

Electrical Conductivity of Molten LiCl-KCl Eutectic with Components of Spent Nuclear Fuel

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Abstract. The electrical conductivity of a number of quasi binary melts $(\text{LiCl-KCl})_{\text{eut.}}$, containing CeCl_3 , NdCl_3 , UCl_3 , as well as CsCl and CdCl_2 , and some of 3-4 component $(\text{LiCl-KCl})_{\text{eut.}}$ - CeCl_3 - NdCl_3 - UCl_3 mixtures was measured. The densities of the melts under study were evaluated and their molar conductivities were calculated. Liquidus lines were built for the measured systems from the breaks on conductivity polytherms. The results are discussed in terms of coexistence and mutual competition of complexes formed by Li^+ and Cd^{2+} , Ce^{3+} , Nd^{3+} , U^{3+} cations.

Key Words: Molten salts, electrical conductivity, rare earths and uranium, cadmium.

1. Introduction

Pyroelectrochemistry is one of the most prospective approaches for spent nitride nuclear fuel (nitride SNF) reprocessing. It includes the anode dissolution of the SNF pellets into the molten LiCl-KCl eutectic melt with the subsequent electrochemical separation of U, Pu, Np, Am from other constituents [1]. Physical-chemical properties of such complex melts are still insufficiently studied.

The aim of this work is to obtain experimental data on the electrical conductivity of the melts formed during SNF reprocessing. These data should become the experimental basis for the development of model to evaluate the electrical conductivity of arbitrary complex melts used for SNF reprocessing. To achieve this goal we measured the electrical conductivity of a large number of multicomponent mixtures based on the molten LiCl-KCl eutectic.

2. Experimental

High-purity (≥ 99.2 - 99.9%), anhydrous alkali metal chlorides, CdCl_2 , NdCl_3 and CeCl_3 were prepared as described in [2, 3]. Finally, LiCl, KCl and CsCl were purified by the threefold zone recrystallization with a boat speed of 2-3 cm/h. At the last stage CdCl_2 , NdCl_3 and CeCl_3 were additionally purified by a distillation under reduced pressure (about 1 Pa). The $(\text{LiCl-KCl})_{\text{eut.}}$ + UCl_3 mixtures were prepared by diluting of $(\text{LiCl-KCl})_{\text{eut.}}$ + 30 mol. % UCl_3 master alloy. The master alloy was prepared according to reaction: $3\text{PbCl}_2 + 2\text{U} = 2\text{UCl}_3 + 3\text{Pb}$ directly in the (58.8 mol. % LiCl - 41.2 mol. % KCl) melt. The synthesis was performed at the temperature of 588 K during 23 h. According to chemical analysis the final composition of the solidified melt turned out $[\text{UCl}_3] = 30.0$ mol. %, and the residual lead content of was less than 0.025 wt. %.

A capillary quartz cell with platinum electrodes was used to measure electrical conductivity (see Fig. 1). The charged and sealed cell was heated in the electric furnace. The melt temperature was registered with the accuracy of ± 1 K by Pt-PtRh (10 % Rh) thermocouple. The melt resistance was measured by the AC-bridge at the input frequency of 10 kHz. In all cases, the correction for the frequency dependence did not exceed 0.25 %. The cell was calibrated against the standard 1-molal KCl solution. The cell constant was $(91.1-66.2) \text{ cm}^{-1}$. The total conductivity measurements error did not exceed 1%. The design of the cell and measuring procedure were described in detail elsewhere [4].

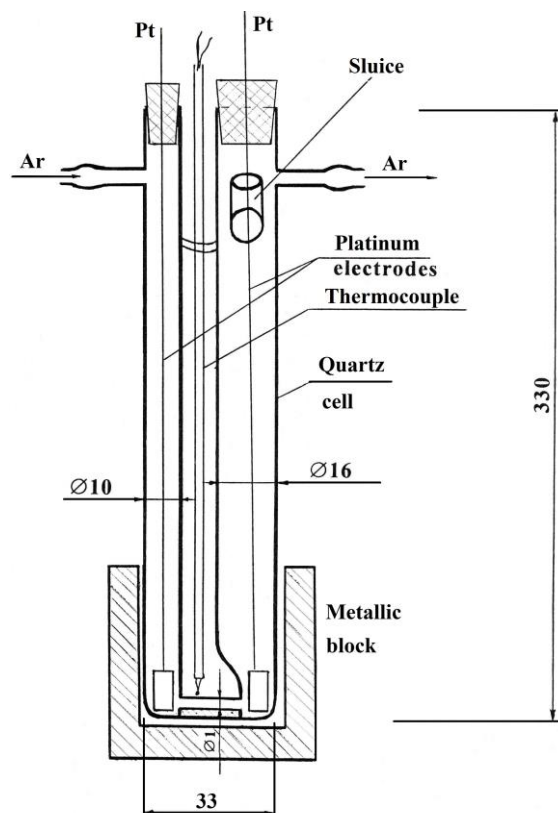


FIG. 1. Capillary quartz cell with platinum electrodes for molten mixtures electrical conductivity measurements.

3. Results

By now the electrical conductivities of $(\text{LiCl-KCl})_{\text{eut.}} + \text{CsCl}$, $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$, $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$, $(\text{LiCl-KCl})_{\text{eut.}} + \text{NdCl}_3$ mixtures were studied over the full concentration range. The conductivity of $(\text{LiCl-KCl})_{\text{eut.}} + \text{UCl}_3$ was measured up to UCl_3 concentration of 10.45 mol.%. Also several $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3 + \text{NdCl}_3$ and $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3 + \text{NdCl}_3 + \text{UCl}_3$ mixtures were studied. The majority of measurements were carried out over a wide temperature range from the liquidus point to 900-920°C. The concentration range of 0-10 % was studied in more detail because it is presumably the most important for practical purposes.

