Electrochemical and thermodynamic properties of thulium in molten chlorides

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Abstract

This work presents the electrochemical study of $TmCl_3$ solutions in equimolar NaCl-KCl and NaCl-2CsCl eutectic in the temperature range 823–1 073 K using inert Mo electrodes. It has been shown that Tm^{3+} ions are reduced to metallic thulium through two consecutive steps: $Tm^{3+} + \bar{e} \rightarrow Tm^{2+}$ and $Tm^{2+} + 2\bar{e} \rightarrow Tm$. The electroreduction of Tm^{3+} to Tm^{2+} ions was found to be reversible at low scan rates, controlled by the rate of the mass transfer and irreversible at a high scan range (> 0.1 V s^{-1}), controlled by the rate of charge transfer. The diffusion coefficient of $[TmCl_6]^{3-}$ complex ions was determined at different temperatures. Arrhenius law was verified by plotting the variation of the logarithm of the diffusion coefficient vs. reverse temperature. The results of a study of the Tm^{3+}/Tm^{2+} couple redox potentials vs. Cl^-/Cl_2 reference electrode in a wide temperature range in molten chlorides was carried out by direct potentiometric and cyclic voltammetry methods. Apparent standard redox potentials of the couples $E^*_{Tm^{3+}/Tm^{2+}}$ were determined in different solvents. Basic thermodynamic properties of the reaction $TmCl_{2(l)} + ½\ Cl_{2(g)} \Leftrightarrow TmCl_{3(l)}$ were calculated.

Introduction

Pyrochemical processes provide an interesting option for future nuclear fuel cycles in several aspects. The latter will should provide high-recovery yields for actinide elements, taking into account the sustainable requirement to be safe, resistant versus proliferation risks, and cost-effective. This leads to a rather prolific research, with many innovative concepts for future reactors, future fuels, and obviously future processes. In this context, pyrochemical processes seem to offer significant-established or presumed-advantages: (i) low radiolytical effects versus solvent processes (which increases the ability to process high burn-up, short-time cooled hot fuels); (ii) ability to dissolve new ceramic or dense fuel compounds; (iii) presumed compactness of technology (low number of transformation steps, small size of unit operations) [1-3].

Partitioning and transmutation (P&T) concept is nowadays considered as one of the strategies to reduce the long-term radiotoxicity of the nuclear wastes [4]. To achieve this, the efficient recovery and multi-recycling of actinides (An), especially TRU elements, in advanced dedicated reactors is essential. Fuels proposed to transmute the actinides into short-lived or even stable radionuclides will contain significant amounts of Pu and minor actinides (Np, Am, Cm), possibly dissolved in inert matrices (U free), and will reach high burn-ups. Pyrochemical separation techniques offer some potential advantages compared to the hydrometallurgical processes to separate actinides from fission products (FP) contained in the irradiated fuel. The high-radiation stability of the salt or metallic solvents used, resulting in shorter fuel cooling times stands out [5] [6].

The aim of the separation techniques which are currently being investigated, both hydrometallurgical and pyrometallurgical ones, is to optimise the recovery efficiency of minor actinides minimising at the same time the fission product content in the final product. Special attention is paid to rare earth elements (REE) mainly due to their neutronic poison effect and the high content in spent fuel. In addition, REE have similar chemical properties hence separation between these groups of elements is very difficult. Another important issue is to consider that during the electrochemical separation process the FP builds up in the solvent; this fact can modify the characteristics of the electrolyte and contaminate the final cathodic product. When the FP concentration exceeds about 10 wt% in the melt it must generally be purified or regenerated to avoid affecting the actinide/FP separation efficiency [7]. For this reason, a good knowledge of the basic properties of An [8-19] and REE [20-37] in the proposed separation media is very important.

Also, rare earth elements and its alloys are of importance, particularly in the fields of magnetism, energy and high technology [38-40]. The use of molten salts, as a reaction media, provides a unique opportunity for the electrowinning and electrorefining of high purity rare earth metals, as well as for the electrochemical synthesis of their alloys.

