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

Iurie Ungureanu [a], Gheorghe Duca [b,c], Ionel Humelnicu [a], Gelu Bourceanu [a*]

[a]*Faculty of Chemistry, Alexandru Ioan Cuza University of Iasi, 11, Carol I blvd., Iasi 700506, Romania*
[b]*Institute of Chemistry, Academy of Sciences of Moldova, 3, Academiei str., Chisinau MD-2028, Republic of Moldova*
[c]*Moldova State University, str. Alexei Mateevici, 60, Chisinau MD-2009, Republic of Moldova*
[*]*e-mail: gelub@uaic.ro*

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.

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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-Liebhafsky $\{IO_3^-, H_2O_2, H^+\}$ [4-7,9-15].

In the Bray-Liebhafsky 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].

$$2IO_3^- + 5\,H_2O_2 + 2H^+ \rightarrow I_2 + 5O_2 + 6H_2O \qquad (1)$$

$$I_2 + 5\,H_2O_2 \rightarrow 2IO_3^- + 2H^+ + 4H_2O \qquad (2)$$

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-Liebhafsky oscillating system there are also the reactions Eq.(3) and Eq.(4), known as Dushman reaction [25].

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O \qquad (3)$$

$$I_2 + I^- \rightleftarrows I_3^- \qquad (4)$$

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 cm^3, optical length L= 1 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 λ= 351 nm in the presence and absence of Ce^{3+}. A similar procedure was applied for the Mn^{2+} systems (Figure 2).

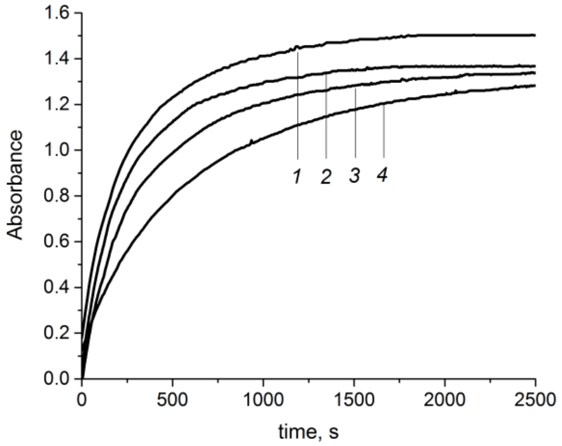

Figure 1. Temporal evolution for the Dushman reaction at λ= 351 nm.
1- $[IO_3^-]_0$= 1.463×10^{-4} M; $[I^-]_0$= 8.778×10^{-4} M; $[H^+]_0$= 1.60×10^{-3} M, (without Ce^{3+});
2- $[Ce^{3+}]_0$= 8×10^{-5} M; 3- $[Ce^{3+}]_0$= 8×10^{-4} M;
4- $[Ce^{3+}]_0$= 8×10^{-3} M.

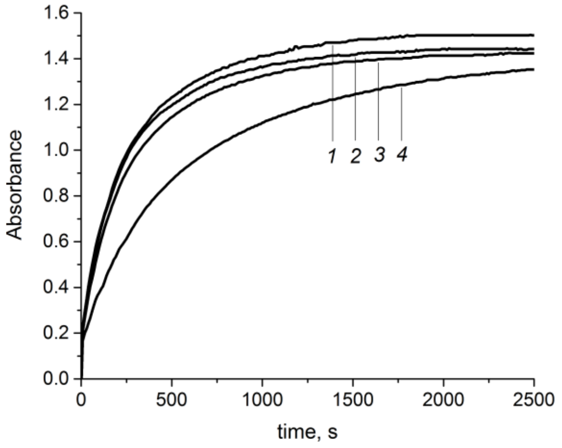

Figure 2. Temporal evolution for the Dushman reaction at λ= 351 nm.
1- $[IO_3^-]_0$= 1.463×10^{-4} M; $[I^-]_0$= 8.778×10^{-4} M; $[H^+]_0$= 1.60×10^{-3} M, (without Mn^{2+});
2- $[Mn^{2+}]_0$= 8×10^{-5} M; 3- $[Mn^{2+}]_0$= 8×10^{-4} M;
4- $[Mn^{2+}]_0$= 8×10^{-3} M.

Molar extinction coefficients derived from the absorbance values registered at 351 nm are $\varepsilon(I_3^-$, 351 nm)= 26400 L mol^{-1}·cm^{-1} and $\varepsilon(I_2$, 351 nm)= 18 L mol^{-1}·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 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.

