

Ionic Melts in Nuclear Power



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1 Introduction

At present, there is a growing interest in studying various ways of organizing a closed nuclear fuel cycle and developing new types of nuclear power reactors and alternative technologies at all stages of nuclear fuel manufacturing and reprocessing. Molten salt reactors with fused halides with gaseous or lead coolants, various compositions of the fuel, and different spent fuel reprocessing technologies (electrolysis, high-temperature extraction, etc.) are considered. Finding an optimal prospective technology is a necessity. One of the possible fuel compositions for the fast-neutron reactors, capable of increased breeding of fissile materials, is a molten mixture uranium and plutonium chlorides with salts diluents (lithium, sodium, potassium, magnesium, calcium, and lead chlorides). Estimate calculations showed that chloride mixtures can be employed in the blanket region of a nuclear reactor [1]. The interest to the molten salt fuel is determined by simplicity and relatively low cost of the fuel production, possibility of continuous purification from the fission products, and adjustment of the molten salt composition during the reactor operation and organization of cooling. All the mentioned points were confirmed by the studies performed on MSRE and MSBR reactors in the USA [2].

The melt must have high radiation and chemical stability, low viscosity and vapor pressure under working conditions, as well as certain thermophysical properties. Molten salts are the most prospective media for the spent nuclear fuel reprocessing. Stability of molten salts toward ionizing radiation allows reprocessing nuclear fuels with short cooling times after removing from the reactor, thus implementing short fuel cycles [3, 4]. Studying corrosion stability of metals, steels, and alloys in these media showed that the problem of choosing construction materials capable of

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prolonged operation under working reactor conditions can be solved. At present, nickel-based alloys with high molybdenum content are considered as prospective materials for constructing a molten salt nuclear reactor [5]. However, making a final conclusion about the possibility of applying such materials is impossible without extensive additional studies of their performance in the melts containing not only uranium but also fission products.

Emerging new types of fuel and reactors result in noticeable changes of the requirements to the reprocessing technology. Therefore, perfecting reprocessing technologies and finding new technical solutions in this field remain relevant tasks. Choosing an optimal composition of salt mixtures, effective ways of cooling, and methods of spent nuclear fuel reprocessing is impossible without comprehensive studies of physicochemical, thermophysical, corrosion, and nuclear properties of the prospective salt compositions. All such information, at present, is very limited.

2 Methods Used in the Study of the Physicochemical and Thermophysical Properties of Molten Salts

The initial chemically pure salts were prepared according to the methods described earlier [6]. The surface of the primary crystallization of ternary systems was studied by differential thermal analysis with recording of the cooling curve. X-ray diffraction analysis was used for identification of the compounds.

The density and surface tension of the fused mixtures were measured by the method of maximum pressure in an argon gas bubble. The experimental technique for this measurement was well described in an earlier work [7].

The kinematic viscosity was determined employing the method based on measuring damped oscillations of a cylindrical crucible filled with the liquid salt and suspended from an elastic filament. The experimental procedure and the apparatus for viscosity measurement were described in a previous communication [8].

The method of a small bridge was used to obtain the data on thermal conductivity of the molten salt mixtures. This method is based on the measurement of the change in resistance caused by electrical heating of a narrow bridge of the material, which joins two larger bodies of the same material [9].

3 The Results of Study of the Physicochemical and Thermophysical Properties of Chloride Melts

This chapter presents the results of a study of the melting, density, viscosity, and surface tension of molten mixture ternary systems NaCl-UCl₃-UCl₄ and KCl-UCl₃-UCl₄ and thermal conductivity of molten binary systems NaCl-UCl₃, KCl-UCl₃, NaCl-UCl₄, and KCl-UCl₄.

