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EXTRACTION-SPECTROPHOTOMETRIC STUDY OF THE COMPLEX FORMATION IN THE SYSTEM VANADIUM(IV) – 4-NITROCATECHOL – IODONITROTETRAZOLIUM CHLORIDE – WATER – CHLOROFORM

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ABSTRACT

The system vanadium(IV) – 4-nitrocatechol (NC) – idonitrotetrazolium chloride (INT) - water – chloroform is studied. The optimum conditions for complex formation and extraction into chloroform are found: pH=3.9-4.5 and reagent concentrations at least 2×10^{-4} mol l⁻¹ NC and 1.2×10^{-4} mol l⁻¹ INT. The composition of the ternary complex is found to be V(IV):NC:INT = 1:2:2 with maximum absorbance at 350 nm. Beer's law is obeyed in the range from 0.1 µg ml⁻¹ to 3.0 µg ml⁻¹ V(IV). Molar absorptivity is found to be $\epsilon_{350} = 2.36 \times 10^4$ l mol⁻¹ cm⁻¹. The following constants are determined: extraction constant $\lg K_{\text{ex}} = 10.6$, association constant $\lg \beta = 9.2$ and recovery factor R=96%. The effect of foreign ions and reagents is studied as well.

Keywords: vanadium(IV), ternary complex, 4-nitrocatechol, idonitrotetrazolium chloride, extraction-spectrophotometry

INTRODUCTION

Vanadium is an element of biological and environmental importance that is why its compounds attract special interest [1]. A considerable number of the studies in the field make use of spectrophotometric methods and are devoted to complexes of vanadium with organic ligands [2]. Complex formation of V(IV) in solutions is less studied as compared to V(V). V(IV) is dominating species in mammals, some natural waters and in various industrial systems. V(IV) exhibits lower toxicity than V(V) [3]. In many cases complexes of V(IV) show better analytical characteristics than the similar complexes of V(V) [4].

V(IV) forms stable oxocations VO^{2+} in aqueous solutions [5]. The most widely applied complexing agents to V(IV) at pH=4-5 are Chrome Azurol S [6,7], Catechol Violet [6,10], Chromoxane Cyanine R [6,8,9] alone or in combination with organic

bases [6-10]. For the quantitative determination of V(IV) are recommended as well the reactions with 9-phenyl-2,3,7-trihydroxy-6-fluorone (Fluorone Black) [11], 9-(2-chlorophenyl)fluorone [12], 3-pyridylfluorone [13] and those reported in ref.[14-16]. The study of V(IV) complexes and comparison of the results with those obtained for V(V) complexes will throw light on the redox processes that may occur during complex formation caused by the ligands or by air oxygen. The system V(V)–NC–INT–water–chloroform has been studied in a previous paper of ours [17]. It has been applied to determination of vanadium in steels [17]. Based on data about complex composition and data reported by other author about similar systems [18] we have assumed that NC reduces V(V) to V(IV), the latter participating in the final complex compound. Having in mind this assumption as well as the insufficient information about complex formation of V(IV) we consider that the system V(IV)–NC–INT–water–chloroform is worthy of studying with a view to theoretical and practical applications.

EXPERIMENTAL

Reagents and Apparatus

- 4-Nitrocatechol (NC), GR from Fluka, 2×10^{-3} mol l⁻¹ aqueous solution;
- VOSO₄·5H₂O, GR from Fluka, 2×10^{-3} mol l⁻¹ in 0.2 mol l⁻¹ H₂SO₄. The concentration was checked by titration with a standard solution of potassium permanganate;
 - Iodonitrotetrazolium chloride (INT), GR from Fluka, 2×10^{-3} mol l⁻¹ aqueous solution;
 - Chloroform, GR;
 - VSU-2P spectrophotometer (Carl Zeiss, Germany).

