ПЛОВДИВСКИ УНИВЕРСИТЕТ „ПАИСИЙ ХИЛЕНДАРСКИ“ – БЪЛГАРИЯ
НАУЧНИ ТРУДОВЕ, ТОМ 36, КН. 5, 2008 – ХИМИЯ, СБ. А
PLOVDIV UNIVERSITY „PAISII HILENDARSKI“ – BULGARIA
SCIENTIFIC PAPERS, VOL. 36, BOOK 5, 2008 – CHEMISTRY

EXTRACTION STUDY ON THE COLOUR REACTION FOR VANADIUM(IV) WITH THE 4-NITROCATECHOL (NC) – THIAZOLYL BLUE TETRAZOLIUM (MTT) – WATER – CHLOROFORM SYSTEM

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ABSTRACT

In slightly acidic medium V(IV) forms with 4-nitrocatechol (NC) and 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyltetrazolium bromide (Thiazolyl Blue Tetrazolium, MTT) a well extractable into chloroform, intensively colored ($\varepsilon_{405}=3.5\times10^{4}$ l mol^{-1} cm^{-1}) 1:2:2 complex. The optimal conditions for extractive-spectrophotometric determination of V(IV) were found: pH 4.0-4.8, $C_{NC}= 2.9\times10^{-4}$ mol l^{-1}, $C_{MTT}= 1.6\times10^{-4}$ mol l^{-1}, extraction time = 3 min. The Beer’s law was obeyed up to 1.6 μg ml^{-1} vanadium(IV). The limit of detection (LOD), limit of quantification (LOQ) and Sandell’s sensitivity were calculated to be 0.07 μg ml^{-1}, 0.23 μg ml^{-1} and 1.46×10^{-3} μg cm^{-2}, respectively. The effect of diverse ions on the determination of V(IV) was studied. The extraction process was investigated quantitatively and the key constants (the extraction constant K_{Ex}, the association constant β, and the distribution constant K_D) were determined: Log K_{ex}=12.9, Log β=11.0, Log K_D=1.9. The recovery factor was calculated to be R=98.4 %.

Keywords: Vanadium(IV), Polyphenol, Tetrazolium salt, Ion-association complex, Extraction-spectrophotometry

INTRODUCTION

4-Nitrocatechol (NC) is a suitable ligand for the formation of stable complexes [1-4] and a well-known analytical reagent [5] used for amperometric [6] and spectrophotometric [7-13] determination of a number of metals. The presence of a nitro substituent on the aromatic ring of this compound enhances the acidity of the catechol function [14] and increases the complexing [4] and chromogenic [12,15] power with respect to catechol and other catechol derivatives. That is why the complexes of NC with many metal ions are perspective for investigations with a view of its application to spectrophotometric analysis.

It is known that the chromophore and extraction properties of vanadium complexes with polyphenolic ligands could be improved in the presence of some cationic reagents [15-17]. A promising ion-pair reagent for the extraction-spectrophotometric determination of metal species incorporated in yellow anionic chelates is 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyltetrazolium bromide (Thiazolyl Blue Tetrazolium, MTT) [18]. MTT^+ absorbs light in the same spectral range as the V(IV) – NC chelate [18] and one can expect promotion of the sensitivity of determination in comparison with the sensitivity [18-21] achieved with other reagents from the same class.

The present paper aims at studying the colour reaction for V(IV) with the NC – MTT – water – chloroform extraction system [9,18].

EXPERIMENTAL

Reagents and Apparatus. A stock V(IV) solution with a concentration of $5x10^{-2}$ mol l^{-1} was prepared by dissolving of $VOSO_4.5H_2O$ (Fluka). The concentration was checked by titration with a standard solution of potassium permanganate. NC (Fluka) and MTT (Loba Feinchemie AG) aqueous solutions were prepared with concentrations of 2×10^{-3} mol l^{-1}. The other reagents were CH_3COOH (0.1 mol l^{-1}), CH_3COONa (0.1 mol l^{-1}) chloroform and solutions of diverse ions. All reagents used were of analytical grade. A Specol–11 spectrophotometer (Carl Zeiss, Germany) equipped with 1.0 cm-in-width cells was employed for reading the absorbance. The pH measurements were made with a HI 83140 pH meter (Italy) with a combined plastic electrode.