There is little information about the electrochemical behaviour of thulium compounds in molten salt media. The electrochemical investigations of $TmCl_3$ solutions in fused 3LiCl-2KCl eutectic on inert and active electrodes were carried out using transient technique [35]. The information about the base thermodynamic properties of the reaction $TmCl_{2(l)} + ½\ Cl_{2(g)} \Leftrightarrow TmCl_{3(l)}$ was presented in molten CsCl [36] and in NaCl-KCl-CsCl eutectic [37] by *emf* method.

The goal of these investigations is to determine the electrochemical and thermodynamic properties of thulium compounds in equimolar NaCl-KCl and fused

NaCl-2CsCl eutectic in large temperature regions by transient electrochemical technique and *emf* method.

Experimental

The solvents NaCl (>99.8%), KCl (>99.5%), and CsCl (>99.9%) were purified under vacuum in the temperature range 293 to 773 K. Then the reagents were fused in the atmosphere of dry argon. Afterwards the solvents were purified by the operation of direct crystallisation [41]. The technique of the operation of direct crystallisation is as follows: Solvents (NaCl, KCl or CsCl) are located in the molybdenum boat (horizontal type of crucible) and then placed into the horizontal quartz tube. The horizontal furnace with a narrow zone of heating (above melting point of the salt) slowly moves along the tube. This operation was repeated for several times. All these experiments were performed in inert gas flow atmosphere. The prepared reagents from the central part of the crucible were saved in glass capsules in inert atmosphere.

Dry thulium trichloride was synthesised by the well-known method [42]:

- First, the crystalline hydrate ($TmCl_3 \cdot nH_2O$, where n is 4.5 to 5.0) was prepared by direct interaction of Tm_2O_3 with HCl acid solution.
- Second, dry $TmCl_3$ was prepared by using the operation of carbochlorination of crystalline hydrate during heating in CCl_4 stream vapour in horizontal furnace.

Thulium (III) solutions were prepared by direct addition of anhydrous $TmCl_3$ to the electrolytic bath consisted of equimolar NaCl-KCl or NaCl-2CsCl eutectic.

The electrochemical measurements were carried out using an Autolab PGSTAT30 potentiostat–galvanostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9). Different transient electrochemical techniques were used such as linear sweep, cyclic and square wave voltammetry, as well as potentiometry at zero current. The experiments were carried out under inert argon atmosphere using an electrochemical quartz sealed cell with a three electrodes setup. The inert working electrode was prepared using a 1 mm metallic Mo wire (Goodfellow, 99.9%). It was immersed into the molten bath between 3 – 7 mm. The active surface area was determined after each experiment by measuring the immersion depth of the electrode. The counter electrode consisted of a 3 mm vitreous carbon rod (SU – 2000) with a large surface. The Cl^-/Cl_2 electrode is the most important reference electrode because it can be used for direct thermodynamic calculations. Its standard construction is the following: The quartz tube with porous membrane at the bottom and the molten solvent in it (NaCl-KCl or NaCl-2CsCl in this case) has a graphite tube for the introduction of chlorine gas into the system. The chlorine gas bubbles through the melt during the experiment [43].

The potentiometric study was carried out with an Autolab PGSTAT30 potentiostat–galvanostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9) using potentiometry (zero current) and coulometry methods. The electrochemical set-up for potentiometric investigations was described in detail in [37]. The inert working electrode was prepared using a molybdenum plate (S = 1.0 to 1.5 sm^2) which was located in the BeO crucible with the investigated melt. During these experiments, Tm^{3+} ions were electrochemically reduced to Tm^{2+} ions up to ratio Tm^{3+}/Tm^{2+} equals one using the galvanostatic method. The ratio of Tm^{3+}/Tm^{2+} in the experiments was controlled by the coulometric method and by chemical analyses of solid samples after experiments. The Cl^-/Cl_2 electrode was used as reference electrode.

