

Electrometric studies on formation of cerium vanadates as a function of pH

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Abstract: The precise nature of the reaction between nitric acid and sodium *ortho*-vanadate solutions has been studied by means of electrometric techniques involving potentiometric and conductometric titrations. The well defined inflections and breaks in the titration curves confirm the existence of the anions, *pyro*-V₂O₇⁴⁻, *meta*-VO₃⁻ and *poly*-H₂V₁₀O₂₈⁴⁻ corresponding to the ratios of VO₄³⁻:H⁺ as 1:1, 1:2 and 1:2.6 in the neighborhood of pH 10.5, 7.4 and 3.6, respectively. The interaction of cerium(III) nitrate with sodium vanadate solutions, at specific pH levels 12.4, 10.5, 7.4 and 3.6 was also studied by potentiometric and conductometric titrations between the reactants. The end-points obtained from the sharp inflections in the titration curves provide definite evidence for the formation and precipitation of cerium *ortho*-Ce₂O₃.V₂O₅, *pyro*-2Ce₂O₃.3V₂O₅ and *meta*-Ce₂O₃.3V₂O₅ vanadates in the neighborhood of pH 7.4, 6.2 and 4.8, respectively. Analytical investigations on the precipitates formed confirm the results of the electrometric study.

Keywords: vanadates; cerium vanadates; electrometry.

Introduction

The chemistry of vanadium is very prominent in both biological and industrial systems [1]. Besides this, a new interest in the chemistry of vanadium has developed during the last decades [1,2]. This has arisen in part from antiviral, including anti-AIDS activity of vanadates and their interaction with biological molecules like proteins [3,4]. Vanadium also exhibits catalytic properties in an extensive variety of chemical reactions. These include the use of vanadium oxide as catalyst in the following: sulfur dioxide to the trioxide, the sulfonation of aromatic hydrocarbons or of pyridine, the reduction of olefines; the oxidation of hydroiodic acid by hydrogen peroxide, of sugar by nitric acid,

of alcohol by air, of stannous salts by nitric acid, of cyclic organic compounds by hydrogen peroxide, of naphthalene by air, and the reduction of aromatic hydrocarbons by hydrogen [5]. A number of recent studies have shown that vanadium oxide catalyst is very promising in oxidative dehydrogenation of alkanes but its activity and selectivity depends on the manner in which the catalyst is pretreated [6-10]. The structure of the vanadia is a very important factor [8,10]. Khodakov et al [11] have recently determined that the oxidative dehydrogenation rates of propane increase as the size of poly-vanadate domain increases. Efforts aimed at relating the structures of the vanadium species to its catalytic activity and selectivity suggest that the catalytic performance depend on the type of structure, bond

length and distance between active and selective sites [2,12-15].

In highly alkaline solution, pH >14, vanadium(V) exists as a tetrahedral VO_4^{3-} anion [16]. On acidification the aqueous solutions turn from colorless to orange-yellow polymeric species. A survey of literature suggests the occurrence of a series of alkali metal vanadates having the ratio of $\text{Na}_2\text{O}:\text{V}_2\text{O}_5$ as 3:1, 2:1, 1:1, 1:2, 1:2.5, 1:3, 2:3, etc. in solution under different conditions [5,17]. The existence of so many polymeric species seems to be doubtful; moreover, there is a great variance in the results published by earlier workers which allows no satisfactory interpretation of the mechanism of the condensation process. A further verification of the vanadate system seems very desirable with a view to rationalizing the conflicting details of the previous workers by employing electrometric techniques, which have provided more conclusive evidences on such systems [18-20]. The knowledge on the formation of different species under different conditions will help in the explanation of the catalytic performance of vanadium and may be a key to understanding the catalytic mechanism. In an earlier publication the results of pH change by HCl on solution of Na_3VO_4 , and composition of nickel vanadates have been reported [21]. The results obtained on pH change of Na_3VO_4 by HNO_3 , and on formation of different vanadates of cerium(III) are presented here.

