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## Electrochemistry of Tm(III) and Yb(III) in Molten Salts

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### 1. Introduction

Pyrochemical processes appeared today gives an interesting option for future nuclear fuel cycles in several aspects. These latter will have to provide high recovery yields for actinides elements, (taking into account the sustainability requirement) to be safe, resistant versus proliferation risks, and cost-effective. This lead to a rather prolific research today, with many innovative concepts for future reactors, future fuels, and obviously future processes. Pyrochemical processes seems in this context 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) [Uozumi, 2004; Willit, 2005].

Partitioning and transmutation (P&T) concept is nowadays considered as one of the strategies to reduce the long-term radiotoxicity of the nuclear wastes [Kinoshita et al., 2000]. 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.

The aim of the separation techniques which are currently being investigated, both hydrometallurgical and pyrometallurgical ones, is to optimize the recovery efficiency of minor actinides minimizing at the same time the fission products (FP) content in the final product. Special attention is devoted to rare earth elements (REE) mainly due to its neutronic poison effect and the high content into the spend fuel. In addition, REE have similar chemical properties [Bermejo et al., 2006, 2007, 2008a, 2008b; Castrillejo et al., 2005a, 2005b, 2005c, 2009; De Cordoba et al., 2004, 2008; Kuznetsov et al., 2006; Novoselova &

Smolenski, 2010; Smolenski et al., 2008a, 2008b, 2009] to those of actinides [Fusselman et al., 1999; Morss, 2008; Osipenko et al., 2010, 2011; Roy et al., 1996; Sakamura et al., 1998; Serp et al., 2004, 2005a, 2005b, 2006; Serrano & Taxil, 1999; Shirai et al., 2000] hence separation between these groups of elements is very difficult. For this reason, a good knowledge of the basic properties of REE in the proposed separation media is very important.

The goal of these investigations is to determine the electrochemical and thermodynamic properties of some fission products (Tm and Yb), their mass transfer, and behavior in different fused solvents using transient electrochemical techniques, and potentiometric method (*emf*).

## 2. Experimental

### 2.1 Preparation of starting materials

The solvents LiCl (Aldrich, 99.9%), NaCl (Aldrich, 99.9%), KCl (Aldrich, 99.9%), and CsCl (Aldrich, 99.9%) were purified under vacuum in the temperatures range 293-773 K. Then the reagents were fused under dry argon atmosphere. Afterwards these reagents were purified by the operation of the direct crystallization [Shishkin & Mityaev, 1982]. The calculated amounts of prepared solvents were melted in the cell before any experiment [Korshunov et al., 1979].

Dry lanthanide trichlorides ( $\text{LnCl}_3$ ) were obtained by the way of well-known method [Revzin, 1967] in two steps:

- First, the crystalline hydrate ( $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ , where  $n$  is 4.5-5.0) was prepared by direct interaction of  $\text{Ln}_2\text{O}_3$  ( $\text{Tm}_2\text{O}_3$  OST 46-205-81 TuO-1 and  $\text{Yb}_2\text{O}_3$  IbO-L TU 48-4-524-90) with HCl acid solution.
- Second, dry  $\text{LnCl}_3$  was prepared by using the operation of carbochlorination of crystalline hydrate during heating in  $\text{CCl}_4$  stream vapor in horizontal furnace.

The obtained lanthanide chlorides ( $\text{LnCl}_3$ ) were kept into glass ampoules under atmosphere of dry argon in inert glove box.  $\text{Ln}^{3+}$  ions were prepared by direct addition of anhydrous  $\text{LnCl}_3$  to the fused electrolytic bath.

### 2.2 Transient electrochemical technique

The experiments were carried out under inert argon atmosphere using a standard electrochemical quartz sealed cell using a three electrodes setup. Different transient electrochemical techniques were used such as linear sweep, cyclic, square wave and semi-integral voltammetry, as well as potentiometry at zero current. The electrochemical measurements were carried out using an Autolab PGSTAT30 potentiostat-galvanostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9).

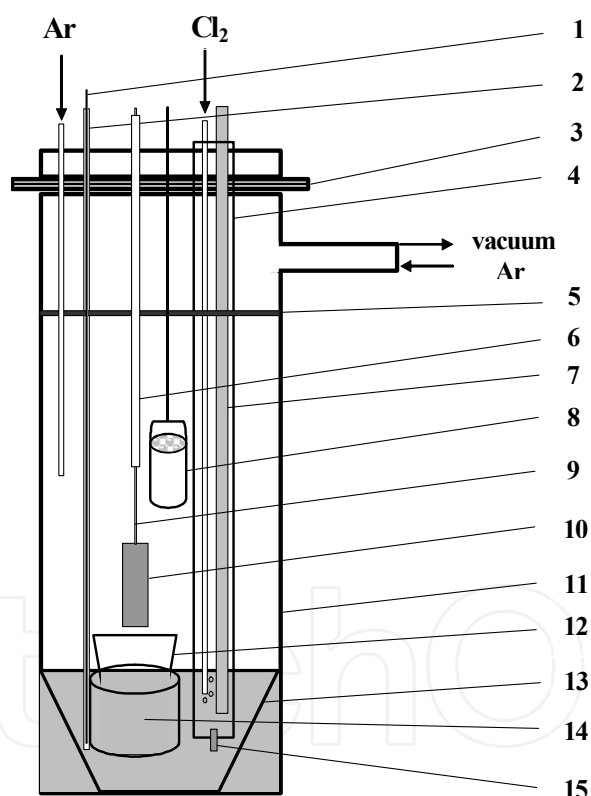
The inert working electrode was prepared using a 1mm metallic W wire (Goodfellow, 99.9%). It was immersed into the molten bath between 3 - 10 mm. The active surface area was determined after each experiment by measuring the immersion depth of the electrode. The counter electrode consisted of a 3 mm vitreous carbon rod (SU - 2000). The  $\text{Cl}^-/\text{Cl}_2$  electrode is the most convenient reference electrode because it can be used for the direct thermodynamic calculations. Its standard construction is the following. The quartz tube with porous membrane in the bottom and molten solvent in it has the graphite tube for chlorine gas introduction into the system. The chlorine gas is bubbling through the melt during the experiment [Smirnov, 1973].

The lanthanide concentrations were determined by taking samples from the melt which were dissolved in nitric acid solutions and then analyzed by ICP-MS.

### 2.3 Direct potentiometric method

The potentiometric study was carried out using an Autolab PGSTAT30 potentiostat-galvanostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9). The electrochemical techniques were used such as potentiometry (zero current) and coulometry methods.

The electrochemical set-up for potentiometric investigations is shown in Fig. 1. The inert working electrode was prepared using a 5 mm vitreous carbon rod (SU - 2000) which was located in BeO crucible with the investigated melt. It was immersed into the molten bath between 3 - 5 mm. During the experiments  $\text{Ln}^{3+}$  ions were electrochemically reduced to  $\text{Ln}^{2+}$  ions up to ratio  $\text{Ln}^{3+}/\text{Ln}^{2+}$  equals one. The counter electrode consisted of a 3 mm vitreous carbon rod (SU - 2000) which was placed in quartz tube with porous membrane in the bottom with solvent melt and located in vitreous carbon crucible (SU - 2000) with pure solvent without lanthanide chlorides. The  $\text{Cl}^-/\text{Cl}_2$  electrode was used as reference electrode.



1 - Pt/Pt-Rh thermocouple; 2- Cover of thermocouple; 3- Section; 4- Capsule of chlorine electrode; 5- Nickel screen; 6- Alumina tube; 7-  $\text{Cl}^-/\text{Cl}_2$  reference electrode/counter electrode; 8- Getter of zirconium; 9- Current contact; 10- Vitreous carbon working electrode; 11- Quartz test-tube with cover; 12- Beryllium oxide crucible; 13- Vitreous carbon crucible; 14- Investigated salt system; 15- Asbestos diaphragm.

Fig. 1. Experimental set-up for potentiometric study

The total lanthanide concentrations were determined by taking samples from the melt which were dissolved in nitric acid solutions and then analysed by ICP-MS. The concentration of the reduced form of lanthanides was determined by volumetric method.

### 3. Results and discussion

#### 3.1 Transient electrochemical technique

##### 3.1.1 Voltammetric studies on inert electrodes

Cyclic voltammetry was carried out on inert tungsten electrodes for all melts tested: eutectic LiCl-KCl, equimolar NaCl-KCl, eutectic NaCl-KCl-CsCl and individual CsCl, at several temperatures (723-1073 K). Fig. 2 (red solid line) shows the electrochemical window obtained in LiCl-KCl at 723 K. The cathodic and anodic limits of the electrochemical window correspond to the reduction of the solvent alkali metal ions and to the oxidation of chloride ions into chlorine gas, respectively.

Fig. 2 also plots the cyclic voltammogram of a LiCl-KCl-YbCl<sub>3</sub> solution on W at 723K (blue solid line). It shows a single cathodic peak at a potential of -1.762V vs. Cl<sup>-</sup>/Cl<sub>2</sub> and its corresponding anodic peak at -1.566V vs. the Cl<sup>-</sup>/Cl<sub>2</sub>. Similar behaviour for the reduction of Yb(III) ions has been observed in the fused equimolar NaCl-KCl mixture (Fig. 3), NaCl-KCl-CsCl eutectic (Fig. 4) and CsCl (Fig. 5). These figures show the linear sweep and the cyclic voltammograms obtained in the above systems with YbCl<sub>3</sub> at several scan rates, respectively.

