

## THE POSSIBILITY OF $Ce^{3+}$ AND $Mn^{2+}$ COMPLEX IONS FORMATION WITH IODINE SPECIES IN A DUSHMAN REACTION

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**Abstract.** This contribution presents investigations into possible effects of  $Ce^{3+}$  and  $Mn^{2+}$  on the reduction of UV-spectral signal for  $I_3^-$  observed e.g. in the Dushman reaction. The potential of the metal ions to form complexes with iodine-containing species was analysed. It was shown that no complex ions are formed between  $Ce^{3+}$  and  $Mn^{2+}$  metals ions with  $IO_3^-$ ,  $I$ ,  $I_2$  species. Only the formation of a very weak  $CeI_3^{2+}$  complex ion was found to occur. An effect of a complex formation on the studied systems could be excluded.

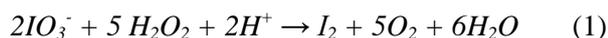
**Keywords:** Dushman reaction, cerium ion, manganese ion, iodine specie.

Received: 03 December 2017/ Revised final: 15 March 2018/ Accepted: 02 April 2018

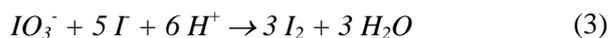
### Introduction

Complex chemical systems, which have a nonlinear dynamics type of evolution and where thermodynamic forces (reactant concentrations) exceed some critical values, sometimes present self organization. This can be recognized as a temporal periodic oscillation of limit cycle type or spatio-temporal oscillations. The reaction mechanism of such a system is very complex, and for this reason it is studied on subsystems of initial reactants. In this manner have been studied the most known oscillating reactions: Belousov-Zhabotinsky,  $\{BrO_3^-, Br^-, H^+, Me^{z+}, MA\}$  [1,2], Briggs-Rauscher,  $\{IO_3^-, H_2O_2, H^+, Me^{z+}, MA\}$  [3] and Bray-Liebafsky  $\{IO_3^-, H_2O_2, H^+\}$  [4-7,9-15].

In the Bray-Liebafsky oscillating system, the  $IO_3^-$  ion is reduced by  $H_2O_2$  to  $I_2$  in acidic medium, according to the global reaction Eq.(1). When  $I_2$  concentration and pH reach critical values, the oxidation reaction Eq.(2) begins and this cycle is repeated [16-21].



Cooke, D.O. found that if a metal with variable valence is added (for example  $Mn^{2+}/Mn^{3+}$ ) in the system  $\{IO_3^-, H_2O_2, H^+\}$  then the rate of  $I_2$  production is considerably increased [8,22-24]. Among the reactions of the Bray-Liebafsky oscillating system there are also the reactions Eq.(3) and Eq.(4), known as Dushman reaction [25].



On the other side, further studies have shown that adding metal ions  $Ce^{3+}$  and  $Mn^{2+}$  to the Dushman reaction induces a decrease of spectral absorbance due to  $\{I_3^-, I_2\}$  pair (see Eqs.(3) and (4)) associated with a decreased rate of production of  $\{I_3^-, I_2\}$ . This decreased rate of production of the pair  $\{I_3^-, I_2\}$  in the Dushman reaction is due to either formation of complex ions  $Ce(III)-X$  and  $Mn(II)-X$ , where X is:  $IO_3^-$ ,  $I$ ,  $I_2$ ,  $I_3^-$  or to the ionic strength effect and to ionic interactions. The study of the ionic strength effect and ionic interactions on kinetics of the Dushman reaction has been presented in a recent paper [26]. Although it was already reported that we did not find the formation of complexes of iodine-containing species with either  $Ce^{3+}$  or  $Mn^{2+}$  [26], in this paper we wanted to report how we arrived at that conclusion.

### Experimental part

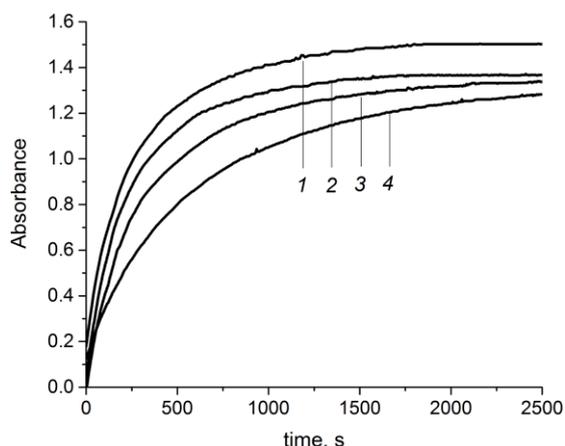
Analytical grade  $KIO_3$ ,  $KI$ ,  $MnSO_4 \cdot H_2O$  (Prolabo),  $Ce_2(SO_4)_3 \cdot 8H_2O$  (Aldrich) and  $HClO_4$  (Merk) were used without further purification. Also, freshly sublimed iodine was used in the study. Stock solutions were prepared from weighted amounts of reagents and were diluted using calibrated pipettes. The spectra and absorbances as function of time at 25°C were recorded using a U-2001, Hitachi