Procedure for establishing of the optimum operating conditions. 3-ml aliquot of the acetate buffer solution (pH=4.3), aliquot of the V(IV) standard solution in the concentration range from 0.1 µg ml⁻¹ to 3.0 µg ml⁻¹, aliquot of the NC solution in the concentration range from 2×10^{-5} mol l⁻¹ to 8×10^{-4} mol l⁻¹ and an aliquot of the INT solution in the concentration range from 0.4×10^{-5} mol l⁻¹ to 4×10^{-4} mol l⁻¹ are introduced (in the mentioned order) into 100-ml separatory funnel. The aqueous phase is diluted to 10 ml with water and extracted with 10 ml of chloroform for 5 min. The phases are allowed to separate and organic layer is filtered through a paper filter impregnated with chloroform. Absorbance is measured in a 1-cm cell against chloroform. A blank is parallelly run and its absorbance measured against chloroform too.

Procedure for determination of the distribution constant. A 3-ml aliquot of the acetate buffer (pH=4.3) followed by 20 µg V(IV), 5×10^{-4} mol l⁻¹ NC and INT in the concentration range from 2.5×10^{-5} mol l⁻¹ to 4×10^{-4} mol l⁻¹ are introduced into 100-ml separatory funnel. The aqueous phase is diluted to 8 ml with water and extracted with 8.0 ml chloroform for 5 min. Organic layer is filtered through a paper filter impregnated with chloroform, collected in 25-ml calibrated flask and diluted to volume with chloroform. A blank is parallelly run. Absorbance is measured at 350 nm against chloroform.

RESULTS AND DISCUSSION

Optimum conditions for formation of the ternary ion-association complex and its extraction with chloroform

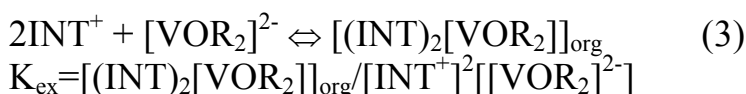
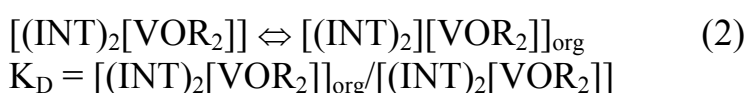
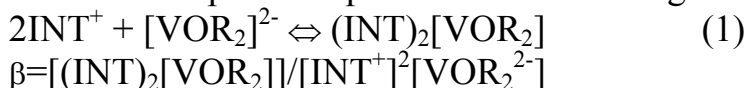
In acidic medium V(IV) forms ternary complex with NC and INT easily soluble in chloroform. Absorbance maximum of the complex in chloroform is at 350 nm. A constant and maximum absorbance of the extracted complex is observed in the pH range of pH=3.9-4.5 (acetate buffer). This pH interval is wider as compared to that established for V(V) complex [17] and is shifted to lower pH values. Optimum concentrations of NC and INT are determined at pH=4.3. The concentration of NC in the aqueous phase should exceed $2 \times 10^{-4} \text{ mol l}^{-1}$ (10-fold excess), while that of INT – $1.2 \times 10^{-4} \text{ mol l}^{-1}$ (6-fold excess). Beer's law is obeyed in the concentration interval from $0.1 \text{ } \mu\text{g ml}^{-1}$ to $3.0 \text{ } \mu\text{g ml}^{-1}$ V(IV). Molar absorptivity calculated using the Beer's law is $\epsilon_{350} = (2.36 \pm 0.07) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$.

The composition of the complex is determined by using the molar ratio method and the Job's method of continuous variations [19] and appears to be V(IV):NC:INT=1:2:2. The following formula of the ternary complex is suggested: $(\text{INT})_2[\text{VO}(\text{NC})_2]$.

The effect of diverse ions on the formation and extraction of the studied complex is summarized in Table 1.

Determination of equilibrium constants K_{ex} , K_D and β in the system V(IV) – NC – INT – H₂O – chloroform.

