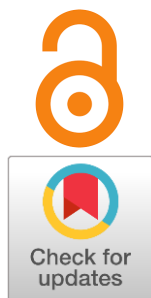


Current state of research on the viscosity of molten fluorides

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The development of new high-precision equipment for the experimental study of the physical-chemical properties of molten salts has led to the emergence of new data. This review examines recent experimental results on the viscosity of molten salt mixtures based on alkali fluorides, which are currently used in modern technologies for the production of metals and alloys and are also promising media for application in molten salt nuclear reactors. Various approaches to the analysis of experimental data are discussed. A different mechanism of viscous flow in the series LiF – NaF – KF and KF – RbF – CsF is well explained from the position of the theory of the autocomplex structure of molten salts. An anomalous decrease in the viscosity of fluorides from lithium to cesium, in comparison with other alkali metal halides, the viscosity of which increases with increasing the cation radius, is confirmed by calculations of the formation energy of the autocomplex and the binding energy between the complex-forming ion and the free ion of the second coordination sphere. To study the mechanism of liquid flow, the temperature dependence of dynamic viscosity is analyzed using the fluidity parameter. Additional information regarding the mechanism of viscous flow can be obtained from the relationship between the viscosity and electrical conductivity of melts. It was assumed that the most promising approach to studying the kinematic properties and the structure of molten salts is the use of both high-precision experiment and mathematical modeling based on first principles.

keywords: molten fluorides, dynamic viscosity, fluidity, electrical conductivity, molar volume, energy activation

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1. Introduction

Molten salts of alkali fluorides and their mixtures with alkaline earth and rare earth fluorides, due to their thermophysical, chemical, and hydrodynamic properties, are widely used in various technological processes: as solvents and participants in the electrolytic production of many metals and alloys, as a fuel salt and coolant in molten salt nuclear reactors (MSR), in solar energy concentration systems in a Concentrated Solar Power (CSP) plant, etc. [1–4].

In technological processes, as a rule, eutectic mixtures are used, the melting point of which is significantly lower than the melting point of individual fluorides and can be about 673–723 K. For example, an eutectic LiF – BeF₂ (FLiBe) has a melting point of 731 K or an eutectic

LiF – NaF – KF (FLiNaK) has a melting point of 727 K. Fluoride salts are characterized by thermal stability (up to temperatures above 1273 K) as well as low vapor pressure compared to chlorides. Mixtures based on alkali fluorides are good solvents for oxides, fluorides of alkaline earth, and rare earth metals. Their physical properties, such as density, electrical conductivity, thermophysical, and hydrodynamic properties, satisfy basic technological requirements [6]. However, the disadvantages include their high aggressiveness at elevated temperatures, which complicates the choice of structural materials.

Viscosity is an important characteristic of a molten salt, which is necessary for assessing mass and heat transfer, hydrodynamic processes in electrolysis and reactor plants. From the fundamental point of view, the study of viscous fluid flow, which is determined by the movement and interaction of molecules, is a contribution to the development of the liquid state theory.

Despite the importance of such a property as viscosity, its value has not been precisely established even

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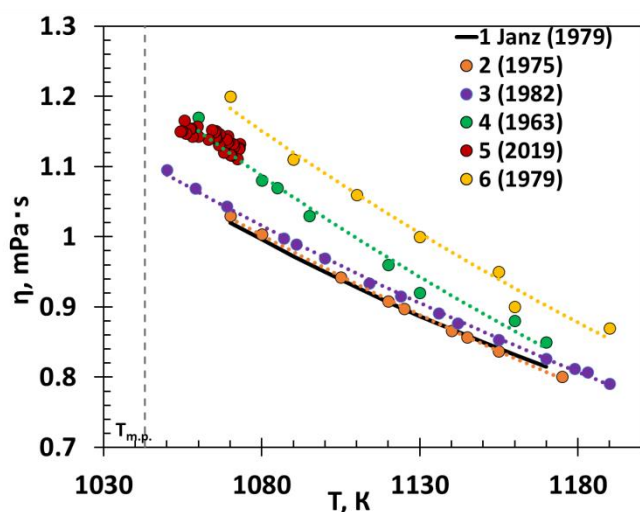


Figure 1 Viscosity of molten KCl: 1 – [8], 2 – [9], 3 – [10], 4 – [11], 5 - unpublished data from the Institute of High Temperature Electrochemistry (IHTE), 6 – [10].

for many widespread salts. For example, according to the available (about 18) references collected in [7], the experimental values of the viscosity for the NaCl melt and the coefficients of the viscosity temperature dependence differ by a factor of 1.5 (near the melting point).

Viscosity of the KCl melt, according to data from 6 references, is displayed in Figure 1. The spread of experimental data is 20 %.

Serious disagreements between the data of different scholars are determined not only by the quality of the chemicals, but also by the measurement method. When choosing a method, it is necessary to take into account the high melting point and chemical aggressiveness of molten fluorides along with quite low values of dynamic viscosity (about 1–10 mPa · s). It is customary to use correlation data of Janz (1988) [12] as reference values for the molten salt viscosity. Considering that, there has been unprecedented development in experimental, computational and analytical methodologies over the past couple of decades, the viscosity data obtained using modern facilities must be considered.

This review observes the latest experimental data on the viscosity of molten fluoride salts, currently applied in conventional technologies to produce metals and alloys, as well as promising salt mixtures for new technological processes associated with the creation of molten salt nuclear reactors. In addition, various approaches to analyzing experimental results are discussed.

2. Methods for measuring the viscosity of molten fluorides

The following methods are mainly used to study the viscosity of molten salts: capillary, falling ball, oscillatory, vibration, rotational. They are based on different

measuring principles over different temperature and viscosity ranges. The capillary and vibration methods are more suitable for low-viscosity liquids, while the falling ball and rotary methods are used to study liquids with higher viscosity [13]. Although the capillary method, which is widely utilized for measuring viscosity, is highly accurate, its use for fluoride melts is limited by the selection of structural materials that are resistant to the effects of the melt at high temperature. As a rule, molten fluorides are studied using the oscillatory [14–18] or rotational [19, 20] technique.

