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Evaluating physical properties of molten salt reactor fluoride mixtures

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ABSTRACT

In the last years, interest in the use of high-temperature molten fluoride salts as fluid fuels and coolants in nuclear power systems has been increasing. The comprehensive information on the properties of molten fuel and coolant salts is necessary for development of new designs. Experimental data on physical properties of some prospective molten salt mixtures of Li, Na, Be, Zr fluorides containing fertile and fissile materials as well as soluble fission products are unknown. At the first stage of the conceptual development estimation of the required properties from the known experimental data can be useful for selection of suitable molten salt compositions. In this paper the approaches for estimation of the physicochemical properties such as density (ρ), dynamic viscosity (η), isobaric heat capacity (c_p), and thermal conductivity (λ) for molten salt fluoride mixtures are proposed. The calculation algorithm was based on the additivity principle for the properties (P_x) of multi-component molten salt mixtures, which can be found from the relationship $P_x = \Sigma N_i P_i$. Here N_i and P_i denote mole fraction and corresponding property of individual molten salts or their binary mixtures as constituents of the more complex systems. The empirical expressions connecting the property with molar volume and molecular mass of selected fluoride compositions are also derived and tested. Estimated values are compared with each other and available experimental data.

1. Introduction

The interest to the molten salt reactors (MSRs) is renewed because of highly efficient balance of neutrons through minimization of the amount of construction materials in the core and the continuous control of the of the fuel salt composition. MSR can be used efficiently for development of a Th–U breeder as well as for utilization of transuranium elements from the spent fuel of light water reactors [1–10]. Recall that the pioneer R&D on MSR performed in 1960–1970s at ORNL (USA) led to the development of a thorium–uranium 1000 MW Molten Salt Breeder Reactor (MSBR) design [1]. The successful testing of the main operating principles for MSR, which was accomplished in 1970s during operation of the Molten Salt Reactor Experimental (MSRE) in the USA, the development of technologies for control of the chemical behavior of the thorium–uranium fuel salt and development of container materials compatible with fuel and intermediate circuits salts provided the technical basis for MSR construction. The feasibility of these systems is beyond doubt today. The reductive extraction methods, which were worked out and experimentally tested under laboratory conditions for removal of protactinium and rare-earth elements from the Li, Be/F-based fuel salt containing uranium and thorium, provide the technological basis for the fuel salt clean up in these systems.

The operating conditions of a fluid fuel in MSR require fulfillment of the following physical and technological conditions:

1. Elements constituting the fuel diluents should not absorb neutrons to anywhere near considerable extent.
2. The melting temperature of the fuel salt composition should not be too high (<800–850 K) at sufficient concentrations of fissile and fertile materials.
3. A low vapor pressure at operating temperatures.
4. Chemical stability at operating temperatures and radiation resistance.
5. The absence of explosive exothermal reactions due to contact with water, air and other substances in the reactor.
6. Compatibility with construction materials and the moderator.
7. Transport properties of the fuel salt composition should ensure efficient removal of the heat generated at operating temperatures.
8. Possibility for the relatively simple extraction from the fuel salt composition of fission products absorbing neutrons in the core.

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The MSR fuel can be UF_4 or PuF_3 dissolved in fluoride mixtures of Li, Be, Na, Zr and Th. The concentration of thorium in these fuel compositions can be brought to the level that ensures breeding of the fuel in thermal or fast neutron spectrum. The optimal fuel salt composition for MSR-Breeder is a mixture of molten LiF and BeF_2 salts, which absorb neutrons very weakly (lithium is enriched to 99.995% in ^7Li), with dissolved fluorides of fissile and fertile UF_4 and ThF_4. The LiF–BeF_2 melt is highly advantageous because UF_4 and ThF_4 are highly soluble in this melt (over 20 mole%) at the melting temperature of the composition equal to about 800 K and the saturated vapor pressure less than 10 Pa at 1000 K.

Transuranium and rare-earth elements are dissolved in this system as trifluorides whose solubility is less than the solubility of UF_4 and ThF_4. The ORNL studies demonstrated that the solubility of PuF_3 is a maximum in molten LiF and NaF systems (see Table 1). The solubility considerably reduces as the concentration of BeF_2, ZrF_4, and ThF_4 grows in the melt. The accumulation of fission products to 1–2 mole% has little effect on their physical properties and does not cause the formation of insoluble compounds under the operating conditions.

Molten fluorides mixtures under consideration ($Pr \approx 8–10$) have satisfactory values of the heat capacity, the thermal conductivity and the viscosity at working temperatures (800–1100 K) and provide an efficient removal of heat when they are used as the coolant over a wide range of compositions. Transport properties of molten salt coolants ensure highly efficient cooling with the natural circulation; the salt-wall heat transfer coefficient is close to the same coefficient for water. The thermal diffusivity of the salt is 300 times smaller than that of sodium. Therefore, all other things being equal, the characteristic solidification time for a volume of the fluoride melt is 300 times longer than that for sodium.

The compositions under discussion have extremely high radiation resistance and a relatively low corrosivity with respect to graphite and some metallic alloys. The mixture of molten LiF–BeF_2–ThF_4–UF_4 fluorides lends itself relatively easily to extraction of actinides and fission products without impairment of the basic LiF–BeF_2–ThF_4 matrix. Considering all these properties of the molten fluorides, they can be viewed as the main constituents of the fuel composition for the thorium–uranium MSR-Breeder.

