TRANSPORT PROPERTIES OF MOLTEN-SALT REACTOR FUEL MIXTURES: THE CASE OF Na, Li, Be/F AND Li, Be, TH/F SALTS

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Abstract

In this paper we have compiled transport properties information, available, on two types of FLiBe based salt mixtures (Na,Li,Be/F and Li,Be,Th/F) that are presently of importance in the design of innovative molten-salt burner reactors. Estimated and/or experimental values measured (particularly, from prior US and Russian studies, as well our recent studies) are given for the following properties: viscosity, thermal conductivity, phase transition behaviour, heat capacity, density and thermal expansion. This effort is done within ISTC Task#1606 supported by EC.

Introduction

In this paper we have compiled transport properties information, available, on two types of FLiBe based salt mixtures that are presently of importance in the design of innovative molten-salt burner (MSB) reactors. The primary user of this transport properties information will, no doubt, be nuclear reactor engineer who require these data for the design and development of MSB concepts. [1]

The choice of salt mixtures has been primarily governed by selection of scenarios: TRU transmuting system of LWR wastes (1) with Th fertile and (2) without any fertile elements. Two most promising mixtures have been selected for possible use as fuel solvents. These are: Na,Li,Be/F and Li,Be,Th/F solvent systems.

These FLiBe based solvent systems selected for MSB configurations appear, on the basis of present knowledge, to resolve all technological problems and in addition, to offer operational advantages regarding increased trifluorides solubility (more 1 mole%), yet not proven, compared to compositions used in prior MSR designs. The freezing point and radiation stability criterions clearly favours for compositions proposed. Differences in corrosivity of the melts towards Ni based alloys, yet unproven for TRU's fueled systems and increased fuel outlet temperatures (till to 750 C), are expected to be not so much. Maintaining of the desired redox potential in the fuel salt is clear for U/Th-based fuels, but not proved yet for U free systems. Obviously, rare earth fission products removal procedure must be more complicate for Th based fuels.

A direct comparison between the attractive solvents for MSB concepts can not now be made in a full scale since the lack of knowledge on some key physical & chemical properties as well as aspects of fuel & material behaviour (operational constraints) for further MSB concept evaluation and development. It is related especially to the ternary sodium-lithium-beryllium fluoride melt, which are known not so good as for Li,Be,Th/F compositions. The additional experimental work was needed to reach such evaluation and comparison. It was decided in our comparison place main emphasis on compositions able to reach solubility of PuF_3 till to 1-2% in mole or possibly more by minimisation of beryllium content in salt composition for well studied in prior MSR programmes $72LiF-16BeF_2-12ThF_4$ mixture and for alternative Na,Li,Be/F salt composition with minimal LiF content (for tritium and economical concern).

Estimated and/or experimental values measured (particularly, from prior US and Russian studies, as well our recent studies) are given for the following properties: viscosity, thermal conductivity, phase transition behaviour, heat capacity, density and thermal expansion. This effort is done within ISTC Task#1606 supported by EC.

Na, Li, Be/F system

Phase diagram. Two available published references gave formation of three ternary compounds $NaLiBe_2F_6$ (melting point 280°C), $Na_2LiBe_2F_7$ (melting point 340°C), and $NaLiBeF_4$ (melting point 305°C). [2,3] Also in [4] melting points for $Na_2LiBe_2F_7$ and $NaLiBeF_4$ are reported to be 355 and 240°C, respectively. $NaLiBe_2F_6$ was not found. Instead of it $NaLiBe_3F_8$ was discovered. Triangulation of $LiF-NaF-BeF_2$ system was made in. [4] Following cross-sections were shown as triangulating: $LiF-Na_2BeF_4$, $LiF-NaBeF_3$, $Li_2BeF_4-NaBeF_3$, $Na_2LiBe_2F_7-NaBeF_3$, $NaLiBe_3F_8-BeF_2$, $NaLiBe_3F_8-Li_2BeF_4$, $NaLiBe_3F_8-NaBeF_3$. Analysis of liquidus isotherms location at $LiF-NaF-BeF_2$ phase diagram was made in. [4]

Prospective compositions selected for detailed experimental studies within ISTC#1606 [5,6] are given below:

Composition in mole%	LiF	NaF	BeF$_2$
A	7.1	64.1	28.8
B	14.3	59.0	26.7
C	22.0	56.7	21.4

According [4] liquidus temperature for composition A is slightly higher than 500°C, and for compositions B and C it is 480 and 500°C, correspondingly.