3.1. Specific conductivity

The primary data on the electrical conductivity of molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$, $(\text{LiCl-KCl})_{\text{eut.}} + \text{UCl}_3$ systems and some of the more complex mixtures are shown in Figs. 2-4 as examples. The electrical conductivity of all melts increases with temperature. The conductivity growth rate does not remain constant, but decreases slightly with temperature.

This is due to the fact that the increase in mobility of ions is gradually compensated by the decrease of the melt density and by the increase in the ions association at higher temperatures. In Figs. 5-7 the specific conductivity isotherms of $(\text{LiCl-KCl})_{\text{eut.}} + \text{CsCl}$, $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$ and $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$ melts are shown. The electrical conductivity gradually decreases with the increasing concentration of CsCl , CdCl_2 or CeCl_3 and the difference between polytherms increases with increasing temperature. For $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$ system, a plateau or even slight maximum is observed in the concentration range of about 30-70%.

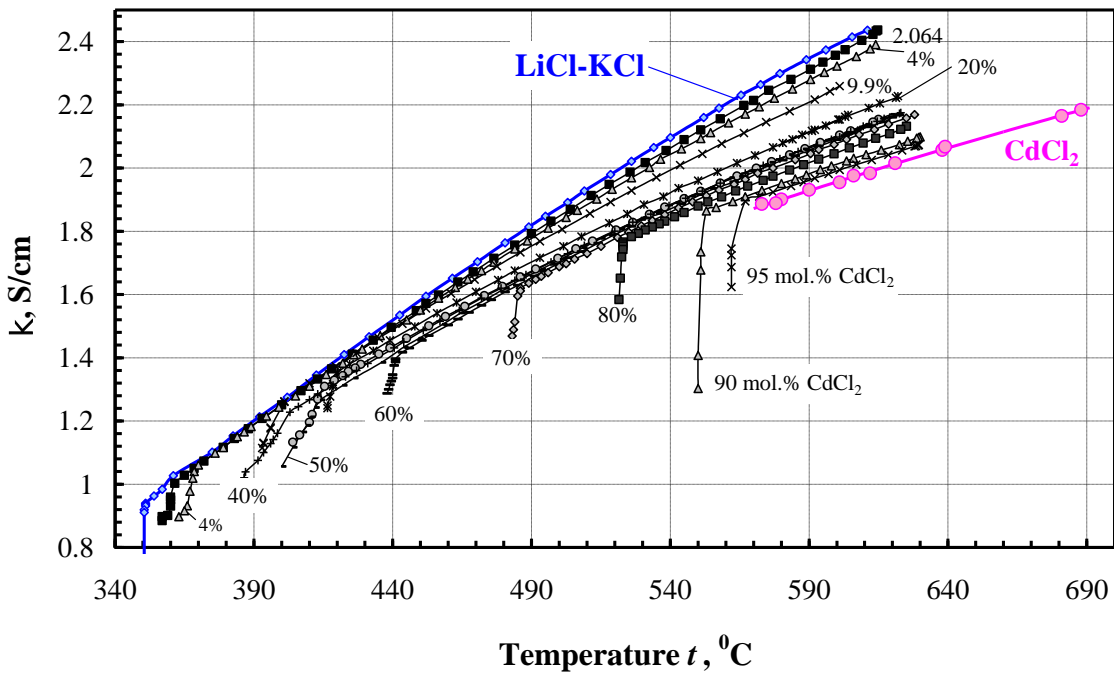


FIG. 2. Specific conductivity polytherms of $(\text{LiCl} - \text{KCl})_{\text{eut.}} + \text{CdCl}_2$ mixtures.

