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Viscosity of fluoride melts promising for molten salt nuclear reactors

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The viscosity of molten salt, as an important hydrodynamic property, should be taken into account when creating and operating molten salt nuclear reactors (MSRs). An eutectic FLiNaK is considered to be one of the most suitable for use in MSR designed for the minor actinides transmutation. The dynamic viscosity of the molten mixtures FLiNaK + NdF_3, FLiNaK + CeF_3 and FLiNaK + LaF_3 was measured in a temperature range of 600–700 °C using the high-temperature rotary rheometer FRS-1600. Lanthanide fluorides were considered as analogues of actinide fluorides. It was revealed that the additions of rare earth fluorides $(REM)F_3$ in amount of 15 mol. % significantly impact the viscosity of the system FLiNaK + $(REM)F_3$, but the effect of NdF_3, CeF_3 and LaF_3 was found to be almost the same. In order to calculate the kinematic viscosity of the molten mixture FLiNaK + NdF_3, a regression equation depending on several parameters was derived. This model equation can be used for predicting the kinematic viscosity of molten mixtures of FLiNaK with other rare earth fluorides.

keywords: molten salts, dynamic viscosity, kinematic viscosity, FLiNaK, FLiBe, rare earth fluorides

1. Introduction

The concept of a molten salt reactor (MSR) originated in the 1940^s and was based on the creation of a new type of high-temperature liquid nuclear fuel. The capabilities of a liquid fluoride fueled reactor were demonstrated in the Aircraft Reactor Experiment (ARE) at the Oak Ridge National Laboratory (ORNL, USA) in 1954 [1]. The reactor (2.5 MW) successfully operated for 9 days at 860 °C. The molten salt NaF-ZrF_4 was chosen as the solvent for UF_4.

In recent decades, an interest in molten salt technology has been renewed as a result of research studying the possibilities of minor actinide (MA) transmutation [2–5]. The absence of complex fuel preparation and compatibility with pyrochemical processing in the liquid-salt fuel cycle have been recognized as important advantages over traditional solid fuels. A characteristic feature of the MSR-burner is that transuranium elements must be introduced into the fuel cycle as the main fissile material. Molten salts based on alkali fluorides are considered as media that ensure the operation of nuclear MSR. These includes eutectics LiF-NaF-KF (FLiNaK), LiF-BeF_2 (FLiBe), KF-ZrF_4 (FKZr), etc., characterized by optimal thermophysical, neutronic and physicochemical properties [6–10]. Molten salts can serve as a fuel salt or are intended to be used as heat transfer fluids. Eutectic compositions of fluoride salts are promising for use as a coolant: they have the lowest liquidus temperature of the system and ensure the homogeneity of the melt properties during reactor operation [11, 12]. Additional requirements are imposed on the fuel salt, the main one being sufficient solubility in the melt of fissile materials and fission products while maintaining acceptable changes in thermophysical properties [13].

Along with FLiBe the eutectic FLiNaK is considered to be one of the most appropriate for use in MSR,

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especially in reactors designed for the MA transmutation since the actinide fluorides have a fairly high solubility in FLiNaK at 600–700 °C [14–16]. Lizin at el. [15] found a high solubility of PuF_3 and AmF_3 in the molten eutectic FLiNaK, which is 30 and 43 wt. % at 700 °C, respectively. Moreover, the analogy of the solubility temperature dependences for AmF_3 and NdF_3 was recognized. Seregin et al. [16] measured the solubility of UF_4, ThF_4, and CeF_3 in FLiNaK and revealed that CeF_3 can be considered as PuF_3 imitator in FLiNaK melt. The analogy of actinides and lanthanides is confirmed by comparable physicochemical properties and similar crystallographic structure [17]. Considering that experimental measurements of the physicochemical properties of fluoride melts containing significant amounts of actinide fluorides are accompanied by large material and labor costs, then the study of these properties using imitators as an example seems quite promising.

Substantial variations in the composition of the molten mixture result in significant changes in its properties. Consequently, mass and heat transfer, hydrodynamic properties such as viscosity must be taken into account at the MSR operating temperatures in order to minimize possible complications in its functioning and melt circulation.