spectrophotometer and a Specord 200 from Analytik Jena. Cuvette capacity was  $V=4\text{ cm}^3$ , optical length  $L=1\text{ cm}$ . The cuvette was closed to avoid sublimation of  $I_2$  and  $I_3^-$ . It should be noted that the signal in the UV spectrum at 351 nm refers to the  $I_3^-$  species.

## Results and discussion

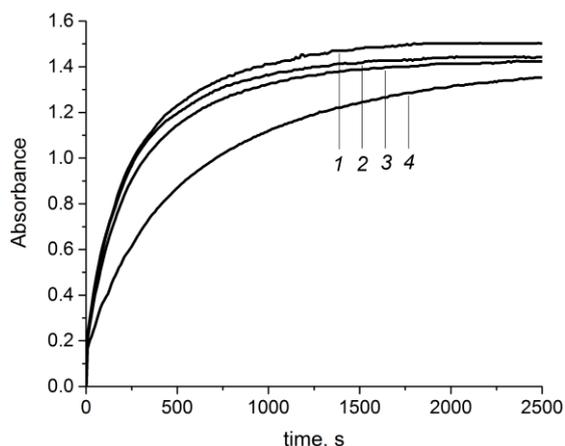
### Temporal evolution of the Dushman reaction

The first step of our study was to investigate the temporal evolution of the Dushman reaction in the presence and absence of metal ions  $Ce^{3+}$  and  $Mn^{2+}$ . Figure 1 presents the temporal evolution of absorbance for the time interval 0-2500 seconds, and wavelength  $\lambda=351\text{ nm}$  in the presence and absence of  $Ce^{3+}$ . A similar procedure was applied for the  $Mn^{2+}$  systems (Figure 2).



**Figure 1. Temporal evolution for the Dushman reaction at  $\lambda=351\text{ nm}$ .**

1-  $[IO_3^-]_0=1.463\times 10^{-4}\text{ M}$ ;  $[I]_0=8.778\times 10^{-4}\text{ M}$ ;  
 $[H^+]_0=1.60\times 10^{-3}\text{ M}$ , (without  $Ce^{3+}$ );  
 2-  $[Ce^{3+}]_0=8\times 10^{-5}\text{ M}$ ; 3-  $[Ce^{3+}]_0=8\times 10^{-4}\text{ M}$ ;  
 4-  $[Ce^{3+}]_0=8\times 10^{-3}\text{ M}$ .



**Figure 2. Temporal evolution for the Dushman reaction at  $\lambda=351\text{ nm}$ .**

1-  $[IO_3^-]_0=1.463\times 10^{-4}\text{ M}$ ;  $[I]_0=8.778\times 10^{-4}\text{ M}$ ;  
 $[H^+]_0=1.60\times 10^{-3}\text{ M}$ , (without  $Mn^{2+}$ );  
 2-  $[Mn^{2+}]_0=8\times 10^{-5}\text{ M}$ ; 3-  $[Mn^{2+}]_0=8\times 10^{-4}\text{ M}$ ;  
 4-  $[Mn^{2+}]_0=8\times 10^{-3}\text{ M}$ .

Molar extinction coefficients derived from the absorbance values registered at 351 nm are  $\epsilon(I_3^-, 351\text{ nm})=26400\text{ L mol}^{-1}\text{cm}^{-1}$  and  $\epsilon(I_2, 351\text{ nm})=18\text{ L mol}^{-1}\text{cm}^{-1}$ , respectively. It should be mentioned that the molar extinction coefficient of the species  $I_3^-$  has the maximum value at 351 nm. Figures 1 and 2 show that in the absence of metal ions ( $Me^{z+}$ ), absorbance has the highest value,  $A(2500\text{ s})=1.502$ , while in the presence of metal ions,  $Me^{z+}$  absorbance decreases with increasing metal concentration. The lowest value is obtained for  $Ce^{3+}$  (see Table 1).