The square wave voltammetry technique was used to determine the number of electrons exchanged in the reduction of Yb(III) ions in different molten compositions. Fig. 6 shows the bell-shaped symmetric cathodic wave obtained in the LiCl-KCl-YbCl<sub>3</sub> melt at 723 K. 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).  $W_{1/2}$  is given by the following equation, valid for reversible systems:

$$W_{1/2} = 3.52 \frac{RT}{nF} \quad (1)$$

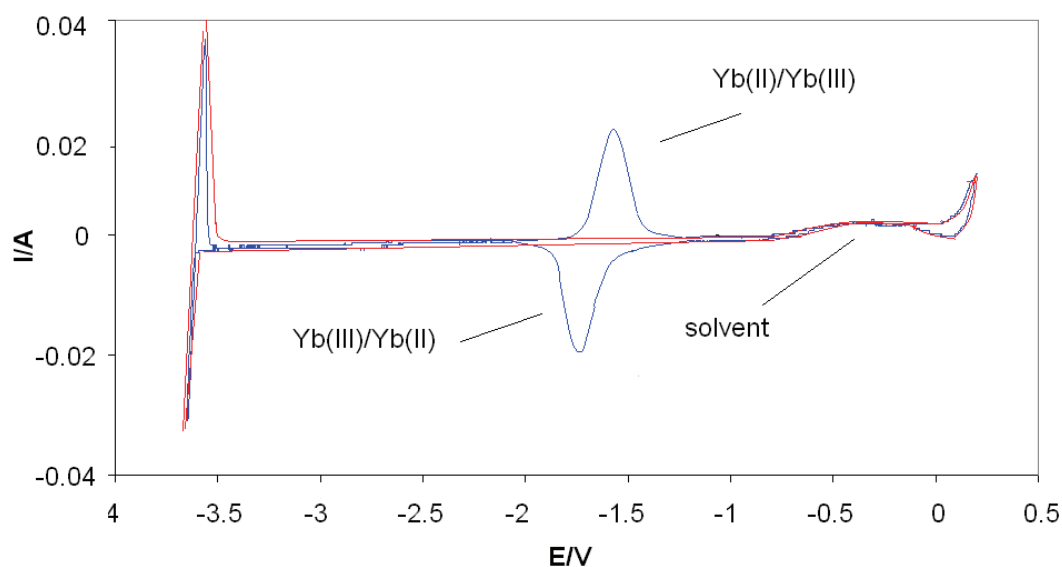


Fig. 2. Cyclic voltammograms of pure LiCl-KCl eutectic melt (red solid line). Cyclic voltammograms of LiCl-KCl-YbCl<sub>3</sub> (9.41·10<sup>-2</sup> mol/kg) melt (blue solid line) corresponding to the reduction reaction  $\text{Yb(III)} + e^- \rightleftharpoons \text{Yb(II)}$  at 723 K. Working electrode: W (surface area = 0.25 cm<sup>2</sup>). Scan rate = 0.1 V s<sup>-1</sup>

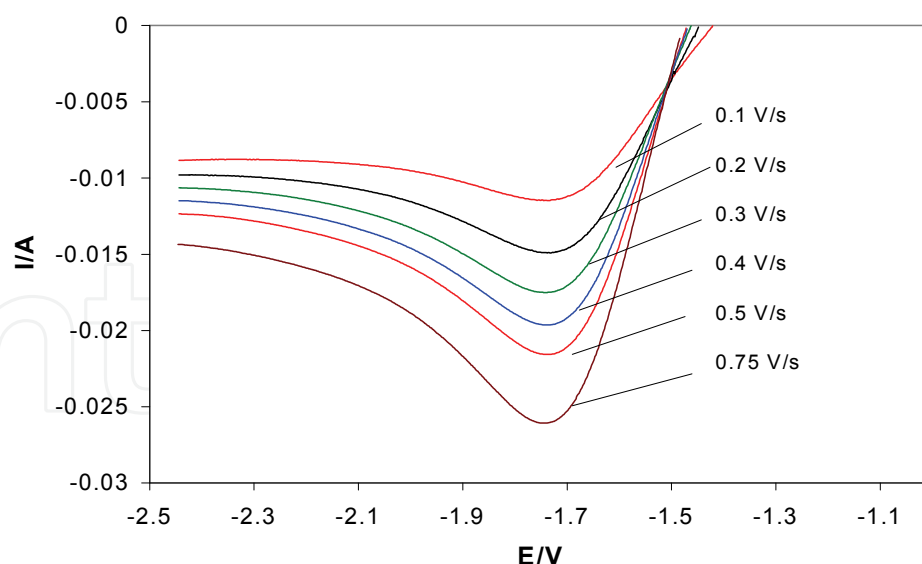


Fig. 3. Linear sweep voltammograms of fused NaCl-KCl-YbCl<sub>3</sub> ( $3.79 \cdot 10^{-2}$  mol/kg) for the reduction of Yb(III) to Yb(II) ions at different sweep potential rates at 973 K. Working electrode: W (surface area = 0.27 cm<sup>2</sup>)

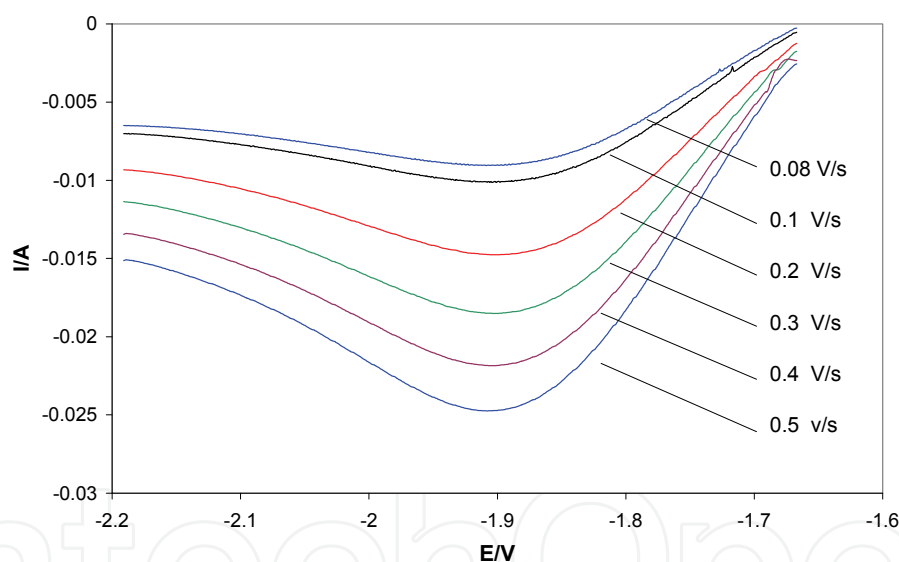


Fig. 4. Linear sweep voltammograms of fused NaCl-KCl-CsCl-YbCl<sub>3</sub> salt at different sweep rates at 873 K. [Yb(III)] =  $7.45 \cdot 10^{-2}$  mol kg<sup>-1</sup>. Working electrode: W (S = 0.36 cm<sup>2</sup>)

At low frequencies a linear relationship between the cathodic peak current and the square root of the frequency was found. Under these conditions the system can be considered as reversible and equation 1 can be applied [Bard & Faulkner, 1980]. The number of electrons exchanged was close to 1. The same results were obtained in NaCl-KCl, NaCl-KCl-CsCl and CsCl media.

Potentiostatic electrolysis at potentials of the cathodic peaks for all systems studied did not show the formation of the solid phase of tungsten surface after polarization. There is no plateau on the dependences potential – time. Also the working electrode did not undergo any visual change. X-ray analysis of the surface of the working electrodes after experiments also show an absence of formation of solid phase.

