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The surfactant sensitized analytical reaction of cerium(IV) with some triphenylformazan derivatives

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Abstract

Cationic surfactant, cetylpyridinium bromide (CPB), sensitizes the colour reaction of cerium(IV) with 1,3-*o*-hydroxyphenyl-5-phenylformazan(I), 1-*m*-hydroxyphenyl-3-*o*-hydroxyphenyl-5-phenylformazan(II) and 1-*m*-carboxyphenyl-3-*o*-hydroxyphenyl-5-phenylformazan(III). The formation of a soluble ternary complex of stoichiometric ratio 1:1:1 (Ce(IV)–R–CPB) is responsible for the observed enhancement in the molar absorptivity and Sandell sensitivity of the formed complex, when a surfactant is present. The ternary complex exhibits absorption maxima at 596, 571 and 607 nm ($\varepsilon = 6.05 \times 10^4$, 6.28×10^4 and $8.06 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) using triphenylformazan derivatives I, II and III, respectively. Beer's law is obeyed between 0.15 and 2.5 $\mu\mathrm{g\,ml^{-1}}$, whereas, optimum concentration range applying Ringbom method is in the range 0.30–2.25 $\mu\mathrm{g\,ml^{-1}}$. Conditional formation constants in the presence and absence of CPB for Ce(IV) complexes have been calculated. The proposed method has been successfully applied to the analysis of magnesium-base cerium alloys and synthetic mixtures corresponding to various cerium alloys.

Keywords: Ternary complex; Cerium(IV) determination; Cetylpyridinium bromide; Spectrophotometry; Triphenylformazans

1. Introduction

Analytically, cerium in its tetravalent state differs significantly from all other lanthanides due to its immense oxidizing ability in acidic solutions. This property of cerium(IV) stands in the way of its determination using organic reagents with the advent of atomic energy programs using thorium extracted from ores, like monazite, a common ore for cerium, the presence of cerium(IV) in the environment proves to be alarming. This necessiated the development of convenient and reliable analytical methods for the determination of cerium. Analytical techniques, such as ICP-AES [1,2], or electrothermal vaporization (ETAA) after HPLC separation [3,4], stripping voltammetry [5,6] and spectrofluorometry [7,8] reported for the determination of cerium are of high cost and may not be available at most laboratories. Hence, it was planned to develop reasonably sensitive and economically viable techniques, like spectrophotometric procedures which are still frequently used because of their relative simplicity and low costs. Various analytical reagents viz, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone [9], 2,4-dihydroxybenzophenonbenzoichydrazone [10], *o*-phenylenediamine [11], *p*-aminophenylmercapto acetic acid [12], hydroxamic acids [13], pyrogallol red [14], phenothiazines, 8-hydroxyquinoline [15], and bisphenylazo-β-diketones [16] have been proposed for the determination of cerium. However, most of these methods suffer from a number of limitations, such as interference by a large number of ions [10,13], low sensitivity [9,11–13,16], need for extraction [9,15] or applicable only at high concentrations of cerium [11].

Concerning the present investigation, we report on a simple, rapid, adequately sensitive and selective spectrophotometric method for the determination of cerium(IV) using some triphenylformazan derivatives.

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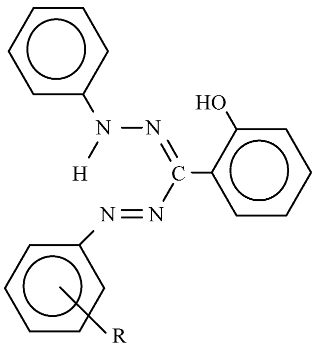

R: *o*-OH (I), *m*-OH (II) and *m*-COOH (III)

Fig. 1. The structure of triphenylformazan derivatives.

2. Experimental

2.1. Apparatus

An Orion research model 601A/digital ionalyzer pH-meter with a combined saturated calomel-glass electrode was used for pH measurements. JASCO 530 V UV–vis spectrophotometer equipped with 10 mm matched silica cells was used, for all spectral measurements.