The oscillatory method is based on measuring the motion parameters of pendulums suspended on an elastic thread: the period of torsional oscillations and the damping amplitude. The fundamental difference in the designs of viscometers is associated with the location of the melt relative to the pendulum: either the stationary vessel contains the melt into which the pendulum is immersed, or the pendulum is the vessel itself with the melt. The period of complete oscillation and the logarithmic decrement depend on the viscosity and density of the liquid, as well as on the parameters of the device: the elasticity of the hanging thread and its length, the moment of inertia of the pendulum. To determine these parameters, viscometers must be calibrated against liquids with well-established viscosities and in the appropriate temperature range. The main sources of error are related to the method of recording vibrations.

For example, Popescu and Constantin [18] measured the viscosity of individual alkali fluorides by the oscillation method. They used a platinum ball suspended on a tungsten thread, which was immersed in the melt. Certain improvements were made to determine the period of vibration damping more accurately, which made it possible to measure the viscosity with an accuracy of $1.5 = 2$ %. Viscosity was calculated using the Verschaffelt equation, which included the values density of liquid, radius of sphere, the moment of inertia of the pendulum, time of swing in liquid and vacuum, logarithmic decrement of the oscillation. Calibration was carried out using the NaCl melt.

Merzlyakov et al. [21] measured the viscosity of binary LiF – ThF₄ and ternary LiF – ThF₄ – BeF₂ fluoride systems using the torsional oscillations of a cylindrical crucible filled with a molten salt mixture. The pendulum had additional weights to increase the moment of inertia, which was determined in preliminary experiments with five rings of the same mass and geometric dimensions. The mass and moment of inertia of the system loaded with rings obviously exceeded the similar parameters of the system with the melt. A cylindrical crucible made of steel

was suspended on an elastic string. The decrement of attenuation and viscosity were measured at cooling.

Abe et al. [22] studied the LiF and FLiBe (0.66LiF – 0.34BeF₂) melts with a high-temperature oscillating-cup viscometer. The cylinder with the test salt was sealed and suspended on a thin Pt-W wire. For precise measurements of the period and the logarithmic decrement, an optical measuring system was used. The accuracy of measurements was estimated to be ± 1.3 %.

It can be assumed that the accuracy of measuring the viscosity of molten fluorides using the oscillatory method is 1–5 %, according to various sources [14–18, 21, 22].

The rotational method is based on measuring the force acting on the rotor (torque) as it rotates at a constant angular velocity (rotation speed) in the melt. The liquid under study is placed in a small gap between two cylinders, one of which is stationary, and the other rotates at a constant speed. Fundamentally, the designs of rotational viscometers differ in which of the cylinders is the rotor – internal or external. The rotational motion of the viscometer rotor is transmitted to another surface through the movement of a viscous medium. Thus, the rotor torque of a rotational viscometer is a measure of viscosity. The basic law that underlies the rotational method and describes the flow of an ideal fluid is Newton's law:

$$\tau = \eta \cdot \dot{\gamma}, \quad (1)$$

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

The dynamic viscosity of fluoride molten mixtures was studied in work [23] by the rotational method using an FRS-1600 rheometer (Anton Paar GmbH, Graz, Austria). When measuring the viscosity of melts using the rotational method, it is necessary, first, to determine the experimental conditions of laminar Newtonian fluid flow. The range of laminar flow is determined by viscosity curves ($\eta = f(\dot{\gamma})$) – viscosity should not depend on the shear rate, or by flow curves ($T = f(\dot{\gamma})$) – viscosity changes proportionally with the shear stress [24]. For example, the viscosity and flow curves obtained in the molten mixture NaF – AlF₃ with cryolite ratio (CR) 2.5 [20] (CR = $X(\text{NaF}) / X(\text{AlF}_3)$, mol/mol) are given in Figure 2.

The maximum values of the shear rate, at which the transition from laminar to turbulent movement occurs, can be determined as by the viscosity as by flow curves. According to both curves this transition takes place at a shear rate of 20 s⁻¹. However, at lower shear rates (below 10 s⁻¹), a large scatter of points is observed on the viscosity

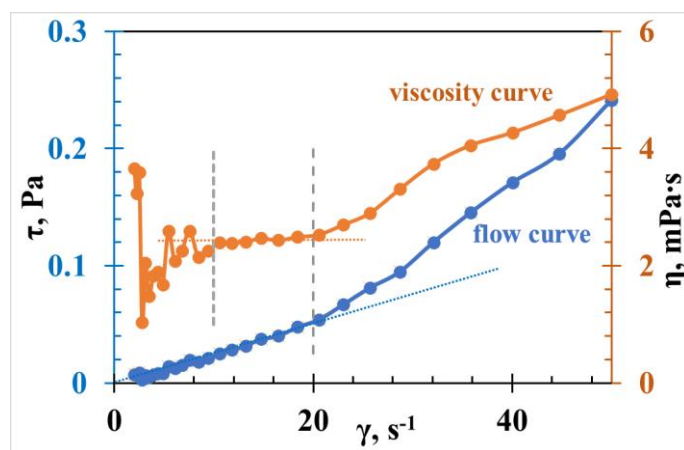


Figure 2 The viscosity and flow curves obtained in the NaF – AlF₃ (CR = 2.5) melt at 1273 K [20].

curve. This is due to the selected measurement conditions, under which the specified measurement time does not correspond to the laminar flow speed [20]. Therefore, the viscosity measurements in the NaF – AlF₃ melts should be performed at shear rates of 10–20 s⁻¹.

