Electrochemical and Spectral Studies of the Interaction of Niflumic Acid with Metavanadate (VO$_3^-$) Ions

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The voltammetric behavior of niflumic acid (HNIF) in the presence and absence of vanadium (V) was investigated using square-wave (SW) voltammetry at physiological pH. SW voltammogram of HNIF exhibited only one cathodic peak at –0.998 V. Due to the complex formation between metavanadate (VO$_3^-$, abbreviated as MV) and HNIF, a cathodic signal was observed at –1.228 V. According to the electrochemical results, the stoichiometry of V(V) complex was found to be 1:1. The spectroscopic characterization of the synthesized solid powder V(V)-NIF complex was also carried out.

Keywords: Niflumic acid, vanadium (V), complex, stoichiometry, voltammetry, spectroscopy.

1. INTRODUCTION

Non-steroidal anti-inflammatory drugs (NSAIDs) have some pharmaceutical effects [1, 2]. HNIF (Scheme 1) is one of NSAIDs [2]. It is generally used to treat inflammatory rheumatoid diseases [2-4].

Vanadium has various pharmacological, biochemical, physicochemical and electrochemical functions [5-8]. In living systems, vanadium is an ultra-trace element and is found both anionic and cationic forms [9-11]. Vanadium goes into cells as vanadate (V) [12-15]. Vanadates bind to some important biological molecules [13-18]. The interactions of MV with cysteine, tryptophan and nicotionamide were reported in the literature [11, 19, 20]. The great interest in vanadium coordination chemistry has sourced from the vanadium complexes, having the insulin-mimetic effect in the treatment of *Diabetes mellitus* [21-25].
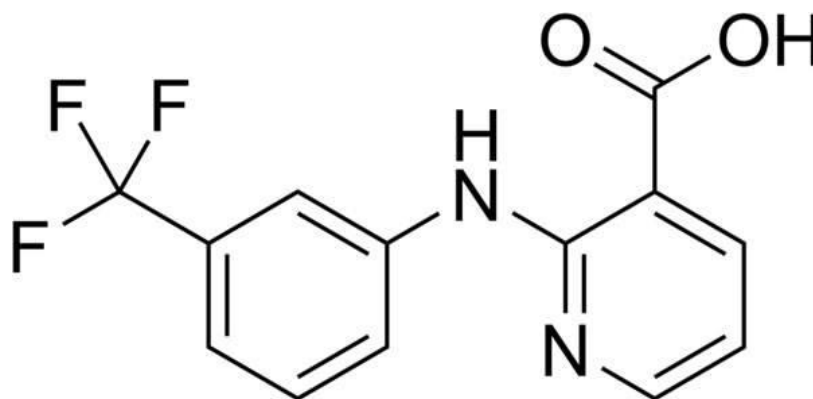
Scheme 1. Chemical structure of HNIF (2-[3-(trifluoromethyl)anilino]pyridine-3-carboxylic acid)

Metal complexes are mostly used in some fields such as biological, pharmaceutical and analytical processes [26-28]. Drugs which have various functional groups can coordinate to metal ions in human organism [27, 29]. Moreover, it is well known that metal complexes of drugs are more effective than parent drugs for many treatments [26, 30, 31]. The binding of HNIF to some metal ions (Cu(II) and Ag(I)) [4, 32-35] has been also studied in the literature. For the characterization of HNIF complexes, their stoichiometries, molecular structures and properties should be investigated. Electrochemistry provides convenient methods for studying mechanism of electrochemical reactions of the metal complexes [36]. In the present study, the identification and characterization of the interaction of ammonium metavanadate (NH_4VO_3, abbreviated as AMV) with HNIF in solution and solid phases have been achieved by the use of spectroscopic techniques, UV-Vis, FT-IR, and NMR as well as square-wave voltammetry (SWV) technique.

2. EXPERIMENTAL

2.1. Reagents and solutions

All the chemicals were of analytical-reagent grade. HNIF and H_3BO_3 were obtained from Sigma. AMV, CH_3COOH, H_3PO_4 and NaOH were purchased from Merck. AMV solution (2×10^{-3} M) was prepared in ultra-pure water. HNIF solution (2×10^{-3} M) was freshly prepared in ethanol. As the supporting electrolyte, Britton-Robinson (B-R) buffer was prepared from a solution including 0.04 M CH_3COOH, H_3PO_4 and H_3BO_3), and adjusted to pH 7.4 with adding of an appropriate amount of 0.2 M NaOH solution.

2.2. Electrochemical measurements

The voltammetric experiments were performed using an EG&G PAR Model 384B polarographic analyzer controlled by a personal computer containing the ECDSOFT [37] software in conjunction with an EG&G PARC Model 303A SMDE stand, including a Hg working electrode, a Pt

auxiliary electrode and an Ag |AgCl| KCl$_{sat.}$ reference electrode. A digital pH meter (Janway 3010) was used to determine the pH value of B-R buffer solution.

Prior to voltammetric experiment, B-R buffer solution was placed in the electrochemical cell and deaerated by N$_2$ gas bubbling for 10 min. Then, a known amount of HNIF solution was added into the voltammetric cell, which was closed, deaerated, and blanketed with N$_2$ gas. The addition of AMV to the cell including HNIF and *vice-versa* were carried out and so, the voltammograms were taken. All results were obtained at room temperature (~ 25 °C). The potential scans at SWV technique (if not stated otherwise) were carried out by using scan rate of 200 mVs^{-1}, frequency of 100 Hz, pulse height of 20 mV, medium drop size and equilibrium time of 5 s. The experimental parameters of cyclic voltammetry (CV) measurements are as follows: scan rate range of 250-1000 mVs^{-1}, medium drop size and equilibrium time of 5 s.

2.3. Synthesis

The vanadium (V) complex was obtained by adding of HNIF in the mole ratio of 1:1 while continuing heating in order to dissolve AMV in water of 30 cm^3. The solution obtained was filtered and then was evaporated slowly at room temperature for solidification. The solid product was recovered by filtering. The melting point of the solid complex (191-193 °C) formed is lower than those of HNIF (203-204 °C [38]) and AMV (200 °C [39]).

2.4. Spectroscopic measurements

Electronic spectra of the solutions of AMV, HNIF, and AMV-NIF complex were taken to follow the changes in absorption bands. Electronic spectra were recorded on a Thermo Scientific Evolution Array EA-1301005 UV-Vis spectrophotometer in the range of 200-900 nm with quartz cell of 1 cm length.