Experimental

V_2O_5 , NaOH, $\text{Ce}(\text{NO}_3)_3$, HNO_3 and ethanol of extra-pure grade were used and their solutions were prepared with deionized distilled water. The solution of sodium *ortho*-vanadate Na_3VO_4 was prepared by digesting one mole of V_2O_5 in boiling solution of NaOH containing six moles of it.

pH measurements were carried out on Metrohm Herisau pH-meter using Scott Gerate glass combination electrode. Conductance values were recorded by employing a Metrohm conductometer. A series of pH and conductometric titrations was carried out between sodium *ortho*-vanadate in concentrations $\geq 10^{-4}\text{mol l}^{-1}$ and nitric acid using same concentration of the reactants in each

technique. All observations were taken at the state of chemical equilibrium. For attaining the equilibrium state the titrations were performed by heating the solution after each addition of titrant and cooling to 25°C before taking observations. All care was taken for maintaining concentration of the solution contents unaltered during the heating operation. The achievement of constant values of pH and conductance required about 30 seconds boiling after each addition of the titrant for the formation of *pyro*-vanadate, whereas the time needed for attaining the state of chemical equilibrium for the formation of *meta*- and *poly*-vanadate was 1 minute and 2.5 minutes, respectively. The curves were plotted between pH and corrected conductance *versus* volume of acid used.

Cerium(III) vanadates

The formation of cerium vanadates was investigated by the action of cerium(III) nitrate with different vanadate anions at specific pH levels 12.4, 10.5, 7.4 and 3.6 using different concentrations of the reactants. For this purpose, the variations of pH of Na_3VO_4 solutions were obtained by progressive additions of determined quantities of nitric acid. A series of pH and conductometric titrations was performed by direct and reverse methods, i.e. when cerium nitrate solution from the microburette was added to sodium vanadate solution and vice-versa. 25 mL of ethanolic solution (20%) was taken in the cell, which was thermostated at $25 \pm 0.1^\circ\text{C}$.

The precipitates obtained at the end-points of titrations between cerium nitrate and sodium vanadates were also analyzed to substantiate the electrometric results. The different cerium vanadates were prepared by mixing stoichiometric amounts of cerium nitrate solution with the respective sodium vanadate solutions. The precipitates obtained were washed several times with 20% ethanolic solution and dried in a vacuum desiccator for 40 h. A known amount (ca 2 g) of each of the above precipitates was dissolved in a minimum quantity of nitric acid and then analyzed quantitatively for cerium by ferrous ammonium sulfate [22a] and vanadium as silver vanadate [22b]. From the proportions of cerium and vanadium in the compounds thus obtained their composition was established.

Results and discussion

In an earlier publication [21] Prasad *et al.* have shown that the addition of HCl to Na_3VO_4 solutions at room temperature causes the formation of various poly-anions of uncertain compositions, but when the solutions were heated after each addition of titrant the three different vanadates viz. *Pyro* ($\text{Na}_4\text{V}_2\text{O}_7$), *meta* (NaVO_3) and *poly* ($\text{Na}_4\text{H}_2\text{V}_{10}\text{O}_{28}$) are formed in the neighborhood of pH 10.5, 7.4 and 3.6, respectively. In the present study related to the formation of different cerium(III) vanadates as a function of pH, by the interaction of cerium(III) nitrate with alkali vanadates at specific pH levels, the use of HNO_3 for pH variation was considered more appropriate because it involves the same cation (nitrate) as present in cerium nitrate. Hence it was considered of interest to ascertain whether similar alkali vanadate species are formed by the action of HNO_3 with Na_3VO_4 solutions. A series of glass electrode and conductometric titrations of Na_3VO_4 solution with HNO_3 were therefore performed. A typical titration curve between pH observed and volume of the acid added is demonstrated in Fig 1 (curve 1). The three inflections in the titration curve at the molar ratios of $\text{H}^+:\text{VO}_4^{3-}$ as 1, 2 and 2.6 corresponding to the stoichiometry for the formation of *pyro*- V_2O_7 , *meta*- VO_3^- and *poly*- $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ anions confirm the formation of the same three vanadate species as obtained by our previous study with HCl [21]. The conductometric titrations between the acid and Na_3VO_4 also confirm the formation of the same species (Fig. 1, curve 2). The stoichiometry obtained by this electrometric study did not correspond to confirm the existence of $\text{V}_6\text{O}_{16}^{2-}$ as reported by Sen Gupta [23] and Russel and Salmon [24], and of V_3O_8^- , $\text{V}_5\text{O}_{14}^{3-}$, $\text{V}_{10}\text{O}_{28}^{6-}$ and $\text{HV}_{10}\text{O}_{28}^{5-}$ as reported by Bystrom and Evans [25] and Naumann and Hallada [26].