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

Although we proved that absorbance decreases due tothe 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:

a) subsystem Ce^{3+} and IO_3^-;
b) subsystem Mn^{2+} and IO_3^-;
c) subsystem Ce^{3+} and I^-;
d) subsystem Mn^{2+} and I^-;
e) subsystem Ce^{3+} and I_2;
f) 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:
$[IO_3^-]_0= [Ce^{3+}]_0= 8\times10^{-4}$ M;
$[HClO_4]_0= 1.6\times10^{-3}$ M.

Total volume of solution= $n_{mL}(IO_3^-) + m_{mL}(Ce_3^+) + 5\ mL(HClO_4) + 5\ mL(H_2O)= 20\ mL$.

The new condition considered in the studied system is:

$$\left[\frac{n_{mL\,[IO_3^-]}}{20}+\frac{m_{mL\,[Ce^{3+}]}}{20}\right]\times 8\times10^{-4}M = 4\times10^{-4}M = const$$

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 λ= 222 nm were used to draw the dependence of the molar fraction of IO_3^- (see Figure 4). We have chosen the absorbance at λ= 222 nm because both species, Ce^{3+} and IO_3^-, have an absorbance at this wavelength.

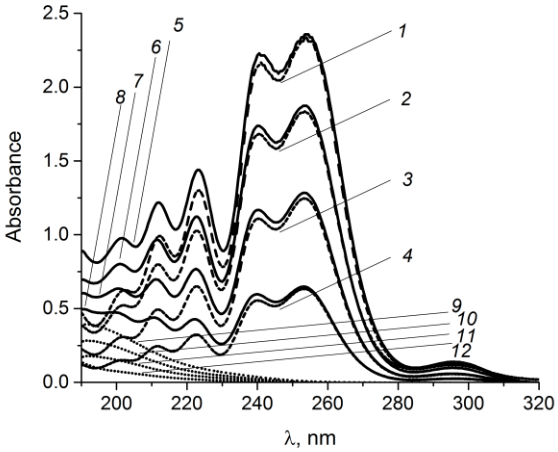

Figure 3. UV-Vis spectra of Ce^{3+}, IO_3^- and of the mixture ($Ce^{3+} + IO_3^-$).
1- $[Ce^{3+}]_0= 4\times10^{-3}$ M;
2- $[Ce^{3+}]_0= 3\times10^{-3}$ M;
3- $[Ce^{3+}]_0= 2\times10^{-3}$ M;
4- $[Ce^{3+}]_0= 1\times10^{-3}$ M;
5- $[Ce^{3+}]_0= 4\times10^{-3}$ M; $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
6- $[Ce^{3+}]_0= 3\times10^{-3}$ M; $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
7- $[Ce^{3+}]_0= 2\times10^{-3}$ M; $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
8- $[Ce^{3+}]_0= 1\times10^{-3}$ M; $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
9- $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
10- $[IO_3^-]_0= 5.5\times10^{-5}$ M;
11- $[IO_3^-]_0= 3.666\times10^{-5}$ M;
12- $[IO_3^-]_0= 1.839\times10^{-5}$ 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.*

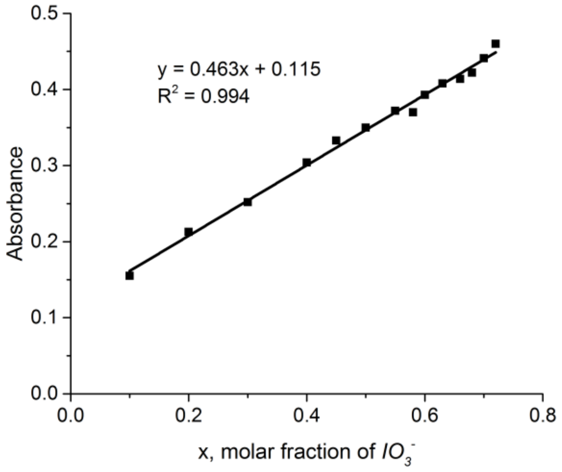

Figure 4. The representation of absorbance at λ= 222 nm as a function of the molar fraction of IO_3^-.

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.