Table 1

**Absorbance values of solutions containing  $Ce^{3+}$  and  $Mn^{2+}$  ions.**

$[Ce^{3+}]$	$8\times 10^{-5}\text{ M}$	$8\times 10^{-4}\text{ M}$	$8\times 10^{-3}\text{ M}$
Absorbance	1.367	1.336	1.281
$[Mn^{2+}]$	$8\times 10^{-5}\text{ M}$	$8\times 10^{-4}\text{ M}$	$8\times 10^{-3}\text{ M}$
Absorbance	1.443	1.423	1.353

Although we proved that absorbance decreases due to the ionic strength effect, given by the presence of ions  $Ce^{3+}$  and  $Mn^{2+}$  [26], further we study the possibility of  $Ce^{3+}$  complex ions formation with iodine species ( $IO_3^-$ ,  $I$ ,  $I_2$ ,  $I_3^-$ ) and  $Mn^{2+}$  complex ions formation with only two iodine species ( $IO_3^-$ ,  $I$ ). According to the aim of this study, we will focus on the following:

- subsystem  $Ce^{3+}$  and  $IO_3^-$ ;
- subsystem  $Mn^{2+}$  and  $IO_3^-$ ;
- subsystem  $Ce^{3+}$  and  $I$ ;
- subsystem  $Mn^{2+}$  and  $I$ ;
- subsystem  $Ce^{3+}$  and  $I_2$ ;
- subsystem  $Ce^{3+}$  and  $I_3^-$ .

### Study of the subsystem $Ce^{3+}$ and $IO_3^-$

The most frequently used methods for the identification of complex formation are the *isosbestic point* [27] method and the *Ostromisslensky-Job* method [28,29]. The *isosbestic point* is the wavelength at which the three absorption spectra cross each other; in our case these are the spectra of the central ion ( $Me^{z+}$ ), that of the ligand ( $IO_3^-$ ) and that of the complex ion.

Figure 3 presents the UV-Vis spectra of  $Ce^{3+}$ ,  $IO_3^-$  and the mixture ( $Ce^{3+}+IO_3^-$ ), for different concentrations. The obtained results show that there is no *isosbestic point* and this means that no  $Ce(III)-IO_3^-$  complex ion is formed.

Further, the *Ostromisslensky-Job* method was applied for the same mixture ( $Ce^{3+}+IO_3^-$ ) to obtain an additional proof that the complex ion  $Ce(III)-IO_3^-$  is not formed in the studied system. This method requires the condition that the sum of

concentrations of the studied species must be constant ( $[Ce^{3+}] + [IO_3^-] = const$ ), in our case it would mean that the sum of molar fractions  $x(Ce^{3+}) + x(IO_3^-) = 1$ .

We worked with the initial concentrations:

$$[IO_3^-]_0 = [Ce^{3+}]_0 = 8 \times 10^{-4} \text{ M};$$

$$[HClO_4]_0 = 1.6 \times 10^{-3} \text{ M}.$$

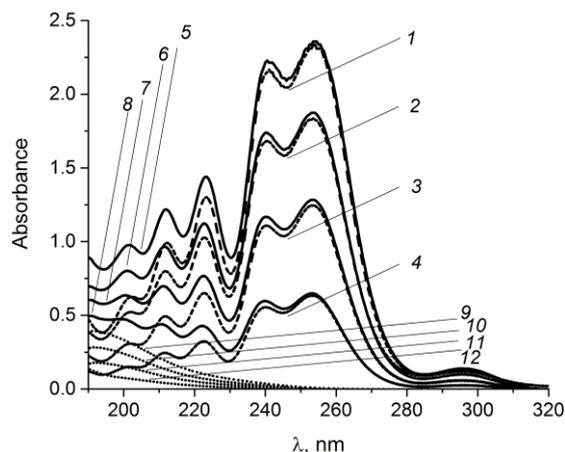
$$\begin{aligned} \text{Total volume of solution} &= n_{mL}(IO_3^-) + m_{mL}(Ce^{3+}) \\ &+ 5 \text{ mL}(HClO_4) + 5 \text{ mL}(H_2O) = 20 \text{ mL}. \end{aligned}$$

The new condition considered in the studied system is:

$$\left[ \frac{n_{mL}[IO_3^-]}{20} + \frac{m_{mL}[Ce^{3+}]}{20} \right] \times 8 \times 10^{-4} \text{ M} = 4 \times 10^{-4} \text{ M} = const$$

where,  $n$  and  $m$  represent the volume of solutions, mL.

In order to obtain the mixture ( $Ce^{3+} + IO_3^-$ ) in accordance with the above condition, the working solutions were prepared according to data presented in Table 2. The spectra were registered in the range 190-300 nm and the absorbance values at  $\lambda = 222$  nm were used to draw the dependence of the molar fraction of  $IO_3^-$  (see Figure 4). We have chosen the absorbance at  $\lambda = 222$  nm because both species,  $Ce^{3+}$  and  $IO_3^-$ , have an absorbance at this wavelength.



