Evaluation of the buffering effect possessed by diluted diammonium hexanitrocerate solutions

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Abstract: *The great scientific interest recently arisen regarding the potential applications of lanthanides, and especially cerium compounds in various technological branches, including alternative energy sources, electrochemical synthesis, corrosion protection, industrial automation, etc. have predetermined the need for detailed investigations on their properties. In this sense, the pH stability of diammonium hexanitrocerate* $(NH_4)_2Ce(NO_3)_6$ *was assessed via systematic potentiometric titrations.*

Key words: *Diammonium hexanitrocerate, pH-stability, titration curves*

INTRODUCTION

The recent environmental regulations in EC [1, 2] and USA [3, 4] have imposed restrictions regarding the use of various substances, for instance compounds of Pb, Cr, Cd, Hg, As, etc. This fact has promoted the recently increased interest to the lanthanides, and especially cerium compounds, since this element is considered as environmentally compliant, non toxic [5], and enough abundant in the Nature [6], as well. Indeed, various Ce-compounds have been investigated for corrosion protection [7 – 15], for alternative energy sources [16, 17], for electrochemical synthesis [18, 19], for elaboration of sensor elements for environmental monitoring and control [20 – 25], etc. Besides, a beneficial effect of Ce(IV) ions on the cross-linking process in sol-gel systems is described by Suegama et al. [26]. Furthermore, the acidic properties of the cerium compounds established during the previous research activities [7, 27, 28], should possess accelerating effect on the sol-gel product formation, due to the stimulation of the indispensable precursor hydrolysis process described by Kozhukharov [29]. Finally, Zacharescu et al. [30] have demonstrated that the precipitation of $Ce(OH)_3$ and/or $Ce(OH)_4$ from aqueous solutions of Ce-compounds provides rather ease methods for nano-material production. All these facts described above, predetermine the necessity for more detailed elucidations on the properties of the cerium compounds, in order to create suitable technological regimes for production of various cerium containing industrial products.

The aim of the present research work is to evaluate pH stability of diluted $(NH_4)_2Ce(NO_3)_6$ solutions, by systematic, potentiometric titration technique.

EXPERIMENTAL

The buffering effect of the aqueous solutions of diammonium hexanitrocerate (anhydrous product of Fluka-Chemica, (Switzerland), Purity > 99.0%) was evaluated by systematic titrations with standardized 0.10 and 0.01M. NaOH solutions, at simultaneous pH recording. The titrant standardization was performed by HCl fixanals, prepared by (Sigma-Aldrich), and the exact values of the NaOH concentrations are shown in Table 1.

Table 1. Approximate and exact NaOH solution concentration values

Titration solutions	Approximate composition	Exact concentration values established by HCl fixanals
Titrant 1	0.01 M NaOH	$9.368x10^{-3}$ M
Titrant 2	0.10 M NaOH	$9.195x10^{-2}$ M

The measurements were performed in triplicate, by titration of 10.00 ml. $(NH_4)_2Ce(NO_3)_6$ solutions with concentrations of 0.10 and 0.01M, respectively. These concentrations were selected on the basis of the experience heaped so far [7, 8, 10 – 14, 27, 28]. The titration curves were acquired on the basis of the experimental data, registered by preliminary calibrated 3505 pH meter, product Jenway (U.K.)., supported by universal glass electrode BA 25 produced by Boeco. ltd. (Germany). For comparison, the measurements were repeated at similar conditions with nitric acid solutions. All the experiments were performed at room temperature.

RESULTS AND DISCUSSIONS

The experimental results have undoubtedly evinced occurrence of buffering effect, in the cases of $(NH_4)_2Ce(NO_3)_6$ solutions, as is shown in the Figure below.

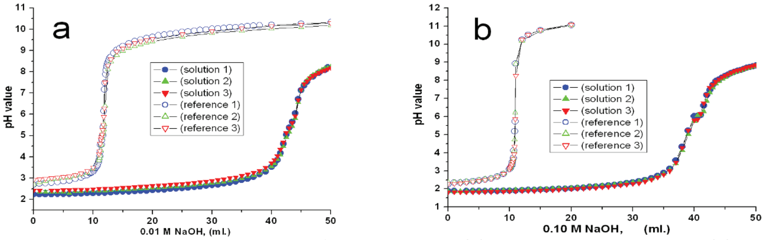

Fig. 1. Titrimetric curves obtained by titration of diluted, 0.01 M (a) and concentrated 0.10 M (b) solutions of the investigated substance $(NH_4)_2Ce(NO_3)_6$ and nitric acid as a reference