Recent advances in Brayton gas-turbine technology now make it possible to convert higher-temperature heat efficiently into electricity and thus have created the enabling technology for more efficient cost-effective high-temperature reactors. The near-term Advanced High-Temperature Reactor (AHTR) uses a graphite-matrix, coated-particle fuel and a liquid salt coolant. A longer term potential exists for a liquid salt-cooled fast reactor that uses metal-clad fuel and a liquid salt coolant [19,20].

The interest showed in the development of MSR, AHTR and other liquid salt cooled designs requires performing comprehensive studies of molten salt mixtures containing alkali metals, beryllium, zirconium, thorium, uranium, and plutonium fluorides [1–10,19,20]. Basic physicochemical parameters of fluoride melts, which show promise with respect to their nuclear characteristics, are not clearly understood. Therefore, prediction of such properties as the density, the viscosity, the heat capacity and the thermal conductivity can constitute basis for the use of high-temperature molten fluoride salts as fluid fuels and coolants in nuclear power systems.

2. Results and discussion

The calculation algorithm was based on the additivity principle for the properties (P_x) of multi-component salt mixtures, which can be found from the relationship $P_x = \sum N_i P_i$. Here N_i and P_i denote

Table 1

Molar compositions, melting temperatures (K) [11] and solubility of plutonium trifluoride (mole%) at 873 K in different molten fluoride salts considered as candidates for the fuel and the coolant circuits in MSR concepts

Alkali metal fluorides	ThF_4-containing	ZrF_4-containing	BeF_2-containing	Fluoroborates
LiF–PuF_3 (80–20) 1016 K [12]				
LiF–KF (50–50) 765 K	LiF–ThF_4 (78–22) 838 K *4.2* [13]	LiF–ZrF_4 (51–49) 782 K	LiF–BeF2 (73–27) 803 K *2.0* [16]	KF–KBF_4 (25–75) 733 K
LiF–RbF (44–56) 743 K	LiF–BeF_2–ThF_4 (75–5–20) 793 K *3.1* [13]	NaF–ZrF_4 (59.5–40.5) 773 K *1.8* [15]	LiF–NaF–BeF_2 (15–58–27) 752 K *2.0* [16,17]	RbF–$RbBF_4$ (31–69) 715 K
LiF–NaF–KF (46.5–11.5–42) 727 K	LiF–BeF_2–ThF_4 (71–16–13) 772 K *1.5* [14]	LiF–NaF–ZrF_4 (42–29–29) 733 K	LiF–BeF_2 (66–34) 731 K *0.5* [16–18]	NaF–$NaBF_4$ (8–92) 657 K
LiF–NaF–RbF (42–6–52) 708 K	LiF–BeF_2–ThF_4 (64–20–16) 733 K *1.2* [13]	LiF–NaF–ZrF_4 (26–37–37) 709 K	LiF–BeF_2–ZrF_4 (64.5–30.5–5) 701 K	
	LiF–BeF_2–ThF_4 (47–51.5–1.5) 633 K	NaF–RbF–ZrF_4 (33–24–43) 693 K	NaF–BeF_2 (57–43) 613 K *0.3* [16]	
		NaF–KF–ZF_4 (10–48–42) 658 K	LiF–NaF–BeF_2 (31–31–38) 588 K *0.4* [16]	
		KF–ZrF_4 (58–42) 663 K		

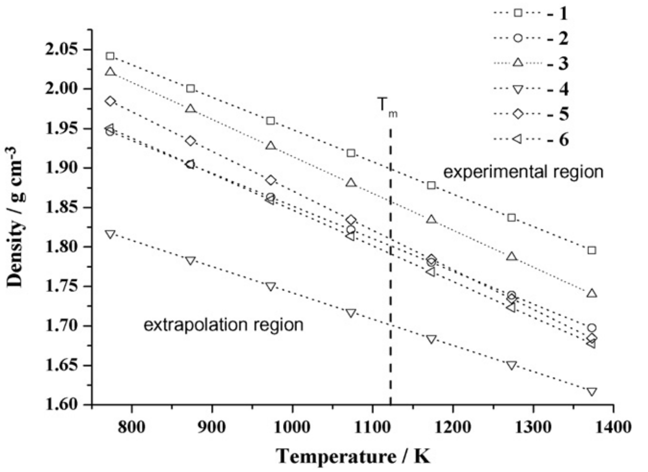

Fig. 1. Density of molten lithium fluoride measured by different researchers. 1 [26], 2 [27], 3 [28], 4 [28] (Porter), 5 [29], 6 [30].

mole fraction and corresponding property of individual molten salts or their binary mixtures as constituents of the more complex systems. Rigorously speaking, the calculations will be more correct if one uses molar characteristics, such as the molar volume ($V = M/\rho$), the molar viscosity ($\eta_M = V\eta = M\nu$), the molar thermal conductivity ($\lambda_M = V\lambda$), and the molar heat capacity ($C_{pM} = Mc_p$). This approach was used most frequently for calculation of thermodynamic (G, H) and volume (V) properties of the salt melts, which in essence represent extensive parameters. The said method has been used for the first time to calculate the transport properties [21].

