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POTENTIOMETRIC DETERMINATION OF STABILITY CONSTANTS FOR TERNARY VANADIUM(III) COMPLEXES WITH DIPICOLINIC ACID AND THE AMINO ACIDS SERINE, THREONINE, METHIONINE AND PHENYLALANINE

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ABSTRACT

In this work, we present the results of the speciation of the ternary complexes formed between vanadium(III), dipicolinic acid (H_2Dipic) and the amino acids serine (Ser, HL), threonine (Thr, HL), methionine (Met, HL) and phenylalanine (Phe, HL), in aqueous solution at 25.0(1)°C using 3.0 mol.dm^{-3} KCl as the ionic medium. The analysis of the potentiometric data using the least squares computational program LETAGROP, indicates the formation of the species $[V(Dipic)(HL)]^+$, V(Dipic)(L), $[V(Dipic)(L)(OH)]^-$ and $[V(Dipic)(L)(OH)_2]^{2-}$, in the ternary V(III)-H_2Dipic-Amino acids (HL) systems studied. The values of Δ log *K*'' for ternary systems involving amino acids have been evaluated and discussed. The species distribution diagrams as a function of pH were briefly discussed. The spectrophotometric spectra were done in order to get a qualitative characterization of the complexes formed in aqueous solution, indicates that the dipicolinate is acting as a tridentade ligand and the complexes formed are all heptacoordinated.

Keywords: Vanadium(III), dipicolinic acid, amino acids, potentiometric studies, speciation, ternary complexes

DETERMINACIÓN POTENCIOMÉTRICA DE CONSTANTES DE ESTABILIDAD PARA COMPLEJOS DE VANADIO TERNARIO CON ÁCIDO DIPICOLÍNICO Y LOS AMINOÁCIDOS SERINA, TREONINA, METIONINA Y FENILANANINA

RESUMEN

En este trabajo se presentan los resultados de la especiación de los complejos ternarios entre el vanadio (III), el ácido dipicolínico (H_2Dipic) y los aminoácidos serina (Ser, HL), treonina (Thr, HL), metionina (Met, HL) y fenilalanina (Phe, HL), en disolución acuosa a 25 ºC usando 3.0 mol.dm^{-3} KCl como medio iónico. El análisis de los datos potenciométricos, usando el programa computacional de mínimos cuadrados LETAGROP, indica la formación de las especies $[V(Dipic)(HL)]^+$, V(Dipic)(L), $[V(Dipic)(L)(OH)]^-$ and $[V(Dipic)(L)(OH)_2]^{2-}$, en el sistema ternario estudiado V(III)-H_2Dipic-amino ácidos (HL). Los valores de Δ log *K*'' para los sistemas ternarios involucran a los aminoácidos previamente evaluados y discutidos. Los diagramas de distribución de especies son brevemente discutidos. Espectros espectrofotométricos se realizaron con el fin de obtener una caracterización cualitativa de los complejos formados en solución acuosa, indicando que el dipicolinato está actuando como un ligando tridentado y los complejos formados están coordinados de forma heptacoordinada.

Palabras clave: Vanadio(III), ácido dipicolinico, aminoácidos, estudios potenciométricos, especiación de complejos ternarios

INTRODUCTION

The importance of pyridinecarboxylic acids stems from their presence in many natural products such as alkaloids, vitamins, and coenzymes. These compounds are of particular interest to medicinal chemists because of the wide variety of physiological properties displayed by natural and synthetic acids. Moreover, many of the pyridinecarboxylates are versatile ligands and their complexes with some metal ions have found use in medicine and in quantitative analysis. Pyridinecarboxylic acid metal complexes are, therefore, especially interesting model systems, (Khalil & Attia, 2000). It has been reported that dipicolinic acid (pyridine-2,6-dicarboxylic acid, H_2Dipic) is a key component for the high heat resistance of bacterial spores, owing to its ability to build stabilizing with divalent metals, (Chung, Rajan, et al., 1971). From the crystal engineering point of view, dipicolinic acid is also a useful tool for constructing crystalline architectures due to its rigid and planar nature, and its proton donating and accepting capabilities for hydrogen bonding via the oxygen atoms of its carboxylate groups (Wang, et al. 2004). Having potential donor oxygen and nitrogen atoms, dipicolinic acid has attracted the scientist from the coordination chemistry and numbers of studies have been carried out with dipicolinate (Dipic) ligand by both inorganic and bioinorganic chemists during the past few years, (Wang, et al., 2001; Yue, et al., 2005).

