# Electrical conductivity of multicomponent chloride melts, containing ions of mono-, di-, and trivalent metals

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**Abstract**

The electrical conductivity of quasi-binary molten mixtures (LiCl-KCl)eut. - MCl, (LiCl-KCl)eut. - MCl2, (LiCl-KCl)eut. - MCl3, where M denotes components of the spent nuclear fuel (M = Cs, Sr, Ce, Nd, U), has been measured. Electrical conductivity is a highly non-additive property. The electrical conductivity of mixtures can deviate from additive values by tens of percent. To calculate the electrical conductivity of complex mixtures, it is proposed to use the additive sum of binary mixtures. In this case, the calculated values differ from those found experimentally by no more than 2-3%.

## INTRODUCTION

At present, in Russia, within the framework of the "Breakthrough" project, a pyrochemical technology for the reprocessing of spent nuclear fuel (SNF) is being developed. The use of molten salts will make it possible to reduce the fuel hold-up time before the processing, to eliminate the formation of liquid waste almost completely, and to implement a system with inherent safety. Special attention is paid to the technology of nitride fuel reprocessing [1], which is the most promising fuel for fast reactors. Molten LiCl - KCl eutectic (58.8 - 41.2 mol%) is proposed as the main technological medium [2]. As a result of the dissolution of SNF in this melt, complex multicomponent mixtures will be formed. The properties of such mixtures have not been sufficiently studied [3]. In the process of SNF reprocessing, electrochemical methods are expected to be widely used for the separation of fission products. Therefore, in particular, it is necessary to know the electrical conductivity of such melts.

The purpose of this work is to study the electrical conductivity of melts, similar to those that are formed during the dissolution of real nitride spent nuclear fuel in (LiCl-KCl)eut., as well as to develop a model that would allow us to estimate the electrical conductivity of multicomponent melts of arbitrary composition based on the electrical conductivity of 2-3 component mixtures.

## Experimental

 The starting salts of the 99.8% purity were dried under vacuum and then purified by 3-4-fold zone recrystallization. Divalent and trivalent metal salts were also dried and purified by distillation. Uranium trichloride was produced by the method described in [4]. Electrical conductivity measurements were performed in capillary-type all-quartz cells with platinum electrodes. The design of the cells was described earlier [3, 5]. The cells were calibrated against standard 0.01 and 0.1 molar KCl solutions [6]. The error in the specific electrical conductivity determination is ± 1% and that of the molar one is ± 2.5%. The preparation of salts and the experimental procedure are described in more detail in [4, 5, 7].

## ELECTRIC CONDUCTIVITY OF SOME QUASIBINARY MELTS BASED ON LICL-KCL EUTECTICS

We have measured the electrical conductivity of a large number of quasi-binary mixtures (LiCl-KCl)eut. - MCl, (LiCl-KCl)eut. - MCl2, (LiCl-KCl)eut. - MCl3, where M is one-, two- or trivalent elements that make up the nitride SNF (Cs, Sr, Cd, Ba, Ce, Nd, U). Within the framework of this work, we will consider the LiCl-KCl eutectic as one component of the system. In addition, the electrical conductivity of a number of ternary and quaternary mixtures was measured. Figs. 1-8 show the molar conductivity of the (LiCl-KCl)eut. - CsCl, (LiCl-KCl)eut. - SrCl2, (LiCl-KCl)eut. - CeCl3, and (LiCl-KCl)eut. - NdCl3 molten mixtures, as well as the relative deviations of the molar electrical conductivity of these mixtures from additive values. All primary data (specific conductivity) were obtained by us. The density of the mixtures required for calculating the molar electrical conductivity was calculated according to the methods described in [8, 9]. These techniques are in fact a generalization of the most reliable experimental data.

## EVALUATION OF ELECTRIC CONDUCTIVITY OF MULTICOMPONENT MIXTURES

As shown in the previous paragraph, electrical conductivity is a highly non-additive property. If we evaluate the electrical conductivity of complex mixtures as an additive sum of individual components, then the error can reach tens of percent.

We suggest to evaluate the electrical conductivity of multicomponent mixtures as an additive sum of binary mixtures. In this case, deviations from additivity are already taken into account in binary mixtures. Figs. 9-12 illustrate the results of this approach.

* Fig. 9 compares the specific conductivities of the (LiCl-KCl)eut. + 2.5 mol% CsCl + 2.5 mol% UCl3 system. The red points are our experimental data for this ternary system. A blue line is a sum of the electrical conductivities of two quasi-binary systems: 0.5·((LiCl-KCl)eut. + 5.0 mol.% CsCl) + 0.5·((LiCl-KCl)eut. + 5.0 mol.% UCl3). The maximum difference from the experimental data at 400° is -0.6%, and at 700 ° it is +0.9%.
* Fig. 10 compares the calculated and experimental data for the (LiCl-KCl)eut. + 7.5 mol% NdCl3 + 7.5 mol%UCl3 system. The difference from the experimental data is 0.7 - 1.2%.
* Fig. 11 compares the calculated and experimental data for the four-component system (LiCl-KCl)eut. + 2.5 mol% CsCl + 2.5 mol% NdCl3 + 5.0 mol% UCl3. The difference at low temperatures reaches 1.3%, at higher temperatures the data practically coincide.
* Fig. 12 compares the calculated and experimental data for the four-component system (LiCl-KCl)eut. + 5.0 mol.% CsCl + 5.0 mol.% SrCl2 + 5.0 mol.% UCl3. The difference from the experimental data at low temperatures is about 0.4% and at high temperatures it reaches 1.9%.