In recent studies on the thorium-containing fluoride melts at JRC ITU (Karlsruhe, Germany) [9] the density (the molar volume) of multi-component melts was estimated on the basis of the additivity principle using values of the corresponding properties of individual components. The choice of the initial data was not substantiated enough. By way of specific example, we can quote considerable discrepancies of the density values obtained for the molten lithium fluoride (see Fig. 1), which is one of the best-studied constituents of the fuel compositions. The discrepancies are still larger for the properties of other main constituents of the molten salt mixtures, e.g., beryllium, thorium or zirconium fluorides. These discrepancies result in the conflicting density values of multi-component fluoride mixtures containing LiF due to extrapolation of initial data to lower operating temperatures (750–850 K).

For the other properties such as viscosity, which are nonlinear functions of temperature, extrapolation effect on final results will be still further. The adoption of available data on the physico-chemical properties of binary salt systems as initial magnitudes is more preferential for like calculations owing to the lesser extrapolation temperature range and rigid consideration of the well known experimental evidence pointing to pronounced deviation of properties of salt mixtures from their additive values [22–25].

2.1. Calculation technique

We have developed the approach and the sequence of calculations and proposed formulas for computation of the density, the viscosity, the heat capacity and the thermal conductivity of multi-component compositions taking into account data on appropriate binary salt mixtures. It is only in the absence of such data we had to use the data on properties of individual salts. In some cases we used physically substantiated empirical expression, which were derived by us and which were held well for the majority of salt melts studied so far, governing the change of properties with the molecular mass, molar volume of the salt mixtures or the crystallochemical radius of ions comprising various salt compositions.

To gain a greater insight into computation model proposed let us consider it by the example of molten ternary LiF–NaF–BeF_2, LiF–NaF–ThF_4, and LiF–NaF–ZrF_4 mixtures which may be written in the general case as LiF–NaF–MeF_n. Considering a small solubility of plutonium, minor actinides and rare-earth trifluorides in this base melts, one may hardly expect any critical changes in properties of the fuel salt (heat carrier, coolant) as density, viscosity, heat capacity and thermal conductivity as compared to the LiF–NaF–MeF_n solvent. They will be governed primarily by the ability of dissolved substances to form strong complex groups.

Unknown properties of LiF–NaF–MeF_n melts may be estimated preferably in the presence of reliable experimental data on LiF–MeF_n and NaF–MeF_n binary systems.

Then some consecutive calculations are performed:

1. Literature data are used to calculate a property of LiF–MeF_n and NaF–MeF_n melts at several fixed temperatures covering the whole operating interval of the selected ternary compositions. This property is described by an equation for the concentration dependence at each temperature ($P_i = P_{\mathrm{LiF\ (NaF)}} + A_{\mathrm{LiF(NaF)}} \cdot N_{\mathrm{MeFn}}$). The change of $A_{\mathrm{LiF(NaF)}}$ is calculated in the sections containing the required mole% MeF_n upon transition from LiF–MeF_n to NaF–MeF_n or vice versa.
2. The property of LiF–NaF melts, whose composition corresponds to their concentration in the selected LiF–NaF–MeF_n ternary compounds, is calculated at the same temperatures using known experimental data.
3. The $A_{\mathrm{LiF(NaF)}}$ is calculated for each concentration section in proportion to the concentration of LiF or NaF, i.e. by the equation $A_x = N_{\mathrm{LiF}} \cdot A_{\mathrm{LiF}} + N_{\mathrm{NaF}} \cdot A_{\mathrm{NaF}}$ (as per item 2) and the required property is found from the expression $P_i = P_{\mathrm{(LiF+NaF)}} + A_x \cdot N_{\mathrm{MeFn}}$ at each temperature.

This problem may be solved differently. The composition of one and the same melt of a ternary mixture is written by different methods using available experimental data on the properties of individual salts and binary melts. The density, the viscosity and the heat capacity can be estimated by calculating these properties for a ternary melt using experimental values obtained for LiF–NaF and MeF_n melts (the first method), LiF–MeF_n and NaF melts (the second method), NaF–MeF_n and LiF melts (the third method). The closer the composition of initial and selected melts, the more reliable is the prediction, which usually is connected with an interpolation of the input data.

It is advisable to use both independent approaches if required experimental data are available. A coincidence of the values of physical properties, which are calculated by different methods, suggests that the prediction is correct and reliable within the experimental error and model assumptions. If experimental data are scarce or absent, one has to use empirical relationships established for compounds having similar chemical bonds.