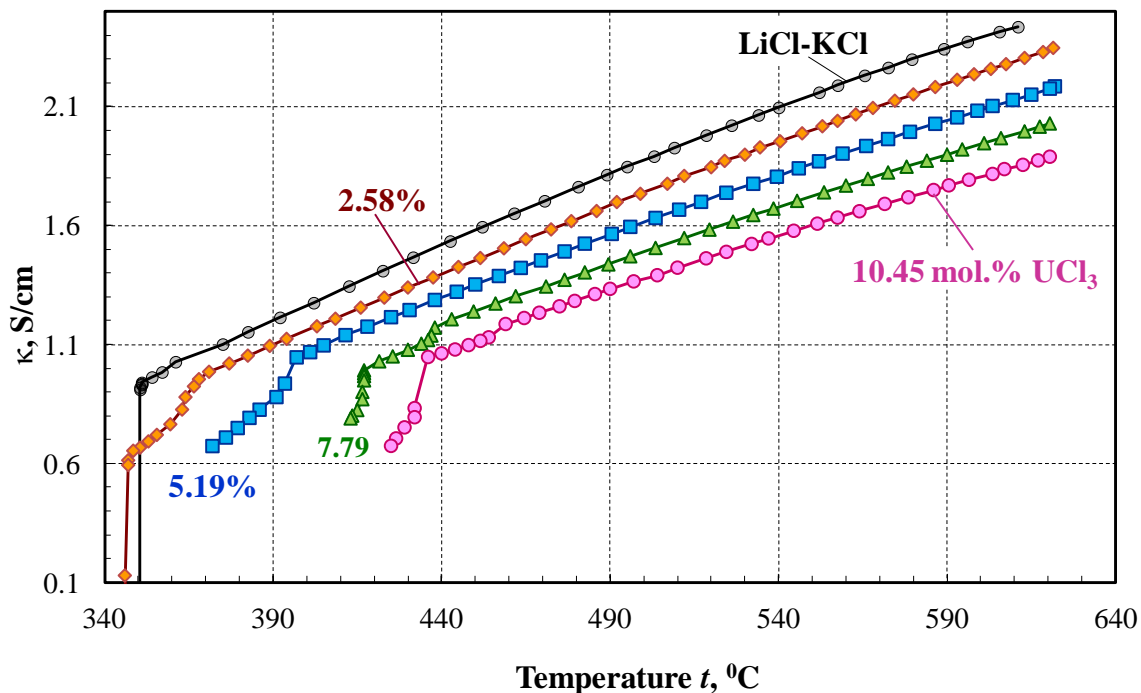


FIG. 3. Specific conductivity polytherms of $(\text{LiCl} - \text{KCl})_{\text{eut.}} + \text{UCl}_3$ mixtures.

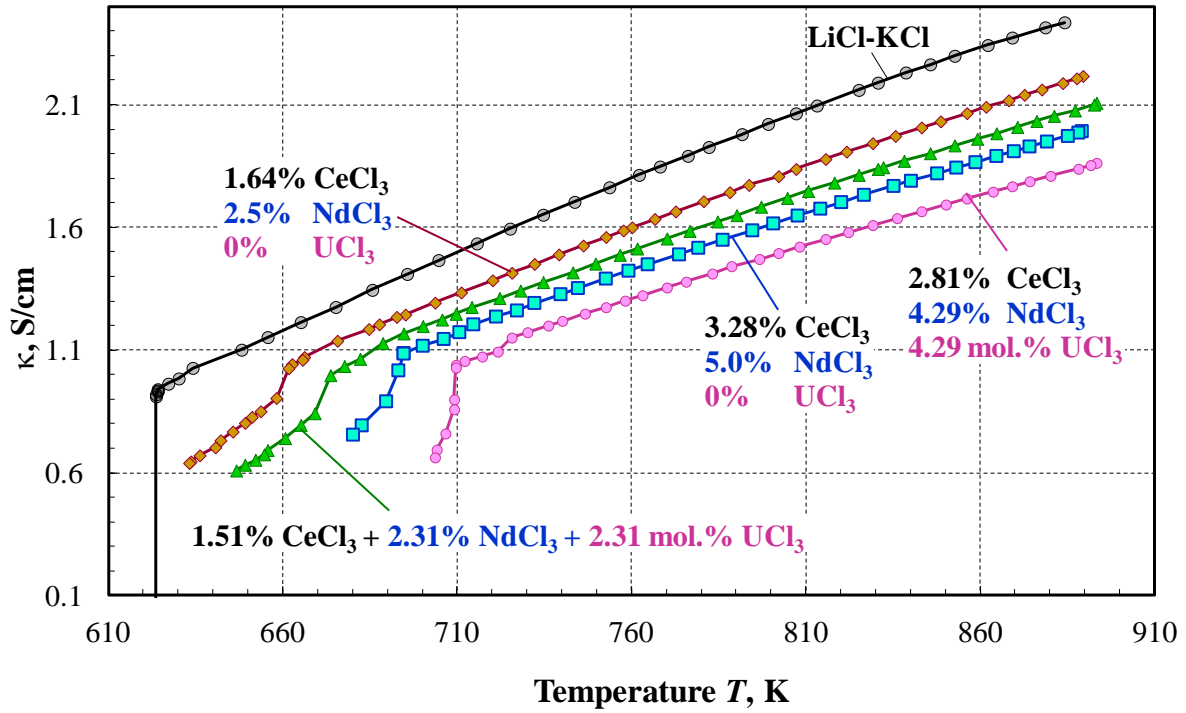


FIG. 4. Specific conductivity polytherms of $(\text{LiCl} - \text{KCl})_{\text{eut.}} + \text{CeCl}_3 + \text{NdCl}_3 + \text{UCl}_3$ mixtures.