The thulium total concentration was determined by taking samples from the melt which were dissolved in nitric acid solutions and then analysed by ICP-MS. The

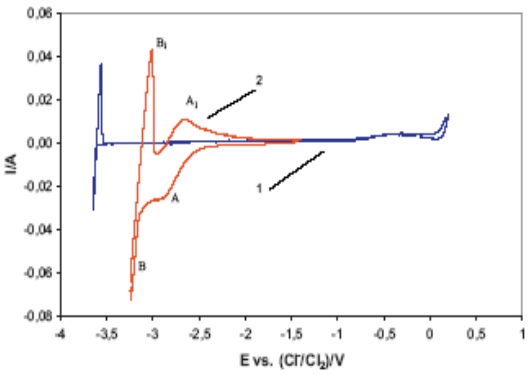
concentration of Tm^{2+} ions in the investigated melts were determined by the volumetric method of analysis.

Results and discussion

Transient electrochemical methods

Cyclic voltammetry was carried out on inert molybdenum electrode in fused NaCl-2CsCl eutectic in the temperature range 823–973 K. Figure 1 shows the electrochemical window obtained at 823 K (1). The cathodic and anodic limits of the electrochemical window correspond to the reduction of the solvent alkali metal ions (Na^+/Na^0 and Cs^+/Cs^0) and to the oxidation of chloride ions into the chlorine gas ($2Cl^-/Cl_2$), respectively. Figure 1 (2) plots the cyclic voltammogram of a NaCl-CsCl-$TmCl_3$ solution on Mo at 823 K. It shows two new cathodic peaks at potentials of –3.068 V (A) and –3.238 V (B) and their corresponding anodic peaks at –3.006 V (B_1) and –2.674 V (A_1) vs. the Cl^-/Cl_2.

Figure 1: Cyclic voltammograms of fused NaCl-2CsCl eutectic (1) and NaCl-2CsCl-$TmCl_3$ solution (2) on molybdenum electrode (S = 0.27 cm^2) at 823 K. Scan rate 0.2 V s^{-1}, m($TmCl_3$) = 9.83·10^{-2} mol kg^{-1}



The reaction mechanism of the soluble-soluble Tm^{3+}/Tm^{2+} redox system was analysed by the voltammetric curves obtained at several scan rates. The analysis shows that the cathodic and anodic peak potential (E_p) is constant and independent from the potential sweep rate at low scan rates. At scan rates more then 0.1 V s^{-1} the cathodic E_p shifts to more negative side and the anodic E_p shifts to more positive side. On the other hand, the cathodic and anodic peak current (I_p) is directly proportional to the square root of the polarisation rate. From these results and according to the theory of the linear sweep voltammetry technique [44] it is concluded that the redox system Tm^{3+}/Tm^{2+} was found to be reversible at low scan rates, controlled by the rate of the mass transfer and was found to be irreversible at high scan ranges (υ > 0.1 V s^{-1}), controlled by the rate of charge transfer.

The square wave voltammetry technique was used to determine the number of electrons exchanged in the reduction of Tm^{3+} ions in the molten NaCl–2CsCl–$TmCl_3$ solution (Figure 2). The number of electrons exchanged is determined by measuring the width at half height of the reduction peak, $W_{1/2}$(V), registered at different frequencies (6-80 Hz), using the following equation [45]:

$$W_{1/2} = 3.52\frac{RT}{nF} \tag{1}$$

where R is the ideal gas constant (J K^{-1} mol^{-1}), T is the absolute temperature (K), n is the number of exchanged electrons and F is the Faraday constant (96,500 C mol^{-1}). At low

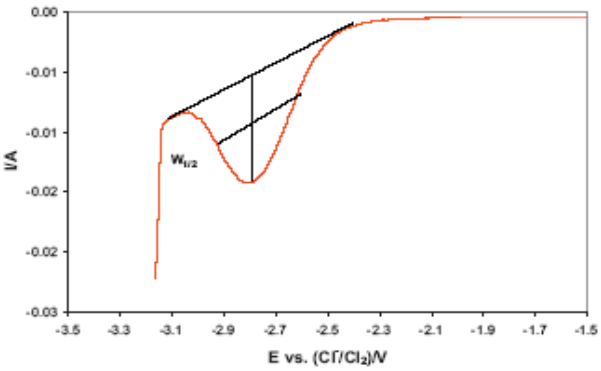
frequencies (8–20 Hz), a linear relationship between the cathodic peak current and the square root of the frequency was found. The experiments at the frequencies more than 22 Hz show nonlinear dependence between the cathodic peak current and the square root of the frequency. In the region (8–20 Hz) Eq. (1) may be applied. The number of electrons exchanged determined this way was close to one (1.01 ± 0.03 in NaCl-2CsCl and 0.98 ± 0.03 in NaCl-KCl).

