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Study On The Character Of Interactions Between Metal-Pyridylazo Resorcinol Complexes And Cationic Surfactants By Spectrophotometry And Liquid Chromatography



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ABSTRACT

Metal-pyridylazoresorcinol complexes are studied in micellar medium by using spectrophotometric and chromatographic techniques. Study shows that divalent cations form uncharged complexes and are little affected by presence of charged surfactants. Metals with higher valence number like vanadium forms negatively charged complexes and due to the formation of ternary complexes with surfactant cause shift in peak position and peak intensity. Addition of surfactant enhances the selectivity of analysis. © 2007 Trade Science Inc. - INDIA

KEYWORDS

Surfactants;
MLC;
Metal complexes.

INTRODUCTION

Since 1960, derivatives of 2-pyridylazo have been extensively studied for analytical purposes. A very important example is 4-(2-pyridylazo)-resorcinol, PAR. This is an excellent metal chromic indicator and also very useful as a chromogenic agent for the quantitative determination of over 50 elements, including at trace levels^[1]. Ghasemi et al.^[2] have reported acidity constants of PAR in acetonitrile-water mixture. It is interesting to note that the nature of solvent composition has fundamental effect on each pure spectrum. PAR behaves as a tetra or

bidentate ligand to form soluble or insoluble coloured complexes with cations of Mg, Al, Ca, Ba, Sr, Sc, Ti, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Ru, Rh, Pb, Bi, Th, U, Np and the lanthanides at specific pH values. Most PAR complexes are red or violet red and in some cases colour changes with pH. In case of divalent cations, the complexes formed are uncharged, co-ordination-saturated with cation to ligand ratio equal to 1:2, M(HL)₂. Due to non-specific nature of reagent it also finds applications in separation of metal ion by chromatography and electrophoresis^[3]. Reverse phase columns eluted with citrate buffers have been used to separate Nb^V and

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Ta^V using PAR in the mobile phase and to separate Pd²⁺, Rh³⁺, Pt²⁺ and Ru³⁺ as PAR complexes by HPLC. Sadanbou Inoue et al^[4] have separated Co³⁺ and V^v using Nitro-PAPS with tetrabutyl ammonium bromide as ion-pairing agent and acetic acid and EDTA in acetonitrile-water system^[5].

With uranium and vanadium this form negatively charged complexes^[6] and can be extracted in chloroform with cations like tetraphenylarsonium and others. Abbas et al^[7] have reported simultaneous determination of uranium and vanadium using cetylpyridinium chloride as ion-pair. They reported the shift of 13 nm in position of λ_{\max} . However, the interesting properties like, interactions with cations and surfactants have not yet been clarified. Careful investigation of literature suggests that pyridylazo resorcinol and its complexes are sensitive to environmental conditions. In this study we selected vanadium (V) and Co(II)-PAR complexes as probe molecules to investigate the interactions of these with cetyltrimethylammonium bromide. CTAB is cationic surfactant, capable of forming micelles and can form ion-pair in monomer form.

EXPERIMENTAL

Reagents

Stock solution 1% 4-(2-pyridylazo)-resorcinol (Fluka) was prepared in methanol. A 1000 $\mu\text{g ml}^{-1}$ stock solutions of cobalt and vanadium were prepared from their corresponding salts of cobalt chloride and ammonium metavanadate and stored in slightly acidic medium. Working solutions were prepared in double distilled de-ionised water. A 0.3 M stock solution of cetyltrimethylammonium bromide (Merck) was prepared in double distilled de-ionised water. HPLC grade acetonitrile (Fluka) was used throughout. Working solutions were prepared by appropriate dilutions of stock solutions.

Liquid chromatography

Liquid chromatography was performed with Hitachi LC-organizer HPLC system with L-6200 pump and Rheodyne injection port. Samples were separated on 25cm x 4.6 m.i.d. SGE Lichrosorb ODS column (particle size 5 μm , pore size 80 \AA). The

mobile phase used was acetonitrile water or CTAB surfactant; in all cases mobile phase contains 0.01 M acetic acid and pH adjusted to 4.3 with ammonium acetate. Detection was performed with Hitachi UV-visible detector at 550 nm. PC running CSW-32, software was used for integration and calculation.

Initially column was equilibrated with surfactant solution only at first, then the required mobile phase was run for at least 30 minutes and reproducibility in retention time was checked to ensure the equilibration of the column. In all cases reproducibility in retention times was not more than 2%. Column backpressure varied from 90-230 kg cm^{-2} , depending on the mobile phase composition. For maintenance and washing of column, method proposed by Hinze (in Micellar Liquid Chromatography) was adopted^[8].