The FT-IR spectra were recorded from KBr pellets with a Bruker 2000 interferometer. ^{1}H NMR spectrum was recorded on a 400 MHz Bruker spectrometer in deuterated DMSO solution using TMS as the internal reference.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization of HNIF in the presence and absence of AMV at pH 7.4

SW voltammogram of HNIF in 0.04 M B-R buffer solution (pH 7.4) showed a broad cathodic peak at −0.998 V on hanging mercury drop electrode (Fig. 1).
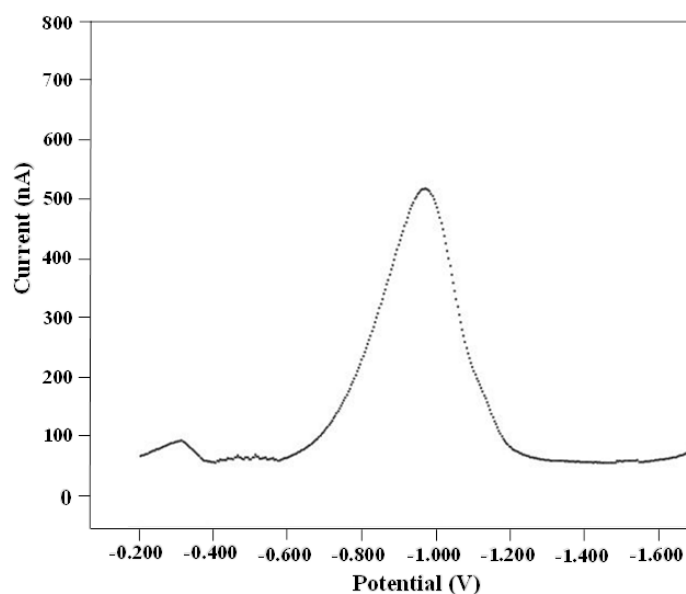
Figure 1. SW voltammogram of 2×10^{-5} M HNIF in 0.04 M B-R buffer (pH 7.4). *Experimental conditions are as given is* Section 2.2.

The electrochemical behaviour of HNIF was also investigated by CV (Fig. 2). CV measurements of HNIF were carried out at different scan rates (250-1000 mVs^{-1}).
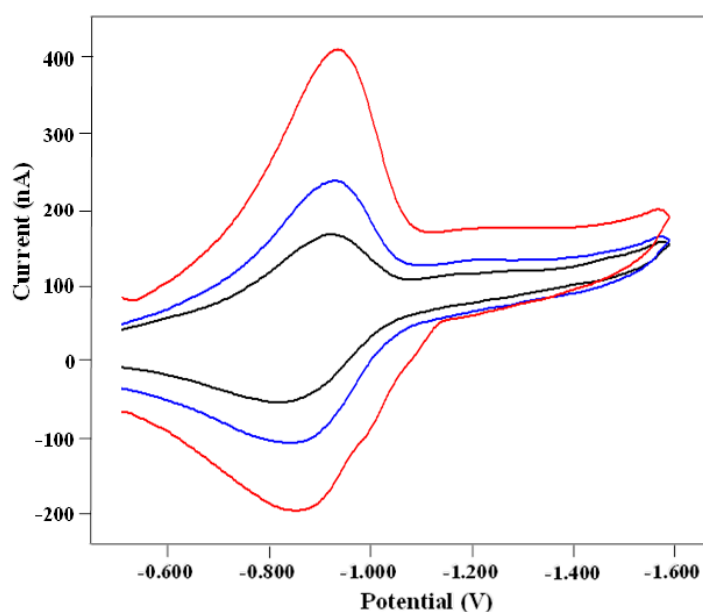
Figure 2. Cyclic voltammograms of 2×10^{-5} M HNIF solution in 0.04 M B-R buffer (pH 7.4) for different scan rates: 333 (black line), 500 (blue line) and 800 mVs^{-1} (red line). *Other experimental conditions are as described in* Section 2.2.

The anodic peak of HNIF was observed on reverse potential scan (Fig. 2). As can be seen in Fig. 3, the current ratio between anodic and cathodic peaks (I_{pa} / I_{pc}) is very close to one at all scan rates used. Moreover, the distance between the anodic and cathodic peak potentials ($\Delta E_p = E_{pa} - E_{pc}$) was in the range of 60-80 mV and also proportionally dependent on the scan rate. In addition, both E_{pa} and E_{pc} shifted to more negative potentials with increasing scan rate. This behavior confirms that the reduction process is quasi-reversible [40, 41]. Under the studied experimental conditions, the linear dependences between the peak currents, (I_{pc}, I_{pa}) and scan rate, v, were found (for 250-800 mVs^{-1}, I_{pc} (nA) = 0.3683 v (mVs^{-1}) − 42.187; R^2 = 0.9982; for 250-1000 mVs^{-1}, I_{pa} (nA) = 0.323 v (mVs^{-1}) − 21.428; R^2 = 0.9974; Fig. 3). As a result, the electrode reaction of HNIF includes an adsorption controlled and quasi-reversible mechanism at physiological pH [40, 42].
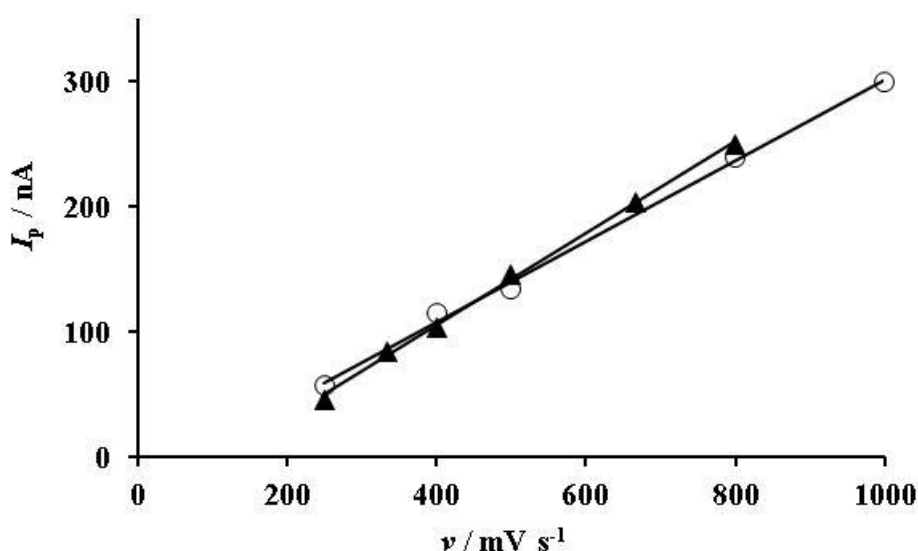
Figure 3. The plots of I_{pc} (▲) and I_{pa} (○) *vs.* scan rate (v) of 2×10^{-5} M HNIF in 0.04 M B-R buffer (pH 7.4).

From the relation ($E_p - E_{p/2}$) = 0.048/αn where $E_{p/2}$ is a potential at half-cathodic peak current [41], the value of αn for the quasi-reversible reduction process of HNIF at pH 7.4 was found to be about 0.5. As can be seen in Scheme 1, HNIF includes >C=N- group in pyridine ring. Therefore it was assumed that the number of electrons transferred, n was 2. So, the value of α was found to be 0.25. This value is very close to α range of 0.45-0.30 for electron transfer slowness relative to mass transfer [40].