As can be seen from the above examples, the electrical conductivity of ternary and quaternary mixtures, calculated by the additive summation of the electrical conductivities of binary mixtures, differs from the experimental values by no more than 2%. That is, the difference is within the experimental error in determining the electrical conductivity.

*Fig. 1. Molar conductivity (Λ) of the molten (LiCl-KCl)eut. - CsCl system.*



Fig. **2**. Molar conductivity relative deviations from additivity (δ) in the molten (LiCl-KCl)eut. - CsCl system.



Fig. **3**. Molar conductivity (Λ) of the molten (LiCl-KCl)eut. - SrCl2 system.



Fig. **4**. Molar conductivity relative deviations from additivity (δ) in the molten (LiCl-KCl)eut. - SrCl2 system.



Fig. **5**. Molar conductivity (Λ) of the molten (LiCl-KCl)eut. - CeCl3 system.



Fig. **6**. Molar conductivity relative deviations from additivity (δ) in the molten (LiCl-KCl)eut. - CeCl3 system.



Fig. **7**. Molar conductivity (Λ) of the molten (LiCl-KCl)eut. - NdCl3 system.



Fig. **8**. Molar conductivity relative deviations from additivity (δ) in the molten (LiCl-KCl)eut. - NdCl3 system.

 FIG. **9**. Specific conductivity (κ) of the molten (LiCl-KCl)eut. + 2.5 mol.%CsCl + 2.5 mol.%UCl3 system. A blue line denotes the conductivity of the system: 0.5·((LiCl-KCl)eut. + 5.0 mol.%CsCl) + 0.5·((LiCl-KCl)eut. + 5.0 mol.%UCl3).



Fig. **10**. Specific conductivity (κ) of the molten (LiCl-KCl)eut. + 7.5 mol.%NdCl3 + 7.5 mol.%UCl3 system. A blue line denotes the conductivity of the system: 0.5·((LiCl-KCl)eut. + 15 mol.%NdCl3) + 0.5·((LiCl-KCl)eut. + 15 mol.%UCl3).

 Fig. **11**. Specific conductivity (κ) of the four-component molten (LiCl-KCl)eut. + 2.5 mol.%CsCl + 2.5 mol.%NdCl3 +

5.0 mol.%UCl3 system. A blue line denotes the conductivity of the system:

0.108·(LiCl-KCl)eut. + 0.25·((LiCl-KCl)eut. + 10 mol.%CsCl + 10 mol.%NdCl3) + 0.642·((LiCl-KCl)eut. + 7.79 mol.%UCl3).



Fig. **12**. Specific conductivity (κ) of the four-component molten (LiCl-KCl)eut. + 5.0 mol.%CsCl + 5.0 mol.%SrCl2 + 5.0 mol.%UCl3 system. A blue line is the conductivity of the system:

0.167·(LiCl-KCl)eut. + 0.25·((LiCl-KCl)eut. + 20 mol.%CsCl) + 0.25·((LiCl-KCl)eut. + 20 mol.%SrCl2) + 0.333·((LiCl-KCl)eut. + 15 mol.%UCl3).

Fig. 13 shows the predicted conductivity of the (LiCl-KCl) + 2mol.%CsCl + 4mol.%SrCl2 + 3.0mol.%CeCl3 + 5.0mol.%NdCl3 + 6.0mol.%UCl3 six-component system. The total concentration of additives is 20 mol. %. The electrical conductivity of this mixture is estimated as the following sum of components: 0.1·((LiCl-KCl)eut. + 20mol.%CsCl) + 0.2·((LiCl-KCl)eut. + 20 mol.%SrCl2) + 0.15·((LiCl-KCl)eut. + 20 mol.%CeCl3) + 0.25·((LiCl-KCl)eut. + 20 mol.%NdCl3) + 0.3·((LiCl-KCl)eut. + 20 mol.%UCl3). There is no experimental data on the electrical conductivity of such a system. Taking into account the above examples, it can be assumed that the error in estimating the electrical conductivity of this mixture does not exceed ± 2%.



*Fig.****13****. Predicted electrical conductivity of the six-component (LiCl-KCl) + 2mol.%CsCl + 4mol.%SrCl2 + 3.0mol.%CeCl3 + 5.0mol.%NdCl3 + 6.0mol.%UCl3 system. The total concentration of additives is 20 mol. %.*

## Discussion

Significant deviations of the electrical conductivity of mixtures from additive values are associated with the complexation in melts. When polyvalent ions with a high ionic potential (ratio of charge to radius) are added to the LiCl-KCl eutectic, complex ions of the $CdCl\_{4}^{2-}$ [10-12], Sr$Cl\_{4}^{2-}$[13, 14], $CeCl\_{6}^{3-}$[15-17], $NdCl\_{6}^{3-}$[16, 17], $UCl\_{6}^{3-}$[16 - 18] types are formed. These large, low-mobile ions provide significant negative deviations of the electrical conductivity of binary mixtures from the additive values. The situation is somewhat different in the (LiCl-KCl)eut. - CsCl system. In the LiCl-KCl mixture, the strongest complexing agent is the lithium cation. Its ionic potential is 13.2 nm-1. It forms $LiCl\_{4}^{3-}$ complexes. K+ cations have a counter polarizing effect, distorting and partially destroying lithium complexes. The ionic potential of Cs+ cations is only 5.99 nm-1. The introduction of these cations lowers the concentration of potassium cations, which leads to the strengthening of lithium complexes. As a result, the mobility both of lithium cations and of associated chlorine anions decreases [19].

If a multicomponent mixture is formed from binary ones, then almost ideal mixing occurs. Complex ions have already formed and their composition and quantity vary slightly. In general, we may state that we managed to bring the multicomponent mixture closer to the ideal one by changing the system components.

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