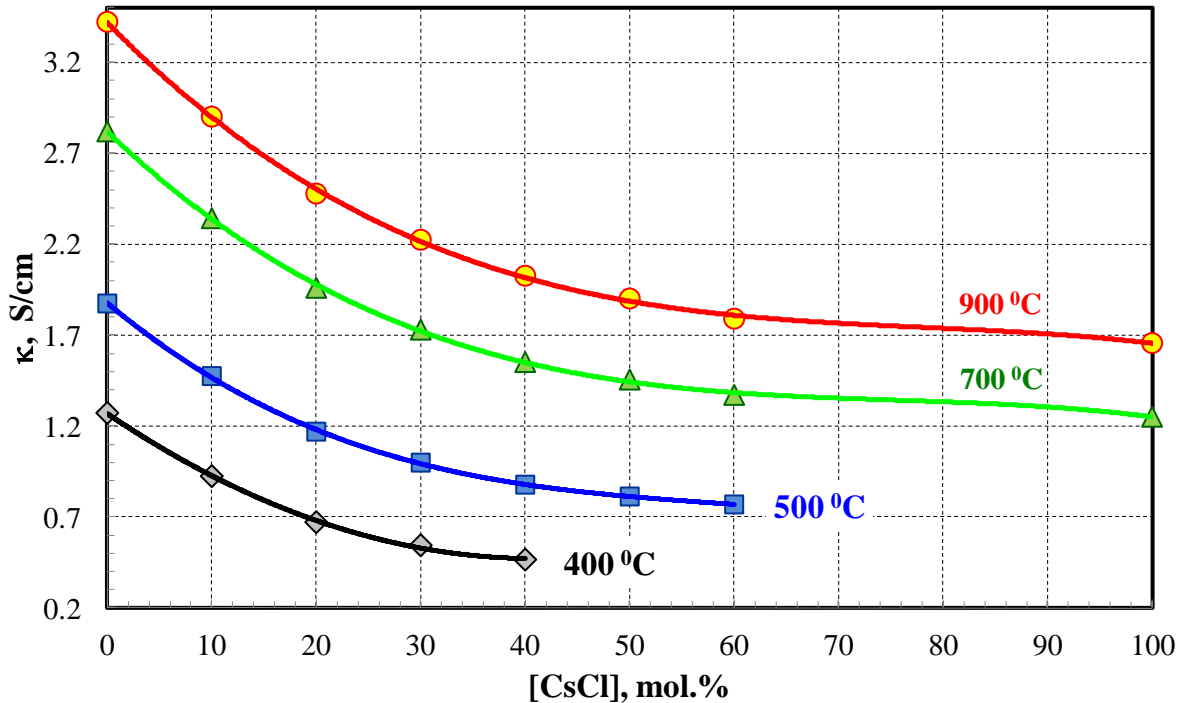


FIG. 5. Specific conductivity isotherms of molten $(\text{LiCl} - \text{KCl})_{\text{eut.}} + \text{CsCl}$ system.

3.2. Molar conductivity

Molar conductivity (Λ) was calculated for all systems according to the conventional equation: $\Lambda = \kappa \cdot V_m$ (V_m - molar volume of the melt). The molar volume was calculated by the general

equations given in [7-10]. In Figs. 8 and 9 the isotherms of the molar conductivity of $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$ and $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$ systems are shown as examples. It is interesting to

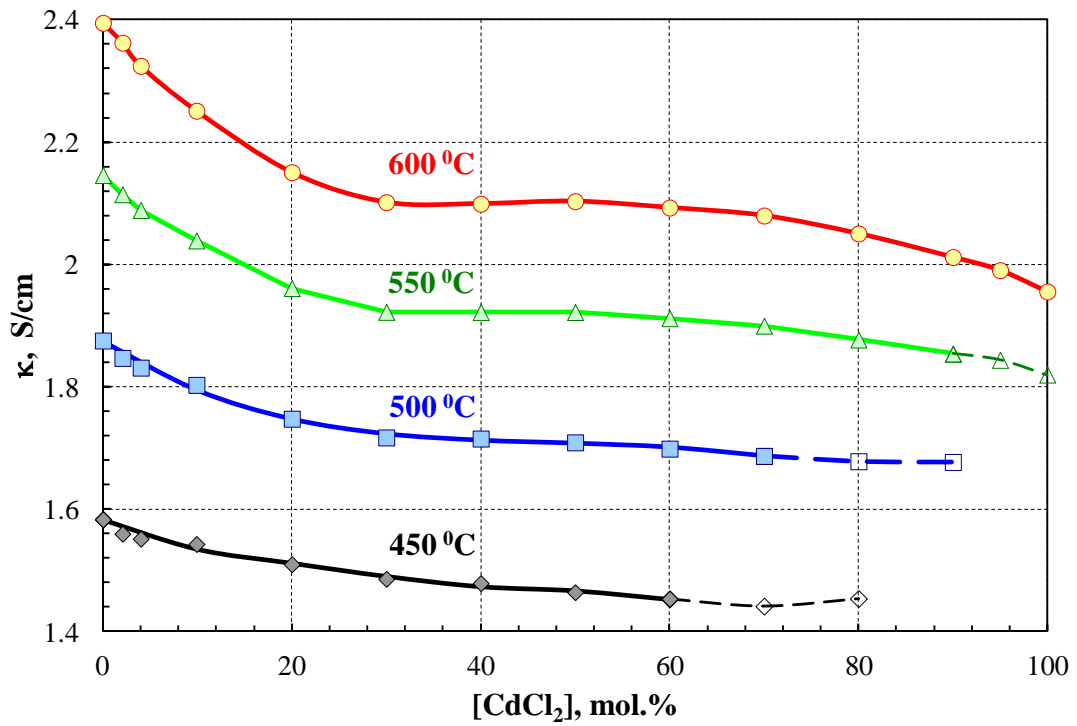


FIG. 6. Specific conductivity isotherms of molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$ system. Extrapolated values are shown in phantom.