Procedure. Aliquots of V(IV) solution, acetate buffer solution, NC solution and MTT solution were introduced into 100-ml separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 ml. Then 10 ml of organic solvent were added and the funnels were shaken for several minutes. A portion of the organic layer was filtered through a filter paper into a cell and the absorbance was read against a blank.

RESULTS AND DISCUSSION

In slightly acidic medium (acetate buffer) and in the presence of the ion-pair reagent MTT vanadium(IV) forms with NC an easily soluble in organic solvents ternary complex. The optimal conditions for its formation and extraction are systematized in Table 1. The spectra of the complex and the blank at these conditions are shown in Fig. 1. The composition of the complex was determined by using the equilibrium shift method [22] (Fig. 2) and the method of Asmus [22] and appears to be V(IV):NC:MTT=1:2:2 at the optimal NC and MTT concentrations. With lower concentrations of NC ($C_{NC} \leq 5\times10^{-5}$ mol l^{-1}), however, the NC to V(IV) ratio was 1:1 (Fig. 2) what is in accordance with Ref. 21.

The following equation of formation of the principal 1:2:2 complex was suggested: $2MTT^{+} + [VO(NC)_2]^{2-} \Leftrightarrow (MTT)_2[VO(NC)_2]$. The association constant β characterizing this equilibrium was determined by using the method of Komar-Tolmatchev [22]. This method allows to calculate both the association constant β and the true molar absorptivity ε of the complex {Log β=10.9±0.4; ε=$(3.0\pm0.2)\times10^{4}$ l $mol^{-1}cm^{-1}$}. The apparent molar absorbtivity ε' determined by using Beer's law and other analytical characteristics of the colour reaction are presented in Table 1. The slightly lower value of ε in comparison with ε' could be explained with the possible existence of the 1:1 (V:NC) complex in the organic phase apart from the principle $(MTT)_2[VO(NC)_2]$.

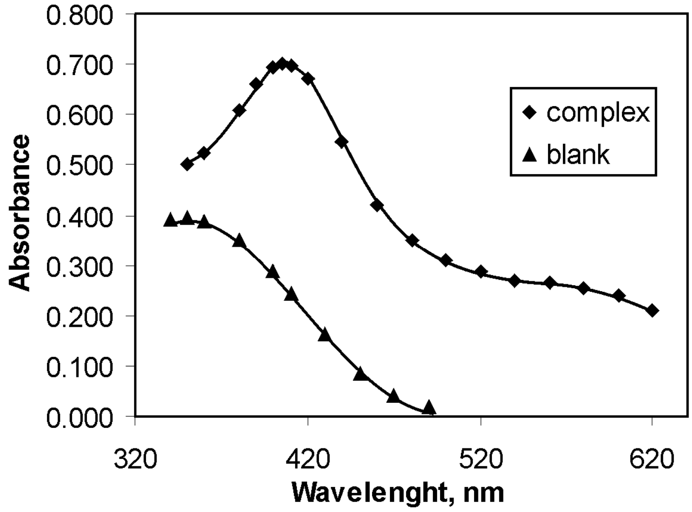

Figure 1. *Spectra of the ternary complex and the blank (NC – MTT) in chloroform.* $C_{V(IV)}=2\times10^{-5}$ mol l^{-1}, $C_{NC}=2.9\times10^{-4}$ mol l^{-1}, $C_{MTT}=1.6\times10^{-4}$ mol l^{-1}, pH=4.7, l=1 cm.