The stepwise condensation of *ortho*-vanadate to *poly*-vanadate can be represented by the following set of equations:

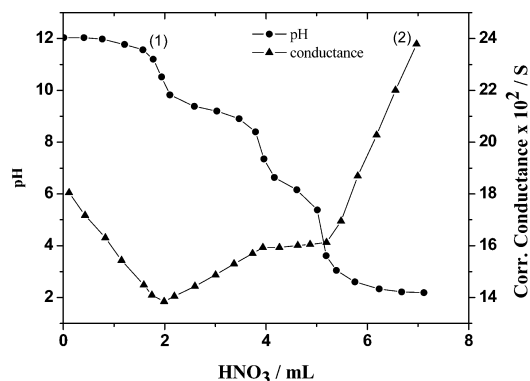
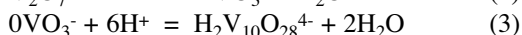
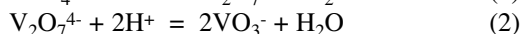
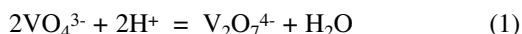
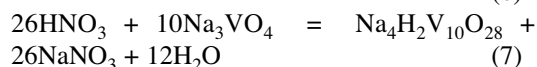
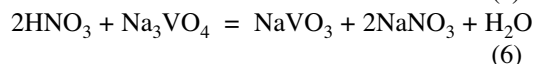
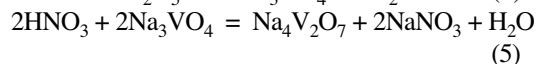
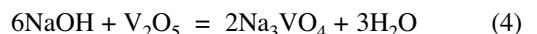


Figure 1. pH (1) and conductometric (2) titrations. 25 mL of M/50 Na_3VO_4 titrated with M/5 HNO_3 .

The above studies show that the addition of acid to sodium *ortho*-vanadate under suitable conditions causes the formation of three different sodium vanadates containing the anions *Pyro*- $\text{V}_2\text{O}_7^{4-}$, *meta*- VO_3^- and *poly*- $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$. Therefore it was considered of interest to ascertain whether similar salts of heavy metals may be precipitated as a result of double decomposition. The reactions of Ce(III) with alkali vanadates have therefore been studied by means of potentiometric and conductometric titrations. A solution of sodium *ortho*-vanadate was prepared by digesting one mole of V_2O_5 in boiling solution of NaOH containing six moles of it. The solutions of sodium *pyro*-, *meta*- and *poly*-vanadates were prepared by adding one, two and 2.6 moles of HNO_3 to one mole of Na_3VO_4 at 100°C.



Formation of cerium(III) vanadates

A series of direct and reverse electrometric titrations between the solutions of cerium(III) nitrate (pH 3.5) and different sodium vanadates at specific pH levels 12.4, 10.5, 7.4 and 3.6 were

Table 1. Summary of results of electrometric study on formation of cerium vanadates.
Volume of titre solution taken in the cell = 25 ml

Molarity of solutions		Equivalence points (ml)			Formula supported
		Calculated	Observed from		
			pH	Conductance	
Ce(NO ₃) ₃	Na ₃ VO ₄				
<i>Direct ortho-vanadate titrations</i> (Fig. 2)					Ce ₂ O ₃ .V ₂ O ₅
M/10	M/125	2.00	2.00	2.00	
M/40	M/450	2.22	2.22	2.20	
M/100	M/1100	2.27	2.25	2.25	
<i>Reverse ortho-vanadate titrations</i>					Ce ₂ O ₃ .V ₂ O ₅
M/125	M/10	2.00	2.00	2.00	
M/450	M/40	2.22	2.22	2.20	
M/1100	M/100	2.27	2.25	2.25	
Ce(NO ₃) ₃	Na ₄ V ₂ O ₇				
<i>Direct pyro-vanadate titrations</i> (Fig. 3)					2Ce ₂ O ₃ .3V ₂ O ₅
M/10	M/150	2.22	2.20	2.20	
M/40	M/550	2.42	2.40	2.42	
M/100	M/1600	2.08	2.08	2.05	
<i>Reverse pyro-vanadate titrations</i>					2Ce ₂ O ₃ .3V ₂ O ₅
M/80	M/10	2.34	2.35	2.35	
M/450	M/50	2.08	2.10	2.10	
M/1750	M/200	2.14	2.15	2.16	
Ce(NO ₃) ₃	NaVO ₃				
<i>Direct meta-vanadate titrations</i> (Fig. 4)					Ce ₂ O ₃ .3V ₂ O ₅
M/10	M/40	2.08	2.08	2.10	
M/40	M/150	2.22	2.20	2.20	
M/100	M/350	2.38	2.40	2.40	
<i>Reverse meta-vanadate titrations</i>					Ce ₂ O ₃ .3V ₂ O ₅
M/350	M/10	2.14	2.14	2.15	
M/1000	M/30	2.25	2.25	2.30	
M/1850	M/60	2.43	2.45	2.45	