Analysis of DTA experimental curves for compositions A, B, C obtained in current VNIITF studies during constant rate heating and natural cooling of salt compositions samples have shown the following:

- Composition A is located on line of melting (crystallisation) of binary eutectics Na$_2$BeF$_4$-NaF. That's why heating (cooling) curves contain two peaks: sharp low temperature one at 482.4±1.6°C corresponds to melting (crystallisation) of ternary eutectics LiF-NaF-Na$_2$BeF$_4$, and protracted high temperature one – to binary eutectics Na$_2$BeF$_4$-NaF. Liquidus temperature being determined on the basis of heating curves is 536±2°C, on the basis of cooling curve - 515±2°C.

- Composition B corresponds to ternary eutectics LiF-NaF-Na$_2$BeF$_4$. Heating (cooling) curves contain one endothermic (exothermic) peak at 482.6±1.5°C, which corresponds to melting (crystallisation) of triple eutectics.

- Composition C is located in the field of primary crystallisation of sodium fluoride. Cooling curves of these samples show three peaks. Sharp low temperature peak at 483.9±2.6°C corresponds to melting (crystallisation) of ternary eutectics LiF-NaF-Na$_2$BeF$_4$ (as in case of composition A). Second peak at 480-500°C corresponds to melting (crystallisation) of binary eutectics LiF-NaF, and third one - to melting (crystallisation) of NaF. Liquidus temperature was 570±1°C. It was determined using cooling curves. It was impossible to determine liquidus temperature using heating curves in this case because all three thermal effects were registered as one wide peak.

Thus measurements have shown that liquidus temperature for salt composition B is 482°C. This value is in good agreement with previously published data. [4] Liquidus temperature for composition A (515-536°C) also coincide with published data satisfactory. Taking under consideration composition C one can see that its liquidus temperature (570°C) is sufficiently higher, than those which was determined using phase diagram (~500°C), shown in [4]. Explanation of this discrepancy may be following – last composition is located on the field of primary crystallisation of sodium fluoride – the most refractory component of investigated ternary system. That's why even small changes in composition can lead to sufficient changes of liquidus temperature.

Preliminary estimated transport properties. 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 chosen ternary solvents. 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, [1,2] the dynamic viscosity, [3-5] the isobaric heat capacity,

[2,6,7] and the thermal conductivity [8,9] of molten fluorides of alkali metals, their mixtures and LiF-BeF$_2$ and NaF-BeF$_2$ melts. Those values were determined by reliable experimental techniques: hydrostatic weighing (ρ), relaxation oscillations of a pendulum (η), high-temperature calorimetry (c_p), and coaxial cylinders (λ). It is significant that the calculation technique used is based on limited experimental data, those of various investigators being different greatly.

The calculation algorithm was based on the principle of additivity of the properties (P_x) of ternary salt compounds, which can be found from the relationship $P_x = \Sigma N_i \cdot P_i$. Here N_i and P_i denote mole fraction and corresponding property of individual salts fused or their binary mixtures, which may make up a test ternary compound. The closer the chemical compositions and, consequently, the closer the properties of the initial melts and a multi-component mixture, the more reliable is the prediction, which usually is connected with an interpolation of the input data. Unknown properties of LiF-NaF-BeF$_2$ melts may be estimated preferably in the presence of reliable experimental data on LiF-BeF$_2$ and NaF-BeF$_2$ binary systems.