Amino acids and their metal complexes are equally important compounds, since they have frequent utilization in both biological and chemical applications.

The vanadium(III) maltolato (ma) complex, $V(ma)_3$, showed a similar activity to normalize the glucose level in the STZ-diabetic rat to the benchmark compound, bis(maltolato)oxovanadium(IV), which is an established insulin-enhancing agent, (Melchior, et al., 1999). Also the vanadium(III) dipicolinate complexes have shown some insulin-mimetic activity, (Buglyó, et al., 2005).

It was studied in vivo coordination structural changes of a potent insulin mimetic agent, bis(picolinato) oxovanadium(IV), by electron spin-echo envelope modulation spectroscopy, (Fukui, et al., 1999) and was observed that the original binary complex is transformed into a ternary complex with a composition of VO(pic)(X), where pic = picolinate and X represents an amino acid. They said that the activity changes substantially by the formation of this ternary complex. Taking into account the possible application of these complexes, we decided to study the formation of the ternary complexes in the vanadium(III), dipicolinic acid (H_2Dipic), and the amino acids: serine (Ser, HL), threonine (Thr, HL), methionine (Met, HL) and phenylalanine (Phe, HL), as a contribution to the knowledge of the speciation of the vanadium(III)-H_2Dipic system in biofluids.

When making an exhaustive bibliographic review, there were no reports on the speciation of the ternary complexes of vanadium(III)-H_2Dipic and the amino acids Serine (Ser, HL), Threonine (Thr, HL), Methionine (Met, HL) and Phenylalanine (Phe, HL), (Martell, Smith, Motekaitis, 1993; Powell, Pettit, 1997).

EXPERIMENTAL

Materials, solutions and methods

VCl_3 (Aldrich) and the amino acids Serine (Ser, HL), threonine (Thr, HL), methionine (Met, HL) and phenylalanine (Phe, HL) (Merck, analytical grade) were used as supplied. The solutions of HCl and KCl were prepared by dissolving the respective acid and salts (Merck, analytical grade) in triply glass-distilled water, that had been boiled in order to remove dissolved CO_2. A carbonate free hydroxide solution (KOH) was prepared from an ampoule of titrisol Merck and standardized against potassium hydrogen phthalate (Kolthoff, & Stenger, 1947). The emf(H) measurements were carried out in aqueous solution at ionic strength 3.0 mol.dm^{-3} in KCl. Nitrogen free of O_2 and CO_2 was used.

The emf(H) measurements were done using the following instruments: pH meter Thermo Orion model 520A, titration vessel Methrom, Lauda Brikmann RM6 thermostatic bath. The sealed 100 ml thermostated double-walled glass titration vessel was fitted with an Orion Ross 8102BN pH electrode and titrant inlet, magnetic stirrer, inert nitrogen atmosphere inlet and outlet tubes. The temperature was maintained at 25.0(1) °C by regular circulation of water from the thermostatic bath. The measurements have been carried out by means of the cell REF//S/GE, 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 Nernst's equation, (equation 1):

$$\mathrm{E} = \mathrm{E^o} + \mathrm{J}h + 59.16\log h \qquad (1)$$

where h represents the free hydrogen ion concentration, E° the standard potential and J a constant which takes into account the liquid junction potential. 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° and J. Then, an aliquot of VCl_3 Stock solution, an aliquot of H_2Dipic and amino acid HL were added. Finally, the titration was continued with KOH 0.1000 mol.dm^{-3}.