Pre-column derivatization

In each case, 0.5 ml of 1% PAR was added to a 20 ml flask containing 20 μg of cobalt vanadium, iron or nickel and diluted to mark with mobile phase. For quantification of cobalt mobile phase G was used TABLE 1.

TABLE 1: Retention data for metal ions using different mobile phases

Mobile phase	% Acetonitrile	CTAB (M)	Retention time (minutes)		
			Cobalt	vanadium	PAR
A	40	0	2.510	2.910	3.8
B	40	4×10^{-4}	4.2	7.44	3.8
C	40	8×10^{-4}	4.95	9.04	3.8
D	20	0.01	24.44	No peak	12.26
E	20	0.03	19.92	No peak	12.26
F	20	0.06	11.73	No peak	12.26
G	20	0.12	6.30	No peak	12.26

Sample preparation of pharmaceutical preparation

Pharmaceutical samples containing 10 – 100 μg Co were wet digested and made up to 20 ml. Aliquot was neutralized with NH_4OH and derivatized as above. .

RESULTS AND DISCUSSION

Spectral characterization of vanadium and cobalt complexes

Position of λ_{\max} and sensitivity of vanadium and cobalt chelate were examined in cationic micellar surfactant solution (Figure 1). No shift in position of λ_{\max} and increase in absorbance was observed for both complexes when the concentration of CTAB is below cmc (spectra of cobalt is not shown). In case of vanadium, shift (550 nm to 563) in position of λ_{\max} on increasing the CTAB concentration was observed with gradual decrease at 550 nm and increase at 563 nm. Then the absorbance becomes constant at 563 nm.

Examination of various spectrum leads to the conclusion: (a) increase in absorbance results in the ion-pair formation between the negatively charged

V-PAR complex and positively charged surfactants (b) shift in λ_{\max} is due to interactions of complex and micelles.

To clarify the findings whether the effect is purely micellar or combined (electrostatic interactions with charged monomers and micelles), keeping other conditions constant cationic surfactant was replaced with non-ionic Brij®-35. No shift in λ_{\max} was observed. This shows that only micellar parameters are not responsible for shift. Further, solution of V-PAR with and without CTAB was extracted with chloroform. The solution containing CTAB as monomer was extracted in chloroform with λ_{\max} 561 nm. This indicates that red shift observed in cationic micellar medium is due to the combined effect of electrostatic intersections between complex and CTAB molecule followed by localization of ion-pair in micellar core.