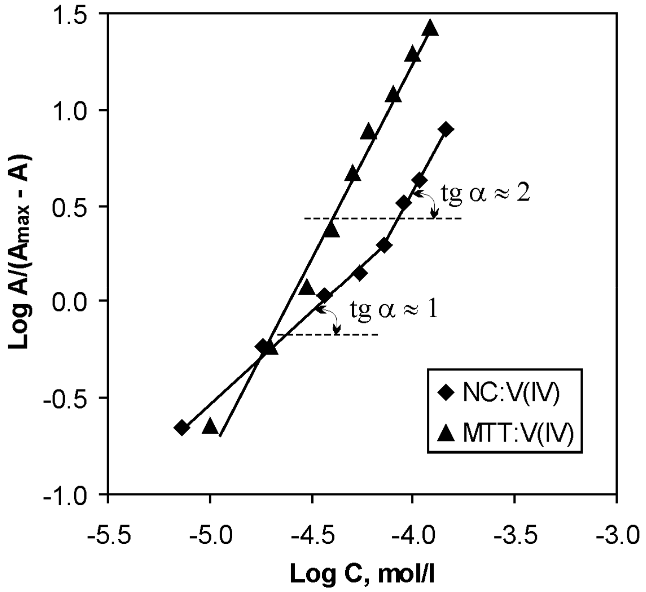

Figure 2. *Determination of the NC to V(IV) ratio and MTT to V(IV) ratio according to the equilibrium shift method.* $C_{V(IV)}=2\times10^{-5}$ mol l^{-1}, pH=4.7, l=1 cm.

Apparent molar absorptivities for some V(IV)-NC-TS systems containing different tetrazolium salts (TS) are juxtaposed in Table 2. It can be concluded that the system studied in this work allows 1.5-3.5 times more sensitive determination of V(IV). The proposed system is superior in terms of sensitivity than the 3,4-dinitrocatechol-diphenylguanidine-water-chloroform system ($\varepsilon'_{max}=2.03\times10^4$ l mol^{-1} cm^{-1}) [15] as well.

The distribution constant K_D, characterizing the distribution of the complex between the phases $\{(MTT)_2[VO(NC)_2]\}_{aq} \Leftrightarrow \{(MTT)_2][VO(NC)_2]\}_{org}$ was evaluated by comparing the absorbance for a single extraction (A_1) to that for triple extraction (A_3) in equal volumes $\{K_D=[V]_{org}/[V]_{aq}=A_1/(A_3-A_1)$; Log $K_D=1.94\pm0.01\}$. Recovery factor R=(98.4±0.1)% was calculated according to the formula $R\% = K_D\times100/(K_D+1)$.

The extraction constant characterizing the total process $2MTT^+ + [VO(NC)_2]^{2-} \Leftrightarrow \{(MTT)_2[VO(NC)_2]\}_{org}$ was determined by the equation Log K_{ex} = Log K_D + Log β = 12.8±0.4.

All calculations were carried out at probability of 95 %.

Table 1. *Optimal conditions and analytical characteristics of the extractive-spectrophotometric determination of V(IV) with 4-NC and MTT*

Optimal conditions	Analytical characteristics
pH 4.0-4.8 (acetate buffer) C_{MTT} (aqueous phase) – 1.6×10^{-4} mol l^{-1} C_{NC} (aqueous phase) – 2.9×10^{-4} mol l^{-1} Volume of the aqueous phase – 10 ml Volume of the organic phase – 10 ml Organic solvent – chloroform Extraction time – 3 min	Wavelength – λ_{max} = 405 nm ε'_{max}= $(3.50\pm0.03)\times10^4$ l mol^{-1} cm^{-1} Beer's law range – up to 1.6 μg ml^{-1} V(IV) Limit of detection – 0.07 μg ml^{-1} V(IV) Limit of quantification – 0.23 μg ml^{-1} V(IV) Sandell's sensitivity –1.46×10^{-3} μg cm^{-2}

The effect of diverse ions on the colour reaction for V(IV) was studied. The following ions do not interfere (in n-fold exsess): Co^{2+} (1100), Ni^{2+} (800), Ce(III) (200), Mg^{2+} (250), Mn^{2+} (1000), Cr^{3+} (5), Zn^{2+} (1500), F^- (100), $H_2PO_4^-$ (250). V(V), Mo(VI), Ti(IV), Nb(V), Fe^{2+}, Al^{3+}, Cr(VI), W(VI), Re(VII), Cu^{2+} and NO_3^- interfere in the same concentration as V(IV). The interfering effect of V(V), Mo(VI), Ti(IV), Nb(V), Fe^{2+} and Cu^{2+} could be attributed to the formation of colored complexes with NC, while that of Cr(VI), W(VI), Re(VII) and NO_3^- is most probably related to the decrease of the effective concentration of the ion-pair reagent MTT.