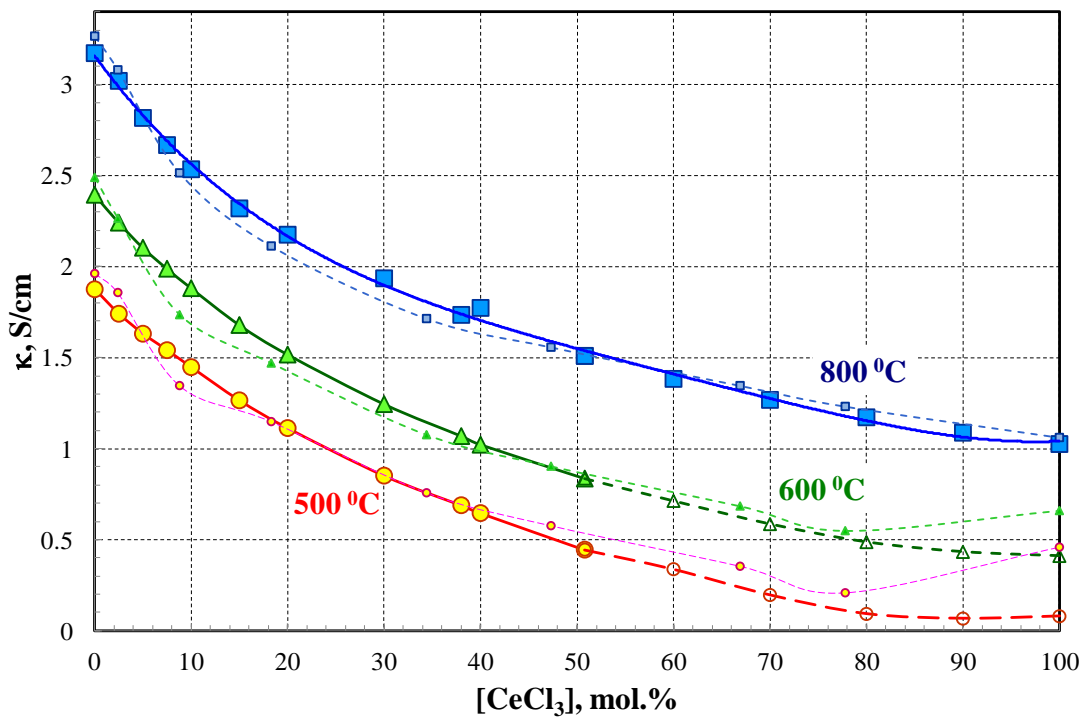


FIG. 7. Specific conductivity isotherms of molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$ system. Solid lines denote our data, dotted lines present our extrapolated values and data from [5, 6].

note that the molar conductivity of molten CdCl_2 is substantially higher than that of LiCl-KCl , whereas in the case with the specific conductivity situation is opposite (see Fig. 6).

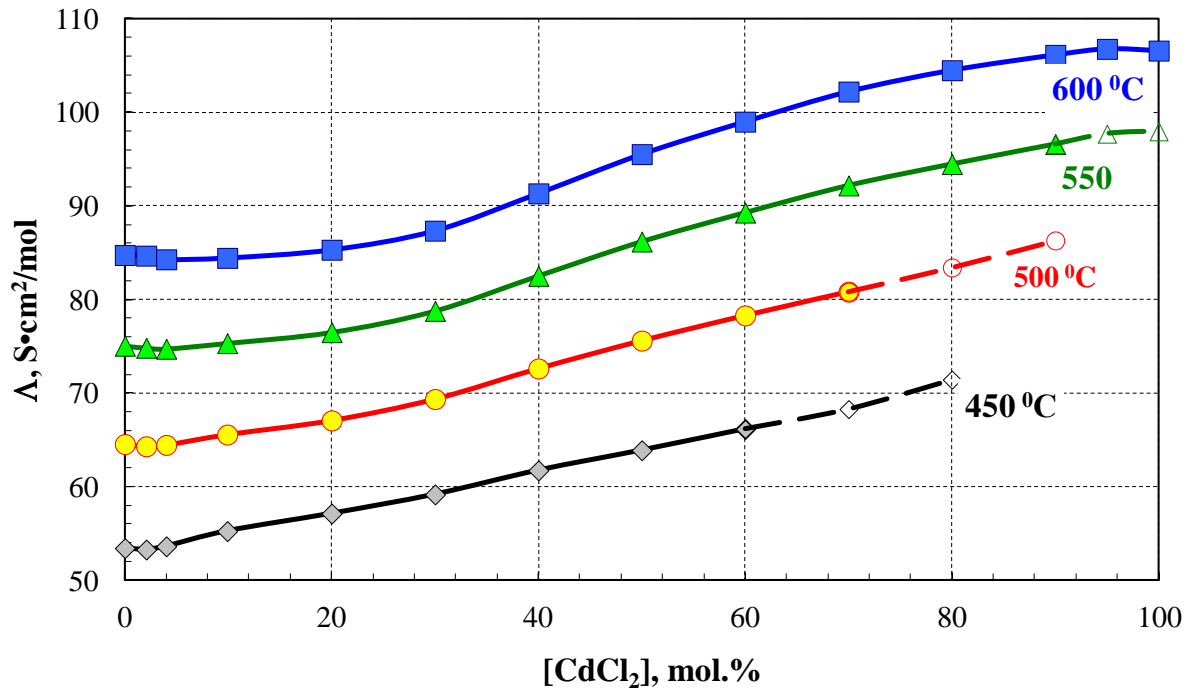


FIG. 8. Molar conductivity isotherms of the molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$ system. Extrapolated values are shown in phantom.

