

Hydroxyanthraquinones in micellar media: Improved spectrophotometric reagents for beryllium(II) and aluminium(III)

Tarasankar Pal* & Nikhil R Jana

Department of Chemistry, Indian Institute of Technology,
Kharagpur 721 302, India

Received 12 December 1994; revised 7 June 1995;
accepted 19 November 1995

Enhancement of absorption spectral intensities have been observed for Be(II) and Al(III) complexes of alizarin and quinalizarin in the presence of cationic and nonionic micelles. This effect has been successfully exploited for the spectrophotometric determination of Be(II) and Al(III). Optimum conditions for complexation, composition of complexes and statistical analysis of the results have also been reported.

The addition of surfactants to aqueous solutions of certain metal-dye complexes results in substantial changes in the UV-visible spectrophotometry of the complexes¹⁻⁴. This is due to the formation of ternary complexes which usually show an increase in molar absorptivity and a bathochromic shift of the absorption maximum relative to that of the binary complexes. Another important factor is the solubilizing capacity of micelles towards metal complexes that are not very soluble in water, so that extractions into organic solvents can be avoided. Anthraquinone derivatives are moderately selective and sensitive reagents⁵ and their performance has been improved by treatment of spectral signals^{6,7}, use of inclusion complexes of cyclodextrins⁸, etc.

Alizarin and quinalizarin are well-known reagents used for the detection as well as estimation of Be(II) and Al(III) in organic or mixed aqueous-organic solvents⁹. Here we report the effective use of different micellar media (cationic, anionic and nonionic) to improve the sensitivity of spectrophotometric method for the estimation of Be(II) and Al(III) using alizarin and quinalizarin over the existing methods. It has been shown that cationic and nonionic micellar media increase the sensitivity of the method. The solubilization of both the reagents in micellar media render them to be efficient and useful spectrophotometric reagents in the absence of organic solvents unlike the earlier known methods. The other metal ions which form complexes with alizarin and quinalizarin include Ca(II), Mg(II), Zn(II), Cu(II) and Ce(III). Howe-

ver, in micellar media the spectral enhancement of these metal complexes was not observed.

Experimental

Absorbance measurements were carried out on a Shimadzu UV-160 digital spectrophotometer using 1 cm quartz cells. A digital pH meter (ECIL, Hyderabad) was used for pH measurements.

All reagents used were of AR grade. Doubly distilled deionised water was used throughout the study. Boric acid (BDH, India) solution (0.01 mol l^{-1}) and sodium hydroxide (BDH, India) solution (0.04 mol l^{-1}) were used to prepare various buffer solutions in the pH range 6.0-12.0. The pH of the buffer solutions was finally adjusted with NaOH solutions using a pH meter. Alizarin and quinalizarin were recrystallized from methanol and stock solutions ($\sim 10^{-4} \text{ mol l}^{-1}$) of these reagents were prepared in buffer solutions of varying pH (6.0-12.0). Be(II) solution 0.016 mol l^{-1} was prepared by dissolving accurately weighed beryllium metal (AD Mackay, New York) (0.036 g) in dil. H_2SO_4 in a 100 ml calibrated flask. The pH of the solution was then increased to the range of 5.0-6.0 using Na_2CO_3 and the volume was made up to the mark. Fresh stock solution (0.01 mol l^{-1}) of Al(III) was prepared by dissolving aluminium nitrate in water and the solution was standardised following EDTA titration¹⁰.

Surfactants used were: cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and polyoxyethylene-isooctylphenyl-ether (TX 100) (all Aldrich, USA). CTAB (0.5 mol l^{-1}) solution was prepared by dissolving 1.82 g of the surfactant in water in a 10 ml volumetric flask. A 4.0 mol l^{-1} stock solution of NaCl (BDH, India) was used to maintain the ionic strength of the reaction medium.

Determination of Be(II) and Al(III)

In a 10 ml calibrated flask, 9.5 ml of reagent solution (pH 8.2) was mixed with varying amounts of surfactant (0.05-0.10 ml) and NaCl (0.0-0.5 ml) solution. To this mixture, was added 5-30 μl of Be(II) [or 5-50 μl Al(III) solution] and the final volume was made up with buffer solution of pH 8.2. The solution was mixed well and spectral measurements were made after 30 min in case of Be(II) and after 2-3 min in the case of Al(III). In the estimation of Be(II), with alizarin as the reagent, absorbance was measured at 525 nm for cationic and nonionic micelles, and while using quinaliz-