The number of electrons exchanged of the reduction of Tm^{3+} ions for reversible system (<0.1 V s^{-1}) was also calculated from cyclic voltammograms for the redox couple Tm(III)/Tm(II) by expression:

$$E_p - E_{p/2} = -2.2\frac{RT}{nF} \tag{2}$$

The number of electrons exchanged determined by this way was 1.03 ± 0.04. The number of electrons exchanged determined this way was close to one (1.03 ± 0.04 in NaCl-2CsCl and 0.97 ± 0.04 in NaCl-KCl).

Figure 2: Square wave voltammogram of NaCl-2CsCl–$TmCl_3$ at frequency 12 Hz at 823 K. m($TmCl_3$) = 2.15·10^{-1} mol kg^{-1}. Working electrode: Mo (S = 0.25 cm^2)



From the transient electrochemical techniques applied it can be concluded that the potential of the system Tm^{2+}/Tm can be observed in molten salt because its potential is more positive than the potential of the solvent (Me^+/Me), with Me: Na, Cs, (see Figure 1).

The diffusion coefficient of $[TmCl_6]^{3-}$ ions in molten chloride media was determined using the cyclic voltammetry technique and applying the Randles–Sevčik Equation, valid for reversible soluble-soluble system (υ < 0.1 V s^{-1}) [45]:

$$I_p = 0.446(nF)^{3/2} C_o S\left(\frac{D\upsilon}{RT}\right)^{1/2} \tag{3}$$

where I_p is the peak current (A), S is the electrode surface area (cm^2), C_0 is the solute concentration (mol cm^{-3}), D is the diffusion coefficient (cm^2 s^{-1}), F is the Faraday constant (96,500 C mol^{-1}), R is the ideal gas constant (J K^{-1} mol^{-1}), n is the number of exchanged electrons, υ is the potential sweep rate (V s^{-1}) and T is the absolute temperature (K).

The estimated expression for the diffusion coefficients versus reverse temperature in fused NaCl-2CsCl eutectic obeys Arrhenius's law by the following equation:

$$\lg D = -2.44 - \frac{2301}{T} \pm 0.02 \tag{4}$$

The diffusion activation energy (EA) of Tm^{3+} ions was calculated from equation:

$$-\frac{E_A}{2.303R} = \frac{\partial \log D}{\partial (1/T)} \tag{5}$$

where EA is the activation energy for the diffusion process (kJ mol^{-1}). The value of the activation energy of diffusion process for thulium (III) ions equalled 44.0 kJ $mol^{-1.}$

The apparent standard potential of the $Tm^{3+/}Tm^{2+}$ couple was determined from the cyclic voltammograms registered in $TmCl_3$ solutions at several temperatures by the following expressions:

$$E^*_{Tm(III)/Tm(II)} = E_p^C + 1.11\frac{RT}{F} \tag{6}$$

$$E^*_{Tm(III)/Tm(II)} = E_p^A - 1.11\frac{RT}{F} \tag{7}$$

$$E^*_{Tm(III)/Tm(II)} = \frac{E_p^C + E_p^A}{2} \tag{8}$$

From the peak potential values measured in the cyclic voltammograms, the following empirical equation for the apparent standard potential of the Tm^{3+}/Tm^{2+} system versus the Cl^-/Cl_2 reference electrode in NaCl-2CsCl was obtained:

$$E^*_{Tm(III)/Tm(II)} = -3.745 + 1.06 \times 10^{-3} T \pm 0.003 \quad V \tag{9}$$

