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Ternary complex formation between vanadium(III) cytosine and some amino acids

Gabriel Enrique Gómez, Lino Hernández, Edgar Del Carpio, Vito Lubes *

Departamento de Química, Universidad Simón Bolívar (USB), Apartado 89000, Caracas 1080 A, Venezuela

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ABSTRACT

In this work we present the results of the speciation of the ternary vanadium(III)–Cytosine (HCyt) complexes with the amino acids Glycine (HGly), Proline (HPro), α-Alanine (HαAla) and β-Alanine (HβAla), studied by means of electromotive force measurements emf (H) using 3.0 mol.dm^{-3} KCl as the ionic medium at 25 °C. The experimental data were analyzed by means of the computational least-squares program LETAGROP, taking into account the hydrolysis of the vanadium(III) cation and the respective stability constants of the binary complexes and the acid base reactions of the amino acids which were kept fixed during the analysis. In the binary vanadium(III)–Cytosine system the formation of the complexes $[V(HCyt)]^{3+}$, $[V(Cyt)]^{2+}$, $[V(Cyt)(OH)]^{+}$, $V(Cyt)(OH)_2$, $[V(Cyt)_2]^{+}$ and $V(Cyt)_3$ was observed. In the ternary systems studied were observed the complexes with the amino acids Glycine, Proline and β-Alanine $[V(HCyt)(HL)]^{3+}$, $[V(Cyt)(HL)]^{2+}$, $[V(Cyt)(L)]^{+}$, $V(Cyt)(L)(OH)$ and $[V(Cyt)(L)(OH)_2]^{-}$ were HL represent the neutral form of the amino acid, with α-Alanine were detected the ternary complexes $[V(HCyt)(HL)]^{3+}$, $[V(Cyt)(HL)]^{2+}$, $[V(Cyt)(L)]^{+}$, $V(Cyt)(L)(OH)$. The species distribution diagrams as a function of pH were briefly discussed.

1. Introduction

Cytosine is one of the four main bases found in DNA and RNA, along with adenine, guanine, and thymine (uracil in RNA). It is a pyrimidine derivative, with a heterocyclic aromatic ring and two substituents attached (an amine group at position 4 and a keto group at position 2). The nucleoside of cytosine is cytidine. In Watson–Crick base pairing, it forms three hydrogen bonds with guanine.

In living systems, almost all the biochemical processes are known to proceed mostly in the solution phase where several metal ions are present in trace quantities. Most of the physiological activities regarding nucleic acid interactions are promoted by metal ions through the formation of ternary (mixed-ligand) complexes [1–3]. Whenever a metal ion exists in solution together with two or more different ligands, the formation of various simple as well as ternary complexes is always possible, depending on the pH of the system. The actual complex formation depends on the affinity of the metal ion towards the various ligands present, and the relative concentrations thereof. The present paper describes the potentiometric study of the binary and ternary complexes involving vanadium(III), cytosine (HCyt), and the amino acids Glycine (HGly), Proline (HPro), α-Alanine (HαAla) and β-Alanine (HβAla), as a contribution to the knowledge of the speciation of the vanadium(III)–HCyt system in biofluids.

Until now, there are no reports on the speciation of the ternary complexes of vanadium(III)–HCyt and the amino acids studied in this work [4,5].

2. Experimental

2.1. Reagents

The VCl_3 (Merck p.a.) and the Cytosine (HCyt) (Merck 99%) and the amino acids HGly, HPro, HαAla and HβAla all (Merck p.a.). Sodium oxalate, potassium permanganate and Mohr's salt (Merck p.a.) were also used to standardize the VCl_3 stock solution. All reagents were used without more purification. The HCl and KOH solutions were prepared using 100.0 mmol.dm^{-3} Titrisol Merck ampoules. The KOH solution was standardized against potassium hydrogen phthalate (Merck p. a.) recrystallized and dried at 120 °C using phenolphthalein as indicator, and the HCl solution was standardized with the KOH solution of known concentration [6]. The solutions were prepared using triple glass-distilled water, boiled before the preparation of the solutions in order to remove dissolved CO_2. To prevent the hydrolysis of the VCl_3 stock solution, it contained 200 mmol.dm^{-3} HCl and was maintained under a H_2 atmosphere in the presence of a Pt platinized net in order to avoid oxidation of the vanadium(III) stock solution to vanadium(IV) [7]. It is important to mention that the VCl_3 is hygroscopic and it must be weighed as fast as possible, for that reason it is necessary to standardized the VCl_3 stock solution, we used a method reported by Mateo and Brito [8]. First, the vanadium(III) is oxidized with a $KMnO_4$ solution to vanadium(V) in acidic medium, the $KMnO_4$ was standardized with