The density of the selected fuel compositions was estimated by both methods (with individual fluorides melts or their binary mixtures), because sufficient data are available in the literature. [7] The density values determined by different methods agree fairly well. Given below are equations for density vs. temperature for Na,Li,Be/F compositions. The calculation accuracy of each coefficient in the linear equation $\rho = a_\rho - b_\rho T$ is specified. The temperature T is shown in Kelvin degrees and ρ in g cm^{-3}.

$$\text{Melt A: } \rho = (2.5720 \pm 3.8 \cdot 10^{-4}) - (5.16 \cdot 10^{-4} \pm 4.2 \cdot 10^{-7})\, T \qquad (1)$$

$$\text{Melt B: } \rho = (2.5748 \pm 2.1 \cdot 10^{-4}) - (5.29 \cdot 10^{-4} \pm 2.3 \cdot 10^{-7})\, T \qquad (2)$$

$$\text{Melt C: } \rho = (2.5777 \pm 5.9 \cdot 10^{-4}) - (5.38 \cdot 10^{-4} \pm 6.5 \cdot 10^{-7})\, T \qquad (3)$$

The viscosity of the selected fuel compositions was calculated similarly to the density. Literature data on the viscosity of LiF-BeF$_2$, NaF-BeF$_2$ and LiF-NaF binary systems [8-11] were used. The values reported in the literature for lithium and sodium fluorides as well as 67.2LiF-32.8BeF$_2$ eutectic mixture coincide within 10% at a temperature from the melting point (T_{melt}) to (T_{melt} + 200 K). Given below are equations of the viscosity temperature dependence and viscosity vs. temperature plots for ternary melts. The calculation accuracy of each coefficient in the linear equation $\log\eta = a_\eta + b_\eta T$ is specified. The temperature T is shown in Kelvin degrees and η in cP.

$$\text{Melt A: } log\eta = (-1.0280 \pm 0.0022) + (1663.8 \pm 2.0)/\, T \qquad (4)$$

$$\text{Melt B: } log\eta = (-1.0018 \pm 0.0020) + (1617.4 \pm 1.8)/\, T \qquad (5)$$

$$\text{Melt C: } log\eta = (-0.9495 \pm 0.0019) + (1519.9 \pm 1.7)/\, T \qquad (6)$$

The isobaric heat capacity of the selected fuel compositions was calculated by both methods using a simplified scheme, because, as is known, this property of salt melts depends slightly on the temperature in the interval T_{melt} + 200 K. [8,12,13] The change of the isobaric heat capacity with temperature, which was determined for some salts, is overlapped by relatively large experimental errors (up to 10-20%). Experimental values of the heat capacity of molten fluorides of lithium and sodium and their mixtures with beryllium difluoride [8] were taken as the input data. To verify the calculation method described above, we compared our calculated values and experimental values [8] of the heat capacity for 24LiF-53NaF-23BeF$_2$ (1) and 7.5LiF-63.5NaF-31BeF$_2$ (2) melts. These values (c_p/cal·g^{-1}·K^{-1}) are compared below (T = 700°C).

Melt 1: $c_{p\,(expl)} = 0.54$ $c_{p\,(calc)} = 0.548$;   **Melt 2:** $c_{p\,(expl)} = 0.51$ $c_{p\,(calc)} = 0.514$

The thermal conductivity of the selected fuel compositions was calculated by an empirical equation describing experimental values of several dozens of salt melts, including alkali-metal fluorides and their mixtures, [15] to within the measurement accuracy provided by the method of coaxial cylinders. This method does not involve any other experimental parameters except temperature. Therefore it is very convenient in estimating the thermal conductivity of unstudied salt compositions. The empirical equation is written as

$$\lambda = -0.34 + 0.5 \cdot 10^{-3}T + 32.0/M \tag{7}$$

Here λ is the thermal conductivity in W/(m·K), T is the temperature in K, and M is the molecular mass in g/mole. The applicability of this equation to prediction of the thermal conductivity of fluoride melts, including those with ions of polyvalent metals, was verified by a comparison of experimental and calculated values of the thermal conductivity of studied salt compositions. The thermal conductivity values, which were estimated from the equation (7) for the selected melts at 800 and 1 000 K, are given in Table 1, which also contains predicted values of density, viscosity and heat capacity.