As similar to the reductions of clonixin [43] and losartan [40], the overall electrode reaction of HNIF can be given as the reduction of >C=N- group in pyridine ring to saturated bond by consuming 2 electrons and 2 protons (Scheme 2).
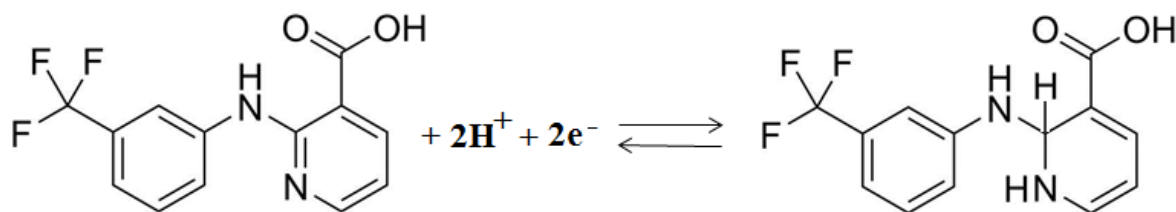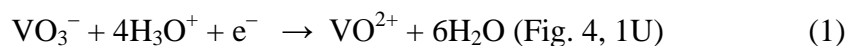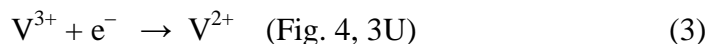
Scheme 2. The proposed electrode reaction of HNIF

Under the same conditions, SW voltammogram of AMV in the absence of HNIF gave three cathodic peaks at –0.272 V, –0.536 V and –1.416 V, respectively (Fig. 4). The numbers of cathodic waves of vanadium (V) change according to both the type and pH of the medium [19, 44].
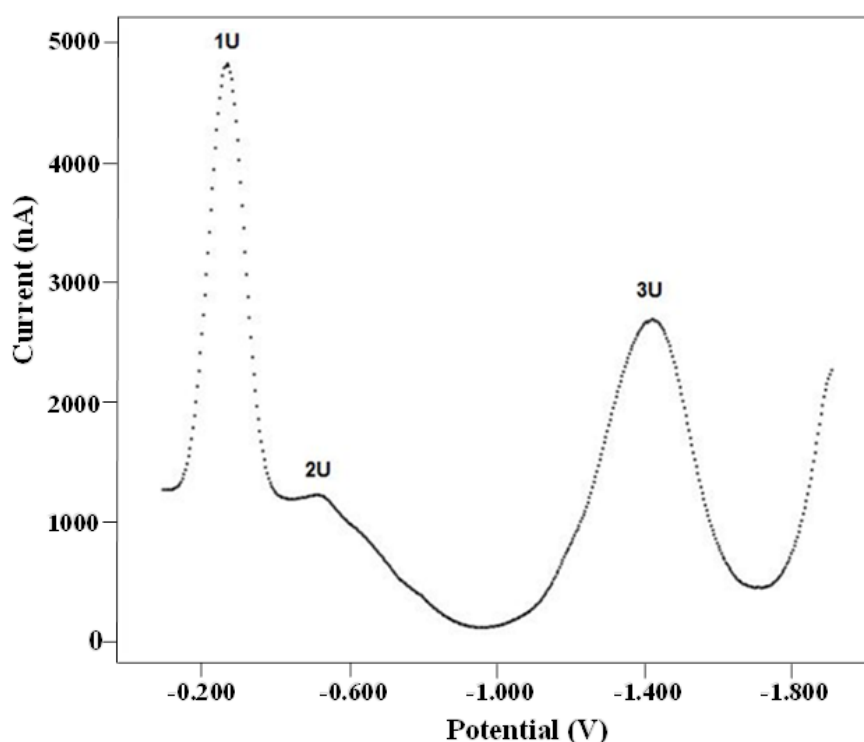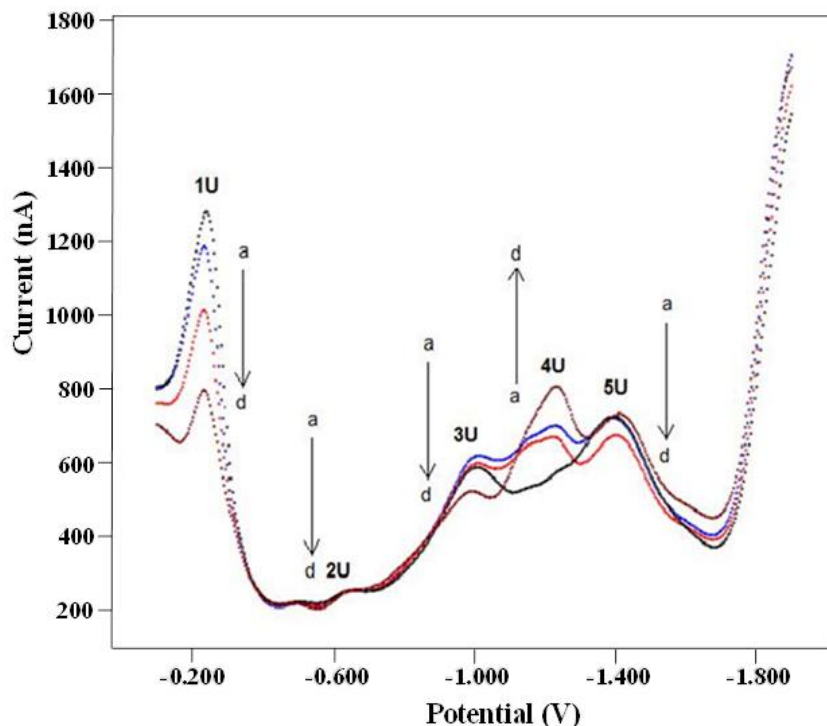

Figure 4. SW voltammogram of 1×10^{-4} M AMV in 0.04 M B-R buffer (pH 7.40). **1U,** the reduction peak of free V(V) to V(IV) (−0.272 V); **2U,** the reduction peak of V(IV) to V(III) (−0.536 V); **3U,** the reduction peak of V(III) to V(II) (−1.416 V). *Experimental conditions are as described in* Section 2.2.

Also, in some complexing media, three cathodic waves are seen, which correspond to the steps, including reductions to V(IV), V(III), and V(II) [44]. In this study, the obtained peaks (at –0.272 V, –0.536 V and −1.416 V, respectively) can be assigned to V(V)-V(IV), V(IV)-V(III) and V(III)-V(II) reduction steps as follows [45, 46]:

$$VO_3^- + 4H_3O^+ + e^- \rightarrow VO^{2+} + 6H_2O \text{ (Fig. 4, 1U)} \qquad (1)$$
$$VO^{2+} + 2H_3O^+ + e^- \rightarrow V^{3+} + 3H_2O \text{ (Fig. 4, 2U)} \qquad (2)$$

$$V^{3+} + e^- \ \rightarrow \ V^{2+} \quad \text{(Fig. 4, 3U)} \qquad \qquad (3)$$

The voltammetric behaviour of AMV in the presence of HNIF has dramatically changed. With adding of HNIF to the electrochemical cell including 1×10^{-4} M AMV, a new reduction peak was observed at -1.228 V (Fig. 5), while the peak currents of free AMV decreased.