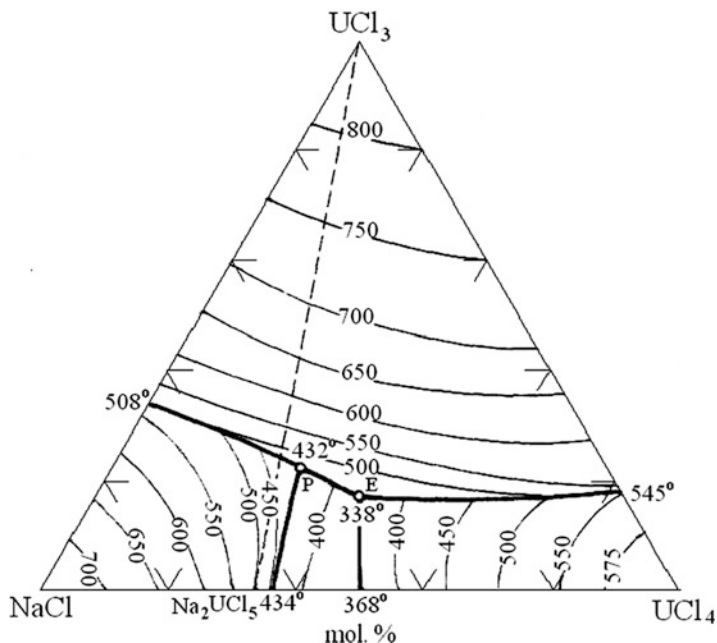


Fig. 1 Melting point diagram for the system NaCl-UCl₃-UCl₄

The surface of the primary crystallization in the system NaCl-UCl₃-UCl₄ is represented by the fields [6] NaCl, UCl₃, UCl₄, and 2NaCl • UCl₄ (Fig. 1). There is one peritectic point and one eutectic point for this ternary system. The eutectic in this system occurs at 338 °C, NaCl-UCl₃-UCl₄ (42.5–17.0–40.5 mol.%). Peritectic point at 432 °C corresponds to the composition (mol.%): NaCl, 49.0; UCl₃, 21.5; and UCl₄, 29.5.

In the system KCl-UCl₃-UCl₄ [7], liquidus surface is represented by five fields of crystallization: KCl, 2KCl • UCl₃, UCl₃, UCl₄, and 2KCl • UCl₄ (Fig. 2). Two quasi-binary sections 2KCl • UCl₃-UCl₃ and 2KCl • UCl₄-UCl₄ divide the system KCl-UCl₃-UCl₄ into three secondary subsystems which have one eutectic point in each of them. One (E₁) with a composition of 74.5% KCl + 7.5% UCl₃ + 18.0% UCl₄ has a melting point of T_m – 795 K (522 °C). Composition of second eutectic point (E₂) is 57.0% KCl + 17.0% UCl₃ + 26.0% UCl₄, which has a melting point of T_m – 791 K (518 °C). Eutectic point (E₃) at 587 K (314 °C) corresponds to the composition: 49.5% KCl + 5.5% UCl₃ + 45.0% UCl₄.

The concentration dependencies obtained for the density in the melts NaCl-UCl₃-UCl₄ and KCl-UCl₃-UCl₄ [10, 11] for 1050 K are presented in Fig. 3. The density of these mixtures increases with increasing UCl₃ concentration.

Figure 4 shows the lines of equal dynamic viscosity of molten mixtures NaCl-UCl₃-UCl₄ [12] and KCl-UCl₃-UCl₄ [13]. The dynamic viscosity was calculated using the results of the investigation of the density and kinematic viscosity.

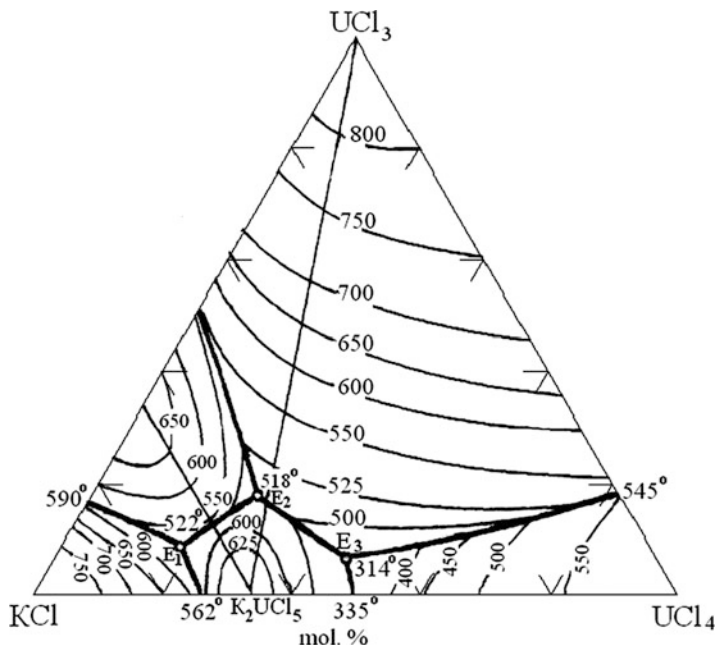


Fig. 2 Melting point diagram for the system KCl-UCl₃-UCl₄

The complicated concentration dependence of the viscosity is determined by the content of uranium chloride. The dynamic viscosity of ternary systems under study increases with increasing UCl₃ concentration in the mixtures.