Potentiometric measurements

Variation of the equilibrium potential of the couple Tm^{3+}/Tm^{2+} as a function of the natural logarithm ratio of concentrations $[Tm^{3+}]$ and $[Tm^{2+}]$ in fused solvent solutions (NaCl-KCl; NaCl-2CsCl) obtained by *emf* method on molybdenum indicated that the electrode obeys the Nernst's law, taking into account the value of thermo-*emf* between molybdenum and carbon electrodes (exp. 10) [43] by the following equations (4) and (5):

$$E_T^{Mo-C} = -0.0076 + 1.74 \cdot 10^{-5} T \pm 0.0008 \quad V \tag{10}$$

$$E_{Tm(III)/Tm(II)} = -(2.529 \pm 0.010) + (0.083 \pm 0.009) \times \ln([Tm^{3+}]/[Tm^{2+}] \pm 0.013 \quad V \text{ (NaCl-KCl, 973K)} \tag{11}$$

$$E_{Tm(III)/Tm(II)} = -(2.920 \pm 0.002) + (0.072 \pm 0.002) \times \ln([Tm^{3+}]/[Tm^{2+}] \pm 0.003 \quad V$$

(NaCl-2CsCl, 833 K) (12)

The number of exchanged electrons (n) taking part in the process of the electrochemical reduction was determined from the slopes of the straight lines. From Equations (11) and (12) the number of exchanged electrons for the reaction (13):

$$Tm^{3+} + e = Tm^{2+} \tag{13}$$

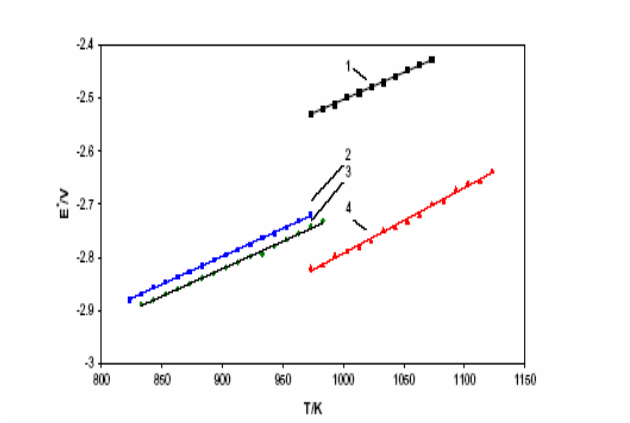
were for the system (NaCl-KCl-$TmCl_3$) is 1.01 ± 0.03 and for the system (NaCl-2CsCl-$TmCl_3$) is 0.99 ± 0.01.

The temperature dependences of apparent standard redox potentials of Tm^{3+}/Tm^{2+} couple in fused solvents were linear in the whole temperature range studied in Figure 3 (lines 1 and 3). The experiment data were fitted to the following equations:

$$E^{*}_{Tm(III)/Tm(II)} = -(3.523 \pm 0.015) + (102.0 \pm 1.4) \times 10^{-5} T \pm 0.001 \quad V \qquad \text{(NaCl-KCl)} \qquad (14)$$

$$E_{Tm(III)/Tm(II)} = -(3.763 \pm 0.013) + (106.0 \pm 1.4) \times 10^{-5} T \pm 0.003 \quad V \qquad \text{(NaCl-2CsCl)} \qquad (15)$$

Figure 3: Apparent standard redox potentials of the couple Tm^{3+}/Tm^{2+} in fused NaCl-KCl (1), Na-KCl-CsCl (2), NaCl-2CsCl (3), CsCl (4) as a function of the temperature



Using the values of the apparent standard redox potentials, the formal free Gibbs energy changes and the apparent equilibrium constants of the redox reaction (16):

$$TmCl_{2(1)} + ½\ Cl_{2(g)} \leftrightarrow TmCl_{3(1)} \qquad (16)$$

can be calculated using the well-known expressions:

$$\Delta G^{*} = nFE^{*}_{Tm(III)/Tm(II)} \qquad (17)$$

$$\Delta G^{*} = -RT \ln K^{*}_{eq.} \qquad (18)$$

The temperature dependence of the Gibbs free energy change can be described by the following equation:

