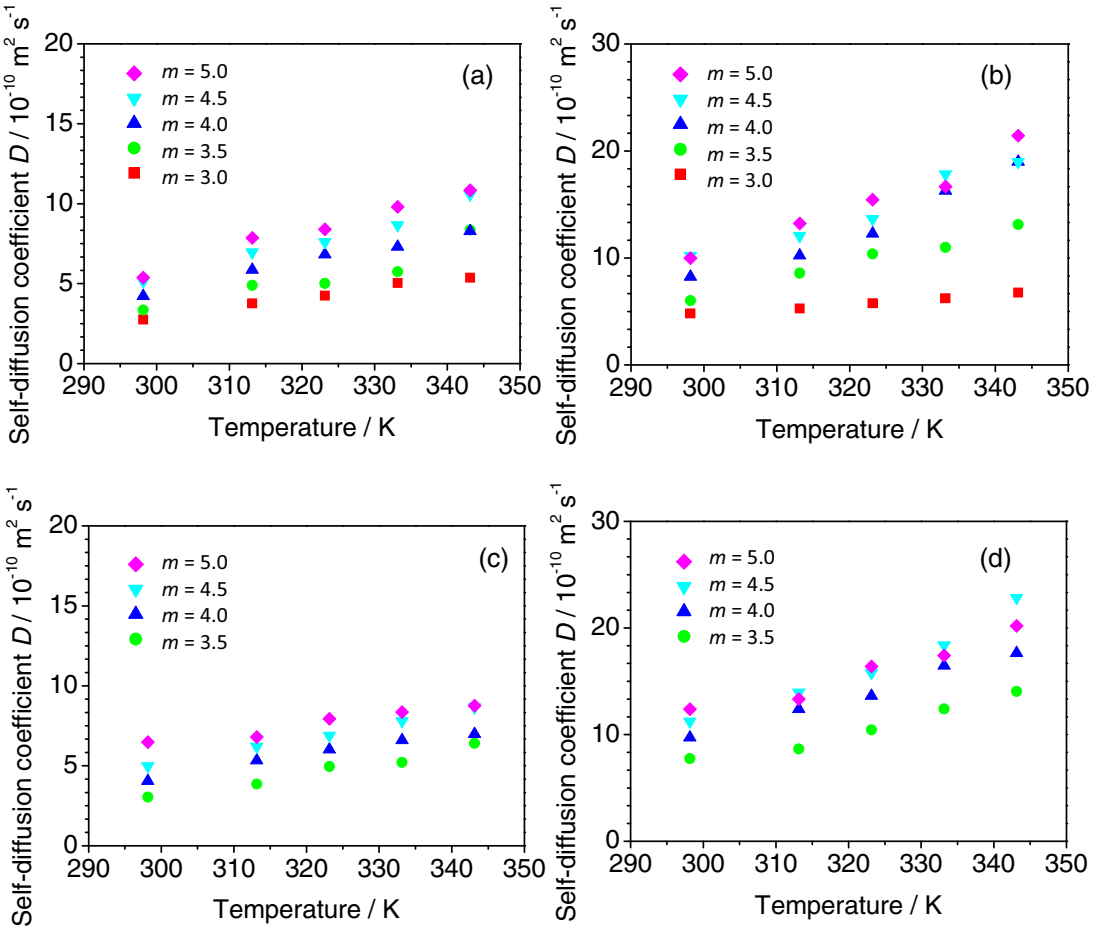

Fig. 1. Temperature dependence of the self-diffusion coefficients of $(CH_3)_3NH^+$ (a) and $(FH)_nF^-$ including HF (b) in the $(CH_3)_3N$·mHF melts and those of $(CH_3)_4N^+$ (c) and $(FH)_nF^-$ including HF (d) in the $(CH_3)_4NF$·mHF melts.