2.2. Reagents

All chemicals were of analytical reagent grade, unless otherwise stated. Formazans used in the present investigation were prepared through the coupling of diazotized substituted anilines with salicylaldehydephenylhydrazone Fig. 1 [17]. A 2×10^{-3} M solutions of reagents I–III were prepared by dissolving an accurately weighed amount of the purified solid reagent in ethanol in a 100 ml measuring flask.

A stock solution of cerium(IV) was prepared using ceric ammonium sulfate (AR) in 0.5 M sulfuric acid and standardized volumetrically [18]. It was further diluted as and when required.

Thiel buffer solutions of pH ranges from 2.0 to 12.0 were prepared as recommended [19].

2.3. General procedure

An aliquot of sample solution containing 1.5–2.5 $\mu g\,ml^{-1}$ of Ce(IV) was transferred into a 10 ml calibrated flask, 0.8 ml of reagent, 6.0 ml buffer solution of the optimum pH value as recorded in Table 1 and 0.5 ml of 0.2% CPB were added, mixed well and then diluted to the mark with water. The flask was allowed to stand for 5.0 min with shaking for complete colour development. The absorbances were measured at 596, 571 and 607 nm using I, II and III, respectively, against a reagent blank prepared similarly.

2.4. Analysis of Ce(IV) in magnesium-base cerium alloys and synthetic mixtures

A magnesium-base cerium alloy was weighed accurately (1.0 g) into a 100 ml beaker and 10 ml of distilled water was added. Concentrated HCl was added in 2.0 ml portions until the alloy dissolved completely. The solution was heated to boiling, cooled and filtered through a Whatman filter paper no. 1. The filtrate was diluted up to the mark in a 100 ml calibrated flask. A 40 ml portion of the prepared solution was transferred into a 250 ml beaker, and 20 ml of saturated oxalic acid solution was added. It was digested on a water bath. The mixture was allowed to stand for one hour and the precipitate was filtered, washing the precipitate with a 0.05 M oxalic acid solution and finally with bidistilled water. The precipitate was dissolved in 2.0 M H_2SO_4 and 20 ml of a 10% ammonium persulfate solution were added, followed by 5.0 drops of a 1.0% silver nitrate solution. It was heated on a water bath until the precipitate had dissolved completely and Ce(III) had been

Table 1
Spectral characteristics of Ce(IV) complexes of reagents I–III

Parameter	I	II	III
pH	5.0	4.0	3.5
λ_{max} (nm)	596	571	607
log Ce–R	4.88	4.20	3.97
log Ce–R–CPB	7.95	6.85	6.13
Stability (h)	24	32	24
Beer's law ($\mu g\,ml^{-1}$)	0.15–2.20	0.2–2.5	0.2–2.0
Ringbom range ($\mu g\,ml^{-1}$)	0.3–2.0	0.4–2.25	0.35–1.85
Detection limit ($ng\,ml^{-1}$)	45	60	65
Quantitation limit ($ng\,ml^{-1}$)	143	186	199
Molar absorptivity ($\times 10^4\,l\,mol^{-1}\,cm^{-1}$)	6.05	6.28	8.06
Sandell sensitivity ($ng\,ml^{-1}$)	2.32	2.23	1.74
Regression equation[a]			
Slope (*a*)	0.43	0.48	0.575
Intercept (*b*)	−0.008	0.005	0.009
Correlation coefficient (*r*)	0.9992	0.9998	0.9996
Relative error (%)	±0.75	± 0.60	± 0.90
R.S.D. (%)	1.15	0.96	1.25

[a] $A = a + bC$ where C is the concentration in $\mu g\,ml^{-1}$, *b*: average of six determinations.

oxidized to Ce(IV) completely. The excess persulfate was destroyed by heating the solution. An appropriate amount of alloy solution (containing cerium within Beer's law range) was analyzed using the procedure described earlier.

Synthetic mixtures corresponding to various cerium alloys [7] were also prepared, and the concentration of Ce(IV) present in each alloy was determined by taking a suitable amount of solution and measuring the absorbance at 596, 571 and 607 nm, after developing the colour by following the general procedure described above using reagents I, II and III, respectively.