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*} \qquad (19)$$

The experimental data were fitted to the following equations:

$$\Delta G^{*} = -(340.0 \pm 1.4) + (98.5 \pm 1.4) \cdot 10^{-3} T \pm 0.1 \quad kJmol^{-1} \qquad \text{(NaCl-KCl)} \qquad (20)$$

$$\Delta G^{*} = -(364.2 \pm 2.2) + (103.2 \pm 2.4) \cdot 10^{-3} T \pm 0.3 \quad kJmol^{-1} \qquad \text{(NaCl-2CsCl)} \qquad (21)$$

By the expression (18) one can calculate the apparent equilibrium constants for the redox reaction (16) in fused NaCl–KCl and NaCl–2CsCl salts. The temperature dependences are the following:

$$\ln K^{*}_{eq.} = -11.85 + \frac{40910}{T} \pm 0.01 \qquad \text{(NaCl-KCl)} \qquad (22)$$

$$\ln K^{*}_{eq.} = -12.38 + \frac{43799}{T} \pm 0.01 \qquad \text{(NaCl-2CsCl)} \qquad (23)$$

It is also possible to estimate the equilibrium chlorine gas pressure above an alkali metal chloride melt containing thulium tri and dichlorides for the reaction (24),

$$TmCl_{3(l)} \leftrightarrow TmCl_{2(l)} + \tfrac{1}{2}\, Cl_{2(g)} \tag{24}$$

by the well-known Equation (25) [43]. Such calculations were performed for the concentration ratio of $[Tm^{3+}]/Tm^{2+}]$ equals one in NaCl-KCl and NaCl-2CsCl melts.

$$\frac{RT}{2F}\ln(P_{Cl_2}) = E^{*}_{Tm^{3+}/Tm^{2+}} + \frac{RT}{F}\ln\left(\frac{[Tm^{3+}]}{[Tm^{2+}]}\right) \tag{25}$$

The calculated values are summarised in Tables 1 and 2. It is obvious that with the increase in the temperature the apparent standard redox potentials and the formal free Gibbs energy change are shifted to more positive side, and the equilibrium constant of the reaction (9) is decreased. The value of an initial chlorine gas pressure above the thulium solution melts also increases with the temperature. It depends on the decrease in the stability of chloride complexes with the increase in the temperature [43].

Table 1: Data of apparent standard redox potentials, formal free Gibbs energy change, and equilibrium gas pressure of chlorine above the melt for thulium compounds in fused equimolar NaCl-KCl at different temperatures

Thermodynamic properties	973 K	993 K	1 023 K	1 043 K	1 073 K
E^{*}/V	- 2.529	- 2.512	- 2.479	- 2.459	- 2.428
ΔG^{*}/(kJ·mol^{-1})	- 244.1	- 242.4	- 239.2	- 237.3	- 234.3
ΔH^{*}/(kJ·mol^{-1})	- 340.0				
ΔS^{*}/(J·K^{-1}·mol^{-1})	98.5				
$K^{*}_{eq.}$	$7.76\cdot10^{14}$	$1.75\cdot10^{13}$	$6.03\cdot10^{13}$	$1.29\cdot10^{12}$	$3.88\cdot10^{12}$
P_{Cl_2}/P_0	$6.11\cdot10^{-27}$	$3.07\cdot10^{-26}$	$3.63\cdot10^{-25}$	$1.67\cdot10^{-24}$	$1.51\cdot10^{-23}$

Apparent standard redox potentials are given in the molar fraction scale.