Figure 5. SW voltammograms of 1×10^{-4} M AMV in the presence of a) 1×10^{-4} M, b) 1.3×10^{-4} M, c) 1.5×10^{-4} M, d) 2×10^{-4} M HNIF at 0.04 M B-R buffer (pH 7.4). 1U: the first cathodic peak of free AMV; 2U: the second cathodic peak of free AMV; 3U: the cathodic peak of free HNIF, 4U: the cathodic peak of V(V)-HNIF complex, 5U: the third cathodic peak of free AMV. *Experimental conditions are as described in* Section 2.2.

The current of peak at -1.228 V increased with the increase in HNIF concentration (Figures 5 and 6). This new peak (at -1.228 V) may be resulted from the reduction of V(V)-NIF complex in the solution medium.

So as to obtain the coordination number (m) of the V(V)-NIF$_m$ complex, the following equation [47, 48] can be utilized:

$$1/I_p = 1/I_{p,max} + 1/\{ \ \beta \ I_{p,max} \ [L]^m\} \qquad \qquad (4)$$

where I_p is the peak current of V(V)-NIF$_m$ complex, $I_{p,max}$ corresponds to the maximum current when all V(V) ions form V(V)-NIF$_m$ complex, [L] is HNIF concentration and β is the stability constant of V(V)-NIF$_m$ complex.
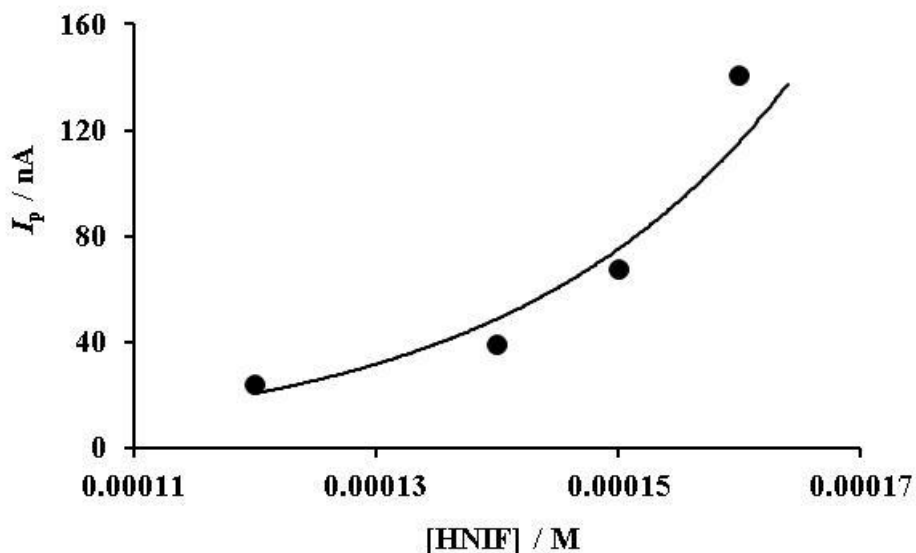
Figure 6. The variation of the cathodic peak current of V(V) complex as function of the HNIF concentration in the presence of 1×10^{-4} M AMV at 0.04 M B-R buffer (pH 7.4). *The experimental conditions are as described in* Section 2.2.
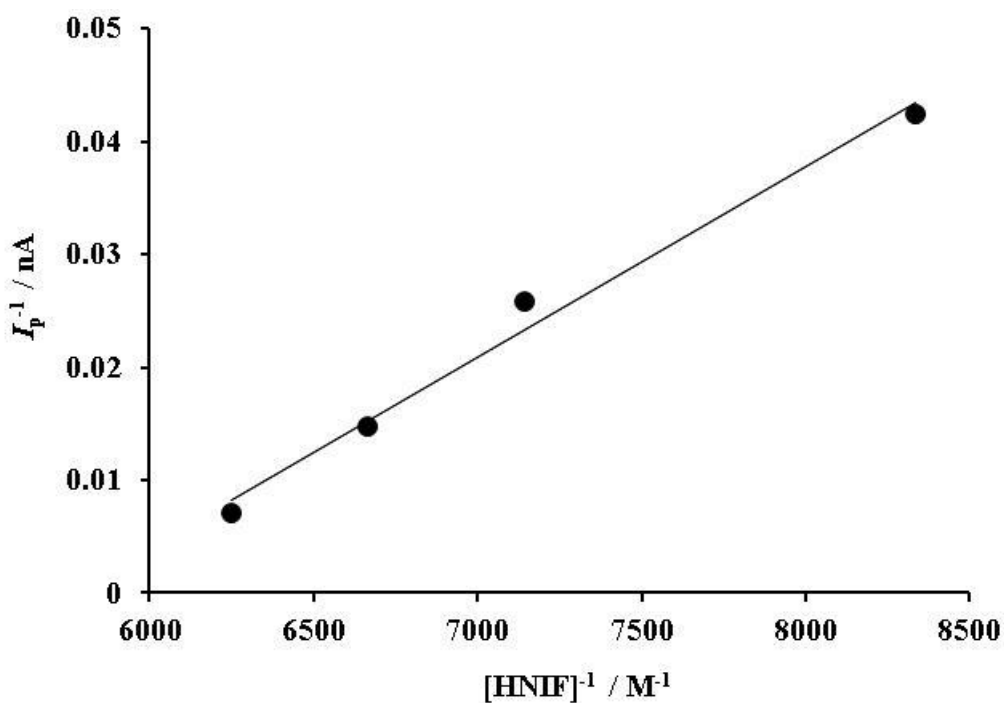

Figure 7. The plot of I_p^{-1} *versus* $[\text{HNIF}]^{-1}$. I_p is the peak current of V(V)-NIF complex. *The experimental conditions are as described in* Section 2.2.

By plotting I_p^{-1} as function of $[\text{HNIF}]^{-m}$ for different m values, a straight line will be obtained for V(V)-NIF$_m$ complex. With analyzing the experimental results, a straight line ($r = 0.9937$) has been seen for $m = 1$ (Fig. 7). According to the above results the stoichiometry of the electroactive V(V)-NIF$_m$ complex can be given as 1:1.