* Corresponding author at: Departamento de Química, Universidad Simón Bolívar (USB), Valle de Sartenejas, Apartado 89000, Caracas 1080 A, Venezuela. Tel.: +58 212 906 39 84; fax: +58 212 906 39 61.
E-mail address: lubesv@usb.ve (V. Lubes).

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Table 1
Values of log β_{pr} for the ligands studied (25 ºC, I = 3.0 mol.dm^{-3} KCl ionic medium).

Equilibrium	log β_{pr}				
	HCyt	Hα-Ala	Hβ-Ala	HGly	HPro
$HL + H^+ \rightleftharpoons H_2L^+$	5.04(1)	2.83(2)	4.09(2)	2.76(2)	2.11(3)
$HL \rightleftharpoons L^- + H^+$	−11.76(9)	−10.08(3)	−10.46(2)	−9.85(2)	−10.88(4)
Dispersion (σ)	0.013	0.023	0.021	0.021	0.027

Values in parentheses are standard deviations [3σ(log β)] on the last significant figure.

Table 2
Equilibrium constants (log β_{pqrs}) for the V(III)–HCyt system (25 °C, I = 3.0 mol.dm^{-3} KCl ionic medium).

Equilibrium	log β_{pqr}
$V^{3+} + HCyt \rightleftharpoons [V(HCyt)]^{3+}$	5.46(3)
$V^{3+} + HCyt \rightleftharpoons [V(Cyt)]^{2+} + H^+$	1.17(8)
$V^{3+} + HCyt + H_2O \rightleftharpoons [V(Cyt)(OH)]^+ + 2H^+$	−2.82(4)
$V^{3+} + HCyt + 2H_2O \rightleftharpoons V(Cyt)(OH)_2 + 3H^+$	−8.00(5)
$V^{3+} + 2HCyt \rightleftharpoons [V(Cyt)_2]^+ + 2H^+$	−0.16(8)
$V^{3+} + 3HCyt \rightleftharpoons V(Cyt)_3 + 3H^+$	−2.48(3)
Dispersion (σ)	0.040

$Na_2Oxalate$, after the oxidation of the vanadium solution it was standardized with a Mohr's salt solution (Fe(II) solution previously standardized with $KMnO_4$) using DAS as indicator. The acidity of the VCl_3 stock solution was determined by the Gran method [9].

The stability of the vanadium(III) stock solution was checked periodically by spectrophotometric measurements and it was shown to be stable for several weeks. The potentiometric measurements were carried out in aqueous solution using 3.0 mol.dm^{-3} KCl as ionic medium. Nitrogen free O_2 and CO_2 were used.

2.2. Methods

The potentiometric measurements were done using the following instruments: Thermo Orion model 520A pH meter, Metrohm EA 876-20 titration vessel, and Lauda Brinkmann RM6 thermostat bath. The sealed 100 mL thermostated double-walled glass titration vessel was fitted with a combined Orion Ross 8102BN pH electrode with a titrant inlet, magnetic stirrer, and an inert nitrogen atmosphere inlet with outlet tubes. The temperature was maintained at 25.0 ± 0.1 °C by constant circulation of water from the thermostat bath.

The emf (H) measurements were carried out by means of the REF//S/GE cell, where REF = Ag / AgCl / 3.0 mol.dm^{-3} KCl; S = equilibrium solution and GE = glass electrode. At 25 °C the emf (mV) of this cell follows the Nernst equation, $E = E^0 + jh + 59.16 \log h$, where h represents the free hydrogen ion concentration, E^0 is the standard potential and j is a constant which takes into account the liquid junction potential [10]. The experiments were carried out as follows: a fixed volume of 0.100 mol.dm^{-3} HCl was titrated with successive additions of 0.100 mol.dm^{-3} KOH until near neutrality in order to get the parameters E^0 and j. Then, aliquots of the cytosine and the amino acid under study were added and finally an aliquot of the vanadium(III) stock solution was added sequentially. And, the titration was continued with 0.100 mol.dm^{-3} KOH. The measurements were done using a total metal concentration, M_T = 2–3 mmol.dm^{-3} and for the binary vanadium(III):HCyt the molar ratios R = 1, 2 and 4 were used, in the case of the ternary vanadium(III):HCyt:amino acids the molar ratios R = 1:1:1, 1:1:2 and 1:2:1 were employed.