Given below are estimated values of the density (ρ), the dynamic viscosity (η), the isobaric heat capacity (c_p), and the thermal conductivity (λ) of the fuel compounds (solvents) adopted for the further study. These properties may be predicted with a sufficient accuracy for the selected compositions, which is comparable with the experimental error. The calculation was made using known experimental values of the density [31–35], the dynamic viscosity [25,36–37], the isobaric heat capacity [38], and

Table 2
Predicted density (ρ/g cm^{-3}) of the selected fluoride melts

Temperature (K)	$0.18LiF–0.58NaF–0.24BeF_2$		$0.72LiF–0.21BeF_2–0.07ZrF_4$	$0.70LiF–0.24BeF_2–0.06ThF_4$ ([32], p. 21)	
T_m	$\rho = 2.166$		$\rho = 2.358$	ρ	$d\rho/dT$
800	(1) $\rho = 2.150$	$\rho_{mean} = 2.147$	$\rho = 2.310$		
	(2) $\rho = 2.147$			$2.754_{(calc)}$	
	(3) $\rho = 2.145$			$2.758_{(expl)}$	6.87×10^{-4}(calc)
1000	(1) $\rho = 2.044$	$\rho_{mean} = 2.043$	$\rho = 2.186$	$2.617_{(calc)}$	6.71×10^{-4}(expl)
	(2) $\rho = 2.045$			$2.624_{(expl)}$	
	(3) $\rho = 2.041$				

the thermal conductivity [39–41] of molten fluorides of alkali metals, their mixtures, and LiF–MeF_4 and NaF–MeF_4 melts. Those values were determined by reliable experimental techniques: hydrostatic weighing (ρ), damped oscillations of a pendulum (η), high-temperature calorimetry (c_p), and coaxial cylinders (λ).

2.2. *The density* may be evaluated with a sufficient degree of reliability, because it is related by a simple expression ($\rho = M/V$) to the molecular mass M and the mole volume V. The latter quantity changes with the composition of an ideal system by the additive law $V = \sum N_i \cdot V_i$, where N_i and V_i are the mole fraction and molar volume of individual salts or their mixtures, which can be used to prepare a more complex compound. It is known also that the relative deviation of the mole volume from additive values is directly connected with the interaction of components (complex formation in salt systems), which can be estimated quantitatively from a simple relationship $\Delta V/V_{add} = f(\Delta\mu_i)$. Here μ_i is the ratio between nominal charges and crystallochemical radii of mutually substituting ions (for example, Li^+, Na^+ Be^{2+}, Th^{4+}, and Zr^{4+} cations in our case).

By now the density of binary LiF–NaF [31], LiF–BeF_2 and NaF–BeF_2 [32], LiF–ZrF_4 and NaF–ZrF_4 [35], LiF–ThF_4 and NaF–ThF_4 [33,34] melts was measured as a function of the temperature and the composition. Those data were used as the basis for calculating the density of the molten $0.18LiF–0.58NaF–0.24BeF_2$ and $0.72LiF–0.21BeF_2–0.07ZrF_4$ mixtures with various model assumptions. To verify the reliability of the method used to calculate the density of unstudied melts, we estimated the density of the $0.70LiF–0.24BeF_2–0.06ThF_4$ melt whose density was known from experiments [32]. The calculated and experimental values are compared in Table 2.

The $0.18LiF–0.58NaF–0.24BeF_2$ melt may be written in three notations: (1) $[0.237LiF–0.763NaF]–0.24BeF_2$; (2) $[0.429LiF–0.571BeF_2]–0.58NaF$; and (3) $[0.707NaF–0.293BeF_2]–0.18LiF$. They were taken into account when the density of ternary mixture was estimated independently from the concentration dependence of the mole volume of the LiF–BeF_2 and NaF–BeF_2 melts at 800 and 1000 K from the equation $V = \sum N_i \cdot V_i$. Here V_i is the mole volume of individual salts or their mixtures whose composition is shown in square brackets. The calculation results are given in Table 2. They were used to derive an equation for the temperature dependence of the density for the $0.18LiF–0.58NaF–0.24BeF_2$ melt:

$$\rho = 2.562 - 5.18 \times 10^{-4}\,T. \tag{1}$$

The density of other promising LiF–NaF–BeF_2 mixtures was calculated with the data for binary LiF–BeF_2 and NaF–BeF_2 melts. The composition of these eutectic mixtures and derived equations of density vs. temperature are presented below.

$$(0.07LiF - 0.642NaF - 0.288BeF_2):\ \rho = (2.5720 \pm 3.8 \times 10^{-5}) - (5.16 \times 10^{-4} \pm 4.2 \times 10^{-8})\,T; \tag{2}$$

$$(0.143LiF - 0.59NaF - 0.267BeF_2):\ \rho = (2.5748 \pm 2.1 \times 10^{-4}) - (5.29 \times 10^{-4} \pm 2.3 \times 10^{-7})\,T; \tag{3}$$

$$(0.22LiF - 0.567NaF - 0.213BeF_2):\ \rho = (2.5777 \pm 5.9 \times 10^{-4}) - (5.38 \times 10^{-4} \pm 6.5 \times 10^{-7})\,T; \tag{4}$$

$$(0.15LiF - 0.58NaF - 0.27BeF_2):\ \rho = (2.5720 \pm 2.8 \times 10^{-4}) - (5.30 \times 10^{-4} \pm 3.1 \times 10^{-7})\,T; \tag{5}$$

$$(0.17LiF - 0.58NaF - 0.25BeF_2):\ \rho = (2.5740 \pm 2.0 \times 10^{-4}) - (5.30 \times 10^{-4} \pm 2.8 \times 10^{-7})\,T. \tag{6}$$

These equations are valid for the temperature interval from the liquidus temperature up to 1270 K.