3. Results and discussion

Cerium(IV) was found to react with reagents I–III instantaneously in acidic media to form a partially soluble pink complex, whereas the addition of CPB leads to dissolution with bathochromic shift of 15–21 nm in the absorption maximum for the binary complex. Investigations were carried out to establish the most effective conditions to achieve maximum colour development in the quantitative determination of Ce(IV). The influences of the following variables on the reaction conditions were tested.

3.1. Effect of surfactant

Five cationic surfactants were tried to increase the sensitivity of the complex reaction namely, benzyldimethyltetradecyl-ammonium chloride (zephiramine), Tricetylmethyllammonium bromide (CTAB), cetylpyridinium bromide (CPB), tetradecyltri-methylammonium bromide (TDTAB) and cetylpyridinium chloride (CPC). Trimethylcetylammonium bromide gave analogous results, whereas non-micelle-forming voluminous cations (*N*,*N*′-diphenyl-guanidinium and tetraethylammonium) or the non-ionic surfactant Trition X-100, Tween 400 and Tween 80, did not produce any change in the absorption band or absorptivity of the binary complex.

The Ce(IV)–formazan complex is dissolved and sensitized by cationic surfactants, whereas colour enhancement is observed in the absorptiometric mode. Moreover, different concentrations of CPB were examined to achieve the best enhancement, 0.5 ml of 0.2% CPB is the optimum for reagents I and III, whereas, 0.8 ml is enough for reagent II. Therefore, 0.8 ml of 0.2% CPB was used for all further studies since the absorbance remained at its maximum values with increase CPB concentration (Fig. 2).

3.2. Effect of pH

In a trial to detected the best medium for quantitative determination of Ce(IV) in aqueous solution, universal, thiel, borate [20,21] and acetate buffer solutions of different pH values were tested. The absorbance readings were maximum on using both universal and thiel buffers. However, thiel buffer solution is used, since universal buffer affected the stability of the coloured complexes. Maximum absorbance values were obtained in the pH ranges, 4.5–5.5, 3.5–4.5 and 3.0–4.0 using formazans I, II and III, respectively. It was also observed that the complex colour remained constant with the addition of buffer solution of appropriate pH value which was used for all further studies.

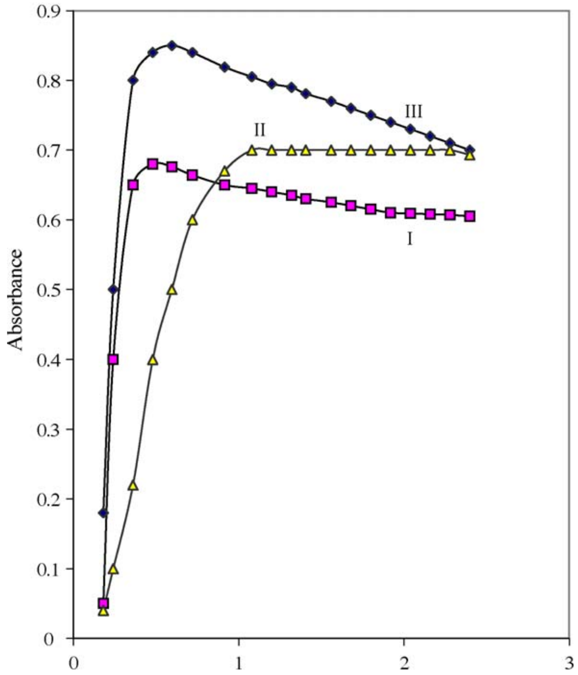

Fig. 2. Effect of 0.2% CPB volume on the absorbance of 1.6×10^{-4} M reagent (I–III) complexed with 1.5 mg ml^{-1} Ce(IV).

3.3. Effect of reagent concentration

Maximum and constant absorbance was obtained using reagent concentration at least 15 times that of Ce(IV), in the presence of CPB. Maximum reporducible absorbances are obtained on using 0.6 ml 2×10^{-3} M for formazan–Ce(IV) complexes. However, 0.8 ml of 2×10^{-3} M formazan was employed for all further studies since the results are highly concordant at this level.