Table 1. **Predicted values for density, viscosity, heat capacity and thermal conductivity of Na, Li, Be/F mixtures**

	Salt A M = 42.303	Salt B M = 41.027	Salt C M = 39.510
Density, g·cm^{-3} ♦ 800 K ♦ 1 000 K	 2.1592 2.0560	 2.1514 2.0456	 2.1473 2.0397
$d\rho/d$**T**, g·cm^{-3}·K^{-1}	5.16·10^{-4}	5.29·10^{-4}	5.38·10^{-4}
Viscosity, cP ♦ 800 K ♦ 1 000 K	 11.28 4.33	 10.48 4.13	 8.92 3.72
Heat capacity, cal·g^{-1}·K^{-1}	0.515	0.529	0.540
Thermal conductivity, W·m^{-1}·K^{-1} ♦ 800 K ♦ 1 000 K	 0.82 0.92	 0.84 0.94	 0.87 0.97

Measurement of viscosity. In current KI experiments the technique was based on method of oscillating cylinder filled by the salt. Kinematic viscosity of two salt compositions (A)- 64.2 NaF + 7.0 LiF + 28.8 **BeF$_2$** (mol %) and (C) 56.7NaF + 22.0LiF + 21.3BeF$_2$ (mol %) have been measured in the temperature range from liquidus up to 800°C with accuracy 4 - 6% (dispersion). Dependence of kinematic viscosity vs temperature for composition (A) - 64.2NaF + 7.0LiF + 28.8BeF$_2$ (mol %) in a range of temperatures 525-800°C can be represented as:

$$\nu(m^2/s) = 0.1344\exp\{2900/T(K)\} \tag{8}$$

And for composition (C):

$$\nu(m^2/s) = 0.1527\exp\{2509/T(K)\} \tag{9}$$

In Figure 1 solid thin line presents correlation dependence of kinematic viscosity of composition (A) - 64.2 NaF + 7.0 LiF + 28.8 BeF$_2$ (mol %) vs temperature, received by processing of experimental data. Similar dependence for composition (C) - 56.7NaF + 22.0LiF + 21.3BeF$_2$ (mol %) is presented by a solid thick line. As one would expect, viscosity grows up with increasing of BeF$_2$ concentration in the system.