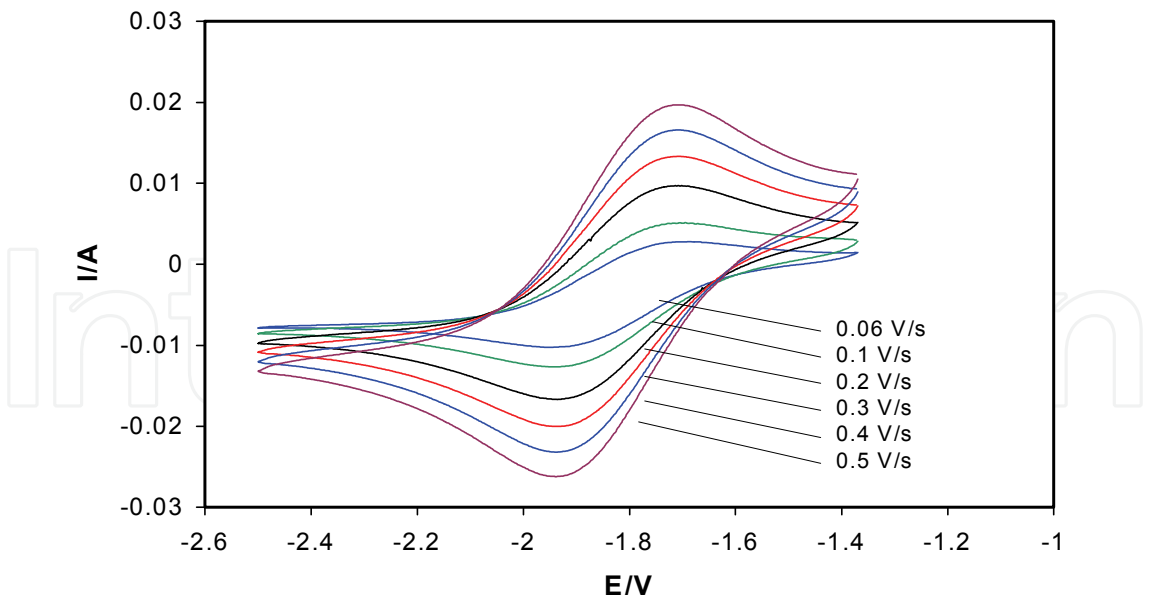


Fig. 5. Cyclic voltammograms of a CsCl-YbCl<sub>3</sub> (3.70·10<sup>-2</sup> mol/kg) solution for the reaction  $Yb(III) + e^- \rightleftharpoons Yb(II)$  at different potential sweep rates at 973 K. Working electrode: W (surface area = 0.31 cm<sup>2</sup>)

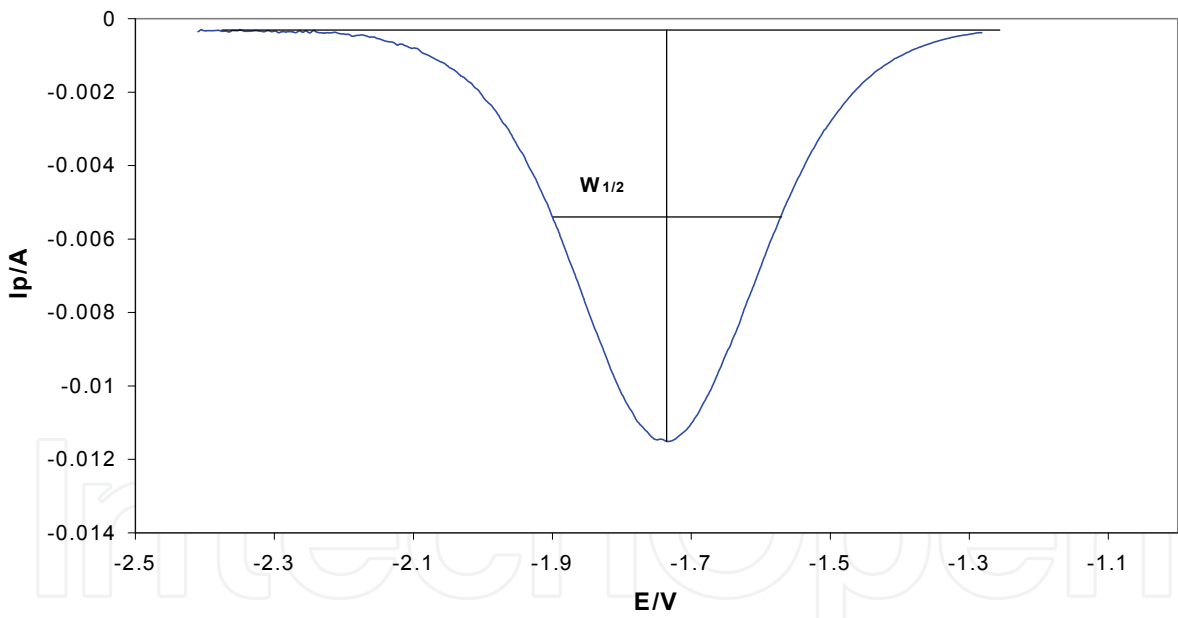
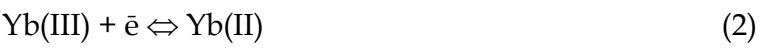


Fig. 6. Square wave voltammogram of LiCl-KCl-YbCl<sub>3</sub> (9.41·10<sup>-2</sup> mol/kg) at 12 Hz at 723 K. Working electrode: W (surface area = 0.25 cm<sup>2</sup>)

The results obtained allow concluding that the reduction of Yb(III) ions takes place in a single step with the exchange of one electron and the formation of a soluble product, according to the following reaction:



The reaction mechanism of the soluble-soluble Yb(III)/Yb(II) redox system was investigated by analyzing the voltammetric curves obtained at several scan rates. It shows that the



cathodic and anodic peak potential ( $E_p$ ) is constant and independent of the potential sweep rate (Fig. 7). On the other hand the cathodic and anodic peak current ( $I_p$ ) is directly proportional to the square root of the polarization rate ( $v$ ) (Fig. 8). A linear relationship between the cathodic peak current density and the concentration of  $\text{YbCl}_3$  ions in the melt was observed (Fig. 9). From these results and according to the theory of linear sweep voltammetry technique [Bard & Faulkner, 1980] it is concluded that the redox system  $\text{Yb(III)/Yb(II)}$  is a reversible and controlled by the rate of the mass transfer.

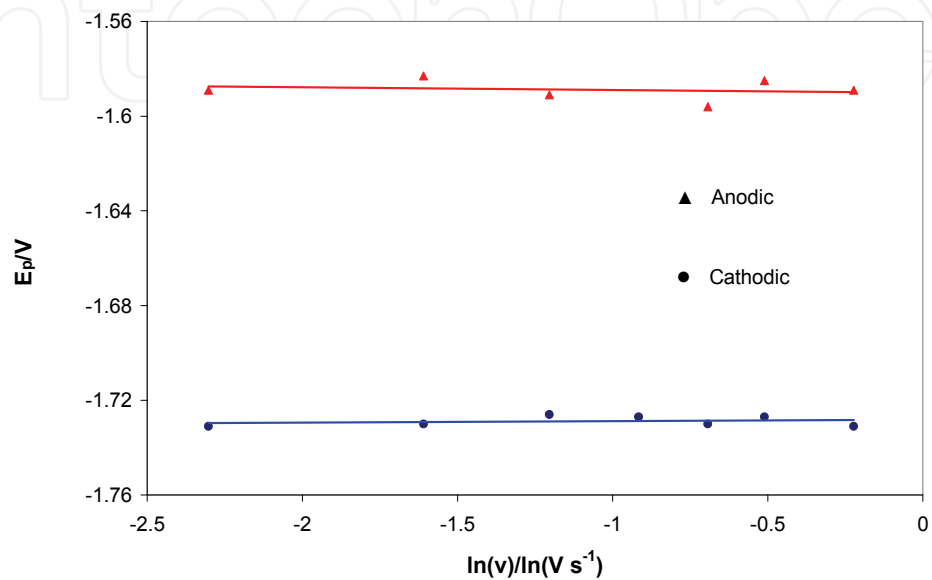


Fig. 7. Variation of the cathodic and anodic peak potential as a function of the sweep rate in fused  $\text{LiCl-KCl-YbCl}_3$  ( $9.41 \cdot 10^{-2} \text{ mol/kg}$ ) at 723K. Working electrode: W (surface area =  $0.25 \text{ cm}^2$ )

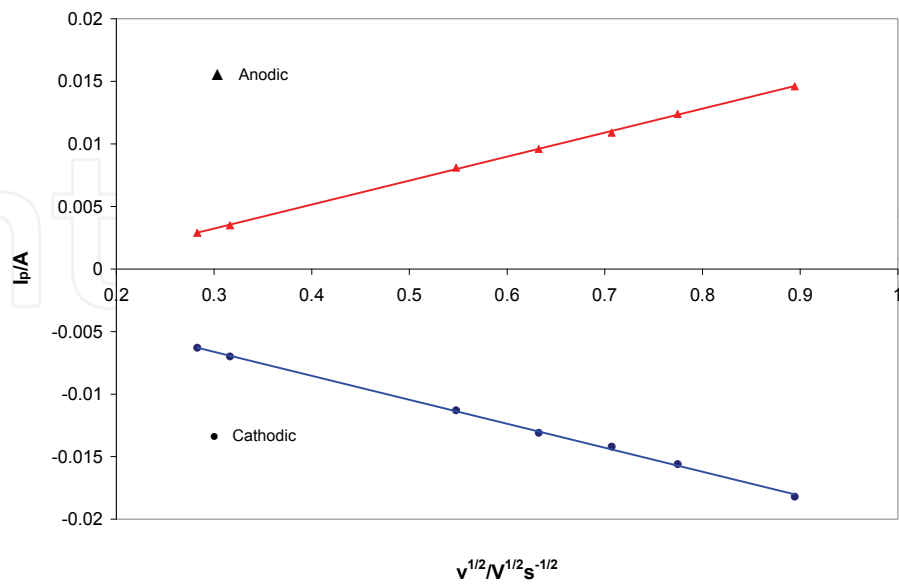


Fig. 8. Variation of the cathodic and anodic peak current as a function of the square root of the potential scan rate in fused  $\text{LiCl-KCl-YbCl}_3$  ( $9.41 \cdot 10^{-2} \text{ mol/kg}$ ) at 723K. Working electrode: W (surface area =  $0.25 \text{ cm}^2$ )