3.4. Effect of time and temperature

The slightly soluble coloured complex was formed instantaneously at ambient temperature (25 ± 1 °C). On increasing temperature up to 70 °C, no change in the stability and sensitivity is observed. Allowing ternary complex to form by addition of CPB, a clear solution is formed and complete colour development is observed after shaking for 5.0 min of mixing. Raising the temperature up to 70 °C, no change in absorbance maximum is observed, whereas, further increase of temperature causes decrease in absorptivity of the formed complex. The colour of the formed complexes is stable for at least 24 h then decreases steadily by 10% for each one hour.

3.5. Order of additions

The absorbance of the ternary complex Ce(IV)–formazan–CPB depends slightly on the order of additions. The optimum order being cerium, formazan, buffer and CPB. Other sequences gave lower absorbance values compared with the above sequence, in addition to long shaking time to achieve maximum colour intensity.

3.6. Nature of the ternary complex

The stoichiometric ratio of Ce(IV) to formazan in the binary complex, was determined by Job's method, indicating 1:1. The composition of the ternary complex was investigated by the molar ratio and continuous variation methods. A molar ratio of Ce(IV):formazan:CPB of 1:1:1 was found for the ternary complex system by Job's method, and by the molar ratio method (by varying the concentration of metal). No definitive conclusion can be reached by varying the concentration of reagent in the molar ratio method because the exact break in the plot depends on the Ce(IV) concentration used. Maximum colour development was achieved at binary complex:CPB ratio close to 1:1.

Additional information on the stoichiometric ratio of the ternary complex was provided by the continuous variation method applied to isomolar solutions of CPB and previously formed 1:1 binary complex. A binary complex:CPB molar ratio of 1:1 was found. Thus, it can be concluded that the ternary complex has a Ce(IV):formazan:CPB molecular ratio of 1:1:1.

3.7. Comparative stability constants

As a quantitative estimate of the effect of CPB on the Ce(IV)–formazan reaction. The stability constant, for the $\beta_{1,1}$ binary complex Ce(IV)–formazan was found from the experimental data for absorbance as a function of formazan concentration. The conditional stability constant values (at the optimum conditions) of the binary complex are 4.88, 4.20 and 3.97 for reagent I, II and III, respectively. This indicates that the stability constant of binary complex $\beta_{1,1}$ depends on substituent effect, electron donating and withdrawing groups.

The stability constant values corresponding to $\beta_{1,1,1}$ for the ternary complex Ce(IV)–formazan(I–III)–CPB were similarly calculated from the data for constant metal and surfactant concentrations and from the isomolar Job's method data. In this case, the values of stability constant are 7.95, 6.85 and 6.13 for reagents I–III and corresponding to $\beta_{1,1,1}$ for ternary complex which are higher than those obtained for binary complex. The calculated values were recorded in Table 1.

3.8. Quantification

The absorbance values of the ternary complex Ce(IV)–formazan–CPB complexes followed Beer's law over the concentration ranges 0.15–2.20, 0.20–2.50 and 0.20–2.00 μg ml^{-1} on using the three formazans I, II and III, respectively in the measured solutions. The complexes exihibit high molar absorptivity (ε) and low Sandell sensitivity (s) values (Table 1). For more accurate results, Ringbom optimum concentration ranges were calculated by plotting the transmittance percent against the logarithmic [Ce] in μg ml^{-1} and recorded in Table 1.

The proposed method offers a slightly higher sensitivity than Gaoker and Eshawar method based on the addition of cetylpyridinium bromide surfactant. Also, the method shows the longer stability of the complexes formed (up to 24 h) compared to stabilities of 1.5 and 2.0 h using 4-(2-thiazolylazo) resorcinol and 1-(2-thiazolylazo)-2-naphthal, respectively [22]. Comparing to the previously work to determine Ce(III) with some bisazophenyl-β-diketone derivatives [16], the proposed method is more sensitive, stable and reproducible. Hsu et al. [23] method for estimation of cerium using *p*-acetylchloro-phosphonazo has higher sensitivity compared to the proposed method. However, it suffers from low stability and highly susceptible to interference.

In order to determine the accuracy and precision of the proposed method, solutions containing six different concentrations of Ce(IV), have been analyzed in quintuplicate. The relative errors and relative standard deviations (Table 1) can be considered satisfactory, at least for the concentration levels examined.