The concentration dependences obtained for the surface tension in the melts NaCl-UCl₃-UCl₄ and KCl-UCl₃-UCl₄ [10, 11] at 1050 K are presented in Fig. 5.

The surface tension of ternary systems NaCl-UCl₃-UCl₄ and KCl-UCl₃-UCl₄ decreases with increasing UCl₄ concentration in the mixtures. More intense changes in the surface tension is observed at concentration up to 60 mol.% UCl₄. Uranium tetrachloride is as a surfactant in the mixtures under study.

The data on the thermal conductivity of molten NaCl-UCl₃, KCl-UCl₃, NaCl-UCl₄, and KCl-UCl₄ binary mixtures [14, 15] are represented as the concentration dependency (Fig. 6).

The thermal conductivity monotonically decreases with increasing UCl₃ concentration in the mixtures and is deflected toward smaller values (Fig. 6a). In molten mixtures of uranium tetrachloride with sodium chloride and potassium chloride, the thermal conductivity isotherms have deviation from linearity in the direction of higher values (Fig. 6b).

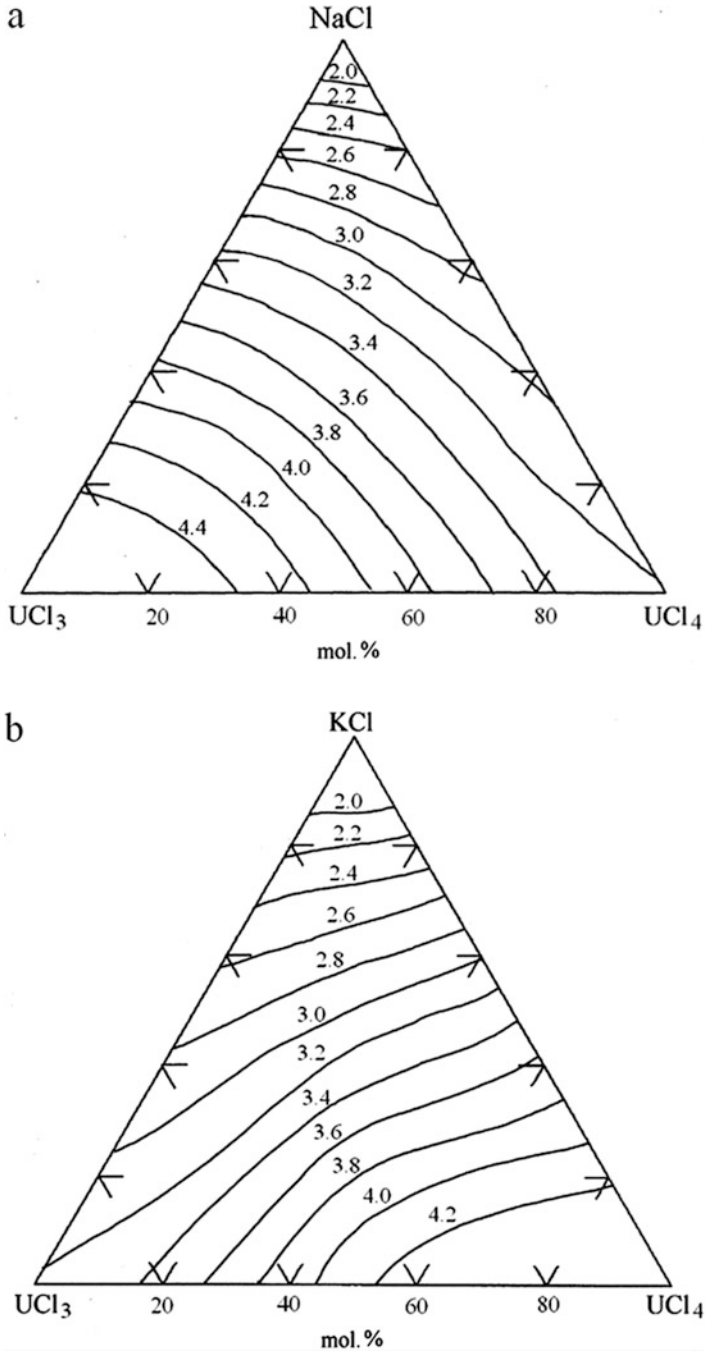


Fig. 3 Isodensities of the ternary melt of the mixtures at 1050 K, g/cm^3 : (a) $\text{NaCl-UCl}_3\text{-UCl}_4$; (b) $\text{KCl-UCl}_3\text{-UCl}_4$