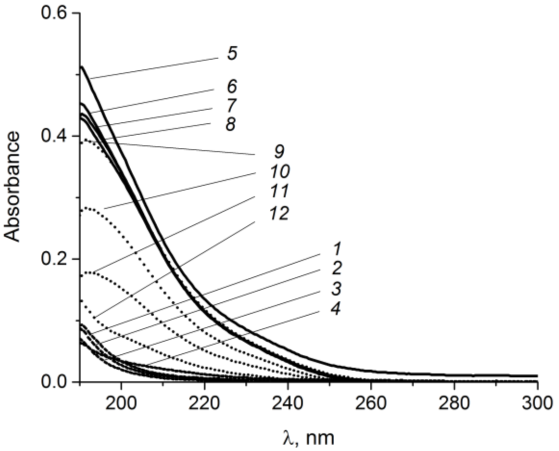

Figure 5. UV-Vis spectra of Mn^{2+}, IO_3^- and of the mixture ($Mn^{2+}+IO_3^-$).
1- $[Mn^{2+}]_0= 4\times10^{-3}$ M;
2- $[Mn^{2+}]_0= 3\times10^{-3}$ M;
3- $[Mn^{2+}]_0= 2\times10^{-3}$ M;
4- $[Mn^{2+}]_0= 1\times10^{-3}$ M;
5- $[Mn^{2+}]_0= 4\times10^{-3}$ M; $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
6- $[Mn^{2+}]_0= 3\times10^{-3}$ M; $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
7- $[Mn^{2+}]_0= 2\times10^{-3}$ M; $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
8- $[Mn^{2+}]_0= 1\times10^{-3}$ M; $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
9- $[IO_3^-]_0= 7.3325\times10^{-5}$ M;
10- $[IO_3^-]_0= 5.5\times10^{-5}$ M;
11- $[IO_3^-]_0= 3.666\times10^{-5}$ M;
12- $[IO_3^-]_0= 1.839\times10^{-5}$ 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):

$[I_2]_0 = 9.7714\times10^{-5}$ M;
$[Ce^{3+}]_0= 3.2\times10^{-2}$ M;
$[HClO_4]_0= 4.24\times10^{-3}$ M.

Table 2

The volumes of initial solutions.

	Solution volume, mL			
Prepared solution	*$V(I_2)$*	*$V(Ce^{3+})$*	*$V(HClO_4)$*	*$V(H_2O)$*
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 λ= 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.

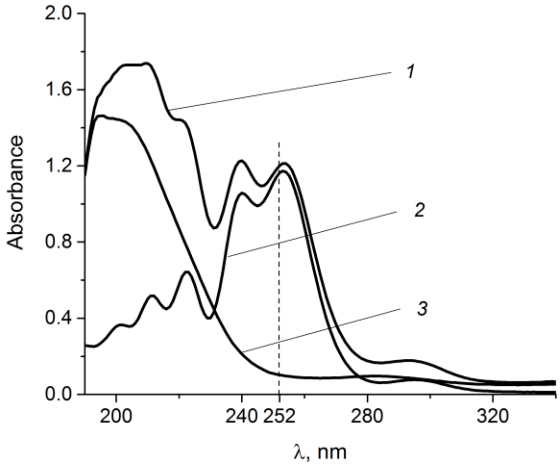

Figure 6. Spectra of Ce^{3+} and I_2 and of the mixture ($Ce^{3+}+I_2$).
1- $[Ce^{3+}]_0= 2\times10^{-3}$ M; $[I_2]_0= 7.643\times10^{-5}$ M;
2- $[Ce^{3+}]_0= 2\times10^{-3}$ M;
3- $[I_2]_0= 7.643\times10^{-5}$ M;

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.

$$I_2 + I^- \rightleftarrows I_3^- \qquad K_4, k_4 \qquad (4)$$

$$I_3^- + Ce^{3+} \rightleftarrows [CeI_3]^{2+} \qquad K_5, k_5 \qquad (5)$$

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):

$[I_2]_0= 7.9156\times10^{-5}$ M;
$[I^-]_0= 1.205\times10^{-2}$ M;
$[HClO_4]_0= 4.24\times10^{-3}$ M;
$[Ce^{3+}]_0= 5.3333\times10^{-3}$ M;
$[Ce^{3+}]_0= 5.3333\times10^{-4}$ M.

Table 3

The volumes of initial solutions*.

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

**The concentrations in cuvettes were:*
$[I_2]= 7.9156\times10^{-5}$ M (8/12)= 5.277×10^{-5} M;
$[I^-]=1.205\times10^{-2}$ M (8/12)= 8.0333×10^{-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:

$[I_2]$= 7.763×10^{-6} M;
$[I^-]$= 7.9883×10^{-3} M;
$[I_3^-]$= 4.5007×10^{-5} M.