The measurements were performed using a total metal concentration, M_T = 3 mmol.dm^{-3} and molar ratios R = 1:1:1, 1:1:2 and 1:2:1 for the V(III):H_2Dipic:amino acids (HL) systems.

The V(III)- H_2Dipic - amino acids (HL) systems were studied according to the reaction scheme:

$$\mathbf{pH_2O + qV^{3+} + rH_2Dipic + sHL \rightleftharpoons [v_4(OH)_p(H_2Dipic)_r(HL)_s] + pH^+}\,\beta_{pqrs} \qquad (2)$$

where HL represents the amino acid studied $[V_q(OH)_p(H_2Dipic)_r(HL)_s]$ are the ternary (p, q, r, s) complexes (the charges were omitted for simplicity), where β_{pqrs} are the respective stability constants.

The potentiometric data was analysed using the program LETAGROP, (Brito, et al., 2005; Sillén, & Warnqvist, 1969), in order to minimize the function (3):

$$Z_B = \frac{(h - \mathrm{H})}{\mathrm{M_T}} \qquad (3)$$

where Z_B is the average number of moles of H^+ dissociated per moles 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 V(III).

Equilibria corresponding to the formation of the hydroxo complexes of V(III) (Lubes, et al., 2010) were considered in the calculation of the stability constants of the ternary complexes. The V(III)-H_2Dipic stability constants were given in, (Lubes, 2005). The V(III)-amino acids systems were previously studied in our group (Lawrence, 2004; Sulbaran M., 2009). The stability constants of the V(III) hydroxo complexes, the dissociation 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, (4), the fittings were done by testing different (*p*, *q*, *r, s*) combinations.

$$\mathbf{U} = \sum (Z_B^{\mathrm{exp}} - Z_B^{\mathrm{calc}})^2 \qquad (4)$$

The species distribution diagrams were done with the computer program HYSS, (Alderighi, et al., 1999) yielding the β_{pqrs} values, which are summarized in Table 1.

Spectrophotometric measurements

The spectrophotometric measurements were performed in order to get information of the complexes formed in aqueous solution. The spectra were measured using the total metal concentration, M_T = 3 mmol.dm^{-3} and the molar ratio, *R* = 1:1:1, at different pH values for the V(III)-H_2Dipic-Ser system.

RESULT AND DISCUSSION

Dissociation constants of the studied ligands

The dissociation constants (Table 2) in the ionic medium 3.0 mol.dm^{-3} KCl are in good agreement with the literature values, considering the differences in ionic strength and ionic medium, (Martell, et al., 1993; Powell & Pettit, 1997). For dipicolinic acid, the first deprotonation H_3L^+/H_2L has a *p*Ka = 0.49, (Funahashi, et al., 1977) but it was impossible to measure it with a glass electrode because of the large contribution of the liquid union potential. The H_2L species should correspond to the zwitterion form of dipicolinic acid. The *p*Ka of the equilibrium H_2L/HL^- corresponds to the deprotonation of the second carboxylic group and the equilibrium HL^-/L^{2-} corresponds to the deprotonation of the pyridine group (pyridine *p*Ka = 5.24), (Martell, et al.,1993). In the case of the amino acids studied it is clear that de pK_{a1} corresponds to the dissociation of the carboxylic group and the pK_{a2} corresponds to the dissociation of the amino protonated group.

TERNARY VANADIUM(III)- H_2DIPIC – AMINO ACIDS (HL) COMPLEXES

Potentiometric Results

In Figure 1 the Z_B(pH) data of the vanadium(III)- H_2Dipic – serine system are observed which is similar for all the amino acids studied, the calculated Z_B *versus* pH curves (continuous line) indicates the correctness of the model obtained which was constructed considering the formation of the complexes $[V(Dipic)(HL)]^+$, V(Dipic)(L), $V(Dipic)(L)(OH)]^-$ and $[V(Dipic)(L)(OH)_2]^2$. In Figure 2 the species distribution diagrams are given for the following conditions: M_T = 3 mmol.dm^{-3} and molar ratio R = 1:1:1, considering the stability constants summarized in Table 1.