3.2. UV-Vis spectra
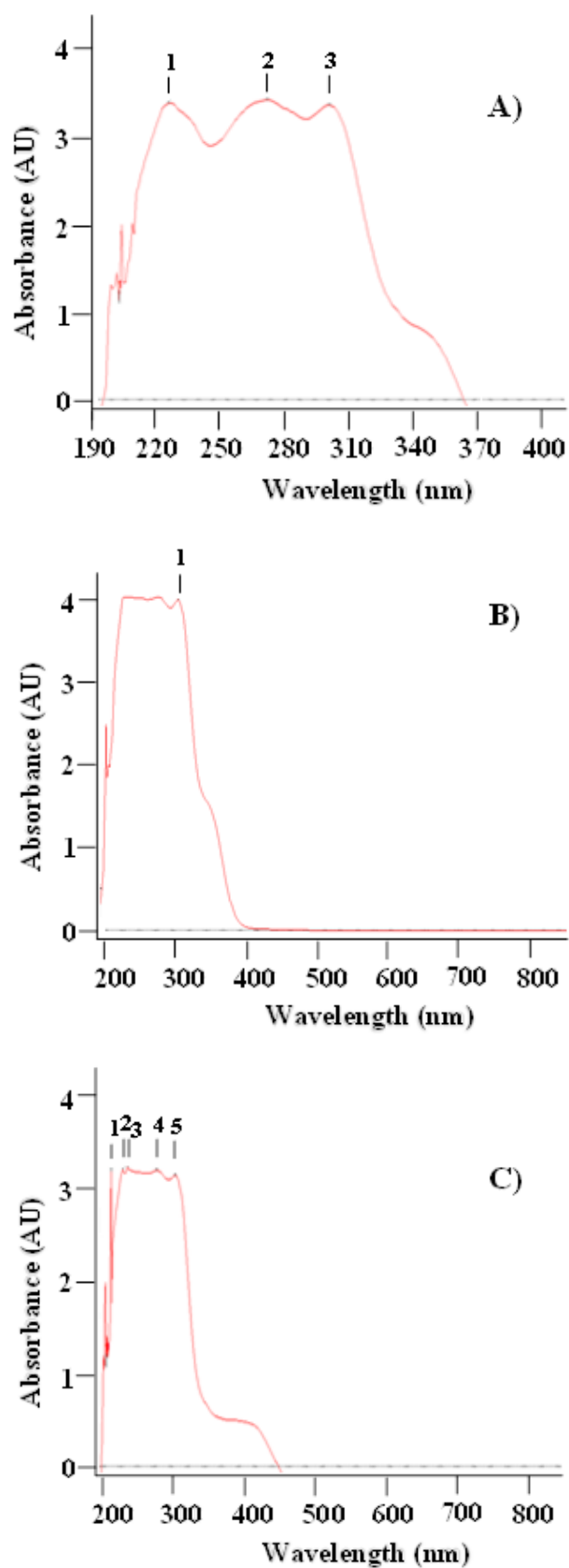
Figure 8. Electronic spectra of A) 1×10^{-3} M HNIF, B) 1×10^{-2} M AMV and C) V(V)-NIF complex solution (0.01 g / 5 mL water).

The UV-Vis spectra of AMV, HNIF and V(V)-NIF complex are shown in Fig. 8. Their electronic spectra data are submitted in Table 1.

Table 1. Characteristic wavelengths for maximum absorbances of AMV, HNIF, and V(V)-NIF complex

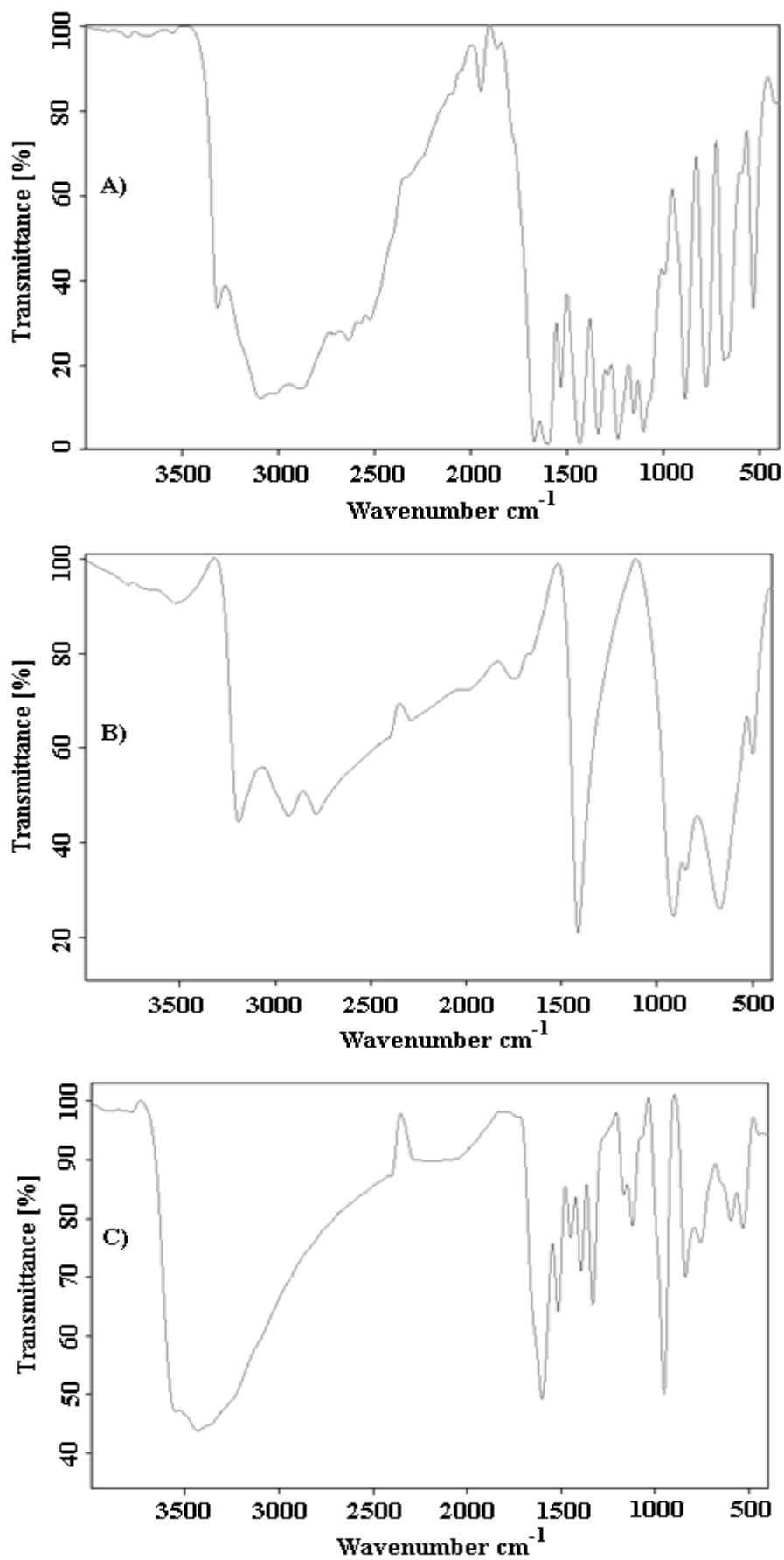| AMV	HNIF	V(V)-NIF complex
	226	227
		235
	272	276
302	301	302
350 (sh)	347 (sh)	419

sh: shoulder

As can be seen in Table 1, HNIF and AMV exhibited four (226, 272, 301 and 347 nm (shoulder)) and two (302 and 350 nm (shoulder)) the characteristic absorption bands, respectively. In the case of V(V)-NIF complex, the shifts in the band positions (from 272 to 276 nm) and new bands (235 and 419 nm) were obtained (Fig. 8 and Table 1). The two bands at 235 and 276 nm correspond to LMCT transitions from oxygen atoms to vanadium, respectively [11]. Also, the band at 276 nm can be attributed to intraligand transitions, presumably combined with the O→V charge transfer which contains the double bonded oxo group [49, 50]. The solutions of many vanadate (V) species and vanadium (V) bound to oxygen donor ligands give a yellow color which is due to intense LMCT bands tailing from the UV region [51]. For V(V)-NIF complex, the bands at 276 and 302 nm substantially involve the O atom, whereas the other one at 419 nm (shoulder) may be owing to the N atom [49, 50]. In the complexes of V(V), LMCT bands may be expected due to the high oxidation state and empty d orbitals of the metal atom [52, 53].