Table 1—Characteristics of Be(II) and Al(III) complexes

Complexes	Medium used								
	H ₂ O			TX 100			CTAB		
	λ_{\max} nm	ϵ l mol ⁻¹ cm ⁻¹	Comp [†]	λ_{\max} nm	ϵ l mol ⁻¹ cm ⁻¹	Comp	λ_{\max}	ϵ l mol ⁻¹ cm ⁻¹	Comp.
Be(II)-alizarin	525	0.3×10^4	III- defined	525	—	NS‡	525	0.9×10^4	1:3
Be(II)-quinalizarin	565	0.5×10^4	2:3	565	—	NS‡	620	1.0×10^4	2:3
Al(III)-alizarin	525	0.3×10^4	2:3	525	0.7×10^4	1:2	530	0.9×10^4	1:1
Al(III)-quinalizarin	565	0.9×10^4	1:3	565	0.9×10^4	1:2	575	1.2×10^4	2:3

†Slope ratio method.

NS: Non-stoichiometric

arin, measurements were made at 565 and 620 nm for nonionic and cationic micelles respectively against reagent blank.

While estimating Al(III), the absorbance against reagent blank was measured at 525 and 530 nm for nonionic and cationic micelles respectively, when alizarin was used as the reagent. In the case of quinalizarin, the absorbance was measured at 565 and 575 nm for nonionic and cationic micelles respectively.

Results and discussion

Absorption spectrum of alizarin and quinalizarin has been studied previously^{11,12}. In order to study the influence of micelles on the absorption spectra of reagents, we have used the surfactant concentration much above their critical micellar concentration (cmc)¹³. The absorption maxima for neutral as well as anionic forms of reagents showed bathochromic shift in cationic micelle compared to that in water but remained almost unaffected in nonionic and anionic micelles. The absorption spectra of metal complexes against reagent blank in different micellar media have also been studied and their spectral characteristics summarised in Table 1. The molar absorptivity values due to Be(II) and Al(III) complexes have been found to increase in cationic and nonionic micellar media associated with/without change in λ_{\max} values.

The effect of pH on the formation of Be(II) and Al(III) complexes of alizarin and quinalizarin have been studied in the pH range of 6.0-11.0. The complex formation is highly influenced by pH of the solution, the optimum pH ranges being different for different media due to the relative shift of acid-base equilibrium of reagents in different media^{2,3}. The calibration graphs have been obtained at pH 8.2 except for Be(II)-alizarin complex in CTAB and Be(II)-quinalizarin complex in water where pH of 10.0 and 9.0 respectively was maintained.

In order to choose the appropriate micellar media for the analytical estimation; the cationic, anionic and nonionic surfactants were tested. Cationic and nonionic surfactants showed promising results in the present study. To avoid adverse effect of ionic strength and precipitation of reagents, surfactant concentrations were always kept above their cmc values.

Surfactants above their cmc extract the reagent in the micellar stern layer and thus the reagent is concentrated in the micellar pseudophase. This leads to the dye-rich complex formation. However, the orientation of the extracted reagent in micelle may favourably open up different binding sites and thus lead to complexes of different nature. The effect of the concentration of surfactants on complexation have been studied at their respective λ_{\max} values. The absorbance values have been shown to increase first and then gradually decrease with the increase in surfactant concentration. The increase in absorbance values may be presumably due to the incorporation of dyes into the micellar pseudophase and the decrease is attributed to the dilution of dyes within the newly formed micellar pseudophase.

Ionic strength has strong influence on acid-base equilibria of charged micellar media¹⁴. This is due to bulk ionic strength dependence of micellar surface charge. This effect was responsible for ionic strength dependence of metal complex in micellar media which was well observed in this case.

Determination of Be(II) and Al(III)

Following the procedure described above, the validity of Beer's law has been tested for Be(II) and Al(III) in water as well as in cationic and nonionic micellar media. Results of linear regression analysis and detection limits (calculated by IUPAC method¹⁵) have been summarised in Table-2. Increase in molar extinction coefficient (ϵ) value decreases the detection limit