The $0.72LiF–0.21BeF_2–0.07ZrF_4$ melt. Experimental data on the mole volume of the $0.647LiF–0.301BeF_2–0.052ZrF_4$ melt [32] were used additionally to calculate the density of the melt under study. The calculation results are given in Table 2. They were used to derive an equation for the temperature dependence of the density of the $0.72LiF–0.21BeF_2–0.07ZrF_4$ melt:

$$\rho = 2.806 - 6.20 \times 10^{-4}\,T. \tag{7}$$

This equation holds for the temperature interval from the liquidus point to 1270 K.

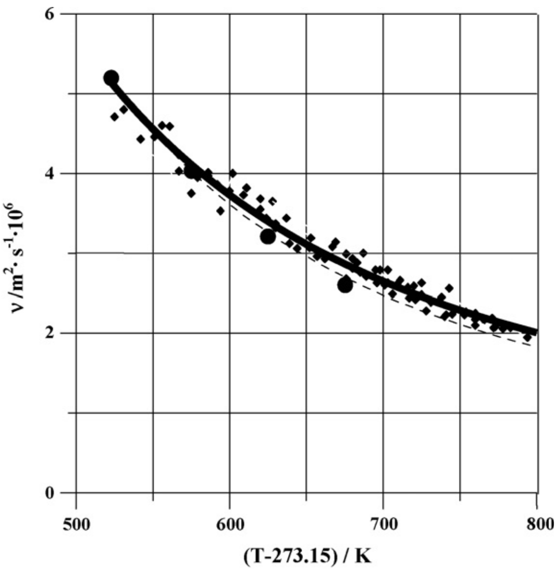

Fig. 2. Kinematic viscosity of ($0.075LiF–0.635NaF–0.29BeF_2$) melt. (■) Experimental data [42,43] and (●) predicted values.

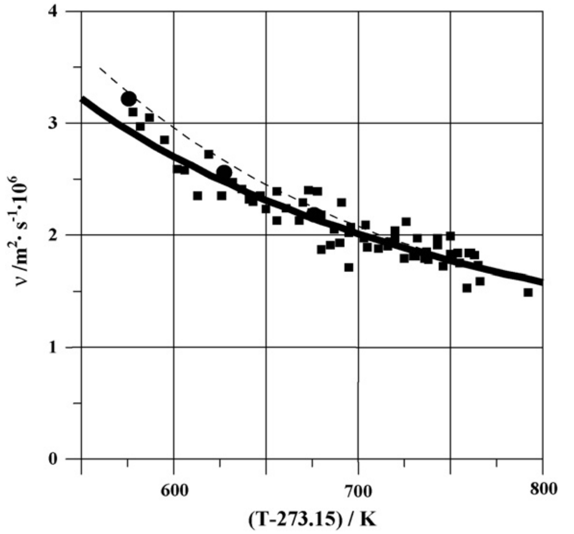

Fig. 3. Kinematic viscosity of (0.22LiF–0.567NaF–0.213 BeF_2) melt. (■) Experimental data [42,43], (●) predicted values, (dash line) data of Powers [38] for (0.24 LiF–0.53NaF–0.15BeF_2) melt.

2.3. *The viscosity* of the selected fuel LiF–NaF–BeF_2 and LiF–BeF_2–ThF_4 compositions was calculated similarly to the density. The input data were experimental results relating to the molar viscosity ($\mu = \eta \cdot V = \nu \cdot M$) of binary LiF–$BeF_2$, NaF–$BeF_2$ [36], LiF–ThF_4, NaF–ThF_4 [37] and LiF–NaF melts [25]. The temperature dependencies of kinematic viscosity of selected LiF–NaF–BeF_2 melt calculated by the above method are correlated with experimental ones in Figs. 2 and 3.

Since the results agree closely with each other, we evaluate the viscosity of other promising ternary eutectic melts. The linear equations of dependence dynamic viscosity (η) on temperature ($\log \eta = a_\eta + b_\eta/T$) are given below. The temperature T is shown in Kelvin degrees.

$$(0.0703\mathrm{LiF} - 0.642\mathrm{NaF} - 0.2877\mathrm{BeF_2}) : \log \eta = (-1.0280 \pm 0.0022) + (1663.8 \pm 2.0)/T; \quad (8)$$

$$(0.1433\mathrm{LiF} - 0.59\mathrm{NaF} - 0.2667\mathrm{BeF_2}) : \log \eta = (-1.0018 \pm 0.0020) + (1617.4 \pm 1.8)/T; \quad (9)$$

$$(0.22\mathrm{LiF} - 0.5666\mathrm{NaF} - 0.2133\mathrm{BeF_2}) : \log \eta = (-0.9495 \pm 0.0019) + (1519.9 \pm 1.7)/T. \quad (10)$$

In a similar manner, the viscosity of (0.701LiF–0.239BeF_2–0.06ThF_4) melt was estimated and correlated with the data of ORNL's researchers [44]. The predicted and experimental values of viscosity are in close agreement at 1000 K while a gap between estimated and observed viscosity is 16% at 800 K as seen in Fig. 4.