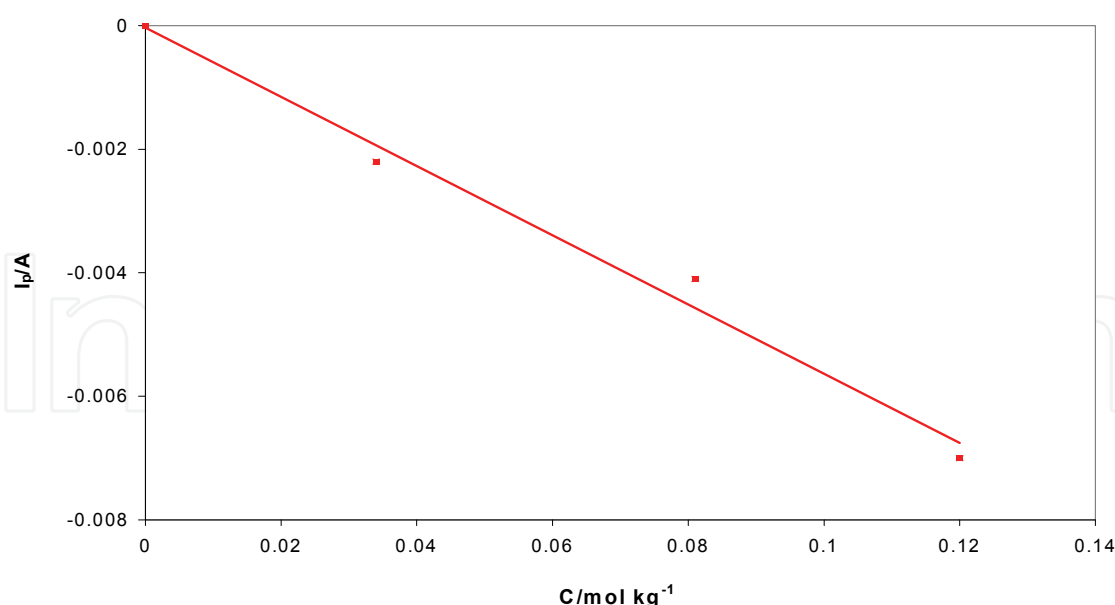


Fig. 9. Variation of the cathodic peak current as a function of the concentration of  $\text{YbCl}_3$  in  $\text{LiCl-KCl-YbCl}_3$  at 723 K. Working electrode: W ( $S = 0.25 \text{ cm}^2$ ). Scan rate =  $0.1 \text{ V s}^{-1}$

From the transient electrochemical techniques applied we concluded that the potential of the system  $[\text{Yb(II)}/\text{Yb(0)}]$  can not be observed in the molten alkali chlorides media because it is more negative than the potential of the solvent  $\text{Me(I)}/\text{Me(0)}$ , being Me: Li, Na, K and Cs, (Fig. 1).

### 3.1.2 Diffusion coefficient of Yb (III) ions

The diffusion coefficient of Yb(III) ions in molten chloride media was determined using the cyclic voltammetry technique and applying the Randles-Sevcik equation, valid for reversible soluble-soluble system [Bard & Faulkner, 1980]:

$$I_p = 0.446(nF)^{3/2} C_0 S \left( \frac{Dv}{RT} \right)^{1/2} \quad (3)$$

where  $S$  is the electrode surface area (in  $\text{cm}^2$ ),  $C_0$  is the solute concentration (in  $\text{mol cm}^{-3}$ ),  $D$  is the diffusion coefficient (in  $\text{cm}^2 \text{ s}^{-1}$ ),  $F$  is the Faraday constant (in  $96500 \text{ C mol}^{-1}$ ),  $R$  is the ideal gas constant (in  $\text{J K}^{-1} \text{ mol}^{-1}$ ),  $n$  is the number of exchanged electrons,  $v$  is the potential sweep rate (in  $\text{V s}^{-1}$ ) and  $T$  is the absolute temperature (in K).

The values obtained for the different molten chlorides tested at several temperatures are quoted in Table 1.

The diffusion coefficient values have been used to calculate the activation energy for the diffusion process. The influence of the temperature on the diffusion coefficient obeys the Arrhenius's law through the following equation:

$$D = D_0 \exp \left( -\frac{E_A}{RT} \right) \pm \Delta \quad (4)$$

where  $E_A$  is the activation energy for the diffusion process (in  $\text{kJ mol}^{-1}$ ),  $D_0$  is the pre-exponential term (in  $\text{cm}^2 \text{ s}^{-1}$ ) and  $\Delta$  is the experimental error.

From this expression, the value of the activation energy for the Yb(III) ions diffusion process was calculated in the different melts tested (Table 1).

The diffusion coefficient of ytterbium (III) ions becomes smaller with the increase of the radius of the cation of alkali metal in the line from Li to Cs (Table 1). Such behaviour takes place due to an increasing on the strength of complex ions and the decrease in contribution of D to the “hopping” mechanism. The increase of temperature leads to the increase of the diffusion coefficients in all the solvents.

| Solvent       | T/K  | D ·10 <sup>5</sup> /cm <sup>2</sup> s <sup>-1</sup> | -E <sub>A</sub> /kJ mol <sup>-1</sup> |
|---------------|------|---|---------------------------------------|
| LiCl-KCl      | 723  | 1.0 ± 0.1   | 38.3                                  |
|               | 848  | 2.7 ± 0.1   |                                       |
|               | 973  | 5.4 ± 0.1   |                                       |
| NaCl-KCl      | 973  | 2.8 ± 0.2   | 45.4                                  |
|               | 1023 | 3.2 ± 0.2   |                                       |
|               | 1073 | 4.1 ± 0.2   |                                       |
| NaCl-KCl-CsCl | 873  | 0.66± 0.1   | 51.3                                  |
|               | 973  | 1.38± 0.1   |                                       |
|               | 1073 | 2.45± 0.1   |                                       |
| CsCl          | 973  | 0.9 ± 0.1   | 54.4                                  |
|               | 1023 | 1.2 ± 0.1   |                                       |
|               | 1073 | 1.7 ± 0.1   |                                       |

Table 1. Diffusion coefficient of Yb(III) ions in molten alkali metal chlorides at several temperatures. Activation energy for the ytterbium ions diffusion process

The variation of the logarithm of the diffusion coefficient as a function of the reverse radius of the solvent cation (r) and reverse temperatures is given by the following expression:

$$\log D_{Yb(III)} = -2.38 - \frac{3596}{T} + \frac{\left(0.0071 + \frac{158}{T}\right)}{r} \pm 0.02$$

(5)

The average value of the radius of molten mixtures ( $r_{R^+}$ ) was calculated by using the following equation [Lebedev, 1993]:

$$r_{R^+} = \sum_{i=1}^N c_i r_i$$

(6)

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

3.1.3 Apparent standard potentials of the redox couple Yb(III)/Yb(II)

The apparent standard potential of the Yb(III)/Yb(II) system was determined from the cyclic voltammograms registered in YbCl<sub>3</sub> solutions in the different alkali metal chlorides tested at several temperatures.

According to the theory of linear sweep voltammetry the following expressions, including the anodic and cathodic peak potentials and the half-wave potential, can be applied in the case of a soluble-soluble reversible system [Bard & Faulkner, 1980]:

$$E_p^C = E_{1/2} - 1.11 \frac{RT}{F} \quad (6)$$

$$E_p^A = E_{1/2} + 1.11 \frac{RT}{F} \quad (7)$$

$$\frac{(E_p^C + E_p^A)}{2} = E_{1/2} \quad (8)$$

where the half-wave potential is given by:

$$E_{1/2} = E_{Yb(III)/Yb(II)}^0 + \frac{RT}{F} \ln \left( \frac{D_{Yb(II)}}{D_{Yb(III)}} \right)^{1/2} + \frac{RT}{F} \ln \left( \frac{\gamma_{Yb(III)}}{\gamma_{Yb(II)}} \right) \quad (9)$$

It is known that for concentrations of electroactive species lower than  $3$  to  $5 \cdot 10^{-2}$  in mole fraction scale, their activity coefficient is almost constant. In these conditions, it is more convenient using the apparent standard redox potential concept ( $E_{Yb(III)/Yb(II)}^*$ ) expressed as follows [Smirnov, 1973]:

$$E_{Yb(III)/Yb(II)}^* = E_{Yb(III)/Yb(II)}^0 + \frac{RT}{F} \ln \left( \frac{\gamma_{Yb(III)}}{\gamma_{Yb(II)}} \right) \quad (10)$$