The range of the shear rate parameter corresponding to laminar flow has to be determined for each melt under study. For example, this range for the molten FLiNaK was 10–20 s⁻¹ (1023 K) [25] and for the FLiBe = 6–20 s⁻¹ (973 K) [26].

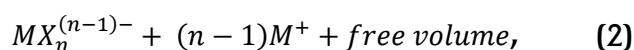
Cohen and Jones [27] determined the viscosity of the FLiNaK using a Brookfield DV-III rotational viscometer with an improved measuring head. The melt was in a graphite crucible (diameter 30 mm, depth 220 mm); a rotor immersed in the melt was connected to the measuring head via a platinum wire. The rotor rotation speed was 30 rpm, which ensured Newtonian movement of the melt. The measurements were carried out at a cooling rate of 1 K/min.

Since the temperature dependence of viscosity is usually obtained in a dynamic mode during cooling, Rudenko et al. [20] studied the effect of the cooling rate (0.5, 2 and 5 deg/min). It was found that measurements of the viscosity temperature dependence for the molten fluorides can be carried out at a cooling rate of 2 deg/min, while the system is almost close to the equilibrium state. It was revealed that the relative error in measuring the viscosity of fluoride melts by the rotational method using the FRS-1600 rheometer does not exceed 1.5 %.

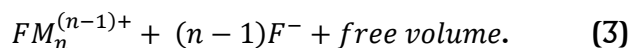
3. Viscosity of alkali metal fluorides

The dynamic viscosity of all alkali metal fluorides over a wide temperature range was measured by Popescu et al. (2015) [18] using the oscillatory method. It is revealed that at temperatures 283–303 degrees above the melting point of each fluoride, the viscosity decreases in the series

$\text{LiF} > \text{NaF} > \text{KF}$ and increases in the series $\text{KF} > \text{RbF} > \text{CsF}$. This fact designates a different mechanism of viscous flow, which is determined by the ionic structure of the melts. The experimental facts obtained are well explained from the position of theory of the autocomplex structure of molten salts, developed for alkali halides by Smirnov with co-workers [28, 29]. According to this model, in ionic melts, an ion-dipole interaction is superimposed on the ion-ion interaction, which arises due to different ionic moments ($\mu = z/r$, z is charge, r is radius). There is a violation of symmetry in the relative arrangement of particles; more polarizable ions are grouped around ions with a large ionic moment, forming autocomplexes. The excess (free) volume resulting from the melting of salts is distributed between complexes and free ions. Thus, molten alkali halides can be represented as a system of ions:



where M is the alkali metal, and X is halogen. However, for KF , RbF and CsF , the formation of complex cations rather than complex anions is more energetically favorable, which is associated with the values of the ionic moments of K , Rb , Cs and F . The ionic structure of these salts can be represented as:



Thus, in a LiF (and NaF) melt, viscosity is determined by the movement of complex anions LiF_4^{3-} (coordination number can vary from 1 to 6) and Li^+ , and in a CsF (RbF , KF) melt – by the movement of complex cations FCs_4^{3+} and F^- .

The dependence of dynamic viscosity calculated using the equations given in [18] on the cation radius at a temperature 10 degrees above the melting point of each salt and at a fixed temperature is given in Figure 3. The ionic radii of alkali metals with coordination number VI were taken into account [30, 31].

The autocomplexes are destroyed as the temperature rises, which leads to a decrease in the viscosity of all salts. However, a trend that is paradoxical from a physical point of view is established – a decrease in the viscosity of alkali fluorides with an increase in the cation radius. Moreover, this dependence is linear, indicating the similarity of the viscous flow mechanism for the $\text{LiF} - \text{NaF}$ and $\text{KF} - \text{RbF} - \text{CsF}$ salt groups.

The binding energy of particles in the melt is equal to the sum of the formation energy of the autocomplex (ΔU_I) and the binding energy between the complex-forming ion

and the free ion of the second coordination sphere (ΔU_{II}). The binding energies ΔU_I and ΔU_{II} for molten alkali fluorides, calculated based on data [29] at a temperature 10 degrees above the melting point of each fluoride and 1350 K are presented in Figures 4 and 5, respectively.

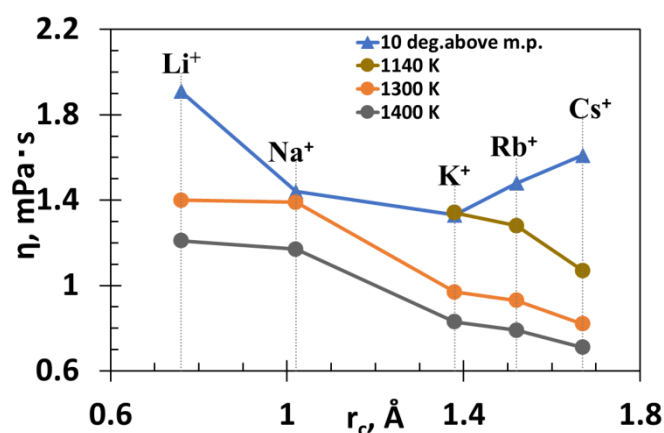


Figure 3 Dependence of dynamic viscosity on the cation radius in alkali fluorides at different temperatures.

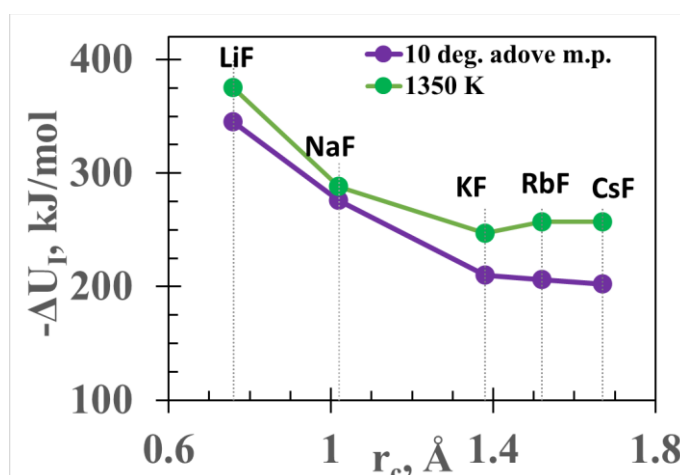


Figure 4 The formation energy of the autocomplex (ΔU_I) in molten alkali fluorides.

