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RESEARCH ARTICLE

Hydroxamic Acids as a Reductometric Titrants: Determination of Cerium in Alloys

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Abstract Hydroxamic acids like acetohydroxamic acid (AHA) and oxalohydroxamic acid (OHA) have been employed as a reductometric titrant for the determination of cerium in 2 N sulphuric acid. Stoichiometry of the reaction is established. One mole of AHA and OHA were found to consume 6.0 and 12.0 equivalents of the oxidant respectively in these reactions. The titre values are obtained by second derivative plots of potentiometric titrations.

Keywords: Stoichiometry, Second derivative Plot, Hydroxamic acids, Equivalents of Oxidant

Introduction

Hydroxamic acids are excellent analytical reagents for organic and inorganic analysis. Extensive works have been carried out on their synthesis[1], complexation with metal ions[2], gravimetry[3], colorimetry[4], kinetics[5-10], spectrophotometry[11] and medical applications[12-15]. Benzohydroxamic acid (BHA) was used as a reductometric titrant for determination of Mn, Cr[16] and Ce, U[17]. The proposed method is based on the reduction property of aliphatic hydroxamic acids such as acetohydroxamic acid (AHA) and oxalohydroxamic acid (OHA).

Cerium is generally found in steels and alloys. It influences the mechanical properties of steels and alloys. It has much significance in various fields such as magnetism, polishing powder, as catalyst for automobile, ceramic technology and nuclear industries[18]. The determination of cerium in cast iron, steels, glass and ceramic materials, control rods used in nuclear industries, *etc.* becomes essential in modern analytical chemical analysis[19]. The reduction of tetravalent cerium proceeds directly to trivalent cerium by a reversible one-electron reaction and thus has an advantage over dichromate and permanganate, with which unstable intermediate stages are encountered.

$$Ce^{+4} + e^{-} \rightarrow Ce^{+3}$$

As an oxidizing agent it is almost as strong as potassium permanganate in acid solution and also has the advantage, over the later, of having stable titre. The redox potential and hence the oxidizing power of ceric cerium is strongly dependent on the concentration and type of the acid used as the medium[20].

Experimental

All titrations were performed using Metrohm 888Titrando-Potentiometric Titrator. This auto titration system consists of a motor-driven titrant dispenser, a mechanical stirrer and electrodes coupled to a pH/ion analyzer and controlled by a personal computer for automatic titration and data acquisition and processing. The titrant from the reservoir was delivered accurately through a calibrated dispenser in the titration vessel. A combination pH electrode, with glass membrane and Ag/AgCl reference electrode was used for these titrations. The glass combination electrodes were calibrated with potassium hydrogen phthalate (pH 4.02), phosphate (pH 6.86) and borax (pH 9.18) buffers.

Reagents

All chemicals used were of AR grade. AHA and OHA were prepared and purified by the literature procedure[21,22]. Solution of ceric ammonium sulphate is prepared by dissolving an accurately weighed quantity of ceric ammonium sulphate in water and solution is standardized[23]. All the solutions were prepared in water twice distilled with alkaline permanganate.

Procedure

10 mL aliquot of Ce(IV) solution containing 10-15 mg cerium was taken in a 100 mL beaker and sufficient standard sulphuric acid solution was added so that the acidity was adjusted to 2 N in a total volume of 50 mL. It was then titrated potentiometrically with standard AHA solution added from a micro burette calibrated to 0.05 mL. Saturated calomel electrode was used as reference electrode and platinum as indicator electrode. The e.m.f. readings were recorded with Metrohm 888 Titrando-Potentiometric Titrator. Titrations in presence of 2 N sulphuric acid were carried out. The same procedure were followed for OHA.

Results and Discussion

The structure of hydroxamic acids such as AHA and OHA are shown in Figure 1. The hydroxamic acids are characterized by Fourier Transform Infra Red Spectroscopy (FTIR). In FTIR spectrum of AHA the broad adsorption bands at 3200 cm^{-1}, is associated with N–H and O–H stretching collectively. So complete overlapping of N–H and O–H peaks resulted in to the 'U' shaped broad adsorption band seen. The stretching at 2850 cm^{-1} represents the C-H stretching in CH_3. The adsorption band at 1631 cm^{-1} is attributable to characteristic C=O stretching of hydroxamic acid (–CONHOH group). The adsorption at 1195 cm^{-1} is associated with C–N stretching, and the two adsorptions at 1039, 1087 cm^{-1} result from the splitting of N–O vibration while absorption at 989 cm^{-1} represents the C-O stretching.