The formal standard redox potentials of  $E_{Yb(III)/Yb(II)}^*$  were calculated from the following equations:

$$E_{Yb(III)/Yb(II)}^* = E_p^C + 1.11 \frac{RT}{F} + \frac{RT}{F} \ln \left( \frac{D_{ox}}{D_{red}} \right)^{1/2} \quad (11)$$

$$E_{Yb(III)/Yb(II)}^* = E_p^A - 1.11 \frac{RT}{F} + \frac{RT}{F} \ln \left( \frac{D_{ox}}{D_{red}} \right)^{1/2} \quad (12)$$

$$E_{Yb(III)/Yb(II)}^* = \frac{(E_p^C + E_p^A)}{2} + \frac{RT}{F} \ln \left( \frac{D_{ox}}{D_{red}} \right)^{1/2} \quad (13)$$

From the peak potential values measured in the cyclic voltammograms and the diffusion coefficients of Yb(III) and Yb(II) the following empirical equation for the apparent standard redox potentials versus the Cl<sup>-</sup>/Cl<sub>2</sub> reference electrode in different solvents were obtained.

$$E_{Yb(III)/Yb(II)}^* = -(1.915 \pm 0.005) + (3.5 \pm 0.2) \times 10^{-4} T, \quad V \quad [723-973 \text{ K}] \quad \text{LiCl-KCl} \quad (14)$$

$$E_{Yb(III)/Yb(II)}^* = -(2.031 \pm 0.005) + (3.7 \pm 0.2) \times 10^{-4} T, \quad V \quad [973-1075 \text{ K}] \quad \text{NaCl-KCl} \quad (15)$$

$$E_{Yb(III)/Yb(II)}^* = -(2.192 \pm 0.016) + (4.3 \pm 0.2) \times 10^{-4} T, \quad V \quad [723-1073 \text{ K}] \quad \text{NaCl-KCl-CsCl} \quad (16)$$

$$E_{Yb(III)/Yb(II)}^* = -(2.262 \pm 0.004) + (4.2 \pm 0.2) \times 10^{-4} T, \quad V \quad [973-1079 \text{ K}] \quad \text{CsCl} \quad (17)$$

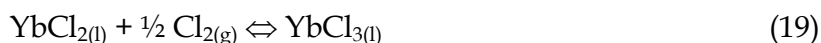
The variation of the apparent standard potential of the redox couple Yb(III)/Yb(II) as a function of the reverse radius of the solvent cation ( $r$ ) and the temperature was calculated. The relation obtained is:

$$E_{Yb(III)/Yb(II)}^* = -3.031 + 8 \cdot 10^{-4} T + \frac{(0.104 - 4 \cdot 10^{-5} T)}{r} \quad (18)$$

Normally, lanthanide chlorides dissolved in alkali chloride melts are solvated by the chloride ions forming different complex ions like  $[LnCl_6]^{3-}$  and  $[LnCl_4]^{2-}$  [Barbanel, 1985; Papatheodorou & Kleppa, 1974; Yamana et al., 2003]. In the case of ytterbium,  $[YbCl_6]^{3-}$  complex ions are present in the melts [Novoselova et al., 2004]. Their relative stability increases with the increase of the solvent cation radius, and the apparent standard redox potential shifts to more negative values. Our results are in a good agreement with the literature ones [Smirnov, 1973].

### 3.1.4 Thermodynamics properties

Using the values of the apparent standard redox potentials the formal free Gibbs energy changes of the redox reaction



was calculated according to following expression:

$$\Delta G^* = -nFE_{Yb(III)/Yb(II)}^* \quad (20)$$

Its temperature dependence allows calculating the enthalpy and entropy of the  $YbCl_3$  formation by means of the relation [Bard & Faulkner, 1980]:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (21)$$

The apparent standard Gibbs energy of formation of  $YbCl_3$  in the different solvents tested can be expressed as:

$$\Delta G_{YbCl_3}^* = -184.80 + 0.033 \cdot T \pm 2.46 \text{ kJ/mol} \quad [723-973 \text{ K}] \quad \text{LiCl-KCl} \quad (22)$$

$$\Delta G_{YbCl_3}^* = -195.96 + 0.036 \cdot T \pm 2.46 \text{ kJ/mol} \quad [973-1075 \text{ K}] \quad \text{NaCl-KCl} \quad (23)$$

$$\Delta G_{YbCl_3}^* = -211.52 + 0.041 \cdot T \pm 2.43 \text{ kJ/mol} \quad [723-1073 \text{ K}] \quad \text{NaCl-KCl-CsCl} \quad (24)$$

$$\Delta G_{YbCl_3}^* = -218.25 + 0.041 \cdot T \pm 2.46 \text{ kJ/mol} \quad [973-1079 \text{ K}] \quad \text{CsCl} \quad (25)$$

The changes of the thermodynamic parameters of the redox reaction (19) versus the radius of the solvent cation show the increasing in strength of the Yb-Cl bond in the complex ions  $[YbCl_6]^{3-}$  in the line from LiCl to CsCl.

### 3.1.5 Voltammetric studies on active electrodes

Linear sweep voltammograms for the reduction of Yb(III) solution at inert tungsten (1) and active aluminum (2) electrodes at 873 K are presented in Fig. 10. The voltammogram on

aluminum working electrode show the existence of two cathodic peaks at the potentials approximately  $-1.92\text{ V}$  and  $-2.92\text{ V}$  vs.  $\text{Cl}^-/\text{Cl}_2$  instead of one on tungsten electrode. Potentiostatic electrolysis at potential  $-1.92\text{ V}$  did not show the formation of solid phase on tungsten and aluminum surfaces after polarization. So we can suppose passing the reaction (2) at this potential on inert and active electrodes.

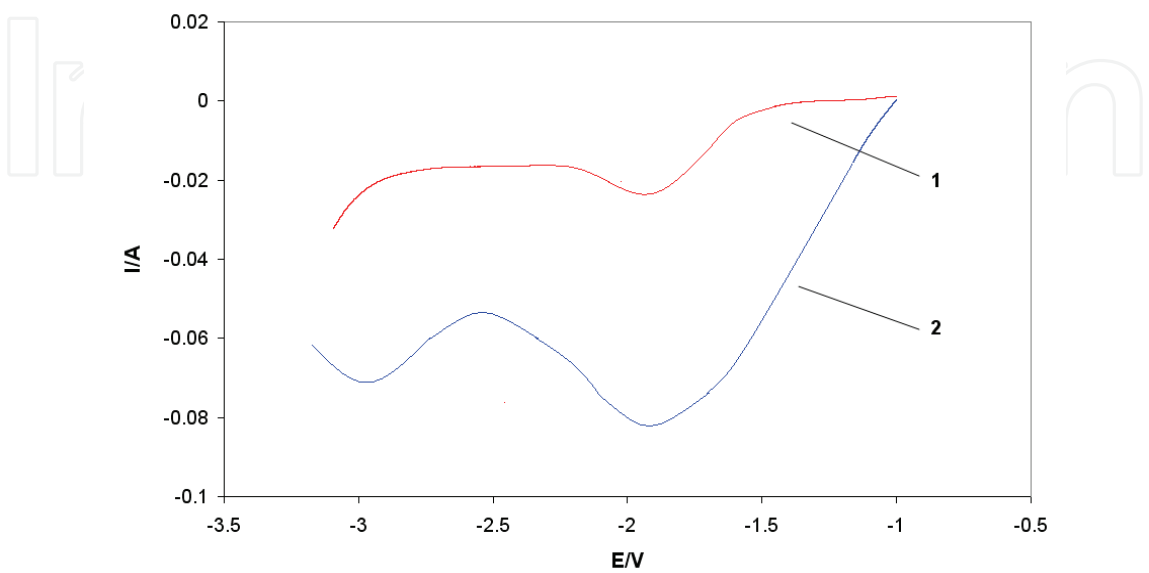


Fig.10. Linear sweep voltammograms of fused  $\text{NaCl-KCl-CsCl-YbCl}_3$  salt on inert W electrode (1) and active Al electrode (2) at  $873\text{ K}$ .  $[\text{Yb(III)}] = 8.26 \cdot 10^{-2}\text{ mol kg}^{-1}$ . Working electrode: W ( $S = 0.23\text{ cm}^2$ ); Al ( $S = 0.47\text{ cm}^2$ )