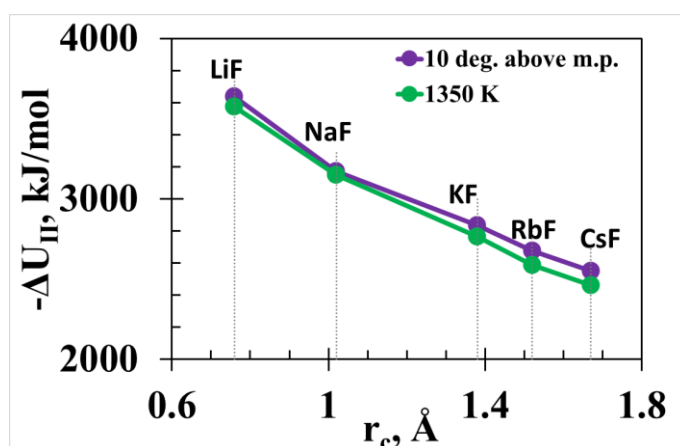


Figure 5 The binding energy between the complex-forming ion and the free ion of the second coordination sphere (ΔU_{II}) in molten alkali fluorides.

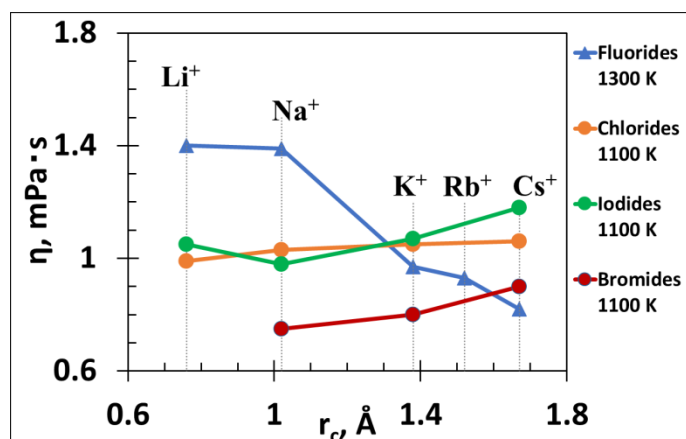


Figure 6 Viscosity of alkali halides calculated according to the reference data [18, 29].

The formation energy of complexes ΔU decreases in the order from LiF to NaF. However, for KF, RbF, and CsF it changes insignificantly, which again confirms the different ionic structure of the alkali fluoride melts. However, as the binding energy ΔU_{II} between the free ions of the second coordination sphere and the complexing ion decreases, the viscosity decreases appropriately, as illustrated in Figure 6.

A comparison of the viscosity of alkali halides in the series of fluorides, chlorides, bromides, and iodides, calculated according to the data [18, 29], is presented in Figure 6.

It should be noted that the decrease in the viscosity of melts in the series of fluorides from lithium to cesium is anomalous in comparison with other alkali metal halides, the viscosity of which increases with increasing cation radius [29].

4. Viscosity of molten mixtures based on alkali fluorides

The dynamic viscosity of binary salt systems LiF – KF, measured by the oscillatory method [32], and NaF – KF, obtained by the rotational method [33], is presented in Figure 7.

The viscosity of the salt mixtures without LiF is higher (at a given temperature). In general, the viscosity values

are low, and, for example, they vary from 2.0 to 2.5 mPa·s at 1000 K. The equations for the viscosity temperature dependence of these systems are given in Table 1.

The data of Janz (1981) [35] based on the results of Torklep and Oye (1980) [36] were considered the most reliable. Over the past decades, values for the viscosity of the FLiNaK have been obtained that coincide with Janz data within 5 % (Figure 8). In this figure, the lines represent the results calculated using the equations borrowed from the corresponding references, the dots denote the experimental points.

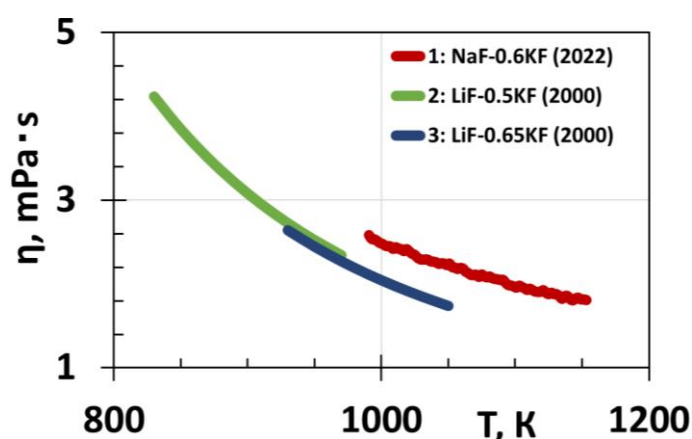


Figure 7 Viscosity of binary salt systems LiF – KF [32] and NaF – KF [33].

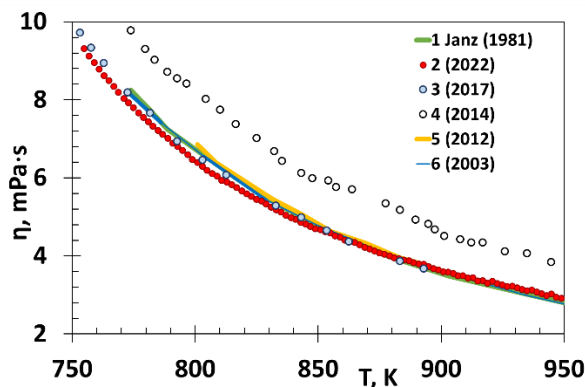


Figure 8 Viscosity of molten FLiNaK: 1 – [35], 2 – [33], 3 – [19], 4 – [17], 5 – [14], 6 – [16].

