Sensitization of Colour Reactions of Lanthanides & Chrome Azurol S with Some Cationic Detergents

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Formation of the complexes, [Ln$_2$(CAS)(CPB)$_2$] and [Ln$_2$(CAS)(CTAB)$_3$] (where CAS is chrome azurol S, CPB is cetylpyridinium bromide and CTAB is cetyltrimethylammonium bromide) at pH 5·4 in the presence of micelle forming cationic detergents is accompanied by marked bathochromic and hyperchromic effects. The increased sensitivity permits the colorimetric determination of microgram amounts of lanthanons. The use of the reaction in the presence of CPB as a complexometric indicator is demonstrated.

THE colour reaction of chrome azurol S (CAS) with lanthanons was reported by Dey and coworkers[1-4]. The sensitization of the reaction of this reagent with UO_2^{2+} by cetylpyridinium bromide (CPB) was studied by Leong[5]. This paper describes the results of sensitization of the Ln-CAS colour reaction by CPB and cetyltrimethylammonium bromide (CTAB) and its use as a complexometric indicator.

Materials and Methods

All chemicals used were of analytical grade purity. Metal solutions ($10^{-2}M$) were prepared by dissolving lanthanide oxides (purity 99·9%) in minimum quantity of hydrochloric acid and making up the volume with distilled water. The stock solutions were standardized by precipitating the metal as their oxalates and estimating volumetrically. A $10^{-3}M$ solution of chrome azurol S (trisodium salt) was prepared by dissolving a calculated quantity of the reagent in distilled water. Solutions ($10^{-2}M$) of the detergents, cetylpyridinium bromide (CPB) and cetyltrimethylammonium bromide (CTAB) were prepared in 20% aqueous methanol and standardized by titrating these against silver nitrate solution.

Detergent solution was added to CAS solution which was kept for at least 30 min for micellar aggregates to form, before the addition of metal ion solution. No change in absorbance was observed for at least 24 hr.

Beckman DU-2 spectrophotometer with matched glass cells of 10 mm light path was used.

Elico pH meter model I=10 fitted with a glass-calomel electrode assembly was used. pH of the solutions were adjusted by using proper concentration of NaOH or HCl.

Results and Discussion

Effect of CPB on absorption spectra of CAS and its lanthanide complexes — CAS does not form stable complexes in alkaline range and hence the effect of detergents was studied in the pH range 4·5 to 6·5. A series of solutions were prepared keeping the ratio of lanthanide-CAS-CPB as 1: 1: 10, 1: 4: 10 and 4: 1: 10. A number of sets were prepared for each ratio and the pH adjusted to 4·0, 5·0, 5·2, 5·4, 5·8 and 6·0. The absorption spectra are then recorded from 400 to 650 nm. For all the lanthanides studied here (La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} and Dy^{3+}) the λ_{max} was found to be at 620 nm in the pH range 5·0 to 6·0. At pH 4·0, it was found to be at 500 nm, which is the λ_{max} of CAS alone at this pH. When the reagent is present in four times excess than the metal, the λ_{max} appeared at 590-600 nm, because it represents the spectra of mixture of complex and excess reagent. A plot of absorbance versus pH shows that the absorbance of Sm^{3+}-CAS chelate in the presence of CPB is constant between pH 5·2 and 5·8; constant absorbance was also noted in this pH range for other lanthanides also. Hence pH 5·4 was selected for further study. CAS alone at pH 5·4 exhibits λ_{max} at 440 nm whereas in the presence of CPB (1: 10 ratio) the λ_{max} is shifted to lower wavelength (430 nm). However, the spectrum in the presence of Sm^{3+} in Sm^{3+}-CAS ratio of 4: 1 shows a λ_{max} at 540 nm as reported by earlier workers[1]. However, when the spectrum is taken in the presence of CPB, the λ_{max} shifts to 620 nm with an increase in the absorbance. It is thus observed that in the presence of CPB the formation of lanthanide complexes is accompanied by a bathochromic shift of maximum absorption by 80 nm.

Effect of varying CPB concentration and of mineral salts on the absorption spectrum of CAS — The absorption of CAS changes gradually depending on the amount of quarternary salt added. The absorbance of different concentrations of CAS shows that the maximum decolourizing effect is reached at the minimal detergent-CAS ratio of 2: 1 in the case of CPB and 3: 1 in the case of CTAB at pH 5·4. When this ratio has been exceeded, the absorbance of CAS remains unaltered even when an excess (ten times) of quarternary salt is added. The concentration range of CAS under which the absorbance of CAS and CPB attains constancy at the minimal ratio of 2: 1 (3: 1 for CTAB) is $1·0 \times 10^{-3}$ to $5·0 \times 10^{-5}M$.

The high concentration of mineral salts prevent the formation of micelles, because of the inorganic anion displacing the dye as counter ion[6]. In the case of sodium chloride and ammonium sulphate, the absorbance of CAS-CPB at pH 5·4 decreases in the early stages and then remains constant. The effect observed on the absorbance is quite small for chloride and sulphate, whereas the maximum effect has been noted for nitrates.

Effect of varying reagent concentration — Different volumes of $5 \times 10^{-4}M$ CAS were taken in each flask to which 5 ml of $4 \times 10^{-3}M$ CPB was added. 2 ml of $1 \times 10^{-3}M$ metal ions were then added in each flask. Total volume was maintained 25 ml. Absorbance readings were recorded at 620 nm. It was found that the amount of CAS needed for full colour development should be twice that of the metal ion.