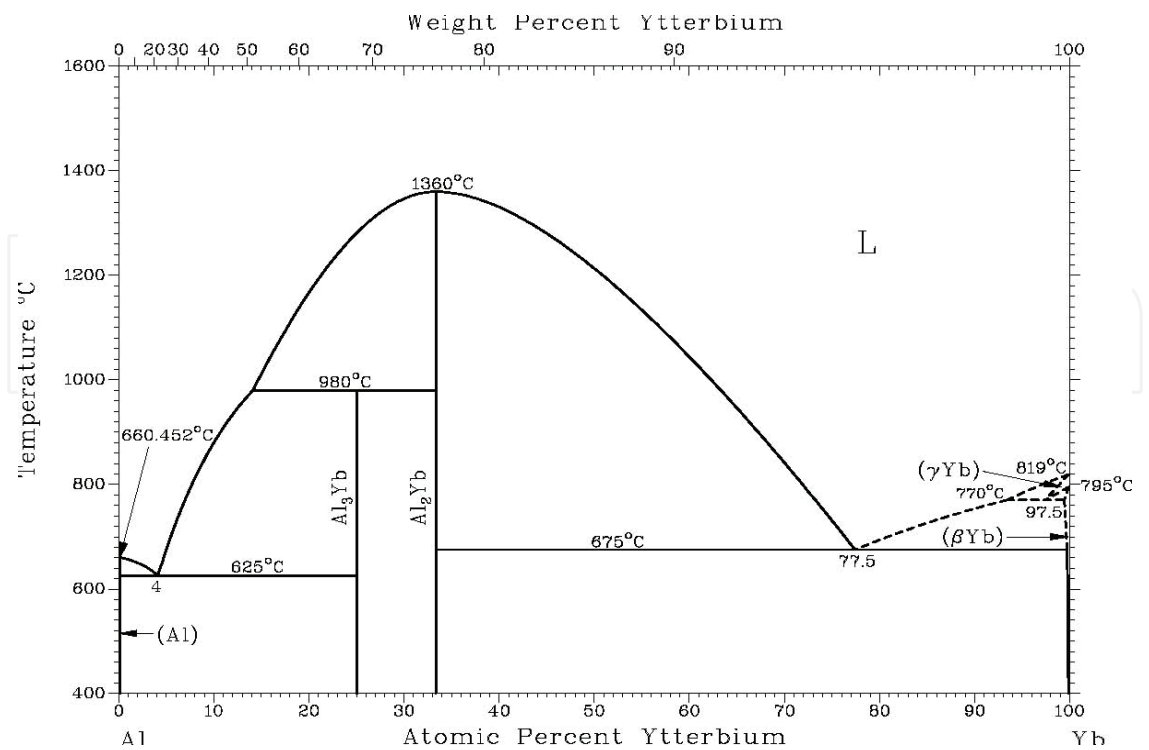


Fig. 11. Phase diagram of Yb-Al system

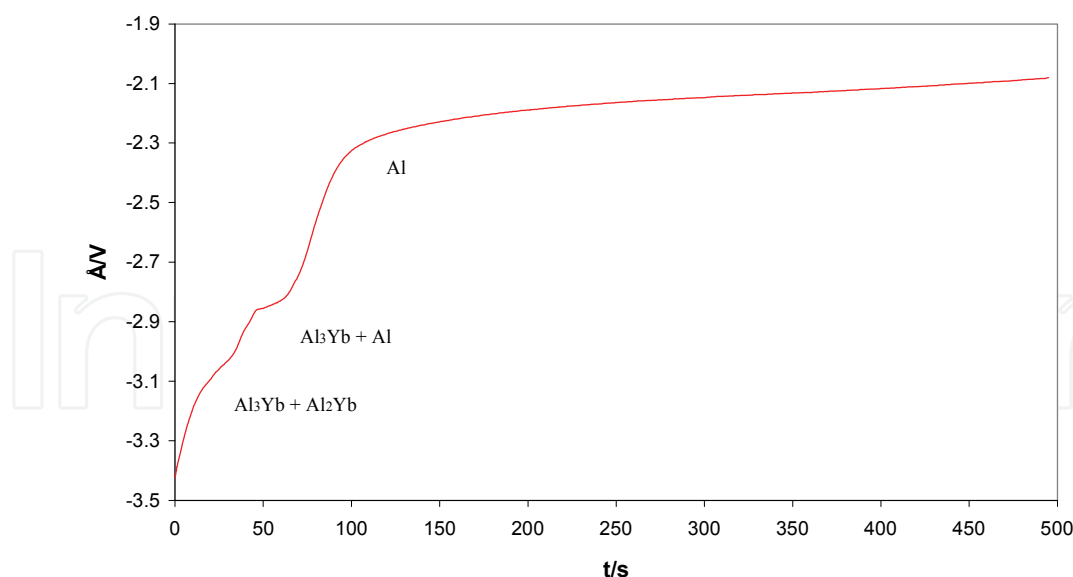


Fig. 12. The dependence of potential – time, obtained after short polarization of Al electrode in NaCl-KCl-CsCl-YbCl<sub>3</sub> melt at 873 K. [Yb(III)] =  $3.17 \cdot 10^{-2}$  mol kg<sup>-1</sup>.  $E_{\text{dep.}} = -3.4$  V;  $t_{\text{dep.}} = 9$  s

Potentiostatic electrolysis at the potential  $-2.92$  V shows the formation of solid cathodic product on a surface of Al electrode. Phase diagram of the system Al-Yb, Fig. 11, show the formation of two intermetallic compounds Al<sub>3</sub>Yb and Al<sub>2</sub>Yb.

The dependence potential – time, obtained after shot polarization of aluminum working electrode, show the existence of two waves at potentials average  $-2.88$  V and  $-3.04$  V vs. Cl<sup>-</sup>/Cl<sub>2</sub>, Fig. 12. It can be combined with the formation of two intermetallic compounds Al<sub>3</sub>Yb and Al<sub>2</sub>Yb. The X-ray analysis of the deposits, obtained after potentiostatic electrolysis at the potential  $-2.88$  V show the existence of Al<sub>3</sub>Yb alloy on the surface of aluminum electrode and at potential  $-3.04$  V show the existence of the mixture of Al<sub>3</sub>Yb and Al<sub>2</sub>Yb alloys.

Analyzing the results of investigations it can be concluded that the mechanism of the reduction of Yb(III) ions in fused NaCl-KCl-CsCl eutectic on active electrode occurs in two steps with the formation of Al<sub>3</sub>Yb and Al<sub>2</sub>Yb alloys:



where  $n$  is equal 2, 3.

Potentiostatic electrolysis allow to deposit Al<sub>3</sub>Yb or the mixture of Al<sub>2</sub>Tm and Al<sub>3</sub>Tm alloys as a thin films on the aluminum surface.

### 3.2 Electromotive force method

#### 3.2.1 Apparent standard potentials of the redox couple Ln(III)/Ln(II)

The typical dependences of the redox potential of the couple Yb<sup>3+</sup>/Yb<sup>2+</sup> with different ratio Yb(III)/Yb(II) versus the duration at the temperature 818 K in NaCl-KCl-CsCl-YbCl<sub>3</sub> melt are presented in Fig. 13.

The same type of the pictures was obtained for Tm<sup>3+</sup>/Tm<sup>2+</sup> and Yb<sup>3+</sup>/Yb<sup>2+</sup> systems in all investigations solvents. The equilibrium potential were fixed after 30-90 minutes after finishing of the electrolysis and depends from the conditions of the experiment. If the value

of potential is constant during 30-40 minutes within the limits of  $\pm 0.001$  V then it is possible to say that the investigation system is in equilibrium conditions.

The value of the apparent redox potential is determined by:

$$E_{Ln^{3+}/Ln^{2+}} = E_{Ln^{3+}/Ln^{2+}}^* + \frac{RT}{nF} \ln \left( \frac{[Ln^{3+}]}{[Ln^{2+}]} \right) \quad (28)$$

where  $E_{Ln^{3+}/Ln^{2+}}$  is the equilibrium potential of the system, V;  $E_{Ln^{3+}/Ln^{2+}}^*$  is the apparent standard redox potential of the system, V;  $n$  is the number of exchange electrons;  $[Ln^{3+}]$  and  $[Ln^{2+}]$  are the concentrations of lanthanide ions in mole fraction.

Variation of the equilibrium potential of the couple  $Ln^{3+}/Ln^{2+}$  as a function of the napierian logarithm ratio of concentrations  $[Ln^{3+}]$  and  $[Ln^{2+}]$  in fused  $LnCl_3$  solutions on vitreous carbon indicated electrode at 818 K (NaCl-KCl-CsCl eutectic) and at 973 K (CsCl) is shown

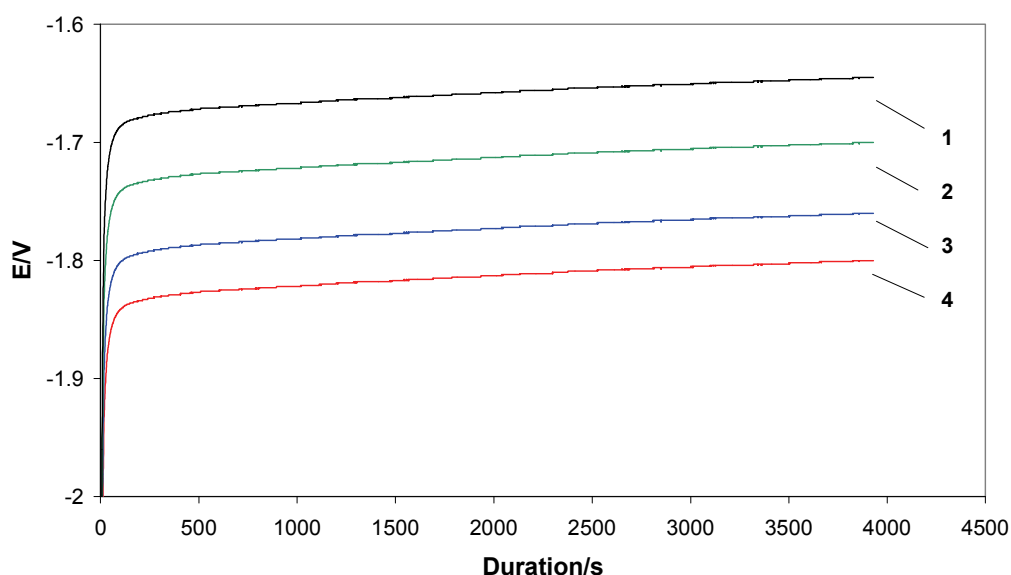


Fig. 13. The typical dependences of the redox potential of the couple  $Yb^{3+}/Yb^{2+}$  versus the duration in NaCl-KCl-CsCl- $YbCl_3$  melt. Temperature – 818 K. Initial concentration of  $[Yb^{3+}] = 3.96$  mol%. Working electrode – GC. 1 –  $\ln[Yb^{3+}]/[Yb^{2+}] = 1.96$ ; 2 –  $\ln[Yb^{3+}]/[Yb^{2+}] = 1.58$ ; 3 –  $\ln[Yb^{3+}]/[Yb^{2+}] = 0.54$ ; 4 –  $\ln[Yb^{3+}]/[Yb^{2+}] = 0$