Table 1 – The equations of the viscosity temperature dependence for some salt mixtures.

Composition	Equation	R ²	Temperature range	Ref.
NaF – 0.6KF	$\ln(\eta) = -1.5898 + 2.504 \cdot 10^3/T$	0.99	990–1153	[33] (2022)
LiF – 0.5KF	$\ln(\eta) = -2.664 + 3.410 \cdot 10^3/T$	–	830–970	[32] (2000)
FLiNaK	$\ln(\eta) = -4.574 + 6.907 \cdot 10^3/T$	0.99	1030–1200	[33] (2022)
0.66LiF – 0.34BeF ₂ (FLiBe)	$\ln(\eta) = -2.5116 + 4.087 \cdot 10^3/T$	1	733–1073	[26] (2022)
NaF–AlF ₃ – 3 wt. %Al ₂ O ₃ (CR = 2.1)	$\ln(\eta) = -3.018 + 4.9438 \cdot 10^3/T$	0.98	1240–1290	[43] (2021)
KF – AlF ₃ (CR = 1.3)	$\ln(\eta) = -5.242 + 6.202 \cdot 10^3/T$	0.98	1034–1073	[20] (2023)

The eutectic LiF – BeF₂ (FLiBe) is considered to be the most promising for use as a solvent medium and coolant in molten salt nuclear reactors [5, 6, 37]. Janz (1974) [38] published reference viscosity values for the eutectic composition LiF – BeF₂ based entirely on Cantor (1968) measurements [39].

The viscosity of the melts with the composition of 0.66LiF – 0.34BeF₂ has been measured by many researchers [34]. The results obtained in recent years are presented in Figure 9.

Fluoride melts, the main component of which is sodium cryolite Na₃AlF₆ (Na₃AlF₆ = 3NaF – AlF₃), are of the greatest practical importance since they are used as an electrolyte-solvent for alumina in the electrolytic production of aluminum. A comparative analysis of the available experimental data on the viscosity of sodium cryolite melts with different CR and concentrations of the key additives (CaF₂, MgF₂) was performed by Robelin and Chartrand [41]. They assumed that the viscosity of cryolite-alumina electrolytes of the conventional composition NaF – AlF₃ – CaF₂ – Al₂O₃ with CR = 1.8–2.6 varies from 1 to 5 mPa·s in the temperature range of 1218–1243 K.

It should be noted that it is quite difficult to compare experimental data, since cryolite electrolytes are usually multicomponent systems, and the melt composition studied by the researchers often does not coincide. In addition, if sodium cryolite is prepared from individual components, it is necessary to take into account the almost always present alumina impurity (up to 3–5 wt. %), which significantly affects the viscosity of the melt. Besides, the experimental difficulties caused by very high temperatures and the chemical aggressiveness of fluoride melts should not be excluded.

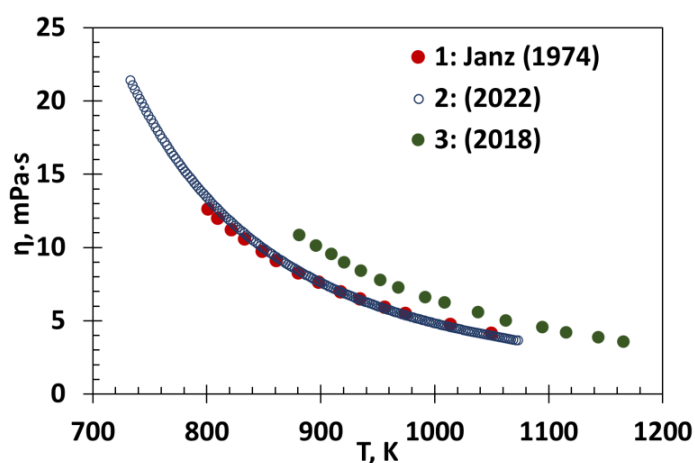


Figure 9 Viscosity of molten 0.66LiF – 0.34BeF₂: 1 – [38], 2 – [26], 3 – [40].

The viscosity of cryolite melts NaF – AlF₃ depending on CR (2.1–2.5), the content of CaF₂ and Al₂O₃ was measured by the rotational method in works [23, 42, 43]. However, the viscosity values of cryolite melts presented by these authors are higher than previously known values [41]. Some results of these references are compared in Figure 10.

Both the Al₂O₃ and CaF₂ additives, as well as the CR increasing, raise the viscosity of the cryolite melt.

Data related to the viscosity of cryolite melts with low CR are scarce. The melt of sodium cryolite NaF – AlF₃ with CR = 1.22 of the eutectic composition was studied by the oscillatory method by Chrenkova et al. [46]; and the melt of potassium cryolite KF – AlF₃ with CR = 1.3, close in composition to eutectic, was measured by the rotational method by Rudenko et al. [20]. These results are presented in Figure 11.