FTIR spectra of OHA represent the absorption band observed at ν_{max} 3263 cm^{-1} arises due to N-H stretching vibration. The OH bonds in crystalline oxalohydroxamic acid are strongly hydrogen bonded and thus the associated vibrational bands are observed at ν_{max} 3184-3074 cm^{-1} and ν_{max} 2862 cm^{-1}. The bands at ν_{max} 1651 cm^{-1} arise due to C=O stretching vibration. The absorption bands at 1531 cm^{-1}, 1444 cm^{-1}, 1226 cm^{-1}, 1099 cm^{-1} and 846 cm^{-1} arises from the vibrations of N-H bending, OH bending, OCN stretching, N-O stretching, and C-NO bending respectively. The observations reveal the presence of –NHOH groups in oxalohydroxamic acid.

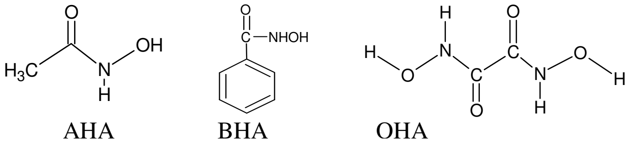

Figure 1. Structures of hydroxamic acid (AHA, BHA and OHA)

Ceric salts have been employed for the oxidation of a variety of organic compounds because of its one-electron change redox reaction[17,20]. During our studies on the oxidation of hydroxamic acids with ceric ammonium sulphate, in sulphuric acid medium; it was observed that the oxidation was rapid at room temperature. The results were recorded by potentiometric titrations. Curves are shown in Figure 2. The first and second derivative curves are shown in Figures 3 & 4. The titre values are obtained by second derivative titration curve. Table 1 shows the number of equivalents per one mole of hydroxamic acids.

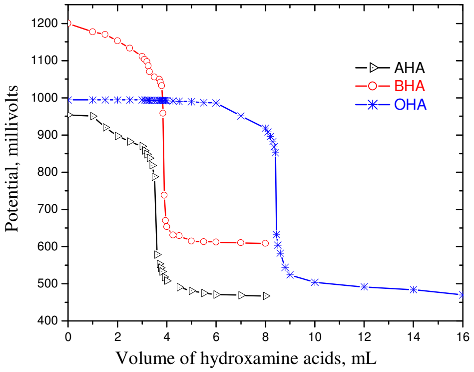

Figure 2. Titration of Ce(IV) with different hydroxamic acid in 2N H_2SO_4 Concentration

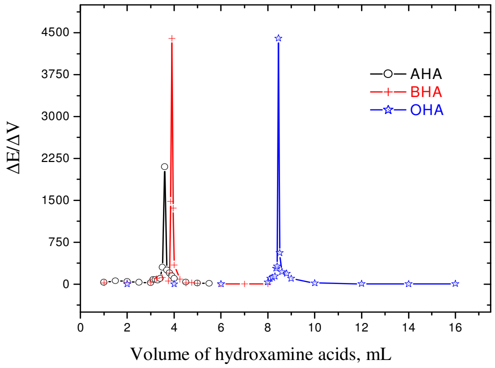

Figure 3. 1st Derivative curve for Ce(IV) with different hydroxamic acids

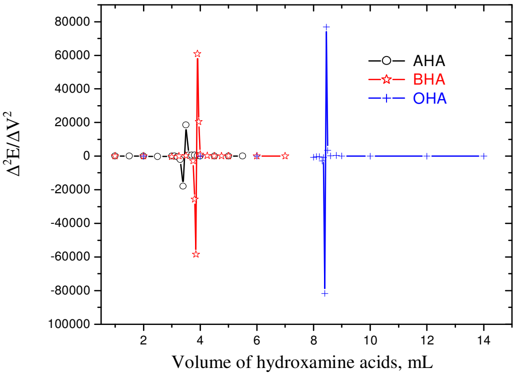

Figure 4. 2nd Derivative curve for Ce(IV) with different hydroxamic acids

Table 1. Ceric oxidation of different hydroxamic acids in 2 N sulphuric acid

S. No.	Volume of Ce(IV), mL	Volume of hydroxamic acids, mL			Equivalents of Ce(IV) per mole of		
		AHA	OHA	BHA[17]	AHA	OHA	BHA[17]
1	05.0	1.68	0.83	1.75	5.95	12.01	5.49
2	10.0	3.33	1.65	3.50	6.00	12.01	5.49
3	15.0	4.99	2.48	5.20	6.01	11.99	5.55
4	20.0	6.65	3.35	7.05	6.01	12.04	5.46
5	25.0	8.35	4.15	8.75	5.98	11.96	5.49
6	30.0	10.0	4.95	10.55	6.00	12.04	5.47