**Figure 3. UV-Vis spectra of  $Ce^{3+}$ ,  $IO_3^-$  and of the mixture ( $Ce^{3+} + IO_3^-$ ).**

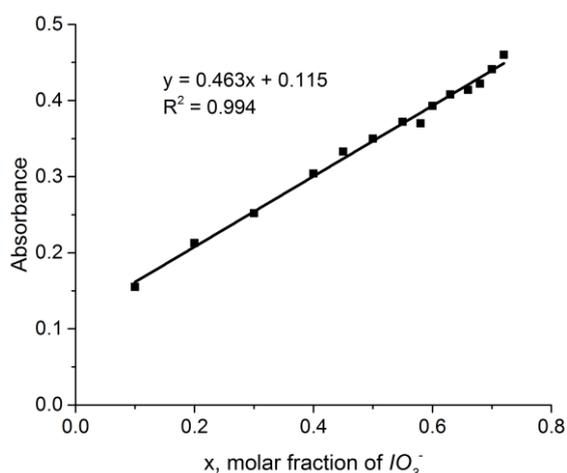
- 1-  $[Ce^{3+}]_0 = 4 \times 10^{-3} \text{ M}$ ;
- 2-  $[Ce^{3+}]_0 = 3 \times 10^{-3} \text{ M}$ ;
- 3-  $[Ce^{3+}]_0 = 2 \times 10^{-3} \text{ M}$ ;
- 4-  $[Ce^{3+}]_0 = 1 \times 10^{-3} \text{ M}$ ;
- 5-  $[Ce^{3+}]_0 = 4 \times 10^{-3} \text{ M}$ ;  $[IO_3^-]_0 = 7.3325 \times 10^{-5} \text{ M}$ ;
- 6-  $[Ce^{3+}]_0 = 3 \times 10^{-3} \text{ M}$ ;  $[IO_3^-]_0 = 7.3325 \times 10^{-5} \text{ M}$ ;
- 7-  $[Ce^{3+}]_0 = 2 \times 10^{-3} \text{ M}$ ;  $[IO_3^-]_0 = 7.3325 \times 10^{-5} \text{ M}$ ;
- 8-  $[Ce^{3+}]_0 = 1 \times 10^{-3} \text{ M}$ ;  $[IO_3^-]_0 = 7.3325 \times 10^{-5} \text{ M}$ ;
- 9-  $[IO_3^-]_0 = 7.3325 \times 10^{-5} \text{ M}$ ;
- 10-  $[IO_3^-]_0 = 5.5 \times 10^{-5} \text{ M}$ ;
- 11-  $[IO_3^-]_0 = 3.666 \times 10^{-5} \text{ M}$ ;
- 12-  $[IO_3^-]_0 = 1.839 \times 10^{-5} \text{ M}$ .

Table 2

**The volumes and the molar fraction,  $x(IO_3^-)$ \***

$n_{mL}(IO_3^-)$	1	2	3	4	4.5	5	5.5	5.8	6	6.3	6.6	6.8	7	7.2
$m_{mL}(Ce^{3+})$	9	8	7	6	5.5	5	4.5	4.2	4	3.7	3.4	3.2	3	2.8
$x(IO_3^-)$	0.1	0.2	0.3	0.4	0.45	0.5	0.55	0.58	0.6	0.63	0.66	0.68	0.7	0.72

\* $n$  and  $m$  represent the volume of solutions in mL and  $x$  represents the molar fraction.

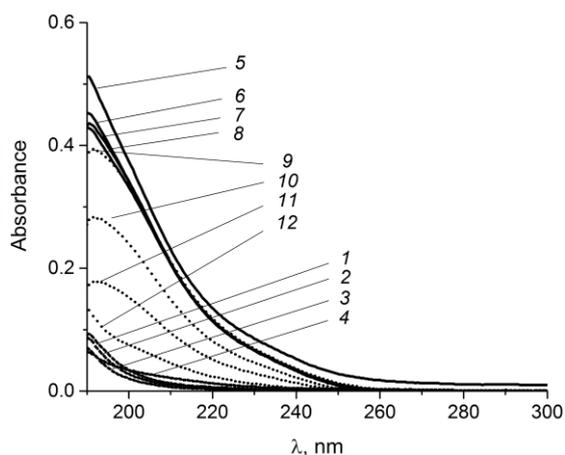


**Figure 4. The representation of absorbance at  $\lambda = 222$  nm as a function of the molar fraction of  $IO_3^-$ .**

The straight line depicted in Figure 4 proves the absence of any complex ions formed by  $Ce^{3+}$  and  $IO_3^-$ . If such a complex ions were formed, there would be a broken line at  $x = 0.5$  or  $x = 0.67$  or  $x = 0.75$  and not a straight one. Thus, the decrease of absorbance is not due to a complex ion between  $Ce^{3+}$  and  $IO_3^-$ .