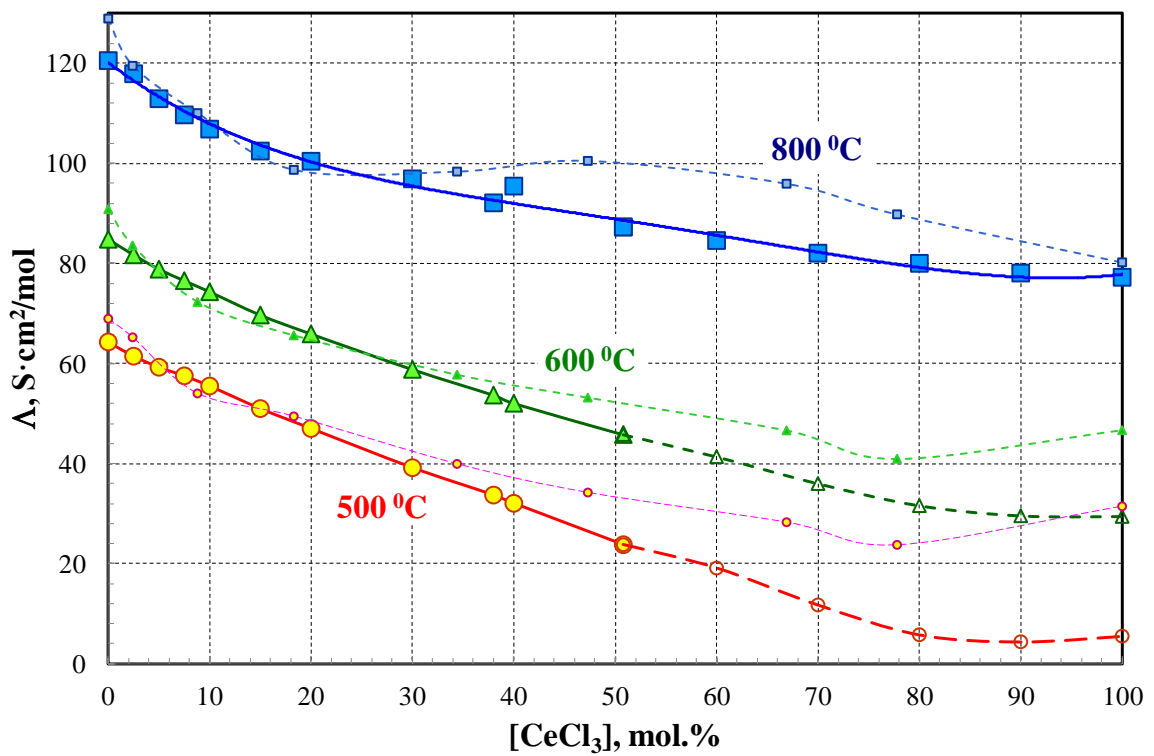


FIG. 9. Molar conductivity isotherms of the molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$ system. Solid lines denote our data, dotted lines demonstrate our extrapolated values and data from [5, 6].

3.3. Molar conductivity relative deviations from additivity

Deviations from additivity reflect the interaction of melt components. Negative deviations are connected with a complexation, i.e. formation of less mobile species. Positive deviations

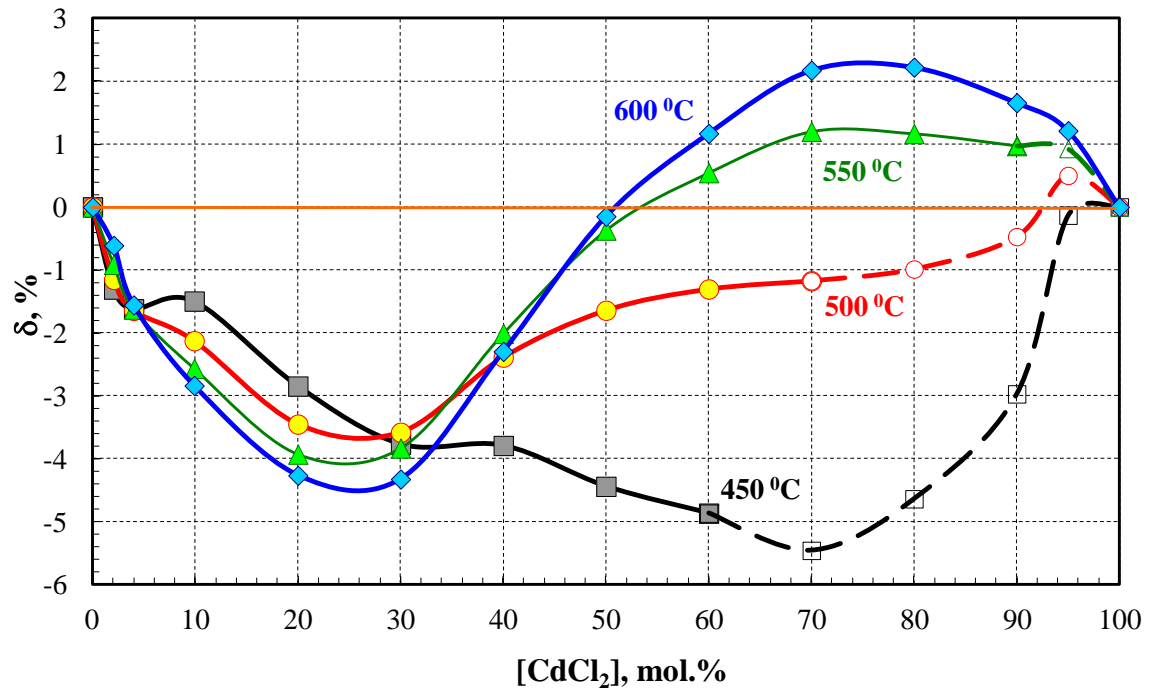


FIG. 10. Molar conductivity relative deviations from additivity in the molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$ system. Extrapolated values are shown in phantom.