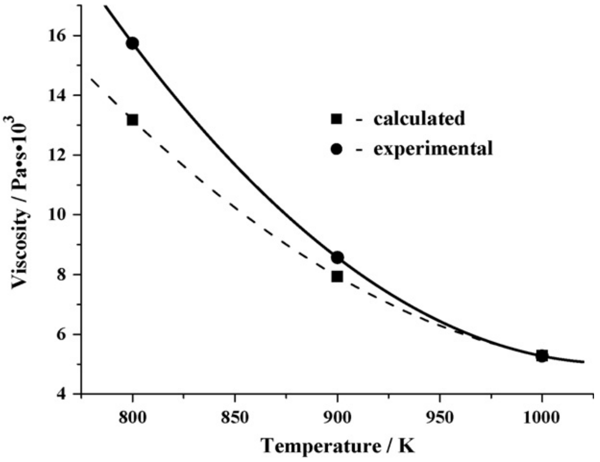

Fig. 4. Dynamic viscosity of (0.701LiF–0.239BeF_2–0.06ThF_4) melt. (●) Experimental data [44] and (■) evaluated values.

Our approach differs essentially from that of van der Meer and Konings [9]. The authors have taken the activation energy of viscous flow as a starting point for calculation of viscosity of ternary salt systems considering that this parameter is constant. In reality the activation energy of viscous flow decreases with increasing temperature as is clear from the results of precision measurements of the viscosity [45]. Therefore the viscosity of multi-component melts at the operating temperatures obtained by extrapolating procedure will be always underestimated in comparison with experimental one. Our estimation method does not depend on the type of temperature changes of viscosity and, in principle, leads to decreasing the prognosis error.

To bring into line and simplify the calculation we have analyzed the molar viscosity isotherms (800, 900, 1000, 1100, and 1200 K) in graphical and analytical forms. As an example the input LiF–BeF_2 and LiF–ThF_4 data are shown in Fig. 5 and Table 3. They are necessary for further calculations and take into account real deviations of this property from the additive values in binary mixtures. The extrapolated values were analyzed at temperatures below 1100 K so as to estimate properties of the ternary fuel salt mixtures whose liquidus temperatures are lower than those of the binary systems. This brings some uncertainty in calculating the viscosity of low-melting ternary compositions, which is larger than the uncertainty of the density. This is because although the viscosity of the initial binary mixtures was measured over a

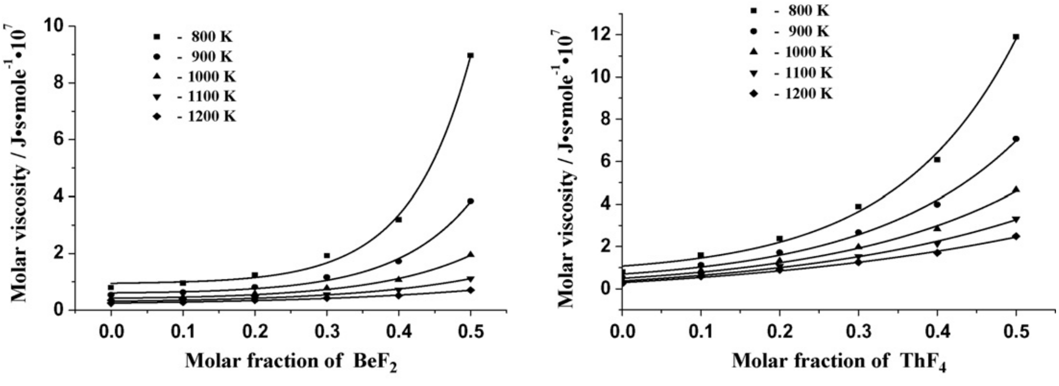

Fig. 5. Concentration dependence of the molar viscosity of the LiF–BeF_2 [36] (a) and LiF–ThF_4 [37] (b) melts at different temperatures.

Table 3
Molar viscosity (J s mole^{-1} × 10^7) of the molten LiF–BeF$_2$ and LiF–ThF$_4$ mixtures containing 0–50 mole% BeF$_2$ or ThF$_4$

Temperature (K)	$\mu = A \times \exp(N/B) + C$ (N is the molar fraction of BeF$_2$ or ThF$_4$)					
	LiF–BeF$_2$			LiF–ThF$_4$		
	A	B	C	A	B	C
800	0.02044	0.08373	0.930	0.41421	0.15183	0.659
900	0.02633	0.10386	0.579	0.46923	0.18736	0.231
1000	0.03638	0.13323	0.385	0.54892	0.23388	−0.056
1100	0.05149	0.17854	0.263	0.66216	0.29734	−0.294
1200	0.08012	0.26408	0.167	0.81656	0.38713	−0.518

sufficiently wide temperature interval (200–300 K), it changed, unlike the density, with the temperature by the exponential law, which is less suitable for extrapolation.