The system V^{3+}–HCyt was studied according to the reaction scheme:

$$pH_2O + qV^{3+} + rHCyt \rightleftharpoons [Vq(OH)p(HCyt)r] + pH^+,\ \beta_{p,q,r}$$

The systems V^{3+}–HCyt–Amino Acids (HL) were studied according to the reaction scheme:

$$pH_2O + qV^{3+} + rHCyt + sHL \rightleftharpoons [Vq(OH)p(HCyt)r(HL)s] + pH^+,\ \beta_{p,q,r,s}$$

where HL represents the amino acids studied, [Vq(OH)p(HCyt)r(HL)s] is the ternary (p, q, r, s) complex (the charges were omitted), and β_{pqrs} is the respective stability constant.

The potentiometric data were analyzed using the program LETAGROP [11,12], in order to minimize the function $Z_B = (h - H)/M_T$, where Z_B is the average number of mole of H^+ dissociates per mole of metal, H is the total (analytical) concentration of H^+, h represents the concentration in equilibrium of H^+, and M_T represents the total (analytical) concentration of vanadium(III).

Equilibria corresponding to the formation of the hydroxo complexes of vanadium(III) were considered in the calculation of the stability constants of ternary complexes. The following species were assumed: $[V(OH)]^{2+}$, $\log \beta_{1,-1} = -3.13(8)$; $[V_2O]^{4+}$, $\log \beta_{2,-2} = -3.76(6)$; $[V(OH)_2]^+$, $\log \beta_{1,-2} = -6.86(2)$; and $[V_3(OH)_8]^+$, $\log \beta_{3,-8} = -27.47(4)$ [13]. The vanadium(III)–Glycine [14], vanadium(III)–Proline [15], vanadium(III)–αAlanine [16] and vanadium(III)–βAlanine systems [16] were previously studied by us.

The stability constants of the vanadium(III) hydroxo complexes, the acidity constants of the ligands and the stability constants of the binary complexes were kept fixed during the analysis. The aim was to find a complex or complexes giving the lowest sum of the errors squared, $U = \sum (Z_B^{exp} - Z_B^{calc})^2$, the fittings were done by testing different (p, q, r) and (p, q, r, s) combinations for the binary and ternary system respectively.

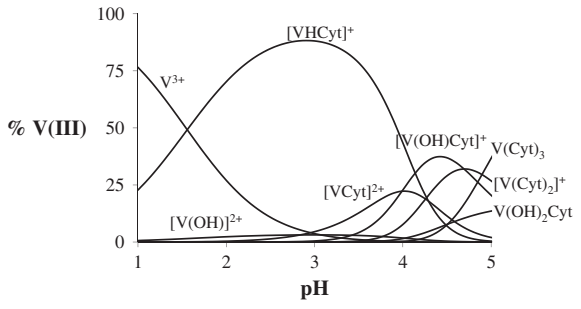

Fig. 1. Species distribution diagram as a function of pH for the V(III)–HCyt system in 3.0 mol.dm^{-3} KCl at 25 °C considering the conditions M_T = 3 mmol.dm^{-3} and molar ratio R = 4.

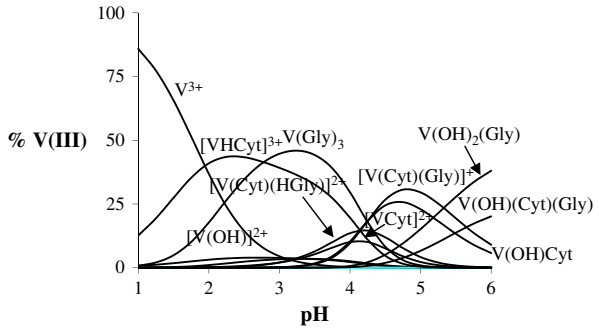

Fig. 2. Species distribution diagram as a function of pH for the V(III)–HCyt–HGly system in 3.0 mol.dm^{-3} KCl at 25 °C considering the conditions M_T = 3 mmol.dm^{-3} and molar ratio R = 1:2:1.