In Fig. 14. Linear dependences of  $E_{Ln^{3+}/Ln^{2+}}$  vs.  $\ln([Ln^{3+}]/[Ln^{2+}])$  obeys the Nernst's law by the following equations using Software Origin Pro version 7.5:

$$E_{Tm^{3+}/Tm^{2+}} = -(2.827 \pm 0.005) + (0.083 \pm 0.005) \ln([Tm^{3+}]/[Tm^{2+}]) \pm 0.007 / V \quad CsCl \quad (29)$$

$$E_{Tm^{3+}/Tm^{2+}} = -(2.906 \pm 0.001) + (0.070 \pm 0.001) \ln([Tm^{3+}]/[Tm^{2+}]) \pm 0.002 / V \quad (Na-K-Cs)Cl \quad (30)$$

$$E_{Yb^{3+}/Yb^{2+}} = -(1.809 \pm 0.001) + (0.086 \pm 0.001) \ln([Yb^{3+}]/[Yb^{2+}]) \pm 0.002 / V \quad CsCl \quad (31)$$

$$E_{Yb^{3+}/Yb^{2+}} = -(1.805 \pm 0.005) + (0.071 \pm 0.004) \ln([Yb^{3+}]/[Yb^{2+}]) \pm 0.006 / V \quad (Na-K-Cs)Cl \quad (32)$$



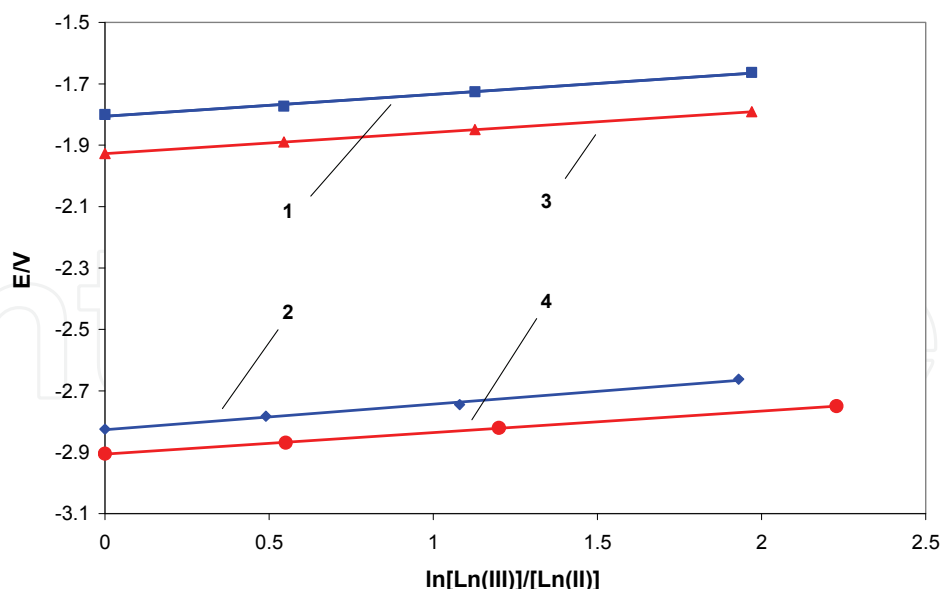


Fig. 14. Variation of the equilibrium potential of the couple  $\text{Ln}^{3+}/\text{Ln}^{2+}$  as a function of the napierian logarithm ratio of concentrations  $[\text{Ln}^{3+}]$  and  $[\text{Ln}^{2+}]$  in fused NaCl-KCl-CsCl eutectic (1 - Yb; 2 - Tm) at 818 K and in fused CsCl (3 - Yb; 4 - Tm) at 973 K on vitreous carbon indicated electrode.  $[\text{Yb}^{3+}] = 3.96 \text{ mol\%}$ .  $[\text{Tm}^{3+}] = 4.28 \text{ mol\%}$

The number of exchange electrons ( $n$ ) taking part in the process of electrochemical reduction of rare-earth trichlorides was determined from the slopes of the straight lines. From equations (29-32) the number of exchange electrons for the reaction (33):



was  $0.99 \pm 0.01$  for Tm and  $0.99 \pm 0.02$  for Yb.

The chemical analysis of the solidified thulium or ytterbium chloride melts performed after experiments confirmed the results of the electrochemical measurements. The difference in concentrations of  $\text{LnCl}_2$  determined by coulometry (i.e., calculated from the amount of electric charge passed through the melt for the reduction of  $\text{Ln}^{3+}$  ions) and analytically did not exceed 2.5 %.

The temperature dependences of apparent standard redox potentials of  $\text{Ln}^{3+}/\text{Ln}^{2+}$  systems on vitreous carbon indicated electrode were linear in the whole temperature range studied, Fig. 15. The experiment data were fitted to the following equations using Software Origin Pro version 7.5:

$$E_{\text{Tm}^{3+}/\text{Tm}^{2+}}^* = -(3.742 \pm 0.006) + (105.0 \pm 0.6) \cdot 10^{-5} T \pm 0.001 / \text{V} \quad [823-973 \text{ K}] \quad (\text{Na-K-Cs})\text{Cl} \quad (34)$$

$$E_{\text{Yb}^{3+}/\text{Yb}^{2+}}^* = -(2.580 \pm 0.013) + (80.6 \pm 1.5) \cdot 10^{-5} T \pm 0.003 / \text{V} \quad [823-973 \text{ K}] \quad (\text{Na-K-Cs})\text{Cl} \quad (35)$$

$$E_{\text{Tm}^{3+}/\text{Tm}^{2+}}^* = -(4.029 \pm 0.03) + (124.0 \pm 2.7) \cdot 10^{-5} T \pm 0.005 / \text{V} \quad [973-1123 \text{ K}] \quad \text{CsCl} \quad (36)$$

$$E_{\text{Yb}^{3+}/\text{Yb}^{2+}}^* = -(2.464 \pm 0.008) + (65.0 \pm 0.7) \cdot 10^{-5} T \pm 0.001 / \text{V} \quad [973-1123 \text{ K}] \quad \text{CsCl} \quad (37)$$

The results of our investigations show that at equal temperatures the apparent redox potentials of thulium ( $E_{Tm^{3+}/Tm^{2+}}^*$ ) are more negative than ytterbium ( $E_{Yb^{3+}/Yb^{2+}}^*$ ). The comparison of data for apparent standard redox potentials of thulium (-2.822 V) and ytterbium (-1.831 V) in molten CsCl ( $r_{Cs^+} = 0.165 \text{ nm}$ ) with data in fused NaCl-KCl-CsCl eutectic ( $r_{eut.} = 0.137 \text{ nm}$ ) [Lebedev, 1993] for thulium (-2.720 V) and ytterbium (-1.796 V) at 973 K show the natural shift of the potential values to more negative region in line LiCl-CsCl.

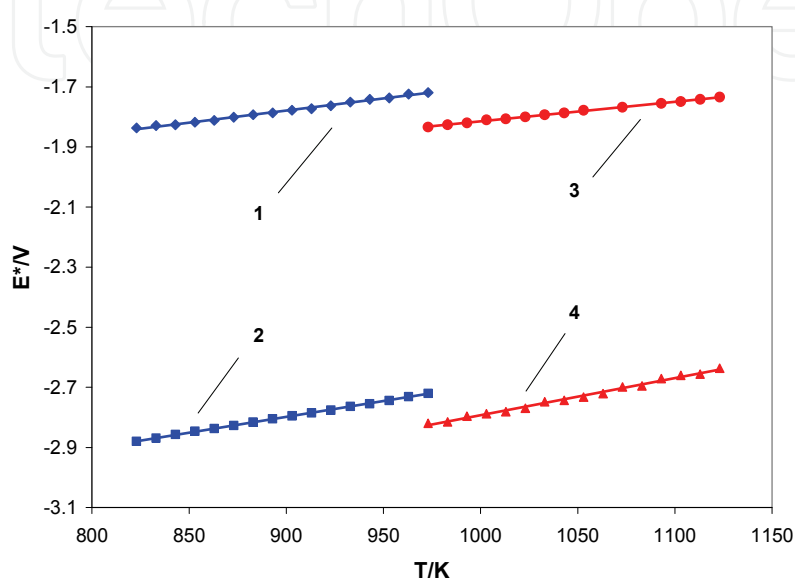


Fig. 15. Apparent standard redox potentials of the  $Ln^{3+}/Ln^{2+}$  system as a function of the temperature on vitreous carbon indicated electrode. 1 – System  $YbCl_3$ - $YbCl_2$ -NaCl-KCl-CsCl. 2 – System  $TmCl_3$ - $TmCl_2$ -NaCl-KCl-CsCl. 3 – System  $YbCl_3$ - $YbCl_2$ -CsCl. 4 – System  $TmCl_3$ - $TmCl_2$ -CsCl

Typical complexes of dilute solution of lanthanide chlorides in alkali chloride melts are  $LnCl_6^{3-}$  and  $LnCl_4^{2-}$  [Papatheodorou & Kleppa, 1974; Yamana et al., 2003]. Their relative stability increases with increasing of solvent cation radius from  $Li^+$  to  $Cs^+$  and the apparent standard redox potentials are shifted to more negative values. These results are in good agreement with literature data concerning the second coordination sphere influence on apparent standard redox potentials.