#### Study of the subsystem $Mn^{2+}$ and $IO_3^-$

Further, we considered the subsystem  $Mn^{2+}$  and  $IO_3^-$ . Figure 5 presents the UV-Vis spectra of  $Mn^{2+}$ ,  $IO_3^-$  and the mixture ( $Mn^{2+} + IO_3^-$ ) for different concentrations proving the absence of the *isosbestic point*. Moreover, the spectra of  $Mn^{2+}$  and  $IO_3^-$  do not cross at all, which proves that the  $Mn(II)-IO_3^-$  complex ion does not exist.



**Figure 5.** UV-Vis spectra of  $Mn^{2+}$ ,  $IO_3^-$  and of the mixture ( $Mn^{2+} + IO_3^-$ ).

- 1-  $[Mn^{2+}]_0 = 4 \times 10^{-3}$  M;  
 2-  $[Mn^{2+}]_0 = 3 \times 10^{-3}$  M;  
 3-  $[Mn^{2+}]_0 = 2 \times 10^{-3}$  M;  
 4-  $[Mn^{2+}]_0 = 1 \times 10^{-3}$  M;  
 5-  $[Mn^{2+}]_0 = 4 \times 10^{-3}$  M;  $[IO_3^-]_0 = 7.3325 \times 10^{-5}$  M;  
 6-  $[Mn^{2+}]_0 = 3 \times 10^{-3}$  M;  $[IO_3^-]_0 = 7.3325 \times 10^{-5}$  M;  
 7-  $[Mn^{2+}]_0 = 2 \times 10^{-3}$  M;  $[IO_3^-]_0 = 7.3325 \times 10^{-5}$  M;  
 8-  $[Mn^{2+}]_0 = 1 \times 10^{-3}$  M;  $[IO_3^-]_0 = 7.3325 \times 10^{-5}$  M;  
 9-  $[IO_3^-]_0 = 7.3325 \times 10^{-5}$  M;  
 10-  $[IO_3^-]_0 = 5.5 \times 10^{-5}$  M;  
 11-  $[IO_3^-]_0 = 3.666 \times 10^{-5}$  M;  
 12-  $[IO_3^-]_0 = 1.839 \times 10^{-5}$  M.

#### Study of the subsystems $Me^{z+}$ ( $Ce^{3+}$ , $Mn^{2+}$ ) and $I^-$

Mayer, S.W. and Schwartz, S.D. [30] measured the association constants for  $Ce^{3+}$  and  $Mn^{2+}$  with  $F^-$ ,  $Cl^-$  and  $Br^-$  but found no associations with  $I^-$ .

#### Study of the subsystem $Ce^{3+}$ and $I_2$

Further on, we studied the spectra of the mixture ( $Ce^{3+} + I_2$ ) to identify the possibility of formation of a  $CeI_2^{3+}$  complex ion type. For this purpose, the following initial concentrations of solutions were used to prepare the studied subsystem (Table 2):

- $[I_2]_0 = 9.7714 \times 10^{-5}$  M;  
 $[Ce^{3+}]_0 = 3.2 \times 10^{-2}$  M;  
 $[HClO_4]_0 = 4.24 \times 10^{-3}$  M.

Table 2

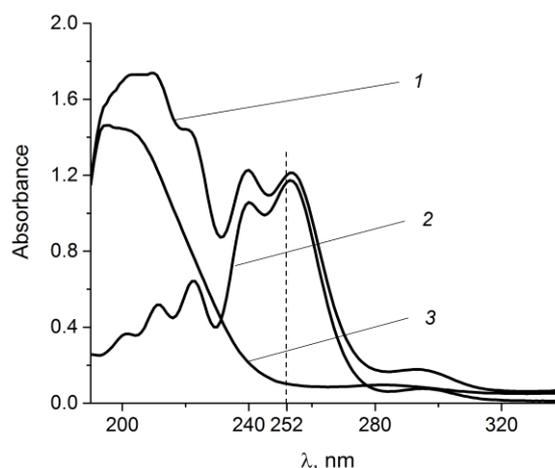
#### The volumes of initial solutions.

Prepared solution	Solution volume, mL			
	$V(I_2)$	$V(Ce^{3+})$	$V(HClO_4)$	$V(H_2O)$
Solution 1	2.5	0.2	0.5	0
Solution 2	2.5	0	0.5	0.2
Solution 3	0	0.2	0.5	2.5

Figure 6 presents the spectra of  $Ce^{3+}$  and  $I_2$  and of the mixture ( $Ce^{3+} + I_2$ ), recorded in the range of 190-590 nm. According to the obtained data, the values of absorbance (A) at  $\lambda = 252$  nm are:  $A(Ce^{3+}) = 1.164$ ;  $A(I_2) = 0.100$ ;  $A(Ce^{3+} + I_2) = 1.210$ .