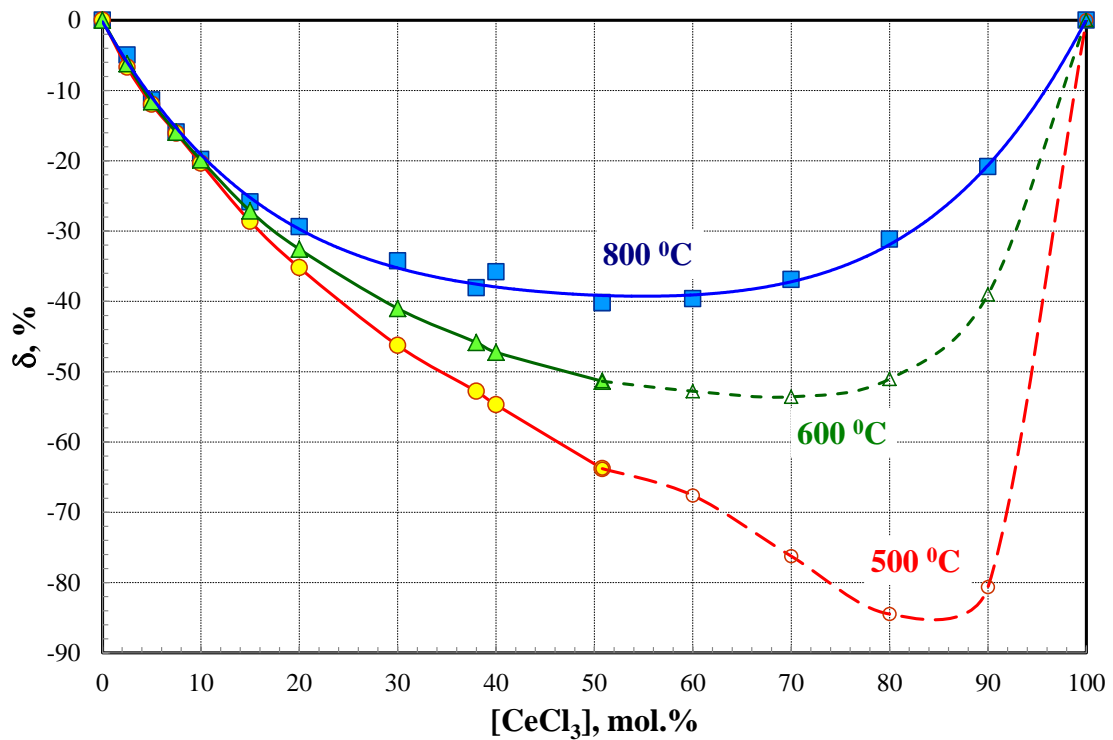


FIG. 11. Molar conductivity relative deviations from additivity in molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$ system. Extrapolated values are shown in phantom.

are usually associated with the destruction of complexes when the solution becomes more ionic than the initial components.

Molar conductivity relative deviations from additivity in molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$ and $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$ systems are shown in Figs. 10 and 11, respectively. For cadmium system the maximum negative value is -4.5% at 25 mol. % of CdCl_2 (600°C), which coincides with the position of maximum on the liquidus line (see Fig. 12). In the molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$ mixture the significant negative deviations (-40% or more) of molar conductivity from additive values are observed over the whole concentration range, which indicates a stronger complexation in the system. It has been known that the intensity of interactions between the components of molten mixtures of salts depends on the difference in the size, polarizability, and ionic moment of the interchanging particles. Species with higher ionic moments, i.e. lanthanide cations, are stronger in comparison with Cd^{2+} complexing agents.

3.4. Liquidus line

In all experiments the breaks on the conductivity polytherms corresponding to the beginning of crystallization were carefully fixed. The liquidus lines in molten $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$ and $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$ systems are shown in Figs. 12 and 13 along with the known literature data. The liquidus lines of these systems have a maximum at approximately 20 mol. % of CdCl_2 or CeCl_3 and a minimum in the area of 40 mol. % CdCl_2 or CeCl_3 . Our and literature data on liquidus temperatures agree well with each other for all systems.