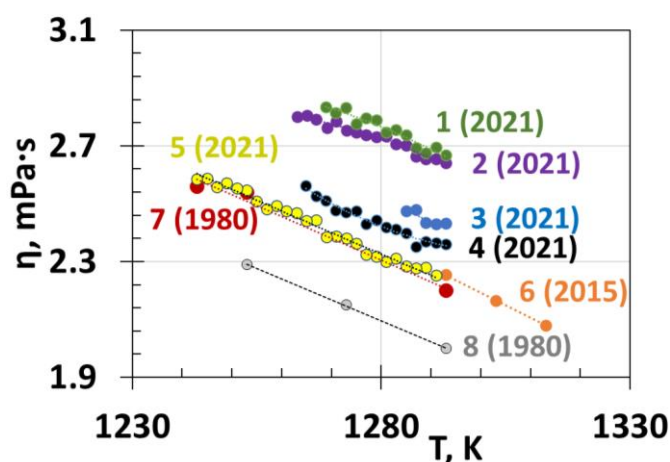


Figure 10 Viscosity of molten cryolite mixtures: 1 – NaF – AlF₃ – 2 wt. %Al₂O₃ (CR = 2.5) [45], 2 – NaF – AlF₃ – 5 wt. %CaF₂ – 2 wt. %Al₂O₃ (CR = 2.3) [44], 3 – NaF – AlF₃ – 5 wt. %Al₂O₃ (CR = 2.5) [45], 4 – NaF – AlF₃ – 2 wt. %Al₂O₃ (CR = 2.3) [44], 5 – NaF – AlF₃ – 3 wt. %Al₂O₃ (CR = 2.1) [45], 6 – NaF – AlF₃ (CR = 3) [46], 7 – NaF – AlF₃ – 8 wt. %Al₂O₃ (CR = 2.3) [47], 8 – NaF – AlF₃ – 4 wt. %Al₂O₃ (CR = 2.3) [47].

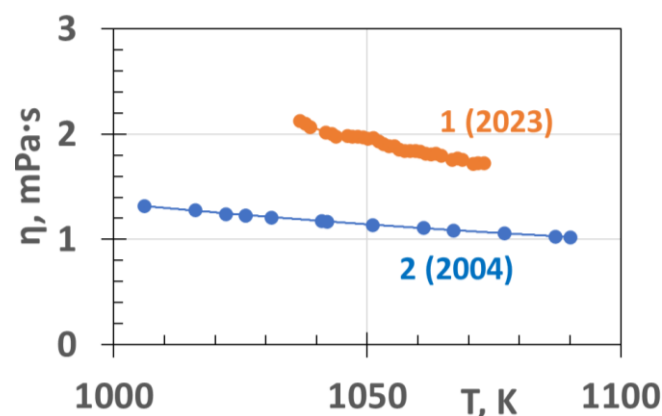


Figure 11 Viscosity of cryolite melts with low CR: 1 – KF – AlF₃ (CR = 1.3) [20], 2 – NaF – AlF₃ (CR = 1.22) [46].

It should be noted that the temperature range for measuring the viscosity of cryolite melts with $CR < 1.3$ is lower by more than 150 degrees than this one for melts with $2.1 < CR < 3.0$, which should significantly affect the decrease in viscosity. Thus, the viscosity of the NaF – AlF₃ (CR = 1.22) is 1.2–1.3 mPa · s in the temperature range of 1000–1020 K, which is almost 2 times less than the viscosity of NaF – AlF₃ with CR = 3. However, the viscosity of KF – AlF₃ melts (CR = 1.3), which are promising for the low-temperature production of aluminum and its alloys, remains quite high (about 2 mPa · s).

5. Temperature dependence of viscosity of the alkali fluorides and their mixtures

As a substance transfer phenomenon, the viscosity of fluorides obeys the exponential law of particle distribution and is described by the Arrhenius equation:

$$\eta = A_{\eta} \cdot \exp(E_{\eta}/R \cdot T), \quad (4)$$

where η – dynamic viscosity (Pa · s), E_{η} – activation energy of viscous flow (J/mol), A_{η} – constant determined experimentally (Pa · s), R – universal gas constant (J/(mol · K)), T – temperature (K). The viscosity temperature dependence of some alkali fluorides and their mixtures is given in Figure 12.

The equations of the viscosity temperature dependence for some salt mixtures, the main component of which is alkali fluoride, are summarized in Table 1.

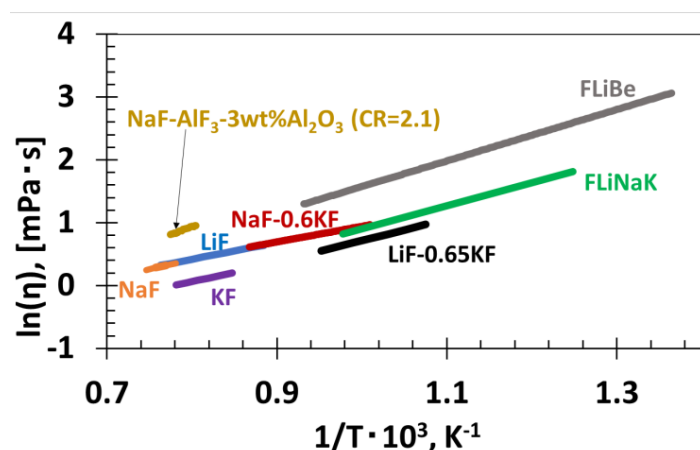


Figure 12 Temperature dependence of the dynamic viscosity of alkali fluorides and their mixtures.

6. Fluidity

To study the mechanism of liquid flow, the temperature dependence of dynamic viscosity is analyzed using the formulas of Batchincki [49], Hildebrand [48] and their modifications [18, 49–51], which relate fluidity (ϕ) to

specific or molar volume (V). For example, Chhabra and Shridhar [51] use the following expression:

$$\phi = 1/\eta = B \cdot [(V - V_0)/V_0], \quad (5)$$

where B and V_0 are empirical coefficients. The coefficient V_0 is found at the point of intersection of the function $\phi = f(V)$ with the abscissa axis – this is the molar volume at $\phi = 0$. For most individual molten salts, this relationship is linear. The dependence of the fluidity of molten alkali fluorides on the molar volume is presented in Figure 13.

From Equation (5) it follows that the viscosity of the liquid is inversely proportional to the free volume ($V - V_0$), which is a function of temperature, and when the melt is heated, only the free volume increases. If the physical meaning of the coefficient V_0 can be attributed to a hypothetical liquid in which there is no free volume, this volume should be close to the free volume of a crystalline substance near the melting point, then the physical meaning of the coefficient B is not so clear. Marcus [49] believes that B is related to the interionic interaction: the stronger the interaction between the ions the less the fluidity.