This paper presents the results of experimental studies of the dynamic viscosity of molten eutectic FLiNaK containing rare earth fluorides (NdF_3, CeF_3, LaF_3) in an amount of up to 15 mol. % and the results of calculation of the kinematic viscosity (using the FLiNaK + NdF_3 system as an example) in the range of operating temperatures MSR 600–700 °C.

2. Experimental

2.1. Salt preparation

The eutectic FLiNaK [(mol. %) 46.5 LiF–11.5 NaF–42.0 KF] was prepared by direct melting of components: lithium fluoride LiF (VECTON, RF); sodium fluoride NaF (GRANCHIM, RF); acid potassium fluoride KHF_2 (GRANCHIM, RF). The KHF_2 was used instead of hygroscopic KF. The KHF_2 decomposes at a temperature of about 400 °C and releases HF, which in turn prevents the hydrolysis of salts and simultaneously fluorinates oxygen containing impurities. The procedure is described in detail elsewhere [15].

The NdF_3 and CeF_3 were prepared by hydrofluorination of their oxides Nd_2O_3 and CeO_2. Techniques for the NdF_3 and CeF_3 preparation were described in detail elsewhere [18, 19]. The obtained products (NdF_3 or CeF_3) were analyzed by the XRD using a MiniFlex 600 instrument (Japan). The presence of single hexagonal phases NdF_3 or CeF_3 with no traces of oxide or chloride was confirmed.

The high purity chemical LaF_3 (99.99 %) was supplied by LANHIT (RF).

Rare earth fluorides (NdF_3, CeF_3, LaF_3) were added to the prepared eutectic FLiNaK in the required amount.

2.2. Viscosity measurement

The dynamic viscosity of fluoride melts was measured by the rotational viscometry using a high-temperature rheometer FRS-1600 (Anton Paar GmbH, Austria). The investigated melt is located between two graphite cylinders in a small 2 mm gap. The rotor is attached to the measuring "head" located at the top of the rheometer. The air-assisted pneumatic motor provides frictionless synchronous motion of the rotor, which increases the measurement sensitivity and allows measuring sufficiently low melt viscosity. The high temperature furnace and the system of two graphite cylinders before measurement are illustrated in Figure 1.

The measurements were carried out at a constant temperature, or according to a given program of cooling in a dynamic mode, in an inert gas atmosphere. Argon was used as an inert gas, which was blown through the furnace from bottom to top at a rate of about 100–150 L/h. The holes at the bottom and the top of the furnace were equipped with rings made of a heat-insulating material.

The thermal expansion of the measuring system (change in the gap width) is automatically controlled by a rheometer. The equipment and procedure for measuring the dynamic viscosity of molten salts are described in more detail elsewhere [20, 21].

The rotational viscometry is based on Newton's law for ideal liquids [22]:

$$\tau = \eta \cdot \dot{\gamma}, \tag{1}$$

where τ is the shear stress; η is the dynamic viscosity; $\dot{\gamma}$ is the shear rate.

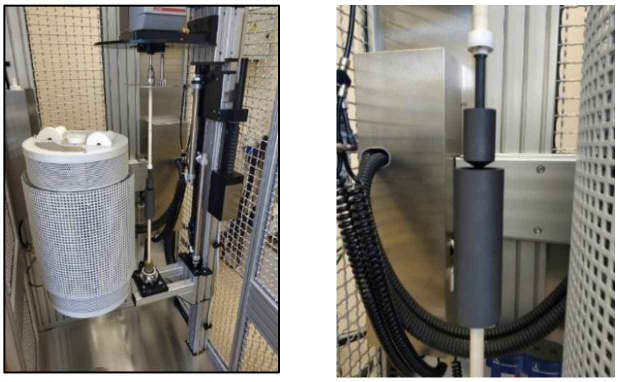

Figure 1 High temperature furnace and inner and outer graphite cylinders before measurement.