Table 2—Statistical data of Be(II) and Al(III) analysis at 0.03 ionic strength

Reagent Metal	Medium											
	H ₂ O				TX 100				CTAB			
	Calibration curve ^a	Beer's law range (ppm)	Correlation coefficient	LOD (ppm)	Calibration curve ^a	Beer's law range (ppm)	Correlation coefficient	LOD (ppm)	Calibration curve ^a	Beer's law range (ppm)	Correlation coefficient	LOD (ppm)
Be(II)	—	—	—	—	—	—	—	—	OD=0.99 × C + 0.005	0.07- 0.43	0.98	0.01
Alizarin Al(III)	OD=0.11 × C - 0.002	0.13- 1.89	0.97	0.03	OD=0.26 × C + 0.004	0.13- 1.89	0.99	0.04	OD=0.34 × C + 0.005	0.13- 1.35	0.98	0.03 (0.15)
Be(II)	OD=0.57 × C - 0.004	0.07- 0.43	0.97	0.03	—	—	—	—	OD=1.06 × C + 0.005	0.07- 0.43	0.93	0.01 (0.15)
Quinalizarin Al(III)	OD=0.33 × C + 0.002	0.13- 0.81	0.98	0.04	OD=0.34 × C + 0.003	0.13- 1.35	0.98	0.04	OD=0.45 × C + 0.005	0.13- 0.81	0.99	0.02 (0.2)

^aRepresents concentration of metal ion in ppm

— Beer's law was not obeyed.

Values in parentheses represent detection limits for existing methods.

[T × 100] was 0.018 mol l⁻¹.

[CTAB] was 2.6 × 10⁻³ mol l⁻¹ and 5.2 × 10⁻³ mol l⁻¹ for alizarin and quinalizarin respectively.

in most cases and thus increases the analytical sensitivity in comparison to water media. The detection limits of the existing methods have also been summarised in Table 2 and it has been observed that the proposed method is more sensitive than the existing methods.

Eight successive measurements were made with stock solutions containing 0.21 ppm of Be(II) and 0.52 ppm of Al(III) for both alizarin and quinalizarin reagents. Relative standard deviations for alizarin and quinalizarin method of Be(II) were 1.5% and 1.0% respectively and those for Al(III) were 2.0% and 1.8% respectively.

Investigations were carried out to examine the influence of foreign ions on the estimation of Be(II) and Al(III), when they were present separately in solution. Both the metal ions can be determined in the presence of Sr(II), Ba(II), Na(I), K(I), NO₃⁻, NO₂⁻, Cl⁻, Br⁻, CH₃CO₂⁻, SO₄²⁻, PO₄³⁻. Ions like Cu(II), Zn(II), Cd(II), Ca(II), Mg(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II) interfere in the determination of Be(II) and Al(III) for both alizarin and quinalizarin due to the formation of complexes. As the complex formation is influenced by the ionic strength of the medium, the interference due to large excess of foreign ions could not be investigated.

The above method for Be(II) has been successfully applied to the determination of Be(II) in pure beryl. Be(II) was estimated in presence of EDTA to avoid interference due to Al(III). The results were in good

agreement with those obtained by atomic absorption spectrophotometry and other techniques¹⁶. Al(III) was estimated in several rock samples and the results were crosschecked by AAS method.

Acknowledgement

The work was supported by the CSIR, New Delhi, India.

References

- 1 Pelizzetti E & Pramauro E, *Anal chim Acta*, 169 (1985) 1.
- 2 Hinze W L, *Use of Surfactants and micellar systems in analytical chemistry, solution chemistry of surfactants*, Vol 1, edited by K L Mittal (Plenum Press, New York), 1979.
- 3 Melntire G L, *Crit Rev Anal Chem*, 21 (1990) 257.
- 4 Callahan J H & Cook K D, *Analyt Chem*, 56 (1984) 1632.
- 5 Diaz A N, *Talanta*, 38 (1991) 571.
- 6 Sanchez F G, Lopez M H & Gomez J C M, *Talanta*, 34 (1987) 639.
- 7 Pal T & Jana N R, *Talanta*, 40 (1993) 1519.
- 8 Sánchez F G, López M H & Heredia A, *Anal chim Acta*, 187 (1986) 147.
- 9 Welcher F J, *Organic analytical reagents*, Vol. 4 (van Nostrand Company), 1948.
- 10 Vogel A I, *A text book of quantitative inorganic analysis*, 4th Edn (Longman, London), 1978.
- 11 Fischer H, *Z Anal Chem*, 73 (1928) 54.
- 12 Zittel H E & Florence T M, *Analyt Chem*, 39 (1967) 320.
- 13 Cline Love L J, Habarta J G & Dorsey J G, *Analyt Chem*, 56 (1984) 113A.
- 14 Diaz-Garcia M E & Sanz-Medel A, *Talanta*, 33 (1986) 255.
- 15 Long G L & Winefordner J D, *Analyt Chem*, 55 (1983) 713A.
- 16 Pal T & Jana N R, *Analyt*, 118 (1993) 1337.