At the UV-Vis spectrum of V(V)-NIF complex, the observed changes at the bands and the formation of new bands according to those of free AMV and HNIF supported the assumption of binding of HNIF to vanadium ions.

3.3. FT–IR spectra

The structure of the V(V)-NIF complex was also studied by IR spectroscopy. The infrared spectra of the V(V)-NIF complex, AMV and HNIF are shown in Fig. 9. The spectrum of AMV in the region of 1000-500 cm^{-1} exhibited the bands at 913, 848 and 671 cm^{-1}, respectively. The NH$_4^+$ ion has two bands: at (N-H stretching) 3193 cm^{-1} and (NH$_4^+$ deformation) 1413 cm^{-1}.

The addition bands also occurred in the region 3000-2500 cm^{-1}. These are characteristic bands of AMV [51, 54]. The bands in the region 950-850 cm^{-1} are due to the stretching vibrations of the V-O bonds [51, 54].

Figure 9. The FT-IR spectra of A) HNIF, B) AMV and C) V(V)-NIF complex in KBr disc

As can be seen in Fig. 9, the symmetric and unsymmetric stretching vibrations of carboxylic acid group in the HNIF molecule at 1669 and 1435 cm^{-1} were shifted to the lower frequencies (1600 and 1394 cm^{-1}) owing to its coordination to vanadium(V) ions. It is already well known that the stretching band of coordinated carboxylate group (COO$^-$) is seen at 1650-1590 cm^{-1} [55, 56].

Also, the very important band of V(V)-NIF was seen at 952 cm^{-1}. This band can be assigned to the vanadyl (V=O) stretching mode [57]. The stretching vibration of V=O in AMV (at 913 cm^{-1}) was shifted to a higher frequency (952 cm^{-1}) due to the coordination of vanadium(V) ions to HNIF. Furthermore, the ν(OH) band at 3431 cm^{-1} shows the presence of coordinating water [58].

It is worthy that the FTIR spectrum of HNIF show two prominent bands at 1669 and 1597 cm^{-1} attributed to C=O and C=N stretching modes, respectively. Upon the complexation, instead of these bands, only one band was seen at 1600 cm^{-1}. Moreover, the spectrum of free HNIF also contains the bands at 3092 and 3312 cm^{-1}. These can be attributed to the stretching vibration of CH groups on the phenyl ring and NH stretching vibration, respectively [59, 60]. However, these bands were not observed in the spectrum of V(V)-NIF complex as similar to the spectrum of ambazone salt with HNIF [59].

Finally, the structure of V(V)-NIF complex can be proposed as illustrated in Scheme 3.
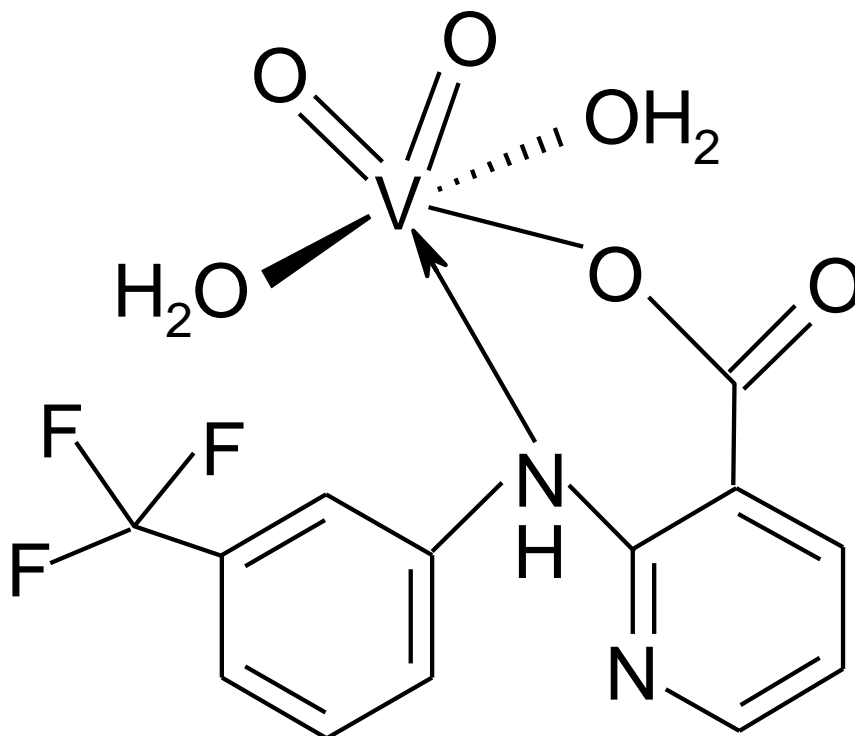

Scheme 3. The proposed structure of V(V)-NIF complex
(mono(niflumato)di(aqua)dioxovanadium(V))

3.4. NMR spectra

In Fig. 10, the ^{1}H NMR spectrum of V(V)-NIF complex in DMSO-d$_6$ is seen. The chemical shifts of the various hydrogen atoms were easily assigned as similar to the ^{1}H shifts of similar