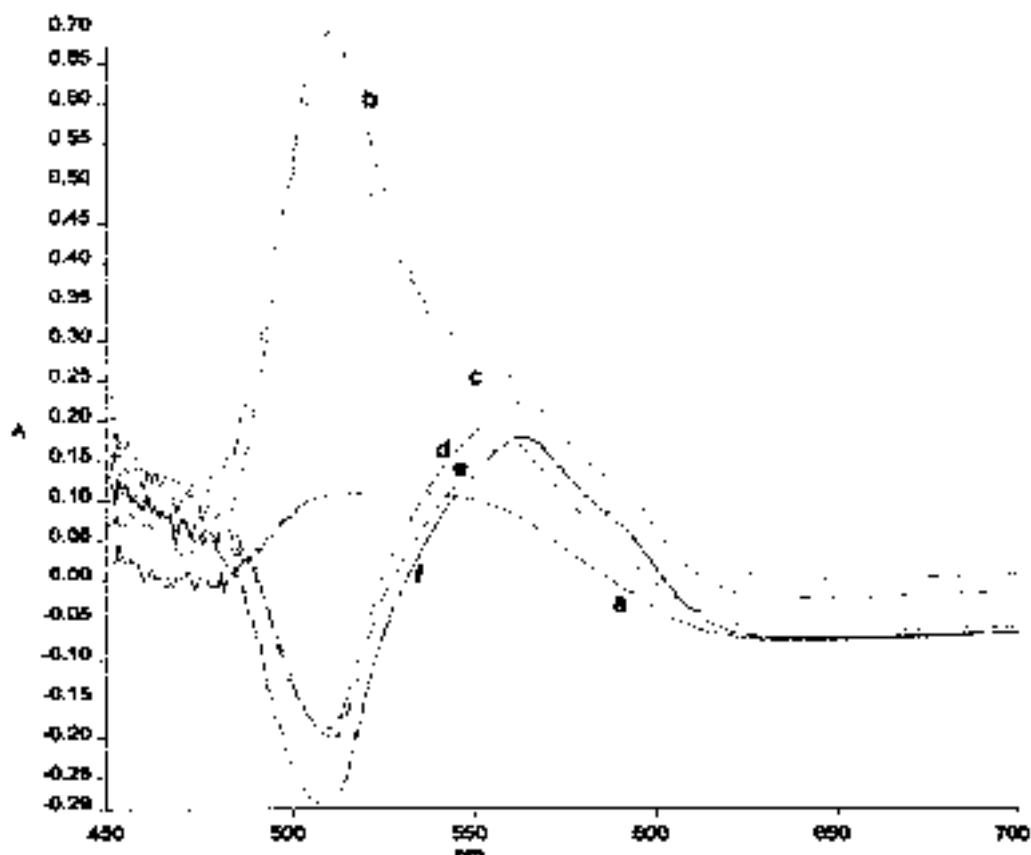


Figure 1: Spectral characterization of vanadium complex, (a) V-PAR at pH 4.3 without CTAB, (b) V-PAR at pH 4.3 with CTAB 2.4×10^{-4} M, (c) with 5×10^{-3} M, (d) 0.015 M, (e) 0.03 M and (f) 0.06 M

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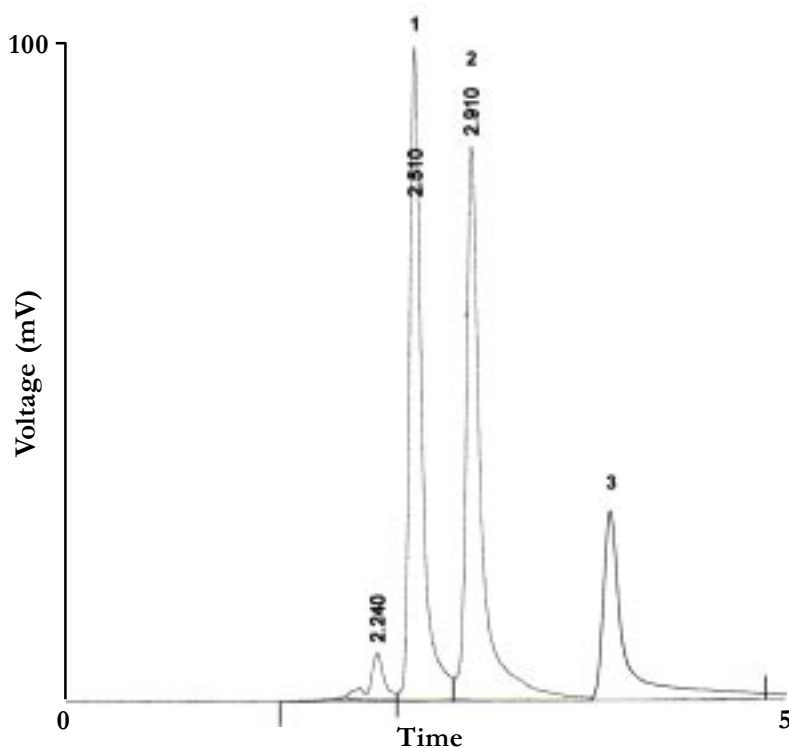


Figure 2: Separation of Co and V using acetonitrile water as mobile phase (Mobile phase A) Cobalt (1), Vanadium (2) and reagent (3)

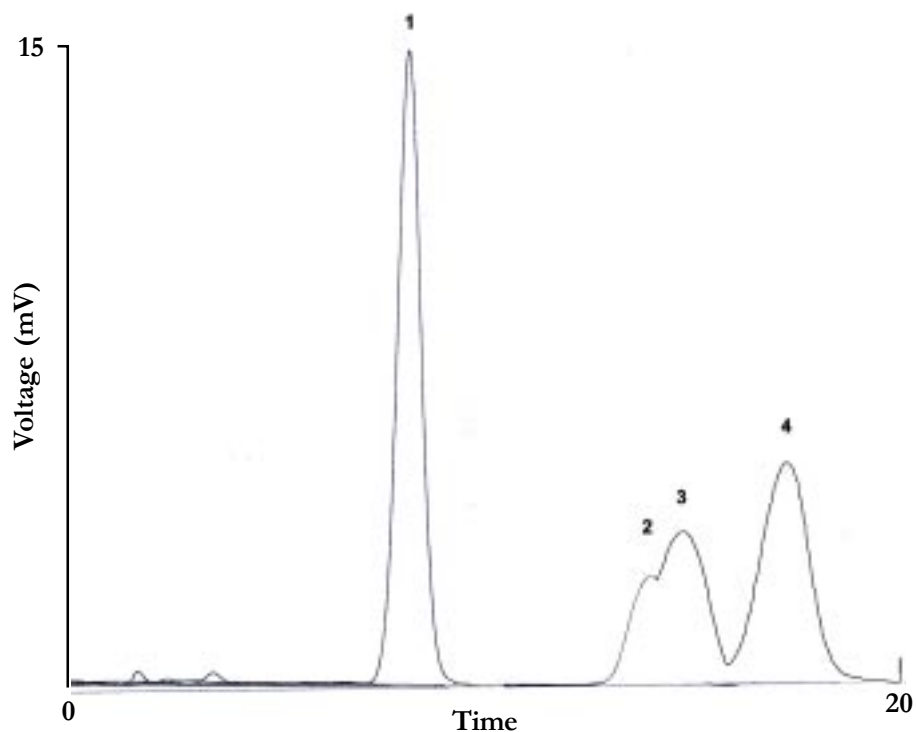


Figure 3: Separation of Co, Fe(II), Fe(III) and Ni using 0.1M CTAB and 20% acetonitrile Co (1), Fe-II (2), Fe-III (3) and Ni (4) with retention times 9.5, 15.1, 15.4 and 18.2 respectively