realized and the results obtained from the stoichiometric end-points are summarized in Table 1.

Only three Figures illustrating the formation of cerium *ortho*-vanadate (Fig. 2), *pyro*-vanadate

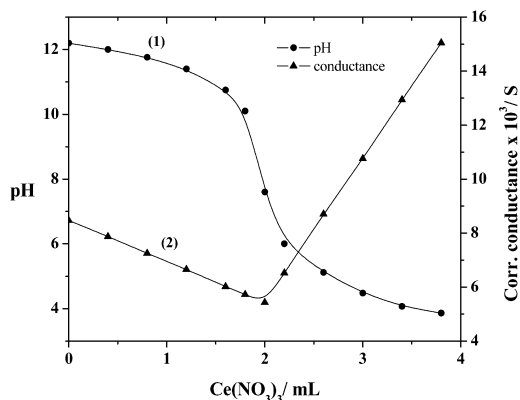


Figure 2. Cerium *ortho*-vanadate titrations. 25 mL of M/125 Na₃VO₄ titrated with M/10 Ce(NO₃)₃.

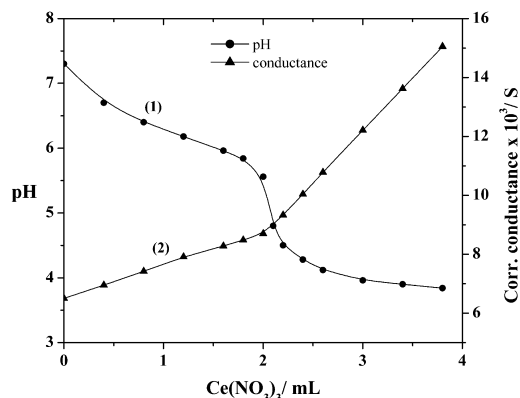


Figure 4. Cerium *meta*-vanadate titrations. 25 mL of M/40 NaVO₃ titrated with M/10 Ce(NO₃)₃.

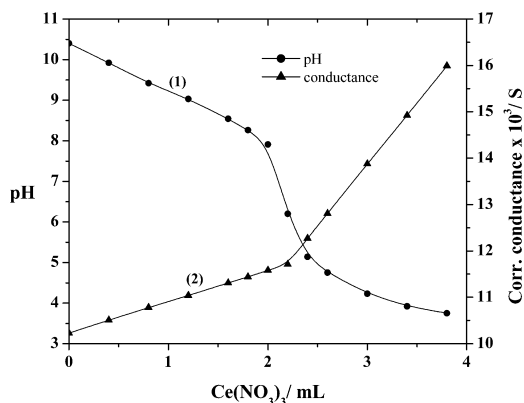


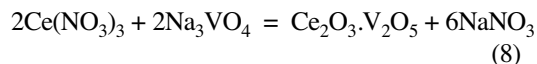
Figure 3. Cerium *pyro*-vanadate titrations. 25 mL of M/150 Na₄V₂O₇ titrated with M/10 Ce(NO₃)₃.

(Fig. 3) and *meta*-vanadate (Fig. 4) by direct titrations have been given for the sake of brevity. The precipitates obtained at the end-points of the electrometric titrations between cerium nitrate and sodium vanadates were also analyzed to substantiate the electrometric results. The analytical results are presented in Table 2.