For calculation of the viscosity of the 0.72LiF–0.16BeF$_2$–0.12ThF$_4$ and 0.75LiF–0.05BeF$_2$–0.20ThF$_4$ melts, the equations in Table 3 were taken first to determine the molar viscosity of the LiF–BeF$_2$ and LiF–ThF$_4$ melts containing 0.72 mole of LiF (the first ternary system) and 0.75 mole of LiF (the second ternary composition). The obtained values were used to calculate the molar and dynamic viscosities of the selected ternary mixtures taking into account the ratio between the molar concentrations of beryllium and thorium fluorides in each melt and the molar volume of these compositions. Given below are temperature dependences of the viscosity (Pa s 10^3) calculated by this method for melts of the selected fuel compositions (two equivalent equations).

$$\left.\begin{aligned}&\eta = 583.8 \times \exp(-T/194.2) + 2.332;\\ &\log\eta = -0.509 + 1.2676 \times 10^3/T \pm 2.07 \times 10^{-3};\end{aligned}\right\}0.72\mathrm{LiF} - 0.16\mathrm{BeF_2} - 0.12\mathrm{ThF_4} \tag{11}$$

$$\left.\begin{aligned}&\eta = 457.6 \times \exp(-T/205.1) + 2.728;\\ &\log\eta = -0.346 + 1.1413 \times 10^3/T \pm 1.16 \times 10^{-3}\end{aligned}\right\}0.75\mathrm{LiF} - 0.05\mathrm{BeF_2} - 0.20\mathrm{ThF_4}. \tag{12}$$

2.4. The isobaric heat capacity

The isobaric heat capacity of the molten LiF–NaF–BeF$_2$ mixtures was calculated by the same method using a simplified scheme, because, as is known, this property of salt melts depends little on the temperature in the interval (T_m + 200 K) [46]. As for density and viscosity, the computation of heat capacity is performed making use of its molar values.

Experimental values of the heat capacity of molten fluorides of lithium and sodium and their mixtures with beryllium fluoride [38] were taken as the starting data. To verify the calculation algorithm described above, we compared our calculated values and experimental values [38] of the heat capacity of molten 0.24LiF–0.53NaF–0.23BeF$_2$ (melt 1) and 0.075LiF–0.635NaF–0.31BeF$_2$ (melt 2) mixtures. These values (c_p/J g^{-1} K^{-1}) are compared below (T = 973 K).

$$\begin{aligned}&\text{Melt 1}: \quad c_{p(\text{expl})} = 2.26; \quad c_{p(\text{calc})} = 2.29.\\ &\text{Melt 2}: \quad c_{p(\text{expl})} = 2.13; \quad c_{p(\text{calc})} = 2.15.\end{aligned}$$

The evaluated heat capacity values for some LiF–NaF–BeF$_2$ melts are given in Table 4.

Table 4
The evaluated values of heat capacity (J g^{-1} K^{-1}) of the selected fluoride melts

0.070LiF–0.642NaF–0.288BeF$_2$	0.143LiF–0.59NaF –0.267BeF$_2$	0.22LiF–0.567NaF –0.213BeF$_2$
c_p = 2.15 (2.22)	c_p = 2.21 (2.25)	c_p = 2.26 (2.32)

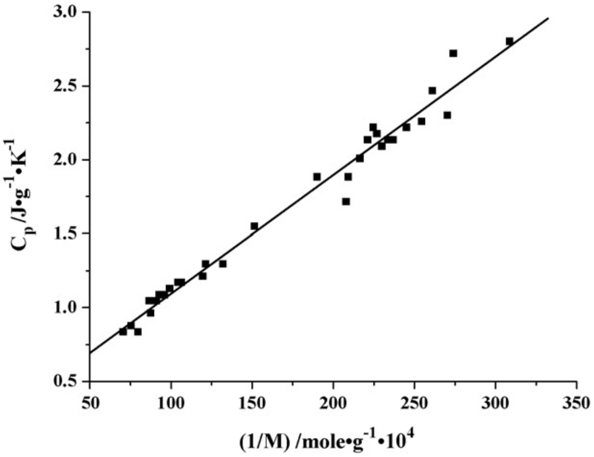

Fig. 6. Relationship between the heat capacity of molten fluoride mixtures and their molar mass.

For the lack of suitable initial experimental data, the evaluation of the heat capacity of molten multi-component mixtures containing zirconium, thorium, uranium, and plutonium fluorides by means of above method is unfeasible. Nevertheless, we have found a simple empirical dependence of the heat capacity (c_p) experimental values [38] on reverse molar mass (1/M) of more than 30 like fluoride melts, which is graphically presented in Fig. 6. In analytical form this straight line is described by the following equation:

$$c_p = (0.2916 \pm 0.0404) + (0.00802 \pm 0.216 \times 10^{-3}) \times 10^4/M. \tag{13}$$

It is seen that the deviations of experimental values from linear equation do not exceed error of measuring the heat capacity of salt melts (3–10%) indicated by the most of researchers [46,47].

When compared the values of heat capacity of ternary LiF–NaF–BeF$_2$ mixtures calculated reasonably rigorously from the experimental data for binary melts (see Table 4) one can see that those agree well with the data found by above equation (the magnitudes put in brackets in this Table). The heat capacities of several useful

Table 5
The predicted heat capacity of molten multi-component fluoride melts

Salt composition	M (g mole^{-1})	c_p (J g^{-1} K^{-1})
0.12UF$_4$–0.76NaF–0.12BeF$_2$	75.244	1.360
0.15UF$_4$–0.25NaF–0.60BeF$_2$	85.822	1.226
0.04UF$_4$–0.48NaF–0.48KF	60.606	1.615
0.011UF$_4$–0.445LiF–0.435KF–0.109NaF	44.849	2.084
0.04UF$_4$–0.55LiF–0.2NaF–0.21ZrF$_4$	70.343	1.435
0.72LiF–0.16BeF$_2$–0.12ThF$_4$	63.174	1.565
0.75 LiF–0.05BeF$_2$–0.20ThF$_4$	83.430	1.255
0.78LiF–0.22ThF$_4$	88.020	1.205