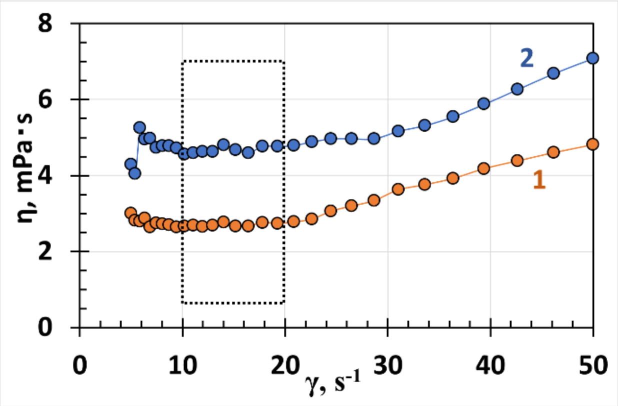

Figure 2 Viscosity curves obtained in the melt at 750 °C: 1 – FLiNaK; 2 – FLiNaK-(15)LaF_3.

The conditions of the melt laminar flow were determined from the viscosity curves, which are the dependences of the dynamic viscosity on the shear rate at a constant temperature. As an example, the viscosity curves for the FLiNaK and FLiNaK-(15 mol. %)LaF_3 at 750 °C are presented in Figure 2. For all compositions under study, the viscosity does not depend on the shear rate in the range of $\dot{\gamma}$ from 10 to 20 s^{-1}. Thus, to measure the viscosity temperature dependence a constant value of $\dot{\gamma}$ equal to 11 s^{-1} was selected.

3. Dynamic viscosity of molten system FLiNaK-(REM)F_3

The dynamic viscosity of the molten eutectic FLiNaK has been obtained by many researchers [23–28]. It was found in our previous work [21] that the dynamic viscosity of the FLiNaK obtained by the rotational method in the temperature range from the liquidus point to 750 °C is in a good agreement (within 7 %) with the literature data. The change in the dynamic viscosity of the FLiNaK and FLiNaK-15 mol. %(REM)F3 in the temperature range of 600–700 °C is given in Figure 3.

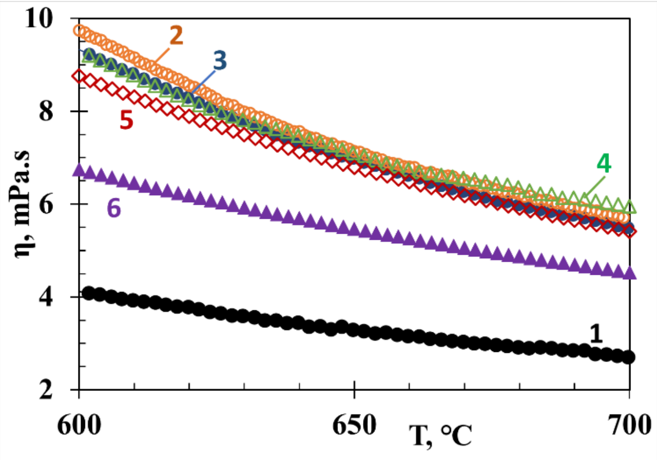

Figure 3 Dynamic viscosity of fluoride melts (mol. %): 1 – FLiNaK; 2 – FLiNaK-(15)NdF_3; 3 – FLiNaK-(15)LaF_3; 4 – FLiNaK-(15)CeF_3; 5 – (66)LiF-BeF_2 [29]; 6 – (73)LiF-BeF_2 [29].

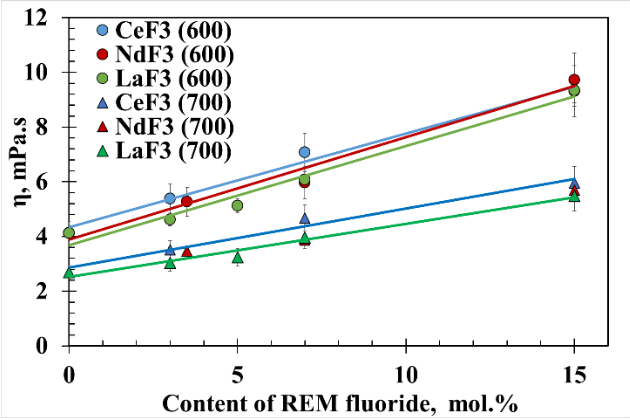

Figure 4 Influence of REM fluoride content on viscosity of the molten system FLiNaK-(REM)F_3 at 600 and 700 °C.