In all the system studied the same results were obtained, so for example he results of the vanadium(III)- H_2Dipic – serine system were only given. It is important to mention that in all complexes the Dipic^{2-} acts as tridentate ligand, (Chatterjee, et al., 1998) in the case of the protonated species $[V(Dipic)(HL)]^+$, the amino acids acts as monodentade ligand coordinated to the vanadium by the carboxylic group and in the rest of complexes the amino acids acts as bidentate ligand by N,COO$^-$ coordination.

The relative stability of the ternary complex, compared with the binary complexes, can be obtained considering the Δ log *K*'' value, (Khalil, & Attia, 1999) where Δ log *K*'' is calculated with this equation (5):

$$\Delta \log_{10} K'' = \log_{10} K^{[V(Dipic)]^+}_{V(Dipic)L} - \log_{10} K^{V^{3+}}_{[VL]^{2+}} \qquad (5)$$

Also, the relative stability of the ternary complex compared to the binary ones, can be obtained from the following reaction, (6):

$$V(Dipic)^+ + V(L)^{2+} \rightleftharpoons V(Dipic)(L) + V^{3+} \qquad (6)$$

The Δ log *K''* expresses the effect of the bound primary ligand (Dipic^{2-}) toward an incoming secondary ligand (L$^-$). Positive Δ log *K''* values were obtained (Table 1) for the systems studied indicating favored formation of the ternary complexes over the corresponding binary complexes. This can be ascribed to interligand interactions or some cooperation between the primary and the secondary ligands such as H-bond formation.

The species distribution diagrams are given in Figure 2, in the range $1 < pH < 3.2$ the protonated complex $[V(Dipic)(HL)]^+$ is very important, between $3.2 < pH < 5$ the species V(Dipic)(L) is formed, the species $[V(Dipic)L(OH)]^-$ is the most important complex at pH > 5, and the formation of the complex $[[V(Dipic)L(OH)_2]^{2-}$ at pH > 6 is formed in low extension; the other amino acids behave in a similar way.

The electronic absorption spectra for the V^{3+}-H_2Dipic-ser system were recorded at different pHs for the conditions $M_T = 3$ mmol.dm^{-3} and molar ratio R = 1:1:1 (Figure 3), an intense band in the 400 nm region is observed that increases when the pH is incremented. This band is the characteristic charge-transfer band of the tricoordination of the dipicolinate to the vanadium(III) ion. The inset shows de d-d transition in the 700 nm region attributed to the formation of heptacoordinated complexes, (Kanamori, 2003; Meier, et al., 1998; Schönherr, et al., 1998). Another important observation, which we can see from the absortion spectra, is the absence LMCT (Lubes, 2005).) that indicate the presence of a dimeric μ-oxovanadium(III) complex in this system. It permits us to confirm the formation of monomeric complexes in this system obtained by the emf(H) measurements.

CONCLUSIONS

The analysis of the potentiometric data indicates in all the V(III)-H_2Dipic-HL systems the formation of the complexes $[V(Dipic)(HL)]^+$, V(Dipic)(L), $[V(Dipic)(L)(OH)]^-$ and $[V(Dipic)(L)(OH)_2]^{2-}$. The species distribution diagrams show that for the molar ratios R = 1:1:1 the predominance of the ternary complexes. The relative stability constants in all the system studied indicated that the ternary complexes are more stable than the binary ones. Finally, the analysis of the spectrophotometric measurements indicate that the dipicolinate is acting as a tridentate ligand and that the ternary complexes are heptacoordinated.