Chromatographic characterization of vanadium and cobalt complexes

TABLE 1 show the retention time observed for cobalt and vanadium on ODS column. In all instances pH of the mobile phase was kept at 4.3 using 0.01 M acetic acid/ ammonium acetate. Figure 1 shows chromatogram obtained with acetonitrile water (mobile phase A) system without surfactant solution. The peaks for two metal ions, cobalt and vanadium are well resolved. Elution of Co and V before PAR shows that the complex formed is more polar. Then the surfactant concentration was systematically increased from below cmc to above cmc. The retention for reagent on adding CTAB below cmc was unaffected (Mobile phase B), while retention time increases for both Co and V from 2.5 to 4.955 minutes and 2.9 to 9.04 minutes, respectively. This shows that PAR form negatively charged complexes with these metal ions, which forms ion-pair with cation produced by CTAB surfactant and results in non-polar species. On using CTAB concentration 8×10^{-4} M (mobile phase D), peak height for vanadium was nearly quarter to the peak observed in acetonitrile-water system. Then the concentration of CTAB was increased from 0.01 to 0.12 M and the percentage of acetonitrile was kept constant at 20%. Acetonitrile percentage cannot be increased than 30% in any case as it is reported that above 30%, acetonitrile disrupts micelles^[8]. On increasing CTAB concentration from 0.01 to 0.12 M retention time for cobalt decreases from 24.44 to 6.3, but for vanadium no peak was observed using surfactant concentration above cmc possibly due to shift in λ_{\max} . This data supplements the results obtained by spectrophotometry.

Nickel and iron were also investigated along with vanadium and cobalt. Increase in CTAB concentration decreases the retention times indicating that results goes concurrent with literature that divalent cations form uncharged complexes with PAR and increase in micelle concentration helps solubilizing the complexes of iron and increases the elution strength of mobile phase. Although the peaks obtained for two metal ions are broad and poorly sensitive (Figure 2) and are analytically not useful. In the

TABLE 2: Quantification of cobalt in pharmaceutical preparations

Sample	Amount of cobalt (labelled)	Amount found
Neurobion (Merck)	8 μ g/tablet	7.92 μ g/tablet
Revitale (SmithKline)	0.02 μ g/tablet	0.018 μ g/tablet

conditions using CTAB above cmc and acetonitrile at pH 4.3, the method is highly selective for cobalt determination. To assess the applicability of method some pharmaceutical preparations containing cobalt as cynocobalamin (Vitamin B₁₂) were investigated. The results obtained are shown in TABLE 2.

CONCLUSION

Pyridylazo resorcinol forms negatively charged complexes with vanadium, which form ion-pair with cetyltrimethylammonium bromide and subsequently gets extracted in micellar core and results in shift in λ_{\max} from 550 nm to 563 nm. No shift in λ_{\max} of cobalt was observed. Using micellar mobile in liquid chromatography, selective determination of cobalt is possible.

REFERENCES

- [1] K.L.Cheng, K.Uno, T.R.Imanmura; 'Hand Book of Organic Analytical Reagents', Florida, CRC Press, 195 (1982).
- [2] Jahnbaksh Ghasemi, Shahin Ahmadi, Mikael Kubista, Amin Fortoon; J.Chem.Eng.Data, **48**, 1178 (2003).
- [3] A.R.Timerbaev, O.P.Semenova, P.Jandik, G.K.Bonn; J.Chrom.A., **699**, 343 (1995).
- [4] Sadanobu Inoune, Bin Chen, Qiangbin Zhang, Hirotsgun Minami; J.Chrom.Sci., **37**, 306 (1999).
- [5] A.K.Babko, A.I.Volkova, T.E.Getman, Zh.Neorgan; Khim, **11**, 374 (1966).
- [6] E.Rex.Shepherd; Coordination Chemsitry Reviews, 147 (2003).
- [7] M.N.Abbas, A.M.Homoda, G.A.E.Mostafa; Anal. Chim.Acta., **436**, 223 (2001).
- [8] A.Berthod, Garcia-Coque Alveraz; 'Micellar Liquid Chromatography', Marcel-Dekker, (2001).