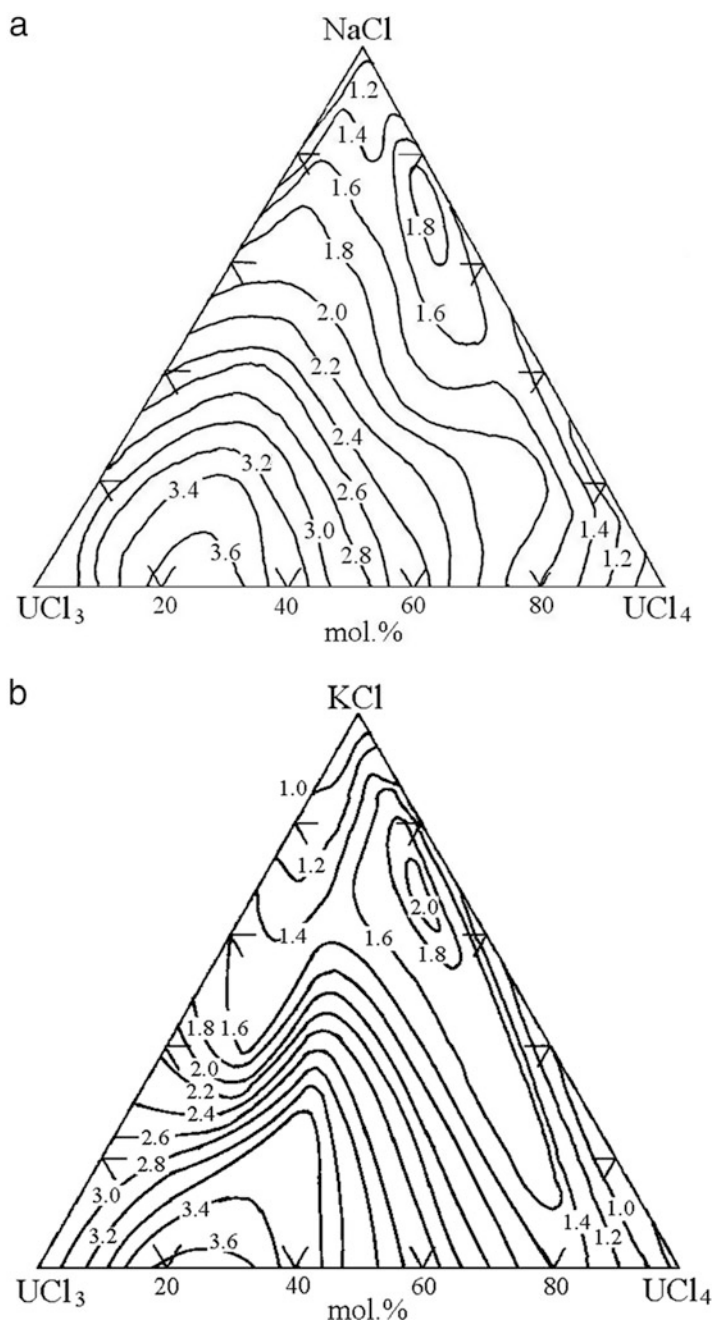


Fig. 4 Dynamic viscosity of the molten mixtures at 1130 K, mPa·s: (a) $\text{NaCl-UCl}_3\text{-UCl}_4$; (b) $\text{KCl-UCl}_3\text{-UCl}_4$