The detection limit ($K = 3$) and quantitative ($K = 10$) limits of the proposed method were calculated according to the IUPAC definitions [24] ($C_1 = KS_0/s$ where C_1 is the limit of detection, S_0 the standard error of blank determination, s the slope of the standard curve, and K is the constant related to the confidence interval). The obtained values are recorded in Table 1.

Table 2
Tolerance limits of diverse ions in the determination of Ce(IV)

Ion or species added	Tolerance limit		
	I	II	III
Ni^{2+}, Cd^{2+}	5500	6000	5250
Cu^{2+}, Co^{2+}	4000	4200	3750
Zr^{4+}, Th^{4+}	2200	3000	2700
Na^{+}, K^{+}	8000	10000	7500
Ca^{2+}, Mg^{2+}	7000	8000	6400
Hg^{2+}, Mn^{2+}	2000	2150	1800
Fe^{3+}, Al^{3+}	1000	1100	900
Y^{3+}, Sc^{3+}	600	650	500
La^{3+}, Nd^{3+}	400	400	320
Sm^{3+}, Gd^{3+}	250	275	225
Eu^{3+}, Dy^{3+}	180	200	150
Pr^{3+}, Er^{3+}	125	140	100
F^{-}, Cl^{-}	7000	7500	8000
$SO_4{}^{2-}$, SCN^{-}	6000	6000	6250
$NO_3{}^{-}$, $ClO_4{}^{-}$	5000	5500	5250
Acetate, borate	3500	3750	3750
Succinate, citrate	9500	10000	10000
Tartrate, CN^{-}	2500	2500	2500
Br^{-}	1000	700	750
EDTA	500	450	400

Table 3
Assay of cerium(IV) in various synthetic mixtures and magnesium-base cerium alloys

Sample no.	Composition (%)	Cerium present (%)	Cerium found[a] (%)	R.S.D. (%)
1	Ce, 0.72; La, 14.2; Pr, 14.43; Nd, 14.71; Sm, 15.32; Eu, 5.52; Mg, 15.64; Cd, 10.37; Tb, 5.24; Ho, 1.09; Y, 3.86	0.72	0.728	0.82
2	Ce, 0.47; La, 9.38; Pr, 9.54; Nd, 9.72; Sm, 10.124; Eu, 3.58; Mg, 15.22; Cd, 6.78; Tb, 3.463; Ho, 0.72; Y, 2.55 (as in sample no. 1) +Yb, 10; Dy, 10; Ca, 10; Zn, 5.0	0.47	0.529	0.91
3	Nd, 0.70; Ce, 1.85; Pr, 0.23; La, 0.82; Zr, 0.52	1.85	1.88	0.77
4	Nd, 3.49; Pr, 0.47; Ce, 0.07; La, 0.09; Zr, 0.56	0.07	0.0701	0.85
5	Nd, 2.43; Pr, 0.33; Ce, 0.06; La, 0.07; Zr, 0.46	0.06	0.0602	0.70

[a] Average of six determination.

3.9. *Effect of foreign ions*

In order to assess the analytical potential of the proposed method, the effect of some diverse ions, which often accompany cerium(IV), were examined by carrying out the determination of 1.5 $\mu g\,ml^{-1}$ of Ce(IV) in the presence of a number of other ions. An ion was considered to interfere with the determination if the obtained absorbance values differed by more than ±3.0% from that for Ce(IV) alone. The results presented in Table 2 indicate that many diverse cations, especially lanthanides, do not interfere with Ce(IV) determination.

4. Analytical applications

The applicability of the proposed method was checked by analyzing magnesium-base cerium alloys and some synthetic mixtures corresponding to cerium alloys. The results are recorded in Table 3.

The percentage contribution of cerium in sample no. 2 was reduced to 0.47 from 0.72% in sample no. 1 due to the presence of additional metal ions (in addition to metal ions already present in sample no. 1) totalling 101.1% as well as in sample no. 1. The low percentage R.S.D. values reflect the good precision of the proposed method.

The results obtained by the proposed method were compared with those of the AAS method using the *t*-test (for accuracy) and the *F*-value (for precision) [25] for five degrees of freedom and a 95% confidence level. The calculated values did not exceed the corresponding theoretical values, indicating insignificant differences between the results (Table 3).

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