### 3.2.2 Thermodynamics properties

Using the values of the apparent standard redox potentials the formal free Gibbs energy changes and the apparent equilibrium constants of the redox reaction (38):



can be calculated using the well-known expressions:

$$\Delta G^* = nFE_{Ln^{3+}/Ln^{2+}}^* \quad (39)$$

and

$$\Delta G^* = -RT \ln K_{eq}^* \quad (40)$$

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

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (41)$$

The experiment data were fitted to the following equations using Software Origin Pro version 7.5:

$$\Delta G^* = -(354.1 \pm 0.6) + (94.5 \pm 0.6) \cdot 10^{-3} T \pm 0.1 \text{ kJ / mol} \quad \text{TmCl}_3\text{-NaCl-KCl-CsCl} \quad (42)$$

$$\Delta G^* = -(249.0 \pm 1.3) + (77.8 \pm 0.1) \cdot 10^{-3} T \pm 0.3 \text{ kJ / mol} \quad \text{YbCl}_3\text{-NaCl-KCl-CsCl} \quad (43)$$

$$\Delta G^* = -(388.8 \pm 0.9) + (119.7 \pm 0.9) \cdot 10^{-3} T \pm 0.2 \text{ kJ / mol} \quad \text{TmCl}_3\text{-CsCl} \quad (44)$$

$$\Delta G^* = -(237.8 \pm 0.8) + (62.7 \pm 0.7) \cdot 10^{-3} T \pm 0.1 \text{ kJ / mol} \quad \text{YbCl}_3\text{-CsCl} \quad (45)$$

By the expression (40) one can calculate the apparent equilibrium constants for the redox reaction (38) in fused salts. The temperature dependences are the following:

$$\ln K_{eq}^* = -13.78 + \frac{44997}{T} \pm 0.01 \quad \text{TmCl}_3\text{-NaCl-KCl-CsCl} \quad (46)$$

$$\ln K_{eq}^* = -10.56 + \frac{31114}{T} \pm 0.01 \quad \text{YbCl}_3\text{-NaCl-KCl-CsCl} \quad (47)$$

$$\ln K_{eq}^* = -14.40 + \frac{46787}{T} \pm 0.02 \quad \text{TmCl}_3\text{-CsCl} \quad (48)$$

$$\ln K_{eq}^* = -7.54 + \frac{28602}{T} \pm 0.01 \quad \text{YbCl}_3\text{-CsCl} \quad (49)$$

The activity coefficients of  $\text{YbCl}_3$  in fused salts was determined from the difference between the apparent Gibbs free energy derived from the experimental measurements and the standard Gibbs free energy for pure compounds obtained in the literature [Barin, 1994]:

$$\log \gamma_{\text{YbCl}_3} = -1.23 - \frac{4436}{T} \pm 0.02 \quad \text{YbCl}_3\text{-NaCl-KCl-CsCl} \quad (50)$$

$$\log \gamma_{\text{YbCl}_3} = -2.09 - \frac{3761}{T} \pm 0.02 \quad \text{YbCl}_3\text{-CsCl} \quad (51)$$

The dependence of the activity coefficient of  $\text{YbCl}_3$  versus the reverse temperature is given by the expressions (50, 51). Database for thulium compounds is absent in the literature [Barin, 1994].

It is also possible to estimate the equilibrium chlorine gas pressure above an alkali metal chloride melts containing thulium or ytterbium tri- and dichlorides for the reaction (52) by



well-known equation (53) [Smirnov, 1973]. Such kind of calculations were done for the concentration ratio of  $[\text{Ln}^{3+}]/[\text{Ln}^{2+}]$  equals one in fused NaCl-KCl-CsCl eutectic and individual CsCl.

$$\frac{RT}{2F} \ln P_{\text{Cl}_2} = E_{\text{Ln}^{3+}/\text{Ln}^{2+}} + \frac{RT}{F} \ln \frac{[\text{Ln}^{3+}]}{[\text{Ln}^{2+}]}$$

(53)

The calculated values are summarized in Table 2. The average value of the radius of these molten mixtures in this line, *pro tanto*, is 0.137; 0.165 nm [Lebedev, 1993]. From the data given in Table 2 one can see that the relative stability of lanthanides(III) complexes ions is naturally increased in the line (NaCl-KCl-CsCl)<sub>eut.</sub> – CsCl.

| Thermodynamic properties                                 | Tm                      |                         | Yb                      |                         |
|--|-------------------------|-------------------------|-------------------------|-------------------------|
|  | NaCl-KCl-CsCl           | CsCl                    | NaCl-KCl-CsCl           | CsCl                    |
| E <sup>*</sup> /V  | -2.721                  | -2.822                  | -1.796                  | -1.846                  |
| ΔG <sup>*</sup> /(kJ mol <sup>-1</sup> )                 | -262.6                  | -272.3                  | -173.3                  | -178.2                  |
| ΔH <sup>*</sup> /(kJ mol <sup>-1</sup> )                 | -354.1                  | -388.8                  | -249.0                  | -258.7                  |
| ΔS <sup>*</sup> /(J ·K <sup>-1</sup> mol <sup>-1</sup> ) | 94.5                    | 119.7                   | 77.8                    | 82.8                    |
| γ  | –                       | –                       | 1.6 ·10 <sup>-6</sup>   | 9.0 ·10 <sup>-7</sup>   |
| K <sup>*</sup> <sub>eq.</sub>                            | 1.31 ·10 <sup>14</sup>  | 4.40 ·10 <sup>14</sup>  | 2.08 ·10 <sup>9</sup>   | 3.80 ·10 <sup>9</sup>   |
| p <sub>Cl<sub>2</sub></sub> / Pa                         | 5.86 ·10 <sup>-29</sup> | 1.05 ·10 <sup>-24</sup> | 2.31 ·10 <sup>-19</sup> | 6.92 ·10 <sup>-20</sup> |

Table 2. The comparison of the base thermodynamic properties of Tm and Yb in molten alkali metal chlorides at 973 K. Apparent standard redox potentials are given in the molar fraction scale

4. Conclusion

The electrochemical behaviour of  $[\text{YbCl}_6]^{3-}$  ions in fused alkali metal chlorides was investigated. It was found that the reduction of Yb(III) to Yb(II) ions is a reversible process being controlled by the rate of the mass transfer. The diffusion coefficient of  $[\text{YbCl}_6]^{3-}$  ions was determined at different temperatures in all investigation systems. The apparent standard electrode potential of the redox couple  $\text{Yb}^{3+}/\text{Yb}^{2+}$  was calculated from the analysis of the cyclic voltammograms registered at different temperatures. The apparent standard redox potentials of  $E_{\text{Tm}^{3+}/\text{Tm}^{2+}}^*$  and  $E_{\text{Yb}^{3+}/\text{Yb}^{2+}}^*$  in molten alkali metal chlorides were also determined by *emf* method. The basic thermodynamic properties of the reactions  $\text{TmCl}_{2(l)} + \frac{1}{2} \text{Cl}_{2(g)} \rightleftharpoons \text{TmCl}_{3(l)}$  and  $\text{YbCl}_{2(l)} + \frac{1}{2} \text{Cl}_{2(g)} \rightleftharpoons \text{YbCl}_{3(l)}$  were calculated. The influence of the nature of the solvent (ionic radius) on the thermodynamic properties of thulium and ytterbium compounds was assessed. It was found that the strength of the Ln-Cl bonds increases in the line from Li to Cs cation.

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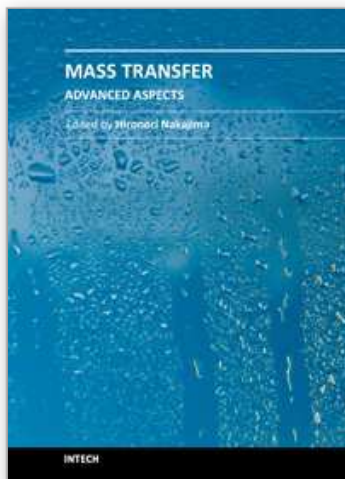
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