compounds [61-67]. The ^{1}H NMR spectrum of the complex (Fig. 10) displays the following signals: aromatic protons at 6.5-7.0 ppm [61], pyridinic protons at 7.3-8.5 [62] and intramolecular hydrogen bonded OH group at 13.6 ppm [63]. The signal at 3.7 ppm may have sourced from the centered NH or crystallization water [64-66]. Other signal at 2.5 ppm is owing to DMSO [66]. The sharp signal at 1.7 ppm may have also sourced from the water adsorbed on the complex as related to different structures of the water [67].
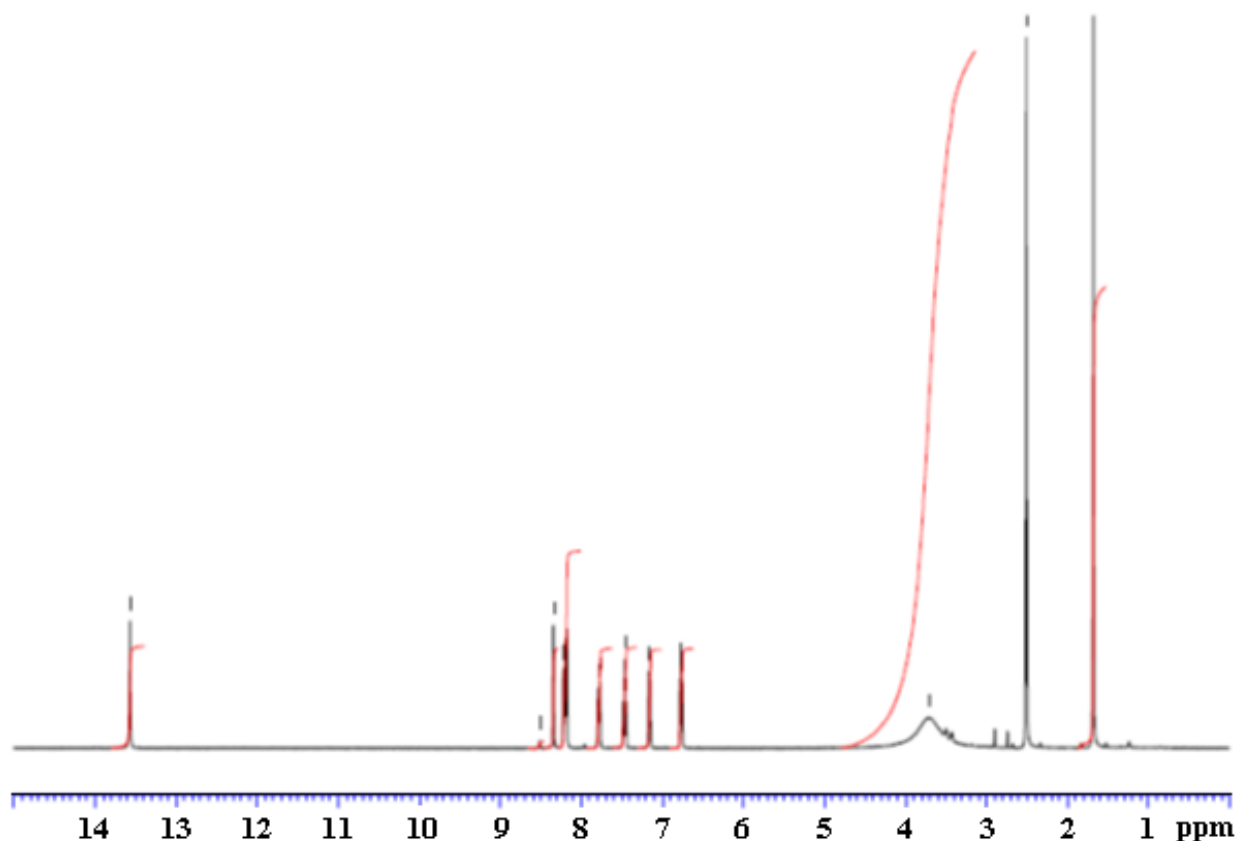
Figure 10. The ^{1}H NMR spectrum (400 MHz) of a solution of V(V)-NIF complex in DMSO-d_6 solvent at ambient temperature (295.1 K).

4. CONCLUSION

The voltammetric data exhibit that V(V)-NIF complex has a stoichiometry of 1:1. At the FTIR spectrum of the complex, the band at 952 cm^{-1} proves the presence of V=O stretching mode. The electronic absorption spectrum shows some peaks as a result of the coordination of oxygen and nitrogen atoms in the V(V)-NIF complex. According to the experimental data, a proper structure of V(V)-NIF complex has been proposed.

References

1. C.P. Duffy, C.J. Elliott, R.A. O'Connor, M.M. Heenan, S. Coyle, I.M. Cleary, K. Kavanagh, S. Verhaegen, C.M. O'Loughlin, R. NicAmhlaoibh and M. Clynes, *Eur. J. Cancer* 34 (1998) 1250.
2. T. Paulina, F. Perdih, I. Turel and G. Psomas, *Polyhedron* 53 (2013) 215.
3. J.R.J. Sorenson, *J. Med. Chem.* 19 (1976) 135.
4. F.T. Greenaway, E. Riviere, J.J. Girerd, X. Labouze, G. Morgant, B. Viossat, J.C. Daran, M. Roch Arveiller and N.-H. Dung, *J. Inorg. Biochem.* 76 (1999) 19.
5. G. Maciejewska, M. Nosek, T. Głowiak, J. Starosta and M. Cieslak-Golonka, *Polyhedron* 22 (2003) 1415.
6. M. Weyand, H.-J. Hecht, M. Kieß, M.-F. Liaud, H. Vilter and D. Schomburg, *J. Mol. Biol.* 293 (1999) 595.
7. A. Butler and J.V. Walker, *Chem. Rev.* 93 (1993) 1937.
8. X. Huang, B. Dai, G. Xu, X. He, S. Zhou, Y. Chen and B. Liu, *Int. J. Electrochem. Sci.* 9 (2014) 6640.
9. M. Garner, J. Reglinski, W.E. Smith, J. McMurray, I. Abdullah and R. Wilson, *J. Biol. Inorg. Chem.* 2 (1997) 235.
10. D. Rehder, *BioMetals* 5 (1992) 3.
11. S. Çakır and E. Biçer, *J. Chil. Chem. Soc.* 55 (2010) 236.
12. Y. Shechter and S.J.D. Kadish, *Nature* 284 (1980) 556.
13. G.R. Dubyak and A. Kleinzeller, *J. Biol. Chem.* 255 (1980) 5306.
14. L.C. Cantley and P. Aisen, *J. Biol. Chem.* 254 (1979) 1781.
15. M. Purcell, A. Novetta-Delen, H. Arakawa, H. Malonga and H.A. Tajmir-Riahi, *J. Biomol. Struct. Dyn.* 17 (1999) 473.
16. J. Li, G. Elberg, D.C. Crans and Y. Shechter, *Biochemistry* 35 (1996) 8314.
17. Y. Shechter, J. Li, J. Meyerovitch, D. Gefel, R. Bruck, G. Elberg, D.S. Miller and A. Shisheva, *Mol. Cell. Biochem.* 153 (1995) 39.
18. L.M. Pierce, F. Alessandrini, J.J. Godleski and J.D. Paulauskis, *Toxicol. Appl. Pharmacol.* 138 (1996) 1.
19. S. Çakır and E. Biçer, *Bioelectrochemistry* 64 (2004) 1.
20. S. Çakır and E. Biçer, *Turk. J. Chem.* 31 (2007) 223.
21. N.S. Youssef, E.A. El Zahany and M.M. Ali, *Phosphorus Sulfur and Silicon and the Related Elements*, 185 (2010) 2171.
22. M.R. Maurya, *Coord. Chem. Rev.* 237 (2003) 163.
23. H. Sakurai, Y. Kojima, Y. Yoshikawa, K. Kawabe and H. Yasui, *Coord. Chem. Rev.* 226 (2002) 187.
24. M. Nakai, M. Obata, F. Sekiguchi, M. Kato, M. Shiro, A. Ichimura, I. Kinoshita, M. Mikuriya, T. Inohara, K. Kawabe, H. Sakurai, C. Orvig and S. Yano, *J. Inorg. Biochem.* 98 (2004) 105.
25. M.M. Lalović, V.M. Leovac, L.S. Vojinović-Ješić, M.V. Rodić, L.S. Jovanović and V.I. Češljević, *J. Serb. Chem. Soc.* 78 (2013) 1161.
26. R.L.Ware, M. Farooqui and S.D. Naikwade, *International Journal of Emerging Technologies in Computational and Applied Sciences,* 5 (2013) 398.
27. R.P. Phase, A.G. Shankarwar, S.G. Shankarwar and T.K. Chondhekar, *Der Pharmacia Sinica* 4 (2013) 54.
28. A.S. Prajapati, S.B. Dalicha and J.J. Vora, *Der Chemica Sinica,* 5 (2014) 7.
29. A.L. Lehninger, *Physical Rev.,* 30 (1950) 393.
30. B. Anilanmert, "*Therapeutic Organometallic Compounds*", in: *Pharmacology*, L. Galelli (Ed.), Intech, Rijeka (2012), Chap. 29, pp. 651-680.
31. K.O. Ogunniran, K.O. Ajanaku, O.O. James, O.O. Ajani, C.O. Nwinyi, C.A. Omonhimin and M.A. Allensela, *Scientific Research and Essay*, 3 (2008) 348.