The viscosity of the eutectic FLiNaK with the addition of 15 mol. % REM fluorides increased by more than 2 times.

For comparison, the viscosity values of molten mixtures (mol. %) 66LiF-34BeF_2 (eutectic FLiBe) and 73LiF-27BeF_2 [29] are also presented in Figure 3. It is obvious that the dynamic viscosity of FLiBe is more than 2 times higher than that of FLiNaK in the range of 600–700 °C. At the same time, an increase in temperature by 100 degrees contributes to a decrease in the viscosity of both eutectics FLiBe and FLiNaK by 1.5 times. However, even a small increase in the proportion of LiF in the LiF-BeF_2 melt significantly reduces its viscosity.

The Influence of the REM fluoride content on viscosity of the molten system FLiNaK-(REM)F_3 at temperature 600 and 700 °C is presented in Figure 4.

As follows from Figure 4, the replacement of the REM metal cation has little effect on the change in viscosity of the molten systems FLiNaK-(REM)F_3. One can notice lower viscosity values of the FLiNaK-LaF_3. However, the discrepancy in the data lies within 5 %.

4. Kinematic viscosity of molten system FLiNaK-(REM)F_3

Based on the obtained experimental data on the dynamic viscosity and the density of the molten mixture FLiNaK + NdF_3 [30], the kinematic viscosity (ν) was calculated using the Equation:

$$\nu = \frac{\eta}{\rho}, \tag{2}$$

where η is the dynamic viscosity, ρ is the density of the melt.

The results of the calculation for compositions with NdF_3 content of 0, 3.5, 7 and 15 mol. % in the temperature range of 600–700 °C are given in Figure 5 as dots.

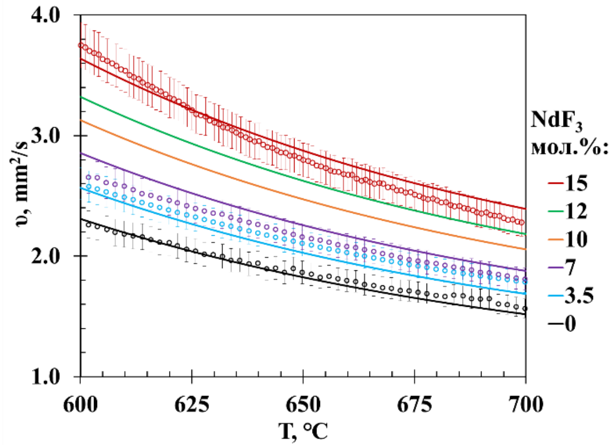

Figure 5 Kinematic viscosity of the FLiNaK + NdF_3 melt: dots – calculation according to equation (2); lines – calculation according to equation (3).

To predict and estimate the kinematic viscosity of the FLiNaK-NdF_3 in wide temperature and concentration ranges, a mathematical equation was obtained by the statistical method of regression analysis (Origin (Graphing & Analysis) software package). The resulting regression equation for the dependence of the kinematic viscosity of the FLiNaK-NdF_3 melt on composition and temperature is the following:

$$\nu = exp(13.25 + 0.03 \cdot X - 0.023 \cdot T + 1.03 \cdot \cdot 10^5 \cdot T^2), \quad (3)$$

where X is the concentration of NdF_3 (mol. %), T is the temperature (K).

The equation is valid for the NdF_3 concentrations of 0–15 mol. % at temperatures 500–750 °C. The results of the kinematic viscosity calculations using the regression Equation (3) in the operating temperature range of 600–700 °C are shown in Figure 5 as solid lines.