Figure 1. **Kinematical viscosity vs temperature for Na, Li, Be/F system**
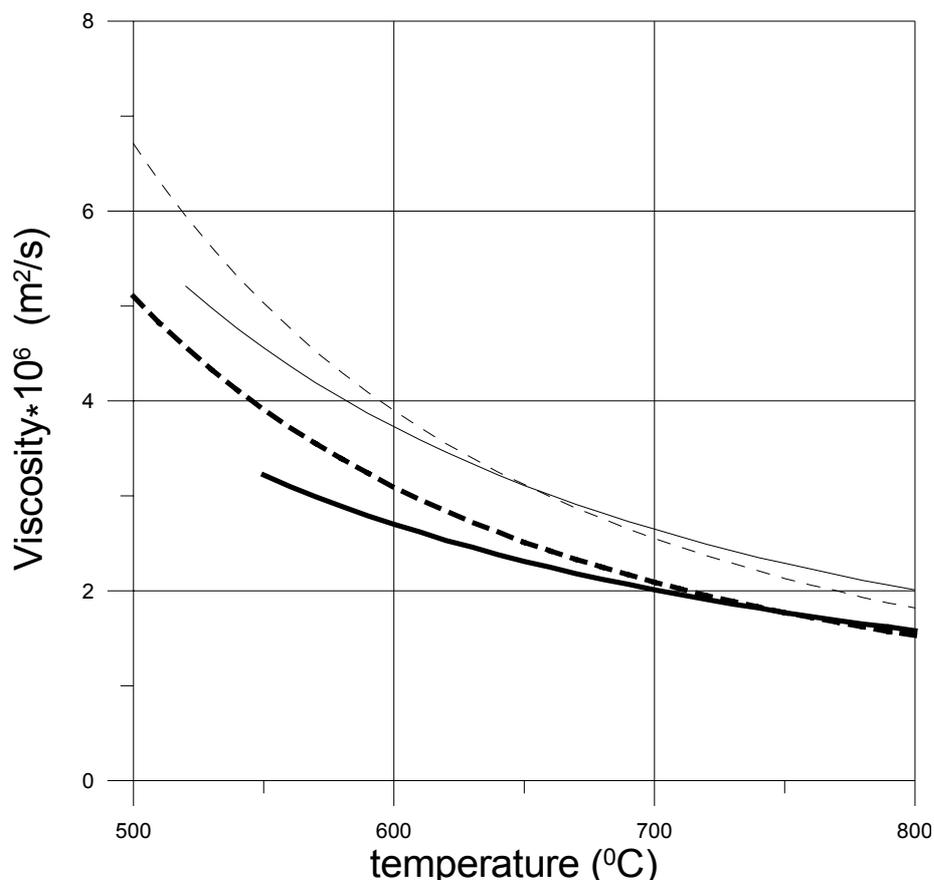
Comparison of the received KI experimental data with the modelling estimations (dashed lines) executed by IHTE in previous section, has shown coincidence of estimations to experimental data at high temperatures (600°C <T <800°C), and significant deviation at temperatures close to liquidus temperature. Note, the KI experimental data in that temperature range are in good agreement with the earlier ORNL data [8] for close Na,Li,Be/F compositions, where viscosity measurements were done in the temperature range of 600-800°C with three different instruments.

Thermal conductivity measurements. The KI data on thermal conductivity measurements for 64.2 NaF + 7.0 LiF + 28.8 BeF$_2$ (mol %) salt composition in temperatures range of 500-750°C are presented in Figure 2 by thick solid line:

$$\lambda=0.8380 +0.0009\bullet[t\ (°C) – 610.3] \tag{10}$$

These values were determined by reliable experimental techniques of coaxial cylinders. Dispersion of data on the thermal conductivity caused by statistical disorder of experimental points and appreciated under the assumption of it homoscedastivity, is evaluated as 0.028 W/m/K or about 3% of measurement value. Total dispersion of these measurements, determined by accuracy of calibration is estimated as 15%.

It is interesting to compare the results received in the present work with results of modelling estimations done by IHTE in previous Section as well as ORNL experimental data. [16] Last paper gives the thermal conductivity value of 1 W/ m/K for two compositions 57 NaF + 43 BeF$_2$ and 41 NaF + 23 LiF + 36 BeF$_2$ (mol %). The value from report [8] on thermal conductivity 0.00992 Cal/(s·cm°C) for 57 NaF + 43 BeF$_2$ (mol %) salt composition should be considered as wrong value.

In Figure 2 the ORNL data [16] are given by the thick dashed line. As can seen, our data are in a good agreement with IHTE modelling estimations (points). Also, at high temperatures (about 750°C) KI data closely correlate with the ORNL experimental data, [16] but the discrepancy increase with the temperature decrease down to 500°C.