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Table 1. Equilibrium constants ($\log_{10}\beta_{pqrs}$) for the ternary V(III)-H_2Dipic – amino acids (HL) systems (25 ºC. I = 3.0 mol. dm^{-3} KCl ionic medium) according to the following reaction scheme:

$$\mathbf{pH_2O + qV^{3+} + rH_2Dipic + sHL \rightleftharpoons [v_4(OH)_p(H_2Dipic)_r(HL)_s] + pH^+}\ \beta_{pqrs}$$

	$\log_{10}\beta_{pr}$			
Species	**HSer**	**HThr**	**HMet**	**HPhe**
$[V(Dipic)(HL)]^+$	8.61(8)	8.66 (4)	8.65 (5)	8.72(6)
V(Dipic)L	5.2(1)	5.55(4)	5.10(6)	5.47(7)
$[V(Dipic)L(OH)]^-$	0.3(1)	0.83(6)	0.28(8)	1.07(7)
$[V(Dipic)L(OH)_2]^{2-}$	-7.1 max -6.7	0.048	-6.8 max -6.2	-5.8(2)
Δ log K”	3.57	3.94	3.83	3.45
Dispersion (σ)	0.087	0.048	0.062	0.071

Values in parentheses are standard deviations [3s($\log_{10}$ b_{pqrs})] on the last significant figure.

Table 2. Values of $\log_{10}\beta_{pr}$ and pK_i for the ligands studied (25ºC. I = 3.0 mol.dm^{-3} KCl ionic medium).

	$\log_{10}\beta_{pr}$				
Equilibrium	**H_2Dipic**	**HSer**	**HThr**	**HMet**	**HPhe**
$H_2L \rightleftharpoons HL^- + H^+$	-1.87(3)				
	-6.62(4)				
$HL + H^+ \rightleftharpoons H_2L^+$		2.29(2)	2.40(2)	2.40(2)	2.65(3)
$HL \rightleftharpoons L^- + H^+$		-8.76(2)	-8.85(2)	-8.99(2)	-9.24(3)
Dispersion(σ)	0.017	0.013	0.015	0.013	0.014
pK_i					
pK_{a1}	1.87 (2.57)[a]	2.29 (2.41)[b]	2.40 (2.41)[b]	2.40 (2.70)[b]	2.65 (2.75)[b]
pK_{a2}	4.75 (4.68)[a]	8.76 (9.64)[b]	8.85 (9.35)[b]	8.99 (9.63)[b]	9.24 (9.61)[b]

Values in parentheses are standard deviations [3s(log b)] on the last significant figure. [a]Reference [14] in 3.0 mol.dm^{-3} KCl. [b]Reference [16].