Table 2. *Influence of the tetrazolium salt (TS) on the apparent molar absorptivity (ε'_{max}) of the ternary V(IV)-NC-TS complex*

Tetrazolium salt	ε'_{max} (l mol^{-1}cm^{-1})	Reference
Triphenyltetrazolium chloride (TTC)	1.0×10^4	19
Neotetrazolium chloride (NTC)	1.9×10^4	21
Iodo-nitro-tetrazolium chloride (INT)	2.36×10^4	20
Thiazolyl Blue Tetrazolium (MTT)	3.50×10^4	present study

CONCLUSION

The extraction-chromogenic V(IV)-NC-MTT-water-chloroform system was studied in details. The sensitivity of the colour reaction for V(IV) was found to be 1.5-3.5 higher than that obtained for similar systems. That is why this system could be used for extractive-spectrophotometric determination of V(IV) in appropriate samples after masking or separation of the interfering ions.

REFERENCES

1. J.P. Cornard, C. Lapouge and J.C. Merlin, *Chem. Phys.*, 340 (2007) 273.
2. A.L.R. Merce, C. Greboge, G. Mendes and A.S. Mangrich, *J. Brazill Chem. Soc.*, 16 (2005) 37.
3. C.J. Macdonald, *Inorg. Chim. Acta*, 311 (2000) 33.
4. J.P. Cornard, Rasmiwetti and J.C. Merlin, *Chem. Phys.*, 309 (2005) 239.
5. L. Sommer, G. Ackermann, D. Thorburn Burns and S.V. Savvin, *Pure Appl. Chem.*, 62 (1990) 2147.
6. A.J. Downard, R.J. Lenihan, S.L. Simpson, B. O'Sullivan, K.J. Powell, *Anal. Chim. Acta*, 345 (1997) 5.
7. K. Kuwada, S. Motomizu, K. Toei, *Japan Analyst*, 26 (1977) 609.
8. A.D. Dimitrov, V.D. Lekova, K.B. Gavazov and B.S Boyanov, *J. Anal. Chem.*, 62 (2007) 138.
9. V.D. Lekova, K.B. Gavazov and A.D Dimitrov, *Chem. Papp.*, 60 (2006) 283.
10. S. Kostova, A. Alexandrov, I. Ilieva, *Nauch. Tr. Plovdiv Univ., Khim.,* 27 (1989) 69.
11. Z. Simeonova, K. Gavazov, A. Alexandrov, *Anaytical Laboratory,* 7 (1998) 184.
12. S. Kostova, A. Dimitrov, A. Alexandrov, *Chem. Pap.,* 54 (2000) 66.
13. K. Gavazov, Z. Simeonova, A. Alexandrov, *Nauch. Tr. Plovdiv Univ., Khim.,* 31 (2002) 13.
14. R.I. Gleb, D.A. Laufer, L.M. Schwartz, K. Wairimu, *J. Chem. Eng. Data*, 34 (1989) 82.
15. A.I. Busev, Z.P. Karyakina, *Zh. Anal. Khim.*, 22 (1967)1506.
16. Z. Marczenko, R. Lobinski, *Talanta*, 35 (1988) 1001.

17. M.J.C. Taylor, J.F. van Staden, *Analyst*, 119 (1994) 1263.
18. K.B. Gavazov, A.N. Dimitrov, V.D. Lekova, *Russ. Chem. Rev.*, 76 (2007) 169.
19. A. Dimitrov, A. Alexandrov, M. Docheva, *Nauch. Tr. Plovdiv Univ., Khim.* 21 (1983) 49.
20. Z. Simeonova, K. Gavazov, A. Alexandrov, *Nauch. Tr. Plovdiv Univ., Khim.,* 33 (2005) 5.
21. K. Gavazov, V. Lekova, A. Dimitrov, Union of Scientists in Bulgaria, National Scientific Conference with International Participation under the heading “20 Years Union of Scientists in Bulgaria – Branch Smolyan” October, 20th-21th, 2006, Scientific papers ISBN 978-954-8329-87-3, p. 808.
22. Bulatov M. I., Kalinkin I. P., Prakticheskoe rukavodstvo po photokolorimetricheskim i spectrophotometricheskim metodam analyza, Khimiya, Leningrad, 1972.