Figure 2. **Comparison of data on thermal conductivity of Na, Li, Be/F systems vs temperature**
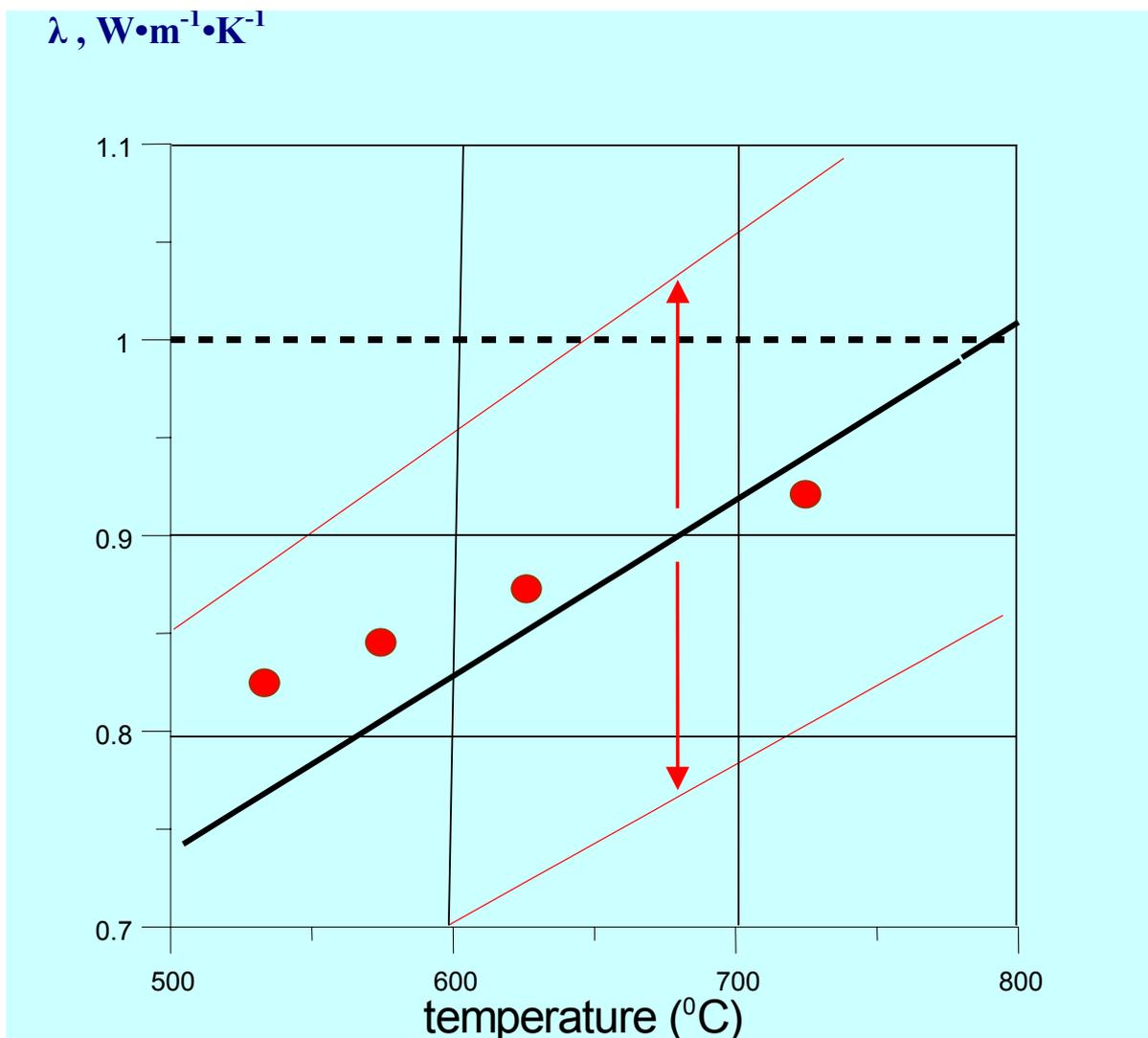
Thick solid line – equation; [10] thick dashed line – ORNL data; [16] points – equation (7).

Li, Be, Th/F system

Many of the physical properties dealing with heat and mass transport processes of Li,Be,Th/F system have been obtained during the development of the MSR programme in ORNL. [4,17] The specific physical properties which were either measured within Russian MSR programme include also phase diagrams behaviour, density, heat of fusion, viscosity, and electrical conductivity of Li,Be,Th/F mixtures. [18] Certainly it is of interest to compare data received within both MSR programmes.

Comparison of ORNL [17] and UPI [18] experimental data on Li,Be,Th/F phase diagram has shown quite satisfactory agreement on composition and temperatures of typical points and train of lines of transformations (see Table 2). Some discrepancy in the position of the typical points and melting temperatures could be explained by different methods of measurement and purity of salts used.