With these equilibrium concentrations and molar extinction coefficients $\varepsilon(I_3^-$, 351 nm$)$= 26400 L mol^{-1}·cm^{-1}; $\varepsilon(I_2$, 351 nm$)$= 18 L mol^{-1}·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 λ= 351 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 $[Ce^{3+}]$= 5.3333×10^{-4} M. Average values on the horizontal (0-50 s) are: 1.1687; 1.1769; 1.1728 (Solution 2);
3. The same for $[Ce^{3+}]$= 5.3333×10^{-3} 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).

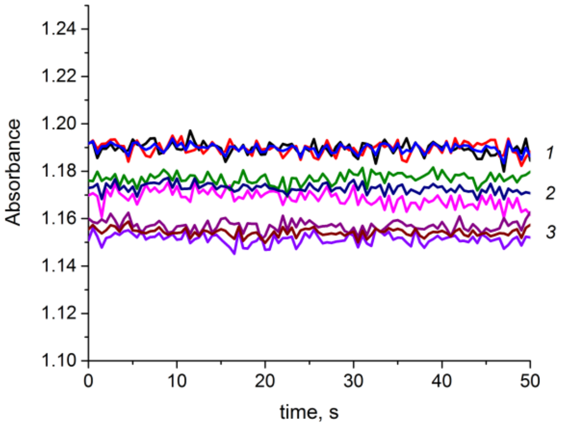

Figure 7. Spectra of solutions *vs* time at λ= 351 nm. *1*-Solution 1, *2*- Solution 2, *3*- Solution 3.

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 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-3} M$)$= 1.1514 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-4}M$)$= 1.1687	$\varepsilon(CeI_3^{2+})$= 26399.96 L mol^{-1}·cm^{-1} K_5= -0.000054 $[CeI_3^{2+}]$= -18259 M $[I_3^-]$= 18253 M	These values have no physical meaning.
2	$A_{exp.}$= 1.1896 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-3} M$)$= 1.1569 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-4} M$)$= 1.1769	$\varepsilon(CeI_3^{2+})$= 21727 L mol^{-1}·cm^{-1} K_5= 909.91 $[CeI_3^{2+}]$= 1.512×10^{-5} M $[I_3^-]$= 18253= 3.208×10^{-5} M	These values suggest the formation of a complex ion, CeI_3^{2+}.
3	$A_{exp.}$= 1.1896 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-3} M$)$= 1.1541 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-4} M$)$= 1.1728	$\varepsilon(CeI_3^{2+})$= 26400+10.744*i* (complex number) K_5= 1.2×10^{-4} - 5.854×10^{-7}*i* $[CeI_3^{2+}]$= 8315.9 +37.08*i* $[I_3^-]$= -8315.8 - 33,62*i*	These values have no physical meaning.
4	$A_{exp.}$= 1.1896 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-3} M$)$= 1.1514 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-4} M$)$= 1.1769	$\varepsilon(CeI_3^{2+})$= 21572 L mol^{-1}·cm^{-1} K_5= 706 $[CeI_3^{2+}]$= 1.25×10^{-5} M $[I_3^-]$= 3.42×10^{-5} 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 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-3} M$)$= 1.1478 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-4} M$)$= 1.1671	$\varepsilon(CeI_3^{2+})$= 26391.96 L mol^{-1}·cm^{-1} K_5= -0.000068 $[CeI_3^{2+}]$= 14548 M $[I_3^-]$= 14543 M	These values have no physical meaning.
2	$A_{exp.}$= 1.1871 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-3} M$)$= 1.1560 $A_{exp.}(Ce^{3+}$; 5.3333×10^{-4} 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 L mol^{-1}·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):

$[IO_3^-]_0$= 1.463×10^{-4} M;
$[I^-]_0$= 8.778×10^{-4} M;
$[HClO_4]_0$= 1.60×10^{-3} M;
$[Ce^{3+}]_0$= 8.0×10^{-3} M.

Also, we considered the following values:

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

The result of numerical integration is given in Figure 8.

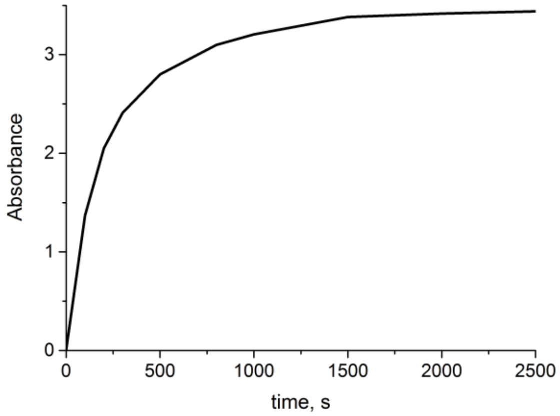

Figure 8. Absorbance calculated by numerical integration.