Viscosity data can be presented as a dependence of fluidity on temperature [52]. At high temperatures, this dependence is linear for ionic salts, when the viscosity is determined by the diffusion nature of the flow. However, for melts prone to glass formation (polymerization), this dependence is not linear. The fluidity of LiF and LiF – BeF₂ melts depending on the reduced temperature is presented in Figure 14. T_0 is the temperature at $\phi = 0$, obtained by asymptotic analysis of the function $\phi = f(T)$ (Figure 15). To derive these dependencies, the experimental data were taken from references [18] and [26].

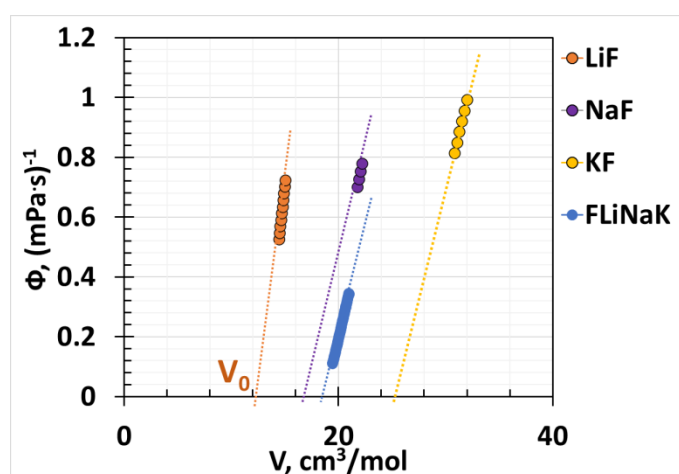


Figure 13 Dependence of the fluidity of molten alkali fluorides on the molar volume.

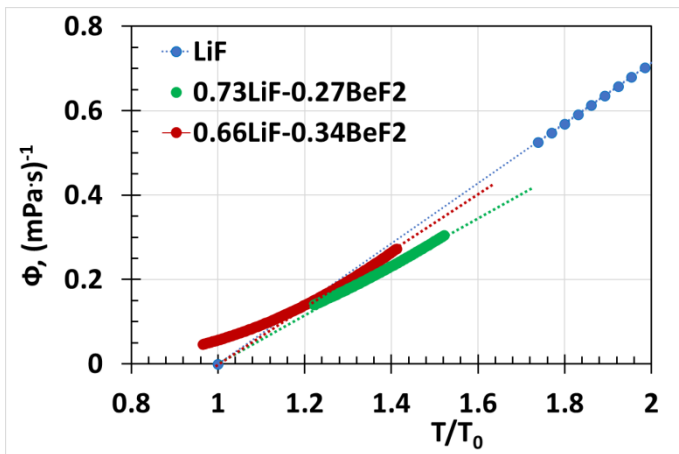


Figure 14 Dependence of melt fluidity on reduced temperature.

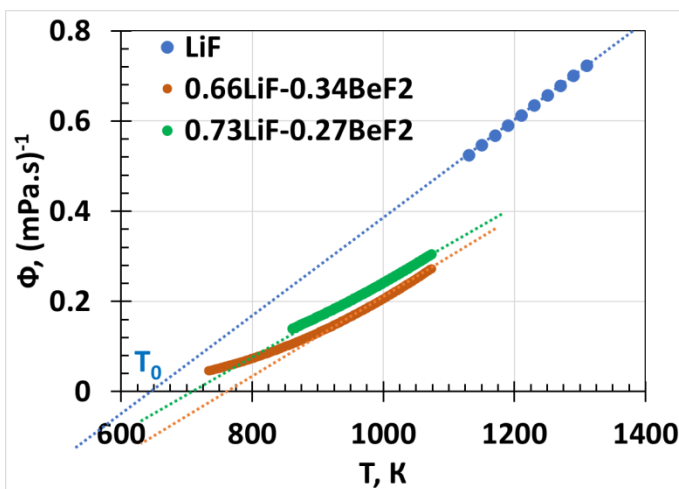


Figure 15 Dependence of the fluidity of molten fluorides on the temperature.

If the dependence $\Phi = f(T/T_0)$ for the LiF melt is linear, then for the LiF – BeF₂ mixtures the linearity is violated with decreasing temperature and increasing the BeF₂ concentration. Indeed, according to structural analysis methods in the LiF – BeF₂ melt, with increasing BeF₂ concentration, polymerization occurs with the formation of BeF₄²⁻, Be₂F₇³⁻, Be₃F₁₀⁴⁻, Be₄F₁₃⁵⁻ [53, 54].

7. Viscosity and electrical conductivity

Additional information regarding the mechanism of viscous flow can be obtained using the Frenkel equation [55], which relates viscosity to the electrical conductivity (k) of melts:

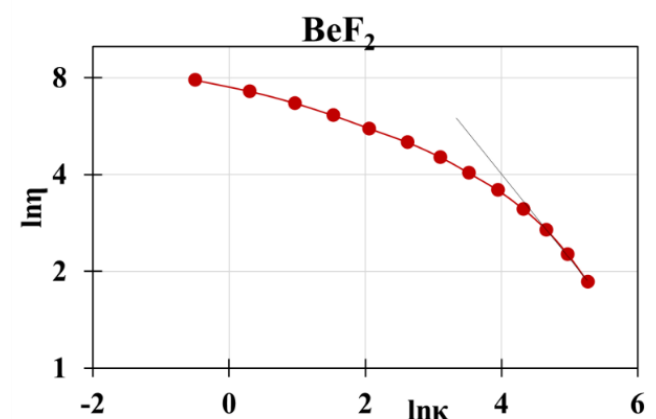
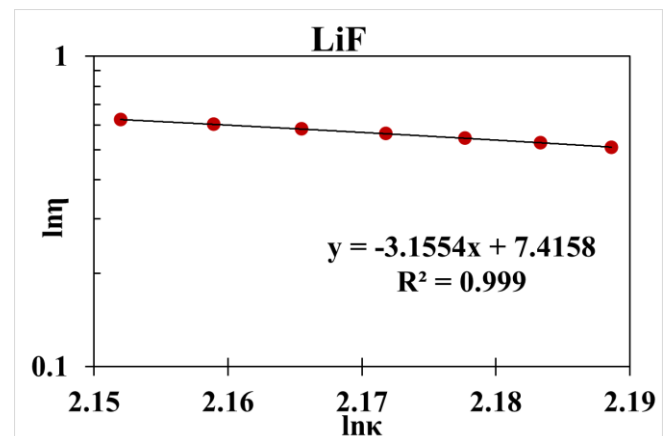
$$k^n \cdot \eta = \text{Const.} \quad (6)$$