Beer's law and photometric ranges — The effective range of metal ion concentration for a concentration of $5 \times 10^{-5}M$ CAS and $4 \times 10^{-4}M$ CPB was computed from Ringbom plots[7] and are given in Table 1. The sensitivities as per Sandell's definition are calculated in the presence and absence of CPB and are also given in Table 1. It can be seen that the sensitivity increases many folds in the presence of CPB using CAS as the reagent.

Effect of foreign ions — The effect of foreign ions was tested by taking 1·2 ppm of lanthanide ions and determining its concentration in the presence of a large number of interfering ions. The results for Sm^{3+} system is given in Table 2. The method suffers from the lack of selectivity but the interferences are not too many. Th^{4+} and Be^{2+} interfere seriously. The determination is also affected by the presence of the metal ions like Ag^+, Fe^{3+}, Co^{2+}, In^{3+} and Y^{3+}.

Procedure for the microdetermination of lanthanides — The pH of the lanthanide solution, containing 17·0 to 135·0 μg of lanthanide was adjusted to 5·4. 2 ml of $1 \times 10^{-3}M$ modified CAS solution of the same pH were added. (The modified CAS is prepared by adding about four fold-excess of CPB solution to CAS solution and keeping it for 1 hr for complete micelle formation.) The volume was made up to 25 ml with distilled water and the absorbance of this solution measured at 620 nm against reagent blank after 1 hr. The absorbance of this unknown solution was compared with the calibration curve obtained under similar conditions.

Absorbance readings showed the average and relative standard deviation values as 0·05 and 2·3% for lanthanides respectively.

Advantages of the new method over the existing one — In the presence of CPB or CTAB, the formation of the complexes with the lanthanides under study at pH 5·4 is accompanied by a large bathochromic shift in the λ_{max} from 540 nm to 620 nm. A large difference in absorbance between the reagent blank and the complexes with and without CPB or CTAB is observed at 620 nm. This results in an increase in the sensitivity of the reaction many folds, as is evident from the data in Table 2.

Procedure for complexometric titration with CAS in the presence of CPB as indicator — The sample solution is diluted to 100 ml and its pH adjusted to 5·4. A ten-fold excess of detergent (CPB or CTAB) and CAS mixture is added. This solution is then titrated with EDTA to the end point. A sharp change in colour from deep blue to pale red occurs. (The indicator was used as 1:100 solid mixture finely ground with potassium chloride.) The results, given in Table 3 show good agreement. The values obtained are the mean of five determinations. The standard deviation shows the excellent reproducibility of the individual results.

TABLE 1 — BEER'S LAW, PHOTOMETRIC RANGES, AND SANDELL'S SENSITIVITIES FOR THE SYSTEMS

Metal ion (L^{3+})	Conc. range for Beer's law (ppm)	Conc. range for effective photometric determination (ppm)	Sandell's sensitivity (μg/cm²)	
			Absence of CPB*	Presence of CPB
La	0·18-3·6	0·63-2·00	0·139	0·0237
Pr	0·18-3·7	0·63-2·08	0·075	0·0042
Nd	0·18-3·8	0·72-2·10	0·070	0·0041
Sm	0·20-4·0	0·79-2·52	0·075	0·0040
Gd	0·20-4·1	0·79-2·57	0·078	0·0039
Dy	0·21-4·3	0·74-2·46	0·069	0·0041

*Data from references 1 and 4.

TABLE 2 — EFFECT OF FOREIGN IONS

(Sm^{3+} taken, 1·2 ppm)

Ion	Amount of interfering ion (ppm)	Sm^{3+} found (ppm)	Error %
Ag^+	1·49	1·50	+25·00
Mg^{2+}	13·44	1·21	+0·83
Ca^{2+}	4·00	1·21	+0·83
Sr^{2+}	3·52	1·19	−0·84
Ba^{2+}	2·74	1·22	+1·6
Be^{2+}	0·108	0·30	−75·00
Mn^{2+}	12·2	1·23	+2·5
Fe(ic)	1·76	1·55	+28·3
Co^{2+}	10·6	1·27	+5·83
Ni^{2+}	10·8	1·22	+1·6
Cu^{2+}	10·08	1·22	+1·6
Zn^{2+}	20·8	1·23	+2·5
Al^{3+}	16·2	1·21	+0·83
Ga^{3+}	1·32	1·21	+0·83
In^{3+}	2·28	0·80	−33·3
Tl^{3+}	1·14	1·21	+0·83
Y^{3+}	7·05	1·00	−16·66
Cd^{2+}	23·2	1·24	+3·33
Pb^{2+}	1·49	1·26	+5·6
F^-	15·2	1·21	+0·83
Cl^-	14·00	1·19	−0·83
Br^-	12·8	1·18	−1·66
I^-	10·1	1·17	−2·5

TABLE 3 — DETERMINATION OF INDIVIDUAL LANTHANIDES

Ion	Lanthanide (mg)		S.D.
	Taken	Found	
La^{3+}	17·12	17·10	±0·020
Pr^{3+}	15·56	15·50	±0·018
Nd^{3+}	15·57	15·50	±0·022
Sm^{3+}	17·24	17·10	±0·046
Gd^{3+}	14·71	14·54	±0·050
Dy^{3+}	26·00	26·06	±0·030

Composition of complexes — The composition of the lanthanide-CAS complexes in the presence of CPB has been determined by the method of continuous variation and the mole ratio method. The complexes are of 2:1 (lanthanide-CAS) stoichiometry. The complexes may therefore be formulated as $[Ln_2(CAS)(CPB)_2]$ where CPB represents associated cetylpyridinium bromide ions. Similar complexes are formed in the presence of CTAB also.

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