Table 2: Data of apparent standard redox potentials, formal free Gibbs energy change, and equilibrium gas pressure of chlorine above the melt for thulium compounds in fused NaCl-2CsCl eutectic at different temperatures

Thermodynamic properties	833 K	873 K	923 K	973 K
E^*/V	- 2.882	- 2.842	- 2.790	- 2.733
$\Delta G^*/(kJ\cdot mol^{-1})$	- 278.1	- 274.2	- 269.2	- 263.6
$\Delta H^*/(kJ\cdot mol^{-1})$	- 364.2			
$\Delta S^*/(J\cdot K^{-1}\cdot mol^{-1})$	103.2			
$K^*_{eq.}$	$2.79\cdot10^{17}$	$2.61\cdot10^{16}$	$1.75\cdot10^{15}$	$1.44\cdot10^{14}$
P_{Cl_2}/P_0	$1.28\cdot10^{-36}$	$1.47\cdot10^{-33}$	$2.34\cdot10^{-31}$	$3.50\cdot10^{-29}$

Note: Apparent standard redox potentials are given in the molar fraction scale.

Figure 3 shows the temperature dependences of apparent standard redox potentials of Tm^{3+}/Tm^{2+} couple in fused different solvents in a large temperature range. They are linear and depend on the nature of solvent. The results are compared with the literature for thulium solutions in individual caesium chloride [36], and in fused NaCl-KCl-CsCl eutectic [37], as shown in Figure 3. It was determined that the values of apparent standard redox potentials of Tm^{3+}/Tm^{2+} couple shift to a more negative field in the line from LiCl to CsCl. The average value of the radius of molten mixtures $\left(r_{R^+}\right)$ was calculated using the following equation [46]:

$$r_{R^+} = \sum_{i=1}^{N} c_i r_i \qquad (26)$$

where c_i is the mole fraction of i cations; r_i is the radius of i cations in molten mixture, consisting of N different alkali chlorides, nm.

The average value of the radius of these molten mixtures in this line, *pro tanto*, is 0.1155 nm for equimolar (NaCl-KCl); 0.137 nm for eutectic (NaCl-KCl-CsCl); 0.143 nm for eutectic (NaCl-2CsCl); 0.165 nm for individual (CsCl). Normally, lanthanide chlorides dissolved in alkali chloride melts are solvated by the chloride ions forming different complex ions like $[LnCl_6]^{3-}$ and $[LnCl_4]^{2-}$ [47-49]. Their relative stability rises with the increase in the solvent cation radius, and the apparent standard redox potential shifts to a more negative values. These results are in a good agreement with the ones reported by Smirnov [43]. The variation of the apparent standard potential of the redox couple Tm^{3+}/Tm^{2+} as a function of the ionic potential (z/r) was calculated at 973 K. The relation obtained is:

$$E^*_{Tm^{3+}/Tm^{2+}} = -(3.525 \pm 0.093) + \frac{(0.113 \pm 0.013)}{r} \pm 0.024/V \cdot \qquad (27)$$

Table 3: The comparison of the base thermodynamic properties of Tm compounds in molten alkali metal chlorides at 973 K

Thermodynamic properties	NaCl-KCl [this work]	NaCl-KCl-CsCl [12]	NaCl-2CsCl [this work]	CsCl [11]
E^*/V	-2.529	-2.721	-2.733	-2.822
ΔG^*/(kJ·mol^{-1})	-244.1	-262.6	-263.6	-272.3
ΔH^*/(kJ·mol^{-1})	-340.0	-354.1	-364.2	-388.8
ΔS^*/(J·K^{-1}·mol^{-1})	98.5	94.5	103.2	119.7
$K^*_{eq.}$	$7.76 \cdot 10^{14}$	$1.31 \cdot 10^{14}$	$1.44 \cdot 10^{14}$	$4.40 \cdot 10^{14}$
P_{Cl_2} / P_0	$6.11 \cdot 10^{-27}$	$5.86 \cdot 10^{-29}$	$3.50 \cdot 10^{-29}$	$5.61 \cdot 10^{-30}$

Apparent standard redox potentials are given in the molar fraction scale.

From the data given in Table 3, it can be concluded that the relative stability of thulium (III) complexes ions is naturally increased in the line $(NaCl\text{-}KCl)_{eq.}$ – $(NaCl\text{-}KCl\text{-}CsCl)_{eut.}$ – $(NaCl\text{-}2CsCl)_{eut.}$ – CsCl concerning the influence of the second co-ordination sphere on the stability of $[TmCl_6]^{3-}$ ions.

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