Table 2. **Phase diagram behaviour of 72LiF-16BeF$_2$-12ThF$_4$ mixture** [17,18]

Typical points	BeF$_2$	LiF	ThF$_4$	[17]	[18]
E	51.5	47.0	1.5	356	360
P$_1$	83.0	15.0	2.0	497	500
P$_2$	64.0	33.5	2.5	455	460
P$_3$	36.5	60.5	3.0	433	445
P$_4$	30.5	65.5	4.0	444	450
P$_5$	30.5	63.0	6.5	448	460

Table 3. **Comparison of transport properties for 72LiF-16BeF$_2$-12ThF$_4$
mixture measured or estimated by different authors at 866 K**

Melting point=773 K	UPI [18]	ORNL [20]	ORNL [19] ([21])
Density, kg m^{-3}	3 347.0	3 236.7	3 356.0
Heat capacity, J K^{-1} g^{-1}	*1.36*[*]	1.42	1.36
Viscosity, cP	8.11	12.61	12.26
Thermal conductivity, W m^{-1} K^{-1}	*0.62*[*]	1.0	1.2 (1.4)
$d\rho/dT$, g·cm^{-3}·K^{-1}	7.2·10^{-4}	6.6·10^{-4}	6.68·10^{-4}

Table 3 shows the key properties of 72LiF-16BeF$_2$-12ThF$_4$ at temperature 866 K. As can seen from the table UPI data [18] on density are in good agreement with data ORNL. [19-21] In UPI paper the density of Li,Be,Th/F mixtures was measured using the method of maximum pressure in gas bubble. The recommended equation for 72LiF-16BeF$_2$-12ThF$_4$ density in a range of temperatures 850-1 150 K can be represented as:

$$\rho \text{ (g cm}^{-3}) = 3{,}970 - 7{,}20 \cdot 10^{-4}\, T(K) \tag{11}$$

The viscosity of this system have been studied quite intensive. In UPI experiments the technique was based on method of torsional oscillations cylinder filled by the salt. Kinematic viscosity of different Li,Be,Th/F compositions have been measured in the temperature range from liquidus up to 1 300 K with accuracy about 2%. Dependence of viscosity VS temperature for composition 72LiF-16BeF$_2$-12ThF$_4$ (mol %) is given as:

$$log\eta \text{ (cP)} = -0{,}4550 + 1181/T \text{ (K)} \tag{12}$$

The value for the viscosity from this equation is 8,11 cP at 866 K. Note that according ORNL data [19-21] the viscosity is varied from 11,99 to 12,67 cP at 866 K.

In ORNL the heat capacity has been derived from drop calorimetry (points)n the basis of this determination and with a simple model for predicting heat capacity of molten fluorides, one can reliably predict the heat capacity of fuel salt. There are also no experimental data received within Russian MSR programme on heat capacity of $72LiF-16BeF_2-12ThF_4$ (mol %) mixture. As can seen from the Table 3 the data on isobaric heat capacity of the selected fuel composition calculated by IHTE are in good agreement with experimental ORNL data.

In ORNL papers [19-21] the thermal conductivity Li,Be,Th/F salt compositions was measured by variable gap method. Particularly for composition $72LiF-16BeF_2-12ThF_4$ the value of thermal conductivity is varied from 1 till to 1,4. Note that in Table 3 is also presented value on thermal conductivity estimated by IHTE from equation (7). It is equal 0,62 W/(m·K) at 866 K. Such significant discrepancy between IHTE predictions and ORNL data could be explained by shortage of IHTE equation or drawbacks of variable gap method used by ORNL.

The disagreement between the ORNL and UPI data on the viscosity and thermal conductivity for the $72LiF-16BeF_2-12ThF_4$ salt, is beyond the uncertainty claimed by the authors. New measurements will be required to obtain the reliable data on the viscosity and thermal conductivity of the fuel salt composition.

Acknowledgement

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