Figure 1 reveals that the diammonium hexanitrocerate solutions demand about four times higher quantities of NaOH for equivalent point reaching compared to the respective HNO_3 referent solutions. The definitely acidic character of the diammonium hexanitrocerate solutions is obvious from Fig. 1. Nevertheless, the exact determination of their buffering effect requires mathematical calculations according to equation 1 [31]:

$$B = \frac{N \cdot V}{\Delta pH \cdot V_p}, \qquad (1)$$

Where: B – is the buffering capability of the investigated solution (1/pH); N.V – is the quantity of the added standard solution (mol/l); ΔpH is the pH change rate (/); V_p – is the volume of the investigated solution (10.00 ml. for the present study).

This formula was employed in order to quantify the pH stability of the diammonium hexanitrocerate solutions investigated. The calculations were done on the basis of the expended quantity of titrant for elevation of pH with about a unit from the initial pH value, corresponding to the horizontal domains of the curves shown in Fig. 1. The results are represented in Table 2:

Table 2. Titrant quantities expended for the initial unit of solution pH

Investigated solutions	Referent solution	Initial solution pH			second solution pH value			Expended titrant volume (ml)		
		First	Second	Third	First	Second	Third	First	Second	Third
0.1010 M $(NH_4)_2Ce(NO_3)_6$	Titrant 1	2.24	2.34	2.43	3.18	3.38	3.50	38.50	39.00	39.00
$1.068x10^{-2}$ M $(NH_4)_2Ce(NO_3)_6$	Titrant 2	1.88	1.88	1.83	2.88	2.84	2.79	35.00	35.00	35.00

On the basis of the average values obtained by the data shown in Table 1, and using equation 1, the following buffering capability values were obtained: $B_{av-1.} = 35.63x10^{-3}$ mol/pH unit, whereas for the diluted solution, and $B_{av-2.} = 33.31x10^{-2}$ mol/pH unit. Besides, the values in Table 2 show a great repeatability, enabling elaboration of reliable technological regimes for production of various products, without of addition of supplemental pH - buffers. The high result repeatability is evidently confirmed by the almost complete overlapping among the titration curves in Figure 1. It is worth to mention, the curve inflexions below pH 3 coincide with precipitation of pale yellow Ce(IV) – oxides/hydroxides, as is well described in the literature [7 - 9, 10 - 14, 27, 28, 30, 32 – 35].

CONCLUSIONS

On the basis of the present brief research work, the following inferences were established:

The literature analysis done reveals that both the environmental compatibility, and the high abundance in the nature predetermine continuous intensification of the scientific interest on the lanthanide compounds, and especially – on the cerium ones. Furthermore, the environmental restrictions against the use of hazardous substances in the electrical and electronic industry, additionally favors the increasing scientific interest on the potential application of the Ce-compounds in various industrial branches. The cerium compounds appear to be versatile precursors for preparation of materials for: (i)- corrosion protection in the transport services, (ii)- ingredients of alternative energetic sources, such as Solid Oxide Fuel Cells, (iii)- layer components of environment monitoring and control sensors, (iv)- active electrode elements for the needs of the electrocatalytical chemical synthesis, etc. Finally, the cerium containing substances have revealed peculiar properties, beneficial for the sol-gel synthesis based technologies and even for the nanotechnologies.

The experiments have shown clear acidic buffering effects of the $(NH_4)_2Ce(NO_3)_6$ aqueous solutions. Besides, remarkable repeatability rate was established during the measurements, because the titration curves almost entirely overlap among themselves. Indeed, the numerical data completely confirm the insignificance of the result deviations. The calculations done reveal the pH stability of the 0.01M solution corresponds to about $B_{av-1.}$= $35.63x10^{-3}$ mol/pH unit, whereas for the 0.10 M solution, it is in the range of $B_{av-2.}$= $33.31x10^{-2}$ mol/pH unit, at pH values below pH 3. The investigations reveal that the when $(NH_4)_2Ce(NO_3)_6$ solutions are used as precursors, the addition of pH buffers can be avoided. Further experiments will be performed in order to determine the pH fluctuations with increase of $(NH_4)_2Ce(NO_3)_6$ concentrations and the coinciding precipitation processes.

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