Cerium ortho-vanadate

Using different concentrations of cerium(III) nitrate (pH 3.5) and Na₃VO₄ (pH 12.4) a

series of pH titrations was carried out. Fig. 2 (curve 1) shows the changes occurring in H⁺ ion concentration when the solution of Na₃VO₄ was titrated with cerium nitrate solution. It may be noted that the first addition of acidic cerium nitrate solution to the alkaline vanadate results in gradual decrease in pH to about 11.0. Further addition of the titrant brings about steep fall in pH value at a point where the molar ratio of Ce³⁺:VO₄³⁻ is 1:1 (see Table 1), corresponding to the stoichiometry for the precipitation of cerium *ortho*-vanadate Ce₂O₃.V₂O₅ in the vicinity of pH 7.4. The reaction can be represented as follows:



In the case of conductometric titrations of the solution of Na₃VO₄ with cerium nitrate (Fig. 2, curve 2) the conductance value decreases gradually in the beginning of the titration (due to removal of the VO₄³⁻ ions in the form of a precipitate), but after completion of the reaction, conductance starts rising with the increase in ionic concentration at the ratio Ce³⁺:VO₄³⁻ as 1:1, which coincides with the stoichiometry indicated by the pH study.

Cerium pyro-vanadate

Fig. 3 (curve 1) illustrates the changes

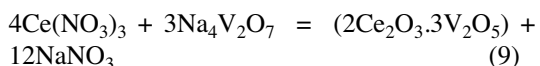
Table 2. Summary of analytical results of the precipitates of cerium vanadates

Proposed formula of the compound	Mode of analysis	Analysis %: Found (Calculated)	
		Ce	V
<i>Analysis of cerium ortho-vanadate precipitates</i>			
Ce ₂ O ₃ .V ₂ O ₅	Direct ^a	54.89(54.94)	20.01(19.97)
	Reverse ^b	54.97	19.94
<i>Analysis of cerium pyro-vanadate precipitates</i>			
2Ce ₂ O ₃ .3V ₂ O ₅	Direct	46.58(46.62)	25.45(25.43)
	Reverse	46.67	25.40
<i>Analysis of cerium meta-vanadate precipitates</i>			
Ce ₂ O ₃ .3V ₂ O ₅	Direct	32.02(32.07)	35.04(34.98)
	Reverse	32.11	34.95

^a Cerium nitrate solution added to sodium *ortho*-vanadate solution.

^b Sodium *ortho*-vanadate solution added to cerium nitrate solution.

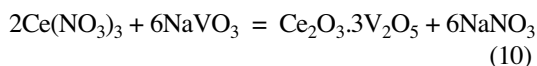
occurring when cerium nitrate solution (pH 3.5) was added from the microburette to the solution of sodium *pyro*-vanadate (pH 10.5). The titration curve shows a well-defined inflection at the equivalence point, where the molar ratio Ce³⁺:V₂O₇⁴⁻ is 4:3, corresponding to the stoichiometry for the formation of cerium *pyro*-vanadate 2Ce₂O₃.3V₂O₅, in the neighborhood of pH 6.2. The reaction can be represented by the following equation:



Employing similar concentrations of the reactants a series of conductometric titrations between the solution of cerium nitrate and sodium *pyro*-vanadate was carried out. Well-defined breaks in the titration curves (Fig. 3, curve 2) were obtained at 4:3 molar ratio of Ce³⁺:V₂O₇⁴⁻, which confirm the formation of the identical compound, cerium *pyro*-vanadate 2Ce₂O₃.3V₂O₅. In these titrations, when cerium nitrate solution was added from the microburette to sodium *pyro*-vanadate solution in the titration cell, a gradual increase in conductance value was observed until the stoichiometric end-point, after which the conductance increased sharply with the increase in ionic concentration.

Cerium meta-vanadate

Using different concentrations of cerium nitrate (pH 3.5) and sodium *meta*-vanadate (pH 7.4) a series of pH and conductometric titrations (Fig. 4) was carried out. The breaks and inflections in the titration curves at the stoichiometric end-point corresponding to the molar ratio Ce³⁺:VO₃⁻ as 1:3, suggest the formation of cerium *meta*-vanadate Ce₂O₃.3V₂O₅ in the neighborhood of pH 4.8, according to the equation:



Similar studies using the different sodium vanadate solutions as titrant (reverse titrations) was also realized (Table 1). The breaks and inflections in titration curves confirmed the results obtained by the direct titrations. As the curves were normal in shape and nature the figures of these titrations are not presented for the sake of brevity.