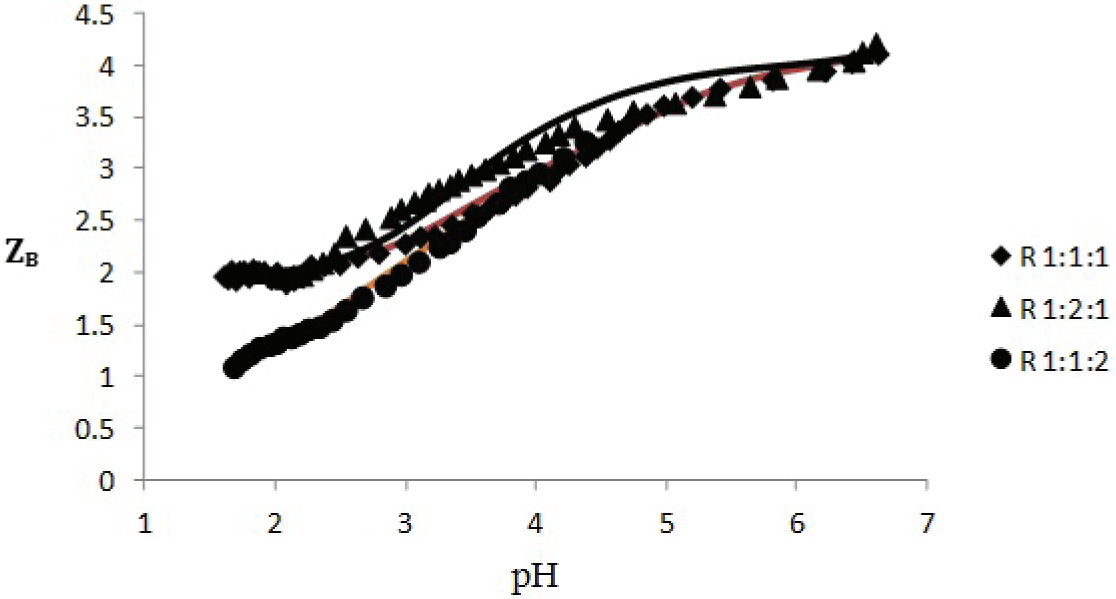

Figure 1. Z_B(pH), data average number of H^+ dissociated per mole of vanadium(III) for the vanadium(III) – H_2Dipic-HSer system. The continuous curve was drawn using the stability constants of Table 1

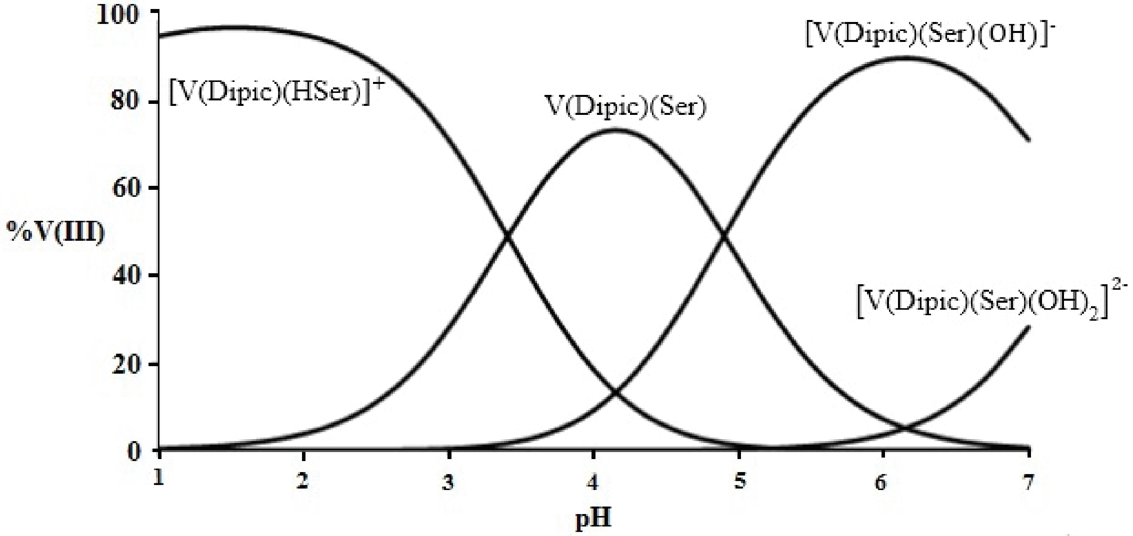

Figure 2. Species distribution diagrams as a function of pH for the Vanadium(III) – H_2Dipic – HSer system in 3.0 mol. dm^{-3} KCl at 25 °C considering the conditions M_T = 3 mmol.dm^{-3} and molar ratio R = 1:1:1. Calculated considering the β_{pqrs} values of Table 1