Table 6
The predicted thermal conductivity of the selected fluoride melts

Temperature (K)	LiF $M = 25.94$ [40]	NaF $M = 41.99$ [40]	FLINAK $M = 41.29$ [40]	0.75NaF 0.25AlF$_3$ $M = 52.48$ [41]	0.72LiF 0.21BeF$_2$ 0.07ZrF$_4$ $M = 40.25$	0.18LiF 0.58NaF 0.24BeF$_2$ $M = 40.30$
800	–	–	0.84 (calc) 0.81 (exp)	–	0.86 (calc)	0.86 (calc)
1000	–	–	0.94 (calc) 0.92 (exp)	–	0.96 (calc)	0.96 (calc)
1200	1.49 (calc) 1.53 (exp)	–	–	–	–	–
1300	1.54 (calc) 1.74 (exp)	1.07 (calc) 1.20 (exp)		0.92 (calc) 0.80(exp)	–	–

in the MSR application multi-component fluoride melts evaluated the same manner are listed in Table 5.

2.5. The thermal conductivity

The thermal conductivity of the selected molten salt mixtures cannot be calculated by algorithm proposed as the density, viscosity or heat capacity owing to limited sources of initial experimental data. Moreover, available data on thermal conductivity of the most studied fluoride melts are contradictory, to say nothing of their mixtures with beryllium, zirconium, thorium, and uranium fluorides. As a rule, large difficulties encountered in experiments at high temperatures as well as inadequacy of the investigation techniques are responsible for the great discrepancies in literature data on the thermal conductivity. The thermal conductivity may be predicted from the equations taking into account a fundamental relationship of the thermal conductivity with the molecular mass (*M*), the packing density of the salt melt particles (the mole volume, *V*), and the oscillation frequency of ionic energy exchange. For the most part ionic melts near the melting point are likened to a crystal and equations for calculating the thermal conductivity of the melts contain the oscillation frequencies of particles in a quasilattice. Otherwise the heat transfer in the molten salts has been identified with propagation of the sound though experimental values of sound velocity and thermal conductivity show temperature dependencies opposite in direction. Attempts to use the modified Rao–Osida equation, derived on the base of the molecular-kinetic theory of liquids and the Maxwell representations of the relaxation of energy-exchanging particles, were successful only in the case of simple molten salts (alkali halides and their mixtures) [39].

The aforementioned approaches cannot be used today to evaluate the thermal conductivity of salt melts having a complicated chemical composition (e.g., the selected fuel compounds), because their physical parameters, which are determined mostly from experiments, are lacking. That is not to say that it impossible to evaluate the thermal conductivity of multi-component salt mixture at all. We have to use empirical rules found from the analysis of the experimental data available to us. Analyzing the experimental values of the thermal conductivity determined earlier for molten chlorides, bromides and iodides of alkali metals and their mixtures, we deduced an equation describing the experimental data on several dozens of the similar salt melts within the measurement error of the method of coaxial cylinders [40]. This equation does not include any parameters except molecular mass and temperature. Therefore it is very convenient for evaluating the thermal conductivity of unstudied salt melts. The equation has the form:

$$\lambda = -0.34 + 0.5 \times 10^{-3}T + 32.0/M. \tag{14}$$

Here λ has dimensionality W m^{-1} K^{-1}, *T* is the temperature (K) and *M* is the molecular mass (g mole^{-1}).

The thermal conductivity calculated by the said equation for molten fluorides of alkali metals, FLINAK (eutectic LiF–NaF–KF mixture), and molten cryolite (0.75NaF–0.25AlF$_3$) agreed with our experimental data [41–43] as a whole. This formula was also used for other ternary fluoride mixtures as can be seen from Table 6.

Thermal conductivity of the 0.67LiF–0.18BeF$_2$–0.15ThF$_4$ melt at 1000 K calculated with the value of thermal diffusivity measured by Japanese researchers [48], proved to be much larger (1.17 W m^{-1} K^{-1}) than the thermal conductivity estimated with the above empirical dependence (0.604 W m^{-1} K^{-1}).

Only direct measurements of the thermal conductivity of other multi-component fluoride mixtures can answer the question if the equation describes the experimental results in a proper way.

3. Concluding remarks

Analytical equations have been developed for evaluation of density, viscosity, heat capacity, and thermal conductivity of various molten salt mixtures of Li, Na, Be, Zr fluorides containing fertile and fissile materials. The methods were used to predict values of the said properties for the melts containing actinides fluorides at temperatures from 800 to 1000 K. In most cases, especially as applied to solvent salts, the deduced equations describe experimental values within their measurement accuracy. Note, that due to forced extrapolation of the initial data to operating temperatures the significant uncertainties can be introduced in the prediction of thermophysical properties, such as the viscosity, which, as a rule, vary nonlinearly with the temperature. In further studies it is also necessary to pay special attention to the thermal conductivity measurements of fluoride melts, including binary ones.

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