The reaction between cerium nitrate and sodium *poly*-vanadate Na₄H₂V₁₀O₂₈ (pH 3.6) was also studied, but the curves did not exhibit any appreciable break or inflection at the stoichiometric end-point. This may be ascribed to too small difference in the pH values of the reactants for getting inflection in the potentiometric

titration curves and the presence of NaNO_3 in appreciable amount in *poly*-vanadate solution (see Eqn. 7) for preventing occurrence of breaks in the conductometric titration curves.

The precipitates obtained at the end-points of the titrations of cerium nitrate with sodium vanadates were analyzed by classical methods. Cerium was determined volumetrically by ferrous ammonium sulfate and vanadium gravimetrically as silver vanadate, and oxygen was calculated from the difference in the percentage. From the proportions of cerium, vanadium and oxygen in the compounds thus obtained, their compositions were established, which were found to be the same as obtained by the electrometric study (Table 2).

It was noted that the presence of ethanol in cerium vanadate titrations slightly improves the end-points and gives better results as it decreases solubility of the precipitates formed and minimizes hydrolysis and adsorption. 20% ethanolic medium was therefore employed for the entire course of the study. A thorough stirring in the vicinity of the end-point had a favorable effect.

As the structure of these compounds is not known these are represented as double oxides, the manner, which is usually adopted for such, compounds [27,28].

Conclusions

The results of the electrometric investiga-

tions on the system nitric acid and sodium *ortho*-vanadate, at the specific concentration level of $\geq 10^{-4}\text{M}$, suggest the formation of *para*- V_2O_7 , *meta*- VO_3^- and *poly*- $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ vanadate anions in the neighborhood of pH 10.5, 7.4 and 3.6, respectively. The results obtained by this study are similar to those obtained by using hydrochloric acid [21]. The electrometric and analytical investigations on the interaction of cerium(III) nitrate with sodium vanadate at specific pH levels 12.4, 10.5 and 7.4 provide cogent evidence for the formation and precipitation of cerium *ortho*- $\text{Ce}_2\text{O}_3 \cdot \text{V}_2\text{O}_5$, *pyro*- $2\text{Ce}_2\text{O}_3 \cdot 3\text{V}_2\text{O}_5$ and *meta*- $\text{Ce}_2\text{O}_3 \cdot 3\text{V}_2\text{O}_5$ vanadates in the vicinity of pH 7.4, 6.2 and 4.8, respectively. The composition of heavy metal vanadates can thus be represented by the general formula $n\text{M}_2\text{O}_3 \cdot 3\text{V}_2\text{O}_5$ for a trivalent metal and the proportion of the metal oxide in the vanadate obtained decreases with the pH of the medium. Therefore by controlling the pH of the medium one can control the composition of the vanadate.

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S. Prasad, V. D. Leite, R. A.C. Santana e E. A. Medeiros. Formação de vanadatos de cério(III) em função do pH.

Resumo: A natureza precisa da reação entre soluções de ácido nítrico e de *ortho*-vanadato de sódio foi estudada por técnicas electrométricas envolvendo titulações potenciométricas e condutométricas. As inflexões e degraus bem definidas nas curvas de titulações confirmaram a existencia de anions, *piro*- $V_2O_7^{4-}$, *meta*- VO_3^- e *poli*- $H_2V_{10}O_{28}^{4-}$ correspondendo as razões de $VO_4^{3-}:H^+$ como 1:1, 1:2 e 1:2,6 na vizinhança do pH 10,5; 7,4 e 3,6, respectivamente. A interação entre soluções de nitrato de cério(III) e vanadato de sódio a específicos níveis de pH 12,4; 10,5; 7,4 e 3,6 também foi estudada por titulações potenciométricas e condutométricas entre os reagentes. Os pontos finais obtidos a partir de inflexões nítidas nas curvas de titulações forceram evidências incontestáveis sobre a formação e precipitação de vanadatos *orto*- $Ce_2O_3.V_2O_5$, *piro*- $2Ce_2O_3.3V_2O_5$ e *meta*- $Ce_2O_3.3V_2O_5$ de cério nas proximidades dos valores de pH 7,4; 6,2 e 4,8, respectivamente. Investigações analíticas sobre os precipitados formados confirmam os resultados do estudo eletrométrico.

Palavras-chave: vanadatos; vanadatos de cério; eletrometria.

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