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.

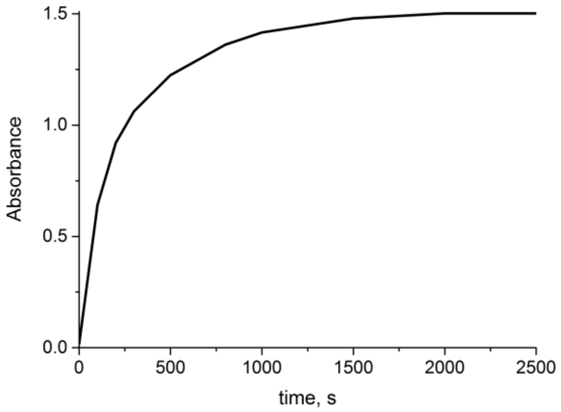

Figure 9. Absorbance calculated in absence of reaction Eq.(5).

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.

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References

1. Belousov, B.P. Periodically acting reaction and its mechanism. Sbornik Referatov po Radiatsionnoi Meditsine, 1958, Moscow: Medgiz, 1959, pp. 145-146 (in Russian). http://www.medlit.ru
2. Zhabotinsky, A.M. Oscillatory processes in biological and chemical systems. Symposium proceedings; Nauka: Moscow, 1967, 445 p.