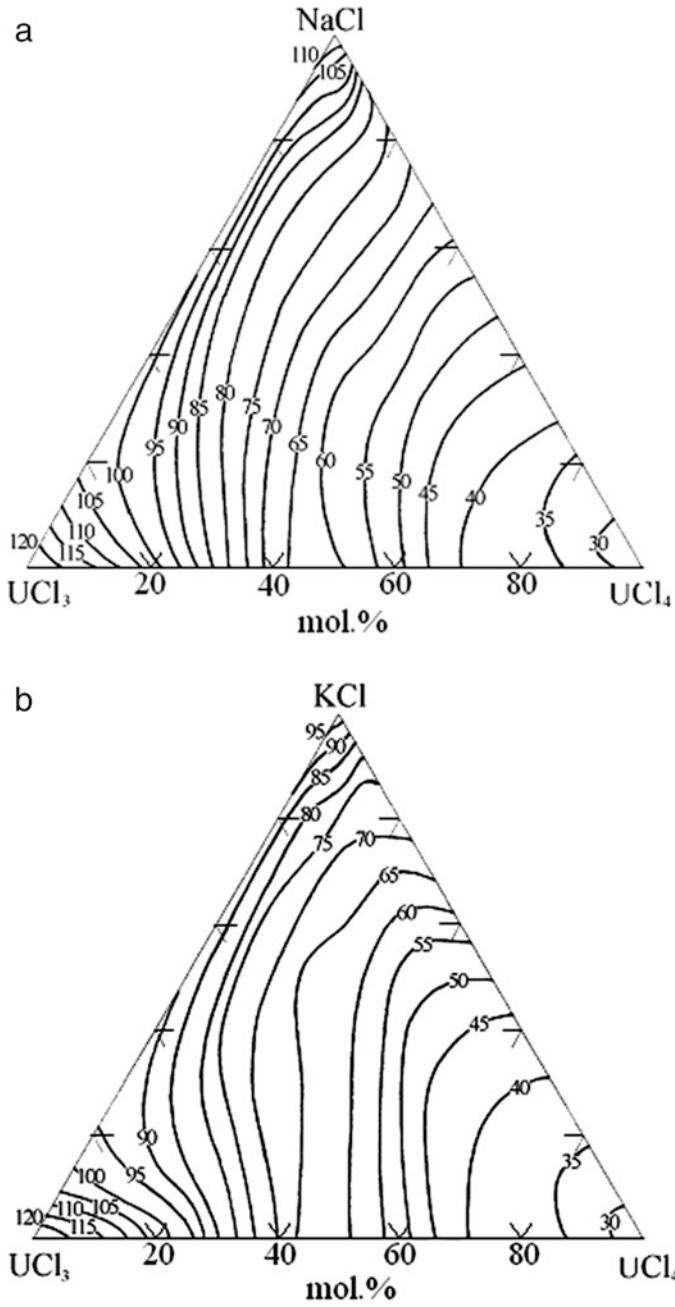


Fig. 5 Lines of constant surface tension of the melts at 1050 K, mJ/m²: (a) NaCl-UCl₃-UCl₄; (b) KCl-UCl₃-UCl₄

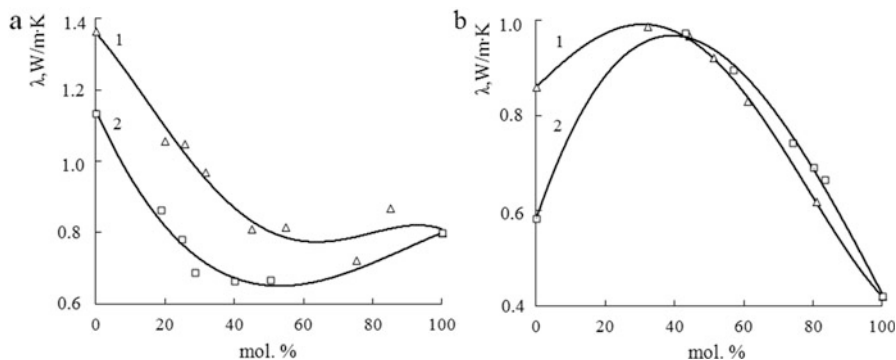


Fig. 6 Thermal conductivity (λ) isotherms of molten mixtures of: (a) uranium trichloride at 1123 K (1, with sodium chloride; 2, with potassium chloride); (b) uranium tetrachloride at 873 K (1, with sodium chloride; 2, with potassium chloride)

4 Conclusion

The presented data on the phase diagrams, viscosity, surface tension, and heat conductivity of the binary and ternary uranium containing mixtures with sodium and potassium chlorides represent part of systematic studies in this field. Magnesium, calcium, and lead chlorides can also be used as the solvent salts because they fully satisfy the nuclear-physical requirements for the fast neutron reactors. For the systems studied already, a number of low melting mixtures with high uranium chlorides content have already been found.

Studying temperature dependencies of density, surface tension, and viscosity of these salt mixtures showed that the melts containing uranium chlorides have sufficiently high density and low surface tension and viscosity.

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