Comparison of the kinematic viscosity values for the FLiNaK + NdF_3 melts obtained according to the experimental data on dynamic viscosity (Equation (2)) and the calculated results using the mathematical Equation (3) revealed that the average percentage of the deviation of the calculated viscosity from the experimental one does not exceed 5 %.

Merzlyakov et al. [25] studied the kinematic viscosity of the molten eutectic FLiNaK containing 5 and 10 mol. % of CeF_3 by the torsion oscillation method. When comparing the kinematic viscosity temperature dependences of the FLiNaK-CeF_3 system, calculated using the approximating equations of Ref. [25], and of the FLiNaK+NdF_3 system, calculated using the model Equation (3), some disagreements were found. The mentioned temperature dependences are presented in Figure 6.

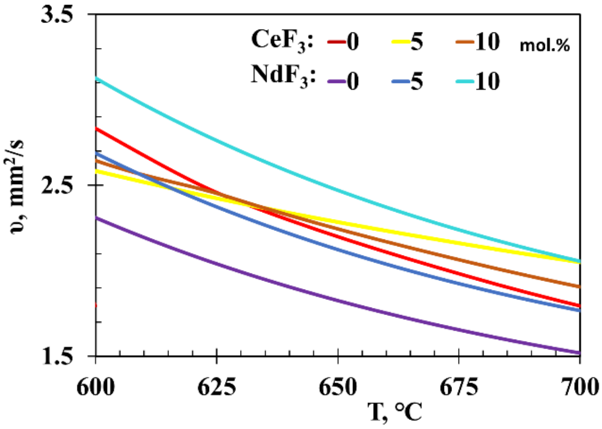

Figure 6 Kinematic viscosity of the FLiNaK + NdF_3 melt calculated according to the Equation (3) and of the FLiNaK + CeF_3 system calculated according to the equations in Ref. [25].

First, it should be noted that the kinematic viscosity of the FLiNaK without additives obtained in work [25] and in the present study differs by 20 %. It was also revealed in Ref. [25] that the addition of CeF_3 (5 and 10 mol. %) significantly reduced the viscosity at low temperatures and slightly increased it – at high temperatures. Moreover, the impact of 5 mol. % CeF_3 was more significant both at low and high temperatures. The Figure 6 indicates that the critical point is 630 °C. The authors explain this behavior by the destruction of cluster groups, present in the molten FLiNaK, due to the CeF_3 introduction. Nevertheless, this phenomenon is not observed for the FLiNaK + NdF_3 system. According to our data, there is a systematic and natural increase in the viscosity of the FLiNaK with increasing concentration of the NdF_3 additives.

When creating and operating molten salt nuclear reactors aimed at the transmutation of minor actinides, it is necessary to have information regarding the thermophysical and physicochemical properties of molten mixtures containing a sufficient concentration of minor actinides. However, it is extremely difficult and expensive to perform experimental studies with such objects. The solution to the problem lies in conducting research using analogues of actinides as well as *ab initio* modeling of processes. Both approaches have their limitations, which can be circumvented, for example, by using several methods at once. The first work is already underway [31–33].

5. Conclusion

The dynamic viscosity of molten eutectic FLiNaK increased by more than 2 times with the addition of 15 mol. % (REM)F_3. However, the replacement of the REM metal cation (Nd^{3+}, Ce^{3+}, La^{3+}) in fluorides does not noticeably affect the viscosity of the FLiNaK-(REM)F_3 systems. A regression equation was derived that relates several parameters (kinematic viscosity, concentration of NdF_3, and temperature) for calculating the kinematic viscosity of the FLiNaK + NdF_3 mixture. The values calculated by the model equation and the experimental data coincide within 5 %; in this way, the model equation can be used to predict the kinematic viscosity of FLiNaK with other rare earth fluorides.

Supplementary materials

No supplementary materials are available.

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Author contributions

Olga Tkacheva: Conceptualization; Data curation; Writing – Original draft; Writing – Review & Editing.

Alexey Rudenko: Investigation; Formal Analysis; Software; Visualization.

Alexander Kataev: Investigation; Resources; Validation.

Conflict of interest

The authors declare no conflict of interest.

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