The following equilibria and the corresponding constants are considered based on data about complex composition and according to the method described in ref. 20:



Distribution coefficient $D = A / (A_{\text{max}} - A)$ is determined at constant vanadium concentration and variable concentration of INT as a ratio between equilibrium concentrations of vanadium species in aqueous and in organic phase. A_{max} is absorbance of the organic phase measured after triple extraction of the complex with chloroform. At V(IV) to INT molar ratio of 1:2, the method described in ref. 20 can be applied only to determination of K_D . Extraction constant K_{ex} is determined using the method of Likussar and Boltz [21] for three values of $K = C_{\text{V(IV)}} + C_{\text{INT}}$: $K_1 = 6 \times 10^{-5} \text{ mol l}^{-1}$, $K_2 = 8 \times 10^{-5} \text{ mol l}^{-1}$ and $K_3 = 1 \times 10^{-4} \text{ mol l}^{-1}$. The calculated three values of K_{ex} agree very well. Association constant β is calculated according to the equation $\beta = K_{ex} / K_D$. The recovery factor $R = (D / (D + 1)) \times 100$ is 96.0%.

$$\lg K_{ex} = 10.6 \pm 0.2 \quad (P=95\%, n=4)$$

$$\lg K_D = 1.4 \pm 0.02 \text{ (P=95\%, n=6)}$$

$$\lg \beta = 9.2 \pm 0.2$$

Table 1. Effect of diverse ions on the extraction of 10 μg V(IV.)

Foreign ion	Ion to V ratio	R %	Foreign ion	Ion to V ratio	R %
Al(III)	50	98.6 ^b	Mn(II)	3000	100.6 ^a
Br ⁻	1	100.0	Mo(VI)	1	104.4
Cd(II)	500 3000	102.5 102.3 ^a	Nb(V)	1	interfere
Ce(III)	6	98.0	Ni(II)	3000	99.9 ^a
citrate ³⁻	60	99.5	NO ₂ ⁻	1	interfere
Cl ⁻	8	98.5	NO ₃ ⁻	1	interfere
Co(II)	200 3000	101.2 98.5 ^a	PO ₄ ³⁻	200	98.8
Cr(III)	800 ^a	95.1 ^a	ReO ₄ ⁻	1	interfere
Cu(II)	200 ^a	96.8 ^a	SCN ⁻	1	interfere
C ₂ O ₄ ²⁻	10	103.0	SO ₃ ²⁻	2	102.2
Fe(II)	1	interfere	SO ₄ ²⁻	4400	100.0
HPO ₄ ²⁻	10	99.3	tartrate ²⁻	75	102.5
H ₂ PO ₄ ⁻	20	99.2	Ti(IV)	1	interfere
IO ₄ ⁻	1	interfere	W(VI)	1	93.3
Mg(II)	3000	102.4	Zn(II)	3000	100.0 ^a

a – in the presence of 0.5 mg sulfosalicylate

b – in the presence of 0.5 mg sulfosalicylate and 1.5 mg F⁻

CONCLUSION

Vanadium(IV) forms stable ternary ion association complex with 4-nitrocatechol and idonitrotetrazolium chloride easily soluble in chloroform. The characteristic features of this complex are superior as compared to that of the similar complex of vanadium(V) [17] – higher molar absorptivity, complex formation occurs in wider concentration interval and pH range, the recovery factor is higher, larger amounts of Zn(II), Cd(II), Co(II), Cr(III), Cu(II), Ni(II), Mn(II) and Mg(II) do not interfere. Molar absorptivity of the ternary complex (INT)₂[VOR₂] formed in the system vanadium(IV) – NC – INT – H₂O – CHCl₃ is higher than the molar absorptivity of vanadium(IV) complexes with the most often used ligands for this oxidation state, namely triphenyl methane derivatives [6-10]: Chromoxane Cyanine R ($\epsilon=8.5 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$), Pyrogallol Red ($\epsilon=4.5 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$), Bromopyrogallol Red ($\epsilon=5.5 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$) and has similar value to the molar absorptivities of vanadium(IV) complexes with Chrome Azurol S ($\epsilon=1.3 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) and Catechol Violet ($\epsilon=2.15 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). The above mentioned advantages reveal that the studied system is suitable for extraction-spectrofotometric determination of traces of vanadium and can successfully compete with known procedures in the field.

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