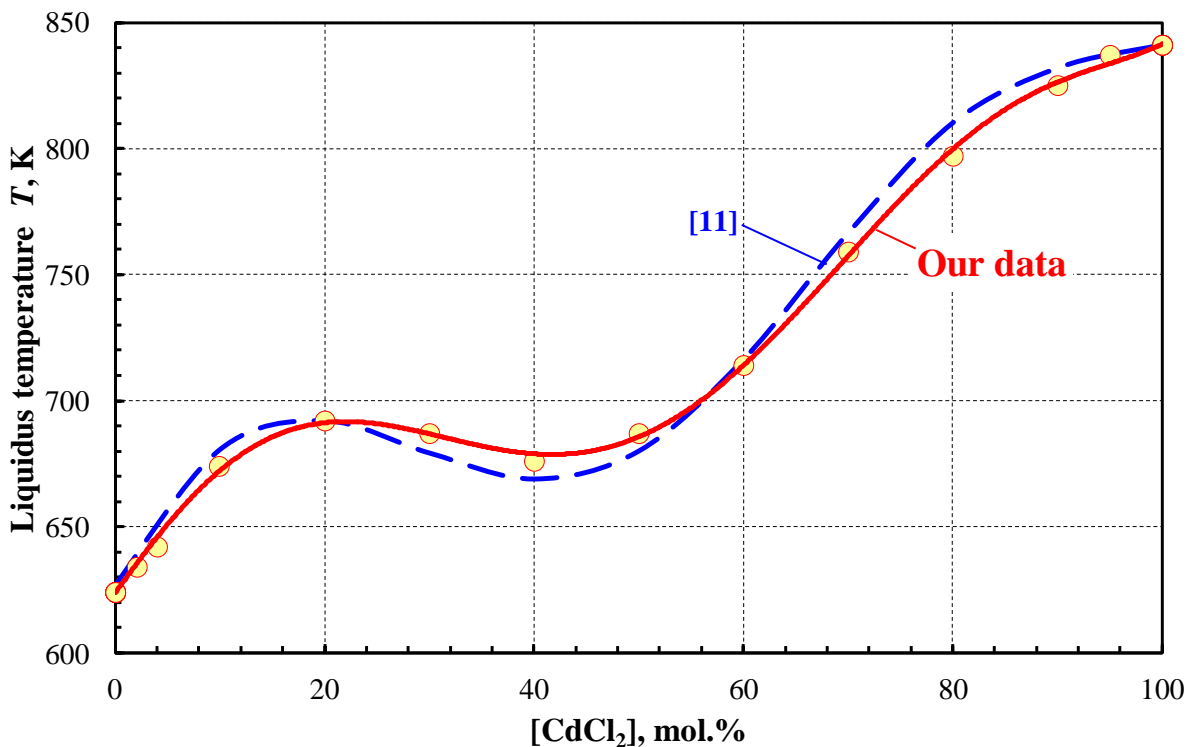


FIG. 12. Liquidus line in $(\text{LiCl-KCl})_{\text{eut.}} + \text{CdCl}_2$ system.
Our data - from conductivity measurements. Data [11] - visual polythermal analysis.

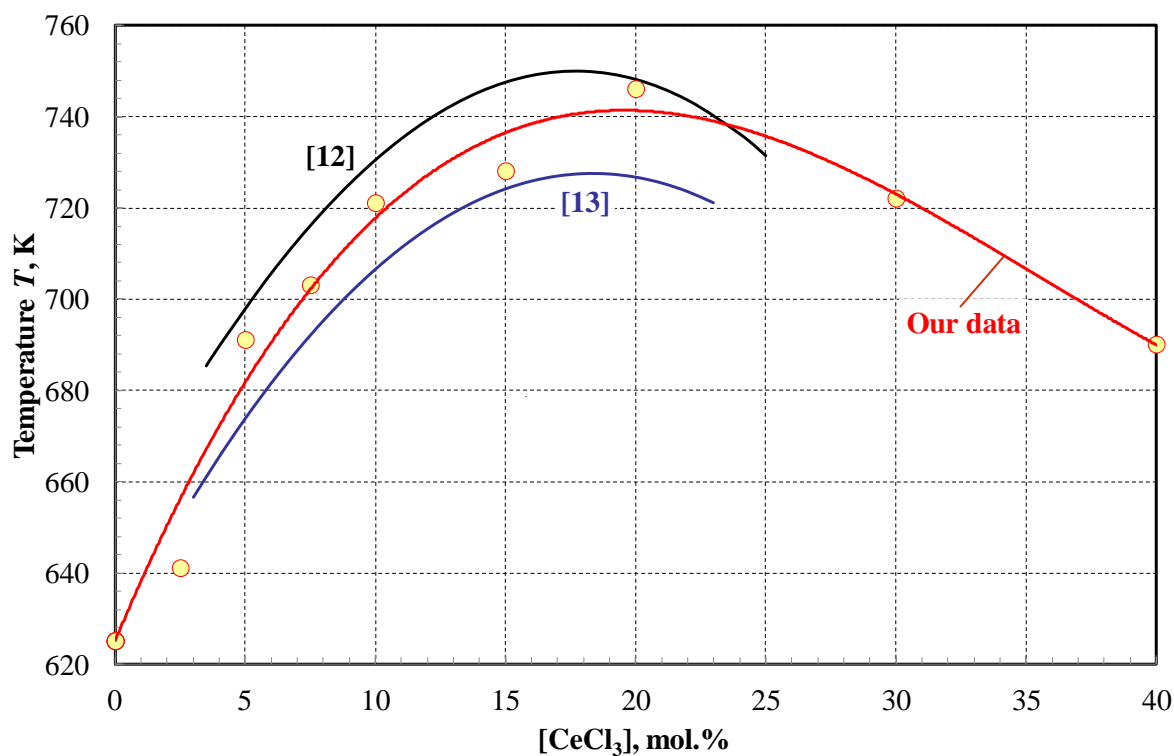


FIG. 13. Liquidus line in the $(\text{LiCl-KCl})_{\text{eut.}} + \text{CeCl}_3$ system according to our conductivity data and data reported in [12, 13].

The obtained results are well interpreted in terms of coexistence and mutual influence of the complexes formed by the mono-, di- and trivalent cations in the investigated molten chloride mixtures [2, 10] taking into account available spectral data related to the structure of melts [14].

4. Conclusions

The electrical conductivity of a large number of quasi-binary and multi-component molten mixtures of the LiCl-KCl eutectic with mono-, di- and trivalent metal chlorides was measured. Densities of the systems were estimated and molar conductivities were calculated. Liquidus lines of these salt systems were built. These data are required to create a general model of the electrolyzer operation and to develop technological equipment.

Acknowledgements

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