The sum of absorbances of the two species:  $A(Ce^{3+}) + A(I_2) = 1.164 + 0.100 = 1.264$ .

In the limits of the experimental errors, we can observe that the sum of absorbances of the two species is equal with the absorbance of the mixture ( $Ce^{3+} + I_2$ ). In conclusion, the complex ion  $CeI_2^{3+}$  is not formed.



**Figure 6.** Spectra of  $Ce^{3+}$  and  $I_2$  and of the mixture ( $Ce^{3+} + I_2$ ).

- 1-  $[Ce^{3+}]_0 = 2 \times 10^{-3}$  M;  $[I_2]_0 = 7.643 \times 10^{-5}$  M;  
 2-  $[Ce^{3+}]_0 = 2 \times 10^{-3}$  M;  
 3-  $[I_2]_0 = 7.643 \times 10^{-5}$  M;

#### Study of the subsystem $Ce^{3+}$ and $I_3^-$

Further, to study the possibility of formation of  $[CeI_3]^{2+}$  complex ion, the reactions Eqs.(4) and (5) were investigated.



For the purpose to study the possibility of formation of  $[CeI_3]^{2+}$  complex ion, the following initial concentrations of solutions were used to prepare the studied subsystem (Table 3):

- $[I_2]_0 = 7.9156 \times 10^{-5}$  M;  
 $[I^-]_0 = 1.205 \times 10^{-2}$  M;  
 $[HClO_4]_0 = 4.24 \times 10^{-3}$  M;  
 $[Ce^{3+}]_0 = 5.3333 \times 10^{-3}$  M;  
 $[Ce^{3+}]_0 = 5.3333 \times 10^{-4}$  M.

Table 3

#### The volumes of initial solutions\*.

Prepared solution	Solution volume, mL			
	$V(I_2, I^-, I_3^-)$	$V(Ce^{3+})$	$V(HClO_4)$	$V(H_2O)$
Solution 1	8	0	2	2
Solution 2	8	2 of conc. $5.3333 \times 10^{-4}$ M	2	0
Solution 3	8	2 of conc. $5.3333 \times 10^{-3}$ M	2	0

\*The concentrations in cuvettes were:

- $[I_2] = 7.9156 \times 10^{-5}$  M (8/12) =  $5.277 \times 10^{-5}$  M;  
 $[I^-] = 1.205 \times 10^{-2}$  M (8/12) =  $8.0333 \times 10^{-3}$  M.

Taking into consideration the equilibrium constant  $K_4 = 721$ , the calculated equilibrium concentrations of the species, in the absence of  $Ce^{3+}$  ions (Solution 1, Table 3), are:

$$\begin{aligned} [I_2] &= 7.763 \times 10^{-6} \text{ M}; \\ [I] &= 7.9883 \times 10^{-3} \text{ M}; \\ [I_3^-] &= 4.5007 \times 10^{-5} \text{ M}. \end{aligned}$$

With these equilibrium concentrations and molar extinction coefficients  $\varepsilon(I_3^-, 351 \text{ nm}) = 26400 \text{ L mol}^{-1} \text{ cm}^{-1}$ ;  $\varepsilon(I_2, 351 \text{ nm}) = 18 \text{ L mol}^{-1} \text{ cm}^{-1}$ , the calculated absorbance, in the absence of  $Ce^{3+}$ , has the value  $A_{calc.} = 1.1882$ .

Figure 7 shows the spectra of solutions vs time at  $\lambda = 351 \text{ nm}$ , obtained in the following conditions:

1. Three series of numerical values: two series of experimental values and a series of their averages. Average values on the horizontal (0-50 s) are: 1.1896; 1.1896; 1.1896 (without  $Ce^{3+}$ ) (Solution 1);
2. Three series of numerical data: two series of experimental data and one series given by the average of these two with cerium ion of concentration  $[Ce^{3+}] = 5.3333 \times 10^{-4} \text{ M}$ . Average values on the horizontal (0-50 s) are: 1.1687; 1.1769; 1.1728 (Solution 2);

3. The same for  $[Ce^{3+}] = 5.3333 \times 10^{-3} \text{ M}$ . Average values on (0-50 s) are: 1.1514; 1.1569; 1.1541 (Solution 3).

Calculation of the molar extinction coefficient  $\varepsilon(CeI_3^{2+})$  requires the calculated ( $A_{calc}$ ) and experimental ( $A_{exp}$ ) absorbance values. For this purpose, the Maple programme has been used. Considering that  $A_{calc.} = 1.1882 = const.$ , several case-studies were evaluated (see Table 4).