The Equation (6) assumes that the product of viscosity and electrical conductivity is independent of temperature, and the activation energies of viscous flow (E_η) and ion migration (E_k) are proportional:

$$n = E_\eta / E_k. \quad (7)$$

The relationship between the electrical conductivity and the dynamic viscosity calculated for some fluoride compositions NaF – AlF₃, NaF – AlF₃ – Al₂O₃, NaF – AlF₃ – CaF₂ was presented in [56]. For example, for NaF – AlF₃ (CR = 2.3) $E_k = 17.80$ kJ/mol and $E_\eta = 41.94$ kJ/mol, so $n = 2.36$ and the product $k^n \cdot \eta = 20.7 \pm 0.01$ in the temperature range of 30 degrees (1263–1293 K). Another example: for NaF – AlF₃ – (4 wt. %)Al₂O₃ (CR = 2.1) $E_k = 19.50$ kJ/mol, $E_\eta = 46.33$ kJ/mol, so $n = 2.38$ and $k^n \cdot \eta = 16.1 \pm 0.01$ in the temperature range of 60 degrees (1233–1293 K). The product of $k^n \cdot \eta$ is a constant for a given melt composition and does not depend on temperature. This fact testifies the ionic nature of the melt. The ratio (n) of the viscous flow activation energy to the electrical conductivity activation energy is greater than unity because the electrical transfer is performed by the ions of smaller size, and the viscous flow is determined by the particles of larger size.

The E_η/E_k ratio for fluoride melts LiF, BeF₂ and their mixture LiF – BeF₂ is presented in Figure 16. Unlike melts prone to glass formation (polymerization), such as BeF₂, for ionic melts (LiF) the proportionality coefficient n is a straight line.



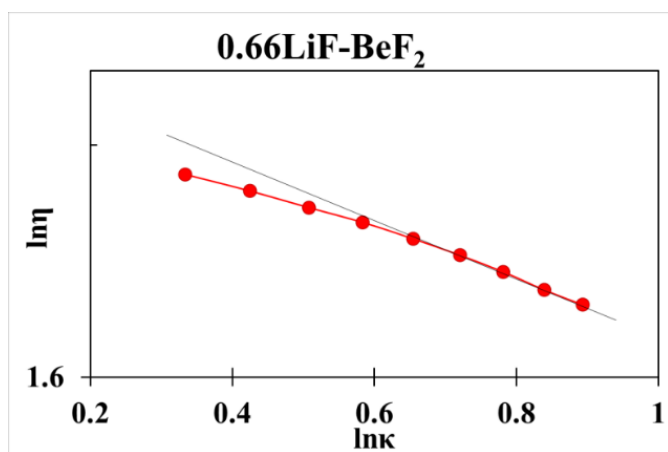


Figure 16 The E_{η}/E_{κ} ratio for fluoride melts KF, BeF₂ and 0.66LiF – 0.34BeF₂.

It should be noted that the Equation (6) proves that the electrical conductivity and the viscosity are exponentially dependent on temperature but does not indicate that these properties depend on each other, since these properties are based on different mechanisms of substance transfer: the electrical conductivity is determined by the most mobile particles (usually cations), while the viscosity is determined by the least mobile particles.

8. Conclusions

To date, *ab initio* molecular dynamics (MD) has become widespread as a computational method for studying the liquid state [57–59]. Molecular modeling provides atomic-scale descriptions of systems and is therefore used both to interpret existing experimental data and to predict unknown properties. The most important component is the consideration of interatomic interactions using physically motivated model potentials as a response of the electronic structure of the ions.

Galashev et al. [57] studied the kinetic properties of molten FLiNaK containing up to 15 mol. % CeF₃ and NdF₃ using the rotational viscometry and MD simulation. To simulate interatomic interactions, the Born–Huggins–Mayer potential was used. The MD calculation of the viscosity of the molten fluoride mixtures FLiNaK – NdF₃ agrees within 2 % with the experimental results.

Recently, a new class of potentials has emerged, called neural network-based machine learning potentials (MLPs), which, compared to classical potentials, do not require knowledge of the mathematical forms of the potential. Rodrigues et al. [60] used MLP to calculate the transport properties of LiF and FLiBe. Configuration data for these substances were taken from *ab initio* MD results. The MD-calculated temperature dependences of the LiF and FLiBe viscosity are closer to the experimental ones than those

obtained by the MLP method (viscosity values are underestimated by ~ 30 %).

However, the symbiosis of modeling and experimental measurements using high-precision viscometers is the most encouraging approach to studying the kinematic properties and the structure of molten salts.

Supplementary materials

No supplementary materials are available.

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Author contributions

Olga Tkacheva: Conceptualization; Data curation; Writing – Original draft; Writing – Review & Editing; Formal Analysis; Software; Visualization. The author expresses deep gratitude to his colleagues for providing unpublished experimental data on the viscosity of alkali metal halides.

Conflict of interest

The author declares no conflict of interest.

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