(in Russian). http://iflorinsky.psn.ru/Molchanov/Editor/Oscillation_Processes-1967.pdf
3. Briggs, T.S.; Rauscher, W.C. An oscillating iodine clock. Journal of Chemical Education, 1973, 50(7), p. 496.
DOI: 10.1021/ed050p496
4. Bray, W.C. A periodic reaction in homogeneous solution and its relation to catalysis. Journal of the American Chemical Society, 1921, 43(6), pp. 1262-1267.
DOI: 10.1021/ja01439a007
5. Liebhafsky, H.A. Reactions involving hydrogen peroxide, iodine and iodate ion. III. The reduction of iodate ion by hydrogen peroxide. Journal of the American Chemical Society, 1931, 53(3), pp. 896-911.
DOI: 10.1021/ja01354a010
6. Noyes, R.M.; Field, R.; Koros, E.; Oscillations in chemical systems. I. Detailed mechanism in a system showing temporal oscillations. Journal of the American Chemical Society, 1972, 94(4), pp. 1394-1395.
DOI: 10.1021/ja00759a080
7. Bourceanu, G.; Bourceanu, M.; Birzu, A.; Joulain, P. A new method to obtain the periodic-chaotic sequence in the oscillating reactions. Revue Roumaine de Chimie, 1998, 43(9), pp. 841-848. http://revroum.lew.ro
8. Cooke, D.O. The hydrogen peroxide-iodic acid-manganese(II)-acetone oscillating system: further observations. International Journal of Chemical Kinetics, 1980, 12(10), pp. 683-689. DOI: https://doi.org/10.1002/kin.550121003
9. Bourceanu, M.; Birzu, A.; Bourceanu, G. Study of the stability systems with a periodical behaviour of limit cycle type. I. Experimental studies. Revue Roumaine de Chimie, 2003, 48(7), pp. 527-533. http://revroum.lew.ro
10. Bourceanu, M.; Birzu, A.; Bourceanu, G. Study of the stability systems with a periodical behaviour limit cycle type. II. Reaction and mathematical models. Revue Roumaine de Chimie, 2003, 48(7), pp. 535-541. http://revroum.lew.ro
11. Onel, L.; Bourceanu, G.; Bitter, I; Wittmann, M.; Noszticzius, Z. Uncatalyzed reactions in the classical Belousov-Zhabotinski system. 2. The malonic acid-bromate reaction in acidic media. The Journal of Physical Chemistry A, 2006, 110(3), pp. 990-996.
DOI: 10.1021/jp055259o
12. Schmitz, G. Oscillations maintained in a homogeneous chemical system. Journal de Chimie Physique et de Physico-Chimie Biologique, 71, 1974, pp. 689-692. (in French).
DOI: https://doi.org/10.1051/jcp/1974710689
13. Schmitz, G. Kinetics of Bray's reaction. The Journal of Physical Chemistry, 1987, 84, pp. 957-965. (in French).
DOI: https://doi.org/10.1051/jcp/1987840957.
14. Schmitz, G. Kinetics and mechanism of the iodate-iodide reaction and other related reactions. Physical Chemistry Chemical Physics, 1999, 1(8), pp. 1909-1914.
DOI: http://dx.doi.org/10.1039/A809291E
15. Schmitz, G. Effects of oxygen on the Bray–Liebhafsky reaction. Physical Chemistry Chemical Physics, 1999, 1(19), pp. 4605-4608.
DOI: http://dx.doi.org/10.1039/A904722K
16. Schmitz, G. Kinetics of the Dushman reaction at low I^- concentrations. Physical Chemistry Chemical Physics, 2000, 2(18), pp. 4041-4044. DOI: http://dx.doi.org/10.1039/B003606O
17. Schmitz, G. The oxidation of iodine to iodate by hydrogen peroxide. Physical Chemistry Chemical Physics, 2001, 3(21), pp. 4741-4746.
DOI: http://dx.doi.org/10.1039/B106505J
18. Schmitz, G. Inorganic reactions of iodine(+1) in acidic solutions. International Journal of Chemical Kinetics, 2004, 36(9), pp. 480-493.
DOI: https://doi.org/10.1002/kin.20020
19. Kolar-Anic, Lj.; Cupic, Z.; Anic, S; Schmitz, G. Pseudo-steady states in the model of the Bray–Liebhafsky oscillatory reaction. Journal of the Chemical Society, Faraday Transactions, 1997, 93(12), pp. 2147-2152.
DOI: http://dx.doi.org/10.1039/A608564D
20. Sevcik, P.; Kissimonova, K.; Adamcikova, L. Oxygen production in the oscillatory Bray−Liebhafsky Reaction. The Journal of Physical Chemistry A, 2000, 104(17), pp. 3958-3963.
DOI: 10.1021/jp993156y
21. Kissimonova, K.; Valent, I.; Adamcikova, L.; Sevcik, P. Numerical simulations of the oxygen production in the oscillating Bray–Liebhafsky reaction. Chemical Physics Letters, 2001, 341(3-4), pp. 345-350. DOI: https://doi.org/10.1016/S0009-2614(01)00486-9
22. Cooke, D.O. Iodine concentration behaviour of the hydrogen peroxide-iodic acid- manganese(II) - malonic acid oscillating system. Inorganica Chimica Acta, 1979, 37, pp. 259-265. DOI: https://doi.org/10.1016/S0020-1693(00)95555-5
23. Cooke, D.O. On the effect of copper (II) and chloride ions on the iodate-hydrogen peroxide reaction in the presence and absence of manganese(II). International Journal of Chemical Kinetics, 1980, 12(10), pp. 671-681.
DOI: https://doi.org/10.1002/kin.550121002
24. Cooke, D.O. The hydrogen peroxide-iodic acid-manganese(II)-acetone oscillating system: further observations. International Journal of Chemical Kinetics, 1980, 12(10), pp. 683-698.
DOI: https://doi.org/10.1002/kin.550121003
25. Dushman, S. The rate of the reaction between iodic and hydriodic acids. The Journal of Physical Chemistry, 1904, 8(7), pp. 453-482.
DOI: 10.1021/j150061a001
26. Schmitz, G.; Bourceanu, G.; Ungureanu, I. Effects of Ce(III) and Mn(II) on the Dushman reaction and simulations of the Briggs–Rausher reaction. Reaction Kinetics, Mechanism and Catalysis, 2018, 123(1), pp. 81-92.
DOI: 10.1007/s11144-017-1264-1

27. Asmus, E.; Kraetschi, J. The 2,3,7-trihydroxy-9-pyridylisoxanthenone- (6) and their complexes with antimony and titanium. Zeitschrift für analytische Chemie, 1966, 216, 4, pp. 391-405.
    DOI: https://doi.org/10.1007/BF00512836
28. Ostromisslensky, I. About a new method of analysis based on the law of mass action of some binary compounds. Berichte der Deutschen Chemischen Gesellschaft**,** 1911, 44, pp. 268-273 (in German).
29. Job, P. Formation and stability of inorganic complexes in solution. Annali di Chimica Applicata, 1928, 9, pp. 113-203.
30. Mayer, S.W.; Schwartz, S.D. The association of cerous ion with iodide, bromide and fluoride ions. Journal of the American Chemical Society, 1951, 73(1), pp. 222-224.
    DOI: 10.1021/ja01145a074