32. B. Viossat, F.T. Greenaway, G. Morgant, J.-C. Daran, N.-H. Dung and J.R.J. Sorenson, *J. Inorg. Biochem.* 99 (2005) 355.
33. F. Valach, M. Tokarcik, P. Kubinec, M. Melnik and L. Macaskova, *Polyhedron* 16 (1997) 1461.
34. M. Koman, M. Melnik and T. Glowiak, *J. Coord. Chem.* 44 (1998) 133.
35. Y.-H. Tan, S.-P. Yang, Q.-S. LI and Y.-L. Tan, *Chin. J. Struct. Chem.* 25 (2006) 1387.
36. E. Ukpong and C. Obadimo, *Int. J. Electrochem. Sci.* 9 (2014) 4405.
37. D. Omanović and M. Branica, *Croat. Chem. Acta*, 71 (1998) 421.
38. http://us.chemicalbook.com/ChemicalProductProperty_US_CB3307557.aspx (Accessed July 19, 2015).
39. http://www.lobachemie.com/Ammonium-salts-01260/AMMONIUM-METAVANADATE-CASNO-7803-55-6.aspx (Accessed July 19, 2015).
40. I.H.I. Habib, S.A. Weshahy, S. Toubar and M.M.A. El-Alamin, *Port. Electrochim. Acta* 26 (2008) 315.
41. I.H.I. Habib, S.A. Weshahy, S. Toubar and M.M.A. El-Alamin, *Pharmaceutical Chemistry Journal* 42 (2008) 438.
42. F. Öztürk, I.H. Taşdemir, D. Altunöz Erdoğan, N. Erk and E. Kılıç, *Acta Chim. Slov.* 58 (2011) 830.
43. A. Álvarez-Lueje, J.C. Sturm, L.J. Núñez-Vergara, J. Carbajo and J.A. Squella, *Anal. Lett.* 33 (2000) 53.
44. Y. Israel and L. Meites, **"*Vanadium*"** in: A.J. Bard (Ed.), *Encyclopedia of Electrochemistry of the Elements*, Vol. VII, Marcel Dekker Inc., New York (1976), Chap. VII-2, pp. 336-378.
45. S. Sander and G. Henze, *Fresenius J. Anal. Chem.* 356 (1996) 259.
46. A.J. Bard and L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Second Edition, John Wiley & Sons, New York (2001), p. 810.
47. P.-h. Deng, J.-j. Fei and Y.-l. Feng, *J. Electroanal. Chem.* 648 (2010) 85.
48. N.Q. Li and J. Min, *Chínese J. Anal. Chem.* (*FenXiHuaXu*e) 17 (1989) 346.
49. A.H. Jubert, A.C. Gonzalez-Baro, R. Pis-Diez and E.J. Baran, *J. Raman Spectrosc.* 23 (1992) 273.
50. A.C. Gonzalez-Baro, O.E. Piro, B.S. Parajon-Costa, E.J. Baran and E.E. Castellano, *Monatsh. Chem.* 129 (1998) 31.
51. C.D. Garner, D. Collison and F.E. Mabbs, In: H. Sigel and A. Sigel (Eds), *Metal ions in biological systems*, Vol 31: *Vanadium and its role in life*, Marcel Dekker, New York (1995), Ch. 19, p. 635.
52. R. Meena and N. Fahmi, *International Journal of Biotechnology and Bioengineering Research* 4 (2013) 437.
53. I. Bulut, *Turk. J. Chem.* 33 (2009) 507.
54. K.-J. Range and R. Zintl, *Z. Naturforsch. Teil B*, 43 (1988) 309.
55. A.A. El-Sherif and M.M. Shoukry, *Inorg. Chim. Acta* 360 (2007) 473.
56. K. Nakamoto, *Infrared and raman spectra of inorganic and coordination compounds*, Third edition, John Wiley & Sons, New York (1978), p. 311.
57. M.E. Brown and B.V. Stewart, *J. Therm. Anal.* 2 (1970) 287.
58. M. Vlad, I. Labadi and O. Costisor, *Chem. Bull. "POLITEHNICA" Univ.* (*Timişoara*), 50 (2005) 61.
59. I. Kacso, L. Rus, M. Pop, G. Borodi and I. Bratu, *Spectroscopy* 27 (2012) 49.
60. K. Balcı, Y. Akkaya and S. Akyuz, *Vib. Spectrosc.* 53 (2010) 239.
61. E.-R. Kenawy, A.E.-R.R. El-Shanshoury, N.O. Shaker, B.M. El-Sadek, A.H.B. Khattab and A. Elzatahry, *Main Group Chem.* 12 (2013) 293.
62. K.A. Ali, M.A. Elsayed and E.A. Ragab, *Green and Sustainable Chemistry* 5 (2015) 39.
63. N.H. Ismail, A. Alias and C.P. Osman, *Alkaloids and Anthraquinones from Malaysian Flora, In: Phytochemicals - A Global Perspective of Their Role in Nutrition and Health*, Dr Venketeshwer Rao (Ed.), InTech, Rijeka (2012), Chapter 14, p. 296.
64. A.M. Asiri and S.A. Khan, *Molecules* 15 (2010) 4784.

65. N. Bıçak, B.F. Şenkal and E. Sezer, *Synthetic Metals* 155 (2005) 105.
66. A. Marteel-Parrish, S. DeCarlo, D. Harlan, J. Martin and H. Sheridan, *Green Chem. Lett. Rev.* 1 (2008) 231.
67. V.V. Turov, V.M. Gun'ko, M.D. Tsapko, V.M. Bogatyrev, J. Skubiszewska-Zieba, R. Leboda and J. Ryczkowski, *Appl. Surf. Sci.* 229 (2004) 197.