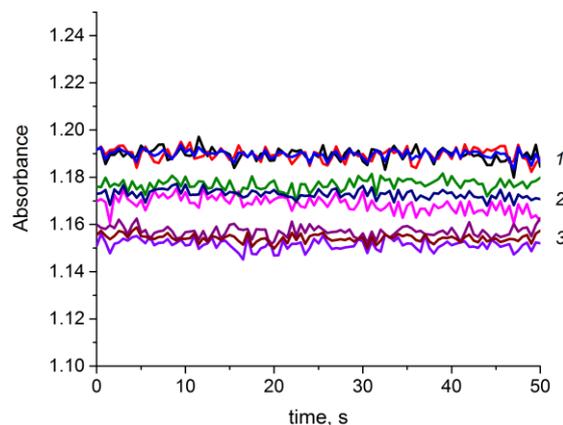


Figure 7. Spectra of solutions vs time at  $\lambda = 351 \text{ nm}$ . 1- Solution 1, 2- Solution 2, 3- Solution 3.

Table 4

Molar extinction coefficient $\varepsilon(CeI_3^{2+})$ and equilibrium constant $K_5$ calculated using Maple programme.			
No.	Input data	Output results	Observations
1	$A_{exp.} = 1.1896$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-3} \text{ M}) = 1.1514$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-4} \text{ M}) = 1.1687$	$\varepsilon(CeI_3^{2+}) = 26399.96 \text{ L mol}^{-1} \text{ cm}^{-1}$ $K_5 = -0.000054$ $[CeI_3^{2+}] = -18259 \text{ M}$ $[I_3^-] = 18253 \text{ M}$	These values have no physical meaning.
2	$A_{exp.} = 1.1896$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-3} \text{ M}) = 1.1569$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-4} \text{ M}) = 1.1769$	$\varepsilon(CeI_3^{2+}) = 21727 \text{ L mol}^{-1} \text{ cm}^{-1}$ $K_5 = 909.91$ $[CeI_3^{2+}] = 1.512 \times 10^{-5} \text{ M}$ $[I_3^-] = 18253 = 3.208 \times 10^{-5} \text{ M}$	These values suggest the formation of a complex ion, $CeI_3^{2+}$ .
3	$A_{exp.} = 1.1896$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-3} \text{ M}) = 1.1541$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-4} \text{ M}) = 1.1728$	$\varepsilon(CeI_3^{2+}) = 26400 + 10.744i$ (complex number) $K_5 = 1.2 \times 10^{-4} - 5.854 \times 10^{-7}i$ $[CeI_3^{2+}] = 8315.9 + 37.08i$ $[I_3^-] = -8315.8 - 33.62i$	These values have no physical meaning.
4	$A_{exp.} = 1.1896$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-3} \text{ M}) = 1.1514$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-4} \text{ M}) = 1.1769$	$\varepsilon(CeI_3^{2+}) = 21572 \text{ L mol}^{-1} \text{ cm}^{-1}$ $K_5 = 706$ $[CeI_3^{2+}] = 1.25 \times 10^{-5} \text{ M}$ $[I_3^-] = 3.42 \times 10^{-5} \text{ M}$	These values also suggest the formation of a complex ion, $CeI_3^{2+}$ .
Further, we used random absorbance values in the presence and absence of $Ce^{3+}$			
1	$A_{exp.} = 1.189$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-3} \text{ M}) = 1.1478$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-4} \text{ M}) = 1.1671$	$\varepsilon(CeI_3^{2+}) = 26391.96 \text{ L mol}^{-1} \text{ cm}^{-1}$ $K_5 = -0.000068$ $[CeI_3^{2+}] = 14548 \text{ M}$ $[I_3^-] = 14543 \text{ M}$	These values have no physical meaning.
2	$A_{exp.} = 1.1871$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-3} \text{ M}) = 1.1560$ $A_{exp.}(Ce^{3+}; 5.3333 \times 10^{-4} \text{ M}) = 1.1725$	-	The calculation is abandoned by computer.

It can be observed that for some values of absorbance, equilibrium constants,  $K_5$  and molar coefficients,  $\varepsilon(CeI_3^{2+})$  would suggest a complex ion  $CeI_3^{2+}$ . On the other side, most of the absorbance values from Figure 7 indicate the absence of the  $CeI_3^{2+}$  complex ion. These results lead to the conclusion that the formation of the complex ion  $CeI_3^{2+}$  is possible but this complex ion is extremely unstable. The differences between the three absorbances for the three solutions is low (Figure 7), suggesting that the complex ion is extremely unstable; its formation is followed by with a very rapid decomposition. The existence of the complex ion  $CeI_3^{2+}$  would allow the verification of experimental curves in Figure 1 using  $\varepsilon(CeI_3^{2+})= 21727 \text{ L mol}^{-1}\cdot\text{cm}^{-1}$  and  $K_5= 909.91$ . For this purpose, chemical reactions Eqs.(3)-(5) were considered. The experimental temporal evolutions obtained for these reactions are represented in Figure 1. For numerical integration of the differential equations we considered the initial conditions (concentrations) (see Figure 1):