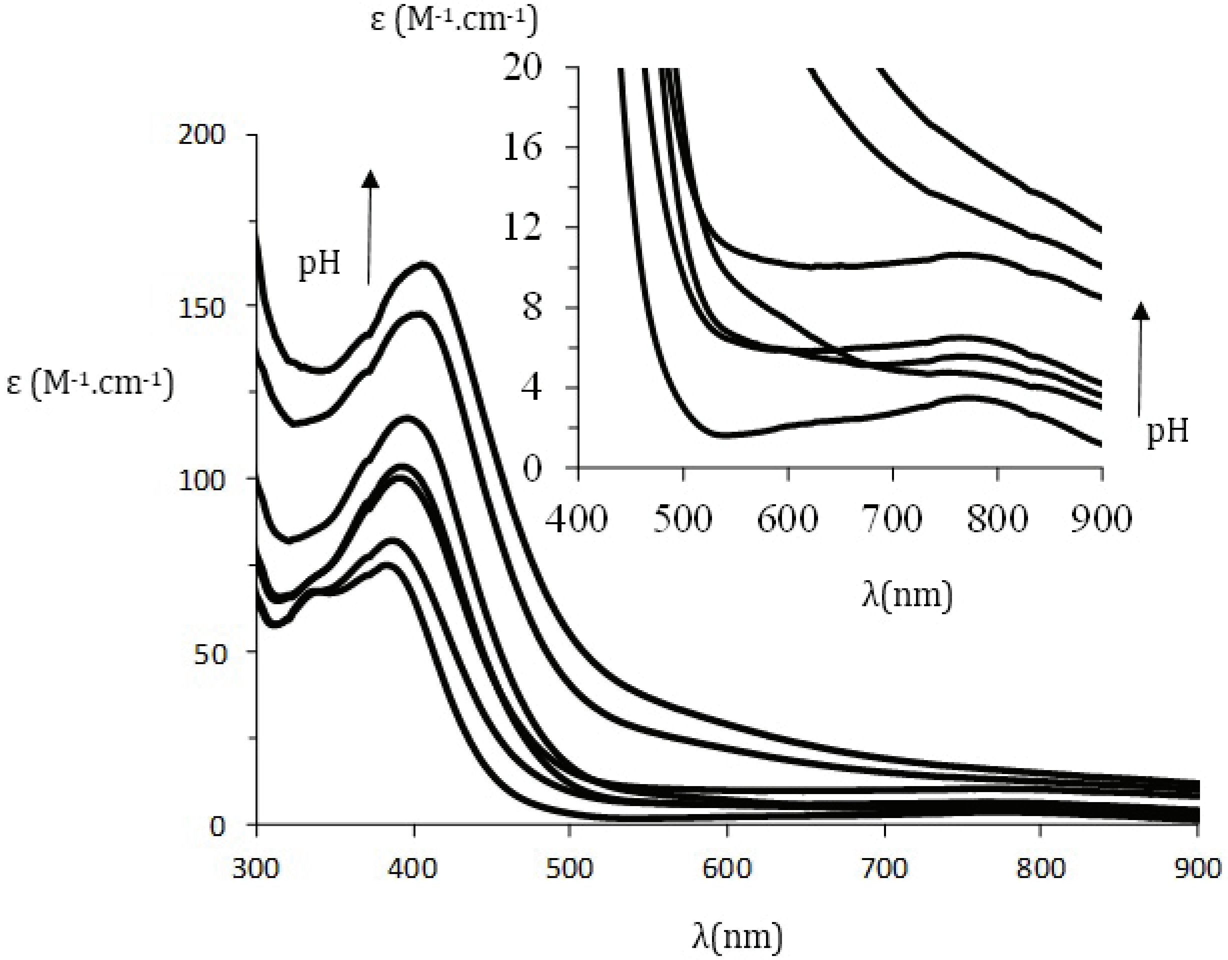

Figure 3*. Electronic absorption spectra for the V(III)-dipicolinic acid-serine system (M_T = 3 mmol.dm^{-3}, R = 1:1:1) at the pH values: 2.02, 3.4, 4.03, 4.25, 4.54, 5.07, 6.07. The inset shows the d-d transition region attributed to the formation of heptacoordinated complexes.*