(AHA = 5.042 x 10^{-3} *M, BHA = 5.036 x* 10^{-3} *M, OHA = 5.033 x* 10^{-3} *M, Ce* $(SO_4)_2 \cdot (NH_4)_2 SO_4 \cdot 2H_2O$ *= 9.988 x* 10^{-3} *M,* H_2SO_4 *= 8.2 N, Total volume = 50 mL)*

The effect of sulphuric acid concentration on the reaction was studied in the range of 1 to 6 N. The results are recorded in Table 2. It was observed that the stoichiometry of the reaction remains unchanged in 1 to 4 N acid and 6.0 and 12.0 equivalents of the oxidant were consumed by one mole of AHA and OHA respectively. In subsequent experiments the oxidation studies were made in 2 N sulphuric acid solutions.

Applications

The established stoichiometry of Ce(IV) - AHA and Ce(IV) - OHA reaction in 2 N sulphuric acid medium has been applied for the determination of cerium[19,24]. The proposed method was applied for the determination of cerium in the standard reference materials, *e.g.* Mischmetal (Composition: iron 19%, cerium 38%, lanthanum 22-50%, neodymium 4-17%, praseodymium 4-6%, magnesium 4% and other non-rare earth impurities 0.01-0.5%) and Aluminum-Cerium master alloy (Composition: iron 0.25%, cerium 2-3%, aluminium 89.7-97.7% and other impurities 0.5%).

The determined values of percentage of cerium in these standard materials are in good agreement with the reported values (Table 3).

Table 2. Effect of sulphuric acid concentration on the ceric oxidation of AHA, BHA and OHA

Normality of H_2SO_4, N	Voluem of hydroxamic acid, mL			No. of equivalents of oxidant (per mole of)		
	AHA	OHA	BHA[17]	AHA	OHA	BHA[17]
1	3.454	1.654	3.519	6.01	12.01	5.49
2	3.325	1.656	3.522	6.01	12.00	5.49
3	3.333	1.652	3.518	6.00	12.02	5.49
4	3.333	1.654	3.518	6.00	12.01	5.49
5	3.395	1.699	3.670	5.89	11.69	5.26
6	3.460	1.699	3.730	5.78	11.69	5.18

(AHA, BHA and OHA = 5.016 x 10^{-3} *M, Ce* $(SO_4)_2 \cdot (NH_4)_2SO_4 \cdot 2H_2O$ *= 1.012 x* 10^{-2} *M, Ce (IV) solution taken = 10 mL, Total volume = 50 mL),* [*]*Values obtained from second derivative plots of potentiometric titrations*

Table 3. Determination of Ce(IV) is standard reference material (Mischmetal and Al-Ce Master Alloy)

S.No	Name and Product code of Alloys	Weight of alloys taken, mg	Theoretical value, %	Observed Value, %	
				Estimated by AHA	Estimated by OHA
1	Misch Metal 58621	352.55	48	47.89	47.67
2	Misch Metal 58624	373.60	67	66.92	65.87
3	Misch Metal 58625	434.60	54	52.69	53.43
4	AlCe-3	375.30	2.5	2.32	2.00
5	AlCe-7	353.22	6.8	6.41	6.73

Conclusion

The developed method is based on the reduction behavior of hydroxamic acids in acidic medium. It is an improved titrimetric method for the establishment of Ce(IV)-AHA and Ce(IV)-OHA reaction stoichiometry in 2N sulphuric acid media. It is a rapid and précised procedure as the reaction is instantaneous at room temperature. The proposed method has the advantage over the earlier reported hydroxamic acid[18] that better number of equivalents is obtained sharply and precisely which facilitate the accurate estimation of Ce in alloys.

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