$$\begin{aligned} [IO_3^-]_0 &= 1.463 \times 10^{-4} \text{ M}; \\ [I^-]_0 &= 8.778 \times 10^{-4} \text{ M}; \\ [HClO_4]_0 &= 1.60 \times 10^{-3} \text{ M}; \\ [Ce^{3+}]_0 &= 8.0 \times 10^{-3} \text{ M}. \end{aligned}$$

Also, we considered the following values:

$$\begin{aligned} \varepsilon(I^-) &= 0; \quad \varepsilon(IO_3^-) = 0; \quad \varepsilon(I_2) = 18; \quad \varepsilon(I_3^-) = 26400; \\ \varepsilon(Ce^{3+}) &= 0; \quad \varepsilon(CeI_3^{2+}) = 21727; \\ k_4 &= 5E+09, \quad k_{-4} = 5E+9/721, \quad k_5 = 5E+09, \\ k_{-5} &= 5E+9/909, \quad k_{03} = 1.19E+09, \quad k_{-03} = 0. \end{aligned}$$

The result of numerical integration is given in Figure 8.

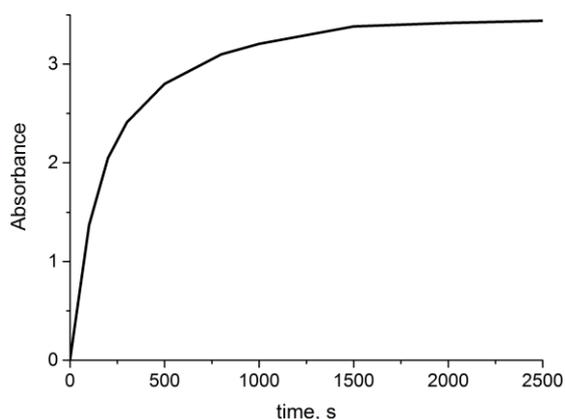


Figure 8. Absorbance calculated by numerical integration.

If we compare the calculated absorbance from Figure 8 with the curve 4 in Figure 1, we find that the calculated absorbance is much higher than the experimental one. If the reaction Eq.(5) of  $CeI_3^{2+}$  complex ion formation is not possible, then we can consider  $k_5= 0$ . In this case, the result

of integration is given in Figure 9. Taking into consideration these results, we can conclude that the complex ion  $CeI_3^{2+}$  is formed according to the reaction Eq.(5), but it is extremely unstable.

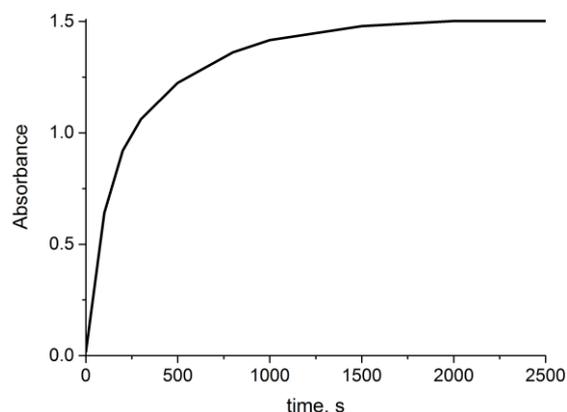


Figure 9. Absorbance calculated in absence of reaction Eq.(5).

Comparison of the calculated absorbance in Figure 9 with curve 4 from Figure 1 ( $A= 1.281$ ) shows that the two absorbances are comparable but slightly different, suggesting that there are other phenomena that induce the decrease of absorbances in the presence of the  $Ce^{3+}$  ion. This difference between experimental and theoretical calculated values of absorbances is due to the ionic strength effect and even to ionic interactions, as it was already shown [26].

## Conclusions

In this article we showed that no complex ions are formed between metal ions  $Ce^{3+}$  and  $Mn^{2+}$  with chemical species  $IO_3^-$ ,  $I^-$ ,  $I_2$  that are usually found in the Dushman system. Instead, we found that the complex ion  $CeI_3^{2+}$  is formed, but it is extremely unstable. So, the decreased absorbance is not associated with the formation of this complex ion and, most probably, it is due to the effect of ionic strength and to ionic interactions.

## Acknowledgments

The authors are grateful to Prof. G. Schmitz, Dr. A. Airinei and Dr. J. Vatamanu for helpful discussions.

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